

ASPECTS OF THE PHOTOCHEMISTRY OF ARYL ETHYLENES

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Abstract. Three aspects of the photochemistry of aryl olefins have been studied. a) The proton tautomerism of the primary photocyclization product of stilbenes, b) the influence of substituents on the photocyclization of stilbenes and on the secondary processes after cyclization, c) the influence of the ground state conformation of stilbenes on the photoproduct formation.

a) The primary photocyclization product of stilbene, the 4a,4b-dihydrophenanthrene (4a,4b-DHP) can undergo several reactions; besides oxidation into phenanthrenes, spontaneous rearrangements and tautomerism under influence of an enolizable group in non-basic medium are known. Also amines and bases appear to induce isomerizations of the compound, leading to 1,4-dihydrophenanthrene and 9,10-dihydrophenanthrene. It is demonstrated that primary amines react in a special way. The predominant formation of the 1,4-DHP is ascribed to a proton transfer from C(4b) to C(4) *via* a single deprotonation/protonation step in which the amine operates as the transferring agent. With other bases, *e.g.* in basic methanolic solution protonation is solvent-mediated and rather unselective at C(2), C(4) and C(9), leading to 1,2-, 1,4- and 9,10-DHP. Deuteration experiments indicate that 1,2- and 3,4-DHP are intermediates in the photoformation of 1,4-DHP.

b) In the past several investigations have been devoted to the influence of substituents on the photocyclization of stilbene-like compounds and the observed substituent effects have usually been ascribed to an influence on the primary cyclization reaction. In the present investigation substituted 1,2-diphenylcyclopentenes have been used to prevent possible interference of reactions from *cis-trans* isomerization and of reactions of the *trans*-isomer. It appeared that the primary photocyclization is almost independent of substituents, but the primary formed 4a,4b-DHP's have substituent dependent oxidation rates if the oxidant is present in low concentration. The rate of the thermal ring opening process also depends on the substituent, especially on its position. The results are discussed.

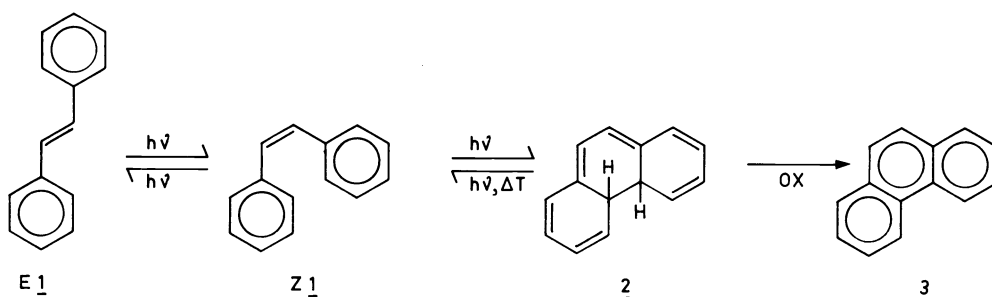
c) The photobehaviour of 2-vinylstilbenes can be divided roughly into three patterns. α -Substituted 2-vinylstilbenes give benzobicyclo[3.1.0]hex-2-enes; β -substituted 2-vinylstilbenes are photostable; α - or β -unsubstituted 2-vinylstilbene forms benzobicyclo[2.1.1]hex-2-enes. An electronic influence of the substituents could not be shown; only steric factors seem to be of importance.

From the fair correlation between a ground state property of the vinyl stilbenes (*viz.* the difference in chemical shifts of the vinylic protons H(1) and H(2)) and the type of photoproduct, we deduce that the ground state conformation of the vinylstilbenes is determining the mode of photocyclization.

A. PROTON TAUTOMERISM IN 4a,4b-DIHYDROPHENANTHRENES

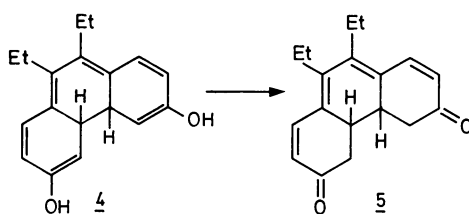
In the last decades the photodehydrocyclization of stilbene (1) and stilbene-like compounds into phenanthrenes (3) has become a well-known photochemical reaction (Scheme 1).

Scheme 1



The *trans* 4a,4b-dihydrophenanthrene (4a,4b-DHP, 2) has been accepted as the initially formed photoproduct¹. Its dehydrogenation occurs under oxidative conditions, mostly in the presence of O₂, I₂, TCNE or other oxidants^{1,2}. Besides an oxidation reaction the 4a,4b-DHP's undergo thermally as well as photochemically a ring opening reaction to the parent stilbene. Several 4a,4b-DHP's can, however, also rearrange into more stable isomers, when they are formed under anaerobic conditions. A well-known example is the enol-keto tautomerism of the 4a,4b-DHP from 4,4'-dihydroxy- α,α' -diethylstilbene (4) in a protic medium³ (Scheme 2).

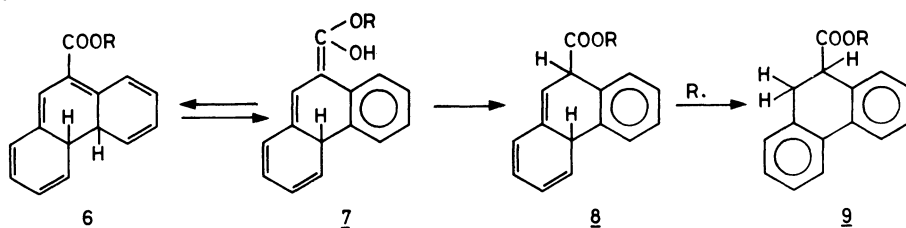
Scheme 2



Another kind of tautomerism occurs in the 4a,4b-DHP's from stilbene which possess enolizable substituents at the olefinic double bond⁴ (Scheme 3).

