THE PHOTOCHEMISTRY OF STILBENES AND 1,2-DIHYDRONAPHTHALENES IN METHANOL

J. WONING

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Contents.

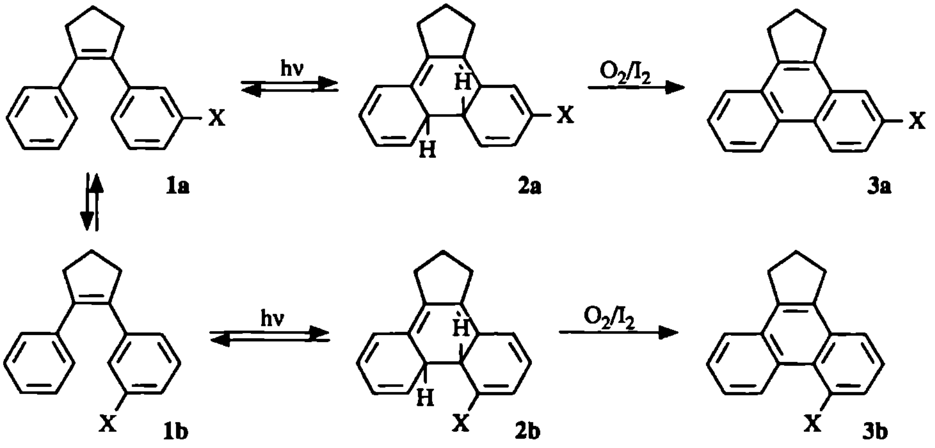
Chapter 1: Introduction.

This thesis deals with the photochemistry of stilbene, 1-, 2-, 3- and 4-phenyl-1,2-dihydronaphthalene, and 1,2- and 3,4-dihydrophenanthrene. As each of the following chapters starts with a short introduction, the present introductory chapter is intended to provide a brief survey of the whole work discussed in this thesis.

Though the photochemistry of the compounds just mentioned has been the subject of previous studies, the effect of solvents thereupon has received comparatively little attention. Almost all information available on this topic concerns stilbene and its derivatives.

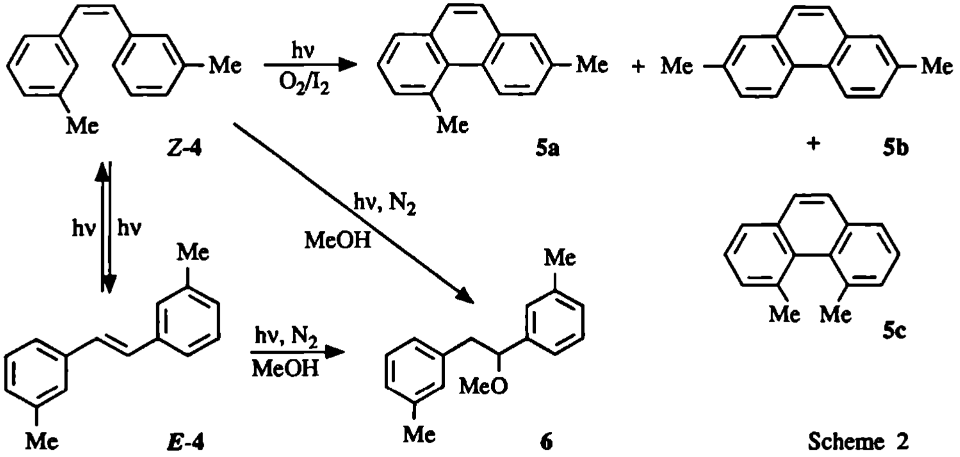
For this class of compounds, *E,Z*-isomerization[1] and conrotatory electrocyclic ringclosure[2] of the *Z*-isomer to the corresponding *trans*-4a,4b-dihydrophenanthrene were established to be the most efficient photoreactions. The usual experimental approach to study the latter reaction, involves scavenging of the unstable 4a,4b-dihydrophenanthrene by oxidation, yielding a phenanthrene as the stable end-product. For *meta*-substituted stilbenes, the *Z*-isomer can occur in two different conformations, which give rise to the formation of different phenanthrenes. A well-documented[3,4] example of this behavior, investigated previously in our research group, is presented in Scheme 1.

Scheme 1



In this case a change of the solvent from cyclohexane to methanol was found to affect the rates of the thermal ring opening and oxidation reactions (to **3a** and **3b**) of the primary cyclization products **2a** and **2b** (Scheme 1) of *m*-substituted 1,2-diphenylcyclopentenes (**1**). From the absence of other photoproducts than **3a** and **3b**, it was concluded that the reactivity of the lowest excited singlet state of **1a** or **1b** remains unchanged on going from a nonpolar to a polar and protic solvent under otherwise similar conditions.

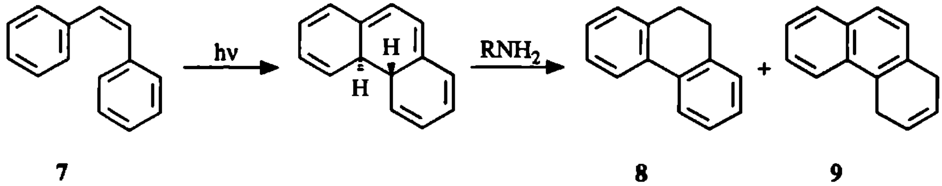
As an extension of this work, the photochemistry of other substituted stilbenes has been studied[4] in methanol and hexane, in the absence of iodine as an oxidizing agent. Among the compounds studied, 3,3′-dimethylstilbene (**4**) appeared[5] to undergo photochemical addition of methanol to the double bond (Scheme 2). Though the compound, like other stilbenes, yields the corresponding phenanthrenes **5a**-**5c** on irradiation in the presence of an oxidant, irradiation of **4** in methanol under strictly anaerobic conditions affords the methanol adduct **6** as the chief photoproduct in good yields. This unexpected result prompted us to investigate the scope and the mechanism of this unusual type of photochemical addition. The results of this work are discussed in Chapter 2.



Scheme 2

Primary amines present another example of a solvent-type, capable of altering the reactivity of the primary photocyclization product of stilbenes. On irradiation in such a solvent, *Z*-stilbene (**7**, Scheme 3) cyclizes to *trans*-4a,4b-dihydrophenanthrene, but, instead of being oxidized, the

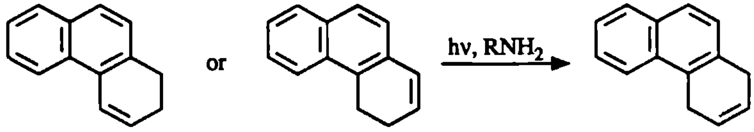
Scheme 3



primary cyclization product rearranges to 9,10- (**8**) and 1,4-dihydrophenanthrene (**9**), even in the presence of air[6]. The compounds 1,2- (**10**) and 3,4-dihydrophenanthrene (**11**) have been identified as precursors of **9** in this rearrangement.

Irradiation of authentic samples of **10** and **11** demonstrated[6], that an efficient, amine-mediated photochemical 1,3-H shift (Scheme 4) is responsible for the formation of **9**. The observation that the photochemical 1,3-H shift could also be brought about by MeO$^-$/MeOH, suggested a deprotonation-protonation sequence to be involved in the hydrogen transfer. However, the results obtained with 1,2-diphenylcyclopentene[6] and 2-styrylbenzo[c]phenanthrene[7] in deuterated primary amines provided evidence favoring either concerted or a radical mechanism.

Scheme 4



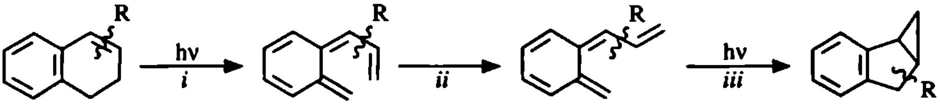
10 **11** **9**

The amine-mediated photochemical 1,3-H shift depicted in Scheme 4 appears to a general feature of compounds, incorporating a 1,2-dihydronaphthalene moiety in their molecular structure: In addition to **10** and **11**[6], which can be considered as benzo-1,2-dihydronaphthalenes, the reaction has been observed with 1,2-dihydronaphthalene[6] itself, phenyl-substituted 1,2-dihydronaphthalenes[8], 3-methyl-1,2-dihydronaphthalene[9] and, indirectly, with 9,10-cyclopenteno-[6] and some other, substituted 1,2- and 3,4-dihydrophenanthrenes[6,10]. Yet, the exact function of the amine, which can be replaced by another basic medium like MeO$^-$/MeOH, is virtually unknown. In view of the lack of mechanistic details, particularly on the role of the reaction medium, it was decided to undertake a systematic study of the amine-promoted 1,3-H shift in 1,2- (**10**) and 3,4-dihydrophenanthrene (**11**). The results of this study are presented in Chapter 3.

In the absence of a primary amine or a base, 1,2-dihydronaphthalenes do not undergo the photochemical 1,3-H shift discussed in the preceding paragraphs. On irradiation in nonpolar solvents like hexane, formation of benzobicyclo[3.1.0]hex-2-enes has been reported[11] as the principal photoreaction for this class of compounds. 3-Phenyl-1,2-dihydronaphthalene and the compounds **10** and **11** provide exceptions to this reactivity pattern.

The mechanism of the bicyclohexene formation from 1,2-dihydronaphthalenes (Scheme 5) is well-established[12] and involves: (*i*) Conrotatory photochemical ring opening of the parent 1,2-dihydronaphthalene **12**, yielding the pentaene intermediate *cZc*-**13**. (*ii*) Thermal conversion of *cZc*-**13** into the *cZt*-conformer *cZt*-**13**. (*iii*) Intramolecular [4+2] photocycloaddition of *cZt*-**13**,

Scheme 5



12 *cZc*-**13** *cZt*-**13** **14**

yielding the benzobicyclo[3.1.0]hex-2-ene **14**.

Previously, the photochemistry of the phenyl-substituted 1,2-dihydronaphthalenes in hexane has been thoroughly investigated[13-15]. In the case of 1- and 2-phenyl-1,2-dihydronaphthalene[13,14], these studies have been devoted in particular to the stereochemistry of the bicyclohexene formation (*exo*- and *endo*-isomers of **14** are possible in this case). In the case of 3- and 4-phenyl-1,2-dihydronaphthalene[14,15], these studies were aimed to verify, whether the photoreactivity of these compounds resembles that of their respective analogs, *trans*-stilbene and 1,1-diphenylethene, or that of the 1,2-dihydronaphthalenes. In each case, the knowledge acquired was insufficient to account in detail for the experimental results. By monitoring more subtle changes in photoreactivity and photoproduct distributions, occurring on replacement of hexane by the polar and protic methanol as the solvent, it was hoped to resolve some of the existing ambiguities concerning the mechanism and excited states involved in the photoreactions of the phenyl-substituted dihydronaphthalenes.

In this context, the photochemistry of 1-phenyl- (Chapter 4), 2-phenyl- (Chapter 7), 3-phenyl- (Chapter 5) and 4-phenyl-1,2-dihydronaphthalene (Chapter 6) in methanol has been investigated in detail.

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Chapter 2: Photochemical addition of methanol to stilbene derivatives.

Introduction

The photochemistry of stilbene (**1**) has been the subject of profound studies over the preceding decades. *E,Z*-isomerization (from either the lowest excited singlet or triplet state)[1] of *E*- and *Z*-**1** and conrotatory electrocyclic ringclosure of *Z*-**1** (from the S_1 state) to 4a,4b-dihydrophenanthrene[2] were established as the most efficient photoprocesses. Exciplex formation of excited *E*-**1** with secondary[3] or tertiary[4] amines presents a relatively new aspect of stilbene photochemistry.

In addition to *E,Z*-isomerization and electrocyclization, many aspects of the photochemistry (e.g. dimerization, [2+2] and [4+2] cycloadditions) of styrenes and non-aromatic alkenes[5], have been observed with **1** and its derivatives. However, photochemical addition of solvents like H_2O, MeOH and EtOH (compounds containing σ-bonds only) to the olefinic bond of **1** itself, has not been described[6].

This type of addition is well-known for aliphatic alkenes and styrenes. In these cases the addition of an alcohol can occur by different mechanisms, viz.: (*i*) By nucleophilic attack on a Rydberg π,R(3s) excited state[5] (*ii*) By protonation of the S_1 state. McEwen[7] demonstrated the photochemical addition of water to styrenes and phenylacetylenes to be subject to general acid catalysis. (*iii*) *Via* a carbene intermediate, arising from a Rydberg π,R(3s) or a π,π^* excited state of the alkene[5,8].

With stilbene derivatives, such photochemical addition reactions have only been observed in a few, exceptional cases. Thus, the occurrence of photochemical addition of methanol to the olefinic double bond is known only for 1,2-diphenylcyclobutene[9], a strained derivative of **1** and the charged 4,4′-(1,2-ethenediyl)bis-1-methylpyridinium ion[10]. The former compound is exceptional in that neither *E,Z*-isomerization nor electrocyclization to the corresponding 4a,4b-dihydrophenanthrene can occur. On the basis of an observed catalytic effect of acids on the rate of methanol addition and the results of irradiations in MeOD and D_2O, it was concluded[9] that the S_1 state of 1,2-diphenylcyclobutene is deactivated through protonation by these solvents. Besides addition of methanol to the olefinic bond, rearrangement of the resulting carbenium ion takes place.

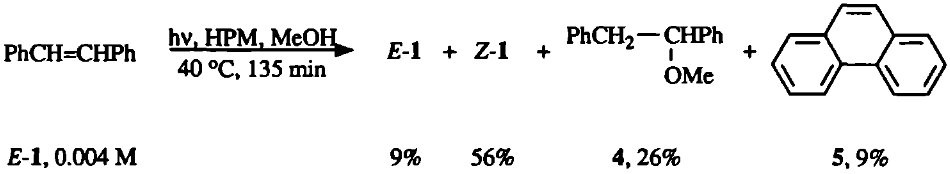
The 4,4′-(1,2-ethenediyl)bis-1-methylpyridinium salts are exceptional in that their S_1 states are said[10] to be electron-deficient at the olefinic positions and hence, prone to be trapped by the addition of nucleophiles to the olefinic bond. It has been stated that photochemical addition of methanol to the olefinic bond of unstrained 1,2-diphenylcyclopentene (**2**)[9] and **1** itself[6] does not take place. In this context, the recently reported[11] photochemical addition of HCl to **1** in dichloromethane presents an unique example.

We observed the photochemical addition of methanol to the olefinic bond of **1** and several of its derivatives. In the following sections, the scope and mechanism of this reaction will be discussed. As far as clarifying to this discussion, results concerning the photochemistry of 1,1-diphenylethene (**3**, in MeOH) are included.

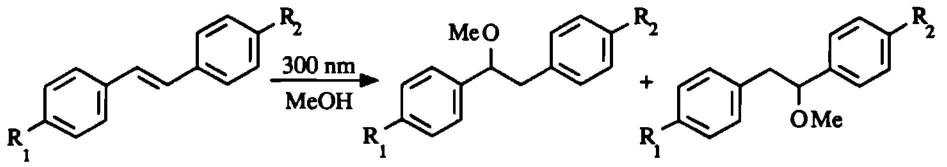
Results and discussion

Scope of the reaction. As part of a continuous research program aimed at elucidation of the structure-reactivity relation concerning the primary photocyclization of *Z*-stilbenes to the corresponding 4a,4b-dihydrophenanthrenes and the effect of solvents thereupon[12], *E*-**1** was irradiated in MeOH under strictly anaerobic conditions. In the ^{1}H-NMR spectrum of the resulting mixture of photoproducts, the occurrence of a sharp singlet at $\delta = 3.18$ ppm, attributable to the presence of a methyl ether, was noted. Chromatographic separation afforded an nonpolar fraction (containing **1** and phenanthrene) and a polar fraction consisting of a single component (GLC). The ^{1}H-NMR and mass spectrum of the latter were assigned to 1-methoxy-1,2-diphenylethane (α-methoxybibenzyl, **4**), the methanol adduct of **1** (Scheme 1). This assignment was confirmed by chemical synthesis of **4**[13]. Preliminary results concerning the scope, indicate the photochemical addition of MeOH to the olefinic bond to be a general reaction of stilbene derivatives. The reaction depicted in Scheme 1 has been performed successfully with several stilbene derivatives, e.g. 1,2-diphenylcyclopentene (**2**), 3-phenyl-1,2-dihydronaphthalene[14], and the symmetrically substituted 3,3′-dimethyl- (**6**) and 4,4′-difluorostilbene (**7**, Scheme 2, $R_1 = R_2 = F$). In case of the asymmetrically substituted 4-methoxy- (**8a**) and 4-methoxy-4′-methylstilbene (**8b**) addition of MeOH was observed to occur regioselectively, affording methanol adducts **10a** and **10b** respectively, in accordance with Markovnikov's rule (Scheme 2). The position of the methoxy group, relative to that of the substituents R was deduced from the CI mass spectra, in which the presence of an intense fragmentation peak at *m/e* 151 due to a $MeOC_6H_4CHOMe^+$ fragment is consistent with structures **10a,b** rather than with **9a,b**. The assignment of structure **10a** to the methanol adduct of 4-methoxystilbene (**8a**) was subsequently verified by chemical synthesis of the regioisomeric α- and -β-methoxy(4-methoxy)bibenzyls **9a** and **10a**. As indicated in Scheme 2, the photochemical addition of MeOH to **8c** does not take place with 100% regioselectivity,

Scheme 1



Scheme 2



8 **9** **10**

8a (R_1=H, R_2=OMe)	**9a** (R_1=H, R_2=OMe) : -	**10a** (R_1=H, R_2=OMe): 100%
8b(R_1=Me, R_2=OMe)	**9b**(R_1=Me, R_2=OMe): -	**10b**(R_1=Me, R_2=OMe): 100%
8c (R_1=H, R_2=Me)	**9c** (R_1=H, R_2=Me) : 25%	**10c** (R_1=H, R_2=Me) : 75%

though in this case too, the Markovnikov adduct α-methoxy(4-methyl)bibenzyl (**10c**) predominates.

For *trans*-stilbene (*E*-**1**) the progress of the photoreaction has been monitored as a function of the irradiation time. The resulting yield *vs.* time curves for conversion of *E*-**1** and formation of *Z*-**1**, phenanthrene (**3**) and the methanol adduct **4** are presented in Fig. 1. Obviously **4** is a primary photoproduct, since its yield *vs.* time curve intercepts at the origin. From the observation that the photostationary *Z*-**1**/*E*-**1** ratio of 6.5 is reached within 2 minutes and the magnitude of the slope of the yield *vs.* time curve of methanol adduct **4**, it emerges that photochemical addition of methanol to stilbene (**1**) is at least 30 times less efficient than *E*,*Z*-isomerization of **1**. On the basis of the known[15] quantum yield (φ = 0.5) of the latter process, the upper limit for the quantum yield of MeOH addition to the olefinic bond of **1** is estimated to be 0.01. This value explains, that under the oxidative irradiation conditions (I_2/O_2) usually employed in previous studies, addition of MeOH to **1** has never been observed along with the rather efficient (φ = 0.1)[16] photoreaction of *Z*-**1** to phenanthrene (**5**).

Referring to *E*,*Z*-isomerization and formation of the corresponding phenanthrenes the addition of MeOH to 3,3′-dimethylstilbene (**6**) appears to be a relatively efficient photoprocess: Even under oxidative irradiation conditions, competition between methanol addition to **6** and conversion into the corresponding phenanthrenes was observed (Table 1).

Reaction mechanism. To elucidate the mechanism of the photochemical methanol addition to stilbene (**1**) and its substituted derivatives, the following studies have been performed:

(*a*) Investigation of the influence of a strong acid on the rates of the photochemical methanol addition reaction. By way of this approach it should be possible to establish whether protonation of the excited state is involved in the formation of methanol adducts from stilbenes.

(*b*) Irradiations in MeOD at different wavelengths, in order to establish the isotope effect and stereochemistry of the photochemical methanol addition reaction and the effect of the wavelength

Figure 1: Irradiation (HPM) of stilbene (*E*-**1**, 4 × 10^{-4} M) in deaerated MeOH. Conversion of *E*-**1** and yields of *Z*-**1**, 1-methoxy-1,2-diphenylethane (**4**) and phenanthrene (**5**) as a function of the irradiation time.

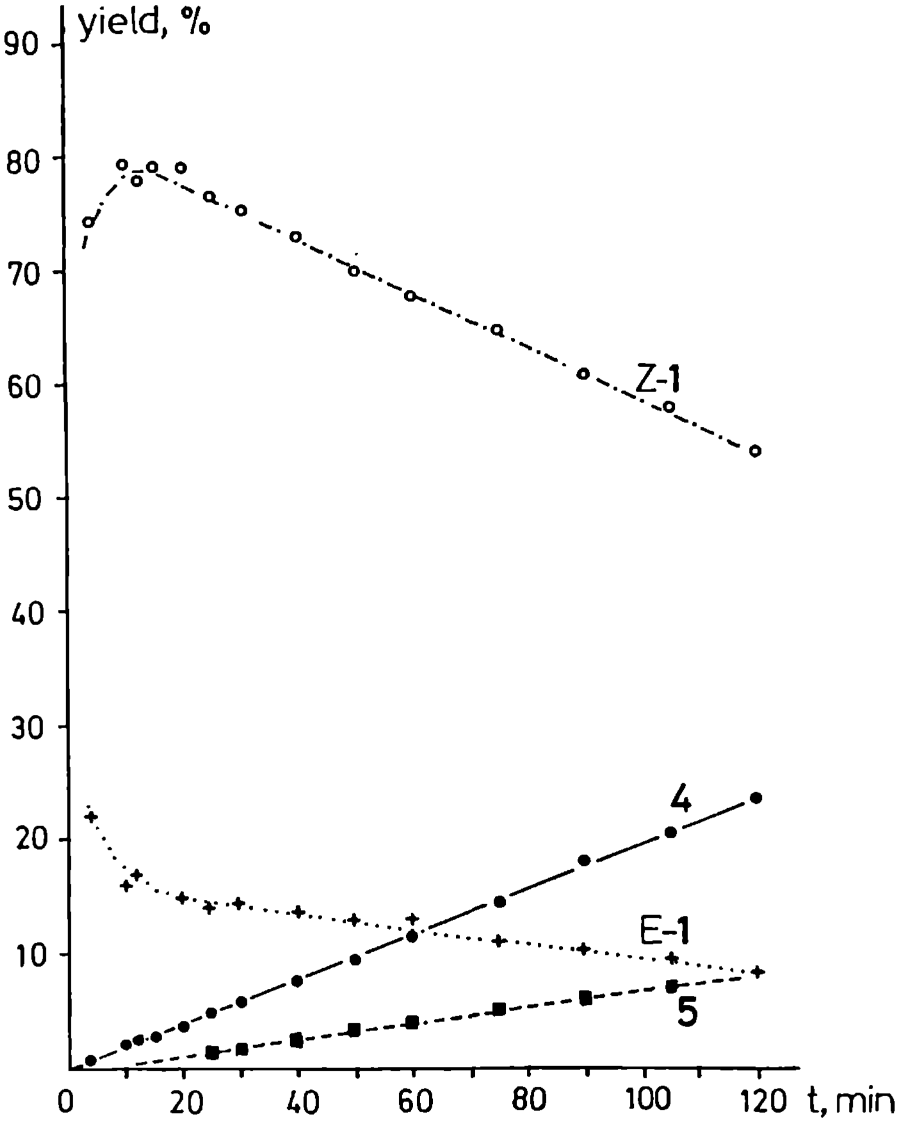


Table 1. Irradiation (HPM, 120 min) of 3,3′-dimethylstilbene (**6**, 1.6×10^{-4} M) in air-saturated methanol. Influence of temperature and concentration of iodine ($[I_2]$) on the yield of the methanol adduct 1-methoxy-1,2-di(*m*-tolyl)ethane.

T, °C	yield of 1-methoxy-1,2-di(*m*-tolyl)ethane, %	
	$[I_2] = 0$	$[I_2] = 1.6 \times 10^{-4}$ M
-80	9.1	0
-60	15.4	1.4
22	18.4	3.6
40	26.0	-

thereupon.

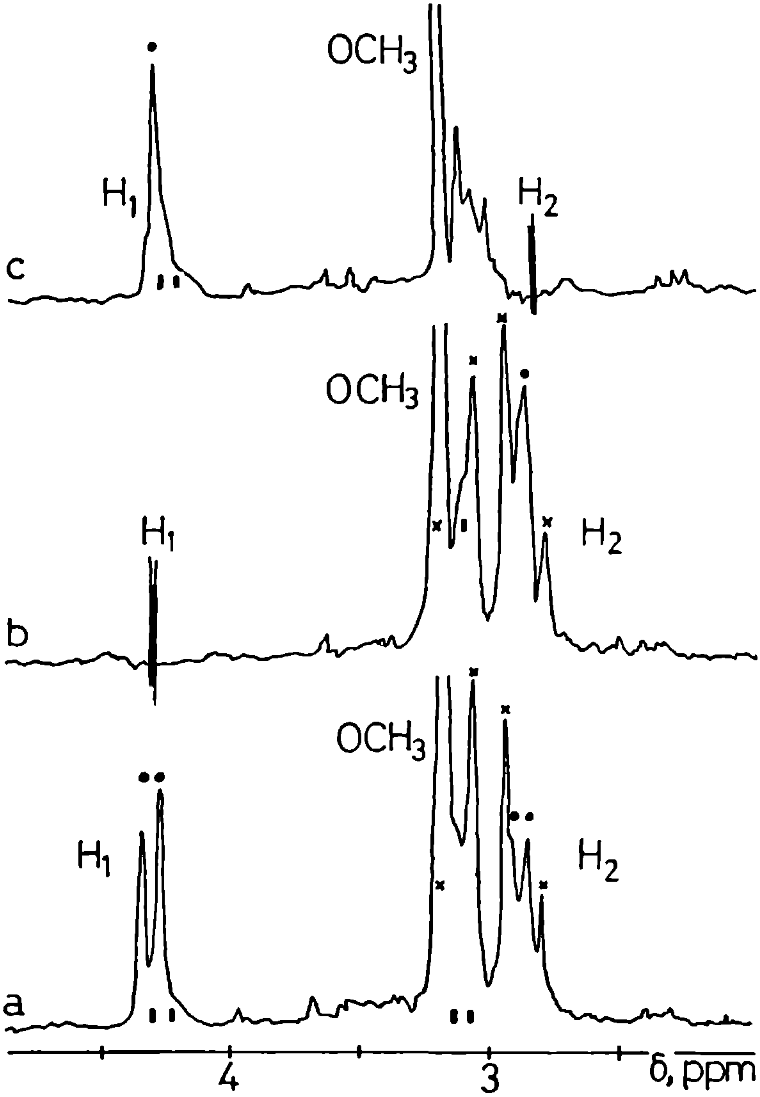
Influence of acid on the rates of the photochemical methanol addition. Repeating the irradiation experiment outlined in Fig. 1 with *trans*-stilbene (*E*-**1**) in the presence of a 20-fold excess (8×10^{-3} M) of H_2SO_4 resulted in a yield *vs*. time plot identical to that in Fig. 1. I.e. that for stilbene (**1**), neither the photochemical addition of methanol leading to **4**, nor the photochemical *E,Z*-isomerization and cyclization reactions, leading to phenanthrene (**5**) are sensitive to acid catalysis.

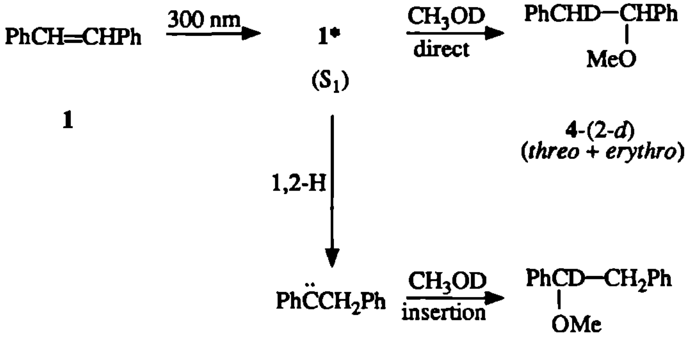
Similar irradiation experiments performed with diphenylcyclopentene (**2**) reproduced essentially the results quoted for *E*-**1**: On irradiation of **2** under the conditions stated in Fig. 1, neither the rate of the photochemical methanol addition to **2**, nor that of conversion into 9,10-cyclopentenophenanthrene were influenced by the presence of a 50-fold excess (0.02 M) of H_2SO_4.

It thus emerges that the photochemical addition of methanol to stilbene (**1**) and diphenylcyclopentene (**2**) does not involve protonation of the S_1 states of these compounds as a rate-determining step. In the case of stilbene (**1**), this conclusion is corroborated by the fact that the fluorescence of *trans*-stilbene (*E*-**1**) in methanol was not quenched observably by H_2SO_4, in concentrations up to 6.0 M.

Irradiations in MeOD. In order to establish the stereochemistry of the photochemical methanol addition to stilbene (**1**), we irradiated *E*-**1** in MeOD at 300 nm. The NMR spectrum (Fig. 2) of the chromatographically separated MeOD adducts demonstrated unambiguously the presence of *threo*- and *erythro*-1-methoxy-2-deuterio-1,2-diphenylethane (**4**-(2-*d*)) as well as the, beforehand unexpected 1-methoxy-1-deuterio-1,2-diphenylethane (**4**-(1-*d*)) (Scheme 3). From NMR integration the ratio **4**-(1-*d*)/**4**-(2-*d*) was found to be 0.8±0.1. (at 300 nm) These data are consistent with the CI mass spectrum which shows fragmentation peaks at *m/e* 122 (due to **4**-(1-*d*)) and at *m/e* 121 (due to **4**-(2-*d*)) in an intensity ratio of 0.85. From these results it follows,

Figure 2: Aliphatic part of the 90 MHz ^{1}H-NMR spectrum of a mixture of 1- (4-(1-*d*)) and 2-deuterio-1-methoxy-1,2-diphenylethane (*threo*- and *erythro*-(4-2-*d*)). Normal spectrum (*a*) and spectra, spin-decoupled at H_1 (*b*) and at H_2 (*c*) of 4-(2-*d*).





Scheme 3 **13** **4**-(1-*d*)

that addition of methanol to **1** involves the two competing pathways outlined in Scheme 3; viz. direct addition of methanol to the olefinic bond of excited **1** (**1***)[17] and insertion[18] of methanol by carbene **13**, emerging from a 1,2-H shift in **1***.

The results presented in Table 2 indicate this conclusion to be valid for substituted stilbenes as well. As can be seen from Table 2, the ratio of the rates of methanol addition *via* the carbene (r_{car}) and direct (r_{dir}) route increases smoothly with decreasing irradiation wavelength λ.

Table 2. Irradiation of stilbene (*E*-**1**), 4,4′-difluorostilbene (**7**, Scheme 2, $R_1 = R_2 = F$) and 4-methoxystilbene (**8a**, Scheme 2) in MeOD. Wavelength dependence of the rate ratio (r_{car}/r_{dir}) of MeOD addition *via* the carbene (r_{car}) and direct (r_{dir}) pathway.

λ, *nm*	r_{car}/r_{dir}		
	1	**7**	**8a**
360	0.6±0.1	0.8±0.3	0
300	0.9±0.3	1.3±0.4	0
254	2.0±0.5	2.1±0.5	1.4±0.5
185	>3	>3	-

The wavelength dependence of the *threo*-**4**-(2-*d*)/*erythro*-**4**-(2-*d*) ratio (k_t/k_e) was also investigated. The results have been collected in Table 3.

To evaluate the deuterium isotope effect on the yields of the direct photochemical methanol addition to stilbene (**1**, Scheme 3), *E*-**1** was irradiated in a 1/1 (molar) mixture of MeOH and

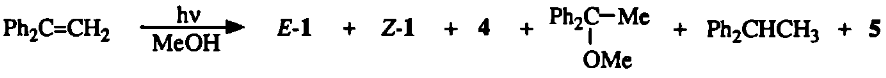
Table 3. Irradiation of stilbene (*E*-**1**), 4,4′-difluorostilbene (**7**, Scheme 2, $R_1 = R_2 = F$) and 4-methoxystilbene (**8a**, Scheme 2) in MeOD. Wavelength dependence of the *threo/erythro* ratio (k_t/k_e) of MeOD adducts emerging *via* the direct pathway and of the photostationary state *Z/E* ratio of the parent stilbene.

λ, *nm*	**1**		**7**		**8a**	
	k_t/k_e	*Z/E*	k_t/k_e	*Z/E*	k_t/k_e	*Z/E*
360	0.7	18	0.04	15	0.5	0.9
300	0.8	5.7	0.04	3	0.4	8.2
254	1.8	1.9	0	1.4	0.1	1.2

MeOD at 300 nm. From the observed yields of the methanol adducts **4**, **4**-(1-*d*) and **4**-(2-*d*), the values of k_t/k_e (Table 3) and the isotope effect for insertion of carbene **13** (See below) into methanol, the isotope effect on the yield of **4**-(2-*d*) (*threo* + *erythro*, Scheme 3) was established to be 2.8±0.5. This value is much higher than for insertion of carbene **13** into methanol ($k_H/k_D = 1.4$, see below) and, considering the high polarity of methanol, points to a rather symmetrical transition state in the direct addition of methanol to the olefinic bond of **1**.

The isotope effect for insertion of carbene **13** in methanol was evaluated by generating this carbene independently, from 1,1-diphenylethene (**3**). On direct irradiation in deaerated MeOH at 254 nm, this compound was observed to undergo Markovnikov addition of MeOH to the olefinic bond, affording 1-methoxy-1,1-diphenylethane (**11**; Scheme 4), as well as rearrangement, leading

Scheme 4



$$\underset{\mathbf{3}}{Ph_2C{=}CH_2} \xrightarrow[\text{MeOH}]{h\nu} E\text{-}\mathbf{1} + Z\text{-}\mathbf{1} + \mathbf{4} + \underset{\mathbf{11}}{Ph_2\underset{\text{OMe}}{\underset{|}{C}}{-}Me} + \underset{\mathbf{12}}{Ph_2CHCH_3} + \mathbf{5}$$

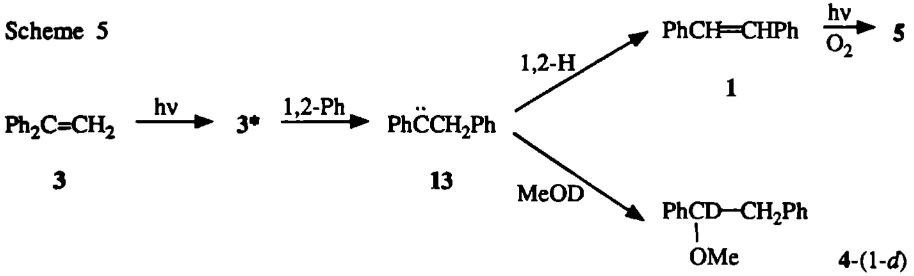
to 1-methoxy-1,2-diphenylethane (**4**), phenanthrene (**5**) and traces of stilbene (*E*- and *Z*-**1**). Along with these photoreactions, photoreduction to 1,1-diphenylethane (**12**), and extensive photopolymerization also take place.

In analogy with the case of stilbene (Fig. 1), the progress of this photoreaction of **3** in methanol was monitored as a function of the irradiation time. The resulting yield *vs.* time curves are given in Fig. 3. The yield *vs.* time curves of *E*- and *Z*-**1** could not be evaluated, due to the very low abundances (<0.5 %, based on reacted **3**) of these compound among the photoproducts of **3**.

According to Fig. 3, the methoxydiphenylethanes **4** and **11** and 1,1-diphenylethane (**12**) are primary photoproducts of **3**. On the other hand, phenanthrene (**5**), being observable only on prolonged (>1 hr) irradiation of **3**, clearly emerges as a secondary photoproduct of **3** in this experiment. This result proves that **4** is not formed from **3** *via* photochemical methanol addition to *E*- or *Z*-**1** (Scheme 2).

Considering the formation of the rearrangement products stilbene (*E* and *Z*-**1**), methanol adduct **4** and phenanthrene (**5**) from 1,1-diphenylethene, rationalizing of these rearrangement products must involve a carbene intermediate **13** (Scheme 5). A radical reaction would involve the relatively stable $^{\cdot}CH_2OH$ rather than the $CH_3O^{\cdot}$ radical[19]. Because methanol adducts deriving from the former radical have not been observed, a radical mechanism appears unlikely. The possibility of an ionic mechanism, involving protonation of excited **3** (**3***, Scheme 6, pathway a) was rejected on the basis of carbenium ion stabilities. Conclusive evidence regarding the intermediacy of carbene **13** was obtained from the results of irradiation of **3** in MeOD: As

Scheme 5



Scheme 6

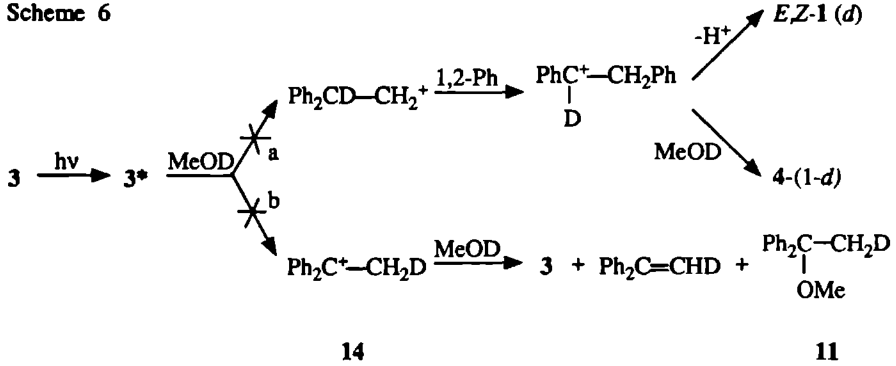
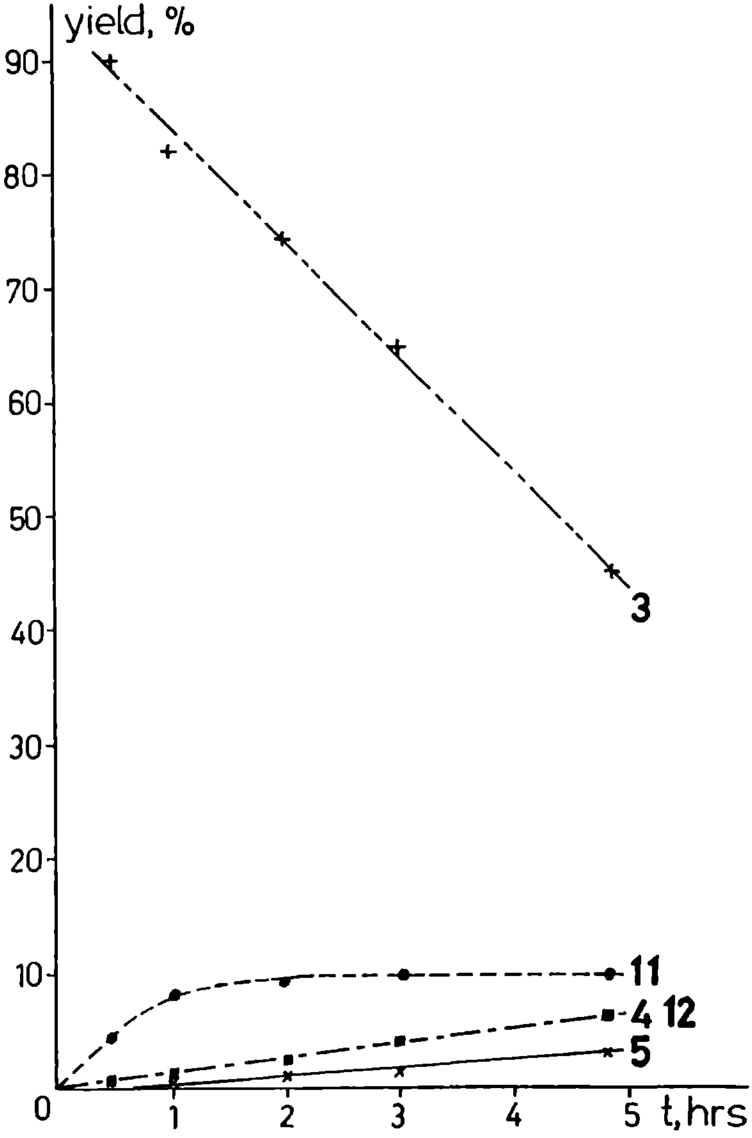
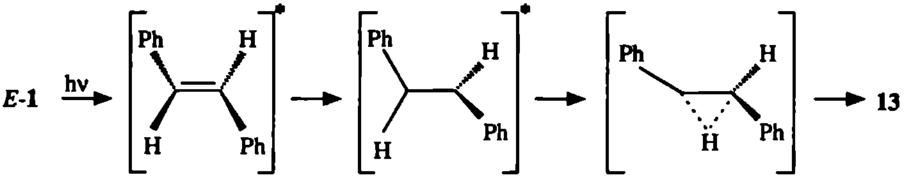


Figure 3: Irradiation (254 nm) of 1,1-diphenylethene (**3**, 10^{-3} M) in deaerated MeOH. Conversion of **3** and yields of 1-methoxy-1,2-diphenylethane (**4**), phenanthrene (**5**), 1-methoxy-1,1-diphenylethane (**11**) and 1,1-diphenylethane (**12**) as a function of the irradiation time. The yield *vs*. time curves of *E*- and *Z*-**1** could not be evaluated due to the low abundances (<0.5%) of these compounds among the photoproducts of **3**.



expected for its formation *via* insertion by carbene **13** in methanol, **4** (Schemes 5 and 6) was obtained exclusively with D and OCH_3 substituents at the same carbon atom (**4**-(1-*d*)). The fact that in this experiment no D incorporation was observed in *E*- and *Z*-**1**, **5** and unreacted **3**, excludes the ionic pathway b depicted in Scheme 6 from being involved in the formation of stilbene (*E*- and *Z*-**1**) and methanol adduct **4** from **3**. In a subsequent experiment, 1,1-diphenylethene (**3**) was irradiated in a 1/1 (molar) mixture of MeOH and MeOD. After chromatographic separation of the methanol adducts, the isotope effect (k_H/k_D) on the yield of **4** was found to be 1.4±0.2, both by NMR and mass spectroscopy. This value is in excellent agreement with that obtained for a genuine insertion of a singlet carbene into the O-H(D) bond of MeOH(D)[18].

Nature of the excited state. The nature of the excited state involved in the photochemical addition of methanol to stilbene (**1**) and the rearrangement of this compound to carbene **13** is the final subject to be considered. As mentioned in the introduction, rearrangement to carbene **13** can occur from a Rydberg π,R(3s) or a π,π^* excited state of **1**. At irradiation wavelengths ≥254 nm[20] (Table 2) the former possibility can be rejected, since the photon energies (3.4-4.9 eV) involved, are well below the $\pi \rightarrow$ R(3s) transition energies reported[21] for alkenes. Because of the absence of radical reaction products from the T_1 state and the failure of stilbene (**1**) to undergo methanol addition on sensitized irradiation[17], the reactive excited state $\mathbf{1}^*$ (Scheme 3) was concluded to be the lowest excited S_1 state. The ability of excited stilbene ($\mathbf{1}^*$) in methanol to rearrange into carbene **13**, obviously implies that the parent S_1 state is highly (~90°) twisted around the olefinic bond; in order to provide the geometry required[22,23] for the 1,2-H shift involved (Scheme 7).



E-$\mathbf{1}^*$
(planar π,π^* S_1)

$\mathbf{1}^*$
(twisted S_1)

Scheme 7

Presumably, a similar consideration applies to the rearrangement (Scheme 4) of excited diphenylethene ($\mathbf{3}^*$) to carbene **13**.

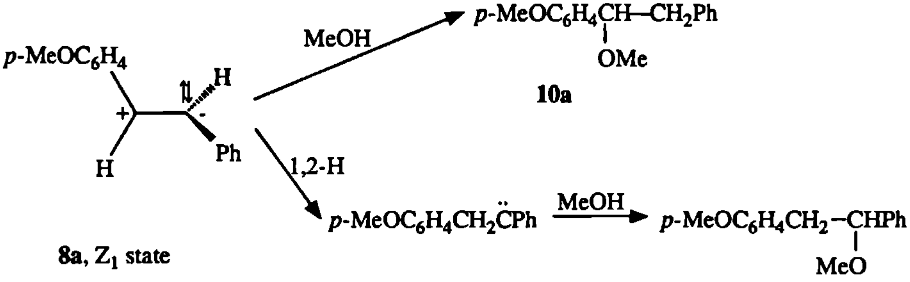
The rearrangement of excited stilbene ($\mathbf{1}^*$) to carbene **13** might involve either a zwitterionic (Z_1) or a non-polar (^1D) twisted excited S_1 state[23] (Scheme 8). MO-CI calculations on propene[24] predict the rearrangement $Z_1 \rightarrow$ **13** to be allowed, hydrogen migrating from the negatively to the positively charged carbon atom. Though these calculations predict the transition $^1D \rightarrow$ **13** to be symmetry-forbidden, it still might occur from a vibrationally unrelaxed ^1D state.

Scheme 8

1^{*}, Z_1 state 1^{*}, ^1D state

The available experimental evidence appears inconsistent with the former alternative. If, in the case of 4-methoxystilbene (**8a**, Scheme 2) the direct and the carbene pathway for addition of methanol are assumed to involve a common Z_1 state, both regioisomeric methoxy(4-methoxy)bibenzyls **9a** and **10a** would be expected (Scheme 9). The fact that on irradiation at 254 nm, where both these pathways are operative, (Table 2) exclusively β-methoxy(4-methoxy)bibenzyl (**10a**) was observed, is not consistent with this theory. Of course, a highly polar Z_1 state should be liable to protonation reactions, particularly by strong acids such as H_2SO_4. This assumption appears in contradiction with the observation, that sulfuric acid does not affect the rate of the photochemical methanol addition reaction to stilbene (**1**) or 1,2-diphenylcyclopentene (**2**). It is also inconsistent with the failure of H_2SO_4 to quench the fluorescence of *E*-**1** in MeOH and with the complete lack of D incorporation (GC-MS) in phenanthrene (**5**) and stilbene (**1**) recovered from irradiations of *E*-**1** in MeOD. Since the presence of electron-donating substituents obviously stabilizes the Z_1 state relative to the nonpolar ^1D excited state and the ground state, enhanced partition of the carbene pathway in the photochemical addition of methanol to stilbenes containing such

Scheme 9



10a

8a, Z_1 state

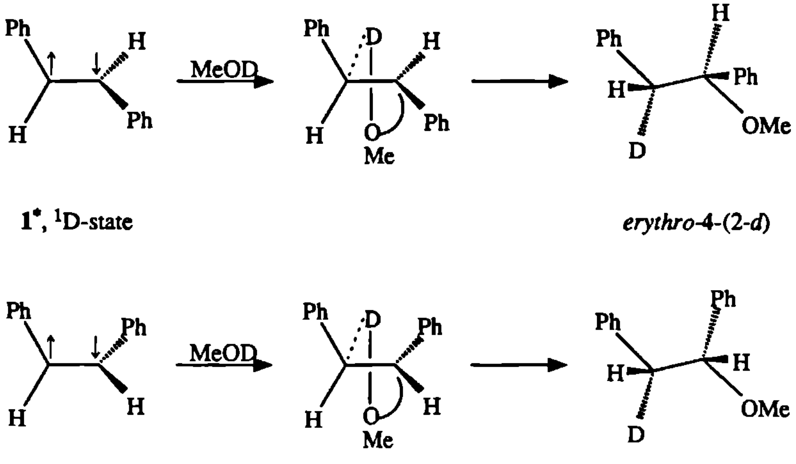
9a

substituents should be expected. Inspection of Table 2 however reveals exactly the opposite trend; the highest r_{car}/r_{dir}-values being observed case of 4,4′-difluorostilbene (**7**, Scheme 2, $R_1 = R_2 =$ F).

The alternative of a non-polar ^{1}D state as the precursor for the stilbene-carbene rearrangement ($\mathbf{1}^* \rightarrow \mathbf{13}$; Scheme 7), provides a more satisfactory account for the experimental data discussed in the previous paragraph. Within this assumption the wavelength dependence of r_{car}/r_{dir} (Table 2) merely reflects the creation of vibrationally unrelaxed ^{1}D states on excitation of stilbenes with highly energetic photons. According to the widths of the UV absorption bands (*E*-**1**: $\Delta\nu_{\frac{1}{2}} = 6000$ cm^{-1}; *E*-**8**: $\Delta\nu_{\frac{1}{2}} = 9000$ cm^{-1}) excited **8** should exhibit a higher rate of internal conversion (through vibrational relaxation) than **1**. This provides an adequate explanation for the observed substituent effect on r_{car}/r_{dir} (Table 2).

In the case of direct addition of methanol to the olefinic bond of stilbene (**1**), the geometry of the excited S_1 state involved is less obvious. According to Scheme 3, direct addition of methanol to excited stilbene ($\mathbf{1}^*$) affords both possible diastereomers *threo*- and *erythro*-**4**-(2-*d*). As outlined in Scheme 10, a twisted S_1 state of stilbene (*E*- or *Z*-**1**) might be considered as a common

Scheme 10



$\mathbf{1}^*$, ^{1}D-state

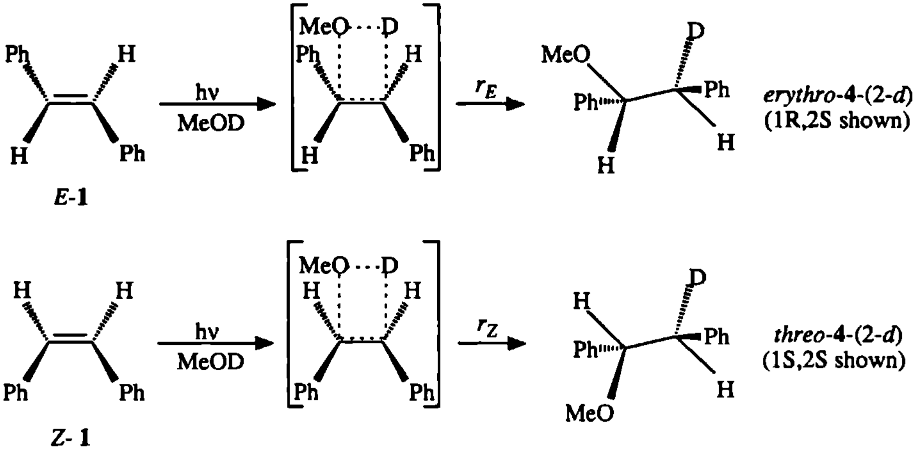
erythro-**4**-(2-*d*)

threo-**4**-(2-*d*)

precursor of these photoproducts: Attack of both enantiomers of this *chiral* S_1 state by MeOD would explain the occurrence of *threo*- and *erythro*-**4**-(2-*d*). In the case of a vibrationally relaxed twisted S_1 state, a wavelength-independent ratio of these diastereomers should be expected. By this assumption alone the experimental data given in Table 3 cannot be accounted for.

On the other hand, it was observed that the obligatory planar diphenylcyclopentene (**2**) undergoes photochemical addition of MeOH at roughly the same rate as stilbene (**1**). This suggests the possibility of direct addition of methanol by attack of MeOD on a planar $^1(\pi,\pi^*)$ state of **1**. Due to efficient photochemical *E,Z*-isomerization, both *E*- and *Z*-**1** are present (Fig. 1) in the photostationary state resulting on irradiation of *E*-**1**. Hence, *threo*- and *erythro*-**4**-(2-*d*) can alternatively be rationalized as the products of *syn* addition of MeOD to the planar, unrelaxed $^1(\pi,\pi^*)$ states of *E*- and *Z*-**1** (Scheme 11), respectively.

Scheme 11



Our present knowledge is insufficient to establish the extent to which twisted and planar S_1 states involved in the direct (Scheme 3) photochemical addition of methanol to stilbenes. The available experimental evidence suggests k_f/k_e to be determined by the competition of a planar, unrelaxed $^1(\pi,\pi^*)$ state and a twisted ^{1}D state for direct addition (Scheme 3) of methanol to the olefinic bond of stilbenes.

