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RESEARCH REPORT

3,3,4,4,5,5-HEXAMETHYL-1,2-BIS(METHYLENE)CYCLOPENTANE: A NOVEL PROBE FOR THE STUDY OF CYCLOADDITION MECHANISMS (*)

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Summary — 3,3,4,4,5,5-hexamethyl-1,2-bis(methylene)cyclopentane, **1**, which is readily accessible *via* electrophilic acylation and alkylation reactions, incorporates a planar *s-cis*-fixed 1,3-diene system, the non-terminal positions of which are sterically shielded. Therefore, compound **1** shows a relatively great tendency to undergo 1,4-additions instead of 1,2-additions. With dihalocarbenes, a 1,2 over 1,4 adduct ratio of only 2.3-2.7 is observed, and diphenylketene undergoes (4+2)-cycloadditions across the CC- and the CO- double bond. Thermal, non-catalysed dimerisation of **1** gives a mixture of [4+2]- and [4+4]-cyclodimer, both products arising through intermediate diradicals. The reaction of **1** with 1,3-diphenylazallyllithium affords the [4+3]-cycloadduct **12** as the main product. Benzonitrile oxide and **1** combine with formation of the regular [3+2]-cycloadduct **15** and the oxime **16**, which are explained through intermediate diradicals. C,N-Diphenylnitrone reacts with **1** and other 1,3-dienes to give the ordinary [3+2]-cycloadducts (*e.g.* **21**, **22**) as well as the [4+3]-cycloadducts **26** and **29-31**, again indicating the intermediacy of diradicals. Possibilities to use **1** as a probe for concertedness are discussed.

INTRODUCTION

Addition reactions to 1,3-dienes can lead to the formation of 1,2- and/or 1,4-adducts (scheme 1)[1].

SCHEME 1

SCHEME 2 - 1,3-DIENES USUALLY GIVE 1,2-ADDUCTS WITH CARBENES, KETENES, ALLYL ANIONS, 1,3-DIPOLES AND 1,3-DIENES
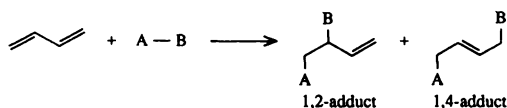
If A-B represents a cycloaddition partner, one of the two reaction modes is usually highly preferred. Dienophiles, for instance, like maleic anhydride, acrylates, etc., undergo 1,4-additions and lead to the formation of cyclohexenes (Diels-Alder reaction)[2]. Carbenes, ketenes, allyl and azallyl anions as well as 1,3-dipoles and related reactants generally add to a $\pi 2$ unit of the 1,3-diene[3], thus exhibiting a strong preference for 1,2-addition (scheme 2). While 1,4-additions of carbenes and ketenes are orbital symmetry allowed processes, the corresponding reactions of allyl anions, 1,3-dipoles, and 1,3-dienes represent ($_\pi 4_s + _\pi 4_s$) processes, and are therefore thermally forbidden reactions[3].

Assuming that less than 0.5% of side products are not usually detected during conventional product analyses, the failure to observe 1,4-adducts in reactions of 1,3-dienes with the cycloaddition partners shown in scheme 2 indicates the activation energies for the 1,4-additions to be at least 3 kcal

mol^{-1} higher than those of the observable 1,2-additions. It is of theoretical interest to learn whether the barrier for the elusive 1,4-additions is just slightly greater ($\sim$3-5 kcal mol^{-1}) than that for the observed 1,2-additions or whether there is a huge difference between the activation energies of the two processes (scheme 3).

SCHEME 3 - HOW BAD ARE 1,4-ADDITIONS? WHAT IS THE BARRIER FOR 1,4-ADDITIONS?
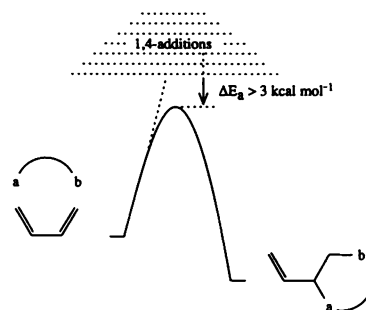
(*) Dedicated to Professor Jürgen Sauer on the occasion of his 60th birthday. Lecture presented at the VI Conference on Practice and Theory of Pericyclic Reactions, Firenze, Italy, May 24-25, 1990.

(°) To whom correspondence should be addressed.

There are two ways to improve the chance of observing 1,4-additions: One can either make the 1,4-additions more attractive by fixing the 1,3-diene in an s-cis conformation, or one can retard the 1,2-additions by attaching bulky substituents at C-2 and C-3 of the 1,3-diene (scheme 4).