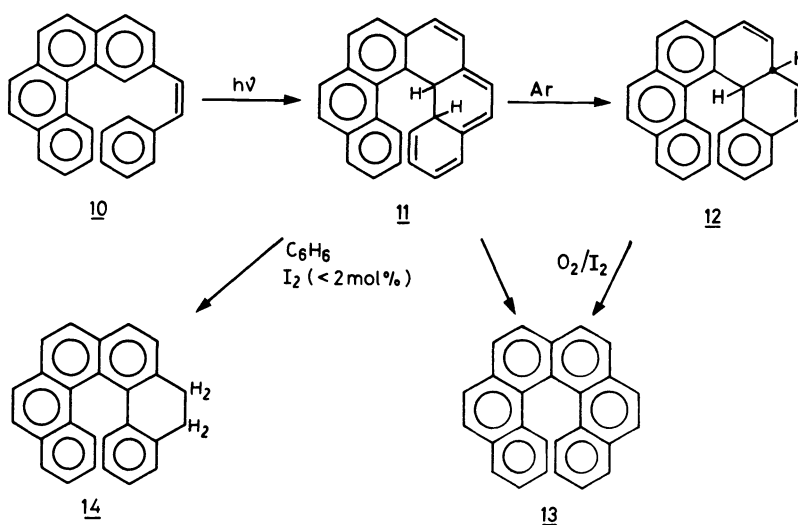
After the prototropic shifts a hydrogen radical abstraction recombination step leads eventually to 9,10-dihydrophenanthrene (9). In this case a protic solvent is necessary, but when two electron accepting groups are present at the stilbene double bond hydrogen shifts are observed also in aprotic solvents and even in the solid state⁴.

Scheme 3



Isomerizations of unsubstituted 4a,4b-DHP's have been observed only incidentally; e.g. a [1.5]suprafacial H-shift in the 4a,4b-DHP (11) of 1-styrylbenzo[c]phenanthrene (10) explains the formation of 6a,16d-dihydrohexahelicene (12), which is more stable than 11 under anaerobic conditions^{5,6} (Scheme 4). In air it is slowly oxidized into hexahelicene (13). Quite remarkable is the formation of 9,10-dihydrophenanthrenes from stilbene-like molecules on irradiation in the presence of only a very small amount of an oxidant. So, 14 (together

Scheme 4

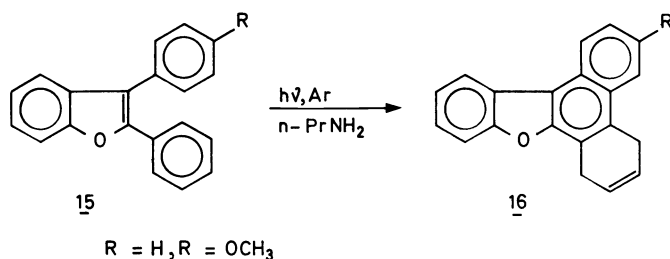


with some 13) is formed when 10 is irradiated in benzene in the presence of about 1 mol % of iodine⁷. In a similar way, irradiation of other stilbenes under these conditions leads to a mixture of dihydrophenanthrenes⁸.

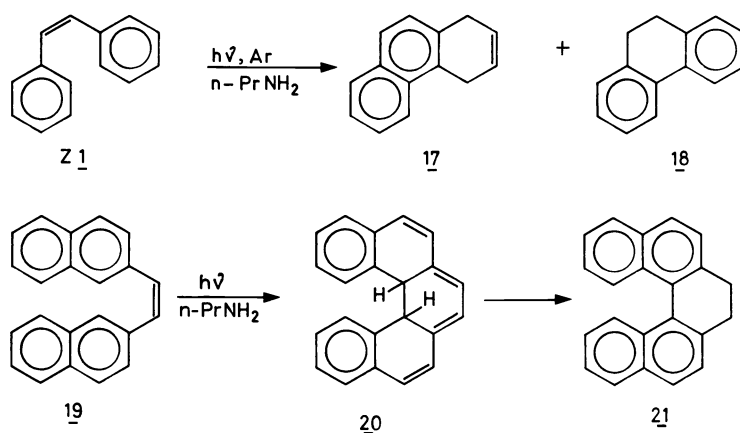
Some years ago the formation of another DHP, viz. a 1,4-dihydrophenanthrene was observed on irradiation of stilbene-like compounds in *n*-propylamine solution (Scheme 5)⁹.

Originally the authors suggested that the amine provoked an ionic pathway contrary to the usual radical pathway for the oxidative reaction. Because 1,4- and/or 9,10 DHP's are not observed upon irradiation of stilbene in methanol or benzene it is clear that the amine enables the formation of 17 and 18 (Scheme 6). No formation of these compounds is described when secondary or tertiary amines are used and no reaction between stilbene and a primary amine occurs. Therefore, we supposed a reaction between the amine and the primary formed 4a,4b-DHP. Addition of a deaerated primary amine to the coloured solution of 4a,4b-DHP (20) from 1,2-di(2-naphthyl)ethylene (19) gave decolorization and the presence of 21 could be

Scheme 5



Scheme 6



demonstrated. The decolorization reaction is first order in **20** with a rate constant $k = 1.1 \pm 0.1 \text{ l}^2/\text{mol}^2 \cdot \text{min}$ (for the oxidation of **20** $k = 0.006 \text{ l/mol} \cdot \text{min}$. These rates are comparable when the amine concentration is about equal to the oxygen concentration). So, 4a,4b-DHP **20** must be an intermediate.