Conclusions

Photochemical addition of methanol to the olefinic bond of stilbene (**1**) is possible under strictly anaerobic conditions. The scope of this reaction appears to be fairly general, including stilbene derivatives substituted with electron-withdrawing as well as electron-donating groups at the aromatic rings. In the case of substituted stilbenes, Markovnikov addition of methanol is preferred.

The photochemical addition of methanol to stilbene (**1**) and its substituted derivatives involves two distinct, competitive pathways; i.e.: (*i*) Rearrangement *via* an 1,2-hydrogen shift, affording an intermediate carbene **13**, which is inserted into the O-H bond of methanol. (*ii*) Direct addition of methanol to the olefinic bond.

Both these pathways were shown to be operative in a very similar photochemical methanol addition reaction to 1,1-diphenylethene (**3**). In this case, carbene intermediate **13** arises *via* a 1,2-phenyl shift.

The insertion of carbene **13** into the O-H bond of methanol represents the second example of intermolecular trapping of a carbene intermediate in the photoisomerization of an alkene. The only other case, in which intermolecular insertion has been shown to compete appreciably with intramolecular insertion into the neighboring β-C-H bond, concerns the carbene intermediate formed on irradiation of tri-*tert*-butylethylene[5,8]. However, unlike **13** the latter carbene is subject to exceptional steric congestion, due to the presence of three *tert*-butyl substituents. The present work demonstrates, that extreme steric congestion is not a prerequisite for competition between intra- and intermolecular insertion of carbene intermediates, formed in the photoisomerization of an alkene.

In the case of stilbenes, the wavelength and substituent dependence of the rates of these competing pathways and the observation that both pathways give the same MeOH adduct, lead to the conclusion that the carbene pathway presumably involves a vibrationally unrelaxed twisted excited singlet (^{1}D) state.

The pathway of direct addition of methanol to the olefinic bond of stilbenes may involve either a twisted (^{1}D) or a planar (π,π^*) excited singlet state. The actual intermediacy of a twisted ^{1}D excited state emerges from its ability to rearrange to carbene **13**. The possibility of concerted addition of methanol to a planar (π,π^*) state of stilbenes emerges from the ability of the obligatory planar 1,2-diphenylcyclopentene (**2**) to undergo photochemical addition of methanol at roughly the same rate as stilbene (**1**) itself.

Experimental evidence, excluding the involvement of highly polar, zwitterionic excited states in both the carbene and the direct pathway of photochemical methanol addition to stilbene has been presented.

Experimental section

Starting materials. *E*-stilbene (*E*-**1**) and 1,1-diphenylethene (**3**) were obtained commercially. 1,2-Diphenylcyclopentene (**2**)[25], 3,3′-dimethylstilbene (**6**), 4,4′-difluorostilbene (**7**), 4-methoxystilbene (**8a**), 4-methoxy-4′-methylstilbene (**8b**) and 4-methylstilbene (**8c**) were synthesized according to known[25,26] procedures. All starting materials were purified by recrystallisation, sublimation, distillation or column chromatography prior to use.

Irradiations. Preparative irradiations were performed in N_2-deaerated methanol (UV: Transmittance >95% at 254 nm), employing the following light sources: Philips UV-A TL (360 and 300 nm), Philips TUV G15T8 (254 nm) and Osram HNS 10 (185 nm; Suprasil irradiation vessel). For the evaluation of yield *vs.* time plots (Fig. 1 and 3), irradiations were carried out either with 50-mL samples, in a Rayonet RPR-100 photochemical reactor equipped with a merry-go-round or in an N_2-purged 200 mL irradiation vessel equipped with a liquid-cooled (MeOH, $-90 < T < 25$ °C) quartz finger and a sampling facility. In the latter case, 0.2-mL aliquots were taken at 2-min intervals and subsequently analyzed by GLC. Samples originating from irradiations in the presence of H_2SO_4 were neutralized with OH^--exchanged Dowex IRA-400 ion-exchange resin prior to injection.

General methods. Isolation of the photoproducts was achieved by TLC and column chromatography on silica gel (Merck 60, 70-230 mesh) employing CCl_4 or hexane-benzene (6:1) as the eluent. Solid components (e.g. **10a**) obtained in this way were recrystallized from MeOH. Compositions of photoproduct mixtures were determined by GLC, employing a HP 5790 gas chromatograph equipped with HP or Chrompack capillary columns, a HP 3390 recording integrator and a flame ionisation detector. The response of the detector was assumed to be proportional to the number of carbon atoms present in the component detected. Characterisation of the photoproducts involved ^{1}H-NMR (Bruker WH-90 (90 MHz) and WM-500 (500 MHz) spectrometers, internal reference: TMS), mass spectroscopy (VG 70-70 MS equipped with a GLC facility similar to that quoted above) and chemical synthesis of authentic samples. In several cases, values of δ, $\Delta\delta$ and J were obtained from a least-squares fit of these quantities into the experimental (AB-, ABX- or AB_2-type) NMR spectrum.

1-Methoxy-1,2-diphenylethane (4). Authentic **4** was prepared from 1,2-diphenylethanol in 70% yield[13]. NMR (90 MHz, $CDCl_3$): $\delta = 2.76 - 3.23$ ppm (m, AB of ABX, 2H) H_2, $H_{2'}$, $J_{2,2'} = 13.68$ Hz, $\delta = 2.88$ ppm H_2, $J_{1,2} = 5.98$ Hz, $\delta = 3.11$ ppm $H_{2'}$, $J_{1,2'} = 7.26$ Hz; $\delta = 3.18$ ppm (s, 3H) OCH_3; $\delta = 4.32$ ppm (t, X of ABX, 1H) H_1; $\delta = 7.08 - 7.34$ ppm (m, 10H) Ar H. CIMS (CH_4); *m/e* (rel. intensity): 209 (M+29($C_2H_5^+$)-32(MeOH), 11), 182 (16), 181 (M+1(H^+)-32 (MeOH), 100), 135 (M+1(H^+)-78(C_6H_6), 23), 121 ($PhCHOMe^+$, 71), 105 (11), 91 (12).

1-Deuterio-1-methoxy-1,2-diphenylethane (4-(1-*d*)). This compound was obtained *via* rearrangement of **3**. NMR (500 MHz, $CDCl_3$): $\delta = 2.877$ ppm (d, 1H) H_2, $J_{2,2'} = 13.82$ Hz; $\delta = 3.108$ ppm (d, 1H) $H_{2'}$; $\delta = 3.183$ ppm (s, 3H) OCH_3; $\delta = 7.08 - 7.33$ ppm (m, 10H) Ar H. GC-CIMS (CH_4); *m/e* (rel. intensity): 210 (11), 183 (15), 182 (M+1(H^+)-32(MeOH), 100), 136 (22), 122 ($PhCDOMe^+$, 57).

2-Deuterio-1-methoxy-1,2-diphenylethane (4-(2-*d*)). *Erythro*-4-(2-*d*): NMR (500 MHz, $CDCl_3$): $\delta = 2.866$ ppm (br. d) H_2, $J_{1,2} = 6.0$ Hz; $\delta = 3.183$ ppm (s) OCH_3; $\delta = 4.315$ ppm (br. d) H_1; $\delta = 7.08 - 7.33$ ppm (m) Ar H. *Threo*-4-(2-*d*): NMR (500 MHz, $CDCl_3$): $\delta = 3.095$ ppm (br. d) H_2, $J_{1,2} = 7.2$ Hz; $\delta = 3.183$ ppm (s) OCH_3; $\delta = 4.315$ ppm (br. d) H_1; $\delta = 7.08 - 7.33$ ppm (m) Ar H. GC-CIMS (CH_4; mixture of *Erythro*- and *Threo*-4-(2-*d*)); *m/e* (rel. intensity): 210 (12), 183 (16), 182 (M+1(H^+)-32(MeOH), 100), 136 (13), 121 (65), 106 (7).

1-Methoxy-1,2-diphenylcyclopentane (MeOH adduct of diphenylcyclopentene, 2). NMR (90 MHz, $CDCl_3$): $\delta = 1.77 - 2.46$ ppm (m, 6H) H_3, H_4, H_5; $\delta = 3.05$ ppm (s, 3H) OCH_3; $\delta = 3.1 - 3.5$ ppm (m, 1H) H_2; $\delta = 6.69 - 7.13$ ppm (m, 10H) Ar H. GC-CIMS (CH_4); *m/e* (rel. intensity):

253 (M+1(H^+), 5), 252 (M^+, 10), 250 (6), 222 (19), 221 (100), 220 (14), 175 (30), 147 (18), 145 (18), 143 (30), 117 (72), 91 (13).

1-Methoxy-1,2-di(*m*-tolyl)ethane (MeOH adduct of 6, Table 1). NMR (90 MHz, $CDCl_3$): δ = 2.31 ppm (s, 3H) 1-(*m*-$CH_3C_6H_4$); δ = 2.35 ppm (s, 3H) 2-(*m*-$CH_3C_6H_4$); δ = 2.70 - 3.17 ppm (m, AB of ABX, 2H) H_2, $H_{2'}$, $J_{2,2'}$ = 13.73 Hz, δ = 2.83 ppm H_2, $J_{1,2}$ = 5.26 Hz, δ = 3.03 ppm $H_{2'}$, $J_{1,2'}$ = 7.90 Hz; δ = 3.17 ppm (s, 3H) OCH_3; δ = 4.27 ppm (q, X of ABX, 1H) H_1; δ = 6.87 - 7.29 ppm (m, 8H) Ar H. GC-CIMS (CH_4); *m/e* (rel. intensity): 237 (12), 210 (17), 209 (M+1(H^+)-32(MeOH), 100), 149 (13), 136 (5), 135 (47), 119 (4), 105 (4).

1-Deuterio-1-methoxy-1,2-di(*p*-fluorophenyl)ethane (MeOD adduct of 7 (Scheme 2, R_1 = R_2 = F), *via* carbene pathway, Table 2). NMR (90 MHz, $CDCl_3$): δ = 2.71 - 3.15 ppm (q, AB, 2H) H_2, $H_{2'}$, $J_{2,2'}$ = 13.6 Hz, δ = 2.81 ppm H_2, δ = 3.05 ppm $H_{2'}$; δ = 3.17 ppm (s, 3H) OCH_3; δ = 6.74 - 7.31 ppm (m, 8H) Ar H.

2-Deuterio-1-methoxy-1,2-di(*p*-fluorophenyl)ethane (MeOD adduct of 7, *via* direct pathway, Table 3). NMR (90 MHz, $CDCl_3$): *Erythro*-isomer: δ = 2.79 ppm (br. d, 1H) H_2, $J_{1,2}$ = 6.2 Hz; δ = 3.17 ppm (s, 3H) OCH_3; δ = 4.24 ppm (br. d, 1H) H_1; δ = 6.74 - 7.31 ppm (m, 8H) Ar H. *Threo*-isomer: δ = 3.00 ppm (br. d, 1H) H_2, $J_{1,2}$ = 7 Hz; δ = 3.17 ppm (s, 3H) OCH_3; δ = 4.21 ppm (br. d, 1H) H_1; δ = 6.74 - 7.31 ppm (m, 8H) Ar H.

1-Methoxy-1-phenyl-2-(*p*-methoxyphenyl)ethane (9a, hypothetical *anti*-Markovnikov MeOH adduct of 8a). The Grignard reaction[26] of *p*-methoxybenzylmagnesiumbromide and benzaldehyde afforded 2-(*p*-methoxyphenyl)-1-phenylethanol, which was converted its Li-salt by treatment of the THF solution with a stoichiometric quantity of n-BuLi at 0 °C. Following the addition of an excess of MeI, this solution was refluxed for 3 hrs.. Evaporation of the solvent afforded a yellow residue, which was boiled with CCl_4 and filtered. The resulting filtrate was concentrated to *ca.* 2 mL and subsequently purified by column chromatography, affording **9a** (Purity (GLC, NMR): 95%) as a colourless oil in 60% overall yield. Elemental analysis: Calculated for $C_{16}H_{18}O_2$: C: 79.31%, H: 7.49%. Found: C: 78.76%, H: 7.54%. NMR (90 MHz, $CDCl_3$): δ = 2.68 - 3.18 ppm (m, AB of ABX, 2H) H_2, $H_{2'}$, $J_{2,2'}$ = 13.9 Hz, δ = 2.82 ppm H_2, $J_{1,2}$ = 6.12 Hz, δ = 3.04 ppm $H_{2'}$, $J_{1,2'}$ = 7.38 Hz; δ = 3.18 ppm (s, 3H) $CHOCH_3$; δ = 3.72 ppm (s, 3H) *p*-$CH_3OC_6H_4$; δ = 4.26 ppm (t, X of ABX, 1H) H_1; δ = 6.70 - 7.05 ppm (q, AB, 4H) *p*-$CH_3OC_6H_4$, $J_{ortho,meta}$= 8.46 Hz, δ = 6.76 ppm *meta*-H, δ = 6.99 ppm *ortho*-H; δ = 7.14 - 7.39 ppm (m, 5H) C_6H_5. GC-CIMS (CH_4); *m/e* (rel. intensity): 243 (M+1(H^+), 7), 242 (M^+, 28), 212 (7), 211 (45), 165 (10), 122 ($MeOC_6H_4Me^{\cdot+}$, 68), 121 ($MeOC_6H_4CH_2^+$, 100), 107 (7), 106 (12), 105 (19), 91 (44), 78 (28), 77 (63).

1-Methoxy-1-phenyl-2-(*p*-tolyl)ethane (9c). NMR (90 MHz, $CDCl_3$): δ = 2.30 ppm (s, 3H) $CH_3C_6H_4$; δ = 2.72 - 3.22 ppm (AB of ABX, 2H) H_2, $H_{2'}$, $J_{2,2'}$ = 13.8 Hz, δ = 2.85 ppm H_2, $J_{1,2}$ = 5.87 Hz, δ = 3.07 ppm $H_{2'}$, $J_{1,2'}$ = 7.36 Hz; δ = 3.18 ppm (s, 3H) OCH_3; δ = 4.29 ppm (t, X of ABX, 1H) H_1; δ = 7.0 - 7.4 ppm (m, 9H) Ar H.

1-Methoxy-2-phenyl-1-(*p*-methoxyphenyl)ethane (10a). This compound was prepared from *p*-methoxybenzaldehyde and benzylmagnesiumbromide according to the procedure outlined for

9a. Contrary to the latter, crude **10a** was isolated as a solid which was readily purified by crystallisation from MeOH (10 mL g^{-1}). Yield: 70%, as colourless crystals of m.p. 51-52 °C and of 99.5% (GLC) purity. Elemental analysis: Calculated for $C_{16}H_{18}O_2$: C: 79.31%, H: 7.49%. Found: C: 79.25%, H: 7.56%. NMR (90 MHz, $CDCl_3$): δ = 2.73 - 3.24 ppm (m, AB of ABX, 2H) H_2, $H_{2'}$, $J_{2,2'}$ = 13.61 Hz, δ = 2.86 ppm H_2, $J_{1,2}$ = 6.19 Hz, δ = 3.11 ppm $H_{2'}$, $J_{1,2'}$ = 7.31 Hz; δ = 3.15 ppm (s, 3H) $\mathrm{CHOC}H_3$; δ = 3.78 ppm (s, 3H) $p\text{-}CH_3\mathrm{OC_6H_4}$; δ = 4.26 ppm (t, X of ABX, 1H) H_1; δ = 6.78 - 7.18 ppm (q, AB, 4H) $p\text{-}\mathrm{CH_3OC_6}H_4$, $J_{ortho,meta}$= 8.50 Hz, δ = 6.84 ppm *meta*-H, δ = 7.13 ppm *ortho*-H; δ = 6.99 - 7.28 ppm (m, 5H) $\mathrm{C_6}H_5$. GC-CIMS (CH_4); *m/e* (rel. intensity): 212 (5), 211 (26), 165 (6), 153 (7), 152 ($\mathrm{MeOC_6H_4CH_2OMe}^{\cdot+}$, 59), 151 ($\mathrm{MeOC_6H_4CHOMe}^{+}$, 100), 136 (29), 135 (60), 121 (9), 108 ($\mathrm{MeOC_6H_5}^{\cdot+}$, 14), 92 (12), 91 (40), 78 (9), 77 (16).

1-Deuterio-1-methoxy-2-phenyl-1-(*p*-methoxyphenyl)ethane (10a-(1-*d*), MeOD adduct of 8a, *via* carbene pathway, Table 2). NMR (90 MHz, $CDCl_3$): δ = 2.74 - 3.18 ppm (m, AB, 2H) H_2, $H_{2'}$, $J_{2,2'}$ = 13.5 Hz, δ = 2.84 ppm H_2, δ = 3.08 ppm $H_{2'}$; δ = 3.15 ppm (s, 3H) $\mathrm{CHOC}H_3$; δ = 3.78 ppm (s, 3H) $p\text{-}CH_3\mathrm{OC_6H_4}$; δ = 6.77 - 7.16 ppm (q, AB, 4H) $p\text{-}\mathrm{CH_3OC_6}H_4$, $J_{ortho,meta}$= 8.5 Hz, δ = 6.82 ppm *meta*-H, δ = 7.11 ppm *ortho*-H; δ = 7.00 - 7.30 ppm (m, 5H) $\mathrm{C_6}H_5$.

2-Deuterio-1-methoxy-2-phenyl-1-(*p*-methoxyphenyl)ethane (10a-(2-*d*), MeOD adduct of 8a, *via* direct pathway, Table 3). NMR (90 MHz, $CDCl_3$): *Erythro*-isomer: δ = 2.84 ppm (br. d, 2H) H_2, $J_{1,2}$ = 6.3 Hz; δ = 3.15 ppm (s, 3H) $\mathrm{CHOC}H_3$; δ = 3.79 ppm (s, 3H) $p\text{-}CH_3\mathrm{OC_6H_4}$; δ = 4.26 ppm (br. d, 1H) H_1; δ = 6.77 - 7.16 ppm (q, AB, 4H) $p\text{-}\mathrm{CH_3OC_6}H_4$, $J_{ortho,meta}$= 8.5 Hz, δ = 6.82 ppm *meta*-H, δ = 7.11 ppm *ortho*-H; δ = 7.00 - 7.30 ppm (m, 5H) $\mathrm{C_6}H_5$. *Threo*-isomer: δ = 3.08 ppm (br. d, 2H) H_2, $J_{1,2}$ = 7 Hz; δ = 3.15 ppm (s, 3H) $\mathrm{CHOC}H_3$; δ = 3.79 ppm (s, 3H) $p\text{-}CH_3\mathrm{OC_6H_4}$; δ = 4.25 ppm (br. d, 1H) H_1; δ = 6.77 - 7.16 ppm (q, AB, 4H) $p\text{-}\mathrm{CH_3OC_6}H_4$, $J_{ortho,meta}$= 8.5 Hz, δ = 6.82 ppm *meta*-H, δ = 7.11 ppm *ortho*-H; δ = 7.00 - 7.30 ppm (m, 5H) $\mathrm{C_6}H_5$.

1-Methoxy-1-(*p*-methoxyphenyl)-2-(*p*-tolyl)ethane (10b). NMR (90 MHz, $CDCl_3$): δ = 2.29 ppm (s, 3H) $CH_3\mathrm{C_6H_4}$; δ = 2.70 - 3.21 ppm (m, AB of ABX, 2H) H_2, $H_{2'}$, $J_{2,2'}$ = 13.8 Hz, δ = 2.83 ppm H_2, $J_{1,2}$ = 6.3 Hz, δ = 3.07 ppm $H_{2'}$, $J_{1,2'}$ = 7.2 Hz; δ = 3.16 ppm (s, 3H) $\mathrm{CHOC}H_3$; δ = 3.80 ppm (s, 3H) $p\text{-}CH_3\mathrm{OC_6H_4}$; δ = 4.25 ppm (t, X of ABX, 1H) H_1; δ = 6.80 - 7.20 ppm (q, AB, 4H) $p\text{-}\mathrm{CH_3OC_6}H_4$, $J_{ortho,meta}$= 8.47 Hz, δ = 6.85 ppm *meta*-H, δ = 7.15 ppm *ortho*-H; δ = 7.01 ppm (s, 4H) $p\text{-}\mathrm{CH_3C_6}H_4$; *ortho*- and *meta*-H's accidentally having identical δ-values. GC-CIMS (CH_4); *m/e* (rel. intensity): 253 (11), 226 (17), 225 (M+1(H^+)-32(MeOH), 100), 165 (6), 151 ($\mathrm{MeOC_6H_4CHOMe}^{+}$, 34), 149 (29), 135 (12).

1-Methoxy-2-phenyl-1-(*p*-tolyl)ethane (10c). NMR (90 MHz, $CDCl_3$): δ = 2.34 ppm (s, 3H) $CH_3\mathrm{C_6H_4}$; δ = 2.74 - 3.24 ppm (m, AB of ABX, 2H) H_2, $H_{2'}$, $J_{2,2'}$ = 13.7 Hz, δ = 2.88 ppm H_2, $J_{1,2}$ = 5.96 Hz, δ = 3.10 ppm $H_{2'}$, $J_{1,2'}$ = 7.34 Hz; δ = 3.17 ppm (s, 3H) OCH_3; δ = 4.29 ppm (t, X of ABX, 2H) H_1; δ = 7.0 - 7.4 ppm (m, 9H) Ar H. GC-CIMS (CH_4); *m/e* (rel. intensity): 195 (M+1(H^+)-32(MeOH), 7), 136 (11), 135 (100), 121 (25), 119 (7), 105 (6), 91 (22), 77 (7).

1-Methoxy-1,1-diphenylethane (11). This compound was synthesized according to the literature[13]. NMR (90 MHz, $CDCl_3$): δ = 1.86 ppm (s, 3H) CH_3; δ = 3.16 ppm (s, 3H) OCH_3; δ =

7.13 - 7.43 ppm (m, 10H) Ar H. CIMS (CH_4); *m/e* (rel. intensity): 209 (8), 198 (6), 197 (M+1(H^+)-16(CH_4), 38), 182 (13), 181 (M+1(H^+)-32(MeOH), 82), 136 (10), 135 (100).

2-Deuterio-1-methoxy-1,1-diphenylethane (11-(2-*d*)). NMR (90 MHz, $CDCl_3$): δ = 1.85 ppm (br. s, 2H) CH_2D; δ = 3.16 ppm (s, 3H) OCH_3; δ = 7.1 - 7.4 ppm (m, 10H) Ar H. GC-CIMS (CH_4); *m/e* (rel. intensity): 210 (8), 197 (M+1(H^+)-17(CH_3D), 28), 183 (17), 182 (76), 137 (11), 136 (100).

2-Methoxy-1,1-diphenylethane (hypothetical *anti*-Markovnikov MeOH adduct of 3). NMR (90 MHz, $CDCl_3$)[13]: δ = 3.37 ppm (s, 3H) OCH_3; δ = 3.87 - 4.37 ppm (m, AB_2, 3H) H_1, H_2, δ = 3.92 ppm H_2, δ = 4.29 ppm H_1, $J_{1,2}$ = 7.32 Hz; δ = 7.25 ppm (br. s, 10H) Ar H. GC-CIMS (CH_4); *m/e* (rel. intensity): 209(11), 182 (16), 181 (100), 167 (57), 165 (7), 135 (15).

1,1-diphenylethane (12). Authentic **12** was obtained by catalytic hydrogenation of **3**. NMR (90 MHz, $CDCl_3$)[27]: δ = 1.64 ppm (d, 3H) H_2, $J_{1,2}$ = 7.32 Hz; δ = 4.15 ppm (q, 1H) H_1; δ = 7.23 ppm (s, 10H) Ar H. CIMS (CH_4); *m/e* (rel. intensity): 211 (8), 184 (14), 183 (100), 105 (42). EIMS; *m/e* (rel. intensity)[28]: 183 (3), 182 (18), 168 (5), 167 (36), 165 (5), 106 (10), 105 (100).

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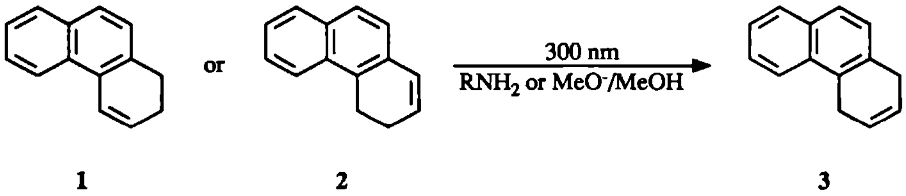
Chapter 3: Mechanism of the amine-promoted photochemical 1,3-H shift in dihydrophenanthrenes.

Introduction

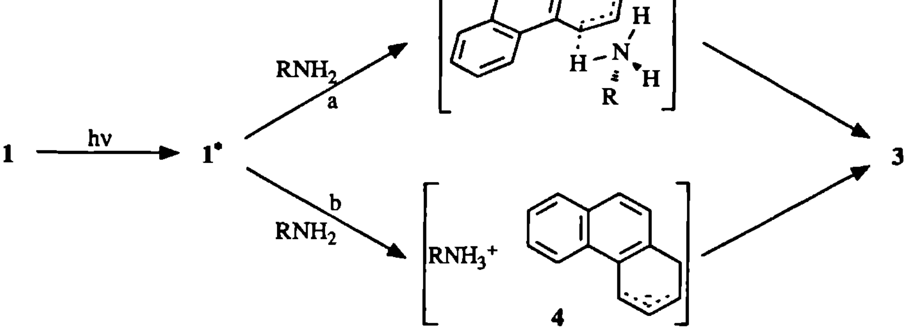
On irradiation of stilbene in the presence of a base, 1,2- (1,2-DHP, **1**) and 3,4-dihydrophenanthrene (3,4-DHP, **2**) have been identified[1,2] as intermediates in the pathway leading from the primary cyclization product 4a,4b-DHP to one of the main end-products; viz. 1,4-DHP (**3**). Subsequent examination of authentic **1** and **2** confirmed[1] that these compounds are readily converted into **3** by a formal photochemical 1,3-H shift (Scheme 1). The presence of a base, e.g. MeO$^-$ in MeOH or, preferably, a primary alkyl amine appeared to be an essential prerequisite for this reaction. Similar amine-promoted photochemical 1,3-H shifts have been observed with several other compounds[1-5].

Scheme 1



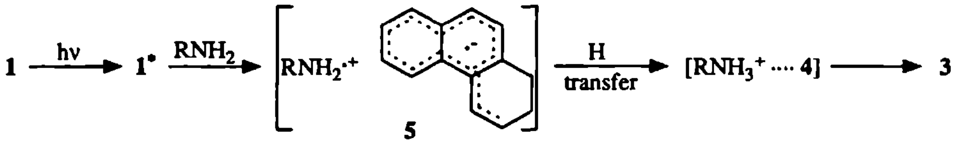
As far as the mechanism of this photoreaction is concerned, the results[1,2] of irradiation of **1** and **2** in *n*-propylamine and in *t*-BuOK/MeOD indicate irreversible formation of **3**, presumably *via*

Scheme 2



deprotonation-protonation reactions involving the base and excited **1** (Scheme 2) or **2**. Whether these deprotonation and protonation reactions occur simultaneously (Scheme 2, route a), as has been proposed for the 4a,4b-DHP's formed by photocyclization of diphenylcyclopentene[1,2] and *cis*-2-styrylbenzo[c]phenanthrene[6], or take place in separate steps *via* an intermediate ion-pair (Scheme 2, route b), is not known. The observation that in **3**, originating from the irradiation of stilbene, the pattern and extent of D incorporation are identical in CH_3O^-/CH_3OD and CD_3O^-/CD_3OD under otherwise identical conditions[1], provides indirect evidence for the absence of radical steps in the photochemical 1,3-H shift of **1** and **2** into **3**. This conclusion needs however, not to be valid with *n*-$PrNH_2$ or other amines as promotors. Many functionalized amines, including primary amines like ethylenediamine and ethanolamine possess a low basicity and a low vertical ionization potential (IP_v). Hence, they should favor the formation of radical ion-pairs by electron-transfer from the amine to an excited species. Excited stilbene in secondary and tertiary amines presents a well-documented example[7] of this behaviour. The possibility of an amine-promoted photochemical 1,3-H shift in **1**, **2** and dihydronaphthalenes *via* an intermediate radical ion-pair (**5**, Scheme 3) should therefore be considered seriously. In this connection, it should be mentioned that an example of a formal 1,3-H shift, involving a radical abstraction-recombination process has been reported[8].

Scheme 3

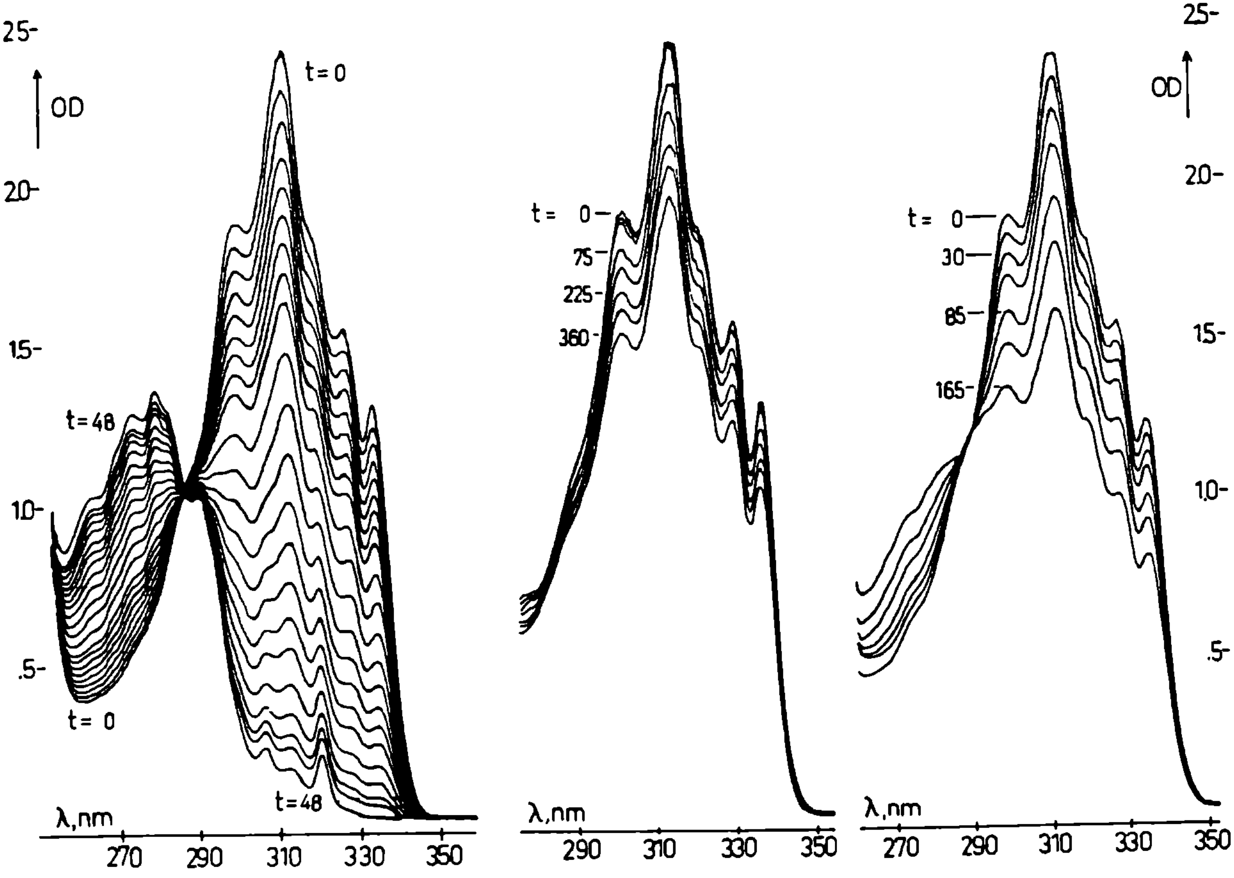


In the following sections the results of a systematic study into the mechanism of the amine-promoted photochemical 1,3-H shift of **1** and **2** to **3** will be presented. The photoreactivity of **1** and **2** and the quantum yield of **3** have been evaluated in various primary, secondary and tertiary amines. Mixtures of these amines with alcohols or with acetonitrile were employed to elucidate the influence of solvent polarity. In corroboration of the conclusions emerging from these experiments, fluorescence spectroscopy and Stern-Volmer quenching experiments as well as time-resolved UV/VIS absorption, fluorescence emission and conductivity measurements have been performed.

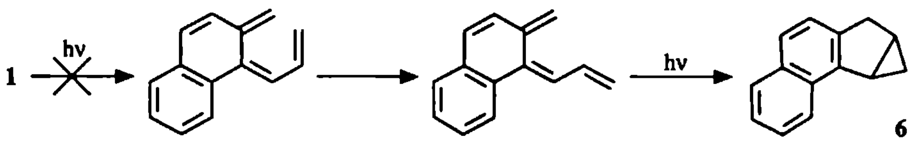
Results and discussion

Irradiation in primary amines. As a starting experiment, the photochemical 1,3-H shift of **1** or **2** into **3**, promoted by *n*-propylamine, was carefully reexamined. The progress of this reaction

Fig. 1. UV spectra from the monochromatic irradiation (313 nm) of 1,2-dihydrophenanthrene (1, 2×10^{-4} M) in neat *n*-PrNH$_2$ (a), in neat Et$_3$N (b) and in a mixture of Et$_3$N and MeOH (6:25 v/v) (c) as a function of the irradiation time (t, min).



Scheme 4



for **1** in neat *n*-$PrNH_2$, monitored by UV spectroscopy, is shown in Fig. 1a. The occurrence of a sharp, well-defined isosbestic point is indicative of a very clean photoconversion of **1** into **3**. This conclusion is supported by the perfect match of the molar extinction coefficients extracted from the UV spectrum of entirely converted **1** with those of authentic **3**[1,2]. Subsequent GLC analysis confirmed the presence of **3** in quantitative yield (99.5%, at 99.7% conversion of **1**). The essential role of the amine in the photochemical 1,3-H shift was confirmed by the complete photostability of **1** and **2** in MeOH and hexane under otherwise identical irradiation conditions. Not even traces of naphthobicyclo[3.1.0]hex-2-enes (**6**, Scheme 4), which should be formed from a photochemical ring opening reaction of **1** and **2** similar to that observed in 1,2-dihydronaphthalenes[9], was found

Table 2. Monochromatic irradiation (313 nm) of 1,2- (**1**) and 3,4-dihydrophenanthrene (**2**) and the deuterated analogs **1**-(2,2-d_2) and **2**-(3,3-d_2) in the presence of amines. Percentage of D incorporation at C(1)+C(4) in the starting material, 1,4-dihydrophenanthrene (**3**) and the side products phenanthrene (Phe) and 1,2,3,4-tetrahydrophenanthrene (THP).

compound	solvent	D-incorporation (%)				k_H/k_D
		DHP	**3**	Phe	THP	
1	*n*-$PrND_2$	< 3	22			0.8
2	*n*-$PrND_2$	< 3	20			0.8
1-(2,2-d_2)	*n*-$PrNH_2$	100 (2D)	76 (1D) 24 (2D)			1.4
2-(3,3-d_2)	*n*-$PrNH_2$	100 (2D)	75 (1D) 25 (2D)			1.3
1	*n*-$PrNH_2$/MeOD 1 : 2 (v/v)	< 3	28		30 (1D)	
2	*n*-$PrNH_2$/MeOD 1 : 2 (v/v)	< 3	26	10	20 (2D)	
1	Et_3N/MeOD 1 : 2 (v/v)	< 3	11	11	47 (1D)	
2	Et_3N/MeOD 1 : 2 (v/v)	< 3	14	15	6 (2D)	

	conversion (%)	solvent	IP$_v$ [12]	pK$_a$ [13]	product yields (%)			Φ(3)
					3	Phe	polymer	
a 1	100 20	n-PrNH$_2$	9.38	10.71	97.5 > 99.5	2.5 < 0.5		0.28
b 1	< 20	n-PrND$_2$	9.3	11.1	100			0.35
c 1	< 20	n-PrNH$_2$/MeOD (1 : 2 v/v)			100			0.11
d 1	< 20 74	 NH$_2$	8.8	8.66	100 > 98	< 2		0.058
e 1	< 20	H$_2$NCH$_2$CH$_2$NH$_2$	7.64	9.96	100			0.25
f 1	< 20	H$_2$NCH$_2$CH$_2$OH		9.50	100			0.21
g 1	< 10	NH$_3$ (16 %)/MeOH		9.25	100			0.025
h 1	< 10	N$_2$H$_4$/MeOH (2 : 1 v/v)		8.23	100			0.029
i 1	33	n-PrNH$_2$/MeOH (1 : 2 v/v)			91	9		0.095
j 1	30	Et$_3$N	8.07	11.01	50		30	0.011
k 1	26	Et$_3$N/t-BuOH (1 : 2 v/v)			77	3	20	0.018
l 1	< 10	Et$_3$N/n-BuOH (1 : 2 v/v)			100			0.042
m 1	< 10	Et$_3$N/EtOH (1 : 2 v/v)			100			0.050
n 1	6-23	(1 : 1 v/v) Et$_3$N/MeOH (1 : 2 v/v) (6 : 25 v/v)			90-100	0-10		0.069 0.083 0.095
o 1	10	Et$_3$N/MeCN (1 : 1 v/v)			27	10	63	0.02
p 1	< 20	(H$_2$N)$_2$C=NH/EtOH (1.4 M) (0.7 M)		13.6	100			0.10 0.05
q 1	80	Et$_2$NH	8.65	10.49	85		15	0.18
r 2	20	n-PrNH$_2$	9.38	10.66	100			0.26
s 2	20	n-PrND$_2$	9.3	11.2	100			0.33
t 2	74	 NH$_2$	8.8	8.66	100			0.057
u 2	20	(H$_2$N)$_2$C=NH(1.4 M)/EtOH		13.6	100			0.10
v 2	23	Et$_3$N	8.07	11.01	50		30	0.01

Table 1. (p. 30) Monochromatic irradiation of **1** or **2** in the presence of amines: Vertical ionization potentials (IP_v), base strenghts (pK_a), chemical yields of 1,4-dihydrophenanthrene, (**3**), Phenanthrene (Phe) and polymeric photoproducts and quantum yields (Φ(**3**)) of **3**.

in either of these solvents. The reluctance of both **1** and **2** to undergo this photoreaction, might be associated with the UV absorption characteristics of these compounds.

Irradiation of **1** or **2** in the presence of other primary amines (RNH_2) afforded **3** again *via* a clean 1,3-H shift. As can be seen from Table 1 (p. 30), the quantum yield of this reaction is highly dependent on the R group of the amine. Inorganic amines, e.g. NH_3 in methanol (Table 1, entry g **1**) are equally effective as primary alkyl amines. As judged from the roughly equal quantum yields of **3** in *n*-propylamine (Table 1, entry a **1**), ethylenediamine (Table 1, entry e **1**) and the highly polar and viscous ethanolamine (Table 1, entry f **1**), the influence of the polarity and viscosity of primary amines on the photochemical 1,3-H shift of **1** or **2** into **3** is marginal.

According to the Tables 1 (Entries a **1** and b **1**, r **2** and s **2**) and 2 ($k_H/k_D = 0.8$), *n*-$PrND_2$ is a more effective promoter of the 1,3-H shift than *n*-$PrNH_2$. Hence, formation of **3** by a concerted, amine-mediated 1,3 hydrogen transfer in excited **1** or **2** (Scheme 1) for which an isotope effect close to the theoretical limit should be expected[10], can be ruled out. This conclusion is consistent with the partial D incorporation (Table 2, p. 29) observed in **3**, originating from irradiations of both **1** and **2** in *n*-$PrND_2$ and of **1** and **2** deuterated at the allylic position (**1**-(2,2-d_2) and **2**-(3,3-d_2), Scheme 5) in *n*-$PrNH_2$. The irreversibility of the photoprocess leading to **3** is demonstrated by the lack of D incorporation (Table 2) in **1** and **2**, recovered from solutions irradiated in *n*-$PrND_2$ and agrees with the predicted[1,2,11] thermodynamic stability of **3**, relative to **1** and **2**.

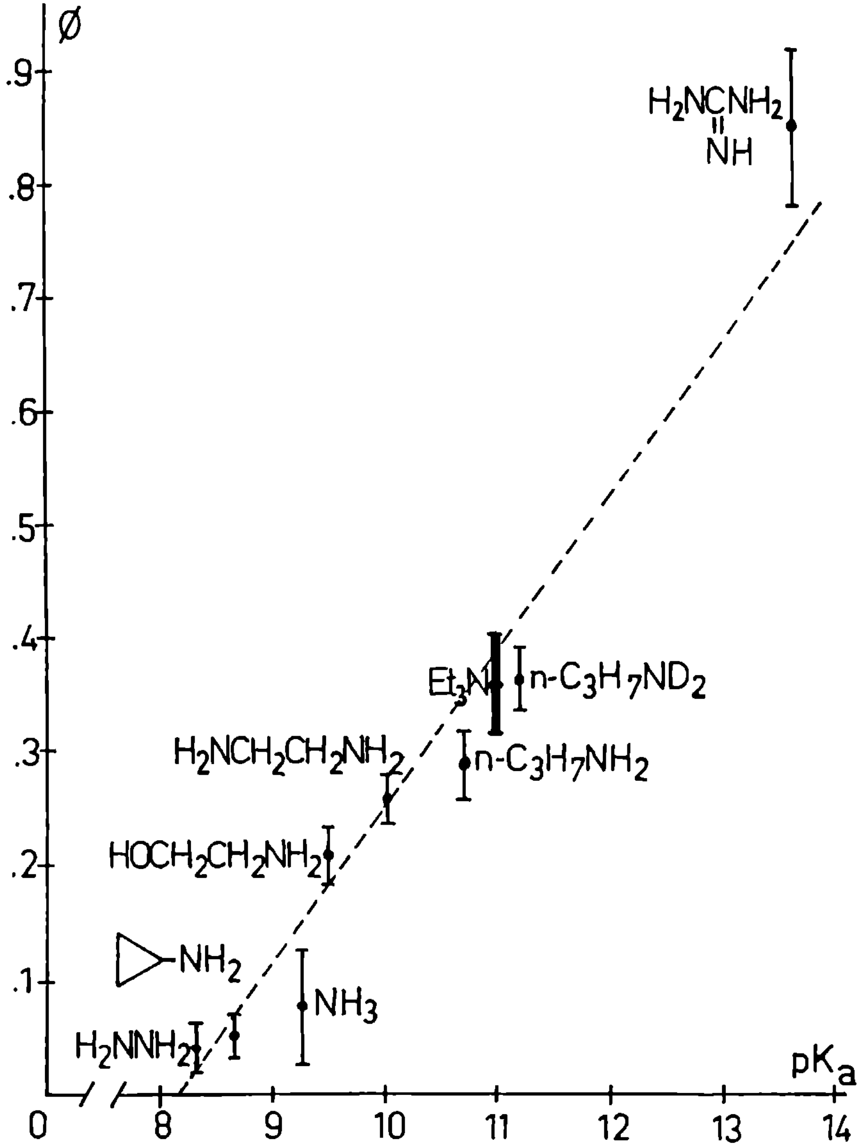
1-(2,2-d_2)

Scheme 5

2-(3,3-d_2)

For a 1,3-H shift involving nonconcerted hydrogen transfer, a relation between the quantum yield of **3** and relevant physical properties of the amine follows from the mechanism of hydrogen transfer. Assuming a pair of radical ions as an intermediate in the pathway to **3** (Scheme 3), the quantum yield will be determined by the energy of electron transfer from the amine to the excited DHP. A correlation between the quantum yield of **3** from **1** or **2** and the IP_v of the amine will then exist. On the other hand, when the intermediacy of a regular ion-pair, emerging from deprotonation of excited 1,2-DHP (**2**) by the amine is assumed (Scheme 2, route b), the quantum yield of **3** will be correlated with the pK_a of the conjugate acid of the amine.

Fig. 2. Monochromatic irradiation (313 nm) of 1,2-dihydrophenanthrene (1) in the presence of primary amines: Quantum yield (Φ(3)) of 1 ,4-dihydrophenanthrene (3) *vs.* amine basicity (pK_a).



Both these correlations have been tested for the primary amines indicated in Table 1. Values of the quantum yield of **3** (Table 1) obtained on irradiation of **1** and **2** in the presence of these amines were normalized to the concentration of *n*-$PrNH_2$ as the neat liquid, assuming that 1,3-H shift obeys first-order kinetics with respect to the amine. This assumption was verified for **1** in solutions of *n*-$PrNH_2$ (Table 1, entries a **1** and c **1**) and guanidine (Table 1, entry p **1**).

From a plot of the quantum yield of **3** *vs.* the IP_v[12] of the primary amine, it emerged that a linear relationship does not exist. On the other hand, Fig. 2 reveals a linear dependence of the quantum yield of **3** on the basicity (pK_a of RNH_3^+)[13] for primary amines with a good correlation coefficient (r^2 = 0.9). These results prove the deprotonation of excited **1** or **2** by the primary amine (Scheme 2, route b) to be the rate-determining step in the 1,3-H shift leading to **3**. The high correlation coefficient is apparently in accordance with the argument[14] that, unlike the pK_a-values themselves, differences in pK_a-values of primary alkyl ammonium ions (RNH_3^+) should not be very solvent dependent.

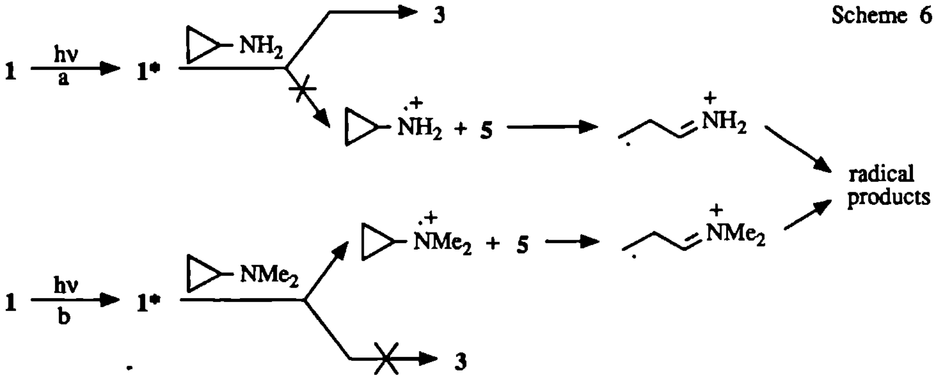
The observation that *n*-$PrND_2$ rather than *n*-$PrNH_2$ is the more effective promoter of the 1,3-H shift can be attributed to the greater basicity of *n*-$PrND_2$[15]. The isotope effects (table 2, obtained with 2,2-dideuterio-1,2-DHP (**1**-(2,2-d_2)) and 3,3-dideuterio-1,2-DHP (**2**-(3,3-d_2)) (Scheme 5) in *n*-$PrNH_2$ appear to be far below the values normally obtained for reactions involving rupture of a C-H(D) bond as a rate-determining step. It should however be realized, that the present case concerns C-H(D) bond rupture in an excited species. In view of the absence of a thermal reaction of **1** or **2** into **3**[1,2], it is evident that excitation enhances the acidity of **1** and **2**[16a] to the extent (*ca.* 25 pK_a-units) necessary[16b] to allow deprotonation at the allylic position by relatively weakly basic primary amines. The conclusion, that this enormous enhancement in acidity is caused by a reduced strength of the allylic C-H(D) bonds in excited **1** and **2** is obvious. The associated decrease in the energy difference of the C-D and C-H stretching vibrations, then accounts for the low isotope effects observed in the present case.

The low percentage of D incorporation in **3** obtained from irradiations of **1** and **2** in neat *n*-$PrND_2$ (Table 2) indicates that protonation of the anion **4** (Scheme 2, route b) presumably involves a contact, rather then a solvent-separated ion-pair and proceeds much faster than H-D exchange between RND_2H^+ and RND_2. In view of this result and the low acidity of the free amine, protonation of anion **4** by RND_2 can be rejected as a mechanism to **3**. In this respect, the reactivity of excited **1** and **2** in primary amines parallels that of other DHP's[1,2] e.g. *trans*-16d,16e-dihydrohexahelicene[6] in these amines. Irradiation of **1** or **2** in a mixture of *n*-$PrNH_2$ and CH_3OD (molar ratio: 0.5) instead of neat *n*-$PrND_2$ gave a substantially higher D incorporation in **3** (Table 2), presumably as a consequence of direct protonation of anion **4** (Scheme 2, route b) by the more acidic CH_3OD molecules present in the solvent cage. In this context, it should be emphasized that photoconversion of **1** or **2** in mixtures of *n*-$PrNH_2$ and CH_3OD proceeds without concomitant H-D exchange between these solvents, as established by NMR. A further indication of the reluctance of anion **4** (Scheme 2, route b) to escape from the solvent cage emerges from the absence of transient electric conductivity on nanosecond excitation

(308 nm) of **1** and **2**, in either neat or methanolic *n*-PrNH$_2$. Moreover, no transient UV/VIS absorption attributable to the DHP-anion could be detected under these conditions. Taking the obviously high quantum yield of formation of the [RNH$_3^+$ 4] ion-pair (Scheme 2, route b) into account, this result points to a life time below 10 ns of this ion-pair in neat and methanolic *n*-PrNH$_2$.

The reported[1,2] absence of radical reaction products in samples of **1** irradiated in the presence of primary amines or in CD$_3$O$^-$/CD$_3$OD contradicts obviously a rationalization of **3** in terms of a mechanism involving radical ions. Decisive proof for the inapplicability of this rationalization to the photochemical 1,3-H shift of **1** and **2** in primary amines emerged from the finding, that irradiation of either **1** or **2** in neat cyclopropylamine affords **3** quantitatively (Table 1, entries d 1, t 2), without concomitant decomposition of the amine. On the basis of reaction mechanisms assuming electron transfer from cyclopropylamine to excited **1** or **2**, extensive rearrangement of the resulting cyclopropylamine radical-cation should be expected (Scheme 6, pathway a)[17].

Scheme 6



Irradiation in secondary and tertiary amines. To obtain a qualitative picture of the relation between the effectivity of an amine as a promoter of the photochemical 1,3-H shift into 1,4-DHP (**3**) and the degree of N substitution, the irradiation experiment outlined in Fig. 1a was repeated with 1,2-DHP (**1**) in Et$_3$N. According to the results (Fig. 1b), the photochemistry of **1** in Et$_3$N is quite different from that in *n*-PrNH$_2$. From the absence of an isosbestic point at *ca.* 290 nm it can be concluded that the 1,3-H shift into **3** is not the major photoreaction of **1** in Et$_3$N. This was confirmed by GLC and UV analysis performed with samples, taken at *ca.* 10% conversion of the starting material **1** or **2**. In both of them, the yield of **3** was found to be only 50%, based on reacted starting material.

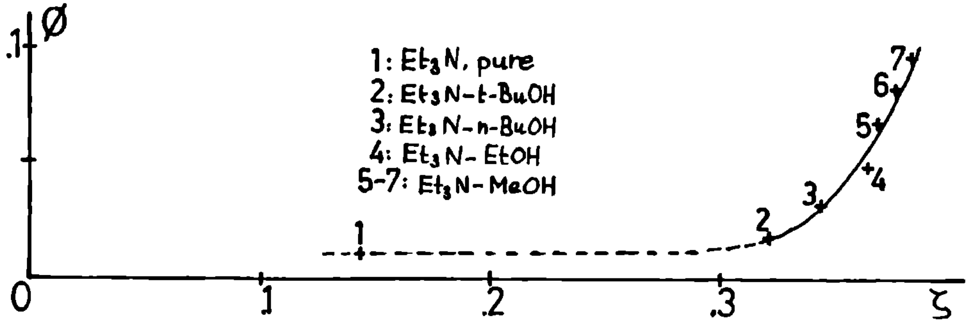
Considering the other photoproducts resulting from irradiation of **1** and **2** in neat Et$_3$N, the formation of phenanthrene (*m/e* 178) and 1,2,3,4-tetrahydrophenanthrene (*m/e* 182) in varying yields (5-30%, based on the amount of converted **1** or **2**) was demonstrated by GC-MS. Following irradiation and treatment with methyl iodide, *ca.* 20% of the contents of a sample obtained on 100% photoconversion of **1** in Et_3N could be extracted into D_2O. The NMR-spectrum of this extract suggested the presence of Et_3N-adducts of **1**, **2** and oligomers of these compounds in the original sample. The remainder (*ca.* 30%) of the photoproducts consisted of MeOH-insoluble polymers.

