

## PHOTOCHEMISTRY OF 2-VINYLSILBENES: IMPORTANCE OF THE GROUND STATE CONFORMATION FOR THE TYPE OF PHOTOREACTION

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### Summary

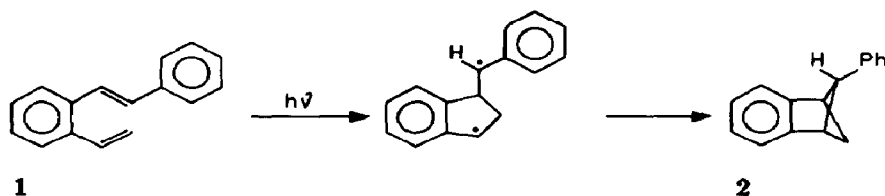
Previous studies on the photochemistry of 2-vinylstilbenes have been extended to  $\beta$  substitution products.  $\beta$ -Methyl-2-vinylstilbene yields 1-(1-indanyl)-1-phenylethene via a radical mechanism which is related to the photochemical behaviour of the parent compound.  $\beta$ -Chloro-2-vinylstilbene undergoes dehydrohalogenation. Other  $\beta$  substitution products in apolar solution do not undergo any other photoreaction than *cis-trans* isomerization.

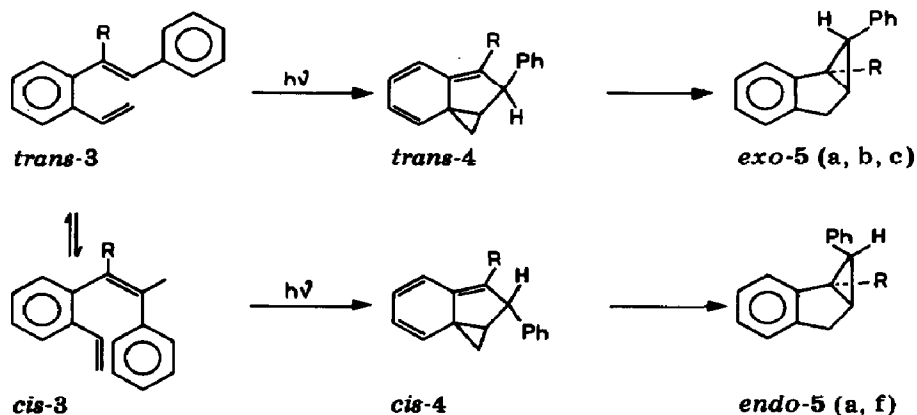
The varying photochemical behaviour of a large number of 2-vinylstilbenes could be related to the difference between the chemical shifts of the methylene protons in the vinyl residue, especially for the *cis* isomers. This has been explained by a predominant influence of the ground state conformation on the course of the photoreactions in this type of compound.

### 1. Introduction

In previous papers on the photochemistry of 2-vinylstilbenes we described the photochemical behaviour of the parent compound **1** [1], a series of  $\alpha$  substitution products **3** [2, 3] and some 2-vinylstilbenes substituted in the  $\beta$  phenyl ring [1].

Irradiation of **1** yields *exo*-5-phenylbenzobicyclo[2.1.1]hex-2-ene **2** as the main product, formed via a radical mechanism:

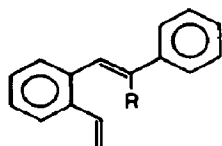




The  $\alpha$  substitution products **3** (**3a**, R  $\equiv$  Cl (the main photoreaction of this compound is dehydrohalogenation (see ref. 4)); **3b**, R  $\equiv$  CN; **3c**, R  $\equiv$  Me; **3d**, R  $\equiv$  CF<sub>3</sub>; **3e**, R  $\equiv$  COOH; **3f**, R  $\equiv$  COOMe), however, give 6-phenylbenzobicyclo[3.1.0]hex-2-enes [**5**] via a [4 + 2] photocycloaddition followed by a vinylcyclopropane rearrangement. With small  $\alpha$  substituents (**3a** - **3c**) the product is obtained as a mixture of the *endo* and the *exo* isomer; with larger substituents (**3d** - **3f**) only *endo-5* is isolated. Introduction of one small *ortho* substituent (Cl, vinyl) in the  $\beta$  phenyl group of **1** has no serious effect on the course of the photoreaction; a substituted benzobicyclo[2.1.1]hex-2-ene is the main primary photoproduct. 2',6'-Disubstituted 2-vinylstilbenes, however, do not yield any photocyclization product.

The varying results evidently could not be ascribed to electronic effects of the substituents; they had to be due to steric factors. It was assumed that the introduction of an  $\alpha$  substituent in **1** leads to another preferred ground state conformation, resulting in a different course of the photoreactions of **1** and **3**. The influence of the size of the  $\alpha$  substituents on the *endo-to-exo* ratio in the product **5** was ascribed to an effect on the reactivity of the *trans* isomer (*trans-3*) either in the first step or in the second step.

In this paper the usefulness of a concept relating the photoreactivity of 2-vinylstilbenes to steric factors is further tested by an extension of the available data to a series of  $\beta$  substitution products **6** - **12**:



**6**, R  $\equiv$  CF<sub>3</sub>  
**7**, R  $\equiv$  CN  
**8**, R  $\equiv$  COOH

**9**, R  $\equiv$  COOMe  
**10**, R  $\equiv$  OMe  
**11**, R  $\equiv$  Me

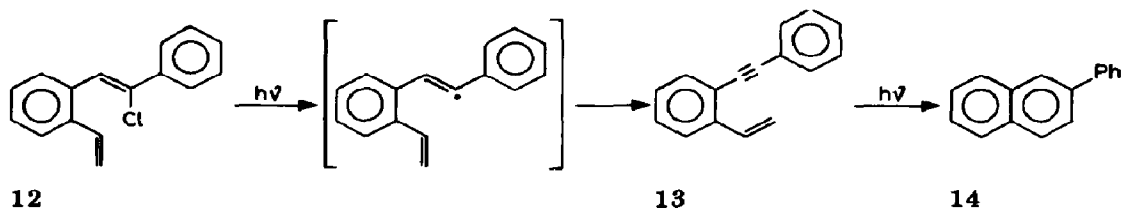
**12**, R  $\equiv$  Cl

The syntheses of **7** and **12** have been given previously [4, 5]. The preparation of the other compounds was carried out via known methods as described in Section 3.