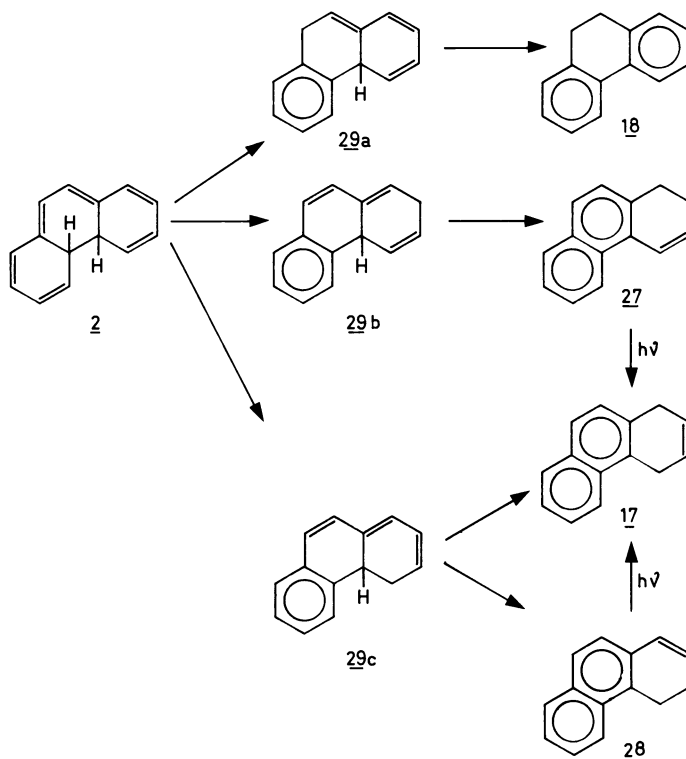
Substituents in the stilbene have a distinct directing influence on the product formation (see Scheme 7). These data point to an ionic mechanism, especially because in tert. butylamine as the solvent the reactions occur as well, showing that the amino-group is responsible for the reaction. Irradiation of **22a** in N-deuterated butylamine results in **23a** having D only at the positions 1, 2, 3 and 4 for 20, 10, 10 and 40%, respectively.

Irradiations of stilbene-like compounds in methanol with dissolved NaOCH_3 give rise to the same products as found in alkylamine solution affirming the base-induced character of the reaction. When stilbene itself is irradiated in methanol with methoxide as base the composition of the products varies with the concentration of the base; moreover, sometimes a third product, 1,2-dihydrophenanthrene (**27**), is present.

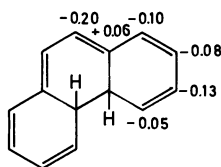
With increasing base concentration the total yield of the products **17** and **18** increases. At lower base concentrations and/or with higher stilbene concentrations **27** becomes detectable. Its yield never exceeds 10% and on longer irradiation times it disappears in favour of **17**.

Using CH_3OD as the solvent the presence of D at C(1), C(2), C(3) and C(4) of **17** and at C(2) of **27** (50% D) was established. The presence of D at C(2) and C(3) of **17** indicated that it is formed via **27** (or **28**). Indeed irradiation of pure **27** and **28** in an alkylamine solution or in a basic methanolic solution resulted readily in **17** (see Figure 1). Thermal rearrange-

Scheme 8



It is assumed that all the steps in Scheme 7 are irreversible, and that the interconversions between the isomers 29 are negligible because the methine hydrogen is much more acidic than the methylene hydrogens. This assumption is in agreement with the calculated stabilities of the various dehydrophenanthrenes (relative to 18). As no conversion of 17, 27 and 28 into 18 or *vice versa* is observed, it can be concluded that the first deprotonation/protonation step determines the structure of the ultimate products. In methanolic solution this step is a solvent mediated reaction, in which the H^+ abstraction is facilitated by a proton transfer from the solvent. The product ratio of this step is kinetically determined and depends on the electron densities at the various positions of 2 in the transition state. Using a weak base (n-propylthiolate) the selectivity is high and only 18 is formed.

Electron densities of 2.

With a strong base (CH_3O^-) the selectivity is lower: 18 remains the main product but side-products arise (27 via 29b and 17 via 29b or 29c) in increasing amounts when the concentration of CH_3O^- is increased.

The D-incorporation in the end products (at C(9) and C(10) in 18; at C(1) and C(2) in

27; at C(1), C(2), C(3) and C(4) in 17) indicates that conversions of the intermediates 29 and the final step 27→17 are again solvent mediated reactions.

Using an amine as the solvent the selectivity is different; 17 is formed as the main product, suggesting another mechanism. The high D-incorporation at C(4) when a deuterated amine is used points to the same conclusion. The preferential protonation at C(4) which has a relative low electron-density, giving 29c is understandable when only one amine molecule is involved in the first deprotonation/protonation step as indicated in Figure 2.

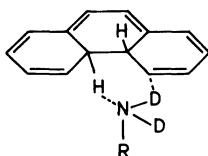


Fig. 2

The observed substituent effect can then be ascribed to the increased (CH_3 , OCH_3) or decreased (CF_3) electron density at the carbon atom next to the substituent position, favouring protonation on the substituted or the unsubstituted ring, respectively.

In bulkier amines the pathway *via* 29a becomes more important because the interaction as in Figure 2 is less favourable. Also in larger diarylethylenes this kind of interaction seems not to occur, only molecules analogous to 9,10-DHP are formed and protonation occurs only at the positions with the highest electron density.

The light induced rearrangements 27→17 and 28→17 are not dependent on the presence of primary amines. In triethylamine these isomerizations occur as well. Though the quenching of the fluorescence of 27 by Et_3N is about four times better than by $n\text{-PrNH}_2$ in hexane, the quantum yield of isomerization in Et_3N is only about half of that in $n\text{-PrNH}_2$.