As far as formation of the photoproducts mentioned in the previous paragraph is concerned, the photochemistry of **1** and **2** in neat Et_3N resembles that reported[7] for stilbene under similar conditions. In analogy with the case of stilbene, the photoproducts arise presumably from radical reactions of excited **1** or **2** with Et_3N. This hypothesis is supported by various experimental results. Thus, the quantum efficiency of the 1,3-H shift into **3** (Table 1, entry j **1**) and of the reaction of starting material **1** ($\phi = 0.025$) in neat Et_3N turned out to be much smaller than in *n*-$PrNH_2$, despite the nearly equal pK_b-values reported[13] for these amines. Hence, in neat Et_3N, deprotonation by the amine according to Scheme 2 (route b) is not the only pathway for deactivation of excited **1** and **2**. The occurrence of extensive D incorporation (Table 2) in the phenanthrene and 1,2,3,4-tetrahydrophenanthrene originating from irradiations of **1** or **2** in Et_3N-MeOD mixtures is also in favor of a radical mechanism. On irradiation (300 nm, 3 hrs) of **1** (2×10^{-4} M) in N,N-dimethyl cyclopropylamine, significant decomposition of the amine occurs; **1** itself being converted into an intractable mixture of volatile and polymeric photoproducts (GLC) (Scheme 6, pathway b). Since N,N-dimethyl cyclopropylamine proved to be photostable in the absence of **1**, the observed breakdown of this amine is caused evidently by excited **1**. As outlined in Scheme 6 (pathway b) this conclusion points to electron abstraction from the N atom by excited **1**, leaving an unstable cyclopropylamine radical-cation. Decisive evidence for the occurrence of photochemically induced charge-transfer from Et_3N to excited **1** and **2** in neat Et_3N will be presented in the following section.

Considering that solvent polarities of tertiary amines are generally low and cover a limited range, it was decided to evaluate the influence of this parameter on the photochemistry of **1** and **2** in tertiary amines by quantum yield measurements in ROH-Et_3N (R = Me, Et, *n*-Bu, *t*-Bu) and MeCN-Et_3N mixtures.

The results, obtained in ROH-Et_3N mixtures (Fig. 3), indicate a drastic enhancement of the quantum efficiency of the 1,3-H shift, with increasing solvent polarity, quantum yields of **3** in MeOH-Et_3N mixtures (Table 1, entry n **1**) rivalling with those obtained in mixtures of MeOH/*n*-$PrNH_2$ (Table 1, entry c **1**) under similar conditions. Simultaneously, all photoreactions others than the 1,3-H shift to **3**, were found to become progressively more suppressed. The most convincing example showing both these trends, is presented in Fig. 1c, which clearly demonstrates that a mixture of Et_3N/MeOH (6 : 25, v/v) resembles primary amines (Fig. 1a) rather than neat Et_3N (Fig. 1b) in giving a clean, efficient photochemical 1,3-H shift of **1** into **3**. Assuming first-order kinetics for promotion of the photochemical 1,3-H shift by Et_3N in Et_3N/MeOH = 6 : 25 (v/v), normalization of the quantum yield of **3** observed in this medium (Table 1, entry n **1**) to the amine concentration (12.15 M, Fig. 2) in neat *n*-$PrNH_2$ yields a value of

Fig. 3. Monochromatic irradiation (313 nm) of 1,2-dihydrophenanthrene (**1**) in mixtures of Et_3N and various alcohols: Qantum yield (Φ(**3**)) of 1,4-dihydrophenanthrene formation *vs.* the solvent polarity parameter ζ (See eqn. 1 in Fig. 6).



0.33. This value fits excellently into the existing linear correlation between the basicity of primary amines and the quantum yield of the photochemical 1,3-H shift of **1** into **3** (Fig. 2). This result proves that in the presence of polar alcohols, the tendency of Et_3N to ionize is apparently small. Like primary amines Et_3N promotes the photochemical 1,3-H shift of **1** or **2** into **3** by a mechanism involving deprotonation of the excited DHP to an intermediate ion-pair (Scheme 2, route b) as the rate-determining step. The low percentage of D incorporation in **3**, formed on irradiation of **1** or **2** in Et_3N/MeOD provides additional support for this conclusion: On the analogy of **1** or **2** in *n*-$PrNH_2$, this result points to protonation of the DHP anion preferentially by Et_3NH^+, at a rate exceeding that of H-D exchange between Et_3NH^+ and MeOD.

Unlike *n*-$PrNH_2$, the tendency of Et_3N to undergo electron-transfer to excited **1** is apparent from the occurrence (Table 1, entry k 1) of radical reaction products in chemical yields up to 23%, on irradiation of **1** in Et_3N/ROH mixtures of low polarity. The ionization potentials (IP_v) of Et_3N (8.08 eV)[12] and *n*-$PrNH_2$ (9.38 eV)[12] are consistent with this trend.

In a 1 : 2 (v/v) Et_3N/MeCN mixture, the quantum yield of conversion of **1** ($\phi = 0.075$) was found to be three times higher than in neat Et_3N and also close to the value obtained with **1** in an equally polar Et_3N/MeOH 1 : 2 (v/v) mixture (Table 1, entry n 1). However, unlike alcohols, MeCN does not suppress the formation of radical reaction products observed in neat Et_3N, as shown by the low chemical yields of **3** observed on irradiation of **1** in neat and MeCN-containing Et_3N (Table 1, entries j 1 and o 1, respectively). It emerges, that, apart from a high solvent polarity common to both MeCN and ROH, alcohols exhibit an additional property which facilitates efficient promotion of the photochemical 1,3-H shift of **1** or **2** into **3** by Et_3N (Scheme 2, route b) and suppresses the concomitant formation of radical reaction products (Scheme 3).

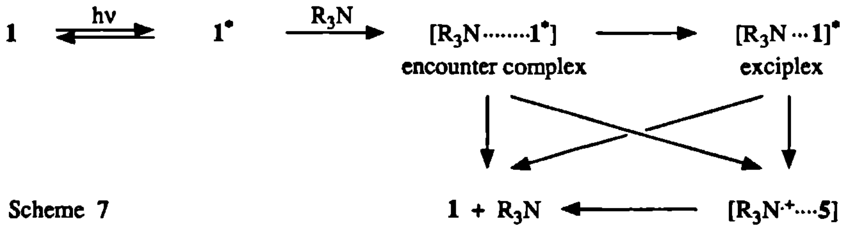
Considering the increase of IP_v in the order $Et_3N < Et_2NH <$ *n*-$PrNH_2$[12], the quantum and chemical yields of the 1,3-H shift in Et_2NH should be intermediate between those in Et_3N and *n*-$PrNH_2$. The experimental results obtained with **1** and **2** in neat Et_2NH are in agreement with this prediction, the quantum and chemical yields of **3** being *ca.* 0.15 and *ca.* 85%, respectively.

Fluorescence spectroscopy and quenching studies. In particular, these studies were aimed to elucidate the underlying causes of the essentially different photoreactivity of **1** or **2** in neat Et_3N and ROH/Et_3N mixtures, respectively.

Kinetic data on the quenching of DHP fluorescence by amines have been collected in Fig. 4 (p. 38). For the secondary and tertiary amines considered here, an excellent linear correlation ($r^2 \geq 0.99$) between the logarithm of the quenching rate constant ($\log k_q\tau$) and the IP_v of the quencher was found, demonstrating an electron-transfer quenching process to be operative[18]. The prediction that the allylic protons of **1** and **2** should not be involved in this type of quenching reaction was confirmed by the absence of deuterium isotope effects on the rate constants of fluorescence quenching of **1**-(2,2-d_2) and **2**-(3,3-d_2) by Et_3N.

According to Fig. 4 the rate constants for quenching of DHP fluorescence by primary amines are more or less independent of the IP_v of the quencher and also 1-2 orders lower than for secondary and tertiary amine quenchers. Furthermore, the data for quenching of DHP fluorescence by *n*-propylamine do not fit into the linear correlation between $\log k_q\tau$ and IP_v, established for the secondary and tertiary amines indicated in Fig. 4 (The correlation coefficient r^2 drops from 0.99 below 0.95 on implementation of $\log k_q\tau$ and IP_v-values concerning *n*-PrNH(D)$_2$). These results obviously imply that a different quenching process, viz. not involving electron-transfer, is involved with primary amines as quenchers. The observation of different quenching processes for primary and, on the other hand, secondary and tertiary amines, coincides with the varying photoreactivity of **1** or **2** in these amines. The absence of a correlation between $\log k_q\tau$ and pK_a for primary amine quenchers and the small isotope effects (k_H/k_D = 1.0-1.1) on the quenching rates of **1**-(2,2-d_2) and **2**-(3,3-d_2) by *n*-$PrNH_2$ and of **1** or **2** by *n*-$PrNH_2$ and *n*-$PrND_2$, suggest that apart from deprotonation by the amine, other pathways exist for quenching of the fluorescence of **1** or **2** in primary amines.

The electron-transfer quenching process, as observed with the secondary and tertiary amines indicated in Fig. 4, can be described with the aid of a radical ion-pair **5** (Scheme 3), or an exciplex of excited 1,2- (**1**) or 3,4-DHP (**2**) with the amine (Scheme 7; depicted for **1** and Et_3N). The



Scheme 7

assumption of the transient existence of radical ion-pairs (**5**, Scheme 3) in Et_3N solutions of **1** or **2**, excited with a 10 ns laser pulse at 308 nm, could not be substantiated by time-resolved UV/VIS

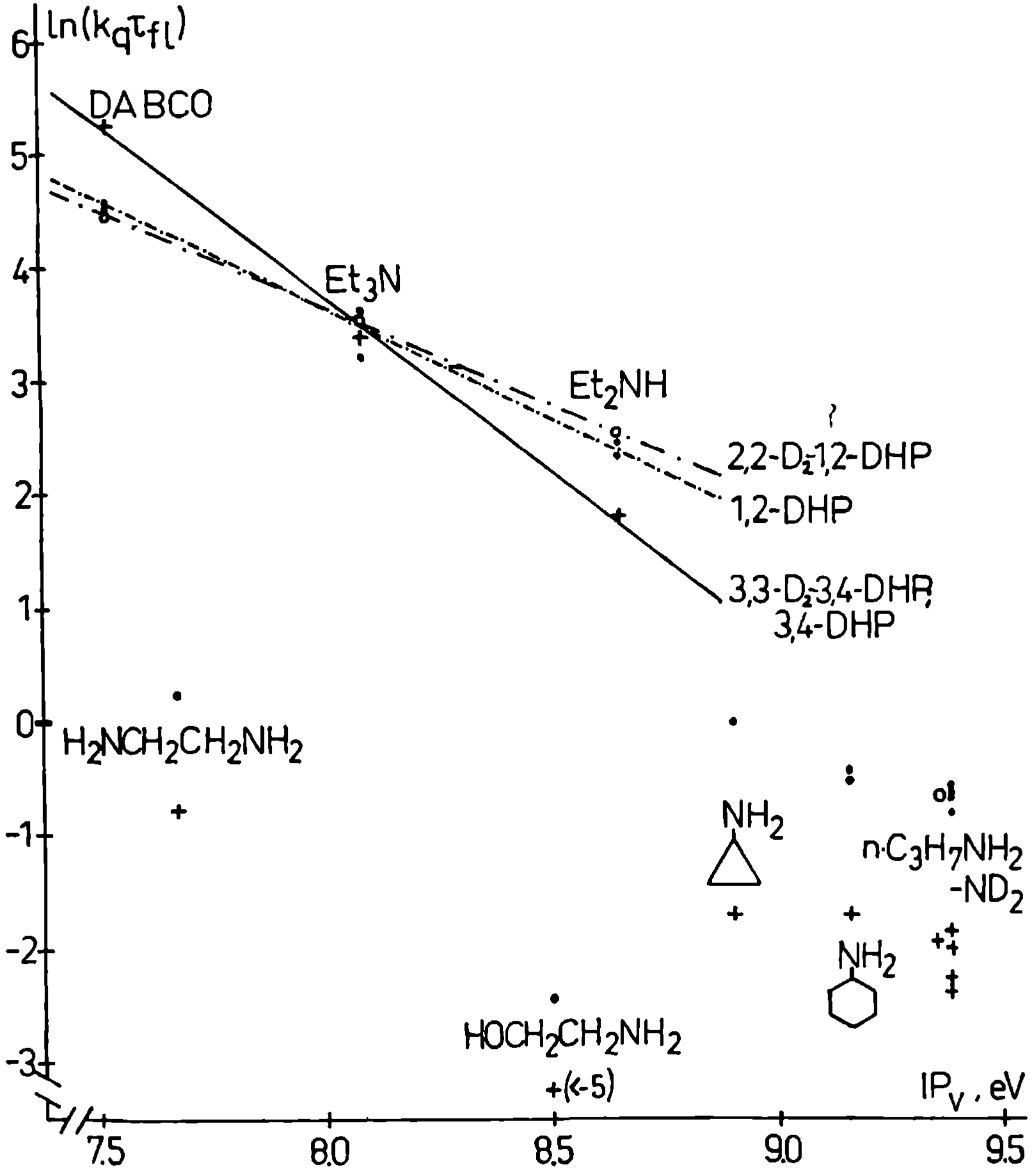


Fig. 4. Quenching of DHP fluorescence in acetonitrile by primary, secondary and tertiary amines: Plot of log $k_q\tau$ *vs*. the vertical ionization potential (IP_v) for **1** ( ), **1**-(2,2-d_2) ( ), **2** (+) and **2**-(3,3-d_2) (**1**-(2,2-d_2) and **2**-(3,3-d_2) with DABCO, Et_3N, Et_2NH and *n*-$PrNH_2$ only). $k_q\tau$-values have been evaluated in triplicate, from Stern-Volmer plots .

Fig. 5. Exciplex fluorescence emission of 1,2-dihydrophenanthrene (**1**) in Et_3N (a), of 3,4-dihydrophenanthrene (**2**) in Et_3N (b) and of **1** in Et_2NH (c, long-wavelength monomer emission given by the dotted line).

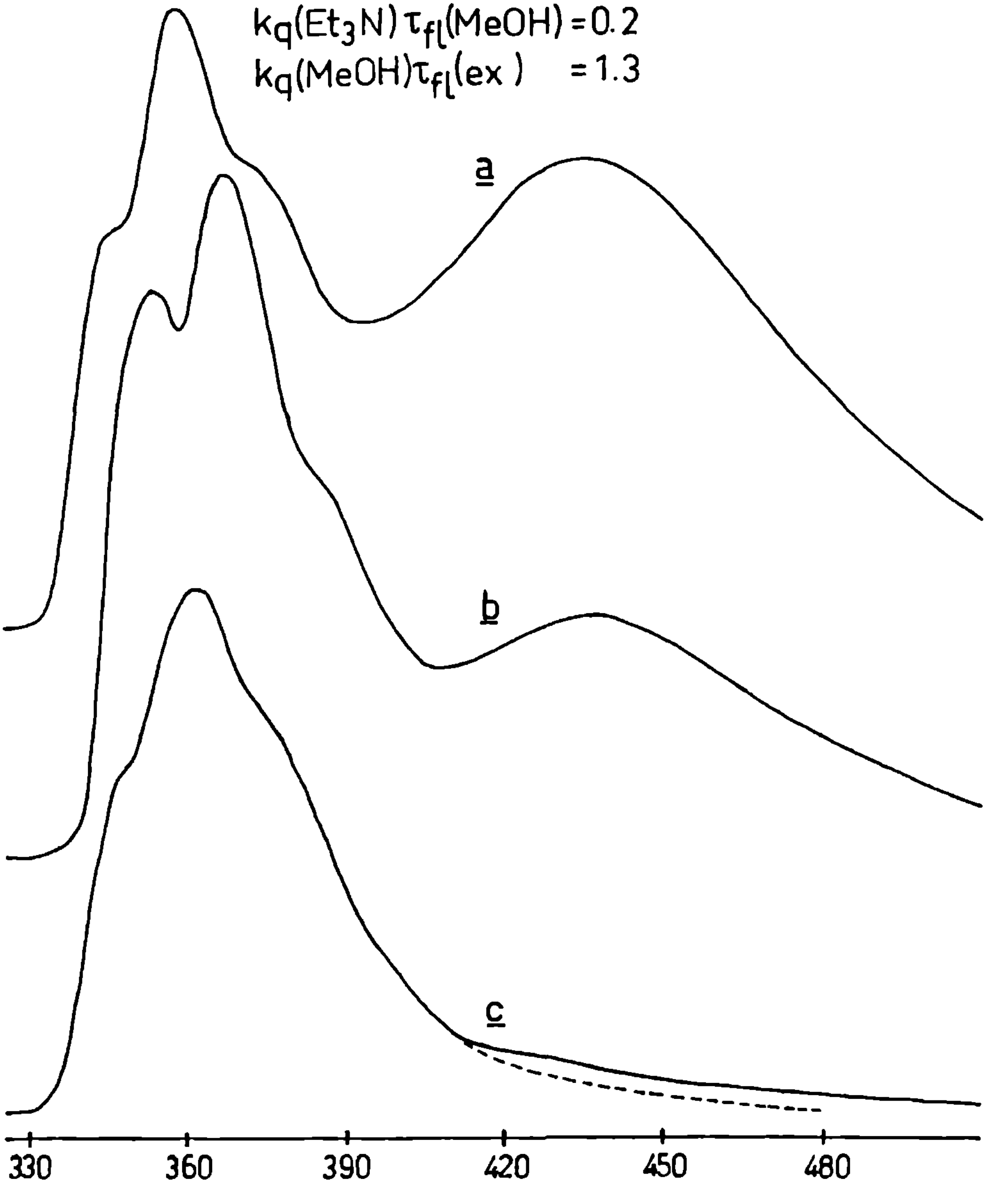
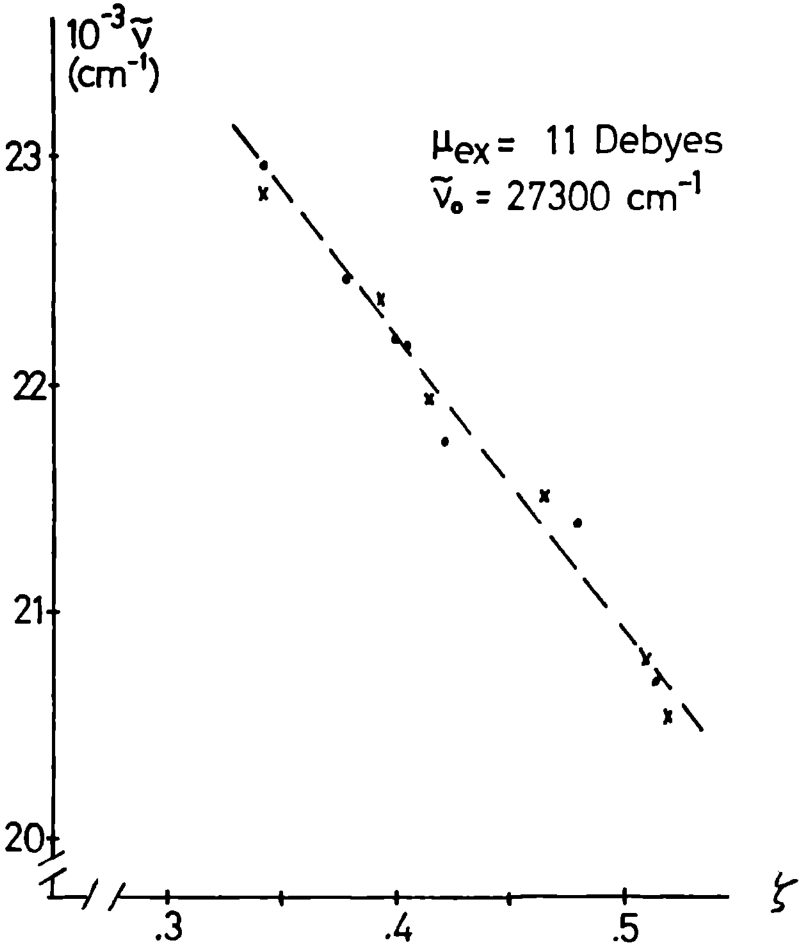


Fig. 6. Solvatochromic shift of the exciplex fluorescence band of 1,2-dihydrophenanthrene (**1**,) and of 2,2-dideuterio-1,2-dihydrophenanthrene (**1**-(2,2-d_2, x) in ROH/Et_3N mixtures: Plot of the wavenumber (ν) of the exciplex emission maximum *vs.* the solvent polarity parameter ζ.

$$\nu = \nu_o - \frac{\mu_{ex}^2}{2\pi\epsilon_o hca^3}\,\zeta \qquad \zeta = (\epsilon - 1)/(2\epsilon + 1) + (n^2 + 1)/(4n^2 + 2)$$

ν_o: wavenumber of the hypothetical emission band of the gaseous exciplex.
μ_{ex}: exciplex dipole moment.
ϵ: relative dielectric constant of the solvent.
n: refractive index of the solvent.



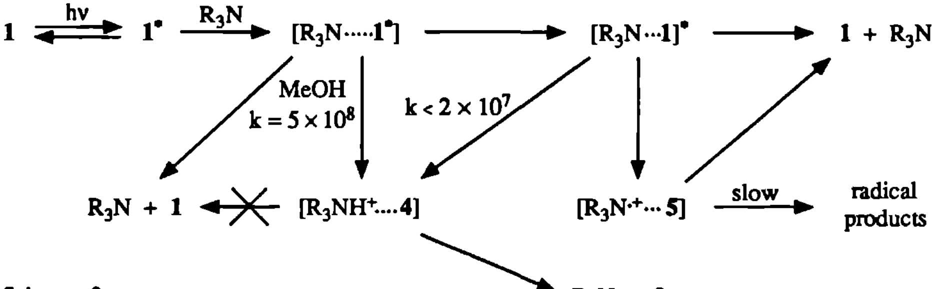
absorption spectroscopy: All attempts to detect the transient UV/VIS absorption band expected[19] for the naphthalene-like radical anions of **1** and **2** were unsuccessful. This failure presumably reflects the low quantum efficiency of formation and the short life time (< 10 ns) of these species in Et_3N solution, since in a similar study the radical-anion of *trans*-stilbene ion was readily indentified by its transient UV/VIS absorption band[20]. This assumption is consistent with the low quantum yields of the reaction of **1** and **2** in neat Et_3N (Table 1, entries j **1** and v **2**).

Exciplex fluorescence was observed with both **1** and **2** in Et_3N or Et_3N/MeOH mixtures and also with **1** in neat Et_2NH (Fig. 5, p. 39) Complexation of Et_3N with ground-state **1** and **2** was ruled out by the identity of the UV-spectra recorded in MeOH, hexane, *n*-$PrNH_2$ and Et_3N.

The charge-transfer character of the exciplex of excited **1** with Et_3N emerged from the linear relation between the wave number (ν) of the exciplex emission maximum and the solvent polarity parameter ζ (Fig. 6, p. 40)[21,22]. Substituting an estimated effective size radius a = 0.45 nm for this exciplex in eqn. 1 leads to an estimated exciplex dipole moment μ_{ex} = 12 Debyes. This estimate agrees with the dipole moment reported for the exciplex between Et_3N and *trans*-stilbene[22]. In neat Et_3N the life times of the exciplexes between **1** or **2** (τ = 2.1 and 2.8 ns, respectively) and this amine were found to exceed that of the corresponding exciplex of *trans*-stilbene (τ = 0.4 ns; deduced from data in Ref. 22). This can be explained by assuming that in the case of **1** and **2**, quenching of an exciplex with Et_3N by a second molecule of the amine occurs less efficiently than in the case of *trans*-stilbene[20,22,23].

The kinetics of exciplex formation between monomeric, excited **1** and Et_3N has been studied with picosecond time-resolved fluorescence spectroscopy (Fig. 7a and 7b, p. 42). The fact that the exciplex fluorescence is seen to grow in (Fig. 7b) at the decay rate of the monomer fluorescence (Fig. 7a) indicates exciplex formation *via* a direct, irreversible complexation reaction[24] between excited **1** and Et_3N.

The monomeric precursor of the exciplex might be either noncomplexed excited **1** itself or an encounter complex of this species and Et_3N. In either case, the shape of the Stern-Volmer plot for the quenching of monomer fluorescence of **1** in Et_3N by MeOH (Fig. 8, p. 43, solid curve) can be rationalized in terms of competitive quenching of excited **1** by Et_3N and MeOH (Scheme 8)[24].



Scheme 8

Fig. 7. Time-resolved (20 ps) exciplex (a) and monomer (b) fluorescence from 3,3'-dideuterio-3,4-dihydronaphthalene (2-(3,3-d_2), 10^{-3} M) in Et_3N. Excitation wavelength: 265 nm, pulse duration *ca.* 6 ps. Time-resolved fluorescence emission was detected with a synchroscan streak camera.

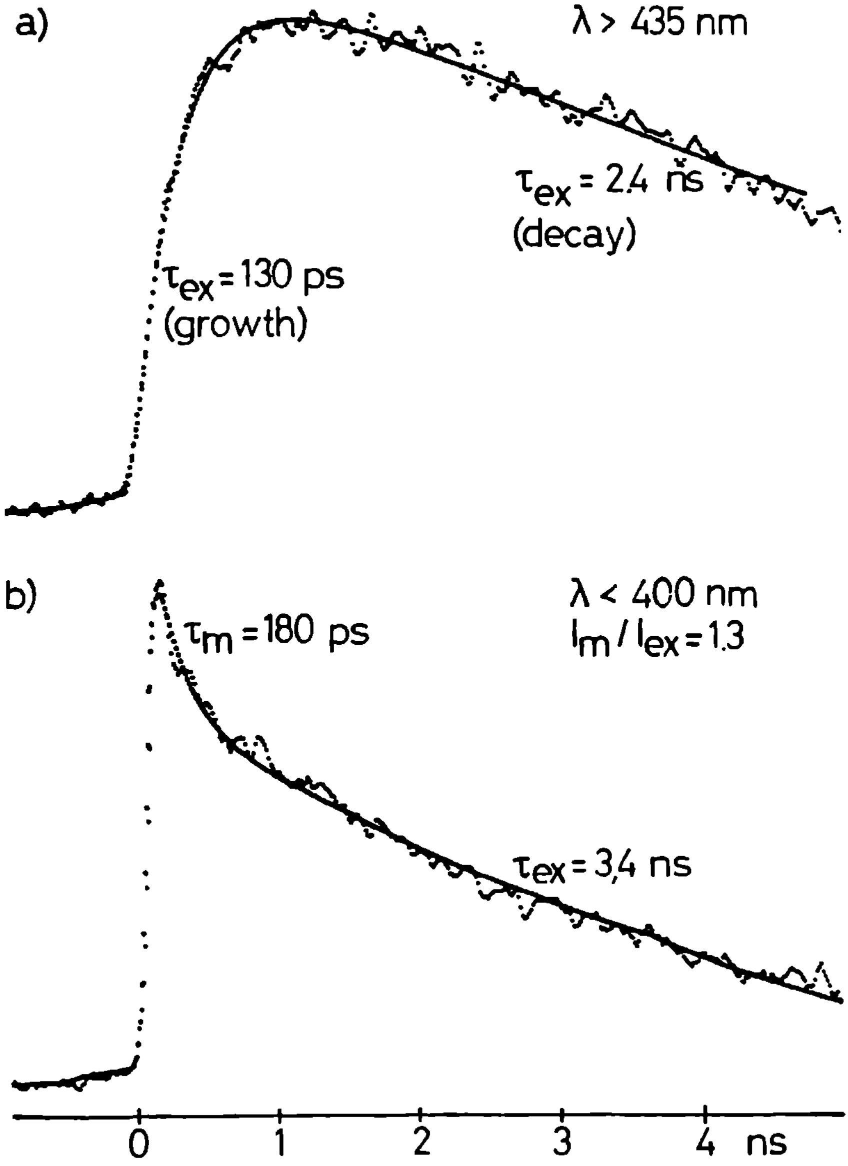


Fig. 8. Quenching of 1,2-dihydrophenanthrene (**1**) fluorescence in Et_3N by MeOH: Stern-Volmer plot of the quantum yield ratio (ϕ/ϕ_o) of monomer (——) and exciplex (- - - - -) fluorescence *vs*. the concentration ([MeOH]) of methanol.

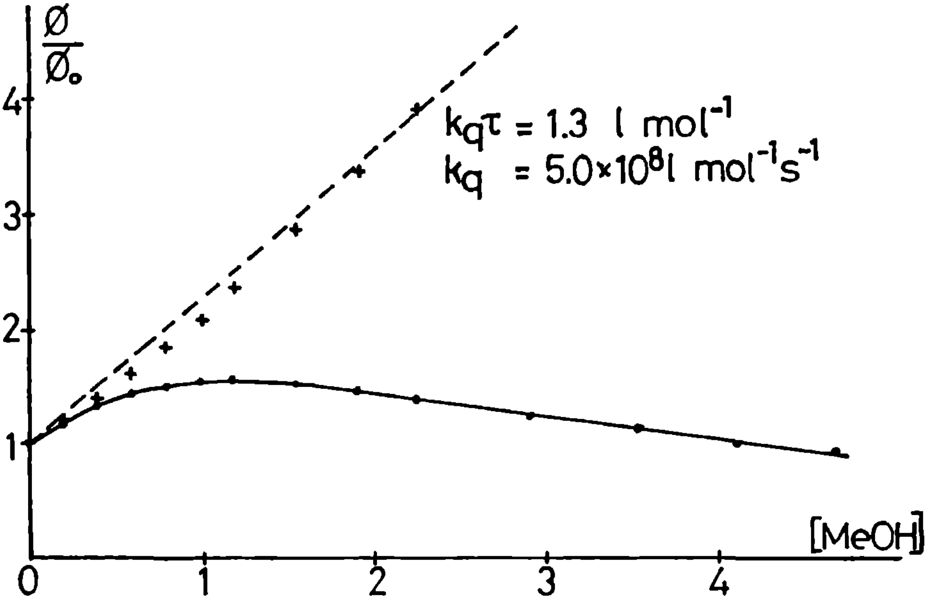
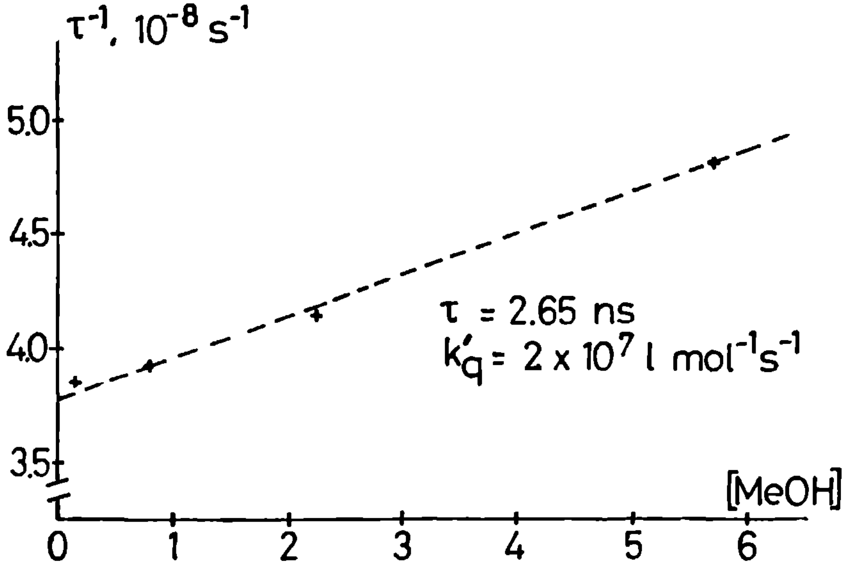


Fig. 9. Quenching of 1,2-dihydrophenanthrene (**1**) exciplex fluorescence in Et_3N by MeOH: Reci-(τ^{-1}) of the exciplex life time *vs*. the concentration ([MeOH]) of methanol.



The recovery of the monomer fluorescence at still higher concentrations (2.5-24.3 M) of methanol can be attributed to enhanced solvation of excited **1** by MeOH.

In contrast with the monomer fluorescence of **1** in Et_3N, quenching of the exciplex fluorescence by MeOH displays normal Stern-Volmer kinetics (Fig. 8), with an apparent rate constant $k_q' = 5 \times 10^8$ l mol^{-1} s^{-1}. The true rate constant (k_q) of this quenching process, evaluated from a plot (Fig. 9) of the exciplex *life time* versus the concentration of MeOH was found to be much lower ($k_q = 2 \times 10^7$ l mol^{-1} s^{-1}). It thus emerges that the decrease in the quantum yield of the exciplex fluorescence caused by the addition of MeOH to **1** in Et_3N arises from quenching of the encounter complex of excited **1** with Et_3N, rather than from enhanced radiative and non-radiative decay of the exciplex itself. On increasing the dielectric constant of the solvent (by addition of MeCN), the pyrene-dimethylaniline system was reported[25] to behave similarly.

The above results are of crucial importance in rationalizing the distinct photoreactivity of the DHP's **1** and **2** in neat and methanolic Et_3N. Obviously, MeOH inhibits exciplex formation of excited 1,2- (**1**) and 3,4-DHP (**2**) with Et_3N and consequently, the formation of radical reaction products by quenching of the intermediate encounter complex involved in exciplex formation. In view of the appreciable quantum yields of the 1,3-H shift to **3** in methanolic, but not in neat Et_3N, this quenching reaction apparently provides an efficient pathway from excited **1** or**2** to **3**. Since the mechanism of the 1,3-H shift in methanolic Et_3N was established to be the same as in primary amines, the MeOH-induced quenching of encounter complexes of excited **1** or **2** with Et_3N must involve at least in part deprotonation of this species by Et_3N to yield the [Et_3NH^+ **4**] ion-pair (Scheme 8). This conclusion presumably applies to mixtures of Et_3N and other alcohols indicated in Fig. 2 as well. So far, the current, alcohol-mediated proton transfer quenching reaction of encounter complexes between excited aromatic hydrocarbons **1** or **2** and Et_3N is unprecedented in the literature.

Conclusions

In the presence of primary amines the photochemical 1,3-H shift of both 1,2- (**1**) and 3,4-dihyrophenanthrene (**2**) into 1,4-dihydrophenanthrene (**3**) occurs *via* an ionic pathway. The rate-determining step involves proton abstraction from the allylic position of excited **1** or **2** by the amine, leading to an ion-pair of the type [RNH_3^+ **4**] (Scheme 2) . In accordance with the relative stability of **3** with respect to **1** and **2**, subsequent protonation of DHP anion **4** (Scheme 2, route b) yields **3** irreversibly. Contrary to MeOD and H^+, the less acidic *n*-$PrND_2$ is not capable of protonating the DHP-anion, what indicates that this reaction involves the ion-pair in a solvent cage. This conclusion is supported by other experimental data, in particular by the high quantum yields of **3** from both **1** and **2**. The finding that irradiation of both **1** and **2** in cyclopropylamine affords **3** quantitatively, excludes an intermediate radical ion-pair definitely from being involved in the formation of **3**.

Considering its reaction with excited **1** and **2**, Et_3N can act either as a base or as an electron donor. The latter property obviously predominates in neat Et_3N, as indicated by the extensive exciplex formation with this amine. It is improbable, that the exciplexes are precursors of **3**, because of their charge-transfer character and tendency to dissociate into radical ion-pairs. In accordance with this supposition, the quantum yield of the 1,3-H shift of **1** and **2** to **3** was found to be low in Et_3N and zero in N,N-dimethyl cyclopropylamine; radical reaction products being obtained instead.

As shown by the results of fluorescence studies, methanol inhibits exciplex formation of **1** with Et_3N by quenching the exciplex precursor, i.e. an encounter complex between Et_3N and excited **1**. In this quenching process, Et_3N acts as a base, capable of deprotonating excited **1**. Under these conditions Et_3N promotes the 1,3-H shift by the same mechanism as primary amines. Presumably, this conclusion holds equally for the photoconversion of **2** and the effect of higher alcohols.

Experimental

General methods. Solvents were purified rigorously before use: Amines were distilled from sodium and KOH. Hydrazine (100%) was obtained by distillation of its hydrate (85% N_2H_4) from KOH. Acetonitrile was distilled from P_2O_5 (2 times) and from dry K_2CO_3. *tert*-Butanol was distilled from NaH till its m.p. exceeded 24.5 °C. A solution of 16% NH_3 in MeOH was prepared by passing dry NH_3 slowly through MeOH at 25 °C.

Irradiations were performed with (2-10) × 10^{-4} M solutions of **1** and **2** in quartz vessels or cuvettes under aerobic conditions either at 300 nm (Philips TL 20 W/12 UVA) or 313 nm (Bausch and Lomb 33-86-79 high-intensity monochromator). Usually conversion levels were kept below 20% in order to avoid light absorption by the photoproducts. The composition of the photoproduct mixture was determined by UV, 90 MHz ^{1}H-NMR and GLC. In order to establish the extent of D incorporation in the individual components, samples originating from irradiation in deuterated solvents were also analyzed by GC-EIMS. Details concerning the equipment have been given elsewhere[26].

Relative quantum yields of photoconversion of **1** and **2** were determined as previously described[1,2]. Conversion into absolute quantum yields was achieved by means of photon flux determinations, employing the Aberchrome 540 actinometer[27]. Values of the quantum yields of the photochemical 1,3-H shift into **3** were obtained by multiplying those of photoconversion of the starting material with the chemical yields of **3**. In order to eliminate the effects of light intensity fluctuations, duplicate quantum yield determinations were made.

Fluorescence spectra and quenching studies were performed with *ca.* 10^{-4} M solutions of **1** and **2**, employing a Perkin Elmer MPF-4 fluorescence spectrophotometer. For both **1** and **2** it was checked that within the given concentration range, reabsorption of the fluorescence did not occur and that the fluorescence spectra were independent of the excitation wavelength.

Time-resolved UV/VIS absorption, fluorescence emission and conductivity neasurements have been performed at the Gorlaeus Laboratorium of the Rijksuniversiteit Leiden, in cooperation with

Drs. P.C.M. Weissenborn and Dr. C.A.G.O. Varma.

Starting materials. 1,2- (**1**) and 3,4-dihydrophenanthrene (3,4-DHP, **2**) were prepared from β-(1-naphthoyl)- and β-(2-naphthoyl)propionic acid[28] according to a known procedure[1,2,29]. For the preparation of 2,2-dideuterio-1,2-DHP (**1**-(2,2-d_2)) and 2,2-dideuterio-1,2-DHP (**2**-(3,3-d_2)) according to this procedure, the β-protons of the relevant naphthoylpropionic acids were exchanged for D by refluxing the dry potassium salts in an excess of D_2O[30]. Physical data of **1**-(2,2-d_2): ^{1}H-NMR($CDCl_3$, TMS): δ = 2.91 ppm (br. s,2H) H_1; δ = 6.24 ppm (d, 1H) H_3, $J_{3,4}$ = 10 Hz; δ = 7.20 - 8.14 ppm (m, 4H) H_4, Ar. H. EIMS; *m/e* (rel. intensity): 183 (16), 182 (M^+, 100), 181 (57), 180 (35), 179 (16), 167 (14), 166 (18), 165 (11). Chemical and isotopic purity: > 99%. Physical data of **2**-(3,3-d_2): ^{1}H-NMR($CDCl_3$, TMS): δ = 3.19 ppm (br. s, 2H) H_4; δ = 6.09 ppm (d, 1H) H_2, $J_{1,2}$ = 9.45 Hz; δ = 6.54 ppm (d, 1H) H_1; δ = 7.14 - 8.05 ppm (m, 6H) Ar. H. EIMS; *m/e* (rel. intensity): 183 (15), 182 (M^+, 100), 181 (67), 180 (44), 179 (22), 167 (13), 166 (19), 165 (12). Chemical and isotopic purity: > 99%.

N,N-dideuterio-*n*-propylamine (*n*-$PrND_2$) was obtained by hydrolysis of $As_4(n\text{-}PrN)_6$ with D_2O[31]. In contrast with a previous report[1], only N-deuteration (> 99%) was observed in this case. Pure N,N-dimethyl cyclopropylamine was synthesized in 10% yield by fusing cyclopropyltrimethylammonium iodide with solid KOH at *ca.* 250 °C[32]. A 1.4 ± 0.05 molar solution of guanidine in EtOH was prepared by mixing a solution of 3.22 g of freshly cut sodium in 50 mL of abs. EtOH with a solution containing 1% excess of (triply recrystallized) guanidinium chloride in 50 mL of EtOH. The mixture was cooled to 0 °C and then liberated from precipitated NaCl by filtration. The resulting, strongly basic guanidine solution was found to be UV-transparent above 255 nm.

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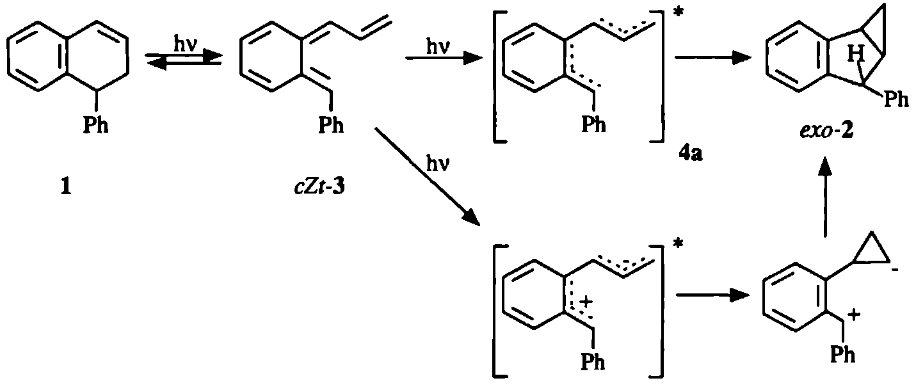
Chapter 4: The photochemistry of 1-phenyl-1,2-dihydronaphthalene in methanol.

Introduction.

Previously, it was reported[1,2] that irradiation of 1-phenyl-1,2-dihydronaphthalene (**1**) with a broad spectrum lamp in hexane affords exclusively the *exo*-isomer of 4-phenylbenzobicyclo-[3.1.0]hex-2-ene (**2**). On the basis of the available experimental data, *exo*-**2** was supposed to arise from excitation of the pe-conformer (**1**-pe, with the phenyl group occupying the pseudo equatorial position) of **1**. Within this assumption two possible reaction pathways leading to *exo*-**2** were postulated[1,2]; i.e. a concerted intramolecular [4+2] photocycloaddition involving an unpolarized excited singlet state of *cZt*-**3**, or a mechanism involving a "sudden-polarized"[3] twisted zwitterionic excited singlet state of *cZt*-**3** (Scheme 1).



Scheme 1

Considering the possibility of a concerted intramolecular [4+2] photocycloaddition of *cZt*-**3**, the structure of the end-product *exo*-**2** requires the excited triene moiety in **4a** to cyclize in a $\pi_4a+\pi_2a$ fashion. Although this conclusion obviously violates the Woodward-Hoffman rules[4], Tanaka et. al.[5] emphasized the possibility of photochemical intramolecular $\pi_4a+\pi_2a$ cross-bicyclization in excited trienes of low symmetry.

The mechanism, involving a sudden-polarized zwitterionic state (**4b**) of the excited *cZt*-triene, was first introduced by Dauben et. al.[6]. Since then it has been used to rationalize the observed stereochemistry of several bicyclo[3.1.0]hex-2-enes originating from apparently concerted, symmetry-forbidden intramolecular $\pi_4a+\pi_2a$ photocycloadditions of *cZt*-hexatrienes[6-10]. In this case, a two step mechanism has been invoked[6] to explain the observation that the configuration of the asymmetric center resulting from the formation of the five-membered ring of the corresponding bicyclo[3.1.0]hex-2-ene, is thermodynamically controlled. The photocycloaddition product *exo*-**2** (Scheme 1) can be rationalized accordingly, as the thermodynamically favorable relaxation product of the "sudden-polarized" zwitterionic excited state **4b**. On the other hand, a sudden-polarized excited state of an s-*trans* 1,3-diene has been postulated[11] to give the corresponding [1.1.0]bicyclobutene *via* a concerted reaction.

Relative stabilities and electron configurations of nonpolar and sudden-polarized, zwitterionic excited *cZt*-hexatrienes, have been the subject of extensive theoretical studies[3,12-17]. For unsubstituted *cZt*-1,3,5-hexatriene, the sudden-polarized, zwitterionic states Z_1 and Z_2 (Scheme 2)

Scheme 2

Z_1 S_1 Z_2

were calculated to be of comparable stability, and to lie 17 kcal mol^{-1} below the corresponding unpolarized excited state (S_1), at a twist angle of 90° [12]. According to the authors, nearly full charge separation (*ca.* 0.8e) between the two perpendicular allyl moieties of Z_1 and Z_2 should exist in this case. It is generally agreed that for twist angles Θ outside the range $88° < \Theta < 92°$ the zwitterionic character of the twisted excited singlet state of *cZt*-1,3,5-hexatriene is negligible[13-16].

In contrast with the great theoretical interest emphasized above, there has been little experimental evidence for the involvement of sudden-polarized excited state in the photochemistry of 1,3,5-hexatrienes and related polyenes[18]. It was therefore decided to initiate an experimental program aimed to elucidate the type of excited state involved in the photoreactions of 1,3,5-hexatrienes, generated by photochemical ring opening of substituted 1,2-dihydronaphthalenes.

Considering the experimental conditions to be employed it was decided to use methanol as the solvent for the following reasons: In the first place, stabilities of zwitterionic excited states relative to nonpolar excited states are expected to be enhanced through more effective solvation of the former by polar solvents[13-17,19]. Secondly, zwitterionic intermediates might be trapped by polar solvents[11,20,21]. I.e. the presence of zwitterionic states might reveal themselves through formation of methanol addition products at a faster rate than formation of the corresponding bicyclo[3.1.0]hex-2-ene. Furthermore, addition of a strong acid was considered as an important tool for trapping of zwitterionic excited states. Provided that their life time exceed *ca.* 10^{-11} s[22], such zwitterionic excited states might be trapped selectively by protonation, what might lead to enhanced rates of photoproduct formation from them in the presence of acid. In addition to this, it should be mentioned that in contrast to unpolarized excited states, trapping of zwitterionic excited states by methanol may give rise to formation of cyclopropane derivatives[11,20,21] *via* polar intermediates like **5**.

Due to annellation within the s-*cis* moiety of **4b**, the extent of charge separation in **4b** will be greater[16] than in zwitterionic twisted excited singlet states of e.g. unsubstituted *cZt*-hexa-1,3,5-triene (Scheme 2). According to the theory of the sudden-polarization effect[14], the life time of zwitterionic **4b** should exceed those of zwitterionic excited states of s-*cis*, s-*trans*-hexa-1,3,5-trienes in which charge separation is less. For this reason, zwitterionic excited states of s-*cis*, s-*trans*-hexa-1,3,5-trienes deriving from 1,2-dihydronaphthalenes appear to be particularly promising candidates for selective trapping by methanol and strong acid.

Considering other arguments for the choice of substituted 1,2-dihydronaphthalenes as the experimental probe, it can be remarked that the photochemistry of these compounds in hexane is well documented[1,2,23]. Further, these compounds provide the advantage of *in situ* generation of hexa-1,3,5-trienes[24] at low photostationary concentrations, thereby avoiding undesirable side reactions e.g. polymerization.

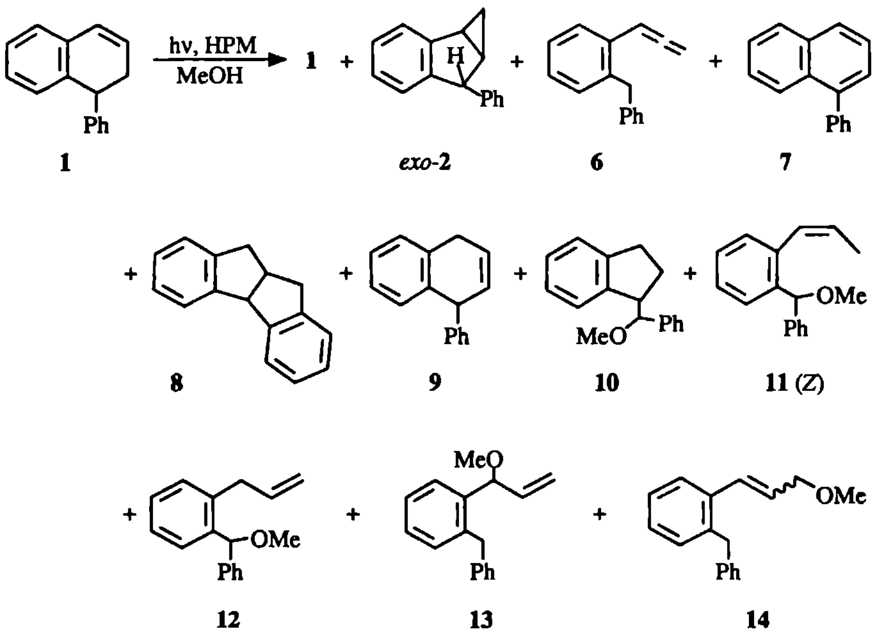
Results

Irradiation of 1 in methanol. Photoproduct analyses were performed with 100 mg samples obtained from broad-spectrum irradiations of **1** (2×10^{-3} M) at room temperature and at -60 °C. The photoproducts were separated into a hydrocarbon fraction and a fraction containing methanol adducts by elution from a 10 cm silica gel column with carbon tetrachloride. All photoproducts were found to be stable to column chromatography and temperature-programmed GLC at 150 °C.

NMR spectra and GC-MS analysis of the hydrocarbon fraction indicated the presence of two major photoproducts, both having *m/e* 206. One of these was recognized immediately as *exo*-**2** (Schemes 1 and 3) by the characteristic NMR absorptions[2,25] of its aliphatic protons. Its presence was confirmed by running an authentic sample of *exo*-**2**[25] along with the hydrocarbon fraction in capillary GLC.

The NMR characteristics of the other major photoproduct included a singlet at $\delta = 4.02$ ppm (2H) and a triplet at $\delta = 6.30$ ppm (1H) coupled ($J = 6.82$ Hz) to a doublet at $\delta = 5.03$ ppm (2H). This suggested the presence of an $ArCH_2Ar$-fragment (Ar = aryl) and a single olefinic proton coupled to apparently equivalent protons of a terminal olefinic methylene group. The only $C_{16}H_{14}$-isomer uniting these structural elements, is *o*-benzylphenylallene (**6**), the formation of which can be envisaged *via* a 1,5-H shift from *cZc*- or *cZt*-**3** (Scheme 1). In accordance with this assignment, the IR spectrum of the hydrocarbon fraction showed characteristic absorptions at 1943 and 1075 cm^{-1} due to the antisymmetrical and symmetrical stretching vibrations[26] of the cumulated olefinic bonds in **6** (Scheme 3). The structure of **6** was confirmed by chemical synthesis. The NMR and IR data of **6** compare favorably to those reported[27-29] for the analogous

Scheme 3



1-phenylallene. In contrast to *exo*-**2**, **6** has not been observed previously[1,2] as a photoproduct from **1** in hexane.