SCHEME 4

1,4-additions are favoured in s-cis-fixed dienes

endocyclic   exocyclic
n = 1,2   n = 1,2,3
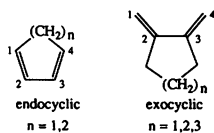
1,2-additions are retarded by bulky groups in 2- and 3-position
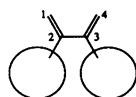
The title compound 1 incorporates both features, and is, therefore, an ideal candidate for 1,4-additions (scheme 5).

SCHEME 5

Facile approach possible ($_\pi$4)

Sterically hindered ($_\pi$2)
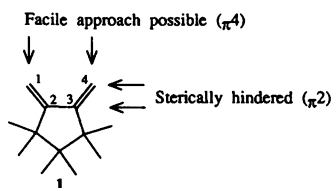
SYNTHESIS AND PROPERTIES OF THE TITLE COMPOUND

Several years ago we have elaborated an efficient access to highly substituted cyclopentenes via [3$^+$+2]-cycloaddition reactions (scheme 6). Hexa- to octa-methyl-substituted cyclopentenes have been synthesised by the ZnCl$_2$-catalysed reaction of allyl chlorides with alkenes[4].

SCHEME 6 - CYCLOPENTYL CATIONS via [3$^+$+2]-CYCLOADDITIONS OF ALLYL CATIONS WITH ALKENES

This reaction type is the key-step in the synthetic sequence outlined in scheme 7, which is self-explanatory. Octamethylcyclopentene, 2, is the only intermediate of this sequence, which has been purified; it is obtained in 58% yield from acetyl chloride and trimethylethylene[5]. A less favourable access to the intermediate tetramethylallyl alcohol, which we had elaborated in the initial period of this project[4b], has recently been published by Lambert and Ziemnicka-Marchant[6]. Bromination of 2 does

not yield an addition product (sterically shielded double bond!), but with excess bromine at room temperature the bisallyl bromide 3 is generated selectively[7]. Treatment with magnesium yields the title compound 1 in 62% yield from 2[5].

SCHEME 7 - SYNTHESIS OF HEXAMETHYL-1,2-BIS(METHYLENE)CYCLO-PENTANE
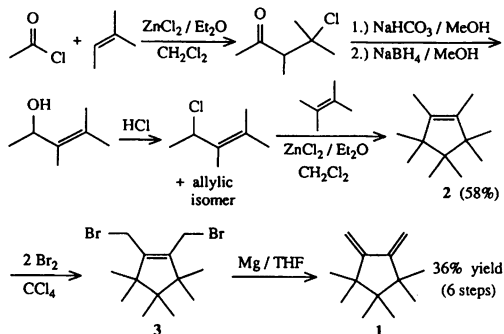
The structurally related 3,3,6,6-tetramethyl-1,2-bis(methylene)cyclohexane can be synthesised in only 3 steps by the sequence shown in scheme 8[8,9].

SCHEME 8
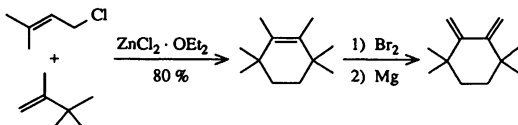
The spectroscopic properties of 1 are not abnormal. Its UV-maximum is almost identical to that of the non-methylated 1,2-bis(methylene)cyclopentane, and the slight lowering of the ionisation potential by the methyl groups can be attributed to CC-hyperconjugation (scheme 9)[10,11]. Analogous effects by branching in allylic position have been observed in the photoelectron spectra of acyclic alkenes[12].

SCHEME 9 - COMPARISON OF UV- AND PE-SPECTROSCOPIC DATA[10,11]

λ_{max}(nm)	250	246
IP$_{v,1}$(eV)	8.73	8.4

Neat 1 can be stored for months at <5 °C in a nitrogen atmosphere. When a drop of it is exposed to atmospheric oxygen at ambient temperature for 24 h, crystals grow out of the liquid which have been identified as an oligomeric peroxide with ¹H NMR singlets at δ 0.88, 1.10 and 4.72 ppm, and ¹³C NMR resonances at δ 21.27 (q), 24.72 (q), 46.69 (s), 49.45 (s), 67.83 (t) and 142.64 ppm (s)[9].

SCHEME 10
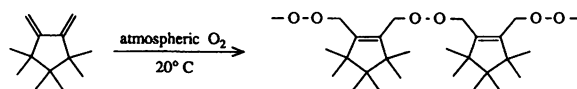
Compound **1** undergoes normal Diels-Alder reactions with dienophiles. The relative reactivities, given in scheme 11, show that the methyl groups in **1** exert only a small influence on the 1,4-reactivity of **1**[11].

