Papers

Synthesis and properties of photochromic furofurans

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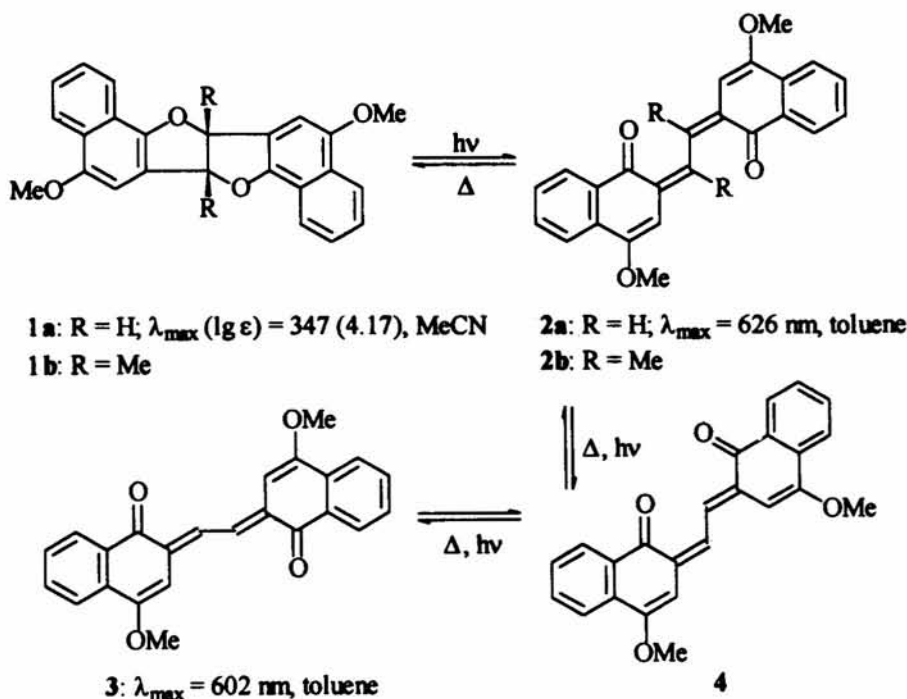
The deep blue-violet bis-*o*-quinonemethide 3 cyclizes thermally in a [4$_s$+4$_a$]cycloaddition reaction, yielding the colourless [3,2- *b*]furofurane 1a. The latter is re-opened by irradiation with UV light back to the methide in its Z,Z- configuration 2a. By metallation of 1a, the highly photoreactive acetylene 8a is obtained which again forms a methide under irradiation, but now in its E,E-configuration 3. The properties of this unique new photochromic system and related furofurans and alkynes have been investigated.

The colourless, stable *cis*-6b,13b-dihydro-5,12-dimethoxynaphtho [2′,1′:4,5] furo [3,2-b] naphtho [2′,1′:4,5]furan (1a) isomerizes in most solvents under UV light ($\Phi = 0.025$ in cyclohexane) or on heating in DMSO *via* 2a rapidly to the deep blue-violet *trans,trans*-bisquinone methide 3. The well characterized 3 formed in this way re-cyclizes thermally under formation of 1a[1]. Both compounds form a novel photochromic system, which might gain technical applicability for optical data storage or photographic image processes, if the influence of the structure on the photochromic behaviour and the

mechanism is predictable and tunable. It belongs to the group of valence isomerizations and is related to the spirobipyranes and the fulgides[2], but photochromism had not been observed in 1-type systems earlier.

As 1a is colourless and 2a/3 are blue-violet, the kinetic parameters of the cyclization can be determined simply by measuring the decolourization rate of the methide at various temperatures: Both methide isomers 2a and 3 cyclize by a first order kinetics back to 1a.

1a: R = H; λ_{max} (lg ε) = 347 (4.17), MeCN   2a: R = H; λ_{max} = 626 nm, toluene
1b: R = Me   2b: R = Me

3: λ_{max} = 602 nm, toluene   4

As **3** has to isomerize to **2a** (*via* **4**) prior to cyclisation, the activation parameters of the **2a**→**1a** reaction (AE = 60.2 kJ/mol in toluene) describe the real cyclisation, but those of the **3**→**1a** reaction concern the **3**→**4** or the **4**→**2a** isomerisation (AE = 101.6 kJ/mol in toluene); in more polar solvents, the values are not lower by more than 1/3, thus excluding ionic transition states. The ground state energies of **2a/1a** and **3/1a** differ by $\Delta G° = -30$ and -25 kJ/mol (toluene) respectively, **1a** being the most stable isomer (see Fig. 1); **4** was not determined due to its low concentration.