Apart from **2** and **6**, the hydrocarbon fraction contained four minor products. 1-Phenylnaphthalene (**7**, Scheme 3) was recognized by its mass spectrum (*m/e* 204), low-field NMR absorptions at δ = 7.75-7.94 ppm and UV absorption at λ_{max} = 290 nm. *Cis*-dibenzobicyclo-[3.3.0]octa-2,7-diene (**8**, Scheme 3) was recognized by the mass spectrum[30] (*m/e* 206) which displays little fragmentation, as compared to its $C_{16}H_{14}$-isomers **1**, **2** and **6**. These assignments were checked by comparing NMR and GC-MS data of the hydrocarbon fraction with those obtained from authentic samples of **7**[2] and **8**[30,31]. The presence of 1-phenyl-1,4-dihydronaphthalene (**9**)[32] among the hydrocarbon photoproducts from **1** in MeOH, was established similarly[1,33]. The structure of the remaining component (*m/e* 206, GC-MS) could not be established with certainty. The retention time of a GLC peak and a set of NMR absorptions, not addressable to hydrocarbons **1**, *exo*-**2** and **6**-**9** suggests it to be *endo*-**2** (NMR ($CDCl_3$): δ = 0.79 ppm (d of t) $H_{6,endo}$, $J_{6\text{-}endo,6\text{-}exo} = J_{5,6\text{-}endo}$ = 4.5 Hz, $J_{1,6\text{-}endo}$= 8.0 Hz; cf. *exo*-**2**[2,19]). In contrast with **7** and **8**, which may occur in yields up to 10%, only traces of **9** and *endo*-**2** are present hydrocarbon fraction.

The composition of the fraction containing the methanol adducts showed a marked dependence on the irradiation time. Irradiation of **1** (2×10^{-3} M) for short periods of time (40 min) yielded four methanol adducts, as indicated by the strong, sharp NMR absorptions at $\delta = 3.14$, 3.18, 3.35 and 3.37 ppm due to methoxy groups. Application of TLC afforded three fractions: The first fraction consisted of two similar components, separable neither by preparative TLC nor by temperature-programmed capillary GLC. The major component showed the NMR characteristics of an aromatic functionality ($\delta = 6.54$ ppm (d, 1H), $J = 7$ Hz; $\delta = 6.83$-7.26 ppm (m, 8H)), a sterically crowded methoxy group ($\delta = 3.18$ ppm (s, 3H)), two coupled methylene groups ($\delta = 2.03$-2.31 ppm (m, 2H) and $\delta = 2.58$-2.88 ppm (m, 2H)) and an $ArCHOCH_3$ fragment ($\delta = 4.19$ ppm (d, 1H), $J = 7.0$ Hz) adjacent to a tertiary CH fragment ($\delta = 3.36$-3.63 ppm (m, 1H)). By the results of spin-decoupling, these NMR-absorptions were assigned to 1-(α-methoxy)benzylindane (**10**, Scheme 3). In agreement with this assignment, the EI mass spectrum (EIMS) showed a parent peak at *m/e* 238 (M^+, 0.4%) and fragmentation peaks at *m/e* 222 ($C_9H_9COPh^+$, 1.1%), 121 ($C_6H_5CHOCH_3{}^+$, 100%), 117 ($C_9H_9{}^+$, 11%) and 115 ($C_9H_7{}^+$, 14%). Obviously, **10** exists as a pair of diastereomers (1R,αR; 1S,αS)-**10** and (1R,αS; 1S,αR)-**10**. The occurrence of NMR satellites at $\delta = 1.52$-1.82 ppm (m, 2H), $\delta = 3.22$ ppm (s, 3H) and $\delta = 4.11$ ppm (d, 1H), $J = 7.0$ Hz is due to this fact. Definite proof for these assignments was obtained from chemical synthesis of a mixture of (1R,αS; 1S,αR)-**10** and (1S,αS; 1R,αR)-**10**. Considering that minimal steric interaction in **10** requires the α-CH fragment to be located either below or above the plane of the indanyl moiety, it emerges that only in (1S,αR; 1R,αS)-**10**, the methylene protons at C(2) can be in the proximity of the shielding zone of the α-phenyl group. Hence the NMR-absorptions at $\delta = 1.52$-1.82 ppm and $\delta = 2.03$-2.31 ppm are assigned to respectively the (1R,αS; 1S,αR) and (1R,αR; 1S,αS) diastereomer of **10**. It should further be mentioned that the observed excess of the (1R,αR; 1S,αS) diastereomer in chemically synthesized samples of **10** is much less ((1R,αR; 1S,αS)-**10**/(1S,αR; 1R,αS)-**10** = 2) than in samples of **10** derived from irradiation of **1**, which have (1R,αR; 1S,αS)-**10**/(1R,αS; 1S,αR)-**10** = 5.

According to both GLC and NMR, the second fraction consisted again of two similar compounds. The chemical shifts of the methoxy substituents ($\delta = 3.35$ and 3.37 ppm) indicated considerably less steric crowding of these groups, as compared to **10**. The NMR spectrum showed olefinic multiplets ($\delta = 4.86$-5.14, 5.63-6.12 and 6.41-6.59 ppm) and an aliphatic doublet ($\delta = 1.60$ ppm) split by allylic couplings, as well as singlets ($\delta = 5.43$ and 5.47 ppm) indicative of the presence of an Ar_2CHOCH_3 fragment[34] in both compounds. From the results of NMR integration and spin-decoupling, the constituents of the second fraction were concluded to be *Z*-1-(α-methoxybenzyl)-2-propen-1-ylbenzene (**11**) and 1-(α-methoxybenzyl)-2-propen-2-ylbenzene (**12**) (Scheme 3). Both CI- and EIMS of **11** and **12** gave weak parent peaks at the correct mass. **11** And **12** were easily be discriminated by the presence of a strong peak at *m/e* 121 in the CI and EI mass spectrum of the former. Similarly, **11** and **12** could be discriminated from **10** by EIMS.

Apart from **11** and **12**, the third fraction contained still another component, the NMR spectrum of which revealed the presence of a methoxy group ($\delta = 3.14$ ppm, (s)), an $ArCH_2Ar$-fragment ($\delta = 4.04$ ppm (s)), and a vinyl group ($\delta = 5.15$ and 5.87 ppm (m)) similar to that in **12**. In accordance with the results of spin-decoupling experiments, these NMR data were assigned to

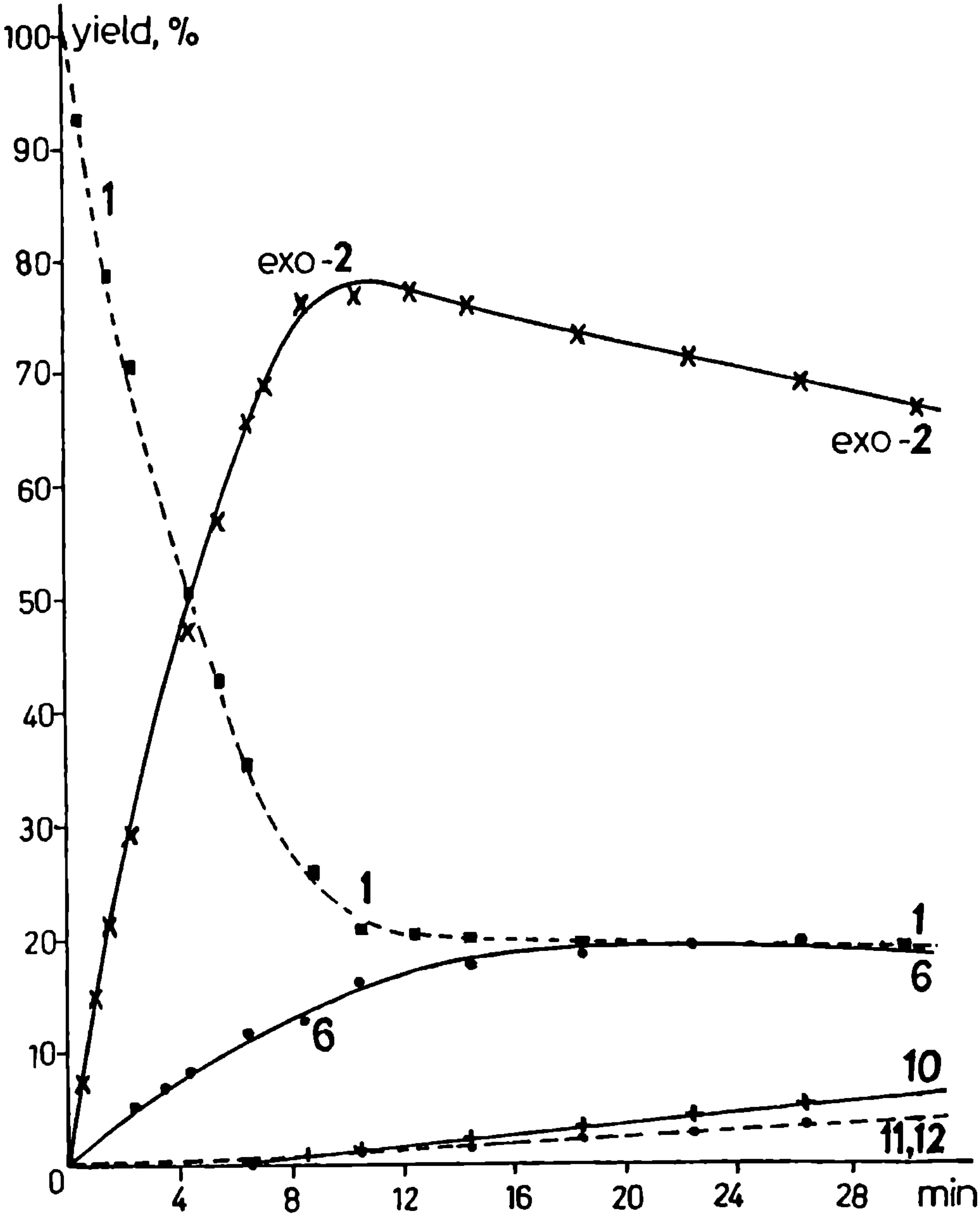
1-methoxy-1-(*o*-benzyl)phenylprop-2-ene (**13**, Scheme 3). Unfortunately, insufficient separability of **13** from **11** and **12** in temperature-programmed capillary GLC, prevented further characterization of this compound by GC-MS.

Prolonged (90 min) irradiation of **1** (10^{-3} M) in H_2SO_4-containing (10^{-2} M) methanol afforded two additional methanol adducts, along with a diminished yield of **10**. The new adducts were separated from compounds **10-13** by TLC and collected as a mixture which proved to be inseparable by capillary GLC. In contrast to compounds **10-13**, the EI mass spectrum of this mixture showed a parent peak (*m/e* 238) of substantial intensity (18%) as well as a relatively weak (18%) fragmentation peak at *m/e* 121, pointing to the absence of an α-methoxybenzyl group. The NMR spectrum of the mixture showed absorptions characteristic of two slightly different methoxy groups ($\delta = 3.23$ and 3.26 ppm (s)) as well as a *cis* ($\delta = 6.56$ (br. d), $\delta = 5.80$ ppm (d of t), $J_{cis} = 11.4$ Hz) and a *trans* ($\delta = 6.80$ ppm (br. d), $\delta = 6.09$ ppm (d of t), $J_{trans} = 16.0$ Hz) olefinic bond, both conjugated with an aryl group. From the results of spin-decoupling the new adducts were concluded to be *Z*- and *E*-3-methoxy-1-(*o*-benzyl)phenylpropene (**14**, Scheme 3), being present in a 1 : 4 ratio in the mixture obtained from TLC. A summary of the photochemistry of **1** in methanol is presented in Scheme 3. On this short irradiation, *Z*- and *E*-**14** were never observed, not even in the presence of H_2SO_4. Hence the occurrence of these compounds upon prolonged (90 min) irradiation of a 10^{-3} M soln. of **1** in acidified methanol is not the result of a primary photoprocess.

From the yield *vs.* time plots of the photoreaction of 1-phenyl-1,2-dihydronaphthalene (**1**) evaluated at various temperatures or in the presence of acid it was concluded that *exo*-**2**, **6**, **8** and **11-13** arise from **1** by primary photoreactions. On the other hand, **10** emerged clearly as a secondary photoproduct. A typical result in support of this conclusion is presented in Fig. 1, from which it can be seen that photoconversion of **1** into *exo*- **2**, **6**, **8**, **11** and **12** starts at t = 0, whereas photoproduction of **10** starts when the yield of *exo*-**2** approaches its maximum value (t = 10 min). Beyond this maximum, **10** is formed at a rate comparable to the decomposition rate of *exo*-**2**. This points to decomposition of *exo*-**2** into **10** as the chief secondary photoreaction in broad-spectrum irradiation of **1** in methanol. The occurrence of this reaction was confirmed by irradiation of an authentic sample of *exo*-**2** under similar conditions: In this experiment **10** was obtained as the major photoproduct, along with small yields of **9** and polymeric compounds. By monitoring the yield *vs.* time curves of **10** in neat and H_2SO_4-containing methanol under otherwise identical irradiation conditions, it was verified that the photodecomposition reaction of *exo*-**2** is not subject to acid catalysis.

Due to the low abundances in the irradiation mixture, the yield *vs.* time curves obtained for *endo*-**2**, **7** and **9** were too inaccurate to decide whether or not these products originate from primary photoreactions. Assuming *endo*-**2** to be a secondary photoproduct, its formation can only be envisaged from *exo*-**2** by a non-concerted photoisomerization reaction of this compound[2,23]. In view of the greater thermodynamic stability of *exo*-**2**, *endo*-**2** is not likely to be formed *via* this route. Hence, *endo*-**2** is most probably a primary photoproduct of **1**. The observed traces of **7**

Fig. 1. Broad-spectrum irradiation (HPM) of 1-phenyl-1,2-dihydronaphthalene (**1**, 2 ×10^{-3} M) in methanol at -72 °C: Yield *vs.* time plots for the conversion of **1** and the formation of *exo*-4-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-**2**), 1-(*o*-benzyl)phenylallene (**6**), 1-(α-methoxy)benzylindane (**10**) and 1-(α-methoxybenzyl)-2-prop-1-enylbenzene (**12**).



presumably arise from aromatization of **1** by residual oxygen. As previously discussed[25], **9** is a minor secondary photoproduct formed *via* photodecomposition of *exo*-**2**.

Under the irradiation conditions stated in Table 1 and Fig. 1, compound **14** could not be detected among the photoproducts of **1**. As mentioned previously this compound is observed as a secondary photoproduct from **1** on prolonged (90 min) irradiation of **1**.

Initial rate constants (r_0) of primary photoproduct formation were calculated form the slopes of the yield *vs.* time curves at zero time. The results concerning the influence of temperature and sulfuric acid on the initial rate constants are collected in Table 1.

Table 1. Influence of the temperature (T) and the concentration of sulfuric acid ($[H_2SO_4]$) on the initial rates (r_0, ±20%) of primary photoproduct formatiom from 1-phenyl-1,2-dihydronaphthalene (**1**, 2×10^{-3} M)in methanol.

T, °C	$[H_2SO_4]$	$r_0 \times 10^6$, mol l^{-1} min^{-1}				
		1[1]	**2**	**6**	**8**	**12 + 13**
- 72	0	300	270	43	<1	2
- 30	0	270	220	38	<1	3
15	0	50	42	10	2.4	3
15	2.5×10^{-2} M	40	30	7	3	3
15	2×10^{-1} M	50	37	10	5	3
15[2]	0	75	76	2.6	1.6	-

[1] Initial rate of disappearence. [2] Solvent: hexane.

Irradiation of 1 in n-hexane. To investigate the influence of solvent polarity on the primary photoreactions of **1**, the irradiation experiment outlined in Fig. 1 was repeated with **1** in hexane. GC-MS and NMR analysis of a 100 mg sample irradiated at 15 °C for 75 min revealed the presence of **1** (11%), *exo*-**2** (54%), **6** (4%), **8** (3%), **9** (14%), five unknown $C_{16}H_{14}$ isomers (8%) and *endo*-**2** (6%). According to the observed yield *vs.* time curves, *exo*-**2**, **6** and **8** are primary photoproducts; the five unidentified $C_{16}H_{14}$-isomers are secondary photoproducts. In agreement with previous reports[1,2], decomposition of *exo*-**2** into **9** was identified as the chief secondary photoreaction. Though all photoproducts mentioned are unstable towards prolonged (>30 min) irradiation, the expected[1,2] polymerization reaction could be suppressed completely by employing highest-purity hexane.

The initial rates of formation of the primary photoproducts *exo*-**2**, **6** and **8** in this solvent at 15

°C have been collected in the last row of Table 1. The results can be directly compared to those obtained in methanol at 15 °C, since in both solvents the initial rates r_0 of the primary photoproducts *exo*-**2**, **6** and **8** have been evaluated under strictly identical irradiation conditions. From this comparison, it emerges that replacement of methanol by the nonpolar solvent *n*-hexane enhances the initial rate of formation of *exo*-**2** from **1** to a greater extent (2.3 times) than the initial rate of disappearance of starting material **1** (1.6 times). Though deriving from primary photoreactions, **9** and *endo*-**2** are formed at rates negligible to r_0(*exo*-**2**).

Monochromatic (254 nm) irradiation of 1. Changing from broad-spectrum to monochromatic irradiation has been reported[30] to alter the photochemistry of **1** drastically. On prolonged irradiation of **1** at 254 nm in hexane or methanol, *Cis*-dibenzobicyclo[3.3.0]octa-2,7-diene (**8**) has been obtained[30,31] in quantitative yield. From an investigation of the effect of H_2SO_4 on the initial rate of formation of **8** from **1** in methanol at 254 nm, this rate emerges to be hardly affected by the presence of acid: After 5 hr irradiation (254 nm) of **1** (10^{-3} M) in MeOH, the yield of **8** is 25% in the absence of acid, and 20% in the presence of a 20-fold excess (2×10^{-2} M) of H_2SO_4. Under identical irradiation conditions (merry go round) the yield of **8** from **1** in hexane is 25%, after a 5 hr irradiation period. This means that the initial rate of formation of **8** from **1** is also independent of the solvent polarity.

These results suggest that formation of **8** neither occurs *via* a non-concerted radical or ionic pathway, nor involves assistance by the solvent. This assumption is in accordance with an earlier observation[30], viz. that irradiation of **1** at 254 nm in CD_3OD yields no detectable D incorporation in **8**.

Influence of conformer equilibrium on the photochemistry of 1 in methanol and hexane. In the literature, the role of the principles of least motion (PLM)[9,10] and non-equilibration of excited rotamers (NEER)[35] in controlling the stereochemistry of the end products obtained from hexatrienes generated through photochemical ring opening of different cyclohexadiene conformers, has been emphasized. Since photoconversion of **1** *via* pentaene intermediates *cZc*- and *cZt*-**3** (Scheme 1) belongs to this class of reactions, it is important to establish whether these principles apply to the present case. If PLM would apply to the photochemical ring opening of the pseudo-equatorial (**1-pe**) and pseudo-axial (**1-pa**) conformers of **1** and simultaneously the NEER principle would be valid for the pentaene intermediates resulting from this ring opening, one would expect ratios of initial rate constants (r_0) for different end products to correlate with the ratios x_{pe}/x_{pa} of **1**-pe and **1**-pa conformers in hexane and methanol.

These ratios were determined from 500 MHz ^{1}H-NMR-spectra of 3,4-dideuterio-1,2-dihydronaphthalene (**1**-(3,4-d_2)) in C_6D_{12} and CD_3OD, according to the procedure described by Lamberts et.al.[1,2]: The required *trans*-couplings ($^3J_{1,2}$) of the protons at C(1) and C(2) were obtained from a computer simulation of the ABX pattern due to these protons. In order to trace the most stable conformer of **1** and to extrapolate x_{pe}/x_{pa} ratios to low temperatures, the ratio was monitored at various temperatures. The data obtained in methanol (Table 2) are the more accurate data since they derive from very reliable (rms error < 0.1) computer simulations of the double AB pattern

Table 2. 500 MHz ^{1}H-NMR data of 3,4-dideuterio-1-phenyl-1,2-dihydronaphthalene in CD_3OD and C_6D_{12}: *Trans* couplings ($J_{1,2}$, in Hz), ratio (x_{pe}/x_{pa}) of the conformers **1**-pe and (**1**-pa) and upfield shifts (in Hz) of H_8, relative to H_5 ($\Delta\delta_{5,8}$), H_6 ($\Delta\delta_{6,8}$) and H_7 ($\Delta\delta_{7,8}$).

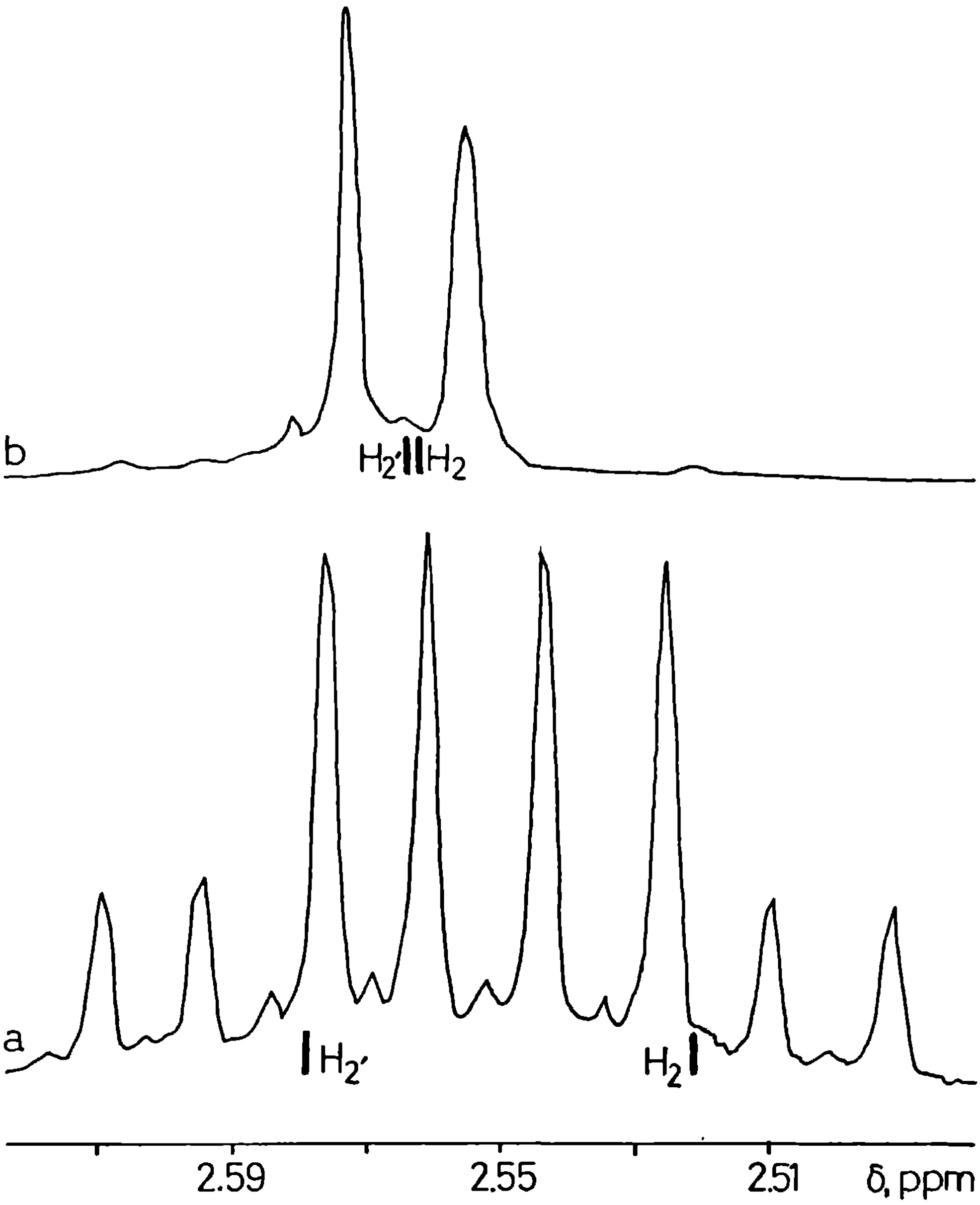
T, °C	CD_3OD					T, °C	C_6D_{12}				
	$J_{1,2}$	x_{pe}/x_{pa}	$\Delta\delta_{5,8}$	$\Delta\delta_{6,8}$	$\Delta\delta_{7,8}$		$J_{1,2}$	x_{pe}/x_{pa}	$\Delta\delta_{5,8}$	$\Delta\delta_{6,8}$	$\Delta\delta_{7,8}$
-10	9.71	1.23	170.7	199.1	146.5	10	11.50	2.5	134.5	168.5	120.6
20	9.49	1.15	159.5	188.5	137.7	30	11.47	2.1	129.2	163.2	116.0
50	9.16	1.05	151.3	180.7	131.7	50	12.10	2.1	124.1	157.9	111.8

(Fig. 2a) due to H_2 and $H_{2'}$. In this case the x_{pe}/x_{pa} ratio decreases smoothly with increasing temperature, indicating the **1**-pe conformer to be the thermodynamically more stable one. As can be seen in Table 2, the x_{pe}/x_{pa} ratio also correlates with the difference between chemical shifts of H_8 and the other aromatic protons of the dihydronaphthalene moiety. This can be ascribed to more shielding of H_8 by the phenyl substituent in the **1**-pe than in the **1**-pa conformer. A similar correlation was observed for the chemical shift values ($\delta(^{13}C)$, Table 3) of the carbon nuclei in **1**, as indicated by temperature dependent 100 MHz ^{13}C-NMR spectroscopy. According to Table 3,

Table 3. Chemical shifts ($\delta(^{13}C)$,in ppm, relative to internal TMS, 24 °C) and temperature dependence ($\delta(^{13}C, T)$ - (^{13}C, 24 °C)) thereof, for 1-phenyl-1,2-dihydronaphthalene (**1**) (Compiled from proton noise decoupled 100 MHz ^{13}C-NMR spectra in CD_3OD).

postion	$\delta(^{13}C)$	$\delta(^{13}C, T) - \delta(^{13}C, 24\ °C)$			postion	$\delta(^{13}C)$	$\delta(^{13}C, T) - \delta(^{13}C, 24\ °C)$		
	24 °C	- 40 °C	- 60 °C	- 80 °C		24 °C	- 40 °C	- 60 °C	- 80 °C
C(1)	44.98	- 0.07	- 0.11	- 0.16	C(7)	128.20	0.10	0.12	0.16
C(2)	33.05	0.08	0.10	0.11	C(8)	128.81	0.00	0.00	0.00
C(3)	127.92	0.16	0.22	0.29	C(8a)	139.16	- 0.06	- 0.09	- 0.12
C(4)	129.08	0.04	0.03	0.03	C(9)	145.96	- 0.11	- 0.14	- 0.17
C(4a)	135.41	0.05	0.06	0.07	C(10,14)	129.35	0.11	0.14	0.18
C(5)	127.18	0.02	0.01	0.01	C(11,13)	129.41	0.15	0.20	0.25
C(6)	127.78	0.12	0.16	0.20	C(12)	127.40	0.13	0.18	0.22

Fig. 2. Aliphatic part (H_2 and H_2') of the 500 MHz ^{1}H-NMR spectrum of 3,4-dideuterio-1-phenyl-1,2-dihydronaphthalene in CD_3OD (a) and C_6D_{12} (b).



the largest variations in $\delta(^{13}C)$ concern the carbons (C(9)-C(14)) of the phenyl substituent and C(3); i.e. those positions where a change of conformation is expected to result into a major alteration of the chemical environment.

In C_6D_{12} the protons H_2 and H_2' provide a deceptively simple NMR pattern (Fig. 2b) due to an extremely small (0.002 ppm) difference of their chemical shifts. Consequently, computer simulations were less accurate (rms errors between 0.1 and 0.25) than in the previous case. This is reflected in the fact that the x_{pe}/x_{pa} ratios (Table 2) derived from the *trans* couplings $^3J_{1,2}$ do not decrease smoothly with increasing temperature. However, the fact that in C_6D_{12}, the chemical shift differences between H_8 and the other protons of the dihydronaphthalene moiety show a smooth temperature dependence similar to that in CD_3OD suggests the x_{pe}/x_{pa} ratio to be a smooth function of temperature in this case too. The observed temperature dependence of the x_{pe}/x_{pa} ratio indicates **1**-pe to be the thermodynamically more stable conformer of **1** in both CD_3OD and C_6D_{12}. From a comparison of the x_{pe}/x_{pa} values in methanol, hexane (Table 2) and $CDCl_3$[1,2], the stability difference between the **1**-pe and the **1**-pa conformer is concluded to be largest in nonpolar solvents.

In Table 4 the observed correlations between ratios of initial rate constants and x_{pe}/x_{pa} are given. The results are compatible with the assumption of PLM and the NEER principle as the factors controlling the stereochemistry of the photoreactions of **1**-pe and **1**-pa to *exo*-**2**, **6** and **8** in hexane and methanol.

Table 4. Comparison of the **1**-pe/**1**-pa conformer ratio (x_{pe}/x_{pa}) of 1-phenyl-1,2-dihydronaphthalene (**1**) with the ratios of initial rates of *exo*-4-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-**2**) and 1-(*o*-tolyl)phenylallene (r_0(*exo*-**2**)/r_0(**6**)) and of *exo*-**2** and *cis*-dibenzobicyclo[3.3.0]octadiene (r_0(*exo*-**2**)/r_0(**8**)) in methanol and hexane at 15 °C.

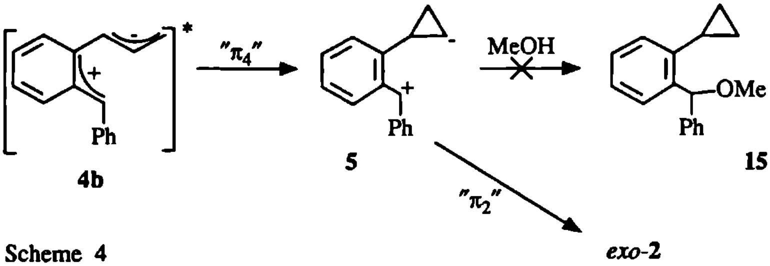
solvent	x_{pe}/x_{pa}	r_0(*exo*-**2**)/r_0(**6**)	r_0(*exo*-**2**)/r_0(**8**)
CH_3OH	1.17	4.2	17.5
C_6H_{12}	2.1	29	47.5

Discussion

The absence of a significant effect of the concentration of H_2SO_4 on the initial rates of photoproduct formation (Table 1) in the broad-spectrum irradiation of **1** in methanol, indicates that trapping by methanol or sulfuric acid of a sudden-polarized excited state of the pentaene *cZc*- or *cZt*-**3** (Scheme 1) does not occur: Either the life time of the zwitterionic excited states of these pentaenes is too short to allow selective trapping by methanol and H_2SO_4 or the lowest excited singlet state is not zwitterionic at all.

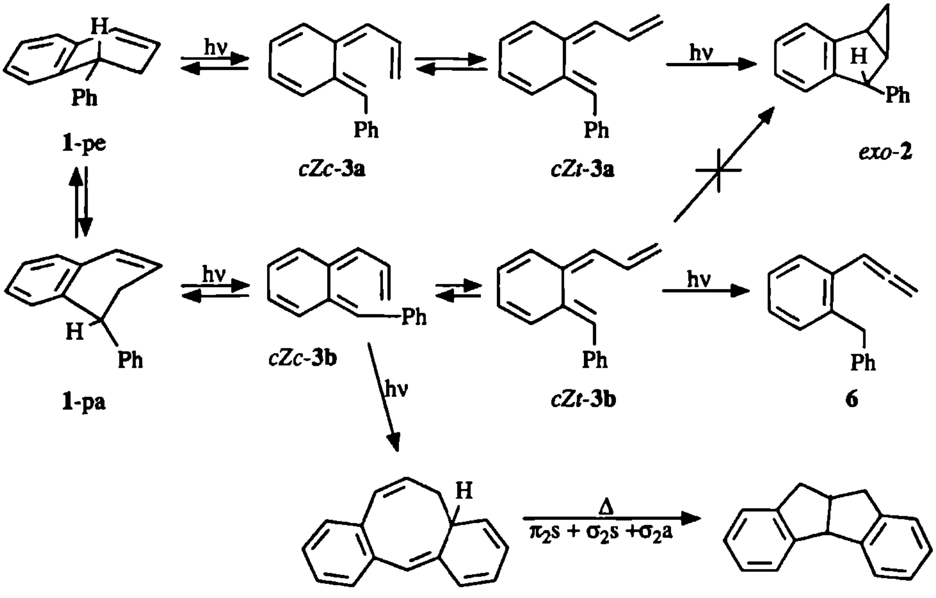
Though conclusive evidence on this issue has not been obtained, the available experimental results suggest that sudden-polarized zwitterionic excited states of the pentaene intermediates *cZc*- and *cZt*-**3** (Scheme 1) are not involved in the photoreactions of **1** in methanol.

When a zwitterionic excited state of *cZc*- or *cZt*-**3** is assumed to be involved in the photochemistry of **1**, the formation of cyclopropane derivative **15**[11,20,21] might be expected (Scheme 4). The presence of this compound among the photoproducts from **1** should reveal itself by high-field NMR absorptions due to the cyclopropane ring protons. Experimentally, however, **15** has not been observed, neither in the crude mixture of photoproducts nor in chromatographically purified fractions of the methoxylated photoproducts. On the other hand, the formation of compounds **11**-**13** (Scheme 3, Table 1) only upon broad-spectrum irradiations of **1**, obviously implies that they arise from photochemical methanol addition to *cZc*- or *cZt*-**3**; apparently the life time of the zwitterionic excited state of the pentaenes *cZc*- or *cZt*-**3** is sufficiently long for intermolecular addition of MeOH leading to **11**-**13**, but is too short to allow selective trapping by protons from methanol or H_2SO_4 and formation of cyclopropane **15**. Furthermore, a consistent rationalization of primary photoproduct **13** in terms of the sudden-polarization effect involves zwitterionic excited state **4c** rather than **4b** (Scheme 4). According to the theory[16] of the sudden-polarization effect, however, **4c** should be less stable than **4b**, because in zwitterionic excited states of hexa-1,3,5-trienes the negative charge is best accommodated by the least substituted allyl moiety. From these considerations it emerges that the assumption of a zwitterionic excited state for the pentaenes *cZc*- and *cZt*-**3** does not provide a consistent rationalization of the experimental results obtained from irradiation of **1** in MeOH.



Scheme 4

A mechanism rationalizing the formation of the primary photoproducts is given in Scheme 5. The validity of the NEER principle governs that photochemical interconversion between 1-pe and 1-pa does not occur, whereas PLM ascertains that photochemical conrotatory ring opening of 1-pe yields only *cZc*-**3a** and that photochemical conrotatory ring opening of 1-pa yields only *cZc*-**3b**. Though photochemical interconversion of *cZc*- (or *cZt*-) **3a** and **3b** cannot be ruled out, the rates of these processes are assumed to be lower than the rates of equilibration of 1-pe and 1-pa and of thermal reversion of *cZc*-**3a,b** to **1**. The photostationary **3a**/**3b** ratio will then be related to the



Scheme 5

conformer ratio x_{pe}/x_{pa}. From Table 4, the following relations between the ratio x_{pe}/x_{pa} of the conformers **1-pe** and **1-pa** and the ratios $r_0(exo\text{-}\mathbf{2})/r_0(\mathbf{6})$ and $r_0(exo\text{-}\mathbf{2})/r_0(\mathbf{8})$ of photoproduct formation in hexane and MeOH are obtained:

$$\left(\frac{x_{pe}}{x_{pa}}\right)_{\text{hexane}} \qquad \left(\frac{x_{pe}}{x_{pa}}\right)_{\text{MeOH}} = 1.8 \pm 0.5 \qquad (1a)$$

$$\left(\frac{r_0(exo\text{-}\mathbf{2})}{r_0(\mathbf{8})}\right)_{\text{hexane}} : \left(\frac{r_0(exo\text{-}\mathbf{2})}{r_0(\mathbf{8})}\right)_{\text{MeOH}} = 2.7 \pm 0.5 \qquad (1b)$$

$$\left(\frac{r_0(exo\text{-}\mathbf{2})}{r_0(\mathbf{6})}\right)_{\text{hexane}} : \left(\frac{r_0(exo\text{-}\mathbf{2})}{r_0(\mathbf{6})}\right)_{\text{MeOH}} = 7 \pm 2 \qquad (1c)$$

From Eqn. (1a) and (1b) the interesting conclusion emerges that the ratio $r_0(exo\text{-}\mathbf{2})/r_0(\mathbf{8})$ of the initial rates of formation of *exo*-**2** and **8** varies according to the ratio x_{pe}/x_{pa} on going from methanol to hexane. This is compatible with the hypothesis put forward in the introduction, that *exo*-**2** arises from an intramolecular $\pi_4a+\pi_2a$ photocycloaddition of *cZt*-**3a**, generated exclusively by excitation of **1-pe** and that **8** arises exclusively from **1-pa**, *via* a $\pi_6s+\pi_2s$ photocyclization reaction of *cZc*-**3b**.

The validity of this interpretation is subjected to the condition that the relative rates of the reaction steps indicated in Scheme 5 are not affected by the solvent polarity: Formation of *exo*-**2**, **6** and **8**. involves only concerted, unimolecular (thermal and photochemical) reaction steps.

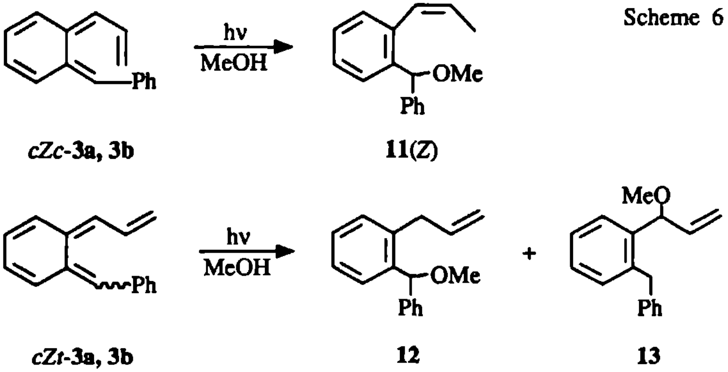
As far as **8** is concerned, this point of view is supported by the results of monochromatic (254 nm) irradiations of **1** in hexane, MeOH and CD_3OD[30], which indicate the absence of interaction between the polar protic solvent methanol and the transition state involved in the thermal $\pi_2s+\pi_2a+\sigma_2a$ rearrangement[30] (Scheme 5) leading to **8**. As far as the formation of *exo*-**2** and **6** is concerned the experimental results of Table 1 suggest that formation of these compounds does not involve zwitterionic excited states of *cZc*- or *cZt*-**3**.

The attractiveness of the present interpretation of Eqn. (1a) and (1b) is in that it complies with other experimental results and theoretical considerations. Considering the geometries of the four pentaene intermediates *cZc*-**3a,b** and *cZt*-**3a,b**, (Scheme 5) it is noted that only *cZc*-**3b** is capable of undergoing an allowed $\pi_6s+\pi_2s$ photocyclization, eventually leading (stereospecifically) to **8**[30]. The present interpretation also associates the chief photoprocess (formation of *exo*-**2** through intramolecular $\pi_4a+\pi_2a$ photocycloaddition of *cZt*-**3a**) with the most abundant of the pentaene intermediates. As noted in the introduction, a photocyclization of the $\pi_4a+\pi_2a$-type is not rigorously symmetry-forbidden in hexa-1,3,5-trienes of low symmetry[5]. Further it is consistent with the observed temperature effect (Table 1) on the initial rates of formation of *exo*-**2** and **8** in methanol. A decrease in temperature will cause the equilibrium between **1**-pe and **1**-pa to shift towards the more stable **1**-pe conformer. In agreement with this expectation, r_o(*exo*-**2**) and r_o(**8**) (Table 1) were found to increase and decrease, respectively with increasing temperature. Obviously the lowering of the rate of the allowed thermal $\pi_2s+\pi_2a+\sigma_2a$ rearrangement[30] (Scheme 5) provides an additional contribution to the aforementioned decrease of r_o(**8**).

In an attempt to shed more light on the underlying causes of the wavelength effect on the photochemistry of **1**, some kinetic experiments have been performed[36]. The results of these experiments prove that, in accordance with previous reports on related 1,2-dihydronaphthalenes[37,38], irradiation of **1** at 254 nm affords the intermediate pentaenes **3** (Scheme 5) in appreciable photostationary concentrations. According to the results obtained on irradiation of **1** at 254 nm in hexane, MeOH and H_2SO_4-containing MeOH, the reactivity of these species is low at this wavelength. This may be attributed[24] to the fact that the pentaenes **3** will compete strongly with **1** for the absorption of incident light at 254 nm, but not at longer wavelengths where only the pentaenes exhibit appreciable UV/VIS absorption. By this argument, the highly selective photoreaction of pentaene *cZc*-**3b** into **8** at 254 nm cannot be accounted for. The formation of **8** might involve selective excitation of the phenyl group in *cZc*-**3b** at 254 nm.

Along with the intramolecular photocycloaddition leading to *exo*-**2**, formation of **6** is seen to be suppressed completely on changing from broad-spectrum to monochromatic (254 nm) irradiation of **1**; both in hexane and methanol. This indicates a photochemical 1,5-H shift to be responsible for its formation from the pentaene precursor **3**. Apart from this argument, the assumption of a thermal pathway to **6** would not be consistent with the lacking temperature effect on the rate of formation (r_0(**6**), Table 1) of this product. From Eqns. (1a) and (1c) it emerges that **6** derives presumably from excitation of both **1**-pe and **1**-pa. This is consistent with the consideration that both *cZt*-**3a** and *cZt*-**3b** provide a geometry suitable for a symmetry-allowed photochemical 1,5-H shift.

The primary photoproducts **11-13**, observed in the case of broad-spectrum irradiations in methanol can be rationalized as adducts of the pentaene intermediates **3** (Scheme 6). In accordance with this rationalization these products, like *exo*-**2** and **6**, were not observed to form on irradiation of **1** at 254 nm.

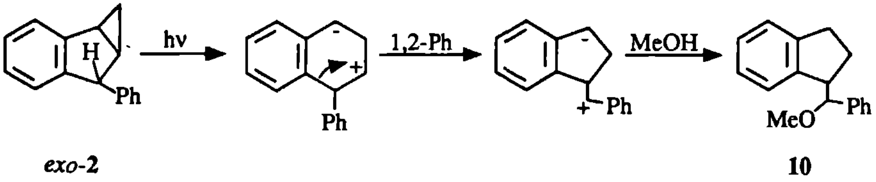


cZc-**3a, 3b** **11(Z)**

cZt-**3a, 3b** **12** **13**

Considering the observed secondary photoreactions, the mode of photodecomposition of *exo*-**2** in methanol is quite unusual for a benzobicyclo[3.1.0]hex-2-ene. The usual pathway for photodecomposition of these compounds involves homolytic cleavage of the C(1)-C(5) cyclopropane bond and subsequent 1.2-H shifts, yielding 1,2- or 1,4-dihydronaphthalenes[1,2,25,39]. This reaction was also observed with *exo*-**2** in hexane[25]. The formation of **10** from *exo*-**2** in methanol can be rationalized when heterolytic fission of the cyclopropane C(1)-C(5) bond[40] is invoked in the reaction mechanism (Scheme 7). The lacking influence of H_2SO_4 on the photodecomposition rate of *exo*-**2** into **10** in MeOH might be rationalized by assuming the sequence of reactions depicted

Scheme 7



exo-**2** **10**

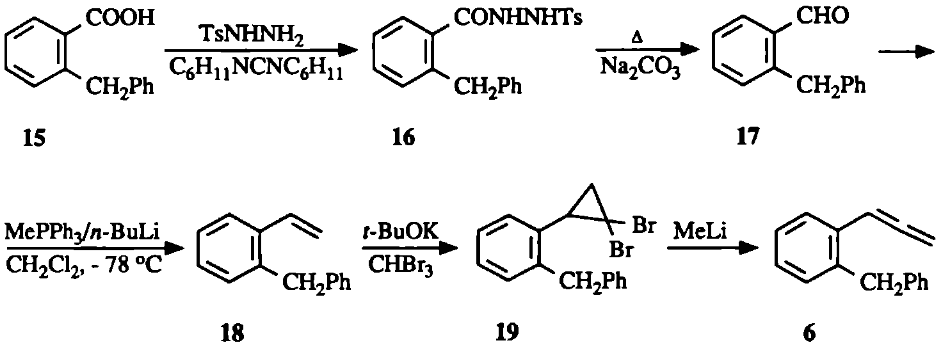
in Scheme 7 to take place in a more or less concerted fashion. Examples of similar heterolytic photochemical methanol addition to a cyclopropane bond, not subject to acid catalysis have been published[41].

Experimental

Preparations. The starting materials 1,2-dihydronaphtalene (**1**), 3,4-dideuterio-1,2-dihydronaphthalene (**1**-(3,4-d_2)) and 4-phenylbenzobicyclo[3,1,0]hex-2-ene (**2**, mixture of isomers, predominantly containing *exo*-**2**) were prepared as previously described[1,2].

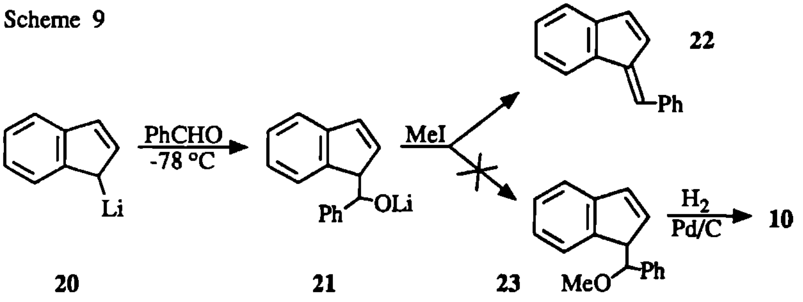
1-(*o*-Benzyl)phenylallene (**6**) was prepared from *o*-benzylbenzoic acid (**15**) according to the procedure (Scheme 8) described for 1-phenylallene[42,43].

Scheme 8



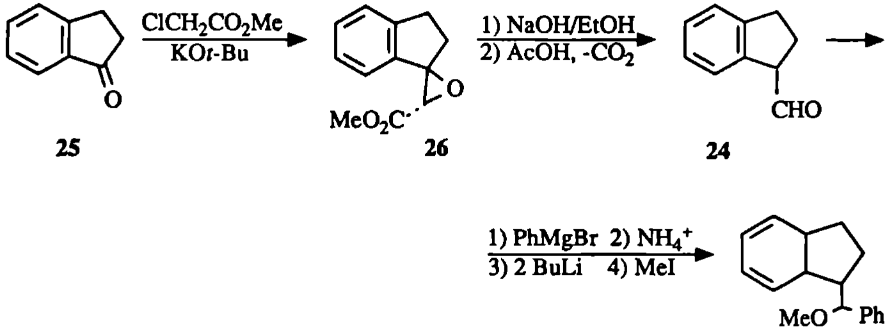
1-(α-Methoxy)benzylindane (**10**) proved to be inaccessible by strategies based on 1-metalated indane or indene: Reaction of the readily accessible 1-lithio-2(1H)indene **20**[44] with benzaldehyde in THF at -78 °C apparently yielded **21** (Scheme 9) as a colorless compound. Attempts to

Scheme 9



methylate this product with MeI resulted in elimination of LiOH at -25 °C to yield yellow 1-benzylidene-2(1H)indene (**22**, m.p.: 87-88 °C[45], yield: >50 %) instead of the desired compound **23**. Attempts to synthesize **10** from benzaldehyde and 1-metalated indane failed: Heating 1-chloroindane[46] with Mg in THF yielded indene and $MgCl_2$ instead of the desired Grignard reagent. Attempts to synthesize 1-lithioindane by reaction of 1-methoxyindane[47] with Li in THF at-15 °C[48] were also unsuccessful.

Fortunately, the reversed strategy, viz. synthesis of **10** by reaction of 1-formylindane (**24**) and phenylmagnesiumbromide (Scheme 10) proved to be effective. The experimental details are given



Scheme 10

10

along with the physical data of **10**.

Irradiations. Irradiations were performed with N_2-purged 2 × 10^{-3} M solutions of **1**, employing Philips 125 W HPM or Philips TUV G15T8 (254 nm) lamps. Spectrophotometric grade MeOH or hexane was used as the solvent. For the evaluation of yield *vs.* time plots (Fig. 1) **1** was irradiated with a HPM lamp in an N_2-purged 200-mL irradiation vessel equipped with a liquid-cooled (MeOH, $-90 < T < 25$ °C) quartz finger and a sampling facility. During irradiation 0.2-mL aliquots were taken at 2-min intervals and, subsequently, analyzed by GLC.

General methods. Separation of the photoproducts was achieved by TLC or column chromatography on silica gel (Merck 60, 70-230 mesh) employing carbon tetrachloride or hexane-toluene as the eluent. Compositions of photoproduct mixtures were determined by GLC, employing a HP 5790 gas chromatograph equipped with HP or Chrompack capillary columns, a HP 3390 recording integrator and a flame ionisation detector. The response of the detector was assumed to be proportional to the number of carbon atoms present in the component detected. Samples originating from irradiations in H_2SO_4-containing methanol were neutralized with OH^--exchanged Dowex-IRA-400 ion-exchange resin, prior to GLC or GC-MS analysis.

Characterization of photoproducts and synthetic intermediates involved ^1H-NMR (Hitachi Perkin-Elmer R-24B (60 MHz) and Bruker WH-90 (90 MHz) spectrometers, internal reference:

TMS), GC-MS (VG 70-70 MS equipped with a GLC facility similar to that quoted above), IR (Perkin-Elmer 397) and UV (Perkin-Elmer 555) spectroscopy and chemical synthesis.

500 MHz ^{1}H-NMR spectra of 3,4-dideuterio-1,2-dihydronaphthalene (**1**-(3,4-d_2)) in C_6D_{12} and CD_3OD were recorded on a Bruker AM 500 spectrometer. The procedure for obtaining ratios (x_{pe}/x_{pa}, Table 2) of the **1**-pe and **1**-pa conformers from these NMR spectra is described in refs. 1 and 2.

100 MHz ^{13}C- and 2D ^{13}C-^{1}H correlated NMR spectra of **1** were recorded on a Bruker AM-400 spectrometer employing a dual ^{13}C-^{1}H-probe. In the 100 MHz ^{13}C-NMR spectrum (Table 3), the low-field resonances due to the quaternary carbon atoms in **1** were assigned on the basis of known[49] $\delta(^{13}C)$-values of alkyl-substituted 1,2-dihydronaphthalenes in combination with empirical increment systems[50] for estimating the effect of the phenyl substituent on these $\delta(^{13}C)$-values.

1-(*o*-Benzyl)phenylallene (6). This compound was synthesized according to Scheme 8.

For the preparation[41] of hydrazide **16**, a solution of 2-benzylbenzoic acid (**15**, 10.6 g, 50 mmol), dicyclohexylcarbodiimide (11.3 g, 55 mmol) and *p*-toluenesulfonylhydrazide (9.3 g, 50 mmol) in dry THF (130 mL) was stirred overnight, at ambient temperature. Removal of the dicyclohexyl urea precipitate followed by evaporation of the solvent afforded crude **16**, which was recrystallized from hot hexane. Recrystallization from ethanol afforded pure **16**.

Extrusion of N_2 from **16** was brought about by the addition of anhydrous sodium carbonate to a hot (160 °C) solution of **16** in ethylene glycol[41]. The extrusion reaction was allowed to proceed for 75 seconds and then quenched by pouring the reaction mixture into water. Crude **17** was isolated by extraction with hexane, drying of the organic phase and evaporation of the solvent. Purification by flash chromatography (Silica gel, eluent: $CHCl_3$) afforded **17** as a colorless oil in 80% yield.