SCHEME 11 - ATTACK TO THE TERMINAL METHYLENE GROUPS OF THE 1,3-DIENE IS ONLY SLIGHTLY AFFECTED BY THE METHYL SUBSTITUENTS
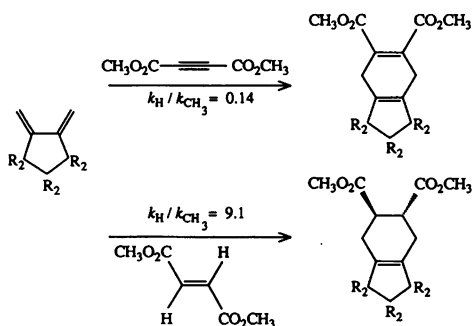
CARBENES

1,3-dienes usually react with singlet carbenes in a 1,2-fashion to give vinylcyclopropanes[13]. Homo-1,4-additions to norbornadiene[14] and intramolecular 1,4-additions in the synthesis of benzvalenes[15] are among the few cases, which show a different reactivity pattern. Bickelhaupt observed 1-3% of 1,4-adducts in reactions of dichlorocarbene to 1,2-bismethylenecycloalkanes (ring size 5-8) and 4-19% of 1,4-adducts in the corresponding reactions of dibromocarbene[16]. Scheme 12 shows that the ratio (1,4-/1,2-adducts) is considerably increased by adding methyl groups. Assuming the rate of the 1,4-additions to be unaffected by the methyl groups, one can derive that the methyl groups raise the barriers for the 1,2-additions by 1.5-1.7 kcal mol⁻¹, with the consequence that **1** gives the highest proportion of 1,4-adduct in intermolecular carbene additions reported up to now[17].

SCHEME 12 - COMPETING 1,2- AND 1,4-ADDITIONS OF CARBENES
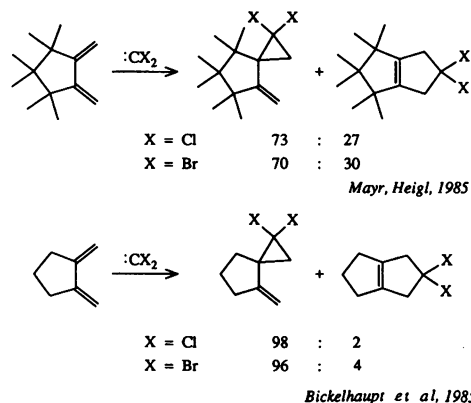
Lambert *et al.*[6] investigated the reaction of **1** with CBr_2 (from $PhHgCBr_3$) at different diene concentrations and found the product ratio to be independent of the concentration of **1**. This observation supports the assertion that the 1,4-adducts, like the 1,2-adducts, are produced *via* free carbenes. In accord with this conclusion, similar product ratios were observed when the dihalocarbenes were generated from $HCBr_3$. When 11,11-dibromo-1,6-methano[10]-annulene was used as a carbene precursor, **1** gave 57-65% of 1,4-adduct, indicating that now a complexed carbene was reacting (scheme 13)[6].

SCHEME 13
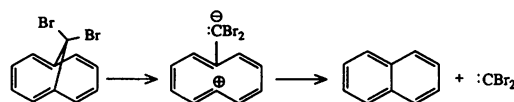
KETENES

Ketenes react with 1,3-dienes to give 3-vinylcyclobutanones[3,18]. Stepwise [4+2]-cycloaddition reactions across the C=O double bond take place when donor(alkoxy or trimethylsiloxy)-substituted 1,3-dienes are combined with alkyl-, aryl- or haloketenes[19], and when the electron-deficient bis(trifluoromethyl)ketene reacts with buta-1,3-diene[20]. Only in reactions with heterodienes (*e.g.* α,β-unsaturated ketones and imines), the CC-double bond of diphenylketene had been reported to act as a dienophile[21].

SCHEME 14
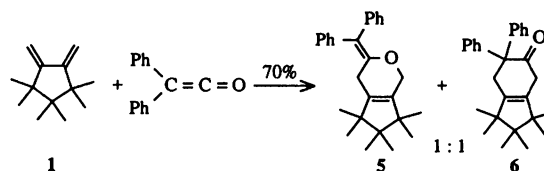
When **1** is combined with diphenylketene, the [4+2]-cycloadducts **5** and **6** are produced in a 1:1 ratio, and **6** represents the only cyclohexenone which has been formed in a Diels-Alder-reaction of a ketene[22]. Since cases with concomitant formation of vinylcyclobutanones and cyclohexenones are not known, and kinetic data for the reaction described in scheme 14 are not available either, the difference of the activation energies of [2+2]- and [4+2]-cycloadditions for reactions of ketenes with ordinary 1,3-dienes cannot yet be estimated.

[4+4]-CYCLODIMERISATION OF **1**

When **1** is heated at temperatures above 80 °C, dimerisation takes place with formation of the Diels-Alder dimer **8** and the [4+4]-cyclodimer **9**[23]. The product ratio shown in scheme 15 reflects kinetic control since both **8** and **9** have been found to be persistent at 150 °C. While **8** may be produced by a concerted process ($_\pi 4_s + _\pi 2_s$) or by cyclisation of an intermediate (*e.g.* **7**), orbital symmetry rules[3] require a stepwise mechanism to account for the formation of **9**.

