

## PHOTOCHEMISTRY OF 2-VINYLSILBENES: CONFIGURATIONAL AND CONFORMATIONAL CONDITIONS FOR THE [2 + 2]-PHOTOCYCLOADDITION INTRAMOLECULAR TRAPPING OF THE TWISTED SINGLET STATE OF STILBENE

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(Received October 10, 1984; in revised form January 10, 1985)

### Summary

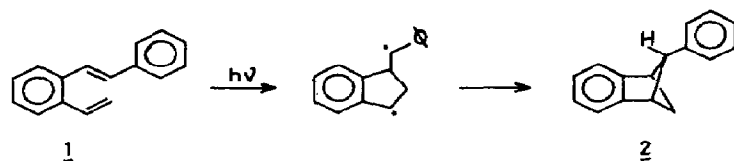
The photoproduct formation and relative reaction rates of 2-vinylstilbenes bearing alkyl substituents at the vinyl group are compared. The normal photoproduct, a 5-*exo*-phenylbenzobicyclo[2.1.1]hex-2-ene, appears to originate from the conformer 1-*s-trans*-(styryl)-2-*s-cis*-(vinyl)benzene.

The vinyl moiety has to be in the E configuration (when applicable); the configuration of the stilbene moiety is irrelevant for formation of the product, which can be regarded as the intramolecular trapping of the twisted singlet biradical of stilbene by the vinyl group.

According to this concept 2-(1-cycloheptenyl)stilbene forms 1,6-pentamethylene-5-*exo*-phenylbenzobicyclo[2.1.1]hex-2-ene. However, 2-(1-cyclopentenyl)stilbene and 2-(1-cyclohexenyl)stilbene do not form any photocyclization product. This is ascribed to a poor orbital overlap and/or the occurrence of other relaxation processes of the intermediate biradical.

### 1. Introduction

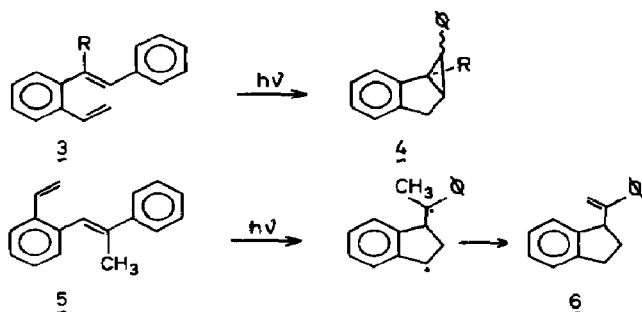
Investigations of the photochemistry of 2-vinylstilbenes and several derivatives have been reported previously [1 - 6]. It was shown that the parent compound (1) and derivatives which are free from steric hindrance or show only moderate steric interactions give benzobicyclo[2.1.1]hexene having the phenyl substituent in the 5-*exo*-position (2) or derivatives of 2 via a radical mechanism. The 5-*endo*-phenyl derivative is only formed in a very small amount (Scheme I) [1].



Scheme I.

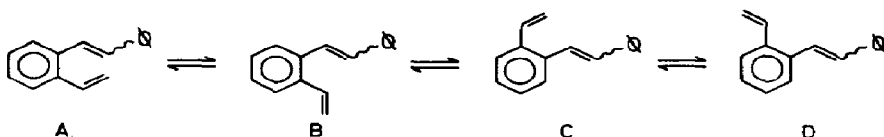
In general,  $\alpha$  substitution products (3) form benzobicyclo[3.1.0]hexene derivatives (4) on irradiation. Small  $\alpha$  substituents give rise to both 5-*endo*-phenyl-4 and 5-*exo*-phenyl-4, whereas bulky  $\alpha$  substituents only give the endo product [2].

As a rule, derivatives of 1 containing a  $\beta$  substituent do not form any intramolecular photocycloaddition product [3]. In general, they undergo only photoisomerization under anaerobic conditions in apolar solvents, except for  $\beta$ -methyl-2-vinylstilbene (5) which forms 1-(1-indanyl)-1-phenylethylene (6) via a first step similar to that in the formation of bicyclo[2.1.1]hexenes (Scheme II).



Scheme II.

From the good correlation between the photobehaviour of more than 20 derivatives of 1 and the chemical shift difference of the methylene protons in the vinyl group ( $\Delta\delta = \delta H(1) - \delta H(2)$ ) we decided that the type of photoreaction depends on the conformation equilibrium in the ground state; the non-equilibration of excited rotamers (NEER) principle [4] should be valid for these photoreactions. From the four extreme conformers of 1 (A - D), which all occur in a *cis* and a *trans* configuration (Scheme III), B is most suited for the formation of 4 whereas D is most probably unreactive.