B. INFLUENCE OF SUBSTITUENTS IN THE PHOTOCYCLIZATION OF 1,2-DIARYLETHYLENES

Several authors have reported that rate constants and quantum yields for processes originating from the excited state can be correlated with ground state σ -constants. For the phenanthrene formation from stilbene and related reactions all explanations and interpretations of the effect of substituents given in the literature have in common the assumption that the influence of substituents on the quantum yield of formation of the final photoproducts parallels their influence on the quantum yield of formation of the primary cyclization product¹⁰⁻¹⁷.

To get more insight into the effect of substituents on this photocyclization a series of substituted 1,2-diphenylcyclopentenes was investigated. These compounds cannot undergo *cis-trans* isomerization so that one of the deactivation channels from the S_1 -state is eliminated and no processes from a *trans*-isomer will be interfering. Moreover, the photochemistry of the parent compound has thoroughly been investigated by Muszkat and Fischer¹⁸.

The photocyclizations were performed under different oxidative conditions in methanol and in cyclohexane.

Oxidation with iodine may involve molecular as well as atomic iodine and is much faster than oxidation with oxygen.

From Table I it can be concluded that para substituents do not have much influence on the quantum yield of photocyclization of 22. An effect of the substituents is found, when an oxidant with low efficiency is used. Substituents having a negative σ_p -value tend to enhance

Scheme 9

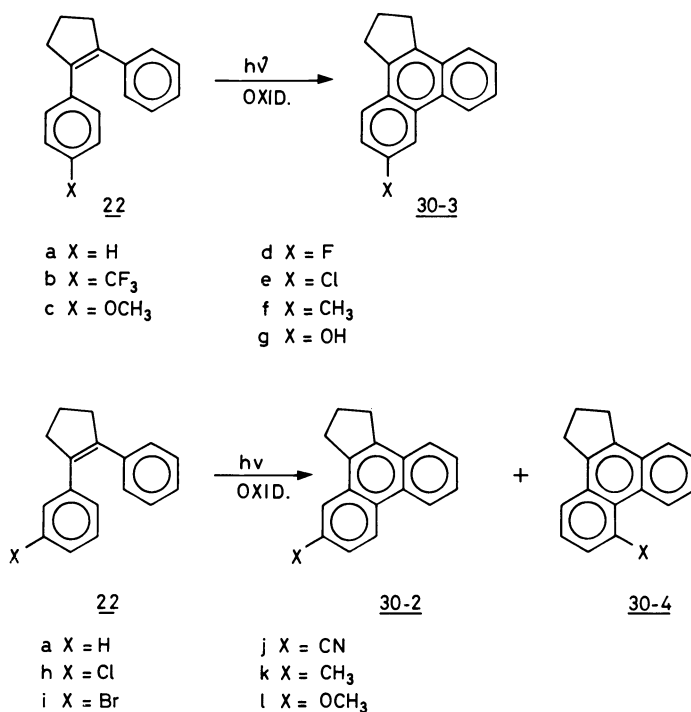


Table I RELATIVE QUANTUM YIELDS OF 3-SUBSTITUTED PHENANTHRENE FORMATION

Oxidant	Solvent	Methanol		Cyclohexane		
		Air	I ₂ /air	Air	I ₂ /air	I ₂ /N ₂
substituted phenanthrene 30		ϕ _{rel}	ϕ _{rel}	ϕ _{rel}	ϕ _{rel}	ϕ _{rel}
a	H	1.0	1.0	1.0	1.0	1.0
b	CF ₃	0.92	0.94	1.1	1.0	1.0
c	OCH ₃	1.7	1.1	1.1	1.0	1.1
d	F	0.93	0.84	0.83	1.0	1.0
e	Cl	0.71	1.1	0.95	1.1	1.0
f	CH ₃	1.9	1.0	1.2	1.2	1.1

the product formation but a linear Hammett plot is not obtained. The differences are smaller in cyclohexane than in methanol. These results are in contrast with those obtained for correspondingly *p*-substituted stilbenes¹⁰, where a decrease in ϕ_{rel} was observed with increasing magnitude of σ_p .

From the data of Table II for meta-substituted compounds 22 it appears that also these compounds do not obey the Hammett equation using ground state substitution constants. Both in methanol and in cyclohexane the quantum yields are almost substituent-independent when I₂ is used as an oxidant. Using air as the oxidant the quantum yields very much more and the same is true for the ratios between the 2- and 4-substituted phenanthrenes. This ratio does not only depend on the type of oxidant but also on its concentration and on the concentration of the stilbene. These results are in contrast to those reported by Mallory¹⁹

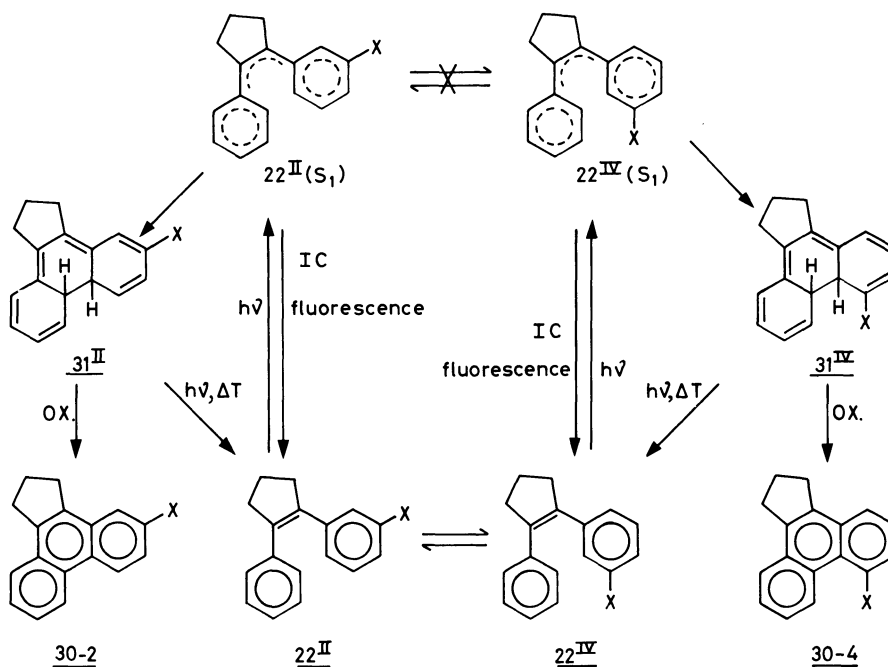
Table II RELATIVE QUANTUM YIELDS OF THE PHOTOFORMATION OF 2- AND 4-SUBSTITUTED PHENANTHRENS AND THE RATIO OF PHENANTHRENS 30-2 AND 30-4