The capability for photochromism is not easily predictable, but depends at least in part on thermodynamic stabilities. As furofuran/methide rearrangements may proceed thermally in both directions, a co-existence of both forms under equilibrium conditions is only possible if the ground state energies do not differ too much. As AM1 calculations and measurements show, this is fulfilled only in the naphthalene ($\Delta G°_{calc} = -28$ kJ, exp. value -30 kJ, see Fig. 1) and perhaps in the phenanthrene system ($\Delta G°_{calc} = -67$ kJ). In the benzene series, the furofuran again is the stable form, but the methide may be too unstable to exist ($\Delta G°_{calc} = -109$ kJ). Indeed, in solution the benzofurofurans did not form coloured methides on irradiation, and most efforts to synthesize benzoquinone methides of type **2a/3** have been unsuccessful; only by photo-rearrangement of **29b**, a transient blue coloration was obtained perhaps due to the methide. Oppositely, in the anthracene series, the methide **5** [$\lambda_{max} = 597$ nm (log ε 3.37, CCl_4)][3] was the stable isomer ($\Delta G°_{calc} = +70$ kJ), and on heating of **5** only traces of the corresponding furofuran were obtained. With furofurans of anthracenes and higher condensed systems, only a single photocycle should be possible therefore. These furofuranes could be used only for irreversible photographic imaging processes.

In spite of suitable ground state energy differences, some dinaphthofurofurans (e.g. **17,18**) did not show photochromisms, and additional reasons must be responsible for this behaviour. The thermal cyclisation of the corresponding bis-methide can be treated as a [4s+4a]cycloaddition of two independent heterobutadienes, and HOMO/LUMO considerations should be allowed. As a result of our experiments and PM3-calculations, thermal cyclisation of methides seems to be restricted to systems where the sum of coefficient squares of the reacting atom pairs
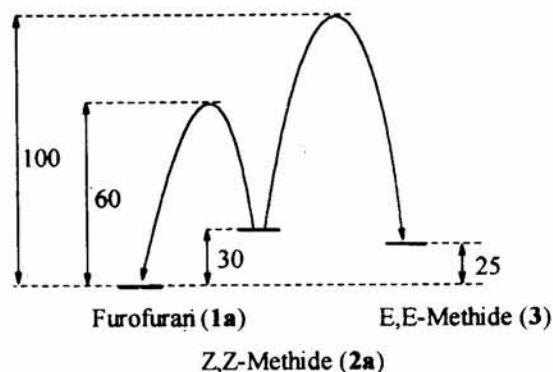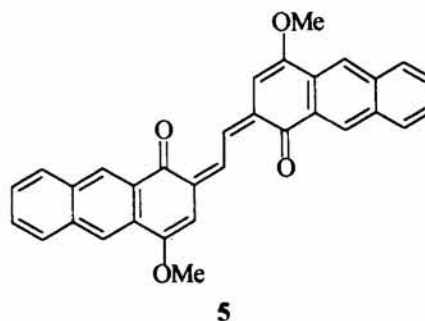

Fig. 1 —Experimental ground state free energy differences and activation energies for the furan/methide rearrangement in toluene; energy values in kJ/mol


5

in the bis-methide is $c^2 (LUMO_{01}) + c^2 (HOMO_{C4'}) \geq 0.11$. This was fulfilled only with one of our benzene derivatives (from 2-*tert.*-butyl-4-methoxyphenol) and certain naphthalenes and phenanthrenes. Corresponding methides of all photostable furofurans (e.g. **1b**, $\Sigma = 0.075$; **17**, $\Sigma = 0.113$; **18**, $\Sigma = 0.088$) showed much lower sums.

In the naphthalene system, the photochemical and acid-catalyzed formation of phenolic side products as **7** reduced the number of photochromic cycles greatly. This unwanted side reaction may be explained as [1,5]hydrogen shift yielding **6**, and a subsequent [1,4]addition, starting from the dimeric methide in a *cis*- configuration **2a**.

A stabilisation against such a rearrangement seemed to be possible by bridgehead substitution of furofurans with alkyl groups. But metallation of **1a** (or **7**) and treatment with methyl iodide yielded solely the dinaphthylalkyne **8b**, and without the iodide, the dihydroxyalkyne **8a** was obtained in high yield[4].

This reaction is related to the behaviour of certain simple furan derivatives[5] and might have been predictable; but it was very surprising that the alkyne was even much more photosensitive than the furofuran **1a**, giving exclusively the E,E-quinone methide **3** [$\Phi = 0.092$ (MeCN), 0.27 (cHex)]. This reaction is