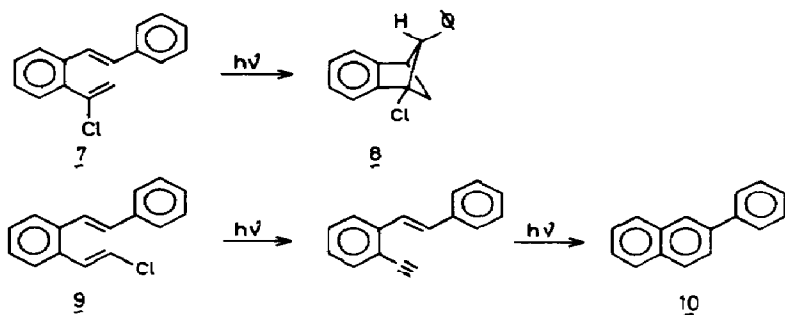


Scheme III.

It is obvious from molecular models that steric crowding will reduce the population of conformers C and D in both *Z* and *E* isomers when an  $\alpha$  substituent is present. In the presence of a  $\beta$  substituent, conformations A and B probably have a low weight, at least in the *E* isomers.

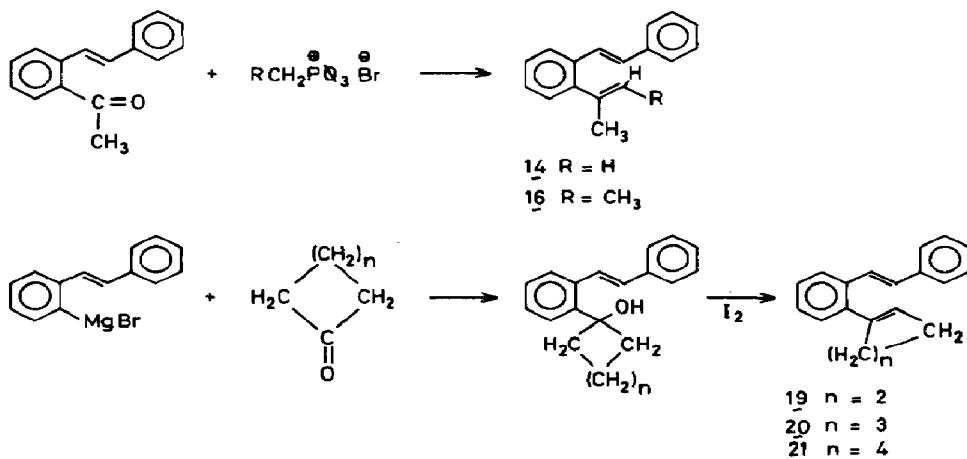
Both conformers A and C seem to be suitable for the formation of 2 (via a radical mechanism). From the rather narrow range of  $\Delta\delta$  values in the *Z* stilbene series which correlate with the formation of derivatives of 2 it seems, however, that conformer C is mainly responsible for this type of reaction.

Until now only a limited number of derivatives of 1, substituted at the vinyl group, has been investigated. The results show large differences in photobehaviour. Irradiation of either the *Z* or the *E* isomer of 2-( $\alpha'$ -chlorovinyl)stilbene (7) gives 1-chloro-5-*exo*-phenylbenzobicyclo[2.1.1]hex-2-ene (8) with a high quantum yield [5]. 2-( $\beta'$ -chlorovinyl)stilbene (9), however, loses hydrogen chloride on irradiation and the resulting acetylenic compound photocyclizes to 2-phenylnaphthalene (10) [6] (Scheme IV). 2-Propenylstilbene (11) forms two photoproducts [1]: 6-*endo*-methyl-5-*exo*-phenylbenzobicyclo[2.1.1]hex-2-ene (11) and 4-*exo*-methyl-6-*endo*-phenylbenzobicyclo[3.1.0]hex-2-ene (13). Both products are apparently formed stereoselectively because out of eight possible isomers only these two are formed (Fig. 1).



Scheme IV.

Finally, 2-isobutenylstilbene (18) is photostable [6]. This restricted number of data suggests at least that substituents in the vinyl group cause a "position-dependent" photoreactivity similar to that observed with substituents at the stilbene double bond of 1. In an attempt to determine the preferential conformation from which derivatives of 1 substituted at the vinyl group undergo photocyclizations, some more alkyl-substituted derivatives (14, 16, 19, 20 and 21) have been synthesized and photolysed. The syntheses were performed using known methods as indicated in Scheme V.



Scheme V.

The results of the irradiation experiments are shown in Fig. 1.