Solvent		Methanol				Cyclohexane			
oxidant		air		I ₂ /air		air		I ₂ /air	
phenanthrene	Ø _{rel}	30-2 30-4	Ø _{rel}	30-2 30-4	Ø _{rel}	30-2 30-4	Ø _{rel}	30-2 30-4	
a	H	1.0	-	1.0	-	1.0	-	1.0	-
h	Cl	0.56	5.0	0.84	1.2	0.61	25	0.90	2.2
i	Br	0.51	7.0	0.83	1.4	0.44	60	0.78	2.4
j	CN	0.48	2.9	1.0	1.2	0.97	1.7	1.0	1.0
k	CH ₃	1.0	3.5	1.2	1.3	0.80	3.0	0.95	1.1
l	OCH ₃	0.93	1.4	1.0	1.0	0.92	1.2	1.0	1.0

for some meta-substituted stilbenes. He ascribed the observed ratio (1.1) to a difference in steric crowding in the parallel photocyclization steps and the increase in the ratio with increase of time to a selective destruction of the 4-substituted phenanthrene.

In the present case the differences cannot be explained by differences in energy barriers in the primary photocyclization steps $22 \rightarrow 31^{\text{II}}$ and $22 \rightarrow 31^{\text{IV}}$ (Scheme 10). Irradiation at different temperatures and in different solvents revealed that the ratio of the products is not viscosity-dependent and that a lowering of temperature decreases the ratio 30-2/30-4. (For 22k 1.1 at -25°C , 8.0 at 197°C ; for 22l 1.0 at -25°C and 3.0 at 197°C .) This indicates that no selective excitation of ground state rotamers occurs. According to the NEER

Scheme 10



principle equilibration of excited rotamers is not likely as is verified for 1,2-di(2-naph-

thyl)ethylene by Fischer²⁰. The internal conversions will be comparable for all conformers because the differences in torsion angles and bond lengths are very small for the several conformers as was calculated by a force field method.

Consequently the quantum yields of the primary photocyclization of step $22 \rightarrow 31^{II}$ or 31^{IV} will be equal. Since the ratio $30-2/30-4$ approaches 1.0 at lower temperatures a difference in the energy barriers does not give an explanation, as it would cause an enlargement of the ratio. Therefore, the unequal amounts of 2- and 4-substituted phenanthrenes must be due to differences in the reactions of the intermediate 4a,4b-DHP's (31), either in thermal ring opening or in their oxidation. Force field calculation of the ground and excited state energies of the methyl substituted DHP's of $22k$ relative to the energy of $22k$ point to a decreased stability of the 4-substituted DHP in its S_0 -state and consequently a reduced half lifetime for its thermal decay. The kinetics of the thermal ring opening in methanol for some compounds is given in Table III. The two DHP's of the meta substituted compounds $22i$ and $22l$ could well be distinguished by their different decay at lower temperatures.

Table III RATE CONSTANTS (k_{0p}), ACTIVATION ENERGIES E_a AND ACTIVATION ENTROPIES ΔS^\ddagger FOR THERMAL RING OPENING OF SUBSTITUTED DHP'S (31) IN METHANOL

Compound	Substituent in product	$10^4 k$	Temp ($^\circ C$)	E_a (kJ/mol)	ΔS^\ddagger (J/mol. $^\circ C$)
$22a$	H	3.7	20	45.2	-164.4
b	3-CF ₃	3.3	20	51.9	-142.2
f	3-CH ₃	3.9	20	60.0	-116.3
i	2-Br	1.2	11	60.2	-114.2
	4-Br	3.0	-16	27.2	-213.0
l	2-OCH ₃	1.2	11	61.9	-109.2
	4-OCH ₃	8.3	11	32.5	-199.6

In general, the influence of substituents on the rate constant of the thermal ring opening is rather small in reactions leading to 2- or 3-substituted products, but large in the formation of 4-substituted products. For the whole series E_{act} -values show a linear, isokinetic relationship to $-\Delta S^\ddagger$ -values. No correlation with Hammett σ -constants is found.

Comparison of the rates of thermal decay with the estimated rates of oxidation (at 11 $^\circ C$: $k_{ox} = 5 \times 10^{-4}$ [DHP]^{18,21}) reveals that they are of comparable magnitude. The differences in the rate of ring opening of corresponding 2- and 4-substituted DHP's can well be reflected in the ratio of the resulting phenanthrenes. Accepting that the pairs of DHP's from $22h-1$ are originally formed in 1:1 ratio, the relative quantum yields of phenanthrene formation that should be obtained when the 2- and 4-substituted DHP are oxidized to an equal extent can be calculated from the data of Table II. It appears then that the photocyclization of meta substituted compounds $22h-1$ using iodine as the oxidant do also not obey the Hammett equation.