2a   6   7

1a   8a
                                          8b: OMe instead of OH

9   10
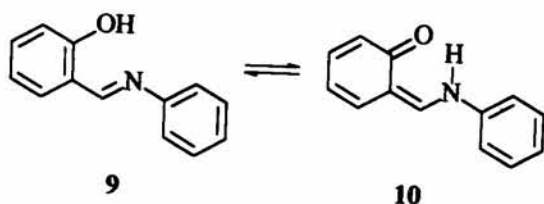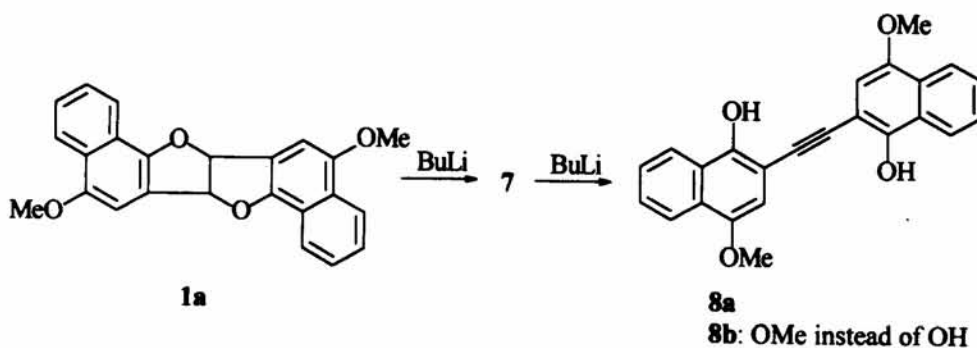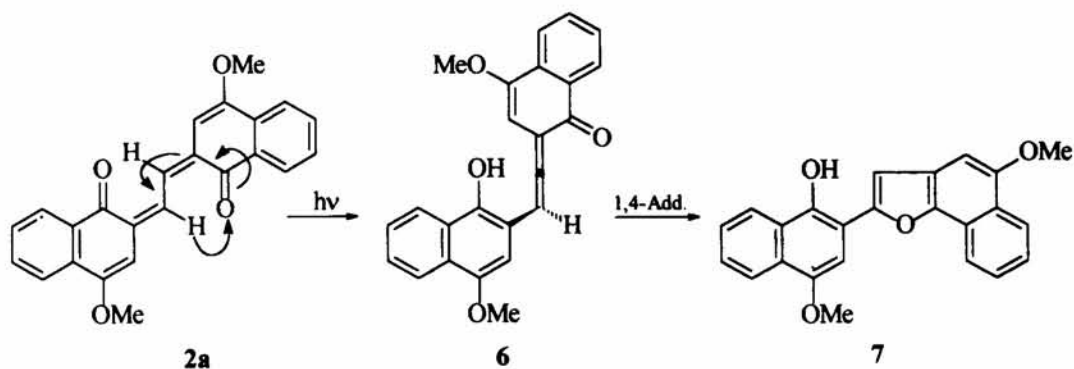
extremely quick even at temperatures of liquid nitrogen and is complete within less than 20 ns which excludes the possibility that (excited) **2a** or **4** are intermediates. Such a reaction was not known before in the acetylene series, but proceeds in a similar manner in salicyliden-anilides (**9**) which react photochemically[6] to anilino-*o*-quinone methides (**10**).
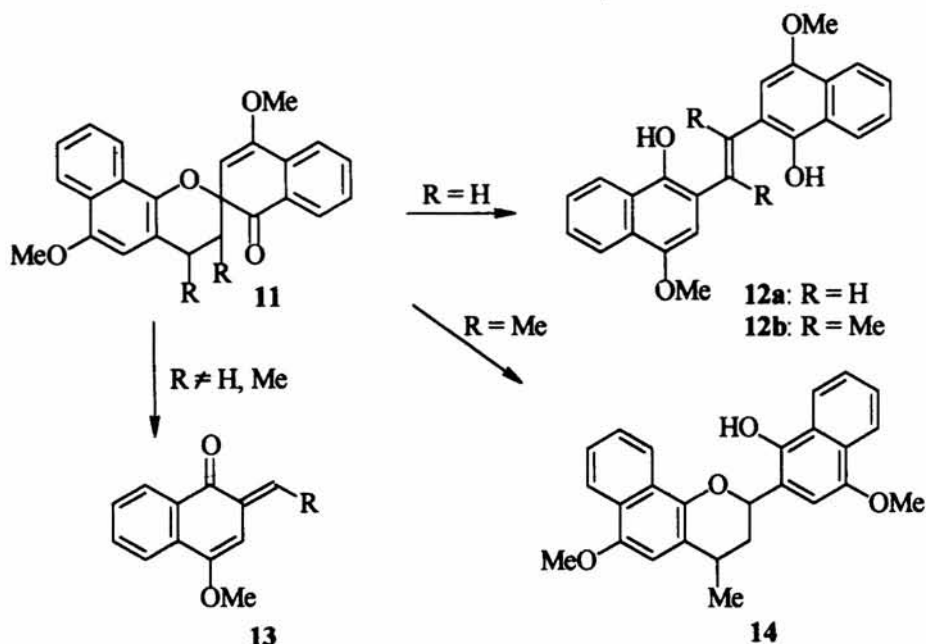
Syntheses

Although all the involved structures are very simple, some syntheses have been remarkably difficult or gave unexpected results: In the naphthalene series,

thermolysis of the spiroquinole ether **11** (R = H) gave the stilbene **12a** or the parent furofuran **1a** in high yield[1], but **11** (R = Me) delivered only **14**, and **11** (R = alkyl > Me) gave the monomeric methide **13**, as also did the corresponding benzene derivatives. Of other aromatic systems, only the anthracene derivative **5** was obtained in good yield by this way.