The following methods were used for the elucidation of the structure of the products. By comparing the proton nuclear magnetic resonance

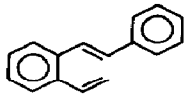
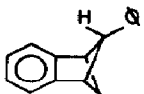
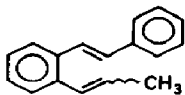
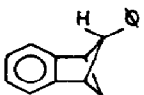
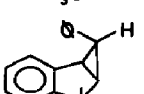
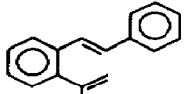
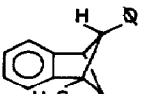
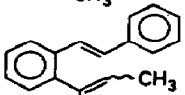
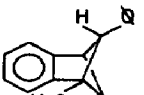
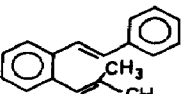
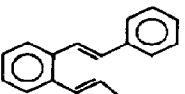
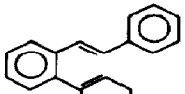
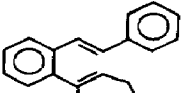
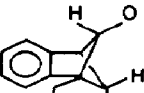
no	compound	no	product	$\Phi$ rel
1		2		1.0
11		12		0.24
		13		
14		15		2.5
16		17		1.4
18		-	-	0
19		-	-	0
20		-	-	0
21		22		0.9

Fig. 1. Products and relative quantum yields of irradiations of substituted 2-vinylstilbenes.

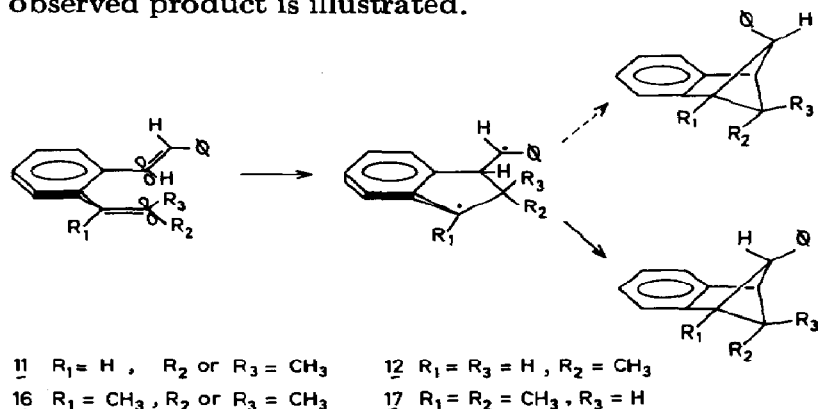
( $^1\text{H}$  NMR) spectra of the photoproducts with those of reference compounds it could be decided whether a bicyclo[3.1.0]hexene or a [2.1.1]hexene was formed. Moreover, pyrolysis of the photoproducts is a straightforward method of obtaining the same information because pyrolysis of bicyclo[2.1.1]hexenes yields vinylstilbenes [1], whereas bicyclo[3.1.0]hexenes in general form 1,2-dihydronaphthalenes under these conditions. The position of the 5-phenyl and 6-methyl groups in derivatives of 2 was deduced from coupling constants.  $J(5\text{-endo},6\text{-endo})$  is rather large (about 7 Hz) whereas  $J(5\text{-endo},6\text{-exo})$  is zero [1]. The position (endo or exo) of the 5-phenyl group was established from the chemical shift data of the benzylic proton H(5) which is at a higher field and of *exo*-H(6) which is at a lower field when the 5-phenyl group is in the endo position. Moreover, the pattern of the aromatic protons in compounds with a 5-*endo*-phenyl group is more extended. In Table 1 the NMR data of the photoproducts are given together with those of some reference compounds.

On comparison of the results shown in Fig. 1 it is obvious that the  $\alpha'$ - $\text{CH}_3$  group of 14 increases the rate of the photoreaction considerably. This must be due to a conformational preference for A and/or C above B and D. A similar increase in the rate has been observed with  $\alpha'$ -chloro-2-vinylstilbene [5]. Because of this substituent effect the photocycloaddition rate becomes comparable with that of the photoisomerization. By separate irradiation of both isomers of 14 it can be established that they give the product at almost equal rates. The formation of 15 from *E*-14 as well as *Z*-14 is in accordance with the radical mechanism.

The equality of the photocyclization rates of the isomers is an indication that conformer C is the more probable precursor for bicyclo[2.1.1]hexene because for this conformation (not in A) the relevant structural relationships are similar in the *Z* and *E* isomers.

Having accepted that C is the preferred conformation for product formation only one of the two possible configurations of the substituted vinyl group in 11 and 16 should participate in the photoreaction as only one derivative of 2 is formed: its formation proceeds quite stereoselectively.

In Scheme VI the course with the least steric hindrance leading to the observed product is illustrated.

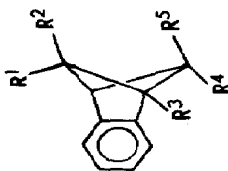


Scheme VI.