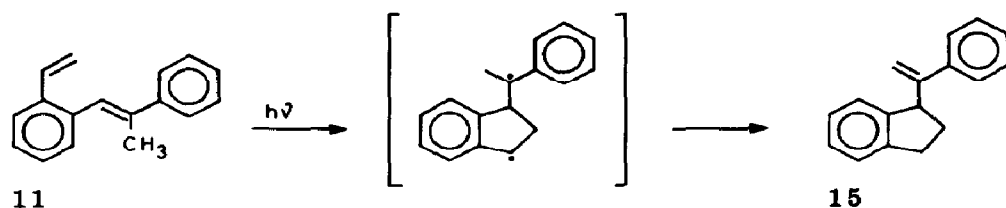
### 1.1. Irradiations

None of the compounds **6** - **12** yielded a substituted benzobicyclo[2.1.1]hex-2-ene or a benzobicyclo[3.1.0]hex-2-ene on irradiation under the

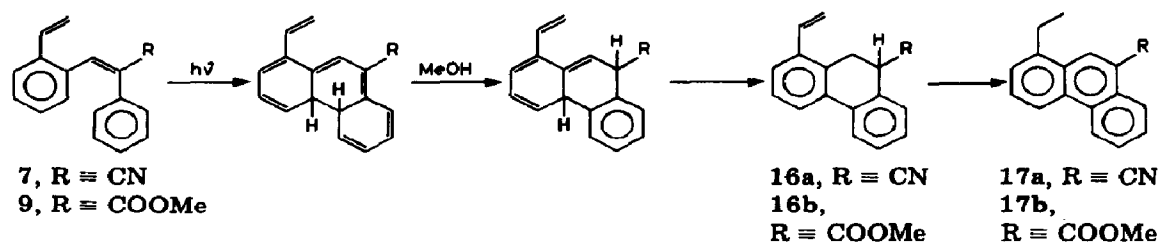
usual conditions (deaerated  $10^{-3}$  M solutions in hexane). In the experiments with 6, 7, 9 and 10 only *cis-trans* isomerization was observed. Very long irradiation (30 h) of the carboxylic acid 8 in a mixture of hexane and benzene gave a low yield (15%) of *unsubstituted* 2, apparently due to decarboxylation of the starting compound. The chloro compound 12 gave mainly the same photoproducts as previously found [4, 6] in irradiation experiments with  $\alpha$ -chloro-2-vinylstilbene 3a, *i.e.* 2-vinyldiphenyl acetylene 13 originating from the fast photo-elimination of HCl and 2-phenylnaphthalene 14 formed through photocyclization of 13:



Irradiation of the methyl derivative 11 also led to disappearance of the starting compound. The nuclear magnetic resonance (NMR) spectrum of the main product (63%) contained a complex pattern for nine aromatic protons ( $\delta = 6.55 - 7.58$  ppm) and two signals belonging to coupled olefinic protons ( $\delta = 4.90$  ppm and  $\delta = 5.33$  ppm;  $J = 1.35$  Hz). One of them ( $\delta = 4.90$  ppm) was also coupled ( $J = 1.1$  Hz) with a methine proton occurring as a double triplet at  $\delta = 4.82$  ppm ( $J = 1.1$  Hz,  $J = 7$  Hz). At higher field two multiplets at  $\delta = 1.75 - 2.58$  ppm (2 H) and  $\delta = 2.78 - 3.00$  ppm (2 H) were present. The data point to 1-(1-indanyl)-1-phenylethene 15 which can be formed via a biradical similar to that which occurs in the photocyclization of 1. Hydrogen exchange instead of ring closure in the biradical will then lead to 15:



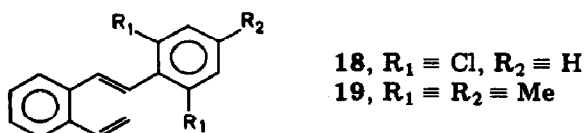
Irradiations of 7 and 9 under argon in a *protic* solvent (MeOH) gave the corresponding 9-substituted 1-vinyl-9,10-dihydrophenanthrenes 16, which converted completely into 9-substituted 1-ethylphenanthrenes 17 on longer irradiation (with 9 ring closure proceeds partly at the substituted *ortho* position, leading to 9-carbomethoxyphenanthrene):



An analogous reaction has been observed for stilbenes containing an enolizable  $\alpha$  substituent [7], but for  $\alpha$ -cyanostilbene the addition of an acid (HCl) to the methanolic solution is required.

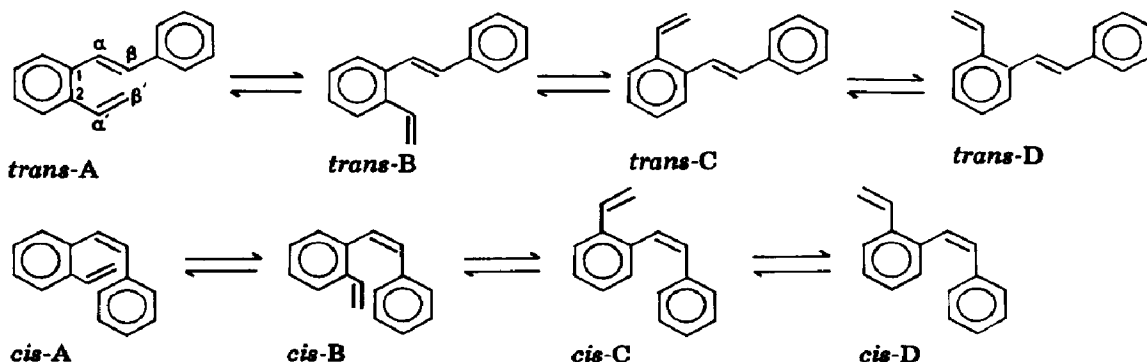
## 2. Discussion

It is clear that the comparable behaviour of 2-vinylstilbenes containing an electron-donating or an electron-accepting  $\beta$  substituent (*e.g.* 9 and 10) cannot be explained by electronic factors. Most of the  $\beta$  substitution products show a reluctance to undergo any photocyclization, in common with 2',6'-disubstituted 2-vinylstilbenes [1] such as 18 and 19:



In both types of compounds (6 - 12 and 18 and 19) the steric factors will be comparable, as appears from the similar hypochromic and hypsochromic shifts of the UV maximum in stilbene on introduction of either an  $\alpha$  substituent or two *ortho* substituents into the same ring [8, 9]. Therefore, it is reasonable to ascribe the differences in the photochemical behaviour of 1 and its  $\beta$  substitution products again to steric factors. The primary photo-reaction of 11, which has the smallest  $\beta$  substituent of our series, fits well into such an explanation. (Similar behaviour expected for 12 is masked by fast photodehydrohalogenation.)

Vinylstilbenes occur in *cis* and *trans* configurations, which equilibrate on irradiation, and in solution several conformations are possible for both isomers. The four extreme conformations for both *cis*- and *trans*-2-vinylstilbene are pictured as follows:



Although all conformations tend to coplanarity as a consequence of the conjugation in the basic system most of the conformers cannot be completely planar for steric reasons. This implies that the above formulae are projections of three-dimensional structures. A and B, which interconvert by rotation around the C(2)—C( $\alpha'$ ) bond, are different, however, because they

are on different sides of the labile structure, in which the  $\alpha$  phenyl ring and the vinyl moiety are perpendicular to each other, and C and D, B and D and A and C are different in a similar way.