SCHEME 15

Dimerization of the Diene 1 in Toluene
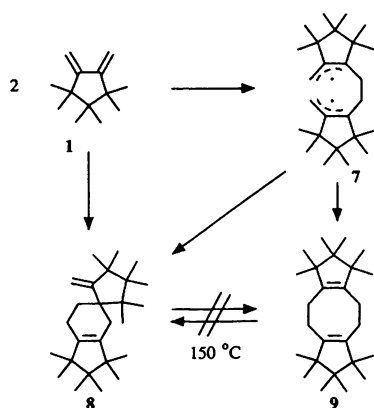
Temperature Effect on Product Ratio (1 bar)

T / °C	80	100	125	150
[8] / [9]	3.4	3.7	3.9	4.2

Pressure Effect on Product Ratio (79 °C)

p / bar	1	500	6000	9000
[8] / [9]	3.4	3.1	3.5	4.0

From the product ratio determined at different temperatures (scheme 15) one can calculate $\Delta S^{\neq}$ for the formation of **8** to be 5 entropy units less negative than $\Delta S^{\neq}$ for the formation of **9**. Since concerted processes are usually characterised by *more negative* activation entropies than analogous stepwise mechanisms[24], this finding is an argument for **8** being formed through an intermediate. From the influence of pressure on rate and product ratio, activation volumes of –15.8 (for **8**) and –15.5 cm^3 mol^{-1} (for **9**) have been determined. These values are to be compared with the reaction volume of –51.2 cm^3 mol^{-1} for the formation of **8**. Since in ordinary Diels-Alder-reactions, the activation volumes are closely similar to the reaction volumes[25], the strong discrepancy between $\Delta V^{\neq}$ and ΔV° indicates that **8** like **9** is produced by a stepwise pathway. In analogy to related studies[26], the diradical **7** appears to be a reasonable intermediate.

2-AZALLYL ANIONS

The 1,3-diphenylazallyl anion **10** has been reported to react with 1,3-butadiene and isoprene with exclusive formation of the 3-vinylpyrrolidine, **11**[27]. Analogous reactions with **10** have also been observed with several s-cis-fixed dienes (scheme 16)[28].

When the sterically hindered diene **1** was treated with 1,3-diphenylazallyllithium, **10**, compound **12** was the only cycloadduct isolated after hydrolysis[28]. Under certain conditions, **12** is accompanied by the acyclic adduct **13**, suggesting a stepwise process being responsible for the formation of **12**.

SCHEME 16

2-azallyl anions undergo [3⁻+2]-cycloadditions with butadiene and isoprene

Th. Kauffmann, 1971
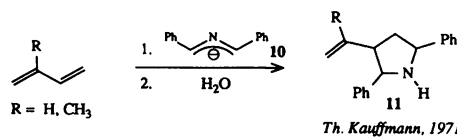
[3⁻+2]-cycloadditions also with s-cis-fixed dienes

But:
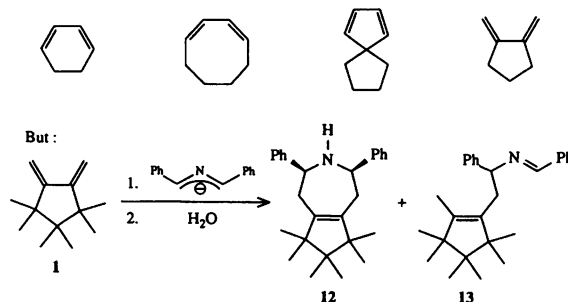
NITRILE OXIDES

Since 1,3-dipoles incorporate the 4 electron - 3 centre π-orbital characteristic for allyl anions, the isolation of **12** encouraged us also to look for [4+3]-cycloadducts with 1,3-dipoles. Nitrile oxides have first been selected, since their reaction with aryl-acetylenes has been known to yield isoxazoles and oximes concomitantly[29]. The intermediate formation of diradicals or zwitterions has been inferred from this observation[30,31].

SCHEME 17
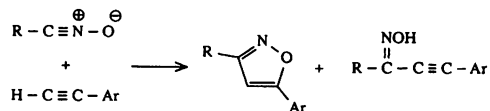
When benzonitrile oxide, **14**, was generated from benzohydroxamoyl chloride and trimethylamine in diethyl ether[31a] in the presence of diene **1**, the [3+2]-cycloadduct **15**, the oxime **16**, and the bisadducts **17** and **18** were produced[32]. Evidence for the formation of a [4+3]-cycloadduct has not been obtained. As indicated in scheme 18, treatment of **15** with benzonitrile oxide, **14**, affords **18** (not **17**), while **17** is produced from the reaction of **16** with **14**.