TABLE 1

NMR data of some substituted benzobicyclo[2.1.1]hex-2-enes<sup>a</sup> in CDCl<sub>3</sub>

R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	H <sup>5</sup> endo	H <sup>5</sup> exo	H <sup>6</sup> endo	H <sup>6</sup> exo	J(4,5- exo)	J(4,6- exo)	J(5-endo,6- exo)	J(6-endo,6- exo)	δ(CH <sub>3</sub> )
2	H	H	H	H	3.34	3.34	2.40	3.14	—	2.5	7.5	6.3	—
2	Ph	H	H	H	3.44	3.44	2.35	2.66	2.5	2.5	—	5.5	—
8	H	Cl	H	H	—	3.65	2.83	3.43	—	3.0	6.9	6.0	—
15	H	Ph	H	H	—	3.51	2.38	3.04	—	2.4	7.3	6.4	1.31 (s)
12	H	Ph	H	H	3.28	3.28	—	3.62	—	2.25	—	—	0.55 (d)
17	H	Ph	CH <sub>3</sub>	H	—	3.43	—	3.40	—	2.4	—	—	0.50 (d)
22	H	Ph	-(CH <sub>2</sub> ) <sub>5</sub> -	H	—	3.40	—	3.53	—	2.5	—	—	1.24 (s)

<sup>a</sup>Structure:

It is obvious that the first cyclization step determines the configuration at C(6) of the end product, as the intermediate biradical can undergo ring closure at only one side of the five-membered ring. Because in the products 12 and 17 the 6-methyl group is in the endo position the precursors must be 11 and 16 respectively, with the vinyl group in the E configuration. (Upon short irradiation of the isomer of 16, having both double bonds in the E configuration, besides 17 the four stereoisomers of 16 appeared to be present.)

The highly stereoselective photocyclization of 16 can be ascribed to the rate-increasing effect of the  $\alpha'$ -methyl group, as was observed for 14. The stereoselective photocycloaddition of 21 ( $\phi = 0.9$ ) is in complete accordance with the results obtained with 11 and 16. The photobehaviour of compounds 19 and 20 raises, however, the question of why they do not give rise to benzobicyclo[2.1.1]hexenes on irradiation, notwithstanding their fixed E configuration in the "vinyllic" moiety.

There are two considerations which may contribute to an explanation of the unexpected photobehaviour of 19 and 20. Firstly, the primary ring closure requires sufficient overlap between the orbitals of C( $\alpha$ ) and C( $\beta'$ ) to form a bond. Secondly, the flexibility of the intermediate biradical has to be sufficiently high to form the bicyclo[2.1.1]hexene within the lifetime of the intermediate, *i.e.* before it reverts into the stilbene or is converted into other end products.

Both requirements appeared to be relevant to an explanation of the behaviour of 19 and 20. Even after long irradiation of 19 (48 h), unchanged 19 (both E and Z isomers) was recovered in high yield, indicating that cyclization does not take place at all or that the primary cyclization step is highly reversible. Long irradiation of 20 did not lead to a similar high recovery of the starting compound (about 50%) but several other products appeared to be formed in minor amounts, as could be concluded from the number of spots in the thin-layer chromatography of the reaction mixture. Apparently, the first cyclization step is less reversible than with 19, but the intermediate biradical is stabilized by pathways other than the intramolecular radical pairing.

The formation of 6 from 5 (Scheme II) is another example of the existence of other pathways after the first cyclization step.

Since the effect of substituents at all double bond positions of the 2-vinylstilbene skeleton on its photochemical behaviour is known and it appears that this behaviour is controlled by the ground-state conformation of the compound concerned, we have to answer the question of why certain conformations of a 2-vinylstilbene give rise to a benzobicyclo[2.1.1]hex-2-ene and others give rise to a benzobicyclo[3.1.0]hexene. An inspection of the UV spectra of some vinylstilbenes may help in finding the answer.

In general, the UV spectra of *trans*-stilbenes consist of four bands [7, 8]. The longest wavelength band with a large oscillator strength is shifted to a shorter wavelength and  $\epsilon_{\max}$  is reduced in derivatives which show steric hindrance. The other three bands which arise from the various partial