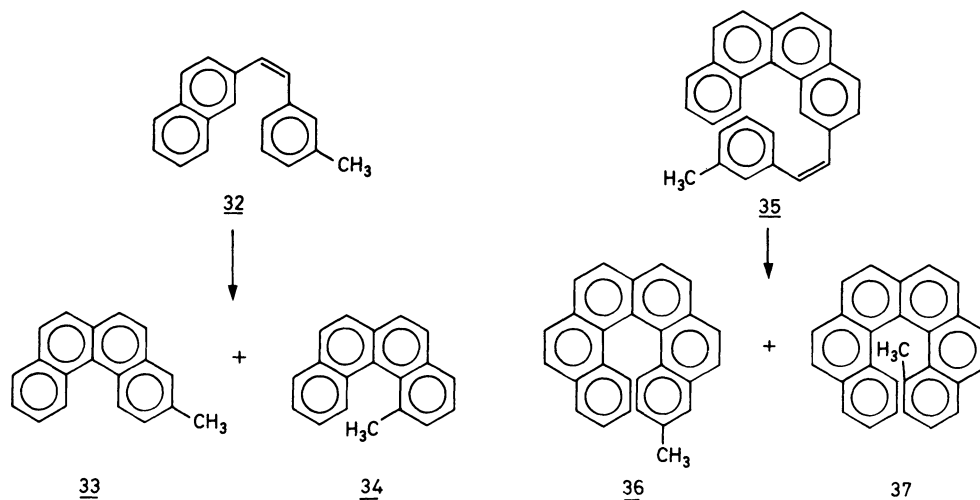
The differences observed for the substituted diphenyl cyclopentenes (22) and the substituted stilbenes 1^{10-12} are, therefore, most likely not caused by a substituent effect on the primary photoreaction but by differences in the rate of oxidation or thermal decay of the DHP's. Similarly, the correlation between quantum yields of phenanthrene formation from para-substituted stilbenes (1) and the maxima of their UV absorption bands¹¹ is not observed for the diphenylcyclopentenes (22). The observed correlation by Jungman¹⁰ may actually be a correlation between the quantum yields or the rate of deactivation of the excited molecule and the absorption maxima. For stilbene (1) the decay of the excited molecules takes place partly *via* an excited twisted configuration, which can be converted into

the *cis*- and the *trans*-ground states²², whereas such a configuration will not be attainable for 22.

In contrast to the above observations a steric substituent effect had to be assumed in the irradiation of 2-(*m*-methylstyryl)naphthalene (32) which results in the formation of 1- and 3-methylbenzo[*c*]phenanthrene (33 and 34) in a ratio of 1:1.3. The ratio is unaffected by the I₂ concentration or the temperature (-40-25 °C) (see also ref. 19).

However, irradiation of 1-(*m*-methylstyryl)benzo[*c*]phenanthrene (35) results in 3- and 1-methylhexahelicene (36 and 37) in a ratio of 9:1 when 5 mol % iodine is present²³ but in a ratio of 1:1 in the presence of 100 mol % iodine (Scheme 11).

Scheme 11



Apparently in the latter photodehydrocyclization the primary DHP's can be formed in a 1:1 ratio on account of the flexibility of the helical compound which is larger than in the smaller aromatic systems in 32.

C. IMPORTANCE OF GROUND STATE CONFORMATIONS FOR THE TYPE OF PHOTOREACTION

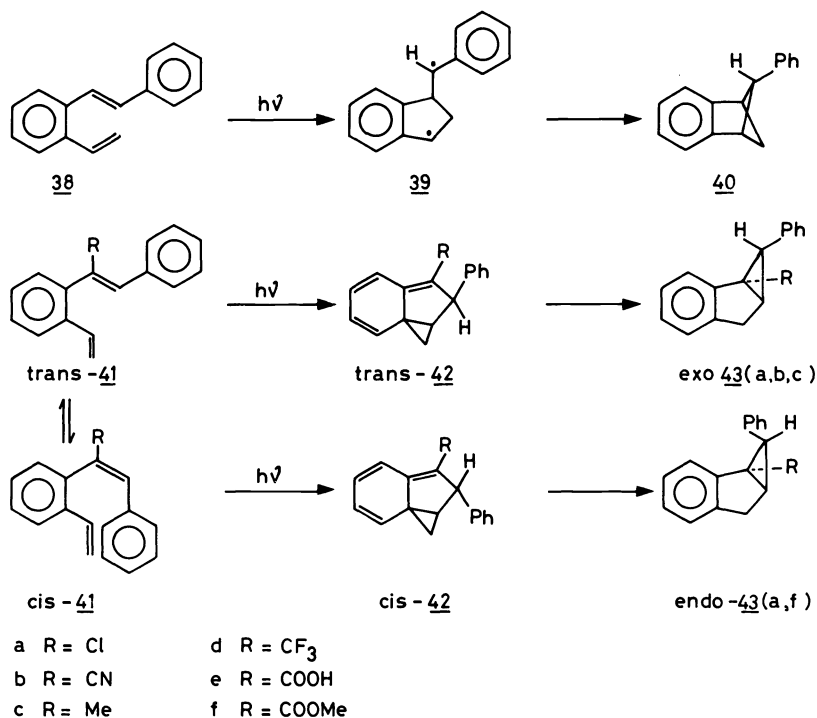
In the preceding paragraph the validity of the NEER principle (non equilibration of excited rotamers) has been assumed for the stilbenes. Only in a few cases, however, the validity of this principle has been proven. Havinga, who formulated the concept for the first time²⁴, could show unambiguously the importance of different rotamers for the course of a photoreaction by exciting simply substituted hexatrienes at different wavelengths and analyzing the photoproducts. The different composition of the product mixture indicated clearly that no equilibration occurs between the excited rotamers.

Using an advanced fluorescence technique Fischer was able to show the existence of different fluorescent species of *trans*-diarylethylenes on excitation at various wavelengths demonstrating the validity of the NEER principle²⁵. For more complicated molecules a direct proof is not well possible in most cases, though several indications for the usefulness of the concept in the explanation of certain photoreactions have been obtained.