SCHEME 18
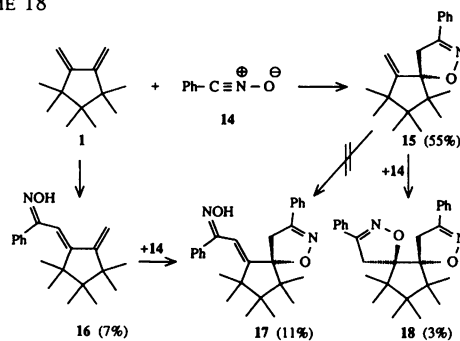
While the reactions of nitrile oxides with aromatic π-systems have previously been reported to yield small amounts of oximes[33], compounds **16** and **17** are the first oximes that have been produced from benzonitrile oxide **14** and a non-aromatic CC double-bonded dipolarophile. The analogous reaction of **14** with the non-methylated bismethylenecyclopentane **4** proceeds with exclusive formation of the regular 1,3-dipolar cycloaddition product **19** (scheme 19)[32].

SCHEME 19
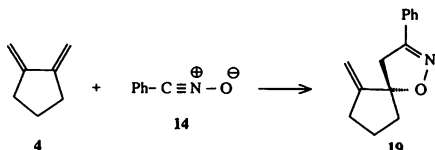
If one assumes the oxime **16** to be generated by intramolecular hydrogen abstraction in an intermediate diradical, the different behaviour of methylated and non-methylated bis(methylene)-cyclopentane (schemes 18 and 19) can be rationalised in two ways.

SCHEME 20

Assumption: oxime and [3+2]-cycloadduct are formed through an intermediate diradical.
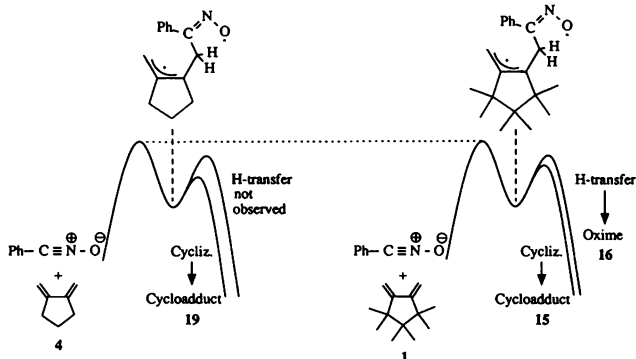
One assumption (scheme 20) is that both products, oxime and [3+2]-cycloadducts, are produced through intermediate diradicals. If the barrier for cyclisation is considerably lower than the barrier for hydrogen transfer in the non-methylated compound, the exclusive formation of the cycloadduct takes place (scheme 20, left). The methyl groups in **1** should increase the barrier for cyclisation, while the barrier for hydrogen transfer should hardly be affected. Thus, the activation energies for the competing reactions become similar, and a mixture of products is formed (scheme 20, right).

According to the second assumption (scheme 21) only the oxime **16** arises from a diradical, while a concerted cycloaddition mechanism accounts for the formation of the isoxazolines. Now, the exclusive formation of a cycloadduct (scheme 21, left) would be due to the fact that the activation energy for the concerted cycloaddition reaction is considerably lower than that for the formation of the diradical. Introduction of the methyl groups can now be

SCHEME 21

Assumption: oxime is formed *via* a diradical, isoxazoline is formed by a concerted cycloaddition pathway.
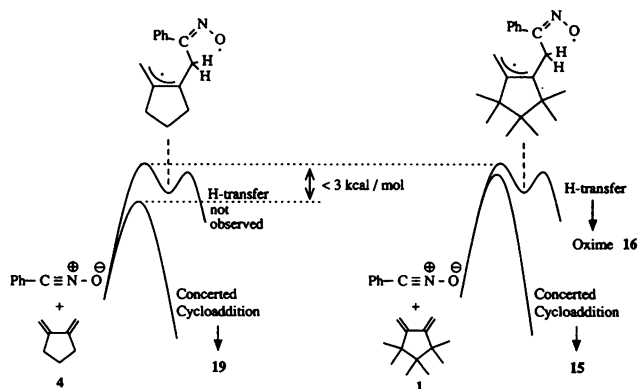
expected to affect only the barrier of the cycloaddition, thus giving rise to the formation of **15** and **16**. While methyl substitution affects the rate-determining step in scheme 21, it only affects the product-determining step in scheme 20. Therefore, kinetic experiments should allow these two possibilities to be differentiated. Competition experiments (CCl₄, 20.5 °C) showed that **1** is 26 times less reactive than the non-methylated compound **4**. This value implies that the cycloaddition of benzonitrile oxide with bis(methylene)cyclopentane **4** does not profit highly from concertedness. If the oxime **16** is produced through an intermediate diradical, the «energy of concert»[34] for the formation of **19** must be less than 3 kcal mol⁻¹.