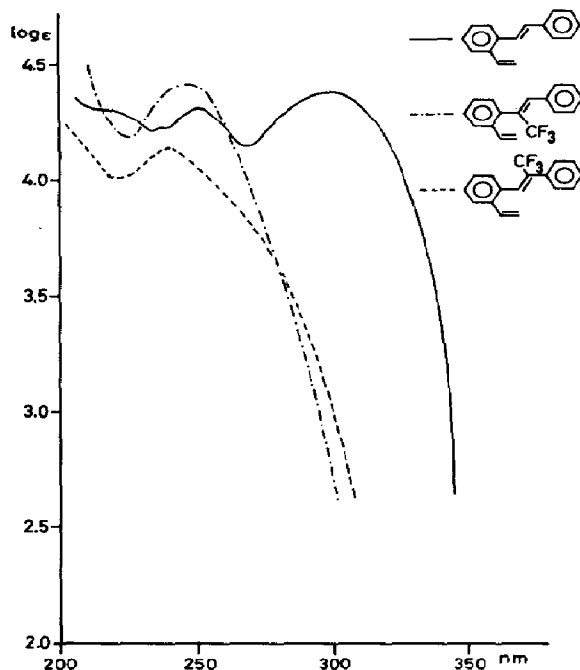


Fig. 2. UV spectra of the *trans* isomers of 2-vinylstilbene, 2-vinyl- $\alpha$ -trifluoromethylstilbene and 2-vinyl- $\beta$ -trifluoromethylstilbene.

chromophores in the molecule do not show a large dependence on steric hindrance. Analogous effects are observed with *cis*-stilbenes [8] but to a much smaller extent. As a consequence of the non-planar conformation of *cis*-stilbene itself, which is apparent from the occurrence of the first absorption band at a shorter wavelength, the effect of additional steric crowding is much smaller.

Inspection of the UV spectra of 2-vinylstilbene (Fig. 2) and its  $\alpha$ - and  $\beta$ -substituted derivatives (the  $\text{CF}_3$  derivatives are used as examples) reveals that the spectra fit quite well into the general pattern found for substituted stilbenes. In comparison with 2-methylstilbenes, the spectra of 2-vinylstilbenes show an additional absorption band at about 230 - 250 nm caused by the additional chromophore; for the  $\alpha$  and  $\beta$  substitution products and also for the *cis* compounds (Fig. 3) this additional absorption is largely hidden under the overlapping stilbene band.

We found (at least in two cases, *viz.*  $\alpha'$ -chloro- and  $\alpha'$ -methyl- vinylstilbene) that benzobicyclo[2.1.1]hexene formation competes with *cis*-*trans* (and *trans*-*cis*) stilbene isomerization of the molecules. Moreover, it is possible that the photoproduct is formed by a reaction from the excited singlet state of vinylstilbene [1]. These facts together with the large stilbene absorption of vinylstilbenes without an  $\alpha$  or a  $\beta$  substituent lead to the conclusion that the reactive state for both the isomerization and the [2 + 2]-cyclization is analogous to the singlet excited state of stilbene, which can be described



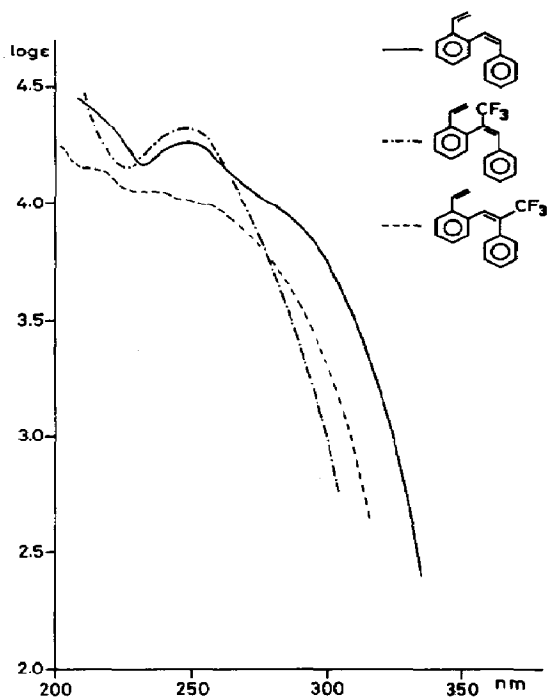


Fig. 3. UV spectra of the *cis* isomers of 2-vinylstilbene, 2-vinyl- $\alpha$ -trifluoromethylstilbene and 2-vinyl- $\beta$ -trifluoromethylstilbene.

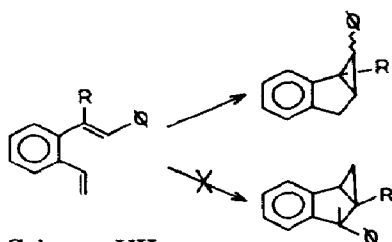
as a singlet biradical having a twisted geometry (for a review and discussion on this subject see ref. 9) in which the two halves of the molecule are more or less perpendicular; the reactive state is named the phantom singlet state ( $^1p$ ).