A more general access to the photoreactive system should be possible *via* three independent ways, i.e. the synthesis of (a) furofurans, (b) of *o,o'*-dihydroxyarylalkynes and (c) the generation of bismethides by oxidation of stilbenes. The latter should be accessible by catalytic reduction of tolane derivatives as **8a** with stoichiometric amounts of hydrogen, by Wittig or McMurry reactions, etc.
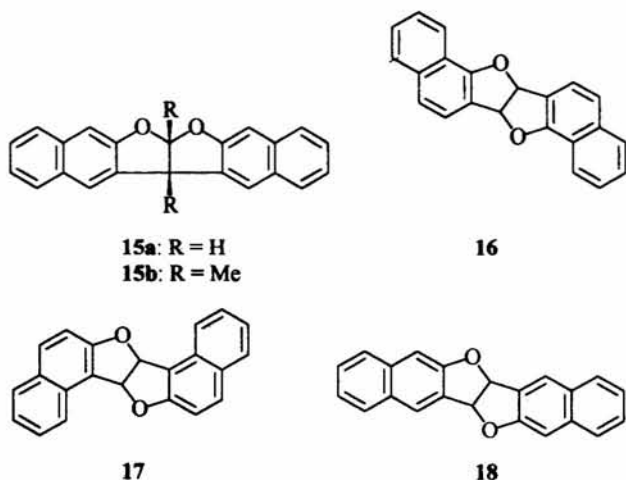
Synthesis of furofurans

Furofurans have been claimed to be obtained already in the last century by reductive coupling of

11

12a: R = H
12b: R = Me

13

14

15a: R = H
15b: R = Me

16

17

18

aromatic aldehydes with magnesium. Yet recent investigations have shown that in these reactions a pinacol rearrangement occurs forming predominantly acetal-type [2,3-b]furofurans 15a. The expected reaction proceeded, however, in some cases very smoothly when titanium(III) salts were used in aqueous solution[7]. Furo[3,2-b] furans have also been obtained by Claisen rearrangement of 1,4-diaryloxy-2-butynes[8].

We obtained the furofurans 16, 17 and 18 by reduction of the corresponding aldehydes, but acid-sensitive furofurans like 1a underwent a further ring-opening with the formation of 7-type phenols and were not accessible under these conditions. All benzaldehydes gave only benzofurans, and trials to obtain bridgehead-substituted benzene or naphthalene

derivatives by reduction of arylalkylketones failed as no (or different) reactions occurred.

Only 16 showed photochromism and turned purple red on irradiation; the furofurans 17 and 18 were stable in light and even did not rearrange forming ring-opened naphthofurans of type 7, as it was predicted by the values of their frontier orbital sum.

Furo[2,3-b] furans by double Dötz-Reaction

In a variation of the Dötz reaction developed by Semmelhack et al.[9], alkynes react with chromium carbene complexes leading to formation of annellated naphthalenes. Using a corresponding procedure starting from rac-diyn-dioles it should be possible to build also acid-sensitive furofurans in a one-pot reaction. In this way, a wide range of substitution patterns should be accessible; such a double Dötz reaction has not been reported before.

The sensitive rac-diyn-diols 19 were accessible by osmium-catalysed bishydroxylation of (E)-endiynes in moderate yield, but we were not able to perform this reaction with the chromium carbene.

Syntheses via stilbenes

Bridge-head substituted furofurans are of special interest, as substituents at the exocyclic double bonds of the isomeric quinone methide (type 2b) should have a substantial influence on the cis/trans isomerisation and hence on its thermal cyclisation. Additionally, they should stabilize the furofuran against protic ring opening.

19   **20**   **21**

22a: R = Bz
22b: R = p-Ts   **23**   **24**
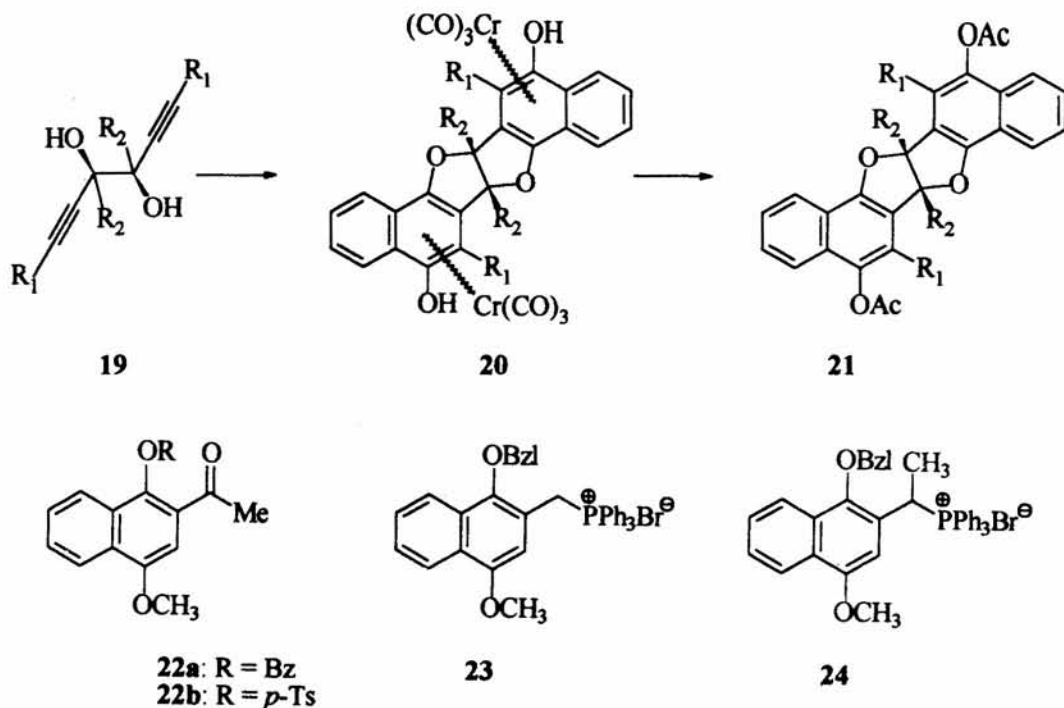
For their synthesis, we have used the McMurry reaction which is known to be very insensitive to steric hindrance. Reductive coupling of salicylaldehyde or o-hydroxyacetophenones to stilbenes was easy. But when we treated various naphthaldehydes and naphthophenones with low-valent titanium reagents, predominantly deoxygenated products were obtained[10]. On reductive coupling of **22b**, after hydrolytic work-up the desired dihydroxystilbene **12b** was not observed, but upon prolonged standing of the reaction mixture, the furofuran **1b** was formed, presumably *via* oxidation of **12b** and cyclization of the intermediate **2b**. The *cis*-fusion of the rings had been demonstrated for **1a** by NMR measurements previously, but now a direct proof by crystal structure analysis was possible (Fig.2).