SCHEME 22
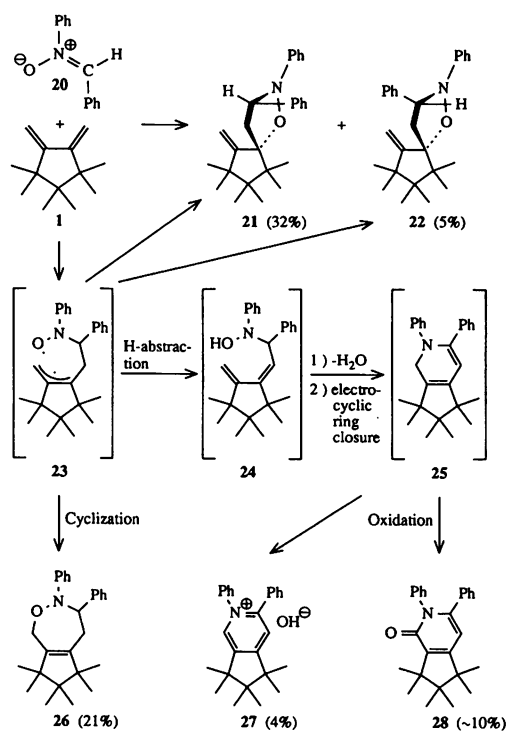
NITRONES

The reaction of C,N-diphenylnitrone, **20**, with **1** affords several types of products, as shown in scheme 22[35,36]. For the formation of the spiranes **21** and **22**, a concerted cycloaddition mechanism as well as a stepwise pathway with formation of an intermediate (*e.g.* **23**) has to be considered. In contrast, the formation of the [4+3]-cycloadduct **26** by a concerted process is orbital symmetry forbidden[3]. If an intermediate with zwitterionic character were involved, trapping with the solvent ethanol should be possible[37]. Since the yields of the cycloadducts were very similar in benzene, toluene, dimethyl sulphoxide, acetonitrile and ethanol, we suggested the intermediacy of the diradical **23**. This intermediate may also account for the formation of **27** and **28** since intramolecular hydrogen transfer, as discussed for the reactions of nitrile oxides, might give the hydroxylamine **24**, a potential precursor of **27** and **28**.

Is the formation of an intermediate diradical a special property of our model compound **1**, or is the isolation of **26-28** an indication that reactions of nitrones with 1,3-dienes generally involve diradical intermediates?

SCHEME 23 - RELATIVE RATE CONSTANTS FOR THE REACTIONS OF C,N-DIPHENYLNITRONE WITH 1,3-DIENES

Baran, Mayr, 1989

Considering the small reactivity difference between **1** and **4** (scheme 23) and following the same line of arguments employed for the discussion of schemes 20 and 21, we came to the conclusion, that cycloadditions of diphenylnitrone **20** with ordinary 1,3-dienes also cannot profit highly from concertedness, *i.e.*, the appearance of intermediates has to be generally considered. Therefore, a detailed analysis of the products formed from **20** and several other 1,3-dienes has been carried out.

Apart from the normal [3+2]-cycloadducts, the [4+3]-cycloadducts **29**, **30** and **31** were formed in low yields from bis(methylene)cyclopentane, **4**, 2-phenyl-1,3-butadiene, and 2,3-dimethyl-1,3-buta-

SCHEME 24 - [4+3]-CYCLOADDUCTS FROM **20** AND «NORMAL» DIENES
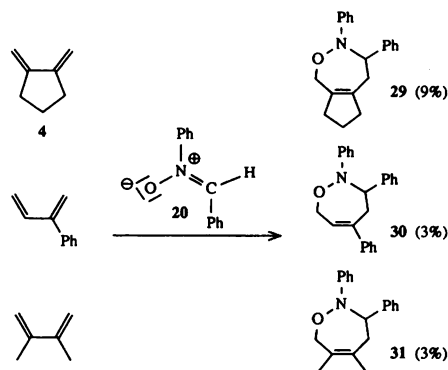
diene, respectively. Since their formation through concerted mechanisms is orbital symmetry forbidden, the intermediacy of diradicals is again deduced. The following section shows that these intermediates are not thermally equilibrated.

When the spirane **21** is heated at 100 °C, decomposition with formation of unidentified high molecular weight products takes place. After 60 h, more than half of the material is lost and only 6% of the [4+3]-cycloadduct **26** is observable (expt. 1, scheme 25). Under the same conditions, **22**, a diastereomer of **21**, selectively rearranges into **26** (expt. 2, scheme 25). Compound **26** is stable under these conditions (expt. 3, scheme 25).