It can now be anticipated that in the conformation of 2-vinylstilbene in which C( $\beta'$ ) (of the vinyl group) is in the neighbourhood of C( $\alpha$ ) (of the twisted bond) the phantom state can be trapped by the vinyl group. (An intermolecular trapping of the  $^1p$  state of stilbene with 2,3-dihydropyran has been described by Rosenberg *et al.* [10].) The efficiency of this process, which competes with isomerization, depends on the weight of ground state conformer C. Only when the trapping results in a biradical in which the second cyclization can take place will a derivative of 2 be formed. For 19 and 20 such a cyclization step does not occur as argued above.

In principle the formation of 2 can also be explained by assuming a twisted singlet state around the vinyl group (which is more unfavourable with 19). However, since a much higher energy is required for excitation of the styrene system compared with that of the stilbene system this can be rejected. The fact that irradiation of 1 at 360 nm also gives rise to 2 [1] is in agreement with the assumption that a twisted singlet state of stilbene is an intermediate. Therefore, the formation of benzobicyclo[2.1.1]hex-2-ene from 2-vinylstilbene can be regarded as proof of the occurrence of the (twisted) singlet biradical of stilbenes.

Conformations not suited to trapping the singlet biradical cannot form a benzobicyclo[2.1.1]hexene and will only lead to isomerization. For this reason  $\alpha$ - and  $\beta$ -substituted vinylstilbenes do not form derivatives of 2. However, because  $\alpha$ - and  $\beta$ -substituted derivatives of 1 absorb mainly in the lower wavelength region, arising from part of the stilbene chromophore, in principle other photoreactions can occur when they are sterically allowed.

In  $\alpha$ -substituted vinylstilbenes excitation involves mainly the styryl chromophore. Their photobehaviour is expected to be comparable with that of 1,2-divinylbenzene, which forms benzobicyclo[3.1.0]hex-2-enes on irradiation [11]. However, there is a difference. Whereas substituted divinylbenzenes lead to more than one photoproduct,  $\alpha$ -substituted vinylstilbenes form only 6-phenyl- and never 4-phenyl-substituted derivatives of the [3.1.0]hexenes, because in the [4 + 2]-photo-Diels-Alder reaction both vinyl groups can participate as a part of the 4- $\pi$  unit.



Scheme VII.

This is an indication that in the  $\alpha$ -substituted vinylstilbenes styryl excitation concerns only the more highly substituted ( $\alpha$ -halogen,  $\beta$ -phenyl) styryl moiety, possibly because of lower energy, so that the 2-vinyl substituent operates as the dienophile in the [4 + 2]-photocycloaddition.

The possibility that in the present cases the [3.1.0] formation occurs via a suddenly polarized excited state in which there is a rotation around the central double bond [12] seems very unlikely because the central double bond here is part of a benzene ring.

The photostability of the  $\beta$ -substituted 2-vinylstilbenes can be explained in the same way. The position of the absorption band of these derivatives is very similar to those of the  $\alpha$ -substituted vinylstilbenes. Excitation of the  $\beta$ -substituted molecules will concern especially the more highly substituted styryl moiety, which in this case cannot lead to a photoreaction with the vinyl group. Only when a small  $\beta$ -substituted group is present (a methyl group (5)) does the stilbene absorption band occur at an energy sufficiently low to compete with the styryl absorption. In this case trapping of the stilbene biradical can occur, forming a biradical which leads to end product 6 (Scheme II).

## 2. Experimental details

NMR spectra were recorded using a Perkin-Hitachi R-24 or a Bruker WH-90 instrument with  $\text{CDCl}_3$  as the solvent and tetramethylsilane ( $\delta = 0$ ) as an internal standard.

UV spectra were measured using a Cary 15 or a Perkin-Elmer 555 spectrometer; the wavelengths given below are in nanometers. Mass spectra were obtained by using a Varian SM2B or a Finnigan 2000 mass spectrometer; the relative intensities are given below in parentheses.

The irradiations were performed in a Rayonet RPR-100 or an RPR-200 photoreactor fitted with 300 nm lamps using Pyrex vessels. The anaerobic irradiations were carried out in an argon atmosphere. Oxygen was removed from the argon by using a BTS catalyst, and it was dried over phosphorus pentoxide, silica and potassium hydroxide.

Alumina (Baker) or silica (Merck, 0.063 - 0.200 mm) was used for chromatographic separations. The syntheses of 1, 11 and 18 have been described previously (see ref. 1 for 1 and 11 and ref. 13 for 18).