This compound was converted into *o*-benzylstyrene (**18**) by a Wittig reaction with methyltriphenylphosphonium bromide and *n*-BuLi in CH_2Cl_2, at -78 °C[42]. 60 MHz ^{1}H-NMR ($CDCl_3$): δ = 4.0 ppm (s, 2H) $ArCH_2Ar$; δ = 5.0 ppm (d of d, 1H), 5.3 ppm (d of d, 1H) $CH{=}CH_2$, $^{3}J_{cis}$ = 11 Hz, $^{3}J_{trans}$= 17 Hz, ^{2}J = 2 Hz; δ = 6.3 - 7.4 ppm (m, 10H) Ar H, $CH{=}CH_2$. EIMS; *m/e* (rel. intensity): 195 (4), 194 (M^+, 26), 180 (12), 179 (100), 178 (33), 165 (9), 152 (4), 115 (16), 91 (9).

2-(*o*-Benzyl)phenyl-1,1-dibromopropane (**19**) was prepared by dropwise addition of a solution of *t*-BuOK (63 mmol) in *t*-BuOH (50 mL) to a solution of **18** (29 mmol) and $CHBr_3$ (58 mmol) in pentane (50 mL) at *ca.* -10 °C[43]. The reaction mixture was allowed to warm to room temperature, diluted with diethyl ether (250 ml) and extracted with water. Drying of the organic layer, followed by filtration, evaporation of the solvent and purification by column chromatography afforded **19** as a colorless oil. 60 MHz ^{1}H-NMR ($CDCl_3$): δ = 1.7 ppm (dist. d, 2H) H_3, $H_{3'}$, $J_{2,3}$ = 9; δ = 2.5 ppm (dist. t, 1H) H_2, δ = 3.8 ppm (s, 2H) $ArCH_2Ar$; δ = 6.8 ppm (s, 9H) Ar H. EIMS; *m/e* (rel. intensity): 368 (1.3), 366 (M^+, 2.7), 364 (1.4), 287 (3.6), 285 (3.9), 206 (48), 205 (31), 181 (11), 180 (84), 179 (100), 178 (23), 165 (18), 128 (29), 115 (18), 91 (89).

For the preparation of 1-(*o*-benzyl)phenylallene (**6**) a solution of **19** in diethyl ether, cooled to

-78 °C, was treated with a slight excess of MeLi in hexane, followed by dilute hydrochloric acid. The reaction mixture was allowed to warm and extracted with water. Drying of the organic phase ($MgSO_4$), followed by filtration and evaporation of the solvent afforded crude 1-(*o*-benzyl)-phenylallene (**6**) which was purified by column chromatography. 90 MHz ^{1}H-NMR ($CDCl_3$): δ = 4.04 ppm (s, 2H) $ArCH_2Ar$; δ = 5.03 ppm (d, 2H) H_3, $^4J_{1,3}$ = 6.9 Hz; δ = 6.30 ppm (t, 1H) H_1; δ = 7.0 - 7.3 ppm (m, 9H) Ar H. IR(NaCl, cm^{-1}): 3080 (sh), 3060 (s) 3020 (s) C-H str. alkene, aryl; 2910 (w), 2855 (w) C-H str. aliphatic; 1940 (s) C=C=C str. as.; 1602 (m), 1493 (m-s) C=C str. aryl; 1453 (s),H-C-H bend.; 1075 (w) C=C=C str. s.. GC-EIMS; *m/e* (rel. intensity): 207 (16), 206 (M^+, 100), 205 (41), 191 (38), 178 (25), 165 (17), 152 (6), 129 (24), 128 (41), 115 (17), 101 (12), 91 (84).

1-(α-Methoxy)benzylindane (10). This compound was synthesized according to Scheme 10.

(±)1-Formylindane (**24**) was prepared according to a known[51] procedure with some modifications: A Darzens condensation with **25** and methyl chloroacetate yielded crude methyl indane-1-spiro-2′-oxirane-3-′carboxylate (**26**) as a thick brown syrup. Crystalline **26** (m.p. 83-86 °C) was obtained in 50 % yield by addition of abs. ethanol (1 mL g^{-1} of crude **26**). This product was sufficiently pure for further use. A very pure sample of **26** was obtained by crystallization from abs. ethanol (10 ml g^{-1} of **27**) as diamond-shaped colorless crystals; m.p. 85.5-86.0 °C. Elemental analysis: Calculated for $C_{12}H_{12}O_3$: C: 70.58%, H: 5.92%. Found: C: 70.56%, H: 5.97%. 90 MHz ^{1}H-NMR ($CDCl_3$): δ = 2.28 - 2.45 ppm (m, 2H) H_2; δ = 2.96 - 3.18 ppm (m, 2H) H_3; δ = 3.82 ppm (s, 3H) OCH_3; δ = 3.92 ppm (s, 1H) $H_{3'}$; δ = 6.97 - 7.06 ppm (m, 1H) H_7; δ = 7.06 - 7.34 ppm (m, 3H) Ar H. IR (KBr, cm^{-1}): 1747 (s) C=0 str.; 1205 (vs) C-O-str. of oxirane. EIMS; *m/e* (rel. intensity): 204 (M^+, 9), 186 (1), 173 (3), 147 (100), 133 (14), 117 (31), 116 (25), 115 (60), 91 (9). An M^+-57 base peak (in this case at *m/e* 147) has been observed in the mass spectra of other glycidic esters as well[41].

Following saponification of **26** with NaOH in ethanol, crude (solid) sodium indane-1-spiro-2′-oxirane-3′-carboxylate was isolated by evaporation of the solvent, addition of diethyl ether to the residue, filtration of the solid and washing with a little cold abs. ethanol. Decarboxylation in concentrated acetic acid and subsequent work up afforded (±)1-formylindane (**24**) as a colorless oil (bp. 65-70 °C/0.3 mm, n_D^{20} = 1.5534) in 25 % overall yield. 90 MHz ^{1}H-NMR ($CDCl_3$): δ = 2.15 - 2.49 ppm (m, 2H) H_2; δ = 3.00 ppm (dist. t, 2H) H_3, $J_{2,3}$ = 7.40 Hz; δ = 3.94 ppm (d of t, 1H) H_1, $J_{1,2}$ = 7.17 Hz, $J_{1,CHO}$ = 2.74 Hz; δ = 7.23 ppm (br. s, 4H) Ar H; δ = 9.63 ppm (d, 1H) CHO. EIMS; *m/e* (rel. intensity): 147 (M+1(H^+), 48), 146 (M^+, 12), 145 (11), 129 (21), 118 (16), 117 (100), 116 (24), 115 (33), 91 (14).

For the preparation of **10**, 1.59 g (10.8 mmol) of **24** in 5 ml of dry diethyl ether was added to 10 ml of a *ca.* 2 M etheral soln. of phenylmagnesium bromide. The reaction mixture was kept at 0 °C for 15 min, diluted with 10 ml of diethyl ether and extracted with 10 ml of a saturated NH_4Cl soln.. Drying ($MgSO_4$) of the organic layer, followed by filtration and evaporation of the solvent afforded 1.80 g (74 %) of 1-indanylphenyl carbinol as a brown oil. This compound was mixed with 25 ml of dry THF, treated with a 1.2-fold excess (6 mL) of a 1.6 M soln. of n-BuLi in hexane and subsequently with 5 ml of MeI. The mixture was refluxed for 3 hrs. Evaporation of the solvent and purification of the residue by column chromatography (silica gel, eluent CCl_4) afforded 1.25 g (49 %, based on the amount of **24** used) of **10** as a colorless oil. Elemental analysis: Calculated for $C_{17}H_{18}O$: C: 85.67%, H: 7.61%. Found: C: 84.71%, H: 7.41%. 90-MHz ^{1}H-NMR ($CDCl_3$): **10**-(1R,αR; 1S,αS): δ = 2.03 - 2.31 ppm (m, 2H) H_2; δ = 2.58 - 2.88 ppm (m, 2H) H_3; δ = 3.36 - 3.63 ppm (m, 1H) H_1; δ = 4.19 ppm (d, 1H) H_α , $J_{1,\alpha}$ = 7.2 Hz; δ = 6.54 ppm (broad d, 1H) H_7, $J_{6,7}$ = 7.0 Hz; δ = 6.83 - 7.26 ppm (m, 8H) Ar H. **10**-(1R,αS; 1S,αR): δ = 1.52 - 1.82 ppm (m, 2H) H_2; δ = 2.6 - 3.0 ppm (m, 2H) H_1; δ = 3.22 ppm (s, 3H) OCH_3; δ = 3.3 - 3.6 ppm (m, 1H) H_1; δ = 4.11 ppm (d, 2H) H_α , $J_{1,\alpha}$ = 7.0 Hz; δ = 6.8 - 7.3 ppm (m, 9H) Ar H. NMR integration: **10**-(1R,αR; 1S,αS)/**10**-(1R,αS; 1S,αR) = 5 (from irradiation of *exo*-**2** in MeOH), 2 (from chemical synthesis). EIMS; *m/e* (rel. intensity): 238 (M^+, 0.42), 223 (0.52), 222 (1.1), 221 (0.4), 207 (3.8), 122 (18), 121 (100), 117 (11), 116 (5), 115 (11), 105 (5), 91 (16), 77 (17).

Z-1-(α-Methoxybenzyl)-2-prop-1-enylbenzene (11). 90 MHz ^{1}H-NMR ($CDCl_3$): δ = 1.60 ppm (d of d, 3H) propenyl-H_3, $J_{1,3}$ = 1.5 Hz, $J_{2,3}$ = 6.8 Hz; δ = 3.35 ppm (s, 3H) OCH_3; δ = 5.42 ppm (s, 1H) benzylic H; δ = 5.81 ppm (d of q, 1H) propenyl-H_2, $J_{1,2}$ = J_{cis} = 11.4 Hz; δ = 6.50 ppm (d of q, 1H) propenyl-H_1; δ = 7.0 - 7.4 ppm (m, 9H) Ar H. EIMS; *m/e* (rel. intensity): 238 (M^+, 0.56), 223 (0.26), 207 (58), 206 (100), 191 (27), 179 (41), 178 (28), 165 (22), 161 (30), 152 (7), 129 (47), 128 (32), 121 (25), 115 (21), 105 (12), 91 (89), 77 (31). GC-CIMS (CH_4); *m/e* (rel. intensity): 239 (M+1(H^+), 6), 208 (17), 207 (100), 206 (21), 179 (6), 161 129 (67), 121 (93), 91 (28).

1-(α-Methoxybenzyl)-2-prop-2-enylbenzene (12). 90 MHz ^{1}H-NMR ($CDCl_3$): δ = 3.3 - 3.5 ppm (m, 2H) propenyl-H_1, $J_{1,2}$ = 6.3 Hz, $J_{1,3}$ = 3.3 Hz, $J_{1,3'}$ = 3.1 Hz; δ = 3.36 ppm (s, 3H) OCH_3; δ = 4.97 ppm (m, 1H) propenyl-H_3, $J_{2,3}$ = J_{trans} = 16.5 Hz, $J_{3,3'}$ = 2.0 Hz; δ = 5.04 ppm (m, 1H) propenyl-$H_{3'}$, $J_{2,3'}$ = J_{cis} = 10.5 Hz; δ = 5.47 ppm (s, 1H) benzylic H; δ = 5.91 ppm (m, 1H) propenyl-H_2; δ = 7.0 - 7.4 ppm (m, 9H) Ar H. GC-EIMS; *m/e* (rel. intensity): 238 (M^+, 0.52), 223 (1.7), 206 (100), 191 (31), 179 (37), 178 (26), 165 (20), 152 (7), 128 (19), 127 (31), 115 (17), 91 (87). GC-CIMS (CH_4); *m/e* (rel. intensity): 239 (M+1(H^+), 3.5), 208 (14), 207 (100), 206 (30), 179 (11), 128 (25), 119 (16), 117 (20), 91 (100).

1-(1-Methoxyprop-2-enyl)-2-benzylbenzene (13). 90 MHz ^{1}H-NMR ($CDCl_3$): δ = 3.14 ppm (s, 3H) OCH_3; δ = 4.04 ppm (s, 2H) benzylic H; δ = 5.14 ppm (m, 1H) propenyl-H_3, $J_{2,3}$ = J_{cis} = 9.3 Hz; δ = 5.15 ppm (m, 1H) propenyl-$H_{3'}$, $J_{2,3'}$ = J_{trans} = 18.0 Hz; δ = 4.81 (br. d, 1H) propenyl-H_1, $J_{1,2}$ = 6.3 Hz; δ = 5.87 ppm (m, 1H) propenyl-H_2; δ = 6.8 - 7.4 ppm (m, 9H) Ar H. GC-EIMS (mixture of **11**, **12** and **13**); *m/e* (rel. intensity): Highest mass at *m/e* 238 (presumably M^+, 0.5).

1-(3-Methoxyprop-1-enyl)-2-benzylbenzene (14, *Z*/*E* = 4). 90 MHz ^{1}H-NMR ($CDCl_3$): *Z*-**14**: δ = 3.23 ppm (s, 3H) OCH_3; δ = 4.00 ppm (br. d, 2H) propenyl-H_3, $J_{2,3}$ = 6.0 Hz; δ = 4.03 ppm (s, 2H) benzylic H; δ = 5.80 ppm (d of t, 1H) propenyl-H_2, $J_{1,2}$ = J_{cis} = 11.4 Hz; δ = 6.56 ppm (broad d, 1H) propenyl-H_1; δ = 7.0 - 7.4 (m, 9H) Ar H. *E*-**14**: δ = 3.26 ppm (s, 3H) OCH_3; δ = 4.00 ppm (d of d, 2H) propenyl-H_3, $J_{1,3}$ = 1.2 Hz, $J_{2,3}$ = 5.7 Hz; δ = 4.03 ppm (s, 2H) benzylic H; δ = 6.09

ppm (d of t, 1H) propenyl-H_2, $J_{1,2} = J_{trans}$ = 16.0 Hz; δ = 6.80 ppm (br. d, 1H) propenyl-H_1; δ = 7.0 - 7.4 ppm (m, 9H) Ar H. EIMS (mixture, *Z*-**14**/*E*-**14** = 4); *m/e* (rel. intensity): 238 (M^+,18), 207 (23), 206 (95), 205 (23), 193 (12), 192 (13), 191 (30), 180 (50), 179 (100), 178 (67), 165 (37), 152 (10), 129 (17), 128 (20), 121 (17), 117 (18), 115 (44), 105 (10), 91 (88), 77 (18). UV (MeOH, mixture, *Z*-**14**/*E*-**14** = 4); λ_{max} (nm) (log ϵ_0): 240 (3.75) sh.

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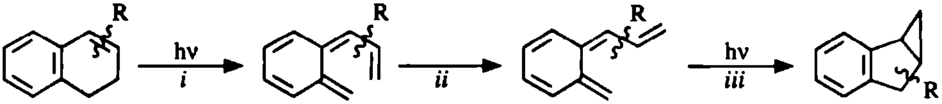
Chapter 5: The photochemistry of 3-phenyl-1,2-dihydronaphthalene and some derivatives in methanol.

Introduction.

The photochemistry of 1,2-dihydronaphthalene (1,2-DHN) and its derivatives has been studied exhaustively over the past decades. Transformation of the 1,2-dihydronaphthalene skeleton into the benzobicyclo [3.1.0]hex-2-ene moiety has been identified as the basic photoreaction of this class of compounds[1]. The mechanism of the transformation is well-established[2], and involves the following steps: (*i*) Photochemical conrotatory ring opening of the 1,2-dihydronaphthalene at the C(1)-C(2) bond yielding a *cZc*-pentaene; (*ii*) Thermal conversion of the *cZc*- into the *cZt*-rotamer and (*iii*) Intramolecular photocycloaddition involving the cyclohexatriene moiety of the *cZt*-pentaene, yielding a benzobicyclo[3.1.0]hex-2-ene as the stable end-product (Scheme 1).

Scheme 1



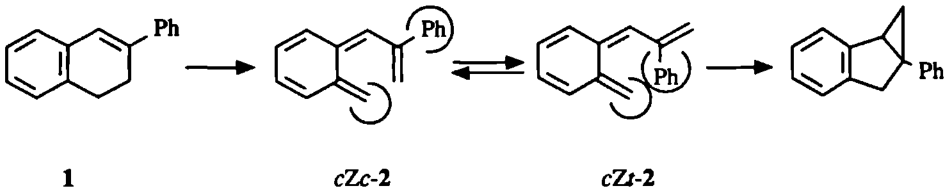
In several cases[3-6] the pentaene intermediate involved in this sequence has been observed and characterized spectroscopically at low temperature, where its life time is usually sufficiently long to allow the build-up of an appreciable steady-state concentration. The formation of substituted benzobicyclo[3.1.0]hex-2-enes *via* this route has been reported for several alkyl-[4,7-10]and aryl-substituted[5,6,11-13] 1,2-dihydronaphthalenes. A ring opening reaction similar to step (*i*) in Scheme 1 was found to be responsible for the photochromism of various 1- and 2- heterosubstituted 1,2-dihydronaphthalenes[14].

In a previous paper[12], it has already been noted that the compound 3-phenyl-1,2-dihydronaphthalene (**1**) presents an exception to this general reactivity pattern: On irradiation in hexane under reaction conditions, which allow 1-,2- and 4-phenyl-1,2-dihydronaphthalene to give the corresponding phenylbenzobicyclo[3.1.0]hex-2-enes in fair yields,[11,13] **1** proved to be photostable.

As has been pointed out in Refs. 11-13, the difference in photoreactivity of **1** and the other phenyl-substituted 1,2-dihydronaphthalenes can be interpreted in two ways.

First, it has been argued[13] that **1**, like 1-, 2- and 4-phenyl-1,2-dihydronaphthalene undergoes the photochemical ring opening (Scheme 1, step (*i*)) to yield the corresponding pentaene (*cZc*-**2**, Scheme 2). This fails however, to give the rotamer *cZt*-**2** in a subsequent step (Scheme 1, step (*ii*)).

Scheme 2



Owing to considerable steric crowding between the bulky phenyl substituent and the exocyclic methylene group, the activation barrier for thermal conversion of *cZc*-**2** into *cZt*-**2** should be very high, making thermal or photochemical reversion to **1** the only feasible reaction route for *cZc*-**2**.

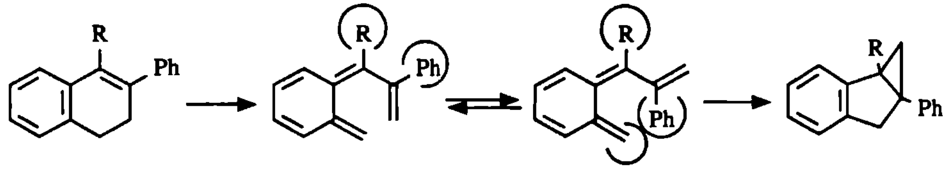
For 1-,2- and 4-phenyl-1,2-dihydronaphthalene the mechanism does not include appreciable steric crowding in the corresponding *cZt*-pentaenes. Hence, it rationalizes correctly the observed formation of phenylbenzobicyclo[3.1.0]hex-2-enes from these compounds. The observation, that quantum yields of fluorescence for 3- (**1**) and 1-, 2- and 4-phenyl-1,2-dihydronaphthalene are nearly equal corroborates the suggestion, that **1** resembles the isomeric phenyl-dihydronaphthalenes in most respects, except for its photostability.

Supporting evidence, in agreement with this hypothesis, has been put forward by Padwa.[15] On irradiation of 2-oxa-3-phenyl-1,2-dihydronaphthalene (3-phenylisochromene, (**5**)) he observed photoproducts attributable to elusive pentaene and bicyclo[3.1.0]hex-2-ene intermediates.

As an alternative explanation of the exceptional behavior of **1**, it has been argued[13] that **1** may be an intrinsically photostable compound, not capable of undergoing the primary photoreaction to *cZc*-**2** (Scheme 2). This hypothesis is based on the obvious structural resemblance between **1** and *trans*-stilbene. This analogy is also reflected in the nearly identical UV absorption spectra [12,13] and quantum yields of fluorescence[13] of **1** and *trans*-stilbene. Extending this analogy to the photochemistry of these compounds, it would emerge that isomerization to the *cis*-isomer being the only very efficient photoreaction for *trans*-stilbene is not possible for the rigid 3-phenyl-1,2-dihydronaphthalene (**1**); this might rationalize the intrinsic photostability of the compound.

This chapter deals with experiments aimed to elucidate the true cause of the photostability of 3-phenyl-1,2-dihydronaphthalene (**1**). To this aim both hypotheses outlined above will be tested for their validity.

The experimental approaches used to test the hypothesis outlined in Scheme 2 have been focussed chiefly on lowering the energy barrier between the *cZc*- and *cZt*-conformers of the pentaene intermediate **2**. A trivial way to achieve this, is by increasing the reaction temperature. Another approach involves introduction of bulky substituents R at C(4) of **1**. As outlined in Scheme 3, this leads to steric crowding between R and Ph in the *cZc*- but not in the *cZt*-conformer of the pentaene intermediate. Consequently, the energy barrier between these conformers will decrease with increasing size of the substituent R. An similar approach has been applied



1, R = H
3, R = Me
4, R = Et

cZc

cZt

Scheme 3

successfully in altering the photoreactivity within a series of substituted hexa-1,3-5-trienes[16]. Following this approach, we examined the cases R = Me (4-methyl-3-phenyl-1,2-dihydronaphthalene, **3**), R = Et (4-ethyl-3-phenyl-1,2-dihydronaphthalene, **4**) and R = H (**1** itself)[17].

Another strategy for testing the hypothesis outlined in Scheme 2 is based on the assumption that owing to the absence of steric crowding the stability of *cZc*-pentaenes, originating from the photochemical ring opening of substituted 1,2-dihydronaphthalenes, should be independent of the size and position of substituents; unlike *cZt*-**2**, *cZc*-**2** (Scheme 2) and the *cZc*-pentaenes derived from 1-, 2- and 4-phenyl-1,2-dihydronaphthalene should be of comparable stability.

Following this strategy we irradiated 3-phenyl-1,2-dihydronaphthalene (**1**) and 4-methyl-3-phenyl-1,2-dihydronaphthalene (**3**) at low temperature and looked spectroscopically or simply by visional[5,6] for colored pentaene intermediates.

When **1** is assumed to be resistant to photochemical ring opening stilbene-like photochemistry should be expected for compounds **1** and **3**-**5**, of course with the exception of *cis-trans* isomerization which is not possible with these cyclic olefins. Apart from efficient photoisomerization to the *cis*-isomer[18], *trans*-stilbene is known to undergo [2+2] photodimerization[19,20] and photochemical addition of small molecules like methanol[6,21] to the double bond. Within the presently considered hypothesis, the last mentioned, inefficient photoreactions might be expected on irradiation of compounds **1** and **3**-**5** in the appropriate solvents.

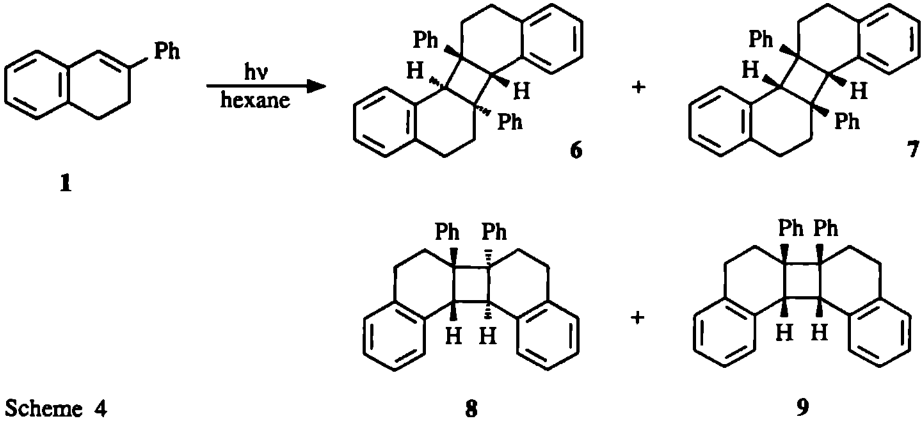
According to this hypothesis **1** and *trans*-stilbene should exhibit different quantum yields of internal conversion. To verify the extent to which this criterion is satisfied, relative quantum yields of internal conversion in **1**, *trans*-stilbene and related compounds have been evaluated by photoacoustic spectroscopy[22] as well as indirectly from the quantum yields of fluorescence.

In addition to the studies indicated above we have performed experiments to establish qualitatively, the polarity of the excited state involved in the photochemistry of **1**, **3** and **4** (Scheme 3). According to MO-CI calculations on *cZc*- and *cZt*-hexa-1,3-5-triene[23] excited singlet states of *cZt*-pentaenes e.g. *cZt*-**2** (Scheme 2) might gain considerable stability from the sudden-polarization effect[24,25]. I.e. in cases where Scheme 1 applies, the possible involvement of a highly polar, twisted excited S_1 state should be considered. Opposite to this, the alicylic olefins **1**, **3** and **4** themselves are not likely to be twisted appreciably at the double bond in their respective S_1 states. Hence, these S_1 states are expected[23,26] to be essentially non-polar.

The experimental approach involved in this study, concerns (*i*) Evaluation of the effect of sulfuric acid on the yields of primary photoproducts in methanol. (*ii*) Fluorescence quenching studies in methanol, employing concentrated sulfuric acid as the quencher.

Irradiations in hexane.

3-Phenyl-1,2-dihydronaphthalene (1). Irradiation of a deaerated solution (5×10^{-3} M) of **1** with a high-pressure mercury lamp at 15 °C for 2 hrs. confirmed the previously reported photostability of this compound. However, prolonged (12 hrs) irradiation under these conditions resulted in appreciable conversion of **1** into volatile and polymeric compounds. On irradiation at -80 °C for 1 hr the formation of polymers turned out to be negligible, and a mixture of three hexane-soluble photoproducts had formed in 45% yield. Attempts to separate the products by column chromatography were unsuccessful. Fortunately a fourth photoproduct had precipitated from the irradiation mixture (in 11% yield). The CI mass spectrum of the precipitate (m/e 413 (M+1, 3%)) provided evidence for the presence of a dimer of **1**, and this evidence was substantiated by X-ray analysis[27], which showed the pre-cipitate to be *trans*-1,7-diphenyldibenzotricyclo-[6.4.0.0^{2,7}]dodeca-3,9-diene (**6**, Scheme 4), one of the four dimers expected from a symmetry-allowed [2+2] photocycloaddition reaction of **1**. The ^{1}H-NMR spectrum of dimer **6** is consistent with the crystal structure, determined by X-ray analysis: The protons of the cyclobutane ring in **6** appear at δ = 4.36 ppm (s, 2H), a value which is very close to the δ-value reported for the configurationally corresponding of the cyclobutane ring in 1-*cis*-2-*trans*-3-*cis*-1,2,3,4-tetraphenylcyclobutane[28].



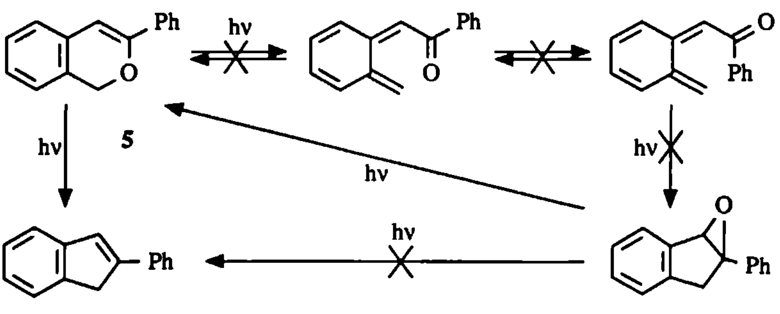
Scheme 4

The ^{1}H-NMR spectrum of the mixture of the hexane-soluble photoproducts was found to be very similar to that of dimer **6**. It exhibited singlets at δ *ca.* 4 ppm (together 2H), overlapping multiplets in the aliphatic (δ = 1.6 - 2.6 ppm (8H)) as well as the aromatic (δ = 6.8 - 7.6 ppm (18H)) region, and no absorptions attributable to olefinic protons. These data were assigned to dimers **7-9** (Scheme 4). The configuration of the protons at the cyclobutane ring in dimers **7-9** could be established by matching their δ-values with those reported[28] for the cyclobutane ring protons in 1,2,3,4-tetraphenylcyclobutanes of known configuration. Unlike **6** which is stable at the m.p. (313 °C), dimers **7-9**, decompose into the monomer **1** at much lower temperature. This leads to identical EI mass spectra and GLC retention times for **7-9** and **1**. Hence, characterization of dimers **7-9** by GLC and GC-MS was impossible. Finally, it should be mentioned that volatile compounds, others than the dimers **6-9** could not be detected (GLC, GC-MS, detection limit 0.1%) among the photoproducts of **1** in hexane.

4-Methyl- (3) and 4-ethyl-3-phenyl-1,2-dihydronaphthalene (4). Irradiation of ca. 5 × 10^{-3} M solutions of these compounds in deaerated hexane at wavelengths of 250 - 350 nm and at temperatures of 183-263 K until 5-100% conversion of the starting material afforded invariably polymeric photoproducts, which could not be eluted from silica gel with carbon tetrachloride. Volatile photoproducts, which might be expected e.g. from photochemical ring opening, 1,3-shifts or dimerization of the starting material could not be detected; not even at low conversion levels and low temperatures.

3-Phenylisochromene (5). Unlike 3-phenyl-1,2-dihydronaphthalene (**1**), **5** was found to be reactive on irradiation (2 hrs) of a 5 × 10^{-3} M solution in deaerated hexane with a HPM lamp at 15 °C. Volatile photoproducts, deriving from photochemical ring opening[15] (Scheme 5) or [2+2] cyclodimerization were not found under these conditions; polymeric compounds were the only photoproducts obtained. However, anaerobic irradiation of **5** (10^{-3} M) at 300 nm and at room temperature for 20 hrs afforded 2-phenylindene (**10**) in strongly varying, but always appreciable yields (up to 30% at 50-100% conversion of **5**). The supposition that this compound might

Scheme 5



10

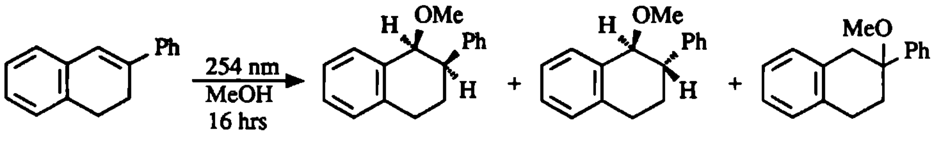
11

originate from a primary photochemical ring opening of **5** *via* 2-phenylindene oxide (**11**, Scheme 5) could be rejected: Irradiation (254 nm) of authentic **11** in hexane afforded **5** in nearly quantitative yield, without a trace of **10** (Scheme 5). The mechanism of the reaction involves presumably breaking of the C-C bond of the 3-membered ring and has been precedented in the irradiation of indene oxide[29] and of benzobicyclo[3,1,0]hex-2-enes[5,6,11-13]. This procedure for the preparation of 3-phenylisochromene (**5**), viz. by irradiation of the easily accessible **11**,[15] is superior to conventional synthetic methods[30a-30c].

Irradiations in methanol.

3-Phenyl-1,2-dihydronaphthalene (1). A deaerated, 2×10^{-3} M solution of this compound was found to be completely photostable to irradiation at -80 °C with a HPM lamp: Even after 24 hrs no conversion into methanol adducts, dimers or other photoproducts had occurred. Prolonged, monochromatic irradiation (16 hrs at 254 nm or 100 hrs at 300 nm, ambient temperature) of **1**, however, gave three methanol adducts (GC-MS) in *ca.* 60% yield. The methanol adducts were readily separated form unreacted **1** by column chromatography. Two of the methanol adducts exhibited very similar ^{1}H-NMR and mass spectra and were identified as *cis*- and *trans*-1-methoxy-2-phenyl-1,2,3,4-tetrahydronaphthalene (*cis*- and *trans*-**12**, (Scheme 6) by chemical synthesis[31,32]. The ^{1}H-NMR spectrum of the third methanol adduct showed the signal of a methoxy group, stereochemically more crowded than that in **12** (δ = 3.06 ppm (s, 3H)), and an isolated methylene group (δ = 3.17 ppm (s, 2H). The data were assigned to 2-methoxy-2-phenyl-1,2,3,4-tetrahydronaphthalene (**13**) (Scheme 6). The identity of this compound was likewise confirmed by chemical synthesis.

Scheme 6



1, 0.002 M　　*cis*-**12**, 6%　　*trans*-**12**, 12%　　**13**, 30%

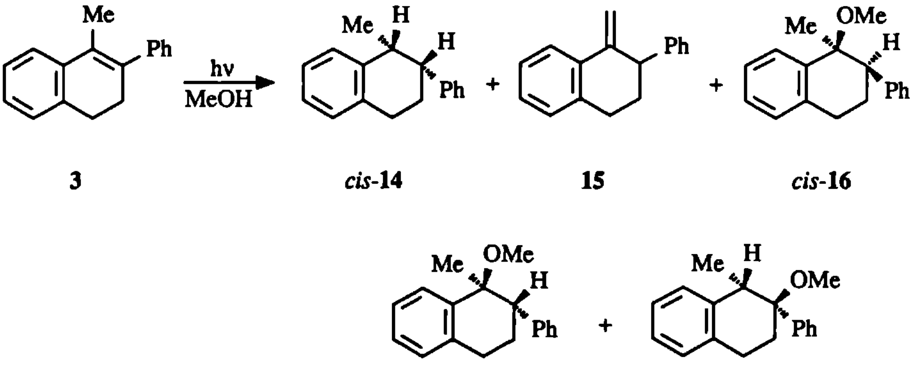
The EI mass spectra of **12-13** were found to be in accordance with the tetrahydronaphthalene structure assigned to these compounds: like many other 1,2,3,4-tetrahydronaphthalenes and related compounds, *cis*- and *trans*-**12** by a retro Diels-Alder reaction.[33] On the other hand the fragmentation pattern (EIMS) of regioisomer **13** is dominated by elimination of MeOH. Owing to these features, EIMS presents a valuable diagnostic tool for establishing the mutual positions of the substituents in substituted 1,2,3,4-tetrahydronaphthalenes, particularly those resulting from the photochemical reactions of **3** and **4** in the next sections.

Methanol adducts **12** and **13** were found to occur at relatively low (<10%) conversion of the starting material **1**. Hence, it was concluded that they are primary photoproducts. By irradiations (254 nm) of authentic **12** and **13** it was demonstrated that these methanol adducts cannot be interconverted photochemically, photodecomposition into polymeric products being the only secondary photoreaction observed with these compounds.

A more detailed study of the primary and secondary photoreaction of **1**, by monitoring the conversion and photoproduct yields as a function of the irradiation time was obstructed by the photoinstability of **12** and **13** and the inseparability of these compounds by temperature-programmed capillary GLC. For the same reason, the effect of temperature and acid on the yield of **12** and **13** could not be evaluated. These studies have been performed, however, with 4-methyl-3-phenyl-1,2-dihydronaphthalene (**3**). As outlined in the next section, this compound undergoes photochemical addition of methanol much faster then **1**, and yields photostable methanol adducts, separable by GLC.

4-Methyl-3-phenyl-1,2-dihydronaphthalene (3). Isolation and analysis of the photoproducts were performed with 100 mg samples, originating from irradiation of **3** (2×10^{-3} M in methanol) with a HPM lamp under anaerobic conditions and at temperatures ranging from 193-338 K. The photoproducts were separated by flash chromatography into fractions containing the nonpolar and polar compounds, respectively.

GC-MS analysis revealed that the nonpolar chromatography fraction consisted of unreacted **3** and two other hydrocarbons, having m/e 222 and 220, respectively. The ^{1}H-NMR spectrum of the hydrocarbon having m/e 222 showed a doublet (δ = 0.91 ppm) due to a methyl group and a multiplet (δ =2.87 - 3.37 ppm) indicating the presence of four benzylic protons in the molecule. These data were assigned to 1-methyl-2-phenyl-1,2,3,4-tetrahydronaphthalene (**14**, Scheme 7).



Scheme 7

trans-**16**

17

The GLC retention time, ^{1}H-NMR data and mass spectrum were found to match those of *cis*-**14**, prepared by catalytic hydrogenation of **3**. The low δ-value of the protons of the methyl group in *cis*-**14**[34] results from shielding by the neighboring phenyl groups at C(1) and C(2), respectively. In methyl-substituted 1,2,3,4-tetrahydronaphthalenes, without such steric crowding, the ^{1}H-NMR absorption due to the methyl protons occurs at 1.2 - 1.4 ppm[34].

The hydrocarbon having m/e 220 showed the ^{1}H-NMR characteristics of a terminal olefinic methylene group (δ = 4.70 and 5.63 ppm, both br. s, 1H) at a carbon atom bearing no hydrogens, a tertiary CH fragment (δ = 3.78 ppm (t, 1H)) bearing two olefinic/aromatic substituents and an aliphatic methylene group (δ = 2.17 ppm (dist. q, 2H)) connecting the tertiary CH fragment with a benzylic methylene group (δ = 2.82 ppm (t, 2H)). These data were assigned to 1-methylidene-2-phenyl-1,2,3,4-tetrahydronaphthalene (**15**, Scheme 7). Unfortunately, attempts to synthesize **15** from 2-phenyl-1,2,3,4-tetrahydronaphthalene-1-one *via* a Wittig reaction[35-37] failed.

According to GC-MS the polar chromatography fraction consisted of three distinct methanol adducts of **3**, all three showing m/e 252 (M^+, 3%) and 220 (M-32(MeOH), 100%). In analogy with the photoproducts of **1** in methanol, two of these adducts exhibited very similar mass and ^{1}H-NMR spectra. Since for both adducts, the ^{1}H-NMR absorption due to the protons of the methyl group at C(1) appeared as a singlet, the adducts were concluded to be *cis*- and *trans*-1-methoxy-1-methyl-2-phenyl-1,2,3,4-tetrahydronaphthalene (*cis*- and *trans*-**16**). This assignment was confirmed by chemical synthesis of a mixture of *cis*- and *trans*-**16** (Scheme 7).

Like *cis*-**14**, *trans*-**16** exhibits the *cis*-configuration for the neighboring methyl and phenyl substituents at C(1) and C(2). Hence, steric crowding of these groups occurs in *trans*-**16**, but not in *cis*-**16**. Accordingly, the ^{1}H-NMR absorptions at δ = 1.18 and 1.40 ppm were assigned to *trans*- and *cis*-**16**, respectively. By similar reasoning the ^{1}H-NMR absorptions at δ = 3.01 and 3.14 ppm were assigned to the methoxy groups in *cis*- and *trans*-**16**, respectively. The assignment of the remaining ^{1}H-NMR data of the isomers was deduced from the results of spin-decoupling and spectrum integration.

The ^{1}H-NMR data of the third methanol adduct of **3** included a doublet at δ = 0.77 ppm (3H) due to a sterically crowded methyl group, attached to a tertiary CH fragment (C(1)) and a singlet (δ = 3.01 ppm (3H)) due to a sterically crowded methoxy group. Moreover, the EI mass-spectrum of this adduct differed noticeably from those of *cis*- and *trans*-**16** by an intense peak at m/e 118 (100%) due to liberation of methyl-*ortho*-quinodimethane. These data were assigned to *trans*-1-methyl-2-methoxy-2-phenyl-1,2,3,4-tetrahydronaphthalene (**17**, Scheme 7). Except for ^{1}H-NMR absorptions arising from the presence of the methyl group at C(1) in **17**, the ^{1}H-NMR spectra of **17** and **13** were very similar.

At low conversion and at temperatures of 183-288 K, the photoreactions of **3** into **14-17** occurred without concomitant formation of side-products. At 338K and 51% conversion of **3**, the chemical yield of **14-17** added up to more than 90%; the remainder consisted of polymeric side products, which could not be eluted from silica gel with carbon tetrachloride.

Despite numerous, minute searches by GC-MS and ^{1}H-NMR, compounds which should have formed when **3** had undergone a photochemical ring opening reaction to an intermediate pentaene (Scheme 2), were never observed among the irradiation products of **3**; not even in trace quantities.

The progress of the photoreaction of 4-methyl-3-phenyl-1,2-dihydronaphthalene (**3**) into **14-17** (Scheme 7) was monitored as a function of the irradiation time. As can be seen from the results obtained at -90 °C, -45 °C and +15 °C (Fig. 1a-1c). **15**, *trans*-**16** and **17** are primary photoproducts. At these temperatures, the formation of the hydrocarbon *cis*-**14** and of the methanol adduct *cis*-**16** sets in at the point where the yield *vs.* time curve of **15** approaches a maximum. This implies that *cis*-**14** and *cis*-**16** are formed by secondary photoreactions, presumably *via* **15**. From the results obtained at 65 °C (Fig. 1d) it was concluded that at this temperature, *cis*-**14** and *cis*-**16** originate in part from primary photoreactions, though in this case too, formation of these products from the exocyclic olefin **15** predominates. Furthermore, Fig. 1d indicates that at 65 °C a significant fraction of the methanol adduct *trans*-**16** derives from a secondary photoreaction of **15**.

The conclusions, presented above for 4-methyl-3-phenyl-1,2-dihydronaphthalene (**3**) are corroborated by the results of irradiations of the exocyclic olefin **15** and of the methanol adducts **16** and **17**, under the conditions used for compound **3**. The results presented in Table 1 confirm, that **14**, *cis*-**16** and *trans*-**16**, but not **17** are formed on irradiation of **15** in methanol. Moreover, these results demonstrate that the photoreaction of **3** to **15** is quasi-reversible. Form the yields of **15** (from **3**, Fig. 1c) and of **3** (from **15**, Table 1) observed after 2 hrs irradiation, the photoreaction of **3** to **15** was estimated to be 10 times more efficient than the reverse reaction. By irradiation of the methanol adducts *cis*-**16**, *trans*-**16** and **17** it was established, that these photoproducts are not interconverted photochemically, slow decomposition into non-volatile, polymeric products is the only photoreaction observed with these methanol adducts.

Table 1. Irradiation (HPM) of 1-methylidene-2-phenyl-1,2,3,4-tetrahydronaphthalene (**15**, 2.3 $\times 10^{-3}$ M) neat methanol and in methanol containing 5.0×10^{-2} M H_2SO_4: Photoproduct yields ($\times 10^5$, min^{-1}) of 4-methyl-3-phenyl-1,2-dihydronaphthalene (**3**), *cis*-1-methyl-2-phenyl-1,2,3,4-tetahydronaphthalene (**14**), *cis*- and *trans*-1-methoxy-1-methyl-2-phenyl-1,2,3,4-tetrahydronaphthalene (*cis*- and *trans*-**16**) and *trans*-2-methoxy-1-methyl-2-phenyl-1,23,4-tetrahydronaphthalene (**17**), and photoconversion rate of **15**.

	3	14	*cis*-16	*trans*-16	17	15
MeOH	8.3	10	16	60	-	- 95
MeOH/H_2SO_4	35	10	8.3	54	-	-108

The effect of temperature on the photoreactions of 4-methyl-3-phenyl-1,2-dihydronaphthalene (**3**) into **14-17** (Scheme 7) has been evaluated by determining the time required for 50% conversion of **3** and subsequently the composition of the reaction mixture (GLC) at this level of

Fig. 1. Irradiation (HPM) of 4-methyl-3-phenyl-1,2-dihydronaphthalene (**3**, 2.3 × 10^{-3} M) in deaerated methanol: Yield *vs.* time curves for the formation of *cis*-1-methyl-2-phenyl-1,2,3,4-tetrahydronaphthalene (**14**), 1-methylidene-2-phenyl-1,2,3,4-tetrahydrmaphthalene (**15**), *cis*- and *trans*-1-methoxy-1-methyl-2-phenyl-1,2,3,4-tetrahydronaphthalene (*cis*- and *trans*-**16**) and *trans*-2-methoxy-1-methyl-2-phenyl-1,2,3,4-tetrahydronaphthalene (**17**) evaluated at -90 °C (1a), at -45 °C (1b), at 15 °C (c, solid curves), at 15 °C,in the presence of 2.5 × 10^{-2} M H_2SO_4 (1c, dashed curves) and at 65 °C (1d).

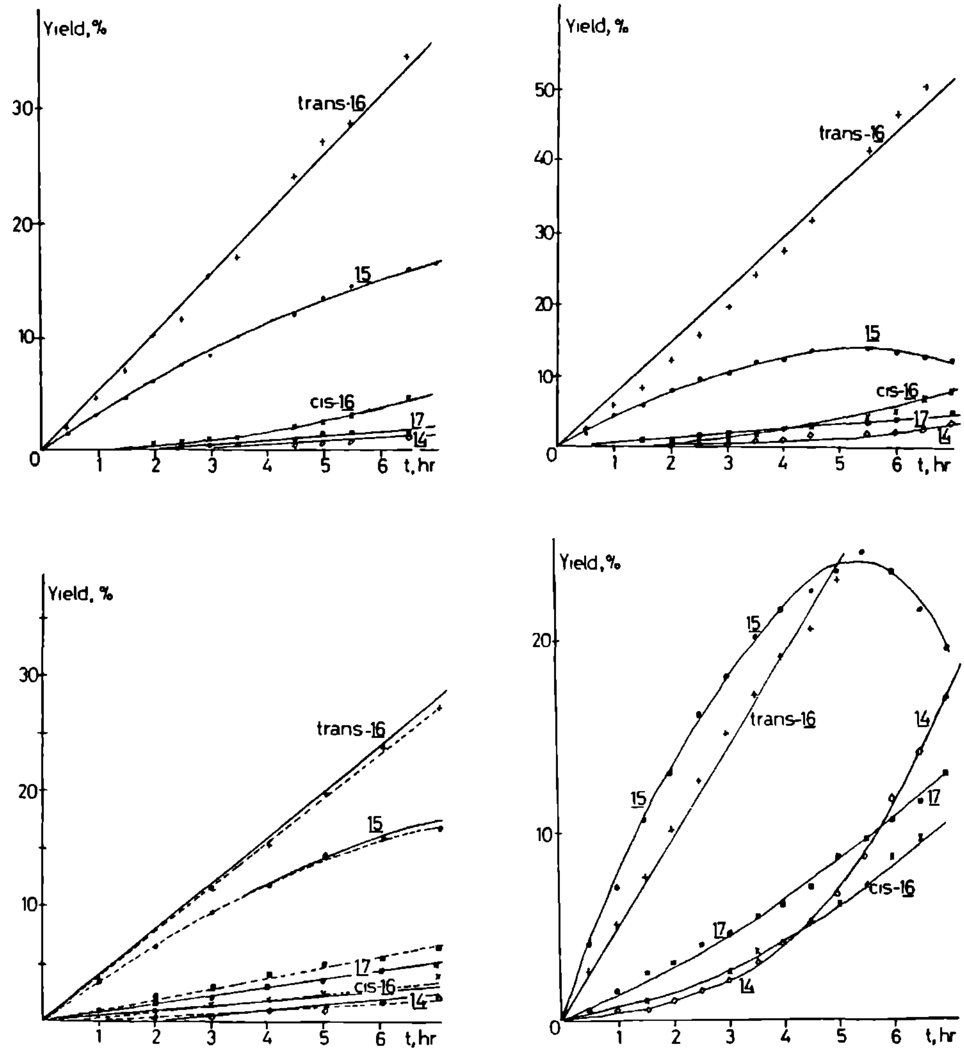


Table 2. Influence of the reaction temperature on the composition of the photoproduct mixture evaluated at 50% conversion of 4-methyl-3-phenyl-1,2-dihydronaphthalene (**3**) in neat MeOH, under the irradiation conditions stated in Fig. 1. Photoproduct yields are given in %, t_{50} represents the time needed to achieve 50% photoconversion of **3**.

T (°C)	-95	-45	15	65
t_{50} (hrs)	5.5	4.5	4	3.5
14	14.5	13	15.5	21
15	0.5	1	1.5	3.5
cis-**16**	3	3	2	1.5
trans-**16**	30.5	30	26	18.5
17	1.5	3	5	5.5

conversion. The results (Table 2) indicate that the rate of photoconversion of **3** increases with increasing temperature. Simultaneously, the yields of the hydrocarbons *cis*-**14** and **15** appear to be enhanced at the expense of the methanol adducts *cis*- and *trans*-**16**. In contrast with the latter compounds, the rate of formation of the methanol adduct **17** increases with increasing temperature.

To track down possible polarized excited states and/or intermediates on the routes from **3** to the photoproducts **14**-**17**, the irradiation experiment outlined in Fig. 1c was repeated with **3** in methanol containing 2.5 × 10^{-2} M of sulfuric acid. The results are represented by the dashed curves in Fig. 1c. In comparison with the results obtained in the absence of acid (Fig 1c, solid curves) causes a *ca.* 30% higher yield of methanol adduct **17**, a doubled yield of *cis*-**16** and a virtually unchanged yield of *trans*-**16**. This is also illustrated in Table 3, where the effect of H_2SO_4 on the *trans*-**16**/*cis*-**16** extrapolated to low conversion of the starting material **3** is given. Moreover Fig. 1c shows, that the rates of conversion of **3** into the hydrocarbons *cis*-**14** and **15** are not affected by the presence of H_2SO_4.

Since starting material **3** and photoproducts *cis*-**14** and **16** have been shown to arise in photoreactions from exocyclic olefin **15**, a reliable interpretation of the results presented in the previous paragraph cannot be given without having established the effect of 2.5 × 10^{-2} M sulfuric acid on the photoreactions of **15** to the starting compound **3**, the hydrocarbon *cis*-**14** and the methanol adducts **16** (Scheme 7). The yield *vs.* time curves of **3**, *cis*-**14** and **16**, evaluated under the irradiation conditions stated in Fig. 1c were found to be linear. Hence, average yields per unit of time have been calculated and collected in Table 1. These data show that formations of hydrocarbon *cis*-**14** and methanol adduct *trans*-**16** from **15** are not sensitive to acid catalysis. However, photoreversion of **15** to **3** occurs much faster in the presence of H_2SO_4. Simultaneously, the yield of methanol adduct *cis*-**16** is somewhat diminished by the presence of acid, emerging

Table 3. Ratio (*trans*-**16**/*cis*-**16**) of the photoproducts *trans*- and *cis*-1-methoxy -1-methyl-2-phenyl-1,2,3,4-tetrahydronaphthalene from 3-phenyl-1,2-dihydronaphthalene (**3**) and from 1-methylidene-2-phenyl-1,2,3,4-tetrahydronaphthalene (**15**) in neat and H_2SO_4-containing methanol at 15 °C. (See Fig. 1 or Table 1 for the reaction conditions)

compound	solvent	*trans*- **16**/*cis*-**16** ratio
3	MeOH	16
	$MeOH/H_2SO_4$	7.5
15	MeOH	6.5
	$MeOH/H_2SO_4$	3.7

into a relatively small increase in the *trans*-**16**/*cis*-**16** ratio (Table 3).

4-ethyl-3-phenyl-1,2-dihydronaphthalene (4). Irradiation of this compound under conditions similar to those employed for the methyl analog **3**, afforded a mixture of six photoproducts. The ^{1}H-NMR spectrum of the mixture and the mass spectra of its constituents (GC-MS) provide convincing evidence for the conclusion that irradiation of **4** yields the ethyl homologues[39] of the photoproducts **14-17** (Scheme 7). Photoproducts, deriving from photochemical ring opening (Scheme 3) of **4**, could not be detected, not even in trace quantities. Thus, it appears that the photochemistry of **4** closely resembles that of the methyl analog **3** and the parent compound 3-phenyl-1,2-dihydronaphthalene (**1**). Since the present photochemical study of the 4-substituted 3-phenyl-1,2-dihydronaphthalenes **1**, **3** and **4** concerns a mere comparison of their respective photoreactivities in polar and nonpolar solvents, a time consuming, rigorous characterization of the photoproducts from **4** has been omitted.

The fact that on irradiation in methanol, **4** afforded one more photoproduct than **3** arises from the occurrence of *cis-trans* isomerism at the double bond in 1-ethylidene-2-phenyl-1,2,3,4-tetrahydronaphthalene. Indeed GC-MS analysis confirmed the presence of two hydrocarbons among the photoproducts, having m/e 234 and fragmentation patterns similar to that of **15**. The ethyl analog[38] of *cis*-**14** was recognized by its mass (m/e 236) and its GLC retention time was equal to that of the product obtained on exposure of **4** to H_2 and Pd/C.