The bottom block of scheme 25 shows that the relative thermodynamic stability of [3+2]- and [3+4]-cycloadducts is reversed, when R = H instead of R = CH₃. Now, three quarters of **21'** and **22'** remain unaffected when heated at 100 °C for 71 h (expts. 4 and 5, scheme 25). In contrast to **26**, the non-methylated [4+3]-cycloadduct **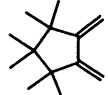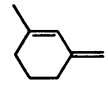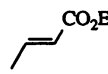26'** rearranges into the spiranes **21'** and **22'** with high preference for the latter stereoisomer, the one which is produced in lower yield during the cycloaddition (expt. 6, scheme 25). The greater rate of the **26** ⇌ **22** (and **26'** ⇌ **22'**) isomerisations compared with the **26** ⇌ **21** (and **26'** ⇌ **21'**) isomerisations clearly shows that the intermediate diradicals are not thermally equilibrated, *i.e.*, internal rotations are not fast compared with radical combinations.

A rationalisation for the stereoselectivities of the rearrangements is given in scheme 25. Let us assume that cleavage of the C-O bond in **21** and **22** is associated with a rotation of the planar nitroxide fragment to give the diradicals **23a** and **23b**, respectively, with *anti*-alignment of the two phenyl groups. In **23b**, the nitroxide oxygen is close to the CH₂-terminus of the allylic radical, and cyclisation to yield **26** *via* a boat-like transition state requires only small geometric reorganisations. The conformer **23a**, on the other hand, has to undergo rotations around bond *a* or bond *b* before cyclisation can give **26**. These rotations are obviously slow, so that side reactions are taking place and the rearrangement **21** → **26** hardly takes place. The reverse order of arguments (principle of microscopic reversibility) can be used to explain the stereoselective rearrangement **26'** → **22'**.

SCHEME 25 - THERMOLYSIS OF THE CYCLOADDUCTS IN TOLUENE

R = CH₃	21	26	22
Expt. 1ᵃ	40ᶜ	6	0
Expt. 2ᵃ	0	88	12ᶜ
Expt. 3ᵃ	1	95ᶜ	0

R = H	21'	26'	22'
Expt. 4ᵇ	74ᶜ	2	6
Expt. 5ᵇ	2	8	74ᶜ
Expt. 6ᵇ	7	20ᶜ	74

a) Composition after 60 h at 100° C; b) Composition after 71 h at 100° C; c) Starting material (=100 at t=0).
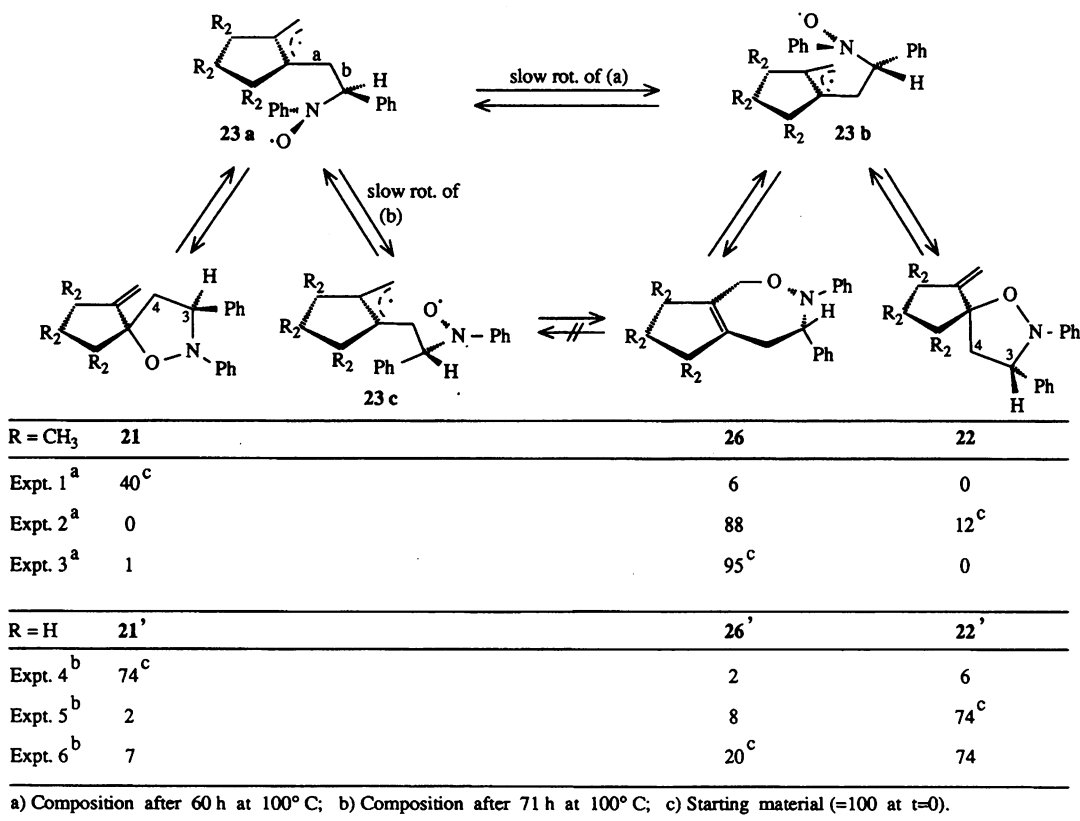
CONCLUSION

Several new types of cycloadditions have been realised by using the sterically hindered 1,3-diene as a cycloaddition partner. Complementing Huisgen's work on stepwise 1,3-dipolar cycloadditions via zwitterionic intermediates (scheme 26)[38], we have found that 1,3-dipolar cycloadditions may also occur stepwise, if the termini of the potential intermediate carry radical-stabilising groups.

