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 photoproduct\(^1\). Its dehydrogenation occurs under oxidative conditions, mostly in the presence of \(O_2\), \(I_2\), 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 medium\(^3\) (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 bond\(^4\) (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 state\(^5\).
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 conditions⁵,⁶ (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 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
demonstrated. The decolorization reaction is first order in \( \text{Q} \) with a rate constant \( k = 1.1 \pm 0.1 \text{i}^2/\text{mol}^2\cdot\text{min} \) (for the oxidation of \( 20 \)). 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 \( \text{NaOCH}_3 \) give rise to the same products as found in alkyamine 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 \( \text{CH}_3\text{OD} \) 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 alkyamine solution or in a basic methanolic solution resulted readily in 17 (see Figure 1). Thermal rearrange-
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Scheme 7

\[
\begin{align*}
\text{22} & \xrightarrow{h\nu, Ar} \text{23} \\
a & R = H \\
b & R = CF_3 \\
c & R = OCH_3
\end{align*}
\]

\[
\begin{align*}
\text{24} & \xrightarrow{h\nu, Pr NH_2} \text{25} + \text{26} \\
\end{align*}
\]

\[
\begin{align*}
\text{27} & \quad \text{28}
\end{align*}
\]

Fig. 1 Sequential spectra from irradiation of 2.5 x 10^{-4} M solution of 27 in n-propylamine in a quartz cuvet using a Philips HPK 125 W lamp. Irradiation times were 0, 2, 4, 8, 16, 24, 32, 64 and 128 min, respectively.

ment did not occur under these conditions and in the absence of a base photoisomerization could not be observed. The product formation can be rationalized as indicated in Scheme 8.

Interaction of a base with \( \mathfrak{Z} \) will result in the abstraction of H(4a) or H(4b). The developing anion will be strongly stabilized by the formation of an aromatic unit. Simultaneous or subsequent protonation will lead to the intermediates 29a-c, which by a second deprotonation/protonation step can be converted into the isomers 17, 18, 27 and 28.
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.

With a strong base (CH\(_3\)O\(^-\)) 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\(_3\)O\(^-\) is increased.

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

The observed substituent effect can then be ascribed to the increased (CH₃, OCH₃) or decreased (CF₃) 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 26→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 Et₃N is about four times better than by n-PrNH₂ in hexane, the quantum yield of isomerization in Et₃N is only about half of that in n-PrNH₂.

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 photoproduct parallels their influence on the quantum yield of formation of the primary cyclization product.

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 S₁-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 Fischer.

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 σπ-value tend to enhance
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 stilbenes$^{10}$, where a decrease in $\Phi_{rel}$ was observed with increasing magnitude of $\sigma_p$.

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 $I_2$ 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 Mallory$^{19}$
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 \(22_1\) and \(22_{11}\) (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 \(-25^\circ C, 8.0\) at \(197^\circ C\); for \(221 1.0\) at \(-25^\circ C\) and \(3.0\) at \(197^\circ C\).) This indicates that no selective excitation of ground state rotamers occurs. According to the NEER principle equilibration of excited rotamers is not likely as is verified for 1,2-di(2-naph-
thyl)ethylene by Fischer^20. 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 22-3111 or 31IV 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 S0-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 (kDOP), ACTIVATION ENERGIES Ea AND ACTIVATION ENTROPIES ΔS* FOR THERMAL RING OPENING OF SUBSTITUTED DHP'S (31) IN METHANOL

<table>
<thead>
<tr>
<th>Compound</th>
<th>Substituent in product</th>
<th>10^4k</th>
<th>Temp (°C)</th>
<th>Ea (kJ/mol)</th>
<th>ΔS* (J/mol. °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22a</td>
<td>H</td>
<td>3.7</td>
<td>20</td>
<td>45.2</td>
<td>-164.4</td>
</tr>
<tr>
<td>b</td>
<td>3-CF3</td>
<td>3.3</td>
<td>20</td>
<td>51.9</td>
<td>-142.2</td>
</tr>
<tr>
<td>f</td>
<td>3-CH3</td>
<td>3.9</td>
<td>20</td>
<td>60.0</td>
<td>-116.3</td>
</tr>
<tr>
<td>i</td>
<td>2-Br</td>
<td>1.2</td>
<td>11</td>
<td>60.2</td>
<td>-114.2</td>
</tr>
<tr>
<td></td>
<td>4-Br</td>
<td>3.0</td>
<td>-16</td>
<td>27.2</td>
<td>-213.0</td>
</tr>
<tr>
<td>l</td>
<td>2-OCH3</td>
<td>1.2</td>
<td>11</td>
<td>61.9</td>
<td>-109.2</td>
</tr>
<tr>
<td></td>
<td>4-OCH3</td>
<td>8.3</td>
<td>11</td>
<td>32.5</td>
<td>-199.6</td>
</tr>
</tbody>
</table>

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 Eact-values show a linear, isokinetic relationship to -ΔS*-values. No correlation with Hammett σ-constants is found.

Comparison of the rates of thermal decay with the estimated rates of oxidation (at 11 °C: kox = 5 x 10^-2 [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-l 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-l 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 110^-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 bands113 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 states\textsuperscript{22}, whereas such a configuration will not be attainable for \textsuperscript{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 uneffectted by the I\textsubscript{2} 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 present\textsuperscript{23} but in a ratio of 1:1 in the presence of 100 mol \% iodine (Scheme 11).

Scheme 11

\[ \begin{align*}
32 & \quad \xrightarrow{\text{CH}_3} \quad 33 + 34 \\
35 & \quad \xrightarrow{\text{CH}_3} \quad 36 + 37
\end{align*} \]

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 time\textsuperscript{24}, 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 principle\textsuperscript{25}. 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-vinylstyrlbenes 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%.

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.

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-isomers.

Vinyl stilbenes substituted at the β-position 44 are photo unreactive, with the exception of 45.
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]hexene. 2-Vinylstilbenes substituted at both ortho positions of the β-ring are photostable as the β-substituted compounds. 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 (δ = 5.62 ± 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 Δ(δH(1)-δH(2)) as the parameter describing the state of the conformational equilibrium in the individual compounds.

In Figure 3 the Δδ-values for cis- as well as trans-isomers are related to the type of photoreaction for these compounds. The Figure shows that the Δδ-values of the cis-isomers correlate rather well with the photochemical behaviour. β-Substituted compounds and 2',6'-disubstituted vinylstilbenes, all being photostable, have Δδ-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.
Δδ-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 Δδ-values might be an indication that the (2+2) cycloaddition occurs mainly from C. Larger Δδ-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 Δδ-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]hexene18. 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 Δδ-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

\[
\begin{align*}
\text{C}_6\text{H}_6 & \xrightarrow{h\nu} \text{dimers} \\
\text{SiO}_2 & \xrightarrow{h\nu} \text{48} \\
& \text{49} + \text{50}
\end{align*}
\]

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