Evidence for the formation of the ethyl analogs of **16** and **17** (Scheme 7) came from the ^{1}H-NMR spectrum of the mixture of photoproducts from **4**, which exhibited three sharp resonances located at precisely the δ-values of the methoxy groups in *cis*-**16**, *trans*-**16** and **17**. Unlike *cis*- and *trans*-**16**, the EI mass spectra of their ethyl analogs did not exhibit a molecular mass peak (at m/e 266). However, the fragmentation patterns of the compounds agree with that expected[33] for 1-ethyl-1-methoxy-2-phenyl-1,2,3,4-tetrahydronaphthalene. The mass spectrum of the ethyl analog of **17** exhibited both a peak at the expected mass (m/e 266 (M^+, 20%)) and fragmentation peaks (m/e 234 (M-32(MeOH), 20%, m/e 132 (ethyl-*ortho*-quinodimethane, 100%)) similar to those of **17**.

Photoacoustic effects and Stokes shifts.

From the evidence accumulated so far, it is obvious that 3-phenyl-1,2-dihydronaphthalene (**1**) and its 4-methyl- and 4-ethyl-substituted derivatives **3** and **4** do not undergo the photochemical ring opening reaction to the corresponding pentaene intermediate. This implies that the high photostability of **1**, not observed in 1-, 2- and 4-phenyl-1,2-dihydronaphthalene, is intrinsic, rather than the consequence of a high energy barrier between the *cZc*- and *cZt*-rotamers of a pentaene intermediate. Considering the low quantum yield of fluorescence ($\phi = 0.06$) reported[13] for **1** in hexane, it emerges from the present results that the lowest excited singlet (S_1) state of **1** relaxes mainly by internal conversion ($\phi_{IC} = 1-\phi_{fl}= 0.94$). This conclusion poses an apparent contradiction, viz. that the stilbene moiety of **1** is usually considered to be a comparatively rigid structure, whereas the established[40,41] physics of internal conversion includes that this type of process is most efficient in flexible molecules, providing a large number of modes for vibrational relaxation. In this connection, acquisition by direct experimental methods of data on the flexibility and efficiency of the internal conversion process of **1**, **3** and structurally related compounds is highly relevant.

Information concerning the flexibilities of molecules in their ground and lowest excited singlet (S_1) state can be obtained from the Stokes shift[42], which measures the change in geometry occurring on excitation from the ground state to the S_1 state. Since flexible molecules are likely to undergo greater changes in geometry on excitation into the S_1 state than rigid molecules, a larger Stokes shift should be observed with the more flexible member of a series of structurally related compounds. The Stokes shifts of 3-phenyl-1,2-dihydronaphthalene (**1**) and the structurally related compounds 2-phenylindene (**10**, Scheme 5) and *trans*-stilbene have been collected in Table 4. The results indicate that compounds **1** and **3** may indeed be comparatively flexible molecules; much more so than 2-phenylindene (**10**) and *trans*-stilbene.

So far, the only experimental method offering direct access to quantum yields of internal conversion processes concerns the measurement of a photoacoustic effect[22,43]. The method involves determination of the amplitudes of acoustic waves, resulting from dissipation into the solvent, of energy released on vibrational relaxation of an excited molecule. Upon excitation with a laser pulse (*ca.* 8 ns) and subsequent internal conversion, the first maximum of the resulting, travelling, acoustic wave is detected (See experimental section) with a time resolution of approximately 10 µs. Thus, energy contributions of intersystem crossing from excited triplet (e.g.: T_1) states having life times exceeding 10 µs, are not detected by this method.

In theory, the amplitude thus detected is proportional to the quantum yield of internal conversion for excited molecules having identical mechanisms and dynamics for the process[44]. In practice this means that even a qualitative, superficial correlation between the photoacoustic

Table 4. Photoacoustic effect (relative to that of *trans*-stilbene), overall quantum yield of non-radiative decay from the S_1 state ($1 - \phi_{fl}$) and Stokes shift of 3-phenyl- and 4-methyl-3-phenyl-1,2-dihydronaphthalene (**1** and **3**, respectively), 3-phenylisochromene (**5**), 2-phenylindene (**10**) and *trans*-stilbene.

compound	photoacoustic effect		$1 - \phi_{fl}$		Stokes shift (cm^{-1})
	MeOH	*n*-hexane	MeOH	*n*-hexane	*n*-hexane
1	2.5	2.3	0.95	0.95	5500
3	-	-	-	-	7000
5	1.6	1.3	-	-	-
10	0.7	0.9	0.2	0.2	3900
trans-stilbene	1	1	0.98	0.95	4000

effect and the quantum yield of internal conversion might be expected only within a set of structurally very similar compounds, exhibiting the same UV absorption characteristics.

A set of molecules, more or less satisfying this requirement, consists of 3-phenyl-1,2-dihydronaphthalene (**1**), 2-phenylindene (**10**), *trans*-stilbene and 3-phenylisochromene (**5**). For these compounds the photoacoustic effects, using *trans*-stilbene as a standard, have been evaluated in hexane and methanol (Table 4).For comparison, the quantity $1-\phi_{fl}$ (ϕ_{fl} being the quantum yield of fluorescence) has also been included in Table 4. The results will be discussed in the next section.

Discussion.

As shown by the results of the irradiation experiments in hexane and methanol the photochemistry of 3-phenyl-1,2-dihydronaphthalene (**1**) and the alkyl substituted derivatives **3** and **4** is quite different from that of 1-, 2- and 4-phenyl-[7-10] and other[11-13] substituted 1,2-dihydronaphthalenes. Unlike the last mentioned compounds, **1**, **3** and **4** fail to give a pentaene intermediate by the usually encountered photochemical ring opening reaction of the cyclohexadiene moiety (Scheme 1): Photoproducts derived from such an intermediate are never obtained on irradiation of **1**, **3** and **4** at various wavelengths and temperatures, neither in hexane nor in methanol.

The difference in behavior of **1**, **3** and **4** on one hand, and 1,2-dihydronaphthalenes which react *via* a pentaene intermediate according to Scheme 1 on the other hand, is also reflected in the relative quantum yields of photoconversion of these compounds, both in hexane and methanol: On anaerobic irradiation of a 2 × 10^{-3} M solution of 3-phenyl-1,2-dihydronaphthalene (**1**)in hexane at -80 °C, it takes *ca.* 1 hr to achieve 50% conversion of **1** into the dimers **7-10** (Scheme 4), whereas in methanol **1** was found to be completely photostable under these conditions. At -72

°C, but otherwise identical irradiation conditions, 50% photoconversion of 1-phenyl-1,2-dihydronaphthalene into the corresponding phenylbenzobicyclo[3.1.0]hex-2-ene is achieved[9] in less than 5 min, both in hexane and methanol. In this experiment the occurrence of a pentaene intermediate was demonstrated[3] by the concomitant, strong coloration of the solution as well as by UV spectroscopy. A similar coloration reaction failed to occur on irradiation of compounds **1**, **3** or **4** in hexane as well as methanol at temperatures as low as -90 °C, indicating that the primary photochemical ring opening reaction (Scheme 1, step (*i*)) does not take place with these dihydronaphthalenes.

It thus emerges that, particularly in comparison with 1-phenyl-1,2-dihydronaphthalene, 3-phenyl-1,2-dihydronaphthalene (**1**) and its alkyl-substituted derivatives **3** and **4** possess a high degree of photostability in hexane and methanol. In contrast with a previous suggestion[13], the photostability of **1**, **3** and **4** is an intrinsic property of these compounds, rather than the consequence of a high energy barrier between the *cZc*- and *cZt*-conformers of a hypothetical pentaene intermediate.

In view of the low quantum yield of fluorescence of **1** in hexane and methanol (ϕ_{fl} = 0.05) this means that excited **1** must undergo very efficient internal conversion from the S_1 to the ground state.

Considering that 3-phenyl-1,2-dihydronaphthalene (**1**) like 2-phenylindene (**10**) should have a rather rigid alicyclic diene substructure, this conclusion seems paradoxical. It is however consistent with the magnitudes of the Stokes shift and photoacoustic effect observed for these molecules.

As can be seen from Table 4, the Stokes shifts and hence the geometry change occurring on excitation into the S_1 state are largest for compounds **1** and **3**. According to this criterion, these molecules should be more flexible than **10** and *trans*-stilbene.

The fact that in both hexane and methanol the photoacoustic effect of 3-phenyl-1,2-dihydronaphthalene (**1**) is much larger than that of 2-phenylindene(**10**) agrees qualitatively with the conclusion that the S_1 states of **1** and **10** deactivate largely by internal conversion and fluorescence, respectively. In this connection it should again be emphasized that care is to be taken in correlating quantitatively the photoacoustic effect with the overall quantum yield ($1-\phi_{fl}$) of nonradiative decay. E.g. according to Table 4, the photoacoustic effect of **1** is 2.3 times larger than that of *trans*-stilbene. Assuming a linear correlation between the photoacoustic effect and ($1-\phi_{fl}$), the latter quantity should differ by the same factor for **1** and *trans*-stilbene. As can be seen from Table 4 this is not the case: The overall quantum yields ($1-\phi_{fl}$) of nonradiative decay of 3-phenyl-1,2-dihydronaphthalene (**1**) and *trans*-stilbene are equal. The difference in the magnitude of the photoacoustic effects displayed by these compounds might be associated with the availability of an additional, chemical mode of radiationless decay (viz. to the ground state of *cis*-stilbene) for excited *trans*-stilbene but not for excited **1** (which decays radiationlessly without chemical changes). In view of this, the efficiency, by which the heat released on internal conversion is converted into acoustic energy is not necessarily equal for these compounds. In a comparison of 3-phenyl-1,2-dihydronaphthalene (**1**) and 2-phenylindene (**10**), which undergo nonradiative decay by physical processes only, the assumption of a correlation between the photoacoustic effect and $(1-\phi_{fl})$ appears less dangerous.

From the experimental results on 3-phenylisochromene (**5**) it can be concluded that the photochemistry of this compound resembles closely that of 3-phenyl-1,2-dihydronaphthalene (**1**) and its alkyl-substituted derivatives **3** and **4**. Like **1**, 3-phenylisochromene (**5**) appears highly photostable in hexane at 300 nm, whereas under more forcing irradiation conditions in this solvent, no volatile photoproduct originating from photochemical ring opening of **5** (Scheme 5) are formed. The fact that 2-phenylindene oxide (**11**) affords **5** quantitatively on irradiation in hexane, without a trace of 2-phenylindene (**10**) excludes the formation of the latter compound from **5** *via* photodeoxygenation of **11**.

In view of the existence of a smooth photochemical pathway from **11** to **5**, the question, whether the photostability of 3-phenylisochromene (**5**) is intrinsic or the consequence of an unfavorable equilibrium between the *cZc*- and *cZt*-rotamers of an elusive oxapentaene intermediate (Scheme 5) can not be answered. As compared to *trans*-stilbene and 2-phenylindene (**10**), **5** displays a relatively large photoacoustic effect (Table 4). This suggests that the lowest excited singlet (S_1) state of **5** deactivate *via* an efficient internal conversion process, so that **5** is intrinsically photostable, like 3-phenyl-1,2-dihydronaphthalene. On the other hand, evidence supporting the reverse conclusion has been reported[15] by Padwa et. al.. On irradiation of 3-phenylisochromene (**5**) in methanol, these workers obtained derivatives of 2-phenylindene oxide (**11**) in fair yields. Unfortunately, several attempts to reproduce this result were unsuccessful: Repeated irradiations (250-313 nm) of **5** (5×10^{-3} M) in deaerated methanol at ambient temperature gave exclusively polymeric photoproducts.

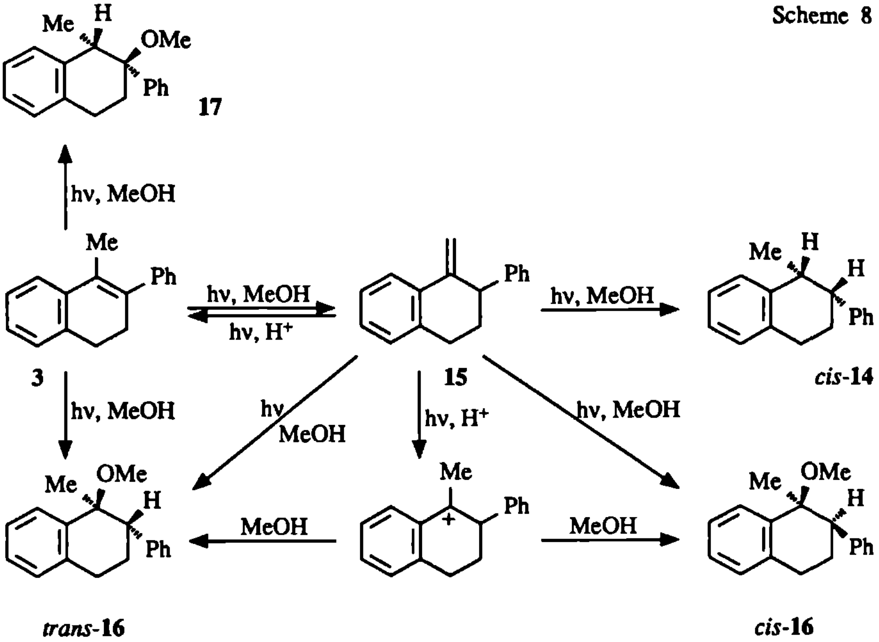
The experimental results concerning the photochemistry of 4-methyl-3-phenyl-1,2-dihydronaphthalene (**3**) in methanol can be rationalized in terms of Scheme 8.

Considering the formation of the exocyclic olefin **15** from **3**, it can be concluded that the photochemical 1,3-H shift involved is assisted by methanol, since the reaction is not observed in hexane. In view of the lacking influence of sulfuric acid on the yield of **15** at low conversion of **3** (Fig. 1c, $t<180$ min) the photochemical 1,3-H shift leading to **15** occurs presumably concertedly, rather than *via* protonation of the lowest excited singlet (S_1) state of **3**. The assumption that this excited state is essentially nonpolar is supported by the fact that sulfuric acid in concentrations up to 0.5 M does not quench observably the fluorescence of **3** (*ca.* 10^{-5} M) in methanol[45].

As can be seen in Figs. 1a-1c and Table 2, the yield of exocyclic olefin **15** from 4-methyl-3-phenyl-1,2-dihydronaphthalene (**3**) increases markedly with temperature. This points to the existence of a thermal barrier, which is not unusual for this type of reaction[46].

On irradiation of exocyclic olefin **15** in methanol, this photochemical 1,3-H shift appears quasi-reversible. Unlike the reverse reaction the photochemical 1,3-H shift of **15** into **3** is sensitive to acid catalysis: The reaction is accelerated more than fourfold by the presence of sulfuric acid. It is tempting to attribute this effect to the involvement of a polar excited singlet

Scheme 8

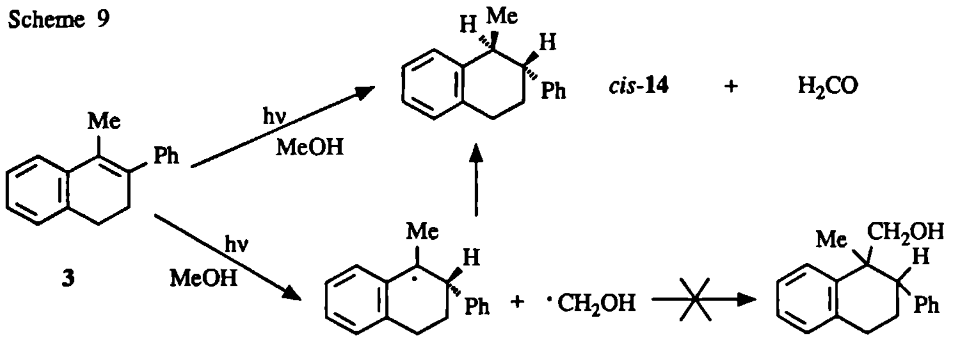


state of **15**, particularly since this assumption would be consistent with the argument, that such a polar excited singlet state should be highly twisted around the double bond[23-26] and hence, be much more likely for the exocyclic olefin **15** than for the alicyclic olefin **3**. According to Table 3, however, the overall rate of photoconversion of **15** into **3**, *cis*-**14** and *cis*- and *trans*-**16** is hardly affected by the presence of sulfuric acid, suggesting that the S_1 state of **15**, like that of **3** is essentially nonpolar. Since the yield of hydrocarbon *cis*-**14** (Table 3) is likewise hardly affected by the presence of sulfuric acid, the acid appears to bring about an enhancement of the 1,3-H shift of excited **15** to **3** at the expense of *cis*- and *trans*-**16**, which are formed by the competing addition of methanol to excited **15**.

From these considerations it emerges that our present knowledge is insufficient to establish the extent to which polar or essentially nonpolar S_1 states are involved in the photoreactions of the exocyclic olefin **15**, Hence, both concerted and non-concerted pathways from **15** to 1-methoxy-1-methyl-2-phenyl-1,2,3,4-dihydronaphthalene (*cis*- *trans*-**16**) have been included in Scheme 8. Evaluation of the temperature-photoreactivity relationship in combination with D labelling experiments and fluorescence quenching studies of 1-methylidene-2-phenyl-1,2,3,4-tetrahydronaphthalene (**15**) might shed more light on this matter. In view of the experimental effort involved, such studies are beyond the scope of this thesis, however.

According to Figs. 1a-1c, the hydrocarbon *cis*-**14** arises chiefly from photoreduction of **15** by methanol, though at 65 °C (Fig. 1d) a small fraction of *cis*-**14** is formed by a primary photoreaction of 4-methyl-3-phenyl-1,2-dihydronaphthalene (**3**). In agreement with this conclusion, the temperature effect on the yield of hydrocarbon *cis*-**14** parallels (Tables 2 and 3) that on the yield of **15** from **3**. Reduction of an olefinic bond by methanol and other alcohols is a well-known photoreaction, occurring[5,6,47] by successive H· radical abstractions from the alcohol (Scheme 9). The insensitivity to acid catalysis of the photoreaction leading to *cis*-**14** is in accordance with a radical mechanism, not involving polar excited states. In view of the stereospecificity for the less stable *cis*- isomer of **14** and the absence of recombination products from the ·CH_2OH radical and the comparatively stable 4-methyl-3-phenyl-1,2,3,4-tetrahydronaphthyl radical, the possibility of a concerted photoreduction of olefins **15** and **3** to *cis*-**14** cannot be ruled out, however.

Scheme 9



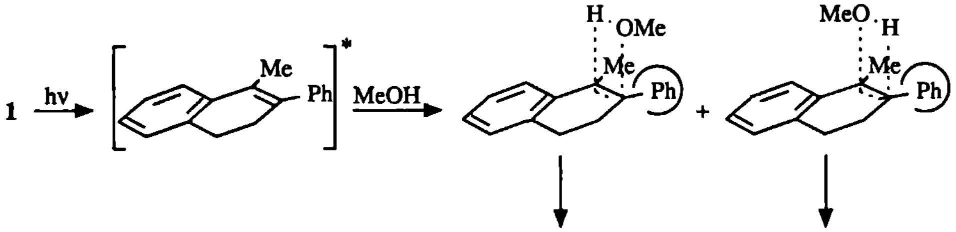
The stereospecific formation of the methanol adduct **17** from 4-methyl-3-phenyl-1,2-dihydronaphthalene (**3**) obviously involves *syn* addition of methanol to excited **3**. The mechanism of this reaction is presumably concerted, involving an essentially nonpolar S_1 state of **3**. This conclusion is corroborated experimentally by the lack[45] of fluorescence quenching of **3** in methanol by sulfuric acid, and theoretically by the argument that polar, highly twisted excited singlet states are not likely for alicyclic olefins of small ring size.

The observed effect of acid on the formation of the methanol adduct **17** from starting olefin **3** does not appear to fit in with the above conclusion. The effect of sulfuric acid on the yield of **17** can however be understood by realizing that **15** reverts to **3** by an acid-catalyzed 1,3-photochemical 1,3-H shift, whereas the reverse photochemical 1,3-H shift leading to **15** is insensitive to acid catalysis. Hence, the quantity of **3** present in the reaction mixture at given irradiation time (Figs. 1a-1d) will be largest in the presence of sulfuric acid, particularly at high photoconverion of **3**. Since methanol adduct **17** is formed exclusively from **3**, the yield of **17** should be highest when **3** is irradiated in H_2SO_4-containing methanol.

The increase in the yield of the methanol adduct **17** with increasing temperature points to the existence of a energy barrier for *syn* addition of methanol to excited **3**.

For the methanol adducts *cis*- and *trans*-**16**, the rationalization of the experimental data (Fig. 1a-1d, Tables 1-3) is much more difficult, since these products can arise directly from 4-methyl-3-phenyl-1,2-dihydronaphthalene **3** as well as *via* secondary photoreactions from exocyclic olefin **15**.

At low irradiation temperature and low conversion of **3** the *trans*-isomer of **16** is obtained highly stereoselectively (Table 2 and 3). From this result it can be concluded that adduct *trans*-**16** arises chiefly from *syn* addition of methanol to excited **3**, by the same mechanism as its regioisomer **17**. This suggests a common, essentially planar S_1 state to be involved in the formation of these methanol adducts from **3** (Scheme 10).



Scheme 10 **17** *cis*-**16**, favored

As can be seen from Figs. 1a-1d and Table 3, the regioselectivity of the methanol addition to excited **3** is also high, particularly at low temperature. The observation that *trans*-**16** is the preferred product of this reaction fits in with the larger steric crowding at C(4) than at C(3) in 4-methyl-3-phenyl-1,2-dihydronaphthalene (**3**).

The available experimental data are insufficient to decide whether the methanol adducts *cis*- and *trans*-**16** arise in part from nonstereospecific methanol addition reactions to excited **3** or **15**.

The experimental data on 4-ethyl-3-phenyl-1,2-dihydronaphthalene (**4**) in methanol reveal a striking resemblance between the photochemistry of this compound and that of the methyl analog **3**. The implications of this conclusion have been discussed at the beginning of this section.

The absence of a substituent at C(4) renders the photochemistry of 3-phenyl-1,2-dihydronaphthalene (**1**) in methanol much simpler than that of its alkyl-substituted analogs **3** and **4**. Considering the experimental data (Scheme 6) of **1**, however, it appear that the photochemical addition of methanol to the olefinic bond does not occur stereospecifically. As interconversion of the methanol adducts *cis*- and *trans*-**12** was ruled out by experiment, the compounds can only be rationalized by the occurrence of *anti* as well as *syn* addition. Since formation of *cis*-**12** by *anti* addition of methanol to the olefinic bond of excited **1** is not likely[48] to occur concertedly, the possibility of a mechanism involving protonation of excited **1** at C(3) followed by attack of MeO^- or MeOH on the resulting carbenium ion has been considered seriously. As pointed out previously, experimental verification of this possibility by evaluating the effect of sulfuric acid on the photoreactivity of 1 in methanol was not possible.

Of course we reasoned that the fluorescence of an excited singlet state capable of undergoing protonation methanol should be quenched by sulfuric acid. Quenching of the fluorescence of 3-phenyl-1,2-dihydronaphthalene (3, 7 × 10^{-6} M) in methanol by sulfuric acid could not be detected for concentrations of sulfuric acid up to 2.5 M.

Experimental.

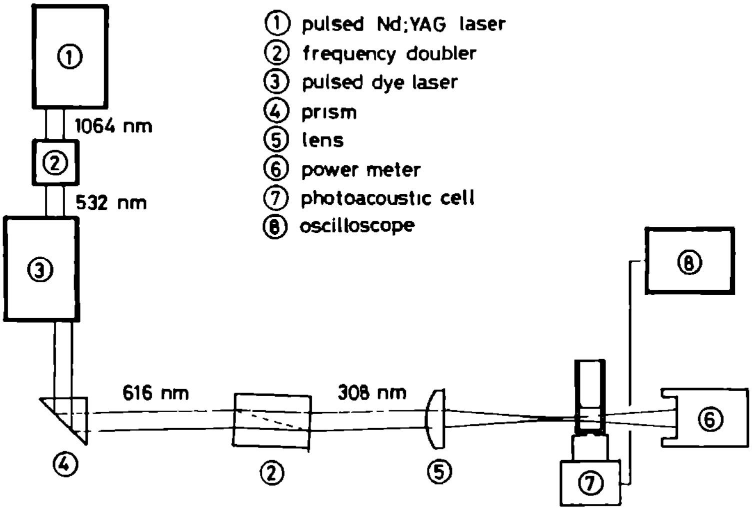
Starting materials. 3-Phenyl-1,2-dihydronaphthalene (1)[13,49,50], 4-methyl-3-phenyl-1,2-dihydronaphthalene (3)[49,51,52] and 4-methyl-3-phenyl-1,2-dihydronaphthalene (4)[52] were prepared from 2-phenyl-1,2,3,4-tetrahydronaphthalene-1-one[53-55] according to the literature.

3-Phenylisochromene (5) was prepared in 6% yield by the method outlined in Ref. 30a. In view of the low yield and limited purity of the product thus obtained, an alternative route based on the photochemical conversion of 2-phenylindene oxide (11) into 5 (Scheme 5) was developed. 2-Phenylindene oxide (11)[15,56] was prepared by epoxidation of 2-phenylindene (10)[57] with *m*-chloroperbenzoic acid.

trans-Stilbene was obtained commercially and recrystallized from ethanol before use.

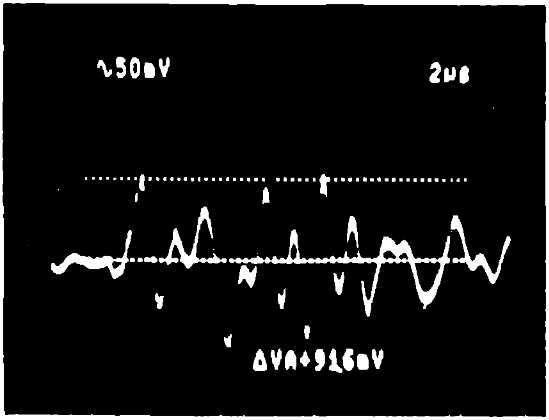
Irradiations. Irradiations were performed with N_2-purged solutions through quartz, employing Philips 125 W HPM, Philips G15T8 (254 nm) or Philips Tl 20 W/12 UVA (300 nm) lamps. Methanol (Merck) or hexane (Baker) of spectrophotometric quality was used as the solvent throughout, except in the synthesis of 5 from 11. Irradiation conditions have been specified along with the experimental data in Figs. 1a-1d and Tables 1-3 or in the text.

Photoacoustic spectroscopy. A block diagram of the experimental set-up used for the



determination of the photoacoustic effect of **1**, **5**, **10** and *trans*-stilbene is given in Fig. 2. The following equipment was used: Quanta Ray DCR-2A Nd-YAG Laser (1); SHG-type II (KDP) frequency doubling crystal (2); Quanta Ray PDL-2 dye laser, dye: Rhodamine-101, pulse duration: 8 ns, energy output: *ca.* 1 mJ/pulse (3); Suprasil I quartz prism (4); Suprasil I quartz lense, f = +30 cm (5); Power meter (6); Home-made photoacoustic cell, consisting of quartz cuvette, external piezoelectric pressure transducer[58]/preamplifier[59] (7); Philips 120 MHz oscilloscope (8).

The scope picture of a typical acoustic transducer response signal is depicted in Fig. 3. As indicated, the magnitude of the photoacoustic effect due to internal conversion processes in the excited molecule corresponds to the amplitude of the first maximum of the transducer response signal.



The actual measurements were performed with solutions of **1**, **5**, **10** and *trans*-stilbene of equal optical densities (OD_{308} typically 0.05) at the excitation wavelength of 308 nm. Values thus obtained have been corrected for contributions of the solvent to the photoacoustic effect and for variations in laser power.

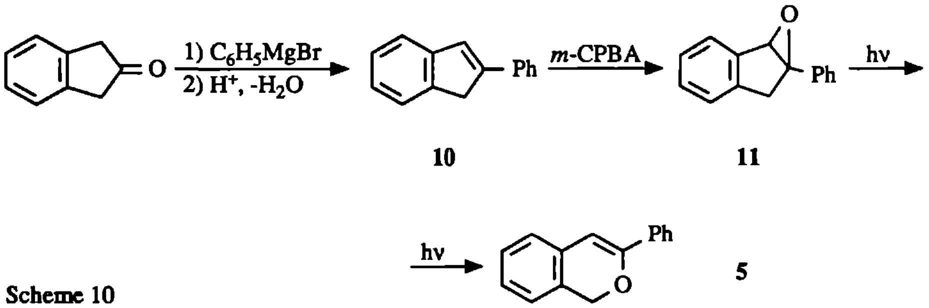
General methods. Photoproducts were separated by column chromatography or preparative TLC and characterized by 90 MHz ^{1}H-NMR, IR, UV, mass (GC-EIMS) spectroscopy, and by chemical synthesis. The purity of starting materials and of individual photoproducts as well as the composition of photoproduct mixtures were determined by temperature-programmed capillary GLC. Samples originating from irradiation in H_2SO_4-containing methanol were neutralized with OH^--exchanged Dowex IRA-400 ion-exchange resin, prior to GLC and GC-MS analysis. Details concerning the equipment involved, have been presented in Chapters 1 and 4 of this thesis.

4-Methyl-3-phenyl-1,2-dihydronaphthalene (3). M.p.: 79.5-79.8 °C (Lit.[49,51]: 75-77 °C). NMR ($CDCl_3$): δ = 1.52 ppm (s, 3H) CH_3; δ = 2.40 - 2.68 ppm (m, 2H) H_3, H_4; δ = 2.75 - 3.02 ppm (m, 2H) H_1, H_2; δ = 6.92 - 7.53 ppm (m, 9H) Ar H. IR (KBr, cm^{-1}): 3045, 3018 (s) C-H str. Ar, 2989, 2923, 2880 (m) C-H str. CH_3, 1592, 1479 (s) C=C str. Ar, 1445 (m) CH_2 scissor.

EIMS; *m/e* (rel. intensity): 221 (17), 220 (M^+, 100), 206 (10), 205 (58), 204 (15), 203 (17), 202 (15), 129 (65), 128 (18), 115 (13), 91 (36). UV; λ_{max}(nm): 278, 224 (sh), 219. λ_{min}(nm): 244, 215.

4-Ethyl-3-phenyl-1,2-dihydronaphthalene (3). M.p.: 63.6-64.2 °C (Lit.[52]: 60-61 °C). NMR ($CDCl_3$): δ = 1.04 ppm (t, 3H) CH_3 of ethyl, $J_{1,2}$ = 7.7 Hz; δ = 2.29 - 2.67 ppm (m, 4H) $CH_2$of ethyl, H_3, H_4; δ = 2.67 - 2.98 ppm (m, 2H) H_1, H_2; δ = 7.06 - 7.42 ppm (m, 9H) Ar H. IR (KBr, cm^{-1}): 3053 (m) C-H str. Ar, 2967, 2953, 2876, 2824 (m) C-H str. CH_3, 1588, 1473 (s) C=C str. Ar, 1452 (m) CH_2 scissor. EIMS; *m/e* (rel. intensity): 235 (17), 234 (M^+, 77), 208 (28), 207 (100), 193 (16),133 (22), 132 (99), 131 (24), 130 (10), 129 (57), 128 (27), 127 (11), 118 (15), 117 (99), 116 (18), 115 (13), 91 (36). UV; λ_{max}(nm): 275. λ_{min}(nm): 243.

3-Phenylisochromene (5). This compound can be conveniently prepared by the three-step synthesis depicted in Scheme 11.



Scheme 10

Crude 2-phenylindene oxide (**10**) was synthesized from 2-indanone and phenylmagnesium bromide according to the literature[57]. Repeated crystallization from methanol afforded pure (100%, GLC) **10** as colorless crystals.

For the preparation of 2-phenylindene oxide (**11**) a solution of 2.00 g (10.4 mmol) of **10** and 2.47 g (*ca.* 12 mmol) of *m*-chloroperbenzoic acid in CH_2Cl_2 (120 mL) was stirred for 20 hrs, in the dark, at ambient temperature. The residue left on evaporation of the solvent, was dissolved in diethyl ether (50 mL) and extracted twice with saturated aq. K_2CO_3. Drying of the organic phase (Na_2SO_4) followed by filtration and evaporation of the solvent afforded pure (>96%, GLC) **11** as a colorless solid in 97% yield. NMR ($CDCl_3$): δ = 3.37 ppm (dist. d, 1H) $H_{1,\ endo}$, $J_{1\text{-}exo,\ 1\text{-}endo}$ = 18.0 Hz; δ = 3.61 ppm (dist. d, 1H) $H_{1\text{-}exo}$; δ = 4.33 ppm (s, 1H) H_3; δ = 7.15 - 7.60 ppm (m, 9H) Ar H.

In the final step, a 5 × 10^{-3} M solution of **11** in N_2-purged hexane (1 L) was irradiated (2.5 hrs) through quartz, in a photochemical reactor equipped with four Philips TL 20 W/12 UVA (300 nm) lamps. Evaporation of the hexane afforded crude 3-phenylisochromene (**5**; Purity 80-90%, GLC) quantitatively. Crystallization from dry ethanol gave pure (99%, GLC) **5** as a fine, yellow-brown precipitate in 80% yield. As reported previously[30b], the brown crystals were found to be unstable, decomposing into a viscous mass on prolonged storage. Sublimation of recrystallized **5** at *ca.* 80 °C/0.2 mm afforded **5** as large colorless plates (Yield: 40%) which could be stored for months. The melting points, ^{1}H-NMR and mass spectra of both recrystallized and sublimed **5** were found to be identical to those, reported in Ref. 30c.

The present procedure for the preparation of **5** surpasses known procedures[30a-30c] in the simple accessibility of the starting materials required, the number of the reaction steps involved, and the overall yield, purity and stability of the end-product.

1-Methoxy-2-phenyl-1,2,3,4-tetrahydronaphthalene (*cis*- and *trans*-12). A mixture of these compounds was prepared by two independent methods.

Treatment[31,32] of 1,2-dihydronaphthalene[49] with phenylmercuric chloride in methanol gave a 1 : 4 mixture (^{1}H-NMR) of *cis*- and *trans*-**12**. The mixture could be liberated from the *cis*- isomer by column chromatography, affording a fraction consisting chiefly of *trans*-**12**. This fraction was recrystallized from methanol, yielding pure (>95%, GLC) *trans*-**12**. NMR ($CDCl_3$)[32]: $\delta = 1.9 - 2.2$ ppm (m, 2H) H_3; $\delta = 2.7 - 3.2$ ppm (m, 3H) H_2, H_4; $\delta = 3.20$ ppm (s, 3H) OCH_3; $\delta = 4.58$ ppm (d, 1H) H_1, $J_{1,2} = J_{trans} = 8.0$ Hz; $\delta = 7.0 - 7.5$ ppm (m, 9H) Ar H. EIMS; *m/e* (rel. intensity): 238 (M^+, 8), 207 (14), 206 (58), 205 (8), 135 (10), 134 (100), 119 (45), 104 (6), 91 (52), 77 (20).

In an alternative procedure, treatment of 2-phenyl-1,2,3,4-tetrahydronaphthalene-1-one with $LiAlH_4$ IN THF[60], followed by addition of an excess of methyl iodide, gave a 1 : 1 mixture of *cis*- and *trans*-**12**. By column chromatography, an oil consisting chiefly of *cis*-**12** (*cis*/*trans* ratio: 7) was obtained. NMR ($CDCl_3$)[32]: $\delta = 1.8 - 2.1$ ppm (m, 2H) H_3; $\delta = 2.4 - 3.0$ ppm (m, 3H) H_2, H_4; $\delta = 3.11$ ppm (s, 3H) OCH_3; $\delta = 4.22$ ppm (d, 1H) H_1, $J_{1,2} = J_{cis} = 2.5$ Hz; $\delta = 7.0 - 7.5$ ppm (m, 9H) Ar H. EIMS (mixture of *cis*- and *trans*-**12**, 7 : 1); *m/e* (rel. intensity): 238 (M^+, 8), 207 (14), 206 (54), 205 (12), 135 (9), 134 (100), 119 (51), 104 (10), 91 (52), 77 (5).

2-Methoxy-2-phenyl-1,2,3,4-tetrahydronaphthalene (13). This compound was synthesized by treating 2-phenyl-1,2,3,4-tetrahydro-2-naphthol[13,50] in THF with an equimolar amount of *n*-BuLi, followed by an excess of methyl iodide. Separation by column chromatography afforded the compound as a colorless oil of *ca.* 90% purity (NMR). NMR ($CDCl_3$): $\delta = 2.1 - 2.4$ ppm (m, 2H) H_3; $\delta = 2.6 - 3.0$ ppm (m, 2H) H_4; $\delta = 3.03$ ppm (s, 3H) OCH_3; $\delta = 3.18$ ppm (br. s, 2H) H_1; $\delta = 7.1 - 7.4$ ppm (m, 9H) Ar H. EIMS; *m/e* (rel. intensity): 238 (M^+, 5), 237 (15), 223 (11), 207 (24), 206 (100), 205 (48), 191 (16), 178 (10), 165 (9), 129 (13), 128 (24), 115 (10), 105 (9), 104 (30), 91 (53), 77 (12).

***cis*-1-Methyl-2-phenyl-1,2,3,4-tetrahydronaphthalene (*cis*-14).** This compound was prepared by catalytic hydrogenation[34] (10% Pd/C, EtOAc, 1 atm.) of **3**. NMR ($CDCl_3$)[34]: $\delta = 0.89$ ppm (d, 3H) CH_3, $J = 6.8$ Hz; $\delta = 1.80 - 2.48$ ppm (m, 2H) H_3; $\delta = 2.80 - 3.37$ ppm (m, 4H) H_1, H_2, H_4; $\delta = 3.18$ ppm (br. s, 2H) H_1; $\delta = 7.02 - 7.42$ ppm (m, 9H) Ar H. EIMS; *m/e* (rel. intensity): 223 (5), 222 (M^+, 28), 118 (100), 117 (30), 115 (10), 91 (21), 77 (5).

1-Methylidene-2-phenyl-1,2,3,4-tetrahydronaphthalene (15). A 2.3×10^{-3} M solution of **3** in deaerated methanol (200 mL) was irradiated with a HPM lamp, through quartz, at -90 °C for 12 hrs (See Fig. 1a). The reaction mixture was allowed to warm up to room temperature. Evaporation of the solvent gave an oil, which was separated by column chromatography (Merck Al_2O_3-E, 50 × 2 cm i.d., eluent: Hexane). The purification step was repeated with the combined samples of crude **15** from five irradiation experiments. GLC analysis of the product thus prepared revealed 98% purity; it was contaminated only with a trace of the starting material **3**. NMR ($CDCl_3$): δ = 2.17 ppm (dist. q, 2H) H_3, $J_{2,3}$ = 6.5 Hz, $J_{3,4}$ = 6.1 Hz ; δ = 2.82 ppm (t, 2H) H_4; δ = 3.78 ppm (t, 1H) H_2; δ = 4.70 ppm (br. s, 1H) H_{exo} of methylidene, $J_{exo,\ endo}$ = 0; δ = 5.63 ppm (br. s, 1H) H_{endo} of methylidene; δ = 7.04 - 7.40 ppm (m, 8H) H_5, H_6, H_7, C_6H_5; δ = 7.60 - 7.90 ppm (m, 1H) H_8. EIMS; *m/e* (rel. intensity): 221 (13), 220 (M^+, 68), 219 (11), 205 (15), 130 (10), 129 (100), 128 (27), 116 (12), 115 (29), 91 (30).

1-Methoxy-1-methyl-2-phenyl-1,2,3,4-tetrahydronaphthalene (*cis*- and *trans*-16). In analogy with the preparation of *cis*- and *trans*-12[31,32], a mixture of *cis*- and *trans*-**16** (*cis/trans* ratio: 0.5) was prepared by treatment of 4-methyl-1,2-dihydronaphthalene[51,52] with phenylmercuric chloride in methanol. Purification by column chromatography and crystallization from methanol afforded *trans*-**16**, slightly contaminated with the *cis*-isomer (Melting points ranged from 71-72 °C to 74-75 °C for different fractions). A sample, enriched in *cis*-**16** was isolated subsequently from the mother liquor, left on crystallization of the *trans*-isomer. Elemental analysis: Calculated for $C_{18}H_{20}O$: C: 85.67%, H: 7.99%. Found: C: 85.44%, H: 8.01%. The NMR and GC-MS data of *cis*- and *trans*-**16** are presented below.

Just as in the preparation of *cis*- and *trans*-**12**, it was also attempted to prepare *cis*- and *trans*-**16** by methylation[52] of the corresponding alcohols, which were available from the synthesis of **3**. These attempts were unsuccessful; dehydration to **3** was the main reaction observed on treatment of these alcohols with *n*-BuLi, followed by the addition of methyl iodide, in THF.

Cis-**16**: NMR ($CDCl_3$): δ = 1.40 ppm (s, 3H) CH_3; δ = 1.74 - 2.09 ppm (m, 1H) and 2.18 - 2.75 ppm (m, 1H) H_3; δ = 2.18 - 2.75 ppm (m, 3H) H_2, H_4; δ = 3.01 ppm (s, 3H) OCH_3; δ = 7.02 - 7.56 ppm (m, 9H) Ar H. GC-EIMS; *m/e* (rel. intensity): 252 (M^+, 2), 238 (3), 237 (10), 221 (22), 220 (100), 205 (35), 148 (62), 147 (33), 134 (27), 133 (88), 129 (40), 128 (14), 119 (33), 118 (16), 117 (20), 116 (11), 115 (61), 105 (22), 104 (10), 103 (13), 91 (61).

Trans-**16**: NMR ($CDCl_3$): δ = 1.18 ppm (s, 3H) CH_3; δ = 2.06 - 2.33 ppm (m, 2H) H_3; δ = 2.78 - 3.07 ppm (m, 2H) H_4; δ = 3.14 ppm (s, 3H) OCH_3; δ = 3.28 - 3.58 ppm (m, 1H) H_2; δ = 6.98 - 7.51 ppm (m, 9H) Ar H. GC-EIMS; *m/e* (rel. intensity): 252 (M^+, 2), 238 (2), 237 (8), 221 (21), 220 (99), 205 (35), 148 (67), 147 (22), 134 (10), 133 (100), 129 (41), 128 (14), 118 (18), 117 (23), 116 (12), 115 (20), 105 (21), 103 (11), 91 (47).

***trans*-2-Methoxy-1-methyl-2-phenyl-1,2,3,4-tetrahydronaphthalene (17).** A pure sample of this compound was isolated from the methanol adducts, obtained on irradiation of **3**. NMR ($CDCl_3$): δ = 0.77 ppm (s, 3H) CH_3; δ = 1.93 - 2.49 ppm (m, 3H) H_1, H_3; δ = 2.84 - 3.09 ppm (m, 2H) H_4; δ = 3.00 ppm (s, 3H) OCH_3; δ = 7.02 - 7.46 ppm (m, 9H) Ar H. GC-EIMS; *m/e* (rel. intensity): 252 (M^+, 3), 220 (38), 205 (12), 119 (10), 118 (100), 117 (29), 91 (17).

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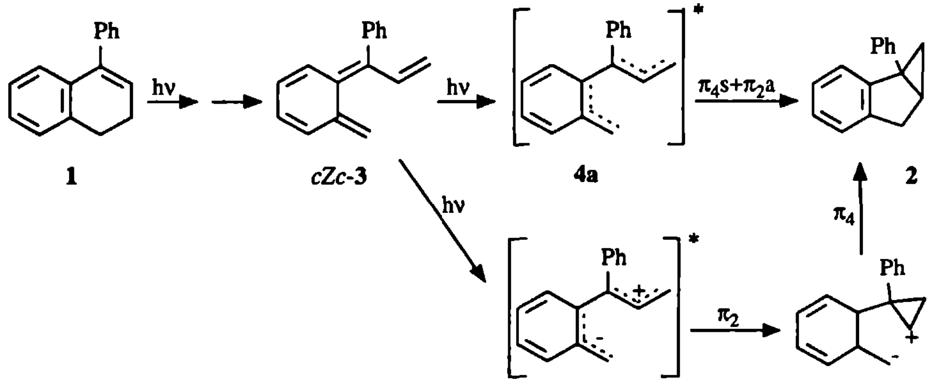
Chapter 6: The photochemistry of 4-phenyl-1,2-dihydronaphthalene in methanol.

Introduction

1-Phenylbenzobicyclo[3.1.0]hex-2-ene (**2**) was reported[1,2] as the main primary photoproduct from broad-spectrum irradiation of 4-phenyl-1,2-dihydronaphthalene (**1**) in hexane. For the formation of this product two routes from the pentaene intermediate[3] *cZt*-**3** can be envisaged (Scheme 1), viz. a concerted intramolecular [4+2] photocycloaddition involving an unpolarized, excited singlet state (**4a**) or a reaction involving a sudden-polarized, twisted zwitterionic excited singlet state (**4b**)[4].



Scheme 1

Considering the first possibility, it should be emphasized that concerted cyclization of the excited triene moiety in **4a** might occur in both $\pi_4a+\pi_2a$ and $\pi_4s+\pi_2a$ fashion. Though a $\pi_4a+\pi_2a$ photocycloaddition violates obviously the Woodward-Hoffmann rules[5], Tanaka et. al.[6] have outlined the possibility of internal $\pi_4a+\pi_2a$ cross-bicyclization in excited *cZt*-trienes of low symmetry.

Though there has been little experimental evidence for the involvement of sudden-polarized, zwitterionic excited states in the photochemistry of other polyenes[7], such excited states have often been invoked[8-11] in rationalizing the stereochemistry observed for bicyclo[3.1.0]hex-2-enes originating from apparently forbidden $\pi_4a+\pi_2a$ photocycloadditions of *cZt*-trienes. However, it has been pointed out[12] that sudden-polarized, zwitterionic excited states are presumably not involved in the photochemistry of 1-phenyl-1,2-dihydronaphthalene. In this case, experimental evidence suggests the formation of *exo*-4-phenylbenzobicyclo[3.1.0]hex-2-ene to take place by an intramolecular $\pi_4a+\pi_2a$ photocycloaddition reaction.

Since the relative stabilities of unpolarized and sudden-polarized, twisted, zwitterionic excited states of *cZt*-hexatrienes were predicted[13] to be sensitive to substitution, it was decided to investigate the photochemistry of **1** in methanol. In this solvent, the formation of zwitterionic excited states should be favored. This might result in selective trapping of such states by methanol or a strong acid.

Further considerations on the photochemistry of **1** in methanol, reveal the presence of a 1,1-diphenylethene substructure in **1** as the next aspect of interest. Unlike 1,2-dihydrophenanthrenes, excited 1,1-diphenylethene and stilbenes have been shown[14] to undergo direct Markovnikov addition of MeOH to the olefinic bond, in competition with rearrangement to a carbene. In this context, the present study concerning mechanistic aspects of the photochemistry of **1** in methanol emerges as a logic continuation of preceding efforts[14] to characterize the excited state involved in these photoreactions. Furthermore we studied the photochemistry of **1** in methanol in the presence of an electron donor or an acceptor. These studies were aimed to elucidate whether **1** is capable to undergo electron transfer senzitized-photoreactions analogous to those reported[15-17] for 1,1-diphenylethene.

Results

Broad-spectrum irradiation of 1 in methanol. Isolation and characterization of the products were performed with 100 mg samples obtained by irradiation (HPM, 40 min) of **1** (10^{-3} M) in deaerated MeOH at 15 °C. The photoproducts were separated into three fractions by column chromatography.

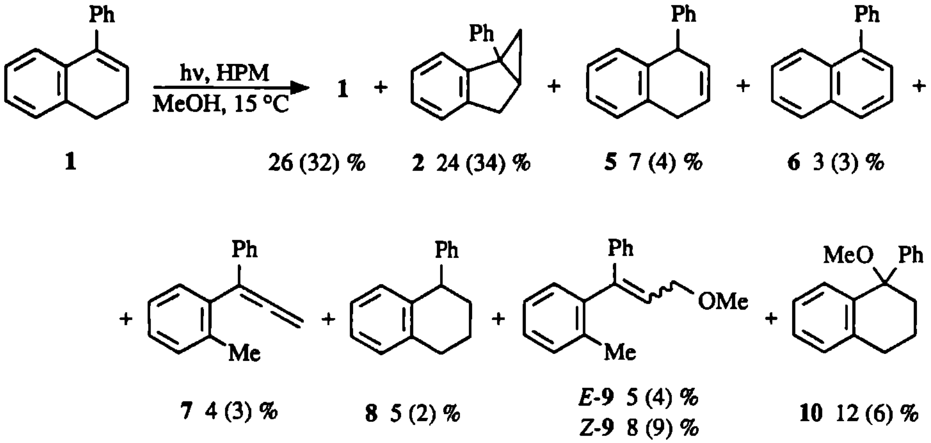
According to the results of GC-MS the first fraction consisted entirely of hydrocarbons. According to the NMR and mass spectra, the main are constituents 1-phenylbenzobicyclo[3.1.0]-hex-2-ene (**2**) and 1-phenyl-1,4-dihydronaphthalene (**5**)[1,2,18,19]. In this respect, the photochemistry of **1** in methanol resembles that in hexane, where **2** and **5** have also been found[1,2] as the principal photoproducts. A third constituent , showing a multiplet at δ = 7.75 - 7.94 ppm in the NMR spectrum, a molecular mass peak at *m/e* 204 in GC-MS, and an UV absorption at 290 nm[20] was identified as 1-phenylnaphthalene (**6**). The structures of **2**, **5** and **6** were confirmed by comparing the spectroscopic data with those obtained with authentic samples[1,2,18,19] of these compounds.

Further GC-MS analysis revealed the presence of two minor hydrocarbons, having *m/e* 206 and 208. The spectral characteristics of these photoproducts included an IR absorption at 1940 cm^{-1} and NMR absorptions at δ = 2.00 ppm (m), δ = 2.20 ppm (s), δ = 4.12 ppm (br. t, J = 6.5 Hz) and δ = 5.18 ppm (s). The IR signal at 1940 cm^{-1} and the NMR singlets at δ = 2.20 and 5.18 ppm (integrated intensity ratio 3 : 2) were assigned to 1-phenyl 1-(*o*-tolyl)-1.2-propadiene (**7**, *m/e* 206). The hydrocarbon having *m/e* 208 and NMR absorptions at δ = 2.00 and 4.12 ppm (integrated intensity ratio 1 : 2) was concluded to be 1-phenyl 1.2.3.4-tetrahedronaphthalene (**8**). The structures **7** and **8** were confirmed by chemical synthesis. An additional check on the composition of the hydrocarbon fraction was made by comparing a GLC run of this fraction with that of a mixture containing known quantities of **1**, **2**, **5**, **6**, and **8**[21].

GC-MS analysis revealed the second chromatography fraction to consist of two components with similar mass spectra. The presence of strong peaks at *m*/*e* 238 (M^+), 223 (M-15(CH_3)) and 206 (M^+-32(MeOH)) in the spectra pointed to methanol adducts of **1**, possessing a readily fissionable methyl group. From the NMR spectrum and the results of spin-decoupling these methanol adducts were concluded to be the *Z*- and *E*-isomer of 3-methoxy 1-phenyl-1-(*o*-tolyl) propene (**9**). A value of 0.55 ± 0.02 for the *E*/*Z* ratio was obtained from both GLC analysis and NMR integration. This value was observed to be independent of the irradiation time, the temperature and the presence or otherwize of 10^{-2} M H_2SO_4.