SCHEME 26

Ion stabilising groups at the intermediate's termini

Radical stabilising groups at the intermediate's termini

Huisgen, Mloston, Langhals

This work
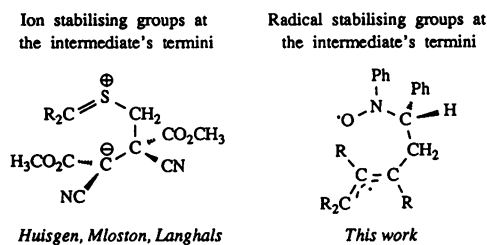
In which cases can compound **1** be used as a mechanistic probe? Scheme 11 has shown that **1** shows a normal ₚ4ₛ reactivity, *i.e.*, this compound will not exhibit special effects for reactions, which normally take place in 1- *and* 4-position of a 1,3-diene. Let us, therefore, consider cycloadditions, for which the simultaneous attack to positions 1 and 4 is orbital symmetry forbidden, and which usually employ a ₚ2-unit of a 1,3-diene. When we now compare the reactivity of **1** and **4**, the methyl groups

can influence *rate and/or products* of the reaction (a-d, scheme 27).

SCHEME 27

Compare the reactivity of **4** and **1**:

	Methylation affects rate	Methylation affects products	Conclusion
a	no	no	None
b	no	yes	Stepwise mechanism with 4 and 1
c	yes	no	Concerted mechanism with 4 and 1
d	yes	yes	Concerted mechanism with 4, stepwise mechanism with 1

CASE a

If compounds **4** and **1** exclusively give 1,2-adducts with similar rates, this may be due to a stepwise mechanism or to a concerted mechanism with an early transition state, which does not experience an extra steric strain by the methyl groups. No mechanistic conclusion can be drawn from the comparison of **4** and **1**.

CASE b

If compounds **4** and **1** give different products with similar rates, one can conclude that the methyl groups only affect the product-determining step, not the rate-determining step. This will be the case if both dienes reacted through an intermediate (scheme 28). However, the observation of different products formed with similar rates is also compatible with a concerted cycloaddition of **4** when the energy of

SCHEME 28 - ENERGY PROFILES FOR THE REACTIONS OF **4** (LEFT) AND
1 (RIGHT) WITH CYCLOADDITION PARTNERS THAT USUALLY PREFER 1,2-
ATTACK

many systems will not provide a clear yes/no answer.
We believe, however, that *a large reactivity difference
between* **1** *and* **4** *is a reliable indication that a concerted
mechanism is operating with ordinary dienes.*

It may seem, as if any cycloaddend with bulky
substituents at one end (*e.g. tert*-butyl-substituted
ethylenes) could serve as an analogous mechanistic
probe. This is not the case, however, since ordinarily
a strong reduction of rate caused by a bulky
substituent may either indicate the increase of the
barrier of the concerted process or signify that the
cyclisation of a reversibly produced intermediate is
slowed down by steric effects. The latter possibility
can be excluded in reactions with compound **1**: In
a potential intermediate, there is always one non-
shielded allylic position (the terminal CH_2-group),
which can be attacked in the cyclisation step. Since
concerted 1,2-additions are also discussed in several
hydrogenation and oxidation reactions, further areas
of application for **1** are conceivable. The convenient
access described in scheme 7 encourages further
experiments.

concert is very small, *i.e.*, when the barriers for the
concerted and the stepwise processes are of similar
height.

CASES c AND d

When methylation strongly reduces the rate, a
concerted reaction of **4** is indicated, since the steric
effect of the methyl groups can only be realised, when
C-2 is attacked in the rate-determining step. If the
energy of concert is very large, the methyl groups
are unable to change the mechanism (case c, schemes
27 and 28). If the steric strain caused by the methyl
groups exceeds the «energy of concert», a change of
mechanism takes place, indicated by the observation
that **1** gives additional or different products than **4**
(case d, schemes 27 and 28). In this case, $\Delta\Delta G^{\neq}$ gives
a rough estimate for the energy of concert, that is
encountered in the reaction with a «normal diene»
(*e.g.* **4**).

As the effect of methyl groups on the attack at the
diene-termini is not exactly zero (see scheme 11),

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