All attempts to open the furofuran **1b** thermally or photochemically to the methide **2b** in analogy to the parent compound **1a**, were unsuccessful. This is difficult to explain on the basis of an antarafacial [4+4]cycloreversion, because PM3 calculations gave nearly identical results for the ground state differences of the thermochromic reactions **1a**→**2a** and **1b**→**2b**. It is explained easily, however, by the low frontier orbital sum of **2b** ($\Sigma = 0.075$).

As the formation of a phenol of type **7** is not possible, **1b** shows indeed a much higher stability against protolytic ring opening than **1a**. But on dis-
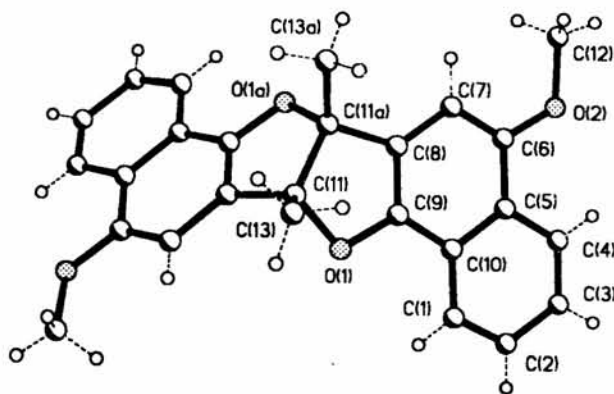

Fig. 2 —Crystal structure of *cis*-5, 12-dimethoxy-6b,13b- dimethyldinaphtho[3,2-*b*]furofuran (**1b**).

solving in trifluoroacetic acid, a slow but irreversible transformation into **15b** was observed. A similar behaviour of other furofurans could explain some irreproducible and contradictory results in the early literature which may reflect changing isomer ratios due to varying acidities during reductive coupling of e.g. salicylic aldehydes.

Similarly, stilbene syntheses using Wittig reactions have been easy in the benzene series. But again in the naphthalene series, the Wittig reaction failed