We found clear indications that the occurrence of different types of product formation in the photochemistry of 2-vinylstilbenes can be due to conformational differences.

Irradiation of 2-vinylstilbene (38) itself and of 2-vinylstilbenes substituted at one ortho position of the β -ring or at non-hindering positions leads to a 5-phenylbenzobicyclo[2.1.1]-hex-2-ene (40). The product formation proceeds *via* an intermediate biradical as could be established by radical scavengers and by trapping the intermediate (39). The yield of the bicyclo compound having the 5-phenyl group in the *exo*-position is about 70%²⁶.

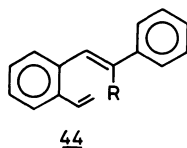
Scheme 12



Only a small amount of the *endo* 5-phenyl derivative is formed. Derivatives of 38 bearing an α -substituent do not form photoproducts like 40, but instead benzobicyclo[3.1.0]hex-2-enes 43²⁷.

This reaction is assumed to be concerted and to proceed *via* a (4+2)photocycloaddition followed by a vinylcyclopropane rearrangement. The electronic properties of the substituents have no influence on this photoprocess, but only the size of the group is of importance. Small α -substituents lead to mixtures of *endo*- and *exo*-6-phenylbenzobicyclo[3.1.0]hexene; large substituents give only the *endo*-isomers²⁷.

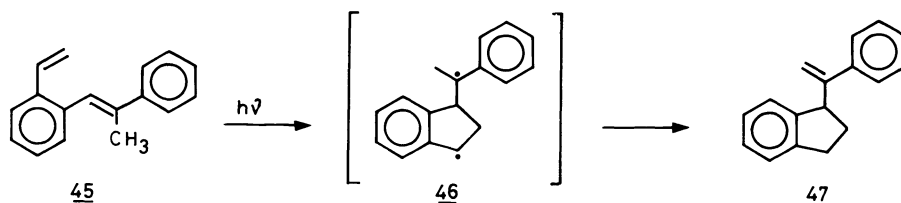
Vinyl stilbenes substituted at the β -position 44 are photo unreactive, with the exception of 45²⁸.



- a R=CF₃
 b R=CN
 c R=COOH
 d R=COOMe
 e R=Cl

In the latter case an indane derivative (47) is formed, presumably *via* a similar intermediate as given for the formation of 40.

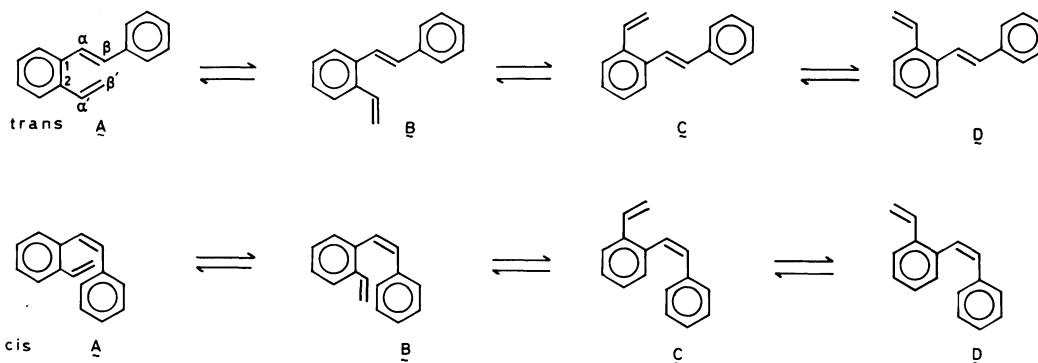
Scheme 13



6-Methyl-2-vinylstilbene forms both a benzobicyclo[2.1.1]hexene as well as a benzobicyclo[3.1.0]hexene²⁶. 2-Vinylstilbenes substituted at both ortho positions of the β -ring are photostable as the β -substituted compounds²⁶. It seems reasonable to ascribe the differences in photochemical behaviour to steric factors.

Vinylstilbenes occur in *cis*- and *trans*-configuration, which equilibrate on irradiation. In solution several conformations are possible for both isomers. In Scheme 14 the four extreme conformations are given for both *cis*- and *trans*-2-vinylstilbenes.

Scheme 14



The formula in this Scheme are projections of three-dimensional structures. A and B which interconvert by rotation around C(2)-C(α') are different conformations, because they are at different sides of the labile structure in which the α -phenyl ring and the vinyl moiety are perpendicular to each other. Conformation C and D, B and D, A and C are different in a similar way.

Steric effects of substituents will be of influence on the deviation from coplanarity in any of the conformations making them slightly different from those of the parent compound.

On irradiation of 2-vinylstilbene with light having a band width of several nanometers all compounds will equally be excited because they cannot differ much in UV absorption. In the excited state the molecules will maintain the ground state conformation to a large extent because the bond order of the bonds over which rotation occurs in the ground state is increased. According to this reasoning it can be anticipated that only the conformations A and C are suited for the formation of a benzobicyclo[2.1.1]hex-2-ene. In these conformations C(α) and C(β') are at relatively short distance. Another possibility for A might be the electrocyclic ring closure, but this kind of reaction is only observed as a side-reaction with α - or β -phenyl substituted 2-vinylstilbenes. For the formation of a benzobicyclo[3.1.0]-

hexene *via* a (4+2) cycloaddition the conformer B is most suited. Conformer D seems not to be suited for the formation of either a benzobicyclo[2.1.1]- or [3.1.0]hexene product. Of course, *cis*-D and *cis*-C can undergo a cyclization into a 4a,4b-DHP but in a deaerated solution these products revert to the parent compound.

Realizing that the vinylstilbene system is much too complicated for a direct coherent explanation of the qualitative and quantitative differences in photochemical product formation based on the NEER principle we wondered whether a correlation could be found between some physicochemical parameters depending in the conformational equilibration in the ground state, and the nature of the main photoproduct.