Steric effects of the substituents can cause further deviation from coplanarity in any of the conformations, making them slightly different from those of the parent compound. Because the effects will be different in the individual conformers, they can also cause shifts in the conformational equilibria.

On irradiation of 2-vinylstilbenes by light with a bandwidth of several nanometres all the conformers will be equally excited because they do not differ much in UV absorption. In the excited state the molecules 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 the Hammond postulate the transition state of any photo-reaction will also resemble the ground state conformation because it must be an exothermic process. According to this reasoning, which involves application of the non-equilibration of excited rotamers (NEER) principle [10], it can be anticipated that only conformations A and C are suited for the formation of a benzobicyclo[2.1.1]hex-2-ene. In these conformers C( $\alpha$ ) and C( $\beta'$ ) are at relatively short distance whereas slight deviation from coplanarity and small torsion around the central bond (C( $\alpha$ )—C( $\beta$ )) bring the orbitals involved in the bond formation into the appropriate orientation. Another possibility for A might be electrocyclic ring closure by bond formation between C( $\alpha$ ) and C( $\beta'$ ), but the experimental results show that product formation along this route is not very attractive. Only with  $\alpha$ - or  $\beta$ -phenyl-substituted 2-vinylstilbenes has this route been observed.

For the formation of a benzobicyclo[3.1.0]hex-2-ene, proceeding via [4 + 2] photocycloaddition, conformers B are most suited. In B the distance between C( $\beta$ ) and C( $\alpha'$ ) is relatively short. The conformers D will yield neither of the photocycloaddition products. *cis*-D (and also *cis*-C) can undergo an electrocyclic reaction in the stilbene moiety leading to a phenanthrene derivative, provided that oxidation of the intermediate 4a,4b-dihydrophenanthrene can occur. In general, the conformers D will behave photostably, however, in deaerated solutions.

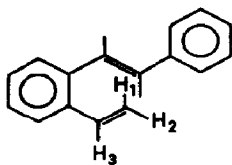
The formation of only one photocyclization product, *i.e.* 2, from the parent compound 1 can only be understood when it is assumed that in this compound the photoreactivity of conformers A and/or C is much higher than that of B, because all the conformers will be present in solution but the photoproduct from B does not arise. However, in  $\alpha$ -substituted vinylstilbenes only the photoproduct of B is formed, which may be ascribed to a strongly reduced occurrence of other conformers (C?) or to an increase in the photoreactivity of B (relative to A and C) or to both factors.

Previously [1] we have supposed that the formation of the benzobicyclo[2.1.1]hex-2-enes occurs mainly from the *cis* isomers. The supposition was based on the difference in photochemical behaviour of the photostable compounds 18 and 19 in comparison with that of 2-vinylstilbenes containing

only one *ortho* substituent in the  $\beta$  phenyl group, which behave similarly to 1. It cannot be seen that the second substituent in 18 and 19 will have much influence on the conformational equilibria of the *trans* isomer. Meanwhile, we have realized that this supposition cannot be generalized to all derivatives of 1, e.g. *trans*- and *cis*-2-( $\alpha'$ -chlorovinyl)stilbene have comparable values for the quantum yield of the photocycloaddition to 1-chlorobenzobicyclo[2.1.1]hex-2-ene [4]. In the formation of [4 + 2] cycloaddition products selective reactivity of *cis* isomers equally cannot be the rule, because some  $\alpha$ -substituted vinylstilbenes give a mixture of *exo*- and *endo*-6-phenylbenzobicyclo[3.1.0]hexene, which points to the photoreactivity of both the *cis* and the *trans* isomer [3].

These considerations illustrate that the vinylstilbene system is much too complex for a coherent explanation of all qualitative and quantitative differences in photochemical behaviour of various types of substitution products according to the NEER principle. All compounds are present as a *cis-trans* mixture, both isomers are involved in a conformational equilibrium between four conformers with different photoreactivity and the *cis-trans* equilibrium, the conformational equilibrium and also the photoreactivity of individual conformers are varied under the influence of substituents.

For this reason we have asked ourselves whether some physicochemical parameter might be found, which depends sufficiently firmly on the spatial relations within an individual vinylstilbene and which might also correlate well with its photochemical behaviour. We considered that the chemical shift of the vinyl protons in the vinylstilbene (Table 1) might serve this purpose. It appeared that the proton at C( $\alpha'$ ) (H(3) in 20)



20

is sometimes hidden under the pattern of aromatic protons. The chemical shift of H(1) is remarkably constant in a large number of vinylstilbenes ( $\delta = 5.62 \pm 0.10$  ppm for *trans* compounds,  $\delta = 5.64 \pm 0.10$  ppm for *cis* compounds).  $\delta$  values for H(2) are strongly variable, however. To eliminate inaccuracies in the measurements and possible solvent effects we chose  $\Delta\delta = \delta_{H(1)} - \delta_{H(2)}$  as the parameter.

In Fig. 1 the  $\Delta\delta$  values for pairs of *cis-trans* isomers are related to the type of photoreaction for the compound in question. The data suggest a better correlation with  $\Delta\delta$  values for the *cis* isomers, especially for photo-stable compounds and compounds yielding benzobicyclo[2.1.1]hex-2-enes. Along the  $x$  axis three groups of five or six points occur within relatively small and well-separated  $\Delta\delta$  intervals.

(1)  $\Delta\delta$  values between 0.25 and 0.32 ppm are found for *cis* isomers of the  $\beta$ -substituted compounds 6, 7 and 9 and the 2',6'-disubstituted com-