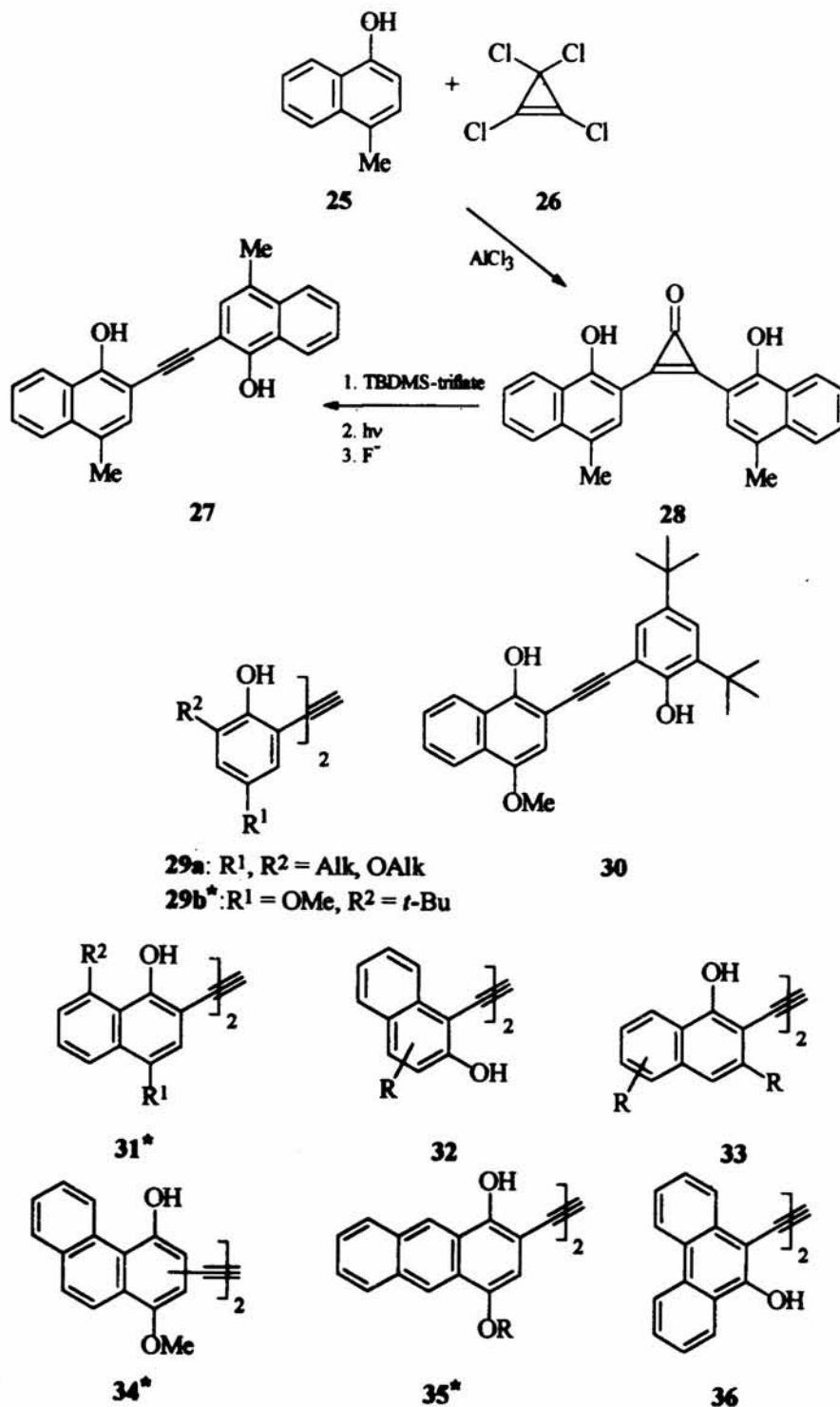due to a lack of reactivity (**22a** + **23**) or the instability of the phosphonium salts (e.g. **24**).

In the benzene series, the syntheses were successful, but none of the stilbene derivatives gave a coloured methide or a furofuran on oxidation; solely phenyl-benzofurans (type **7**) were obtained.

Diarylalkynes by Friedel-Crafts reactions

We have found it most convenient to synthesize o,o'-dihydroxyarylalkynes by reaction of phenol de-

rivatives with tetrachlorocyclopropene (**26**), and photolysis of the cyclopropenone (e.g. **28**) obtained thereby[11].

Using this sequence, a considerable number of benzene and naphthalene derivatives was accessible. Only one of the benzene derivatives tested (2,2'-(ethindiyl)bis(3-*tert.*- butyl-2-hydroxy-5-methoxy-benzene) turned blue on irradiation in solution, probably due to methide formation $[c^2 (LUMO_{01})+c^2 (HOMO_{C4'}) = 0.135]$. Phenyl-benzofurans were iso-

25   **26**

27   **28**

29a: R^1, R^2 = Alk, OAlk
29b*:R^1 = OMe, R^2 = *t*-Bu   **30**

31*   **32**   **33**

34*   **35***   **36**

lated with only one ring closed in all other cases. We got a colour reaction in the naphthalene system and co-existence of methide and furofuran form in some (indicated by an asterix), but no reaction in others cases. The same was true in the phenanthrene system where both **34** isomers were photoreactive (λ_{max} of the methides = 627, 653 mm), but **36** was not.

Donor substituents in *para*-position to the methide carbonyl enhanced the stability of the methides and gave rise to a bathochromic shift, and correspondingly the 4-methyl derivative **27** gave a less stable red-violet methide than alkyne **8a**, as also the 4-chlo-

ronaphthyl alkyne **27** (Cl instead of Me) did on irradiation.