Apart from *Z*- and *E*-**9**, GC-MS revealed the presence of another methanol adduct of **1** in the third chromatography fraction. The mass spectrum, displaying a small peak at *m*/*e* 238 (M^+, 3%) and strong peaks at *m*/*e* 207 and 206, differed noticably from the mass spectra of *E*- and *Z*-**9**. The absence of a readily fissionable methyl group (no peak at *m*/*e* 223) suggested that this adduct originated from methanol addition directly to the olefinic bond of **1**. The adduct should then be 1- or 2-methoxy-1-phenyl-1.2.3.4-tetrahydronaphthalene (**10** or **11**, respectively). The NMR spectrum of the photoproduct mixture showed no clear signals addressable to this third adduct, except for a sharp singlet at δ = 3.15 ppm from the methoxy group. This NMR absorption was also observed for the methanol adduct obtained on irradiation of **1** in MeOH at 254 nm as well as for authentic **10**, but not for authentic **11**, which has $\delta(OCH_3)$ = 3.34 ppm. Hence, we conclude that the last methanol adduct to be **10**. This conclusion was confirmed by the observation that the GLC retention time and mass spectrum of this methanol adduct (capillary GLC) matched that of authentic **10**, but not of **11**.

Scheme 2



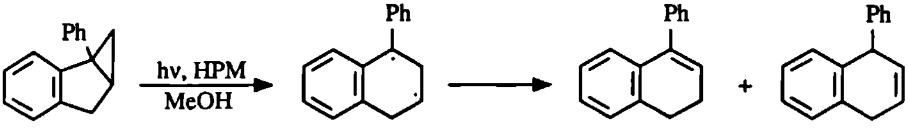
A summary of the above results,including the photoproduct yields (GLC) as obtained from broad-spectrum irradiation of **1** at 15 °C and -72 °C (in parentheses), is presented in Scheme 2. As can be seen from the scheme, the total yield of the photoproducts (93% at 15 °C, 96% at -72 °C) does not add up to 100%. The discrepancy can be accounted for by the occurrence of five other products, present in trace amounts. The most abundant of these products, occurring in *ca.* 3% yield, was found to be a hydrocarbon having *m/e* 206 and showing a triplet at δ = 1.26 ppm (1H) coupled (J = 7.2 Hz) to a doublet at δ = 1.98 ppm (2H) in the NMR spectrum. The remainder included another hydrocarbon of mass 206 and three methanol adducts of **1** (*m/e* 238), displaying mass spectra similar to those of *E*- and *Z*-**9**, but differing from those of **10** and **11**. Closer examination of these products was prevented by their low abundances among the photoproducts of **1**. In this connection it should be emphasized that on broad-spectrum irradiation of **1** in MeOH, photopolymerization does not occur.

Yield *vs.* time plots. The yield *vs.* time plot obtained from broad-spectrum irradiation of **1** in MeOH at 15 °C is presented in Fig. 1. From the figure it can be seen that all photoproducts depicted in Scheme 2 originate from primary photoreactions of **1**: The yield *vs.* time curves of all products intercept at the origin. Relative initial rates (r_0) of primary photoproduct formation, calculated from the slopes of the curves at zero irradiation time, have been collected in Table 1. A comparison of the sum of the initial rates (r_0, at t = 0) of primary photoproduct formation (r_0(**2**) + r_0(**5**-**10**) = 32) with the initial disappearance rate of starting material (r_0(**1**)= 33) demonstrates the excellent mass balance encountered in this type of experiment.

Closer inspection of Fig. 1 reveals that **2**, *Z*-**9** and *E*-**9** are not photostable under the irradiation conditions. The rates of formation of these compounds decrease as a function of the irradiation time. Whereas for *Z*- and *E*-**9** the decrease is relatively small, it is quite substantial for **2**: E.g. at t = 28 min, **2** appears to be decomposed as fast as it is formed. Simultaneously the disappearance rate of **1** decreases sharply, whereas the rate of formation of **5** increases slightly as a function of the irradiation time. From these results, a secondary photoprocess involving decomposition of **2** into **1** and **5** (Scheme 3) is concluded to be operative on broad-spectrum irradiation of **1** in MeOH. This conclusion agrees with previous results on the photochemistry of **1** in hexane[1,18].

To investigate the effects of temperature and the presence of acid on the photochemistry of **1** in MeOH, the irradiation experiment outlined in Fig. 1 was repeated at -72 °C, and at 15 °C in the

Scheme 3



2 **1** **5**

Fig. 1. Broad-spectrum irradiation (HPM) of 4-phenyl-1,2-dihydronaphthalene (**1**, 2×10^{-3} M) in methanol at 15 °C: Yield *vs.* time plots for the conversion of **1** and the formation of 1-phenylbenzobicyclo[3.1.0]hex-2-ene (**2**), 1-phenyl-1,4-dihydronaphthalene (**5**), 1-phenylnaphthalene (**6**), 1-phenyl-1-(*o*-tolyl)-1,2-propadiene (**7**), 1-phenyl-1,4-dihydronaphthalene (**8**), *E*- and *Z*-3-methoxy-1-phenyl-1-(*o*-tolyl)propene (*E*- and *Z*-**9**), and 1-methoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (**10**).

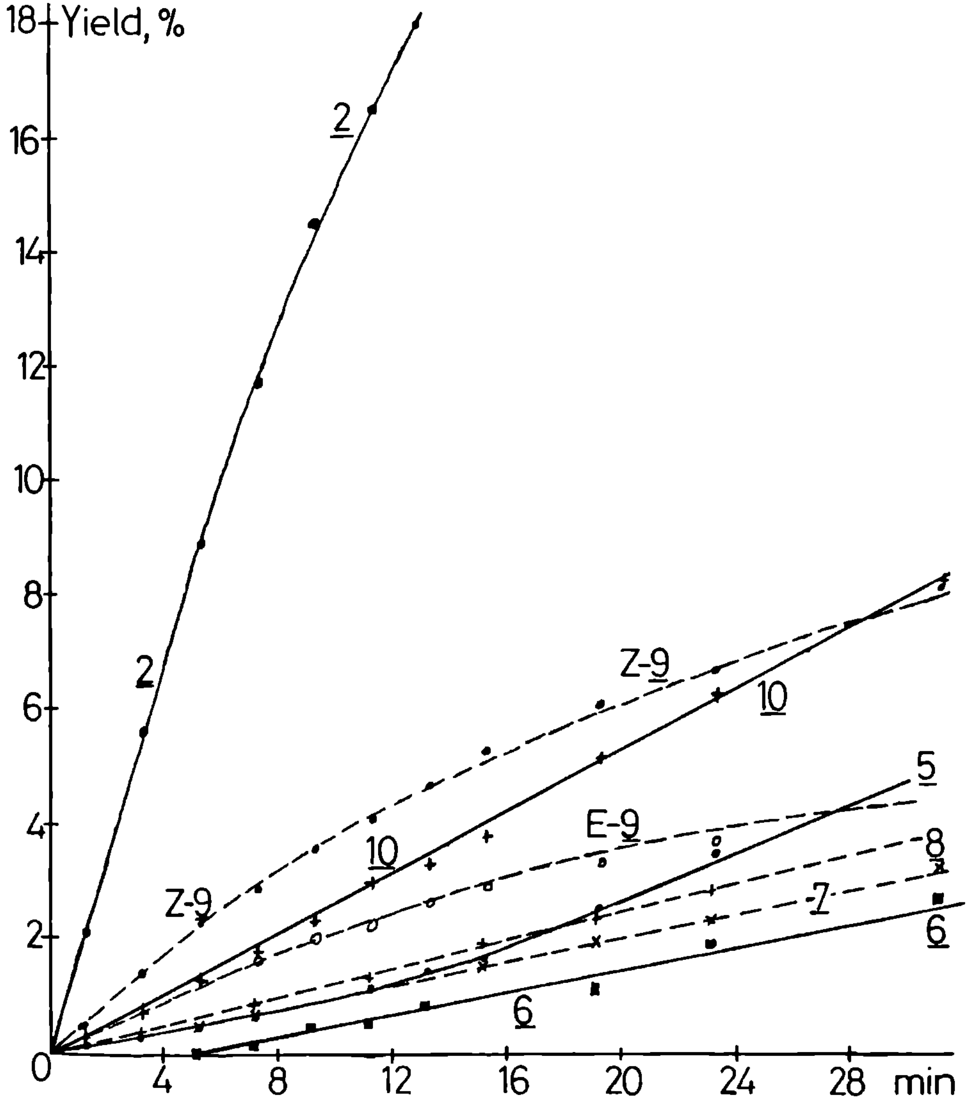


Table 1: Relative initial rates of the primary photoproducts from 4-phenyl-1,2-dihydronaphthalene in methanol.

Compound	HPM[1]			254 nm[2]	
	15 °C	15 °C, H_2SO_4	-72 °C	20 °C	20 °C, H_2SO_4
2	18	22	28	1	1
5	1.1	1.1	0.8	-	-
6	1	1	1	1	1
7	1.0	1.2	1.4	6	6
8	1.2	1.1	1.4	-	-
Z-**9**	2.3	3.1	2.7	-	-
E-**9**	4.4	5.6	4.9	-	-
10	2.7	2.8	2.3	38	38

[1] Broad-spectrum irradiation of **1** (2×10^{-3} M) in methanol, $[H_2SO_4] = 2 \times 10^{-2}$ M.
[2] $[\mathbf{1}] = 10^{-3}$ M, $[H_2SO_4] = 10^{-2}$ M.

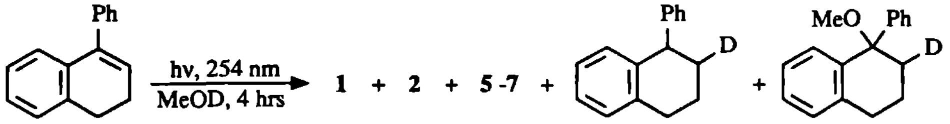
presence of 2×10^{-2} M H_2SO_4. The results (Table 1) demonstrate that neither the reaction temperature nor the presence of H_2SO_4 exerts significant influence on the initial rates of photoproduct formation.

Monochromatic (254 nm) irradiation of 1 in MeOH and MeOD. In comparison with the broad-spectrum irradiation, photoconversion of **1** at 254 nm proceeds more slowly and is accompanied by substantial polymerization. Nearly complete conversion of **1** (2×10^{-3} M) in deaerated MeOH at 25 °C and 254 nm required *ca.*4 hrs, as compared to *ca.* 30 min under similar conditions but with a HPM lamp. Separation of the photoproducts by column chromatography afforded two volatile fractions, representing a yield of *ca.* 30% based on reacted **1**. NMR and GC-MS analysis showed the least polar of these fractions to consist of hydrocarbons **6** and **8** (major products), **1** and **5** (minor products) and **2** and **7** (traces). The other fraction was found to consist of pure **10**.

Apart from the high degree of polymerization (*ca.* 70%), the negligible yields of **2** and **7**, and the absence of *Z*- and *E*-**9** (Scheme 2) are striking.

The irradiation experiment, was repeated with a 5×10^{-3} M solution of **1** in CH_3OD. A GC-MS run of the volatile photoproducts revealed significant D incorporation in hydrocarbon **8** ($\geq$ 0.92 eq D) and methanol adduct **10** ($\geq$ 0.95 eq D), and negligible incorporation in the other photoproducts. The fragmentation pattern of the EI mass spectrum of deuterated **8** pointed to D substitution at C(2) (**8**-(2-*d*), Scheme 4).

Scheme 4



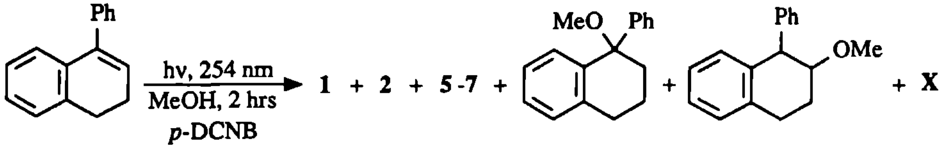
1, 0.001 M 5 % 8-(2-*d*), 10 % 10-(2-*d*), 10 %

In the analysis of deuterated **10**, application of CIMS (CH_4) was necessary to detect the molecular mass peak (*m/e* 240, M+1(H^+), 27%). Unfortunately only fragmentation due to elimination of CH_3OH and C_6H_6 was observed in the EI mass spectrum. Hence, the position of the D atom in deuterated **10** could not be established from the fragmentation pattern. However, the NMR spectrum of the compound demonstrated unequivocally the presence of two protons at C(4) (δ = 2.85 ppm (dist. t, 2H) H_4 and $H_{4'}$, $J_{3,4} = J_{3,4'} = 6.0$ Hz) and two protons at C(3). Since in **10** both the phenyl and the methoxy group (δ = 3.16 ppm (s, 3H)) are present at C(1), it is concluded that the D atom is located at C(2) of **10** (**10**-(2-*d*), Scheme 4).

Irradiation of 1 in the presence of *p*-dicyanobenzene or 1,4-dimethoxynaphthalene. In order to establish the influence of the 1,1-diphenyl substructure on the photochemistry of 1-phenyl-1,2-dihydronaphthalene (**1**), the compound was irradiated in MeOH in the presence of *p*-dicyanobenzene (*p*-DCNB) or 1.4-dimethoxynaphthalene (DMN) as an electron transfer sensitizer.

Irradiation of **1** (2×10^{-3} M) in the presence of *p*-DCNB (4×10^{-3} M) was performed at 254 nm to ensure preferential excitation of the electron acceptor (ϵ_0(*p*-DCNB)/ϵ_0(1) *ca.* 7 at 254 nm (Refs. 22 and 2)). After removal of *p*-DCNB by crystallization at -20 °C and isolation of the volatile photoproducts by column chromatography, characterization by GC-MS and NMR showed the *anti* Markovnikov methanol adduct (**11**, Scheme 5) to be the main photoproduct under this condition.

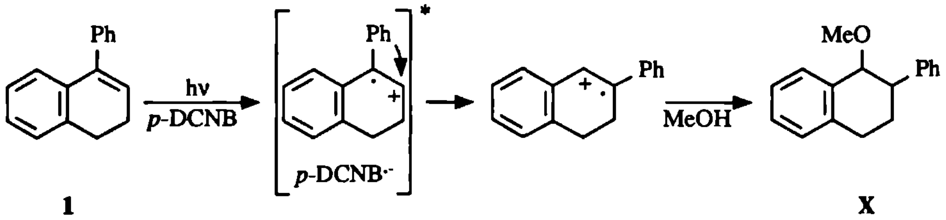
Scheme 5



1, 0.001 M 5 % 10, 3 % 11, 27 % 3 %

An unknown side product X could not be separated completely from **11**. The NMR spectrum (δ = 4.39 ppm (br. d), J = 4.7 Hz; δ = 3.5 - 3.9 ppm (m); δ = 3.42 ppm (s, OCH_3); δ = 2.7 - 3.2 ppm

Scheme 6



(m); δ = 1.9 - 2.4 ppm (m)) and mass spectrum of X suggest, however, a structure very similar to **11**. In view of the obvious resemblance with the photochemistry of 1,1-diphenylethene under similar conditions[15,17,23], X might be 1-methoxy-2-phenyl-1,2,3,4-tetrahydronaphthalene, wich might arise *via* a 1,2-Ph shift from the radical cation of **1** (Scheme 6).

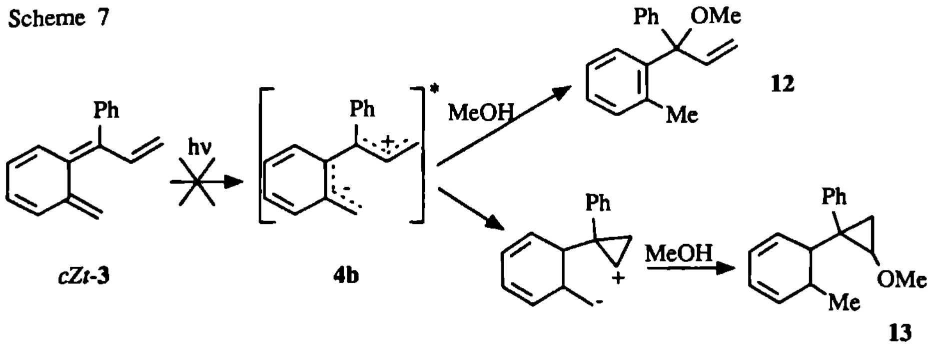
Irradiation of **1** (2×10^{-3} M) in the presence of DMN (4×10^{-3} M) was performed at 313 nm, to ensure preferential excitation of the electron donor. Even after an irradiation period of 48 hrs no appreciable photoconversion into volatile products was observed; the starting material **1** was recovered in about 85% yield. The absence of photoconversion in this experiment may be due to deactivation of excited DMN *via* an efficient fluorescence channel. During irradiation of a solution of **1** and DMN in MeOH at 313 nm an intense blue fluorescence was observed.

Discussion and conclusions

The absence of a significant effect of temperature and acid on the initial rates of photoproduct formation (Table 1) in the broad-spectrum irradiation of **1** in methanol, indicates that trapping by methanol or sulfuric acid of a sudden-polarized excited state of the pentaenes (Scheme 1) does not occur: Either the life time of the zwitterionic excited states of the pentaene is too short to allow selective trapping by methanol and H_2SO_4 or the lowest excited singlet state is not zwitterionic at all.

When a zwitterionic excited state of *cZc*- and *cZt*-**3** is assumed to be involved in the photochemistry of **1**, the formation of methanol adduct **12** and cyclopropane derivative **13** should be expected (Scheme 7)[24-26]. Experimentally, however, **12** and **13** have not been observed among the photoproducts of **1** in methanol, not even in trace quantities. On the other hand, the formation of the compounds *E*- and *Z*-**9** (Scheme 2, Table 1) only upon the broad-spectrum irradiation of **1**, obviously implies that they arise from photochemical methanol addition to *cZc*- or *cZt*-**3**; apparently the life time of the zwitterionic excited state of the pentaene *cZc*- or *cZt*-**3** is sufficiently long for intermolecular addition of MeOH leading to *E*- and *Z*-**9**, but is too short to allow selective trapping by protons from methanol or H_2SO_4 and formation of adduct **12** and cyclopropane derivative **13**. It thus emerges that the assumption of a zwitterionic excited state for

Scheme 7

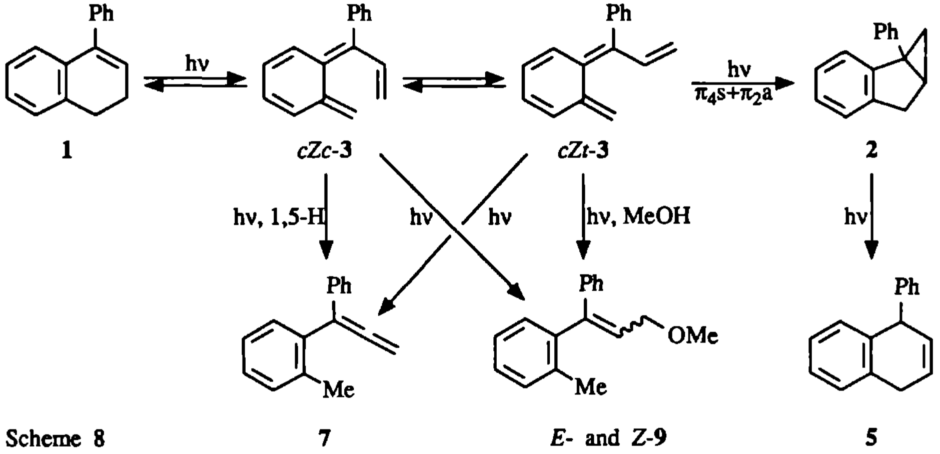


the pentaene does not provide a consistent rationalization of the experimental results obtained from irradiation of **1** in MeOH. To this it should be added that, in view of the higher local symmetry of the triene moiety in *cZc*-**3**, the rotamer is less likely to give rise to a sudden-polarized excited state than *cZt*-**3**[27]. Using this consideration in the consistent rationalization of **9**, the *Z*- and *E*-isomer of this compound will presumably arise from a nonpolar excited state of *cZc*-**3** and a sudden-polarized excited state of *cZt*-**3**, respectively. In this situation the *Z*-**9**/*E*-**9** ratio should be sensitive to the reaction temperature and, in particular, to the presence of acid. It thus appears that the experimentally observed insensitivity of the *Z*-**9**/*E*-**9** ratio to the irradiation temperature and the presence of H_2SO_4 cannot be rationalized consistently in terms of sudden-polarized excited states of *cZc*- or *cZt*-**3**.

The experimental results, presented in Scheme 2 and Table 1 suggest that sudden-polarized excited states of the pentaenes **3** (Schemes 1 and 7) are not involved in the photochemistry of 4-phenyl-1,2-dihydronaphthalene (**1**) in MeOH. A similar conclusion was reached in the case of 1-phenyl-1,2-dihydronaphthalene[12].

From Fig. 1 and Table 1 it can be seen that the addition of MeOH to **1** is slow as compared to the major photoprocess (formation of **2**) occurring on broad-spectrum irradiation of **1** in methanol. Also in this respect, the behavior of **1** resembles that of 1-phenyl-1,2-dihydronaphthalene[12]. The formation of hydrocarbons **2**, **5** and **7** from **1** can be rationalized in terms of an intramolecular [4+2] photocyclization of *cZt*-**3**[1,2], a photodecomposition reaction of **2**[1,18] and a photochemical 1,5-hydrogen shift[12] involving *cZc*- or *cZt*-**3** (Scheme 8). *Z*- and *E*-**9** can be rationalized similarly; viz. as photoproducts originating from the same pentaene intermediates (*cZc*- and *cZt*-**3**) as the hydrocarbons **2** and **7**. In accordance with this rationalization these photoproducts are not formed on irradiation of **1** at 254 nm; at this wavelength the phenyl group in *cZc*- or *cZt*-**3** is the main absorbing chromophore.

The remaining photoproducts from broad-spectrum irradiation of **1** in methanol to be accounted for, are **6**, **8** and **10**. The enhanced yields of these compounds, particularly at the expense of 1-phenylbenzobicyclo[3.1.0]hex-2-ene (**2**) on irradiation of **1** at 254 nm indicate that **6**, **8** and **10** do not arise from **1** *via* a pentaene intermediate.

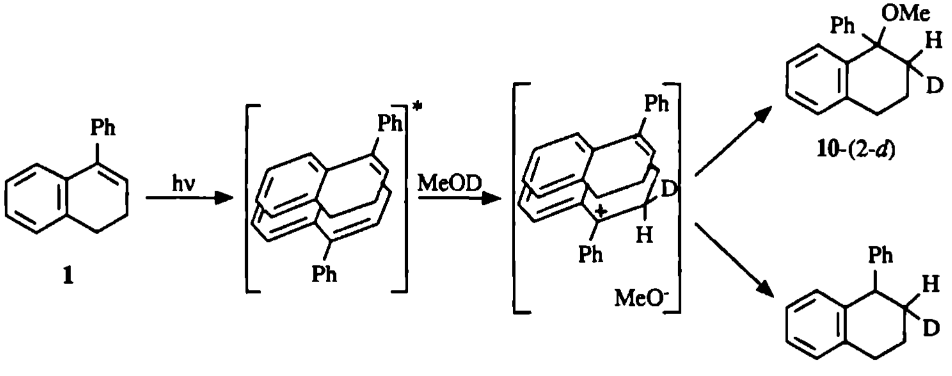


Scheme 8

In contrast with *E*- and *Z*-**9**, **10** is obviously formed by photochemical addition of methanol to the olefinic bond of **1**. Considering the observed wavelength dependence of the appropriate photoproduct yields (cf. Schemes 2 and 4), it can be concluded that the photoprocess leading to **6**, **8** and **10** involves excitation of **1** at 254 nm and competes with ring opening of excited **1** to *cZc*-**3**. The observation that irrespective of the reaction conditions **6** and **8** were always obtained in equimolar yields, suggests these products to arise from a photoinduced disproportionation reaction of **1**.

In the literature the following routes for photoinduced addition of methanol to the double bond of olefins have been reported: (*i*) Nucleophilic attack of MeOH on a Rydberg π,R(3s) excited state of the olefin[17]. (*ii*) Thermal addition of methanol to a photochemically generated *trans* olefinic bond in a ring containing less than 8 carbon atoms[17]. (*iii*) Nucleophilic addition of methanol to the olefin ionized into a radical cation, the ionized electron being solvated[28]. (*iv*) Attack of methanol on an excimer or exciplex[17,23]. (*v*) Markovnikov addition to an olefin excited into either a twisted (^{1}D) or a planar (π,π^*) singlet state[14]. Of these possibilities (*i*) can be rejected at once, since the range of photon energies involved in the present studies is below the reported[20,29] $\pi \rightarrow$ R(3s) transition energies of olefins. Considering route (*ii*) it is obvious that photochemical *cis-trans* isomerization of **1** should result in a highly strained *cis,trans*-benzocyclohexa-1,3-diene. Since methanol addition to such strained intermediates is known to be a rapid, acid-catalyzed thermal reaction[20,30], this route is ruled out by the experimental results of Table 1. Route (*iii*) can also be ruled out since even when **1** has partial radical cation character, by irradiation in the presence of *p*-DCNB (Scheme 6), it give rise to chiefly the *anti* Markovnikov methanol adduct **11**.

The assumption of an intermediate excimer on the route from **1** to **6**, **8** and **10** is outlined in Scheme 9. According to Scheme 9 the assumption accounts for both the highly regiospecific



Scheme 9

8-(2-*d*)

incorporation of D at C(2) in **8** and **10** and the occurrence of photoinduced disproportionation of **1** into **6** and **8**. However, closer examination of the mechanism depicted in Scheme 9 reveals that it is inconsistent with the experimental results: According to Scheme 9 (*a*) **1** should exhibit concentration-dependent fluorescence quantum yields and emission maxima, (*b*) the formation of **8** and **10** should be sensitive to acid and (*c*) photoinduced disproportionation of 2,2-dideuterio 4-phenyl-1,2-dihydronaphthalene (**1**-(2,2-d_2)) in MeOH should give hydrocarbon **8**-(1,3,3-d_3) regioselectively deuterated at C(1). Experimentally, neither self-quenching of the fluorescence of **1**, nor an effect of H_2SO_4 on the initial rates of formation of any of the photoproducts from **1** in MeOH or MeOD was found. Moreover, irradiation of **1**-(2,2-d_2) in MeOH afforded **8**-(2,2-d_2), comletely free from D incorporation at C(1) (NMR, GC-MS). From this result, it is concluded that **8** originates from photoreduction of **1** by MeOH, the observed equimolar quantities of **6** and **8** being a mere coincidence.

On the basis of these considerations, the photochemical addition of MeOH is (*vide infra*) proposed to occur directly to **1** in a planar (π,π^*) or, perhaps, a partially twisted excited singlet state[14]. According to this proposal the photochemistry of **1** should resemble that of the acyclic analog 1,1-diphenylethene. A comparison of the behavior of **1** (Scheme 4) and 1,1-diphenylethene[14] on direct irradiation at 254 nm in MeOH reveals indeed a striking analogy between these compounds. Both **1** and 1,1-diphenylethene undergo Markovnikov addition of MeOH, photoreduction by the solvent and extensive polymerization. Unlike 1,1-diphenylethene, however, excited 1-phenyl-1,2-dihydronaphthalene (**1**) does not rearrange into a carbene *via* a 1,2-phenyl shift. This may indicate that the sterically congested olefinic bond in excited **1** cannot reach completely the 90°-twisted geometry required for a 1,2-phenyl shift.

The resemblance of **1** and 1,1-diphenylethene appears also to include the photoreactivity of these compounds in the presence of electron transfer senzitizers such as *p*-DCNB. In analogy with the case of 1,1-diphenylethene[15,16] the occurrence of the *anti* Markovnikov methanol adduct **11** on irradiation (254 nm, MeOH) of **1** in the presence of *p*-DCNB (Scheme 6) can be rationalized in terms of an exciplex[23] of **1** with *p*-DCNB, wherein charge-transfer to the strong electron-acceptor *p*-DCNB imposes a partial radical-cation character on **1**.

Experimental

Starting materials. 4-Phenyl-1,2-dihydronaphthalene (**1**) and 2,2-dideuterio-4-phenyl-1,2-dihydronaphthalene (**1**-(2,2-d_2)) were prepared by dehydration[1,2] of 1-phenyl- and 3,3-dideuterio-1-phenyl-1,2,3,4-tetrahydronaphthol, respectively. Both naphthols were synthesized[31]from β-benzoylpropionic acid[32]. For the preparation of 3,3'-deuterio-1-phenyl-1,2,3,4-tetrahydronaphthol, the β-methylene protons of the acid were exchanged by refluxing a solution of the dry potassium salt in D_2O[1,2,31]. 1,4-Dimethoxynaphthalene (DMN, m.p. 88.5-88.8 ^{0}C) was synthesized in 60% yield by treatment of 1,4-naphthalenediol in dimethyl sulfate with concentrated KOH under N_2[33,34]. Commercial 1,4-dicyanobenzene (*p*-DCNB) was purified by repeated crystallizations from MeOH prior to use.

Irradiations. Irradiations were performed with (1-2) × 10^{-3} M solutions of **1** in neat or H_2SO_4-containing methanol under anaerobic conditions. Philips 125 W HPM, Philips TUV G15T8 and Philips TL 20 W/12 lamps were employed for broad-spectrum and monochromatic irradiations at 254 and 300 nm, respectively. Irradiations of **1**, sensitized by DMN or *p*-DCNB were performed at extinction ratios $\epsilon(\text{sens})/\epsilon(\mathbf{1}) \geq 7$.

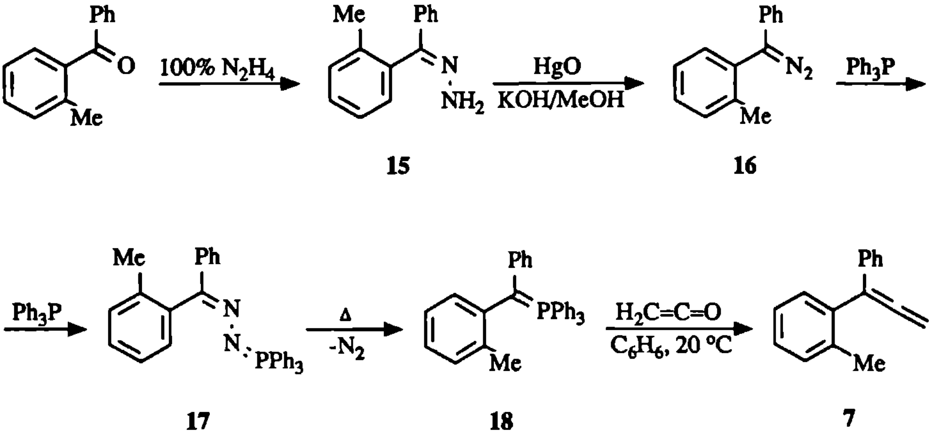
General methods. Photoproducts were isolated by column chromatography from silica gel (Merck 60, 60-230 mesh), employing carbon tetrachloride as the eluent. The photoproducts were characterized by ^{1}H-NMR (Bruker WH 90), IR (Perkin-Elmer 397), GC-MS (VG-7070 including a GLC-MS facility) and chemical synthesis. Kinetic data concerning the primary and secondary photoreactions were obtained by monitoring the yield of the photoproducts from **1** as a function of the irradiation time. Quantitative analysis of photoproduct mixtures was performed with 0.2-mL aliquots by temperature-programmed GLC (HP 5790, equipped with a flame-ionisation detector, a HP 3390 recording integrator and a HP 1157 fused-silica capillary column) and, occasionally, by integration of NMR spectra. Samples originating from irradiations in acidified MeOH were neutralized with OH^--exchanged Amberlite IRA-400 ion-exchange resin prior to GLC analysis.

2,2-dideuterio-4-phenyl-1,2-dihydronaphthalene (1-(2,2-*d*$_2$)). B.p.: 125-130 °C/1 mm, chemical purity: 95% (GLC), isotopic purity: *ca.* 100% (NMR, EIMS). NMR: ($CDCl_3$): $\delta = 2.81$ ppm (br. s, 2H) H_1; $\delta = 6.04$ ppm (br. s, 1H) H_3; $\delta = 7.0 - 7.5$ ppm (m, 4H) H_5-H_8; $\delta = 7.30$ ppm (br. s, 5H) C_6H_5. EIMS; *m/e* (rel. intensity): 209 (17), 208 (M^+, 100).

1-Phenyl-1-(*o*-tolyl)-1,2-propadiene (7). An attempt to synthesize this compound *via* an allylic rearrangement failed: Reaction of 3-bromo-3-phenyl-3-(*o*-tolyl)propyne with $LiAlH_4$ in refluxing THF resulted in overreduction[35] to 1-phenyl-1-(*o*-tolyl)propene (**14**, yield: 95%). NMR ($CDCl_3$): *E*-**14**: $\delta = 1.60$ ppm (d, 3H) H_3, $J_{2,3} = 6.74$ Hz; $\delta = 2.08$ ppm (s, 3H) $CH_3C_6H_4$; $\delta = 6.30$ ppm (q, 1H) H_2; $\delta = 7.0 - 7.3$ ppm (m, 9H) Ar H. *Z*-**14**: $\delta = 1.92$ ppm (d, 3H) H_3, $J_{2,3} = 7.1$ Hz; $\delta = 2.03$ ppm (s, 3H) $CH_3C_6H_4$; $\delta = 5.79$ ppm (q, 1H) H_2; $\delta = 7.0 - 7.3$ ppm (m, 9H) Ar H. EIMS (mixture of *E*- and *Z*-**14**); *m/e* (rel. intensity): 209 (10), 208 (M^+, 57), 193 (10), 179 (100), 115 (26), 91 (10).

The reaction of phenyl-(*o*-tolyl)carbene (generated by photolysis of phenyl-(*o*-tolyl)diazomethane (**16**, Scheme 10)) with a *ca.* 50% solution of acetylene in diethyl ether at -80 °C yielded a complex mixture of hydrocarbons and polymers, rather than the anticipated[36] products 3-phenyl-3-(*o*-tolyl)cyclopropene and **7**.

Scheme 10



Though in very low yields, pure **7** proved to be accessible by a strategy based on a salt-free Wittig reaction of the appropriate phosphorane with ketene (Scheme 10).

o-Methylbenzophenone hydrazone (**15**) was prepared[37] by refluxing 5.6 g of *o*-methylbenzophenone, 75 mL of abs. ethanol and 25 mL of anhydrous N_2H_4 for 4 days. Evaporation of the solvent and crystallization from MeOH afforded **15** as colorless needles (m.p. 116-117 °C) in 75% yield. NMR ($CDCl_3$): $\delta = 2.15$ ppm (s, 3H) CH_3; $\delta = 5.35$ ppm (br.s, 2H) NH_2; $\delta = 7.2 - 7.4$ ppm (m, 9H) Ar H. EIMS; *m/e* (rel. intensity): 211 (17), 210 (M^+, 100), 209 (64), 195 (27), 194 (79), 193 (74), 179 (28), 178 (25), 165 (25), 116 (45), 91 (20). IR (KBr, cm^{-1}): 3370, 3250 (br) N-H str..

Oxidation of **15** with yellow HgO[38] afforded purple-red **16** in quantitative yield. NMR ($CDCl_3$): $\delta = 2.25$ ppm (s, 3H) CH_3; $\delta = 6.8 - 7.4$ ppm (m, 4H) $CH_3C_6H_4$; $\delta = 7.27$ ppm (s, 5H) C_6H_5. IR (KBr, cm^{-1}): 2035 (vs) N=N str.. EIMS; *m/e* (rel. intensity): 180 (M^+-28(N_2), 100). UV; λ_{max}(nm) (ϵ, arbitrary units): 512 (0.01), 284 (3.0)

Conversion of **16** into **7** *via* phosphazine **17** and phosphorane **18** was achieved according to the procedure reported for the analogous diphenyl derivatives[39,40]. Compound **17** was isolated as light-yellow crystals (m.p.: 131 °C) in 57% yield. NMR ($CDCl_3$): $\delta = 2.12$ and 2.17 ppm (s, 3H)

CH_3(*cis*- and *trans*-**17**); δ = 7.2 - 7.6 ppm (m, 19H) Ar H. IR (KBr, cm^{-1}): 1572 (m) C=N str., 1480 (s) C=P str., 1434 (vs) N-N str. EIMS; *m/e* (rel. intensity): 471 (2), 470 (M^+, 5), 263 (20), 262 (100), 261 (11), 184 (11), 183 (48), 180 (30), 179 (49), 178 (27), 165 (16). Five mmols (2.35 g) of this compound were converted into dark-red, crystalline **18**, by heating in vacuo at *ca.* 150 °C until N_2 evolution had ceased[39].

After cooling to room temperature **18** was dissolved in 20 mL of dry, N_2-purged benzene and treated with ketene for 2 hrs[40]. Evaporation of the solvent afforded a dark brown residue, from which a fraction containing volatile reaction products could be separated by flash chromatography. The volatile fraction was purified by column chromatography (Silica gel: Merck 60H 70-230 mesh, eluent: CCl_4) affording 30 mg of pure (> 95% by GLC) **7**. NMR ($CDCl_3$): δ = 2.20 ppm (s, 3H) CH_3; δ = 5.18 ppm (s, 2H) H_3; δ = 7.24 - 7.29 ppm (m, 9H) Ar H. IR (KBr, cm^{-1}): 3064 (s) C-H str. olefin, 3020 (s) C-H str. Ar, 2954, 2920 (m) C-H str. CH_3, 1940 (s) C=C=C str., 1600 (w) C=C str. Ar. EIMS; *m/e* (rel. intensity): 207 (17), 206 (M^+, 100), 205 (50), 204 (19), 203 (23), 202 (24), 191 (72), 189 (25), 179 (25), 178 (26), 165 (23), 129 (16), 128 (31), 115 (16), 91 (43), 89 (17), 77 (13).

1-Phenyl-1,2,3,4-tetrahydronaphthalene (8). The pure compound was obtained quantitatively by catalytic hydrogenation (PtO_2, $P(H_2)$ = 3 bar) of **1** (1 mmol in 10 mL of ethyl acetate). NMR ($CDCl_3$): δ = 1.6 - 2.4 ppm (m, 4H) H_2, H_3; δ = 2.87 ppm (br. t, 2H) H_4, $J_{3,4}$ = 6.1 Hz; δ = 4.12 ppm (br. t, 1H) H_1, $J_{1,2}$ = 6.2 Hz; δ = 6.8 - 7.5 ppm (m, 9H) Ar H. EIMS; *m/e* (rel. intensity): 209 (17), 208 (M^+,100), 180 (63), 179 (43), 178 (23), 165 (21), 131 (15), 130 (52), 129 (14), 115 (14), 104 (14), 91 (23), 78 (14), 77 (14).

2-Deuterio-1-phenyl-1,2,3,4-tetrahydronaphthalene (8-(2-*d*)). This compound was isolated from a mixture of photoproducts formed by irradiation (254 nm) of **1** in MeOD. NMR ($CDCl_3$): δ = 4.11 ppm (br. d, 1H) H_1 of **8**-(2-*d*), $J_{1,2}$ = 6.2 Hz. GC-EIMS; *m/e* (rel. intensity): 209 (M^+, 100), 181 (59), 180 (44), 179 (59), 165 (24), 132 (21), 131 (59), 130 (26).

3-Methoxy-1-phenyl-1-(*o*-tolyl)propene (9, *Z*/*E* = 2). NMR ($CDCl_3$): *Z*-**9**: δ = 2.03 ppm (s, 3H) CH_3; δ = 3.37 ppm (s, 3H) OCH_3; δ = 4.16 ppm (d, 2H) H_3, $J_{2,3}$ = 6.74 Hz; δ = 5.86 ppm (t, 1H) H_2; δ = 7.0 - 7.4 ppm (m, 9H) Ar H. GC-EIMS; *m/e* (rel. intensity): 239 (7), 238 (M^+, 39), 223 (64), 207 (36), 206 (100), 205 (41), 191 (65), 179 (46), 178 (55), 165 (38), 147 (17), 129 (33), 115 (82), 103 (29), 91 (56), 82 (54), 77 (28). *E*-**9**: δ = 2.06 ppm (s, 3H) CH_3; δ = 3.28 ppm (s, 3H) OCH_3; δ = 3.83 ppm (d, 2H) H_3, $J_{2,3}$ = 6.45 Hz; δ = 6.35 ppm (t, 1H) H_2; δ = 7.0 - 7.4 ppm (m, 9H) Ar H. GC-EIMS; *m/e* (rel. intensity): 239 (7), 238 (M^+, 38), 223 (62), 207 (33), 206 (100), 205 (40), 191 (72), 179 (41), 178 (45), 165 (36), 147 (13), 129 (29), 115 (71), 103 (29), 91 (56), 82 (54), 77 (28). Considering the presence of steric interaction between the olefinic proton H_2 and the *o*-CH_3 group in *E*-**9** but not *Z*-**9**, this proton should be more deshielded in *E*-**9**. Hence, the NMR triplets at δ = 5.86 and 6.35 ppm due to H_2 were assigned to *Z*- and *E*-**9**, respectively. The assignments of the other NMR absorptions could then be deduced from the results of spin-decoupling.

1-Methoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (10). Crude 1-phenyl-1,2,3,4-tetrahydronaphthol[1,2] (20 mmol) was added slowly to a suspension of NaH (25 mmol) in DMF (25 mL). The reaction mixture was stirred (30 min) and then treated with an excess of MeI. After 30 min, the excess NaH was quenched by careful addition of water. Repeated extractions with pentane (5 × 60 mL), drying (K_2CO_3) of the combined pentane extracts, filtration and evaporation of the solvent afforded crude **10** which was purified by column chromatography. NMR ($CDCl_3$): δ = 1,5 - 2.5 ppm (m, 4H) H_2, H_3; δ = 2.86 ppm (br. t, 2H) H_4, $J_{3,4}$ = 6.3 Hz; δ = 3.16 ppm (s, 3H) OCH_3; δ = 7.0 - 7.4 ppm (m, 4H) H_5-H_8; δ = 7.3 ppm (s, 5H) C_6H_5. GC-EIMS; *m/e* (rel. intensity): 238 (M^+, 1.9), 237 (1.5), 209 (23), 207 (72), 206 (100), 191 (12), 179 (38), 178 (26), 165 (18), 161 (69), 129 (31), 115 (13), 91 (76), 77 (20).

2-Deuterio-1-methoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (10-(2-*d*)). This compound was separated from the photoproducts obtained on irradiation (254 nm) of **1** (5×10^{-3} M) in MeOD. NMR ($CDCl_3$): δ = 1,5 - 2.3 ppm (m,3H) H_2, H_3; δ = 2.85 ppm (br. t, 2H) H_4, $J_{3,4}$ = 6.0 Hz; δ = 3.16 ppm (s, 3H) OCH_3; δ = 7.0 - 7.4 ppm (m, 9H) Ar H. GC-CIMS; *m/e* (rel. intensity): 241 (5),240 (M+1(H^+), 27), 209 (19), 208 (100), 207 (24), 163 (9), 162 (75), 91 (9).

2-Methoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (11). This compound was obtained as a mixture of *cis* and *trans* isomers (inseparable by column chromatography or GLC) with more than 90% (GLC) purity by sensitized (*p*-DCNB, 4×10^{-3} M) irradiation (254 nm) of **1** (2×10^{-3} M) in deaerated MeOH. NMR ($CDCl_3$): *Component I*: δ = 1,8 - 2.2 ppm (m, 2H) H_3; δ = 2.7 - 3.2 ppm (m, 2H) H_4; δ = 3.36 ppm (s, 3H) OCH_3; δ = 3.55 - 3.82 ppm (m, 1H) H_2; δ = 4.39 ppm (br. d, 1H) H_1, $J_{1,2}$ = 4.75 Hz; δ = 6.8 - 7.4 ppm (m, 9H) Ar H. *Component II*: δ = 1,8 - 2.2 ppm (m, 2H) H_3; δ = 2.7 - 3.2 ppm (m, 2H) H_4; δ = 3.34 ppm (s, 3H) OCH_3; δ = 3.55 - 3.82 ppm (m, 1H) H_2; δ = 4.18 ppm (br. d, 1H) H_1, $J_{1,2}$ = 5.25 Hz; δ = 6.8 - 7.4 ppm (m, 9H) Ar H. A consistent assignment of these NMR data to the *cis*- and *trans*-isomer of **11** could not be made. GC-EIMS (mixture of *cis*- and *trans*-**11**) ; *m/e* (rel. intensity): 238 (M^+, 9), 237 (3), 223 (1), 208 (3), 207 (22), 206 (100), 191 (7),181 (10), 180 (61), 179 (74), 178 (32), 165 (23), 129 (6), 128 (8), 115 (10), 91 (17).

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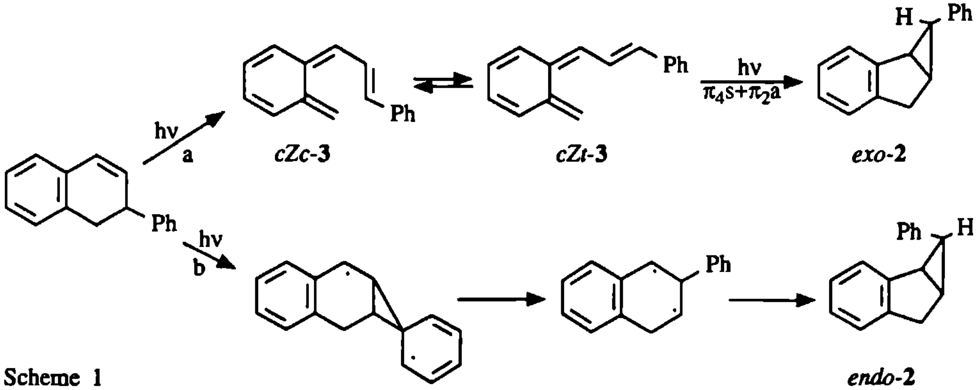
Chapter 7: The photochemistry of 2-phenyl-1,2-dihydronaphthalene in methanol.

Introduction

In Chapters 4 and 6 of this thesis, the photoreactivity of 1- and 4-phenyl-1,2-dihydronaphthalene in methanol has been described and compared to that in hexane. From these studies it emerged that the formation of the corresponding phenylbenzobicyclo[3.1.0]hex-2-ene is not affected seriously for these compounds on changing the solvent from hexane to methanol. The result of experiments, in which the progress of the photoreaction in neat and H_2SO_4-containing methanol, and in hexane was monitored as a function of the irradiation time, suggest that sudden-polarized[1,2] excited states are not involved in the primary photoreactions of these compounds.

Like 1- and 4-phenyl-1,2-dihydronaphthalene, 2-phenyl-1,2-dihydronaphthalene (**1**) has been reported[3,4] to give the corresponding *exo*- and *endo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (**2**) as the principal photoproducts in hexane. However, in contrast with 1- and 4-phenyl-1,2-dihydronaphthalene, experiments[3,4] with deuterated **1** demonstrate that the formation of *exo*- and *endo*-**2** from **1** involves two distinct pathways. In addition to a pathway *via* photochemical ringopening and subsequent intramolecular photocycloaddition of the resulting pentaene intermediate (*cZt*-**3**, Scheme 1, route a) **2** arises from **1** *via* a di-π-methane rearrangement (Scheme 1, route b). Though the latter reaction was shown to give rise to *endo*-**2**, it could not be established whether *exo*- and *endo*-**2** arise stereospecifically *via* routes a and b (Scheme 1), respectively, since photochemical interconversion of these compounds takes place.



Scheme 1

In this chapter the results of studies on the photochemistry of **1** in methanol are presented. In analogy to 1- and 4-phenyl-1,2-dihydronaphthalene the present study has been devoted to: (*i*)

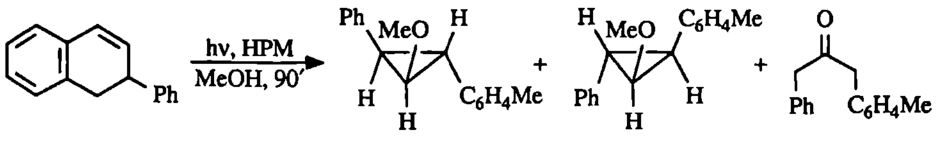
Isolation and characterization of the photoproducts from **1** in methanol. (*ii*) Establishment to which extent primary and other photoreactions are involved in their formation. (*iii*) Elucidation of the nature (sudden-polarized or essentially nonpolar) of the excited state involved in the formation of the primary photoproducts. (*iv*) Elucidation to which extent the routes a and b depicted in Scheme 1 are involved in the photoreactions of **1** to *endo*- and *exo*-**2**.

Results and discussion

Photoproduct analyses were performed with 200 mg samples, obtained from irradiation of **1** (0.001-0.003 M) in N_2-purged MeOH with a HPM lamp. The samples were separated by flash chromatography (Silica gel, eluent: CCl_4) into a fraction containing the hydrocarbons and a fraction containing the polar photoproducts. Separation of the photoproducts from irradiation of **1** (10^{-3} M) in methanol for 90 min in this manner indicated that, apart from polymeric materials, only polar compounds were obtained in this experiment. Further separation of these by column chromatography (Silica gel, 22 cm × 2 cm i.d. column, eluent: $CCl_4/CHCl_3$ 2:1 v/v) afforded two fractions.

According to GC-MS the first fraction collected in this way, consisted of two very similar compounds of stoichiometry $C_{17}H_{18}O$ (m/e: 238 for both of them). The ^1H-NMR spectrum of the fraction indicated the presence of a methoxy group ($\delta = 3.23$ and 3.29 ppm (both s, 3H)) and three other aliphatic protons ($\delta = 2.2 - 3.8$ ppm, all d of d, 1H) in both constituents. The formation of methanol adducts analogous to those reported for 1-, 3- and 4-phenyl-1,2-dihydronaphthalene (i.e. either addition of MeOH directly to the double bond of **1** or to the pentaene rotamers *cZc*- or *cZt*-**3** depicted in Scheme 1)[5] was ruled out by the absence of ^1H-NMR absorptions due to olefinic protons or to methylene and methine protons of a substituted 1,2,3,4-tetrahydronaphthalene. From the results of spin-decoupling the methanol adducts of **1** were concluded to be the (1α,2α,3β) and (1α,2β,3α) isomers of 1-methoxy-2-phenyl-3-(*o*-tolyl)cyclopropane (**4**, Scheme 2). In view of the values of the vicinal coupling constants of the cyclopropane ring protons, there is no ambiguity concerning the geometric arrangement of the substituents at the cyclopropane ring. Moreover, the δ-values and vicinal coupling constants of the cyclopropane ring and OCH_3 protons in (1α,2β,3α)- and (1α,2α,3β)-**4** agree with those reported[6-11] for similar compounds.

Scheme 2

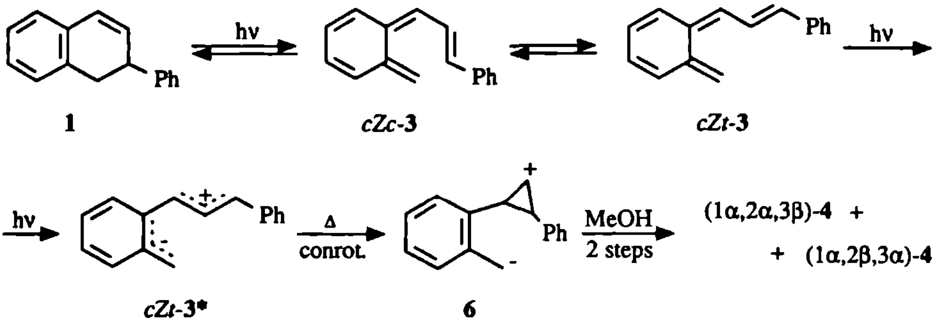


1, 10^{-3} M (1α,2α,3β)-**4** (1α,2β,3α)-**4** **5**

The second chromatography fraction consisted of a single compound of stoichiometry $C_{16}H_{16}O$ (High resolution MS: m/e: 224.1204 (theor. 224.1201)). From the IR (cm^{-1}(KBr) 1700 (s) C=O str., 760 (s) *o*-disubst. benzene) and the ^{1}H-NMR spectrum the compound was recognized as 1-phenyl-3(*o*-tolyl)-2-propanone (**5**, Scheme 2).[12,13] The ketone was shown to be derived from photoreactions of the cyclopropanes **4** in MeOH under the conditions given in Scheme 2.