### 2.1. *trans*-2-(2-Propenyl)stilbene (*trans*-14)

2-Acetylstilbene was prepared according to Reid *et al.* [14] and was then used in a Wittig reaction with methylenetriphenylphosphorane which had been made by the Adlercreutz method [15]. After purification by chromatography over silica the yield was 70%. ( $^1\text{H NMR}$ :  $\delta$  = 2.11 (broad s,  $\text{CH}_3$ , 3H), 4.88 (m,  $\text{H}^2$ , 1H), 5.28 (m,  $\text{H}^1$ , 1H), 6.95 (d,  $\text{H}_\alpha$ , 1H), 7.10 - 7.77 (m, aromatic +  $\text{H}_\beta$ , 10H). UV (methanol):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 325 (3.79 sh), 310 (4.10 sh), 297 (4.16), 225 (4.00). Mass spectrum: 220 (54%), 206 (15), 205 (85), 204 (17), 203 (16), 129 (100), 128 (43), 127 (18), 115 (22), 91 (68), 77 (22);  $\text{M}^+$  calculated for  $\text{C}_{17}\text{H}_{16}$ , 220.125;  $\text{M}^+$  found, 220.121.)

### 2.2. *cis*-2-(2-Propenyl)stilbene (*cis*-14)

*Cis*-2-carboethoxystilbene, obtained by irradiation of the *trans* isomer under argon in hexane at 360 nm, was added to a solution of methylmagnesium iodide in ether. After boiling for 1 h and the usual work-up, dimethyl-(2-styrylphenyl)carbinol was obtained in 80% yield. The carbinol was dissolved in formic acid. After 1 h, water was added and *cis*-14 was isolated by extraction with toluene. After washing the toluene solution with sodium carbonate and water and drying, the solvent was evaporated and the residue was purified by carrying out chromatography over silica. ( $^1\text{H NMR}$ :  $\delta$  = 2.10 (broad s,  $\text{CH}_3$ , 3H), 4.99 (m,  $\text{H}^2$ , 1H), 5.20 (m,  $\text{H}^1$ , 1H), 6.57 and 6.61 (AB pattern,  $\text{H}_\alpha + \text{H}_\beta$ , 2H), 7.0 - 7.3 (m, aromatic, 9H). UV (methanol):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 275 (3.96), 2.04 (4.36).)

### 2.3. 2-(2-But-2-enyl)stilbene (16)

The Wittig reaction of 2-acetylstilbene and ethylidenetriphenylphosphorane gave 16 as a mixture of four isomers in 55% yield. By partial separation on silica gel a mixture of two isomers, both having the *trans* configuration in the stilbene moiety, could be isolated. ( $^1\text{H NMR}$ :  $\delta$  = 1.33 (d of d, *Z*- $\beta'$ - $\text{CH}_3$ ), 1.80 (d of d, *E*- $\beta'$ - $\text{CH}_3$ ), 1.93 (s,  $\alpha'$ - $\text{CH}_3$ , 3H), 5.53 (m, vinyl, 1H), 6.77 - 7.83 (m, aromatic +  $\text{H}_\alpha + \text{H}_\beta$ , 11H). UV (methanol):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 308 (4.31), 224 (4.21), 202 (4.34). Mass spectrum: 234 (50%), 220 (20),

219 (100), 205 (22), 204 (36), 203 (20), 202 (19), 178 (10), 143 (79), 141 (22), 128 (73), 119 (46), 117 (47), 115 (25), 105 (20), 91 (45);  $M^+$  calculated for  $C_{18}H_{18}$ , 234.141;  $M^+$  found, 234.140.)

#### 2.4. 2-(1-Cyclopentenyl)stilbene (19)

Magnesium (0.5 g) was added to a solution of 2-bromostilbene (5.2 g) in dry tetrahydrofuran. When all the magnesium had disappeared the solution was cooled and cyclopentanone (4.0 g) was added dropwise. The mixture was refluxed for 1 h. Then the turbid solution was cooled and the magnesium salt was hydrolysed with a saturated aqueous solution of ammonium chloride. The reaction mixture was extracted with dichloromethane, and the organic layer was washed with water and dried over calcium chloride. The solvent was evaporated and the residue chromatographed over silica. Elution with carbon tetrachloride gave unreacted 2-bromostilbene and a small amount of stilbene. Elution with dichloromethane gave 2-(1-hydroxycyclopentyl)stilbene. After evaporation of the solvent the crude carbinol was dissolved in carbon tetrachloride; iodine was added and the mixture was refluxed for 2 h. After evaporation of the solvent the residue was chromatographed over alumina. Elution with carbon tetrachloride gave *trans*-19 in 50% yield. ( $^1H$  NMR:  $\delta$  = 1.5 - 2.1 (m,  $CH_2$ , 2H), 2.1 - 2.8 (m,  $CH_2$ , 4H), 5.71 (m, vinyl, 1H), 6.8 - 7.8 (m, aromatic +  $H_\alpha$  +  $H_\beta$ , 11H). UV (methanol):  $\lambda_{max}$  (log  $\epsilon$ ) = 326 (3.32), 286 (3.89), 254 (3.96), 218 (4.07). Mass spectrum: 246 (100%), 218 (12), 198 (44), 197 (18), 170 (13), 169 (17), 155 (19), 141 (12), 115 (8), 91 (9);  $M^+$  calculated for  $C_{19}H_{18}$ , 246.141;  $M^+$  found, 246.137.)