TABLE 1

 $\delta$  values of vinyl protons in 2-vinylstilbenes

		$\delta$ (ppm) of vinyl protons in <i>cis</i> -2-vinylstilbenes				$\delta$ (ppm) of vinyl protons in <i>trans</i> -2-vinylstilbenes			
		H(1)	H(2)	H(3)	$\Delta\delta = \delta_{H(1)} - \delta_{H(2)}$	H(1)	H(2)	H(3)	$\Delta\delta = \delta_{H(1)} - \delta_{H(2)}$
Unsubstituted [1]	1	5.54	5.11		0.43	5.55	5.26		0.29
2'-Chloro [1]	21	5.56	5.22		0.34	5.56	5.31		0.25
4'-Me	22	5.66	5.22	6.95	0.44	5.59	5.31	7.03	0.28
4'-Fluoro	23	5.66	5.24	6.73	0.42	5.64	5.37	7.09	0.27
2'-Vinyl [1]	24	5.56	5.22		0.34	5.59	5.30		0.29
2',6'-Dichloro [1]	18	5.61	5.30		0.31	5.61	5.34		0.27
2',4',6'-Trimethyl [1]	19	5.57	5.25		0.32	5.57	5.26		0.31
6-Me [1]	25	5.50	5.08		0.42	5.57	5.17		0.40
$\alpha$ -CN [3]	3b	5.66	5.25	6.82	0.41	5.73	5.35	6.97	0.38
$\alpha$ -Me [3]	3c	5.62	5.13	6.80	0.49	5.69	5.23		0.46
$\alpha$ -COOMe [3]	3f	5.64	5.15	6.69	0.49	5.67	5.22		0.45
$\alpha$ -Cl [3] <sup>a</sup>	3a	5.72	5.25	6.84	0.47	5.75	5.30	7.06	0.45
$\alpha$ -CF <sub>3</sub> [3]	3d	5.62	5.12	6.75	0.50	5.70	5.26	6.88	0.44
$\alpha$ -C <sub>6</sub> H <sub>5</sub> [2]	28	5.52	4.98	6.65	0.54	5.56	5.08		0.48
$\beta$ -OCH <sub>3</sub> <sup>b</sup>	10	5.63	5.26	7.04	0.57	5.64	5.30	7.00	0.34
$\beta$ -CN [5]	7	5.65	5.40	6.85	0.25	5.62	5.44	6.91	0.18
$\beta$ -CH <sub>3</sub> <sup>b</sup>	11	5.65	5.26	7.02	0.39	5.69	5.26	6.92	0.43
$\beta$ -COOH <sup>b</sup>	8	5.63	5.40		0.23				
$\beta$ -COOMe <sup>b</sup>	9	5.66	5.37	6.98	0.29	5.63	5.33		0.30
$\beta$ -Cl [6] <sup>a</sup>	12	5.67	5.31	6.96	0.36	5.69	5.31	6.90	0.38
$\beta$ -CF <sub>3</sub> <sup>b</sup>	6	5.66	5.38	6.91	0.28	5.70	5.37	6.87	0.33
$\beta$ -C <sub>6</sub> H <sub>5</sub> [11]	19	5.51	5.09		0.42	—	—	—	—
1-( $\alpha$ -Naphthyl)-2-( <i>o</i> -vinylphenyl)ethene	26	5.65	5.25	7.04	0.40	5.65	5.40		0.25
1-( $\beta$ -Naphthyl)-2-( <i>o</i> -vinylphenyl)ethene	27	5.69	5.26		0.43	5.66	5.39		0.27

<sup>a</sup>The main photoreaction of this compound is dehydrohalogenation (see ref. 6).<sup>b</sup>See Section 3.

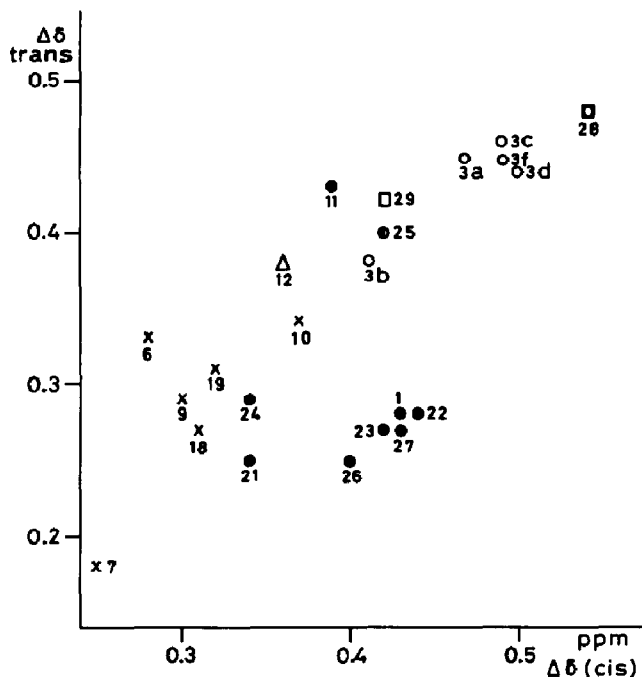


Fig. 1. Correlation between  $\Delta\delta$  ( $\delta_{H(1)} - \delta_{H(2)}$ ) values for the *cis* and *trans* isomers of 2-vinylstilbenes and the type of photoreaction of the compound: x, photostable compound; ●, compound yielding a benzobicyclo[2.1.1]hex-2-ene; ○, compound yielding a benzobicyclo[3.1.0]hex-2-ene; □, △, compound giving another type of photoreaction; ⊙, compound yielding both benzobicyclo[3.1.0]hex-2-ene and benzobicyclo[2.1.1]hex-2-ene; ◻, compound giving both benzobicyclo[3.1.0]hex-2-ene and another type of photoreaction.

pounds 18 and 19, all of which are photostable. The low value of  $\Delta\delta$  fits in well with a strong contribution of the conformer D to the conformational equilibrium, because only in that conformation are both H(1) and H(2) outside the influence of the central olefinic bond and the  $\beta$  phenyl group.

(2)  $\Delta\delta$  values between 0.40 and 0.44 ppm are found for *cis* isomers of the parent compound 1, the 4' substitution products 22 and 23 and the  $\beta$ -naphthyl analogues 26 and 27 which can be seen as 2',3' and 3',4' substitution products of 1 respectively. All these compounds yield benzobicyclo[2.1.1]hex-2-enes, which must arise from A or C. The intermediate value of  $\Delta\delta$  might be an indication that the [2 + 2] cycloaddition occurs mainly from C for *cis* isomers.

(3)  $\Delta\delta$  values between 0.47 and 0.54 ppm are found for the *cis* isomers of the  $\alpha$  substitution products 3a, 3c, 3d, 3f and 28, which yield a benzobicyclo[3.1.0]hex-2-ene as the main product. The high  $\Delta\delta$  values point to higher contributions of the rotamers A and B to the conformational equilibrium. The absence of the photoproduct of A might be another indication that the photoreactivity of A is low and that C is mainly responsible for the formation of [2 + 2] cycloaddition products.

Between the first and the second region some borderline cases are found: two compounds containing only one *ortho* substituent in the  $\beta$



phenyl group (21 and 24) with  $\Delta\delta = 0.34$  ppm which still yield a benzobicyclo[2.1.1]hex-2-ene and two  $\beta$  substitution products containing a relatively small substituent (11 and 12) with  $\Delta\delta = 0.36 - 0.39$  ppm. 11 behaves as a compound of the second group; 12 is a special case because it does not yield any photocycloaddition product as a consequence of fast dehydrohalogenation. The remaining points (3b, 25 and 29) fall within the second region, but the compounds concerned do not behave photochemically as expected. Compound 25 is a true borderline case because it yields a benzobicyclo[3.1.0]hex-2-ene as well as a benzobicyclo[2.1.1]hex-2-ene. It is the only vinylstilbene studied with two *ortho* substituents of comparable size in the  $\alpha$  phenyl ring. By this the stability of the differing conformers will not be very different, which might explain the formation of more than one photoproduct. Compound 29 is a special case. It yields a benzobicyclo[3.1.0]hex-2-ene but the product formation is accompanied by a phenyl shift. Previously, we have argued [11] that the product cannot originate from a [4 + 2] photocycloaddition and subsequent vinylcyclopropane rearrangement. The primary photoreaction must be an electrocyclic reaction, which was indicated above as another possibility for the conformer A. Compound 3b belongs photochemically to the third group. The low  $\Delta\delta$  value may be due to a relatively large anisotropic effect of the cyano substituent.