The chemical shift of the vinyl protons in the vinyl stilbenes proved to be well suited for this purpose. The chemical shift of H(1) is remarkable constant in a large variety of vinylstilbenes ($\delta = 5.62 \pm 0.10$ ppm for the *trans*-compounds; 5.64 ± 0.10 ppm for *cis*-compounds). The δ -values of H(2) vary strongly. To eliminate experimental inaccuracies we used the difference $\Delta(\delta H(1) - \delta H(2))$ as the parameter describing the state of the conformational equilibrium in the individual compounds.

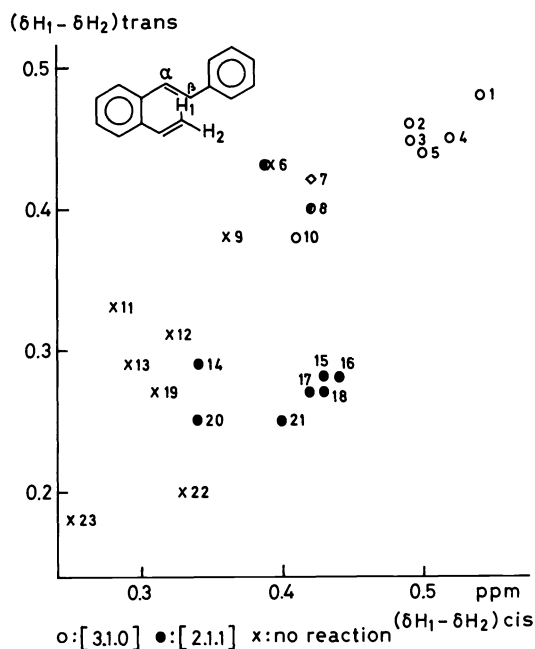


Fig. 3 Correlation between the differences in chemical shifts ($\delta H(1) - \delta H(2)$) for *cis*- and *trans*-isomers of 2-vinylstilbenes and the type of photoreaction. Substituents 1: α -phenyl, 2: α -Me, 3: α -CO₂Me, 4: α -Cl, 5: α -CF₃, 6: β -Me, 7: β -phenyl, 8: 6-Me, 9: β -Cl, 10: α -CN, 11: β -CF₃, 12: 2',4',6'-triMe, 13: β -CO₂Me, 14: 2'-vinyl, 15: none, 16: 4'-Me, 17: 4'-F, 18: 1-(β -naphthyl)-2-(*o*-vinylphenyl)ethene, 19: 2,6'-diCl, 20: 2'-Cl, 21: 1-(α -naphthyl)-2-(*o*-vinylphenyl)ethene, 22: 4-CN, 23: β -CN.

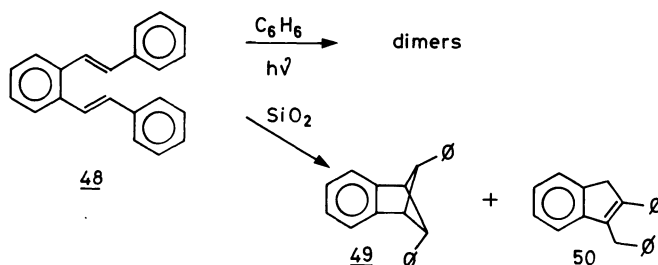
In Figure 3 the $\Delta\delta$ -values for *cis*- as well as *trans*-isomers are related to the type of photoreaction for these compounds. The Figure shows that the $\Delta\delta$ -values of the *cis*-isomers correlate rather well with the photochemical behaviour. β -Substituted compounds and 2',6'-disubstituted vinylstilbenes, all being photostable, have $\Delta\delta$ -values between 0.25 and 0.34. The low values point to a strong contribution of D, in which conformation both H(1) and H(2) are outside the influence of the central olefinic bond and the β -phenyl group.

$\Delta\delta$ -Values between 0.40 and 0.44 ppm are found for the *cis*-isomers of the parent compound, its 4'-substituted and naphthyl derivatives. All form benzobicyclo[2.1.1]hexenes which must arise from A or C. The intermediate $\Delta\delta$ -values might be an indication that the (2+2) cycloaddition occurs mainly from C. Larger $\Delta\delta$ -values between 0.47 and 0.54 are found for the *cis*-isomers of the α -substituted stilbenes which yield benzobicyclo[3.1.0]hexenes. The high $\Delta\delta$ -values point to a high contribution of A or B. The absence of a cyclization product from A might be an indication that the photoreactivity of A is low.

Between the three regions some quite comprehensible borderline cases are found: 6-methyl-2-vinylstilbene (Figure 3, 8) forms both the benzobicyclo[3.1.0]- and [2.1.1]hexene²⁵; β -methyl-2-vinylstilbene (45) (Figure 3, 6) forms a product originating from the same intermediate as occurring in the formation of a benzobicyclo[2.1.1]hexene²⁸. Compound 7 (Figure 3) forms a benzobicyclo[2.1.1]hexene but its formation is accompanied by a phenyl shift²⁹. Only compound 10 does not fit very well; its low $\Delta\delta$ -value may be due to the large anisotropic effect of the cyano group. For the *trans*-isomers a distinction between the compounds forming bicyclo[3.1.0]hex-2-enes and the others can be observed. Anyhow, these data strongly suggest that the ground state conformation of the 2-vinylstilbenes is of predominant influence on the course of the reactions.

It is of interest to note that 1,2-distyrylbenzene (48), which forms only dimers when irradiated in solution³⁰ give rise to a mixture of diphenylbenzobicyclo[2.1.1]hexene (49) and 1-benzyl-2-phenylindene (50) when irradiated absorbed on silicagel. Similar products are formed on irradiation of 2-vinylstilbene on silicagel.

Scheme 15



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