#### 2.5. 2-(1-Cyclohexenyl)stilbene (20)

In the same way as described above the Grignard compound of 2-bromostilbene and magnesium was reacted with cyclohexanone. Treatment of the resulting carbinol with iodine gave *trans*-20 which was purified by chromatography. ( $^1H$  NMR:  $\delta$  = 1.5 - 2.1 (m,  $CH_2$ , 4H), 2.1 - 2.7 (m,  $CH_2$ , 4H), 5.66 (m, vinyl, 1H), 6.9 - 7.8 (m, aromatic +  $H_\alpha$  +  $H_\beta$ ). UV (methanol):  $\lambda_{max}$  (log  $\epsilon$ ) = 310 (3.97 sh), 2.88 - 2.92 (4.05), 252 (3.80), 220 (4.10). Mass spectrum: 260 (73%), 231 (13), 217 (57), 201 (33), 169 (73), 141 (100), 128 (32), 119 (27), 117 (33), 115 (39), 91 (60);  $M^+$  calculated for  $C_{20}H_{20}$ , 260.156;  $M^+$  found, 260.154.)

#### 2.6. 2-(1-Cycloheptenyl)stilbene (21)

In a way analogous to that described for 19, *trans*-21 was prepared from cycloheptanone as the ketone. ( $^1H$  NMR:  $\delta$  = 1.4 - 2.1 (m,  $CH_2$ , 6H), 2.1 - 2.7 (m,  $CH_2$ , 4H), 5.83 (t of m, vinyl, 1H), 6.9 - 7.66 (m, aromatic +  $H_\alpha$  +  $H_\beta$ , 11H). UV (methanol):  $\lambda_{max}$  (log  $\epsilon$ ) = 328 (3.54), 286 (4.09), 252 (4.00), 220 (4.27). Mass spectrum: 274 (100%), 231 (29), 218 (17), 217 (40), 215 (24), 202 (20), 183 (46), 141 (80), 115 (20), 91 (43);  $M^+$  calculated for  $C_{21}H_{22}$ , 274.172;  $M^+$  found, 274.164.)

## 2.7. Irradiations

For irradiation in a spectrophotometer cuvette, the substances were dissolved in hexane then boiled for several minutes and cooled while passing through a stream of oxygen-free argon. The cuvettes were filled with the cooled solution under argon and were stoppered and irradiated using a high pressure mercury lamp for short time intervals. Then the UV spectrum was measured. All compounds showed a rapid trans-cis isomerization. On prolonged irradiation of compounds 14, 16 and 21 the spectrum changed into that of an unconjugated benzene derivative (characteristic bands around 250 nm). With 18, 19 and 20 the spectrum did not change even after 3 h. Longer irradiations led to a decrease of the extinction owing to destruction.

Irradiation of all substances dissolved in hexane without removing air resulted in spectra in which the characteristic peaks of phenanthrene were present.

The relative quantum yields were measured by irradiating the compounds in quartz tubes of volume 50 ml ( $c = 10^{-3}$  M in hexane) in the merry-go-round of the RPR-100 photoreactor fitted with 300 nm lamps. The composition of the irradiation mixture was determined from the NMR spectra because gas-liquid chromatography re-converts the bicyclohexenes into the stilbenes. Compounds 19 and 20 gave no cycloaddition product even after 20 h under conditions in which 1 gave 35% 2 in 3 h. The results are given in Fig. 1.

## 2.8. Determination of the precursor for the photocycloaddition reaction

The ratio of the absorbances at 300 nm of *cis*-14 and *trans*-14 is 0.35. Irradiation of equimolar solutions of *cis*-14 and *trans*-14 ( $c = 10^{-3}$  M in hexane) for 60 s and 20 s respectively gave equal amounts of 15 ( $4 \pm 2\%$ ). By employing such short irradiation times interference from *cis*-*trans* isomerization is avoided. Extending the reaction times to 150 and 50 s gave a similar result;  $8 \pm 2\%$  product had been formed from both stereoisomers.

For the isolation of the photoproducts, irradiations were performed in quartz tubes of volume 0.5 l. After evaporation of the solvent the residue was chromatographed over silica. The products were eluted with hexane. Compounds 1, 11, 16 and 21 gave about 70% cycloaddition product after 6 h irradiation.

The products were identified from their NMR spectra (see Fig. 1) and from their thermolysis products. Heating at 150 - 200 °C of all products formed gave the starting compounds, as detected by NMR and UV spectroscopy. Even thermolysis of the photoproducts of 16 and 21, which might give rise to a mixture of isomers, besides some destruction products gave mainly the original compound.

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