As stated before the  $\Delta\delta$  values of the *trans* isomers correlate less well with the photochemical behaviour, although also in this series the third group is well separated from the others. Above about 0.35 ppm the stilbenes give benzobicyclo[3.1.0]hexenes, except 12 and 29 which give different reactions, 11 which gives a different product and 25 which is a borderline case. Clearly the mean conformation of the vinylstilbenes which form bicyclo[3.1.0]hexene differs from that of the vinylstilbenes which form [2.1.1]-hexene and from that of the vinylstilbenes which do not react. The similar  $\Delta\delta$  (*trans*) values for the vinylstilbenes which do not react again indicates that conformer C is responsible for the bicyclo[2.1.1]hexene formations, because similar  $\Delta\delta$  (*trans*) values for conformers A and D can be less well understood.

From the observed correlation between the ground state NMR parameter and the type of photoreaction it can be concluded that the ground state conformation of the 2-vinylstilbenes is of predominant influence on the course of the photoreaction.

### 3. Experimental details

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

UV spectra were measured with a Cary 15 or a Perkin-Elmer 555 UV spectrometer; the wavelengths are given in nanometres. Mass spectra were

obtained by using a Varian SM2B or a Finnigan 2000 mass spectrometer.  $m/e$  values are given together with their relative intensities in parentheses.

The irradiations were performed in a Rayonet RPR-100 or RPR-200 photoreactor using 300 nm lamps. The anaerobic irradiations were carried out under an argon atmosphere. The argon was purified from oxygen through a BTS catalyst (manufactured by BASF, F.R.G.) and dried over phosphorus pentoxide, silica and potassium hydroxide.

The photoreactions were monitored by measuring the UV spectra of samples of the reaction mixture after several time intervals.

Alumina (Baker) or silica (Merck; 0.063 - 0.200 mm) preparative thin layer chromatography was used for the chromatographic separations.

### 3.1. $\beta$ -Trifluoromethyl-2-vinylstilbene 6

A Wittig reaction of trifluoroacetophenone (8.7 g) and 2-methylbenzyl-triphenylphosphonium bromide (22.3 g) with 250 ml methanol as the solvent and sodium methoxide (2.8 g) as a base gave after boiling for 14 h a mixture of *cis*- and *trans*-2-methyl- $\beta$ -trifluoromethylstilbene in 75% yield. The procedure of isolating was identical with that described for the  $\alpha$ -trifluoromethyl-2-methylstilbene [3].

The spectroscopic data for the *trans* isomer (colourless oil) are as follows:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta = 2.29$  ppm (singlet (s);  $\text{CH}_3$ ; 3 H),  $\delta = 6.60 - 7.10$  ppm (multiplet (m); aromatic H; 4 H),  $\delta = 7.20$  ppm (s; aromatic H; 5 H),  $\delta = 7.39$  ppm (quartet (q);  $\text{H}_\alpha$ ; 1 H),  $^4J_{\text{HF}} = 2.1$  Hz; UV (methanol),  $\lambda_{\text{max}} = 248$  nm ( $\log \epsilon = 4.01$ ); mass spectrum, 263 (42), 262 ( $\text{M}^+$ , 100), 261 (15), 248 (15), 247 (77), 227 (38), 193 (56), 192 (19), 191 (19), 179 (37), 178 (67), 165 (12).

The spectroscopic data for the *cis* isomer (colourless oil) are as follows:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta = 2.31$  ppm (s;  $\text{CH}_3$ ; 3 H),  $\delta = 7.08$  ppm (s;  $\text{H}_\alpha$ ; 1 H),  $\delta = 7.13 - 7.30$  ppm,  $\delta = 7.30 - 7.70$  ppm (m; aromatic H; 9 H); UV (methanol),  $\lambda_{\text{max}} = 258$  nm ( $\log \epsilon = 3.86$ ),  $\lambda_{\text{max}} = 203$  nm ( $\log \epsilon = 4.94$ ); mass spectrum, 263 (23), 262 ( $\text{M}^+$ , 100), 261 (9), 247 (55), 231 (15), 227 (25), 193 (32), 179 (25), 178 (45), 154 (27).

The products were transformed into the  $\beta$ -trifluoro-2-vinylstilbene 6 in an analogous way to that described for the corresponding  $\alpha$ -substituted 2-methylstilbene. The yield was 68%.

The spectroscopic data for *trans*-6 are as follows:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta = 5.37$  ppm (doublet of doublets (dd); H(2); 1 H),  $\delta = 5.70$  ppm (dd; H(1); 1 H),  $\delta = 6.87$  ppm (dd; H(3); 1 H),  $\delta = 7.15$  ppm (s;  $\text{H}_\alpha$ ; 1 H),  $\delta = 7.21 - 7.61$  ppm (m; aromatic H; 9 H),  $J_{1,2} = 1.2$  Hz,  $J_{2,3} = 12.0$  Hz,  $J_{1,3} = 17.3$  Hz; UV (methanol),  $\lambda_{\text{max}} = 315$  nm ( $\log \epsilon = 2.37$  shoulder (sh)),  $\lambda_{\text{max}} = 270$  nm ( $\log \epsilon = 3.80$  sh),  $\lambda_{\text{max}} = 247$  nm ( $\log \epsilon = 4.13$ ),  $\lambda_{\text{max}} = 200$  nm ( $\log \epsilon = 4.24$ ); mass spectrum, 263 (42), 262 ( $\text{M}^+$ , 100), 261 (15), 248 (15), 247 (77), 227 (38), 193 (56), 192 (19), 191 (19), 179 (37), 178 (67), 165 (12).

The spectroscopic data for *cis*-6 are as follows:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta = 5.38$  ppm (dd; H(2); 1 H),  $\delta = 5.66$  ppm (dd; H(1); 1 H),  $\delta = 6.91$  ppm (dd; H(3); 1 H),  $\delta = 6.67 - 7.80$  ppm (m; aromatic H; 9 H),  $\delta = 7.47$  ppm (s;  $\text{H}_\alpha$ ;

1 H),  $J_{1,2} = 1.2$  Hz,  $J_{2,3} = 12.0$  Hz,  $J_{1,3} = 17.3$  Hz; UV (methanol),  $\lambda_{\max} = 315$  nm ( $\log \epsilon = 2.71$ ),  $\lambda_{\max} = 278$  nm ( $\log \epsilon = 3.80$ ),  $\lambda_{\max} = 260$  nm ( $\log \epsilon = 3.97$  sh),  $\lambda_{\max} = 234$  nm ( $\log \epsilon = 4.05$ ),  $\lambda_{\max} = 214$  nm ( $\log \epsilon = 4.75$ ).