Considering the occurrence of the cyclopropanes **4** on irradiation of **1**, the photochemistry of this compound appears to be different from that of the related compounds 1- ,3- and 4-phenyl-1,2-dihydronaphthalene[4,14] (see also Chapters 4-6 of this thesis). Assuming the cyclopropanes **4** to be primary photoproducts of **1**, their fromation might be ascribed (Scheme 3) to a sudden-polarized excited state (*cZt*-**3***, Scheme 3) of the pentaene *cZt*-**3**, formed by photochemical ringopening of **1**. The argument, that in *cZt*-**3*** the positive charge is stabilized by the phenyl substituent whereas the negative charge resides on the least substituted carbon atom,[1] provides a plausible explanation for the occurrence of such an excited state in the polar solvent MeOH. Moreover the mechanism, presented in Scheme 3 rationalizes consistently the stereochemistry of the cyclopropanes **4** *via* a conrotatory photochemical ringclosure of *cZt*-**3***.

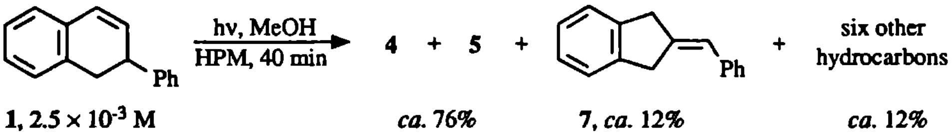
Scheme 3



However, the mechanism does not provide a consistent explanation for the fact that *cZt*-**3*** yields exclusively the dipolar intermediate **6**, without being scavenged itself by methanol addition: According to theoretical calculations[1] on the parent, unsubstituted *cZt*-hexatriene almost complete charge separation should exist in sudden-polarized *cZt*-**3***. Hence, both *cZt*-**3*** and **6** (Scheme 3) should be quenched rapidly by methanol addition.

In view of these considerations a more detailed examination of the photochemistry of **1** in methanol and hexane appeared relevant. According to Scheme 3 the rate of photoconversion of **1** in MeOH should exceed those of the related compounds 1- and 4-phenyl-1,2-dihydronaphthalene (Chapters 4 and 6), which presumably do not react *via* sudden-polarized excited states. This expectation was confirmed by experiment: On irradiation of an N_2-purged, 2.5 × 10^{-3} M solution in MeOH with a HPM lamp photoconversion of **1** was observed to be complete within 20 min, whereas that of both 1- and 4-phenyl-1,2-dihydronaphthalene was incomplete after a 40-min irradiation period (73% and 65%, respectively). Flash chromatography of the photoproducts, obtained from **1** under these conditions gave results different from those presented in Scheme 2: In addition to the cyclopropanes **4** and ketone **5** a mixture of hydrocarbon photoproducts was isolated in *ca.* 25% yield. GLC analysis of the hydrocarbon mixture revealed the presence of 7 components. The ^{1}H-NMR spectrum of the most abundant hydrocarbon exhibited broad singlets at δ = 3.9 and 6.8 ppm (ratio 4:1). This compound was identified as 2-benzylidene indane (**7**, Scheme 4) by comparing the retention time of its GLC peak and the ^{1}H-NMR spectrum of the hydrocarbon mixture with those of authentic **7**[3,4]

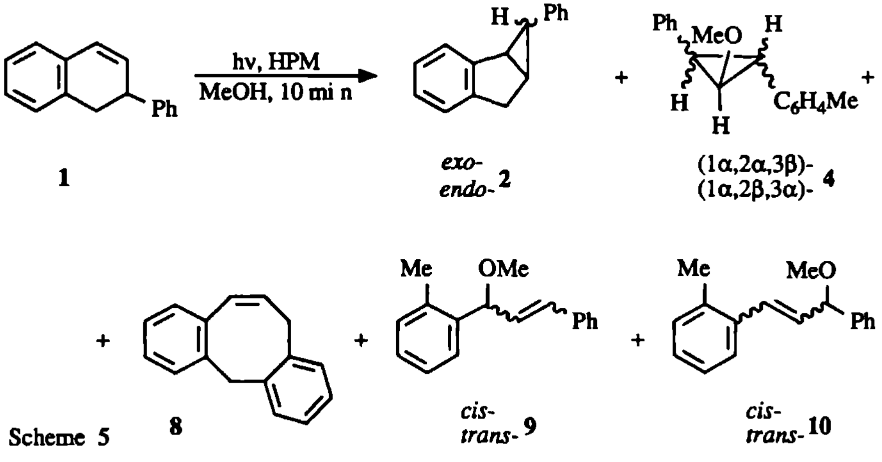
Scheme 4



In hexane **7** has been reported[3,4] as the major secondary photoproduct of **1**, arising *via* photodecomposition of *endo*- and *exo*-**2** (Scheme 1). Hence, the observation that significant yields of **7** but not of *endo*- and *exo*-**2** were obtained from **1** in methanol (Scheme 4), suggested that under these conditions *exo*- and *endo*-**2** are primary photoproducts of **1**.

To verify this supposition, **1** was irradiated in methanol for short periods of time. GLC analysis of the reaction mixture obtained on irradiation of a 2.91 × 10^{-3} M solution of **1** in MeOH with a HPM lamp for 10 min revealed the presence of nine photoproducts. These were separated by flash chromatography into a hydrocarbon and a polar fraction. GC-MS analysis of the hydrocarbon fraction revealed the presence of unreacted **1** and of three $C_{16}H_{14}$-isomers (m/e: 206) of **1**. From their individual mass spectra and the ^{1}H-NMR spectrum of the mixture, the $C_{16}H_{14}$-isomers were recognized as *endo*- and *exo*-**2**, and 1,6-dibenzocycloocta-1,3,6-triene (**8**, Scheme 5), the same photoproducts as formed[3,4] from **1** in hexane under similar conditions.

According to GC-MS the fraction of the polar photoproducts consisted of six compounds, all of stoichiometry $C_{17}H_{18}O$ (m/e 238). The cyclopropanes ($1\alpha,2\alpha,3\beta$)-**4** and ($1\alpha,2\beta,3\alpha$)-**4** (Scheme 2) were found to be the most abundant constituents of this fraction. Separation by column chromatography afforded a mixture of the other methanol adducts. The ^{1}H-NMR spectrum, showing resonances in the olefinic region (δ = 4.5 - 6.5 ppm (4 doublets)) and the region δ = 3 - 3.5 ppm (4 singlets due to methoxy groups), suggested that the new compounds were formed by addition of methanol to the pentaenes *cZc*- or *cZt*-**3** (Schemes 1 and 3). This suggestion was



Scheme 5

corroborated by the data from spin-decoupling experiments and from GC-MS analysis, which could be assigned to *cis*- and *trans*-3-methoxy-3-(*o*-tolyl)-1-phenylpropene (*cis*- and *trans*-**9**) and *cis*- and *trans*-3-methoxy-3-phenyl-1-(*o*-tolyl)propene (*cis*- and *trans*-**10**) (Scheme 5). For *trans*-**9** and *trans*-**10** the assignments were confirmed by chemical synthesis. Ketone **5** and 2-benzylideneindane (**7**), arising as the products of photodecomposition of the cyclopropanes **4** (Scheme 2) and of bicyclohexenes **2** on prolonged irradiation of **1**, were not detected among the photoproducts of **1** in this experiment.

Like the experimental results presented in Schemes 2 and 4 those of Scheme 5 are still compatible with Scheme 3. Thus the formation of the bicyclohexene *exo*-**2**, and of compounds **9** and **10** (Scheme 5) can be envisaged from the sudden-polarized excited state *cZt*-**3*** (Scheme 3). The preferred polarity[1] of the excited state rationalizes, that photoproducts derived from nucleophilic attack of methanol on the exocyclic methylene group in *cZt*-**3*** are not observed. In accordance with the results reported with **1** in hexane the occurrence of *endo*-**2** and **8** on irradiation of **1** in methanol can be rationalized in terms of a photo-di-π-methane reaction from **1** and of a concerted $\pi_6s+\pi_2s$ intramolecular photocyclization[3,4,14] reaction from *cZc*-**3**, respectively.

In order to obtain information concerning the polarity of the excited states of *cZc*- and *cZt*-**3** and the intermediacy of **6** (Scheme 3), the progress of the photoreaction of **1** in methanol has been monitored as a function of the irradiation time in neat and in H_2SO_4-containing MeOH. The resulting yield *vs*. time curves for the disappearance of **1** and the formation of *endo*-**2**, *exo*-**2**, **4**, and **7**-**10** (Scheme 5) are given in Fig. 1 and 2.

The results of these experiments reveal that, in contrast with the basic assumption involved in Scheme 3, the isomeric cyclopropanes **4** are not primary photoproducts of **1**. From the observation that the formation of the cyclopropanes **4** sets in when the yields of *trans*-**9** and *trans*-**10** approach their maximum values (Fig. 2, solid curves), these compounds are assumed to be the main

Fig. 1. Broad-spectrum irradiation (HPM) of 2-phenyl-1,2-dihydronaphthalene (**1**, 2.9 ×10^{-3} M) in neat and in H_2SO_4-containing (0.1 M) methanol at 15 °C: Yield *vs*. time plots for the conversion of **1** and the formation of *endo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (*endo*-**2**) and of (1α,2α,3β)- and (1α,2β,3α)-1-methoxy-2-phenyl-3-(*o*-tolyl)cyclopropane (**4**).

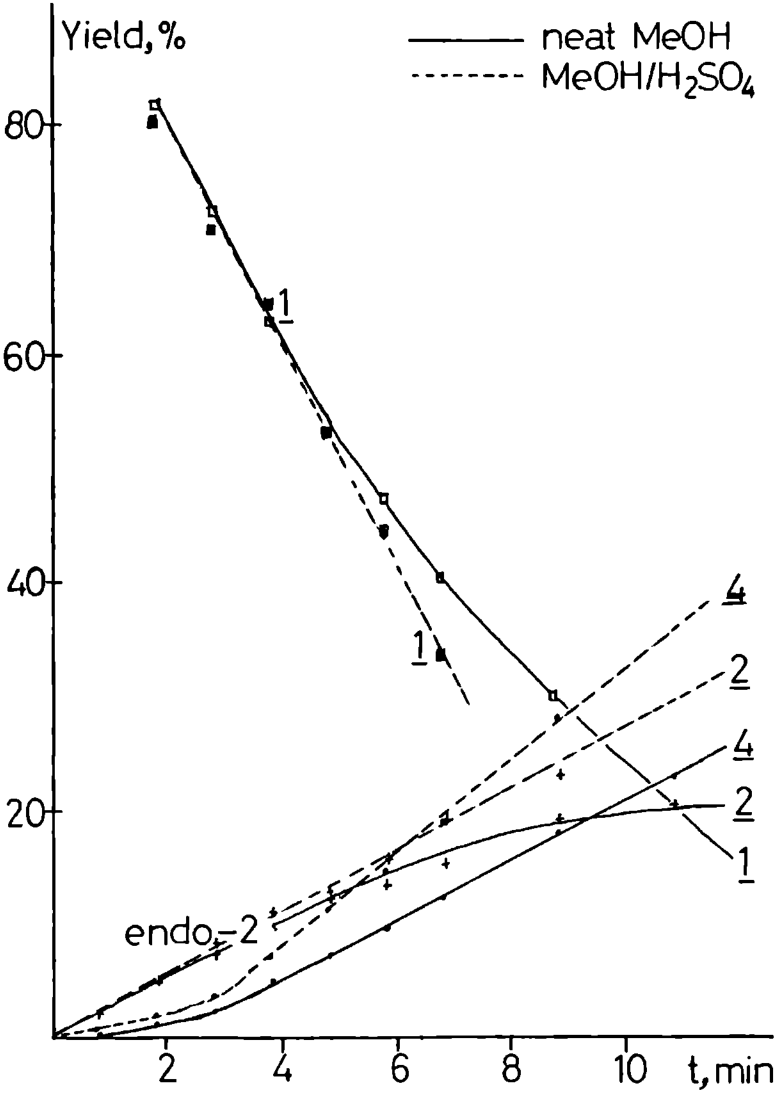
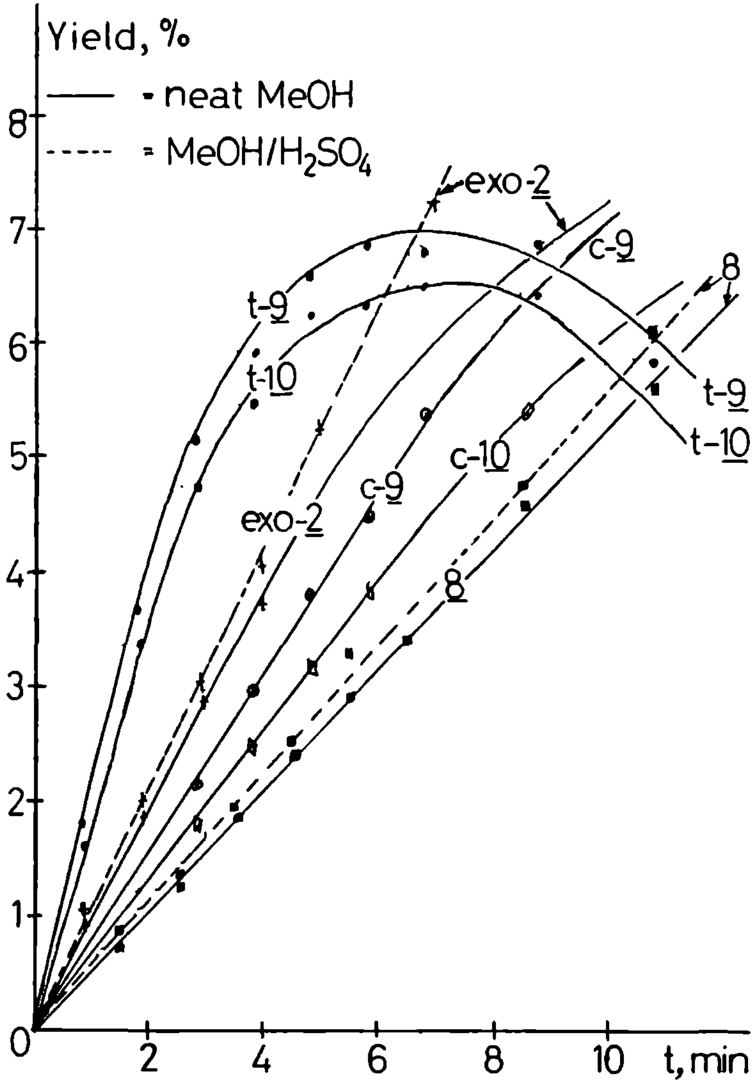


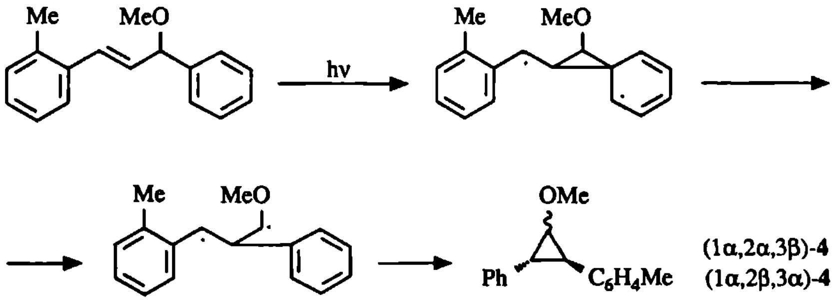
Fig. 2. Broad-spectrum irradiation (HPM) of 2-phenyl-1,2-dihydronaphthalene (**1**, 2.9×10^{-3} M) in neat and in H_2SO_4-containing (0.1 M) methanol at 15 °C: Yield *vs.* time plots for the formation of *exo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-**2**), 1,6-dibenzocycloocta-1,3,6-triene (**8**), 3-methoxy-3-(*o*-totlyl)-1-phenylpropene (*cis*- and *trans*-**9**) and 3-methoxy-3-phenyl-1-(*o*-tolyl)propene (*cis*- and *trans*-**10**).



precursors to **4**. In view of the perfect (100%) mass balance and the high yield of **4** obtained, even after irradiation for a few minutes, the transformation of *cis*- and *trans*-**10** into the cyclopropanes **4** appears to be a clean, efficient photoprocess. Supporting evidence for this conclusion has been obtained from the irradiation (300 nm) of an authentic mixture of *trans*-**9** and *trans*-**10** (10^{-3} M) in methanol, which afforded the cyclopropanes **4** in 92% yield at 100% conversion.

As an explanation of these results, we propose the transformation of *trans*-**9** and *trans*-**10** into the isomeric cyclopropanes to involve a photochemical di-π-methane rearrangement (Scheme 6, depicted for *trans*-**10**). Though examples of a photochemical di-π-methane rearrangement with simple 3-arylpropenes are rare[15], the reaction has been reported[16,17] to take place efficiently with 3-methoxy-1,1,3-triaryl-1-propenes, which are structurally similar to **9** and **10**.

Scheme 6

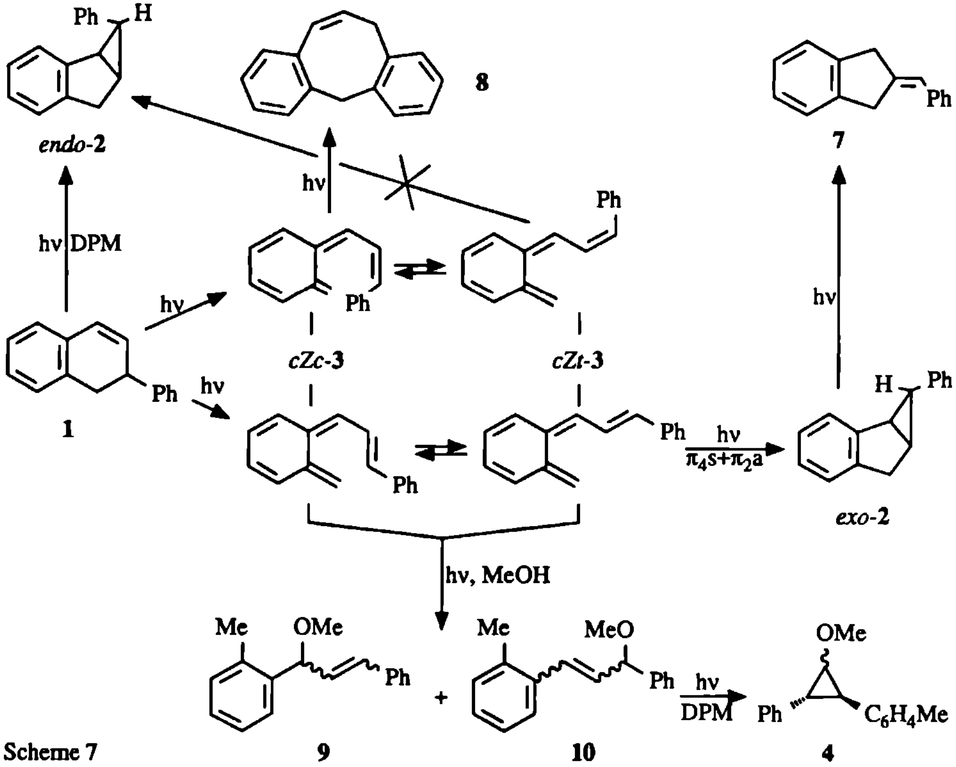


According to the yield *vs.* time curves of the cyclopropanes **4** (Fig. 2) their formation is apparently catalyzed by H_2SO_4. A simple explanation for this effect in terms of Scheme 6 cannot be given. The observation that the isomer ratio (1α,2α,3β)-**4**/(1α,2β,3α)-**4** (2.6 ± 0.3 and 2.9 ± 0.3 in neat and in H_2SO_4-containing MeOH) is not affected by H_2SO_4, indicates the mechanism of the di-π-methane rearrangement of **10** into **4** to be the same in neat and in H_2SO_4-containing MeOH. Furthermore, it can be seen in Fig. 1 that the rates of the photochemical di-π-methane rearrangement **1** of into *endo*-**2** in neat and in H_2SO_4-containing MeOH are equal. Irradiation of a mixture of authentic *trans*-**9** and *trans*-**10** in neat and in H_2SO_4-containing methanol indicated this conclusion to hold equally for the di-π-methane rearrangement leading to the cyclopropanes **4**. Therefore, the enhanced yields of the cyclopropanes **4** in H_2SO_4-containing methanol reflect a catalytic effect of H_2SO_4 on the formation of the precursors **9** and **10** from **1**.

In addition to the conclusion that cyclopropanes **4** are not formed directly from a sudden-polarized excited state *cZc*-$\mathbf{3}^*$ (Scheme 3), the experimental results presented in Figs. 1 and 2 suggest also that this excited state is not involved in the formation of the hydrocarbons *exo*-**2** and **8** and the methanol adducts **9** and **10** from **1**.

According to the mechanism of Scheme 3 enhanced scavenging of the polar intermediates *cZt*-**3*** and **6** should be expected on going from neat to H_2SO_4-containing MeOH. On the other hand, the theory of the sudden-polarization effect predicts the excited singlet state of *cZc*-**3** to be nonpolar[1,2]. Thus, according to Scheme 3 the photostationary state concentration ratio of the intermediates *cZc*-**3** and *cZt*-**3** and related yield ratio **8**/*exo*-**2** should increase on going from neat to H_2SO_4-containing methanol. By similar reasoning the mechanism of Scheme 3 predicts an increase in the ratios (**4**+**9**+**10**)/*exo*-**2** and *endo*-**2**/*exo*-**2** on going from neat to H_2SO_4-containing methanol. In all three cases the experimental yield ratios, evaluated from the data in Figs. 1 and 2, turned out to be equal in neat and H_2SO_4-containing methanol.

A mechanism rationalizing all experimental data presented so far is given in Scheme 7.

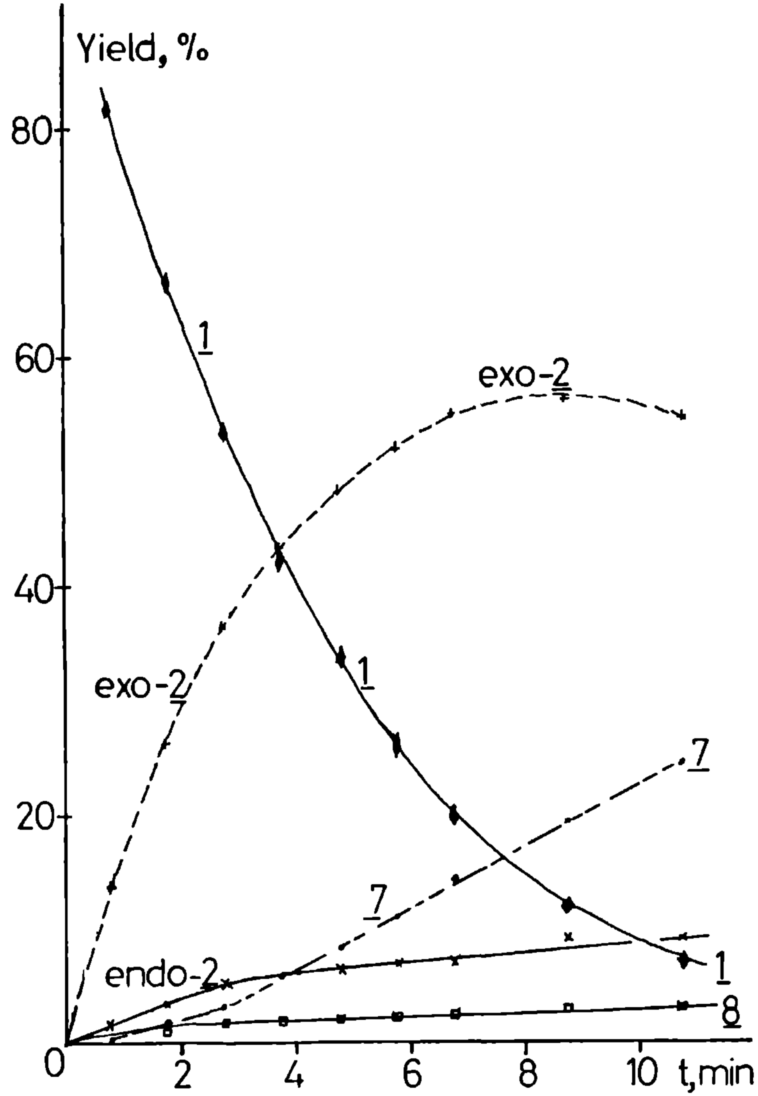


Scheme 7

According to this scheme the photochemistry of **1** in MeOH resembles closely that of 1- and 4-phenyl-1,2-dihydronaphthalene in this solvent, except of course for the observed photochemical di-π-methane rearrangements of **1** itself and of the methanol adducts **9** and **10**.

As mentioned previously, the primary photo di-π-methane rearrangement of **1** to *endo*-**2** is a concerted reaction and hence, expected to be insensitive to the polarity of the solvent. The results

Fig. 3. Broad-spectrum irradiation (HPM) of 2-phenyl-1,2-dihydronaphthalene (**1**, 2.9×10^{-3} M) in hexane at 15 °C: Yield *vs.* time plots for the formation of *endo*- and *exo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (*endo*- and *exo*-**2**), 2-benzylideneindane (**7**) and 1,6-dibenzocycloocta-1,3,6-triene (**8**).



(Fig. 3) obtained on irradiation of **1** in hexane under the conditions given in Figs. 1 and 2 are in accordance with this prediction: From a comparison of the results in Figs. 1, 2 and 3 it emerges that the rates of formation of *endo*-**2** from **1** are about equal in these media. Together with the results of previous work[3] with deuterated **1** in hexane this observation provides evidence for the conclusion that formation of *endo*-**2** from **1** occurs exclusively by a photochemical di-π-methane reaction and not *via* an intermediate *cZc*-**3** (Scheme 7). This conclusion is corroborated by the observation that the concomtiant formation of **8** and *exo*-**2** (which involves the pentaene intermediates *cZc*- and *cZt*-**3**) is suppressed significantly on going from hexane to MeOH. This points again to the involvement of different precursors of *endo*- and *exo*-**2**. In methanol, photochemical addition of the solvent competes effectively with intramolecular photocycloaddition for the precursor (*cZt*-**3**, Scheme 3) of *exo*-**2**.

Summary and conclusions.

On prolonged irradiation in methanol 2-phenyl-1,2-dihydronaphthalene (**1**) affords the (1α,2α,3β)- and (1α,2β,3α)-isomers of 1-methoxy-2-phenyl-3-(*o*-tolyl)cyclopropane (**4**) in appreciable yields. Though formation of these photoproducts may be envisaged *via* a sudden-polarized excited state of a pentaene intermediate (*cZc*-**3**) arising from ringopening of **1**, this possibility is ruled out by the results of irradiation of **1** in methanol for short periods of time: According to these results the isomeric cyclopropanes **4** arise entirely in secondary photoreactions of **1**. As the precursors of **4**, the compounds (**9** and **10**) deriving from photochemical ringopening of **1** have been identified. The transformation of these methanol adducts into the isomeric cyclopropanes involves presumably a concerted, photochemical di-π-methane rearrangement. Though examples of the rearrangement are scarce[16,17] for the type of compounds presently considered, irradiation of authentic **9** and **10** indeed afforded the cyclopropanes **4** in high yield.

As far as the primary photoreactions are concerned, the photochemistry of **1** in MeOH parallels that of 1- and 4-phenyl-1,2-dihydronaphthalenes. Like these compounds **1** undergoes photochemical ringopening to the corresponding pentaene intermediates, which subsequently undergo either intramolecular photocyclization yielding *exo*-**2** and **8**, or photochemical addition of methanol to a double bond yielding **9** and **10**. In the case of **1** the photochemical addition of methanol competes much more effectively with the intramolecular photocycloaddition of the pentaene intermediates than in the case of 1- and 4-phenyl-1,2-dihydronaphthalene.

The observation that the presence of a large excess of H_2SO_4 (0.102 M) does not catalyze the overall photoconversion of **1** and, especially not the formation of the hydrocarbons *endo*-**2**, *exo*-**2**, and **8** in MeOH points to the absence of a sudden-polarized excited state on the photoproducts. Together with previously reported results with deuterated **1** in hexane the present work provides evidence for the conclusion that both in methanol and hexane, the formation of *endo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (*endo*-**2**) from **1** involves a stereospecific, photochemical di-π-methane rearrangement.

Experimental.

Preparations. 2-Phenyl-1,2-dihydronaphthalene (**1**) was prepared in 100% yield and purity from pure 3-phenyl-1-tetralone (recrystallized 3 times from EtOH, prior to use) according to the literature[3,4]. As a starting compound for the synthesis of *trans*-3-methoxy-3-(*o*-tolyl)-1-phenylpropene (*trans*-**9**) and *trans*-3-methoxy-3-phenyl-1-(*o*-tolyl)propene (*trans*-**10**) 3-phenyl-1-(*o*-tolyl)allylalcohol was prepared[18] by a Grignard reaction of *o*-methylbenzylmagnesium bromide and cinnamaldehyde. The alcohol was methoxylated[19] by stirring in MeOH with 10% H_2SO_4 to yield a mixture of *trans*-**9** and *trans*-**10**.

Irradiations and general methods. Irradiations were performed with N_2-purged $(1\text{-}3)\times10^{-3}$ M solutions of **1**, through quartz using a Philips HPK 125 high-pressure mercury (HPM) lamp as the light source. Spectrograde methanol or hexane was employed as the solvent in the experiments. The experimental procedures and equipment[20] involved in the isolation and characterization of the photoproducts, and the determination of the yield *vs.* time curves (Figs. 1, 2 and 3) have been adopted from the studies on the photochemistry of 1- and 4-phenyl-1,2-dihydronaphthalene (Chapters 4 and 6 of this thesis). Particular care was been taken to ensure strictly identical irradiation conditions in the evaluation of the yield *vs.* time curves. Thus, the evaluation of the yield *vs.* time plots of primary photoproduct formation from **1** in MeOH/H_2SO_4 and in hexane were flanked by similar experiments in neat MeOH. The strict identity of the irradiation experiments emerged from the reproducibility of the yield *vs.* time curves obtained from these independent flanking experiments in MeOH.

(1α,2α,3β)-1-methoxy-2-phenyl-3-(*o*-tolyl)cyclopropane ((1α,2α,3β)-4). NMR ($CDCl_3$): δ = 2.41 ppm (s, 3H) CH_3; δ = 2.41 ppm (d of d, 1H) H_3, $J_{1,3}$ = 6.0 Hz, $J_{2,3}$ = 7.2 Hz; δ = 2.47 ppm (d of d, 1H) H_2, $J_{1,2}$ = 3.9 Hz; δ = 3.30 ppm (s, 3H) OCH_3; δ = 3.70 ppm (d of d, 1H) H_1; δ = 6.9 - 7.5 ppm (m, 9H) Ar H.

(1α,2β,3α)-1-methoxy-2-phenyl-3-(*o*-tolyl)cyclopropane (1α,2β,3α-4). NMR ($CDCl_3$): δ = 2.25 ppm (d of d, 1H) H_2, $J_{1,2}$ = 6.6 Hz, $J_{2,3}$ = 6.9 Hz; δ = 2.37 ppm (s, 3H) CH_3; δ = 2.60 ppm (d of d, 1H) H_3, $J_{1,3}$ = 3.8 Hz; δ = 3.24 ppm (s, 3H) OCH_3; δ = 3.69 ppm (d of d, 1H) H_1; δ = 6.9 - 7.5 ppm (m, 9H) Ar H.

***cis*-3-Methoxy-3-(*o*-tolyl)-1-phenylpropene (*cis*-9).** NMR ($CDCl_3$): δ = 2.12 ppm (s, 3H) CH_3; δ = 3.29 ppm (s, 3H) OCH_3; δ = 5.16 ppm (d, 1H) H_3, $J_{2,3}$= 9.2 Hz; δ = 5.85 ppm (d of d, 1H) H_2, $J_{1,2}= J_{cis}$ = 11.3 Hz; δ = 6.70 ppm (br. d., 1H) H_1; δ = 6.9 - 7.5 ppm (m, 9H) Ar H.

***cis*-3-Methoxy-3-phenyl-1-(*o*-tolyl)propene (*cis*-10).** NMR ($CDCl_3$): δ = 2.23 ppm (s, 3H) CH_3; δ = 3.21 ppm (s, 3H) OCH_3; δ = 4.85 ppm (d, 2H) H_3, $J_{2,3}$= 9.2 Hz; δ = 5.89 ppm (d of d, 1H) H_2, $J_{1,2} = J_{cis}$ = 11.3 Hz; δ = 6.70 ppm (br. d, 1H) H_1, δ = 6.9 - 7.5 ppm (m, 9H) Ar H.

***trans*-3-methoxy-3-(*o*-tolyl)-1-phenylpropene and *trans*-3-methoxy-3-phenyl-1-(*o*-tolyl)-propene (*trans*-9 and 10).** NMR ($CDCl_3$): δ = 2.34 and 2.36 ppm (both s) CH_3; δ = 3.35 and 3.37 ppm (both s) OCH_3; δ = 4.79 and 4.95 ppm (both d of d) H_3, $J_{2,3}$= 7.0 Hz; δ = 6.0 - 6.5 ppm (m)

H_2, $J_{1,2} = J_{trans}$ *ca.* 16 Hz; $\delta = 6.9 - 7.5$ ppm (m) H_1, Ar H. Due to the complexity and close proximity of the ^{1}H-NMR signals involved, further assignment of the ^{1}H-NMR data to the individual compounds *trans*-**9** and **10** is impossible.

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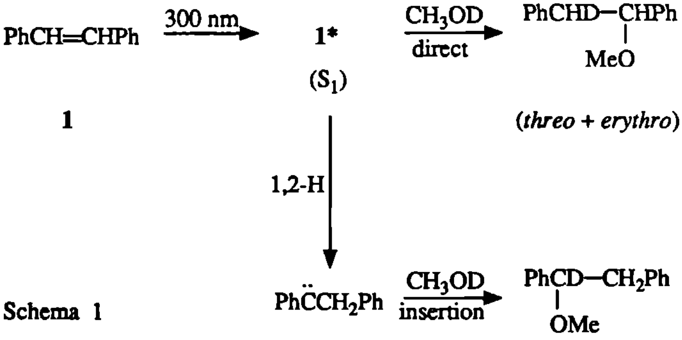
20. Minor modifications included the use of more sophisticated GLC equipment, consisting of a HP 5890 gaschromatograph equipped with a HP 3396 recording integrator and a Chrompack 7703 WCOT fused silica capillary column (10 m). Characterization of the photocproducts involved 90 MHz ^{1}H-NMR (Bruker WH 90 spectrometer).

Samenvatting

Dit proefschrift beschrijft de resultaten van een onderzoek naar het oplosmiddeleffect van methanol en aminen op de fotochemie van stilbenen, van 1,2- en 3,4-dihydrofenantreen en van 1-, 2-, 3- en 4-fenyl-1,2-dihydronaftaleen. Het betreft hier een uitbreiding van eerder onderzoek (J.J.M. Lamberts, Proefschrift: Nijmegen, 1982 en J.B.M. Somers, Proefschrift: Nijmegen, 1984) naar de fotochemie van deze verbindingen.

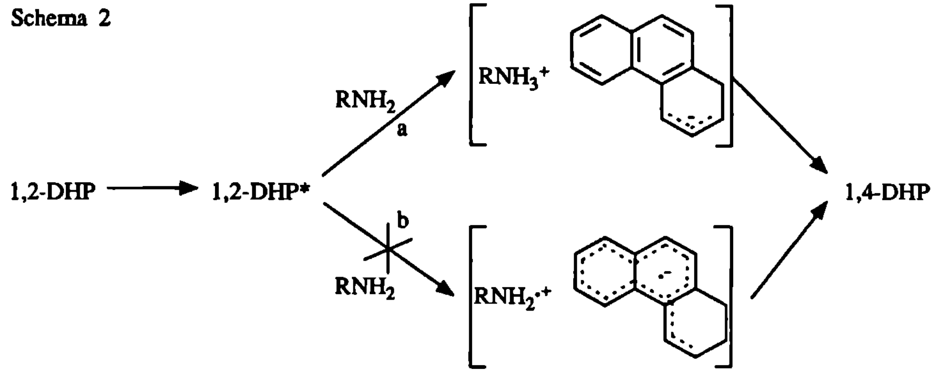
De fotochemie van stilbeen en een aantal, op aromatische posities gesubstitueerde stilbeen derivaten is beschreven in Hoofdstuk 1. Onder strikt anaerobe bestralingscondities blijkt deze klasse van verbindingen een nog niet eerder gerapporteerde fotoreactie te ondergaan, nl. additie van methanol aan de olefinische binding. Asymmetrisch gesubstitueerde stilbenen ondergaan deze reactie met een in de regel hoge regioselectiviteit, waarbij de methoxy substituent op het meest positief geladen C-atoom wordt ingevoerd. Uit de resultaten van bestralingen in CH_3OD, blijkt dat voor stilbeen zelf, de reactie *via* twee competetive routes verloopt (Schema 1), nl. (*i*) door rechtstreekse additie van MeOH aan de olefinische binding en (*ii*) door methanol additie aan een, *via* een fotochemische 1,2-waterstof verhuizing uit stilbeen gevormd carbeen intermediair. De gevonden effecten van subtituenten en van de golflengte op de competitie suggereren, dat in beide gevallen de reactie *via* een apolaire, laagste aangeslagen ^1D singulettoestand van stilbeen verloopt.



Schema 1

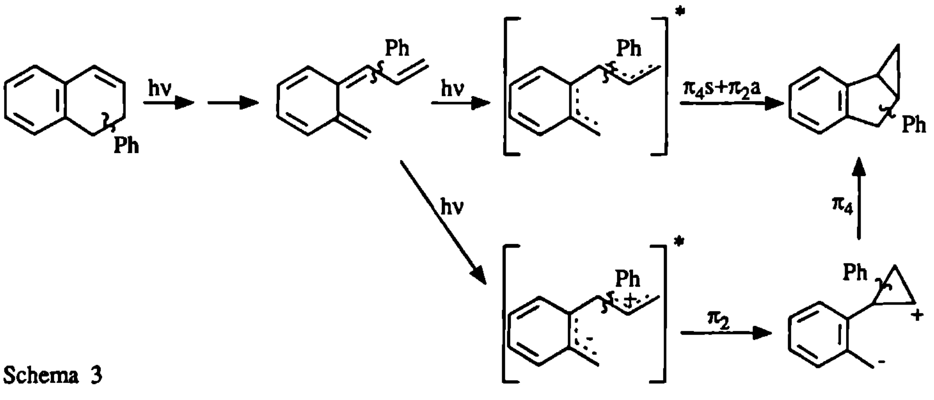
Het onderzoek naar het mechanisme van de door aminen bevorderde fotochemische 1,3-waterstof verhuizing in 1,2- en 3,4-dihydrofenantreen (resp. 1,2- en 3,4-DHP) tot 1,4-DHP is beschreven in Hoofdstuk 3. Uit het gevonden, lineair verband tussen de kwantumopbrengst van deze reactie en de basesterkte van primaire aminen, volgt, dat in deze aminen de reactie *via* deprotonering van het aangeslagen 1,2- of 3,4-DHP verloopt (Schema 2, route a). Op grond van de resultaten van tijdsopgeloste UV/VIS en fluorescentie spectroscopie en van bestralingen van 1,2- en 3,4-DHP in cyclopropylamine kan een radicaal mechanisme (Schema 2, route b) worden

Schema 2



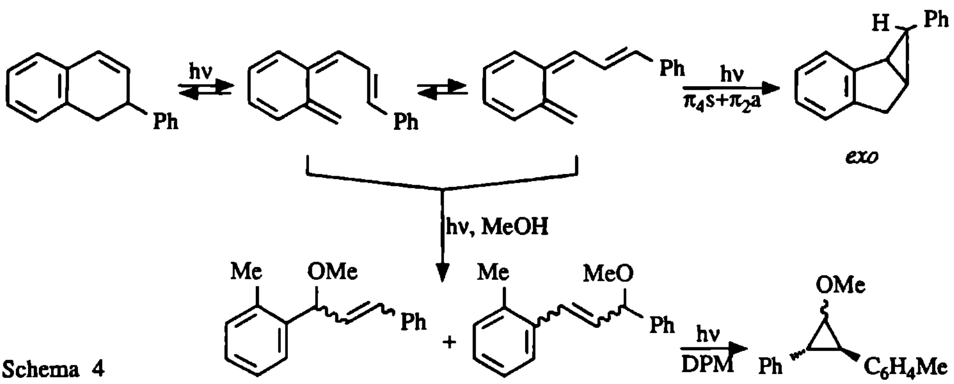
uitgesloten. Bij bestraling in triethylamine verloopt de reactie in slechte kwantum- en chemische opbrengst, onder vorming van vnl. polymere bijprodukten. Laastgenoemde fotoprodukten worden verondersteld afkomstig te zijn van radicaal reacties (Scheme 2, route b). Wordt de bestraling daarentegen uitgevoerd in mengsels van triethylamine en alkoholen, dan wordt 1,4-DHP, evenals in primaire aminen, in goede kwantum en chemische opbrengst *via* route a in Schema 2 verkregen.

Doel van het in Hoofdstuk 4 t/m 7 beschreven onderzoek naar de fotochemie van de phenyl-gesubstitueerde dihydronaftalenen in methanol betrof de vraag, in hoeverre zwitterionische aangeslagen toestanden (z.g. "sudden-polarized, excited states", Schema 3) betrokken zijn bij de



Schema 3

vorming van fenylbenzobicyclo[3.1.0]hex-2-een derivaten en overige fotoproducten uit deze verbindingen. Pogingen, dergelijke zwitterionische aangeslagen toestanden met methanol en een daarin opgelost sterk zuur (H_2SO_4) af te vangen hadden een negatief resultaat. Bij bestraling van zowel 1-, 2-, als 4-fenyl-1,2-dihydronaftaleen in methanol blijken aard en vormingssnelheid van

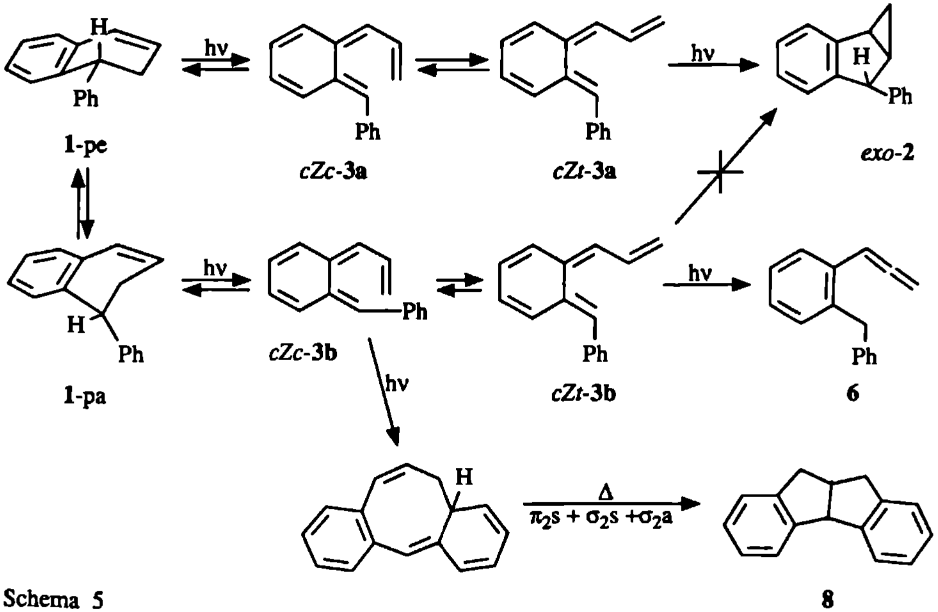


Schema 4

de primaire fotoprodukten niet noemenswaardig te worden beinvloed door de aanwezigheid van H_2SO_4. Dit gegeven suggereert dat, m.b.t. de genoemde dihydronaftalenen, het in Schema 3 aangegeven type zwitterionische aangeslagen toestand niet betrokken is bij de fotoproduktvorming.

Hoewel bij bestraling van 2-fenyl-1,2-dihydronaftaleen in methanol (Hoofdstuk 7) de op grond van Schema 3 te verwachten cyclopropaan derivaten ontstaan, blijkt de vorming van deze verbindingen via een secundaire foto-di-π-methaan (DPM) omlegging te verlopen (Schema 4).

In het geval van 1-fenyl-1,2-dihydronaftaleen (Hoofdstuk 4) lijkt de vorming van de



Schema 5

fotoprodukten te worden bepaald door de verhouding van de conformeren 1-pe en 1-pa in de grondtoestand (Schema 5): Gaande van hexaan naar methanol als oplosmiddel blijkt de verandering in de verhouding van de conformeren 1-pe en 1-pa gecorreleerd te zijn aan de waargenomen verandering in de verhouding van de fotoprodukten *exo*-**2** en **8** (Schema 5). Dit wijst erop dat de vorming van *exo*-**2** en **8** plaatsvindt vanuit resp. de 1-pe en de 1-pa conformeer (Schema 5). Bicyclohexeen *exo*-**2** zou in dit geval voornamelijk worden gevormd *via* een symmetrie-verboden intramoleculaire $\pi_4s+\pi_2a$ fotocycloadditie.

Bij bestraling van 1- en 4-fenyl-1,2-dihydronaftaleen in methanol werd, naast bekende fotoprodukten, in beide gevallen een alleen derivaat en methanol additie produkten gevonden. De vorming van alleen kan worden verklaard m.b.v. een fotochemische 1,5-waterstof verhuizing vanuit de pentaeen intermediaren (zie Schema 5, verbinding **6**). De vorming van de methanol additie produkten verloopt niet *via* een sudden-polarized aangeslagen toestand.

Verder is onderzoek verricht naar de aard van de in hexaan waargenomen fotostabiliteit van 3-fenyl-1,2-dihydronaftaleen (Hoofdstuk 5). Hiertoe is het gedrag van deze verbinding, alsmede dat van een aantal derivaten, bij bestraling in methanol en hexaan onderzocht. Uit dit onderzoek blijkt dat 3-fenyl-1,2-dihydronaftaleen, evenals stilbeen, in zeer lage kwantumopbrengst, fotochemische additie van methanol aan de olefinische binding ondergaat. De voor 1,2-dihydronaftalenen gebruikelijke fotochemische ring opening en vorming van benzobicyclo[3.1.0]hex-2-een derivaten (Schema's 3-5) treedt echter niet op. Uit de waargenomen fotochemie en de gemeten waarden voor het fotoacoustisch effect en de Stokes shift volgt, dat de fotostabiliteit van 3-fenyl-1,2-dihydronaftaleen en zijn derivaten een intrinsieke eigenschap van deze verbindingen is; vermoedelijk de consequentie van een efficient stralingloos vervalproces vanuit de laagste aangeslagen singulettoestand. De additie van methanol aan 4-alkyl gesubstitueerd 3-fenyl-1,2-dihydronaftaleen verloopt met een hoge stereoselectiviteit. Het mechanisme van deze reaktie is bediscussieerd.

Curriculum vitae

De auteur van dit proefschrift werd geboren in Rheden op 27 april 1956. Na het behalen van het diploma atheneum B aan het Christelijk Lyceum Arnhem in 1974, werd in hetzelfde jaar begonnen met de scheikundestudie aan de Katholieke Universiteit te Nijmegen. Het kandidaatsexamen werd afgelegd in december 1977. De doctoraalstudie omvatte als eerste hoofdrichting Organische Chemie (Prof. Dr. W.H. Laarhoven) en als tweede hoofdrichting Molecuulspectroscopie (Prof. Dr. W.S. Veeman en Prof. E. De Boer). Voor het in het kader van de tweede hoofdrichting verrichte onderzoek naar de laagste aangeslagen triplettoestand van 4,4′-dijoodbenzofenon werd hem in 1980 de faculteitsprijs toegekend. Het doctoraalexamen werd *cum laude* afgelegd in maart 1981.

Van 1 april 1981 tot 1 november 1984 was hij als research scientist werkzaam aan het Koninklijke Shell/Laboratorium Amsterdam, waar zowel praktisch als theoretisch onderzoek aan TiO_2-katalysatoren voor het styreen-monomeer propyleen oxide proces werd verricht (Prof. Dr. W.M.H. Sachtler). Van 1 november 1984 tot 1 november 1988 was hij, in dienst van SON/NWO, als wetenschappelijk medewerker verbonden aan het Laboratorium voor Organische Chemie van de Katholieke Universiteit te Nijmegen, waar hij onder leiding van Prof. Dr. W.H. Laarhoven het in dit proefschrift beschreven onderzoek heeft verricht.

Dankzij financiele steun van SON/NWO werd hij in staat gesteld deel te nemen aan het XI IUPAC Symposium on Photochemistry te Lissabon en aan de EPA Summer School on Photochemistry te Noordwijk, beide in 1986.

Stellingen.

1. Voor beheerders van computersystemen verdient het aanbeveling Nederlands als taal te gebruiken in de communicatie met computergebruikers.

   Brief C & CZ aan computergebruikers, dd. 11 oktober 1988.

2. De door Baldry gepostuleerde protonering van aangeslagen 1-fenyl-1,3-butadieen is niet in overeenstemming met de door hem waargenomen afwezigheid van een effect van toegevoegd zwavelzuur op de opbrengst van de primaire fotoprodukten uit deze verbinding.

   Baldry, P.J. *J. Chem. Soc. Perkin Trans. II* **1980** 809.

3. In tegenstelling met de tot dusverre gepubliceerde onderzoeksresultaten, lijkt de aanwezigheid van een alkyl substituent op het B-atoom geen belemmering te vormen voor het optreden van fotocyclisering en oxidatie (I_2) in B=N analoga van *cis*-stilbeen.

   Grisdale, P.J., Glogowski, M.E., Williams, J.L.R., *J. Org. Chem.* **1971** *36* 3821. Hancock, K.G., Dickinson, D.A. *J. Am. Chem. Soc.* **1973** *95* 280. Müller, K.D. Niedenzu, K. *Inorg. Chim. Acta* **1977** *25* L53. Glogowski, M.E., Williams, J.L.R. *J. Organomet. Chem.* **1980** *195* 123.

4. De door fabrikanten van subwoofer luidsprekersystemen geopperde veronderstelling, dat bas-grondtonen met frekwenties beneden *ca.* 200 Hz zeer moeilijk of in het geheel niet te lokaliseren zouden zijn, is gebaseerd op subjectieve maatstaven en derhalve onjuist.

   Zie bijvoorbeeld: Prospectus Bose Nederland B.V. (1988) p. 35 en 40.

5. Voor het globaal evalueren van de audioprestaties van transistor-eindversterkers op grond van gemeten elektrische specifikaties, vormen de impedantieafhankelijkheid van het uitgangsvermogen en de grootte en frekwentieafhankelijkheid van de dempingsfactor de meest relevante beoordelingskriteria.

6. Bij diskussies over de ethische restrikties t.a.v. de toelaatbaarheid van genetische manipulatie wordt voorbij gegaan aan het feit dat beperking ervan tot plantaardig materiaal op rationele gronden verdedigbaar is.

   Van Kleef, B. *De Achtste Scheppingsdag*, De Volkskrant, 2 april 1988, p. 27. Zie ook: Dessaur C.I. *De Achtste Scheppingsdag*, Gouda Quint: Arnhem, 12 oktober 1988.

7. De door het Ministerie van Onderwijs en Wetenschappen voorgestelde regeling voor vervroegde terugbetaling van bij het Rijk opgebouwde studieschulden getuigt van een inconsistent financieel beleid, zowel op korte als op lange termijn.

8. Voor de door Klett en Johnson gegeven conclusie, dat bij de fotochemische additie van methanol aan trifenylalleen geen, *via* een fotochemische 1,2-waterstofverhuizing gevormd carbeen intermediair betrokken zou zijn, is het experimenteel bewijs niet geleverd.

   Klett, M.W., Johnson, R.P. *Tetrahedron Lett.* **1983** *24* 1107, 2527.

J. Woning

Nijmegen, 24 november 1988