Alkyne-methide rearrangement

We have interpreted this photoreaction as a double thermally allowed [1,5]hydrogen shift which occurs in the following way: On irradiation, the stiff rod-like acetylene reaches the excited state S_1 which should have a *trans*-alkene structure (calcd. naphthalene-alkyne-naphthalene bond angle = 129.8° for **29b**, $R^1 = R^2 = Me$) if diarylalkynes behave similar to unsubstituted acetylene[12] itself. But contrary to the experi-
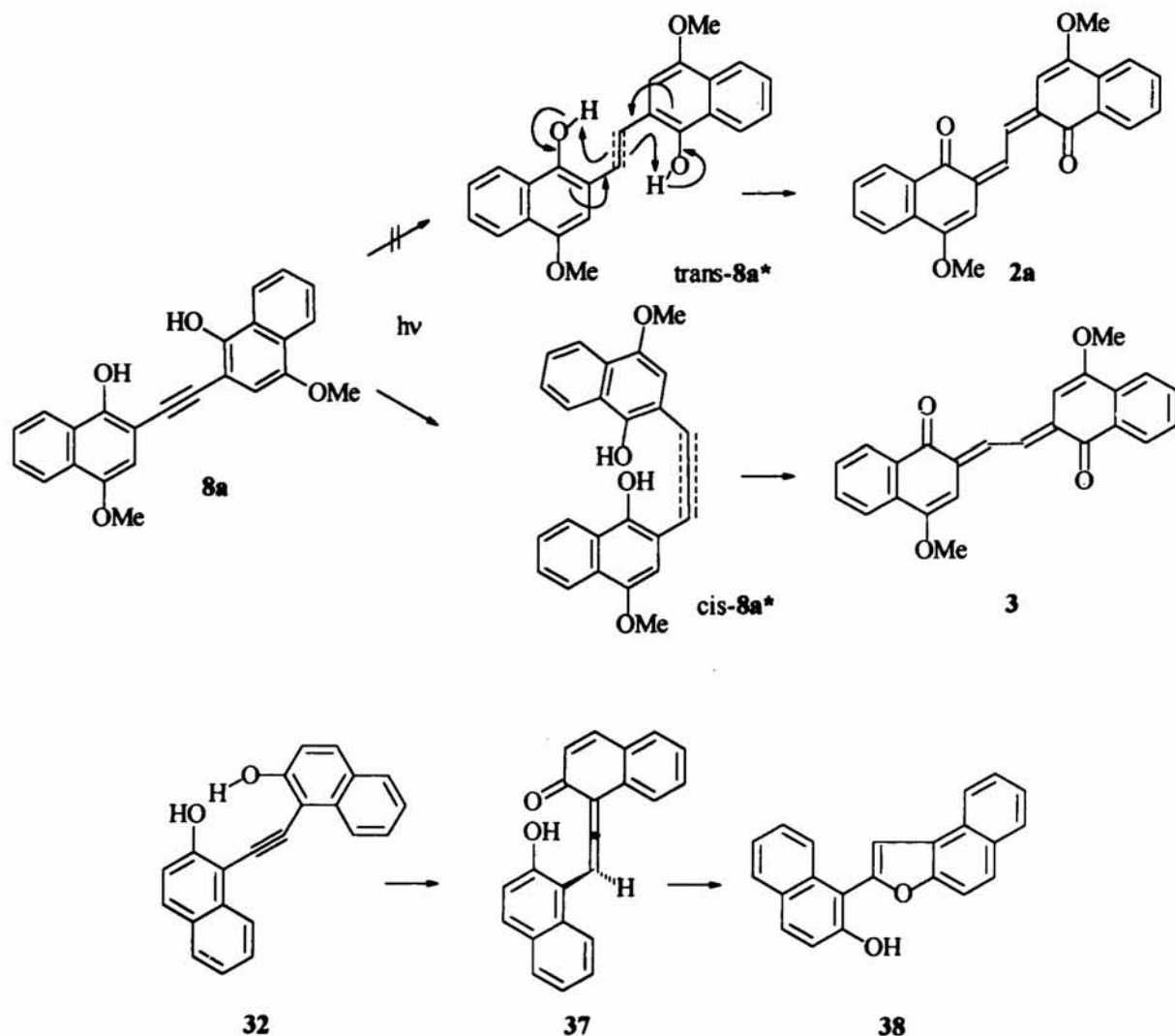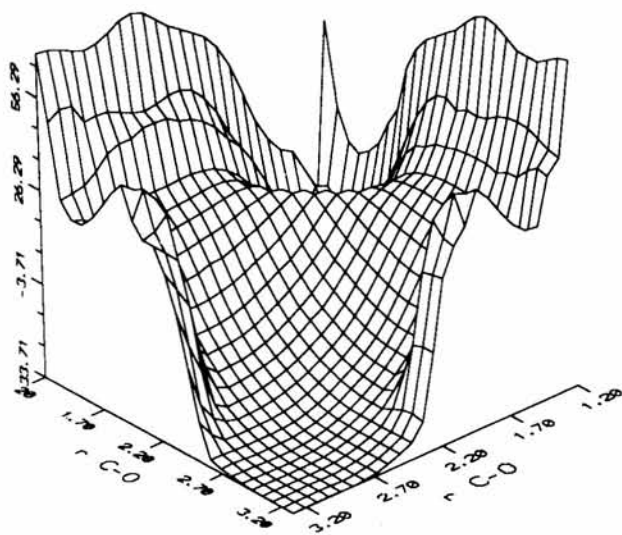
Fig. 3—PM3-Hyper space of the thermal isomerisation of Z,Z- hexa-2,4-diendial to 3a,6a-dihydrofuro[3,2-*b*]furan as a model system of **1a/2a**

mental result, in this case the Z,Z-methide **2a** should be expected.

Only one of the benzene derivatives (**29b**) showed methide formation in solution, and the alkynes **32**, **33** and **36** gave only phenols of type **7**. Besides electronic factors, steric interactions also seem to influence the photochemical behaviour of the *o,o'*-dihydroxydiarylalkynes and therefore the stability of their photo products. As the crystal structure shows, hydrogen bridges are fixing the acetylene **32** (R = H) even in the ground state in a bent "*cis*"-conformation. This seems to be the case in solution also, as **32** and all other o,o'- dihydroxydiarylalkynes show signals of chelated OH groups in the NMR spectra at $\delta \approx 6.3$.