### 3.2. $\beta$ -Carboxy-2-vinylstilbene 8

The Perkin condensation of 2-methylbenzaldehyde and phenylacetic acid yielded  $\beta$ -carboxy-2-methylstilbene in 50% yield (melting point, 165 - 167 °C). This compound was converted into 8 by consecutive bromination with *N*-bromosuccinimide, formation of the phosphonium salt and a Wittig reaction with formaldehyde. The crude product was crystallized from methanol.

The spectroscopic data for *cis*-8 (melting point, 139.5 - 140 °C) are as follows:  $^1\text{H}$  NMR,  $\delta = 5.40$  ppm (dd; H(2); 1 H),  $\delta = 5.63$  ppm (dd; H(1); 1 H),  $\delta = 6.66 - 7.53$  ppm (m; aromatic H, H(3); 10 H),  $\delta = 8.20$  ppm (s;  $\text{H}_\alpha$ ; 1 H),  $\delta = 12.20$  ppm (broad s; COOH; 1 H),  $J_{1,2} = 1.2$  Hz,  $J_{1,3} = 17.5$  Hz,  $J_{2,3} = 11$  Hz; UV (methanol),  $\lambda_{\max} = 287$  nm ( $\log \epsilon = 4.08$ ),  $\lambda_{\max} = 243$  nm ( $\log \epsilon = 4.21$  sh),  $\lambda_{\max} = 221$  nm ( $\log \epsilon = 4.29$ ); mass spectrum, 250 ( $\text{M}^+$ , 79), 238 (11), 232 (26), 205 (20), 204 (100), 203 (63), 202 (47), 201 (37), 200 (9).

### 3.3. $\beta$ -Carbomethoxy-2-vinylstilbene 9

The carboxylic acid 8 was esterified by reflux in benzene, methanol and sulphuric acid for 3 h. After neutralization and evaporation of the solvents the ester was chromatographed on silica with hexane as the eluent. The yield was 35%. The *trans* isomer could not be isolated free of the *cis* isomer.

The spectroscopic data for *cis*-9 (colourless oil) are as follows:  $^1\text{H}$  NMR,  $\delta = 3.82$  ppm (s;  $\text{OCH}_3$ ; 3 H),  $\delta = 5.37$  ppm (dd; H(2); 1 H),  $\delta = 5.66$  ppm (dd; H(1); 1 H),  $\delta = 6.98$  ppm (dd; H(3); 1 H),  $\delta = 6.66 - 7.48$  ppm (m; aromatic H; 9 H),  $J_{1,2} = 1.2$  Hz,  $J_{1,3} = 17.5$  Hz,  $J_{2,3} = 10.8$  Hz; UV (methanol),  $\lambda_{\max} = 290$  nm ( $\log \epsilon = 3.97$ ),  $\lambda_{\max} = 241$  nm ( $\log \epsilon = 4.00$ ),  $\lambda_{\max} = 222$  nm ( $\log \epsilon = 4.10$ ); mass spectrum, 264 ( $\text{M}^+$ , 52), 232 (86), 204 (100), 203 (80), 202 (57), 201 (56).

### 3.4. $\beta$ -Methoxy-2-vinylstilbene 10

A solution of 1.6 g of phenyllithium in hexane was added dropwise to a solution of 8 g  $\alpha$ -methoxybenzyltriphenylphosphonium chloride [12] in tetrahydrofuran with stirring. Then 2.5 g of 2-vinylbenzaldehyde [13] was added to the mixture. After the mixture had been stirred overnight it was worked up as usual and the isomers were separated by chromatography. The total yield was 60%.

The spectroscopic data for *trans*-10 are as follows:  $^1\text{H}$  NMR,  $\delta = 3.58$  ppm (s;  $\text{OCH}_3$ ; 3 H),  $\delta = 5.30$  ppm (dd; H(2); 1 H),  $\delta = 5.64$  ppm (dd; H(1); 1 H),  $\delta = 6.30$  ppm (s;  $\text{H}_\alpha$ ; 1 H),  $\delta = 7.00 - 7.83$  ppm (m; aromatic H; 9 H),  $\delta = 7.00$  ppm (dd; H(3); 1 H),  $J_{1,2} = 1.2$  Hz,  $J_{1,3} = 17.4$  Hz,  $J_{2,3} = 10.8$  Hz; UV (methanol),  $\lambda_{\max} = 291$  nm ( $\log \epsilon = 4.50$ ),  $\lambda_{\max} = 250$  nm ( $\log \epsilon = 4.57$ ).

The spectroscopic data for *cis*-10 are as follows:  $^1\text{H}$  NMR,  $\delta = 3.85$  ppm (s;  $\text{OCH}_3$ ; 3 H),  $\delta = 5.26$  ppm (dd; H(2); 1 H),  $\delta = 5.63$  ppm (dd; H(1); 1 H),  $\delta = 5.87$  ppm (s;  $\text{H}_\alpha$ ; 1 H),  $\delta = 6.86 - 7.44$  ppm (m; aromatic H; 9 H),  $\delta = 7.04$  ppm (dd; H(3); 1 H),  $J_{1,2} = 1.2$  Hz,  $J_{1,3} = 17.4$  Hz,  $J_{2,3} = 10.8$  Hz; UV (methanol),  $\lambda_{\text{max}} = 289$  nm,  $\lambda_{\text{max}} = 247$  nm.

### 3.5. $\beta$ -Methyl-2-vinylstilbene 11

$\alpha$ -Methylbenzyltriphenylphosphonium bromide was prepared by stirring triphenylphosphine (230 g) and  $\alpha$ -bromoethylbenzene (163 g) in 500 ml of chloroform for 16 h. After evaporation of the major part of the solvent the residue was poured into ether. The salt precipitated. It was filtered and dried. The yield was 300 g. A Wittig reaction of this salt and 2-vinylbenzaldehyde [13] gave  $\alpha$ -methyl-2-vinylstilbene 11 in 40% yield.

The spectroscopic data for *trans*-11 (colourless oil) are as follows:  $^1\text{H}$  NMR,  $\delta = 2.08$  ppm (d;  $\text{CH}_3$ ; 3 H),  $\delta = 5.26$  ppm (dd; H(2); 1 H),  $\delta = 5.69$  ppm (dd; H(1); 1 H),  $\delta = 6.92$  ppm (dd; H(3); 1 H),  $\delta = 6.93$  ppm (q;  $\text{H}_\alpha$ ; 1 H),  $\delta = 7.15 - 7.64$  ppm (m; aromatic H; 9 H),  $^4J_{\text{H}_\alpha-\text{CH}_3} = 2$  Hz,  $J_{1,2} = 1.5$  Hz,  $J_{1,3} = 17.4$  Hz,  $J_{2,3} = 10.8$  Hz; UV (methanol),  $\lambda_{\text{max}} = 278$  nm ( $\log \epsilon = 3.99$ ),  $\lambda_{\text{max}} = 246$  nm ( $\log \epsilon = 4.24$ ); mass spectrum, 220 ( $\text{M}^+$ , 100), 206 (21), 205 (89), 204 (36), 203 (37), 202 (37), 191 (19), 190 (14), 189 (20), 169 (20); exact mass,  $220.124 \pm 0.03$ ; theoretical mass, 220.125.

The spectroscopic data for *cis*-11 (colourless oil) are as follows:  $^1\text{H}$  NMR,  $\delta = 2.26$  ppm (d;  $\text{CH}_3$ ; 3 H),  $\delta = 5.26$  ppm (dd; H(2); 1 H),  $\delta = 5.65$  ppm (dd; H(1); 1 H),  $\delta = 6.60$  ppm (broad s;  $\text{H}_\alpha$ ; 1 H),  $\delta = 6.61 - 7.49$  ppm (m; aromatic H; 9 H),  $\delta = 7.02$  ppm (dd; H(3); 1 H),  $^4J_{\text{H}_\alpha-\text{CH}_3} = 1.5$  Hz,  $J_{1,2} = 1.5$  Hz,  $J_{1,3} = 17.4$  Hz,  $J_{2,3} = 10.8$  Hz; UV (methanol),  $\lambda_{\text{max}} = 247$  nm ( $\log \epsilon = 3.91$ ).

## 4. Irradiations

### 4.1. $\beta$ -Cyano-2-vinylstilbene 7

Irradiation of 7 dissolved in hexane under argon at 300 nm resulted in a mixture of the *cis* and *trans* isomers in the ratio 2:1. The product mixture remains unaltered even after 4.5 days of irradiation.

Irradiation of 7 (120 mg) dissolved in methanol under argon at 300 nm for 7 h resulted in 35% 1-vinyl-9-cyano-9,10-dihydrophenanthrene 16a and 35% 1-ethyl-9-cyanophenanthrene 17a. These compounds could not be separated by column chromatography over silica, but by chromatography of enriched fractions over alumina with mixtures of hexane and toluene the isomers could be separated.

The spectroscopic data for 9-cyano-1-vinyl-9,10-dihydrophenanthrene 16a are as follows:  $^1\text{H}$  NMR,  $\delta = 3.15$  ppm (m; H(10); 1 H),  $\delta = 3.49$  ppm (m; H(10); 1 H),  $\delta = 4.04$  ppm (m; H(9); 1 H) (these protons form an ABX pattern with  $J = 11.4$  Hz,  $J = 4.4$  Hz,  $J = -14.8$  Hz),  $\delta = 5.44$  ppm (dd; H(1); 1 H),  $\delta = 5.64$  ppm (dd; H(2); 1 H),  $\delta = 7.01$  ppm (dd; H(3); 1 H),  $\delta =$

7.24 - 7.84 ppm (m; aromatic H; 7 H),  $J_{1,2} = 1.2$  Hz,  $J_{1,3} = 17.4$  Hz,  $J_{2,3} = 11$  Hz; UV (methanol),  $\lambda_{\max} = 316$  nm ( $\log \epsilon = 3.81$ ),  $\lambda_{\max} = 304$  nm ( $\log \epsilon = 3.84$ ),  $\lambda_{\max} = 279$  nm ( $\log \epsilon = 4.28$ ),  $\lambda_{\max} = 258$  nm ( $\log \epsilon = 4.53$ ); mass spectrum, 231 ( $M^+$ , 100), 216 (34), 204 (20), 203 (22), 202 (15), 179 (14); exact mass,  $231.104 \pm 0.003$ ; calculated mass, 231.105.

The spectroscopic data for 1-ethyl-9-cyanophenanthrene 17a are as follows:  $^1\text{H}$  NMR,  $\delta = 1.40$  ppm (triplet (t);  $\text{CH}_3$ ; 3 H),  $\delta = 3.18$  ppm (q;  $\text{CH}_2$ ; 2 H),  $\delta = 7.30 - 7.81$  ppm (m; aromatic H; 4 H),  $\delta = 8.27 - 8.38$  ppm (m; aromatic H; 2 H),  $\delta = 8.55$  ppm (s; H(10); 1 H),  $\delta = 8.65 - 8.79$  ppm (m; aromatic H; 2 H); UV (methanol),  $\lambda_{\max} = 299$  nm ( $\log \epsilon = 3.84$ ),  $\lambda_{\max} = 279$  nm ( $\log \epsilon = 4.28$  sh),  $\lambda_{\max} = 258$  nm ( $\log \epsilon = 4.53$ ); mass spectrum, 231 ( $M^+$ , 68), 217 (23), 216 (100), 204 (21), 203 (38), 190 (18); exact mass,  $231.106 \pm 0.003$ ; calculated mass, 231.105.

#### 4.2. $\beta$ -Carboxy-2-vinylstilbene 8

Compound 8 (250 mg) dissolved in a mixture of hexane and benzene (5:1) was irradiated at 300 nm for 30 h. After evaporation of the solvent the residue consisted of polymeric products and about 15% of 2.

#### 4.3. $\beta$ -Carbomethoxy-2-vinylstilbene 9

Because of the very slight solubility of 9 in hexane only a very dilute solution could be irradiated. No cycloaddition product was detected after evaporation of the solvent.

Dissolved in 500 ml of a mixture of hexane and methanol (10:1) 100 mg of 9 gave after irradiation at 300 nm for 17 h a mixture consisting of several products. The separation of the mixture could not be performed quantitatively, but gave 30% *cis*-9, 20% *trans*-9, 14% 9-carbomethoxy-1-vinyl-9,10-dihydrophenanthrene 16b and 24% of a mixture of 9-carbomethoxyphenanthrene and 1-ethyl-9-carbomethoxyphenanthrene 17b.

The spectroscopic data for 9-carbomethoxy-1-vinyl-9,10-dihydrophenanthrene 16b are as follows:  $^1\text{H}$  NMR,  $\delta = 3.61 - 3.84$  ppm (m; H(10), H(10'), 2 H),  $\delta = 3.97 - 4.10$  ppm (m; H(9); 1 H),  $\delta = 4.07$  ppm (s;  $\text{COOCH}_3$ ; 3 H),  $\delta = 5.58$  ppm (dd; H(2); 1 H),  $\delta = 5.82$  ppm (dd; H(1); 1 H),  $\delta = 7.0 - 7.8$  ppm (m; aromatic H, H(3); 8 H),  $J_{1,2} = 1.2$  Hz,  $J_{1,3} = 17.0$  Hz,  $J_{2,3} = 11.0$  Hz.