Starting with such a geometry, a *concerted* double [1,5]hydrogen shift cannot yield the Z,Z-methide, but must end up with the E,E- configuration, as it was
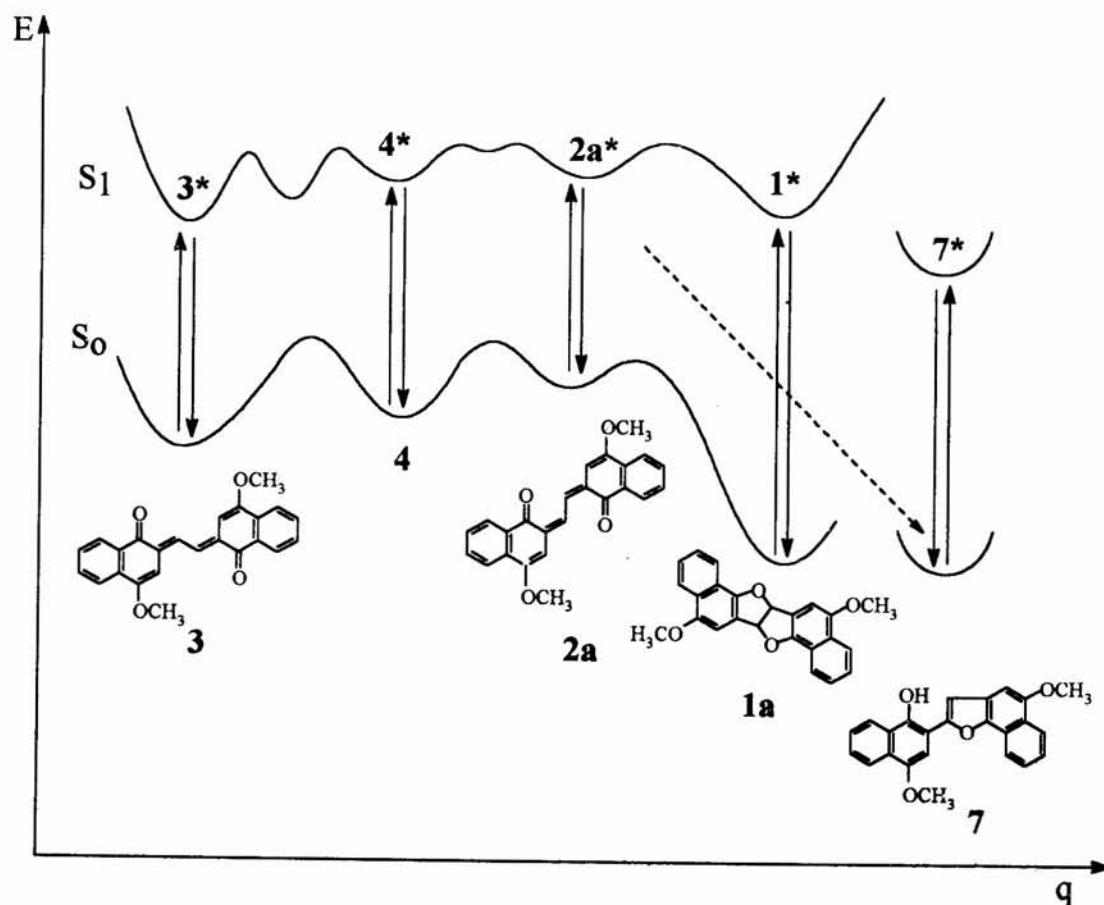

Fig. 4—Jablonski-diagram of the **3** → **1a** cyclization for ground state and excited state; arrows upwards = absorption, downwards = fluorescence.

found experimentally. But a unsymmetrically distorted triple bond as in **32** may give rise to a two-step mechanism: After the first [1,5]-H shift to **37**, a subsequent 1,4-addition reaction yielding **38** presumably is more effective than the formation of the methide by a second [1,5]-H shift. Hydrogen bridges between 1-OH and 8-OR prevented also the photo reaction of **31** (R^2 = OH, OAlk), whereas the 5-OR isomer gave the methide.

Hyper spaces and transition states

Radicals as intermediates of the photochemical methide rearrangement have been excluded on the basis of ESR experiments and ionic states on the basis of the low solvent dependency of the kinetic parameters. The identification of the short-living Z,Z-methide **2a** and also its E,Z-isomer in the rearrangement of **1a** supports the formulation of the thermal cyclisation of **2a** to **1a** as a thermally allowed antarafacial [4_s+4_a] reaction. Corresponding to AM1 and PM3 calculations on model systems and on **1a/2a**, a concerted cyclisation should predominate, but the energy difference to a non-concerted reaction is only 1 kcal/mol (Fig. 3).

Results of experiments and *semi*empirical calculations of ground states and the excited state have led to an understanding of the **1a** $\rightarrow$ **3** isomerization as depicted in Fig. 4. The ground state profile was determined experimentally by thermodynamic and kinetic measurements (see Fig. 1). As **1a** (at -196 °C) and **3** show fluorescence, in the S_1 state, their minima should be opposite to the ground state minima with energy differences corresponding to their fluores-

cence wavelength. For **2a***, the minimum was calculated. Also other results of *semi*empirical calculations are in good agreement with this model but indicate that higher excited states may also be involved in the photo processes.

Acknowledgement

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