The spectroscopic data for 1-ethyl-9-carbomethoxyphenanthrene 17b are as follows:  $^1\text{H}$  NMR,  $\delta = 1.27$  ppm (t;  $\text{CH}_3$ ; 3 H),  $\delta = 3.71$  ppm (q;  $\text{CH}_2$ ; 2 H),  $\delta = 3.80$  ppm (s;  $\text{COOCH}_3$ ; 3 H),  $\delta = 7.3 - 7.8$  ppm (m; aromatic H; 4 H),  $\delta = 8.56 - 8.93$  ppm (m; aromatic H; 4 H). The spectrum of 9-carbomethoxyphenanthrene was in accordance with the data given by Schubert and Fischer [14].

#### 4.4. $\beta$ -Methoxy-2-vinylstilbene 10

Compound 10 (100 mg) dissolved in 50 ml of ether was irradiated under argon at 300 nm. Even after 66 h only a photostationary mixture of the *cis* and *trans* isomers (5.5:4.5) had been formed. Irradiations in methanol

or a benzene-ether mixture also gave no other photoproducts. When no precautions were taken for the neutrality of the solvent during irradiation or work-up some 2-vinylbenzyl phenyl ketone was isolated.

The spectroscopic data for 2-vinylbenzyl phenyl ketone are as follows:  $^1\text{H}$  NMR,  $\delta = 4.37$  ppm (s;  $\text{CH}_2$ ; 2 H),  $\delta = 5.29$  ppm (dd; H(2); 1 H),  $\delta = 5.64$  ppm (dd; H(1); 1 H),  $\delta = 6.85$  ppm (dd; H(3); 1 H),  $\delta = 7.11 - 7.77$  ppm (m; aromatic H; 7 H),  $\delta = 7.97 - 8.10$  ppm (m; aromatic H; 2 H); UV (methanol),  $\lambda_{\text{max}} = 310$  nm ( $\log \epsilon = 2.59$ ),  $\lambda_{\text{max}} = 287$  nm ( $\log \epsilon = 3.14$ ),  $\lambda_{\text{max}} = 277$  nm ( $\log \epsilon = 3.25$  sh),  $\lambda_{\text{max}} = 241$  nm ( $\log \epsilon = 4.15$ ).

#### 4.5. $\beta$ -Trifluoromethyl-2-vinylstilbene 6

Irradiation of 6 dissolved in hexane under anaerobic conditions at 300 nm for different periods resulted only in a 2:1 *cis-trans* mixture of 6. After 22 h about 35% of 6 had been polymerized.

#### 4.6. $\beta$ -Methyl-2-vinylstilbene 11

*trans*-11 (320 mg) dissolved in hexane (500 ml) was deaerated with argon and irradiated at 300 nm in a quartz tube for 70 h. The solvent was evaporated and the residual mixture was separated by column chromatography giving 9% *cis*-11, 5% *trans*-11, 63% 1-(1-indanyl)-1-phenylethene, 5% 1-vinyl-9-methylphenanthrene and 20% polymeric products.

The spectroscopic data for 1-(1-indanyl)-1-phenylethene 15 are as follows:  $^1\text{H}$  NMR,  $\delta = 1.75 - 2.58$  ppm (m;  $\text{CH}_2$ ; 2 H),  $\delta = 2.78 - 3.00$  ppm (m;  $\text{CH}_2$ ; 2 H),  $\delta = 4.32$  ppm (t; CH; 1 H),  $\delta = 4.90$  ppm (q; vinyl H; 1 H),  $\delta = 5.33$  ppm (d; vinyl H; 1 H),  $\delta = 6.55 - 7.58$  ppm (m; aromatic H; 9 H),  $J_{4,4'} = 1.35$  Hz,  $J_{1,4'} = 1.1$  Hz,  $J_{1,2} = 7$  Hz; UV (methanol),  $\lambda_{\text{max}} = 243$  nm ( $\log \epsilon = 3.83$  sh); mass spectrum, 221 (60), 220 ( $\text{M}^+$ , 100), 219 (38), 206 (22), 205 (100), 204 (28), 203 (33), 202 (34); exact mass,  $220.126 \pm 0.003$ ; calculated mass, 220.125.

The spectroscopic data for 9-methyl-1-vinylphenanthrene are as follows:  $^1\text{H}$  NMR ( $\text{CCl}_4$ ),  $\delta = 2.7$  ppm (s;  $\text{CH}_3$ ; 3 H),  $\delta = 5.4$  ppm (dd; H(2); 1 H),  $\delta = 5.7$  ppm (dd; H(1); 1 H),  $\delta = 7.0 - 8.0$  ppm (m; aromatic H, H(3); 7 H),  $\delta = 8.4 - 8.6$  ppm (m; aromatic H; 2 H); mass spectrum, 220 (20), 218 ( $\text{M}^+$ , 21), 205 (21), 203 (26), 192 (100), 191 (47), 178 (26).

## References

- 1 M. Sindler-Kulyk and W. H. Laarhoven, *J. Am. Chem. Soc.*, **100** (1978) 3819.
- 2 M. Sindler-Kulyk and W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas*, **98** (1979) 187.
- 3 P. M. op den Brouw and W. H. Laarhoven, *J. Chem. Soc., Perkin Trans. II*, (1983) 1015.
- 4 P. M. op den Brouw and W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas*, **101** (1982) 58.
- 5 P. M. op den Brouw and W. H. Laarhoven, *J. Org. Chem.*, **47** (1982) 1546.
- 6 P. M. op den Brouw and W. H. Laarhoven, *J. Chem. Soc., Perkin Trans. II*, (1982) 795.
- 7 P. H. G. op het Veld and W. H. Laarhoven, *J. Am. Chem. Soc.*, **99** (1977) 7221.

- 8 H. Suzuki, *Bull. Chem. Soc. Jpn.*, 33 (1960) 396, 406.
- 9 W. H. Laarhoven, R. J. F. Nivard and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, 79 (1960) 1153.
- 10 H. J. C. Jacobs and E. Havinga, *Adv. Photochem.*, 11 (1979) 305.
- 11 M. Sindler-Kulyk and W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas*, 98 (1979) 452.
- 12 F. Straus and H. Heinze, *Justus Liebigs Ann. Chem.*, 493 (1932) 203.
- 13 W. J. Dale, L. Starr and C. W. Strobel, *J. Org. Chem.*, 26 (1961) 2125.
- 14 U. Schubert and E. O. Fischer, *Chem. Ber.*, 106 (1973) 1062.