The Photochemistry of α-Substituted 2-Vinylstilbenes

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Irradiation of a solution of 2-vinylstilbene (1) under anaerobic conditions gives 9-phenyltricyclo-[6.1.1.0^{2,7}]deca-2,4,6-triene. Derivatives of (1), substituted at the α-position of the stilbene double bond, give 2-substituted 3-phenyltricyclo[4.4.0.0^{2,4}]deca-1(10),6,8-trienes, with the exception of the α-methoxy-derivative which is photostable. α-Substituted derivatives of (1) containing a CO_2H, CO_2CH_3, or CF_3 group yield only the *endo*-3-phenyl substituted product. Derivatives of (1) having an α-CN, Cl, or CH_3 substituent yield mixtures of *endo*- and *exo*-3-phenyl derivatives. It is shown that only the size of the α-substituents is responsible for the stereoselectivity of the reaction: derivatives containing small substituents give cycloaddition products from both the *trans*- and *cis*-isomer.

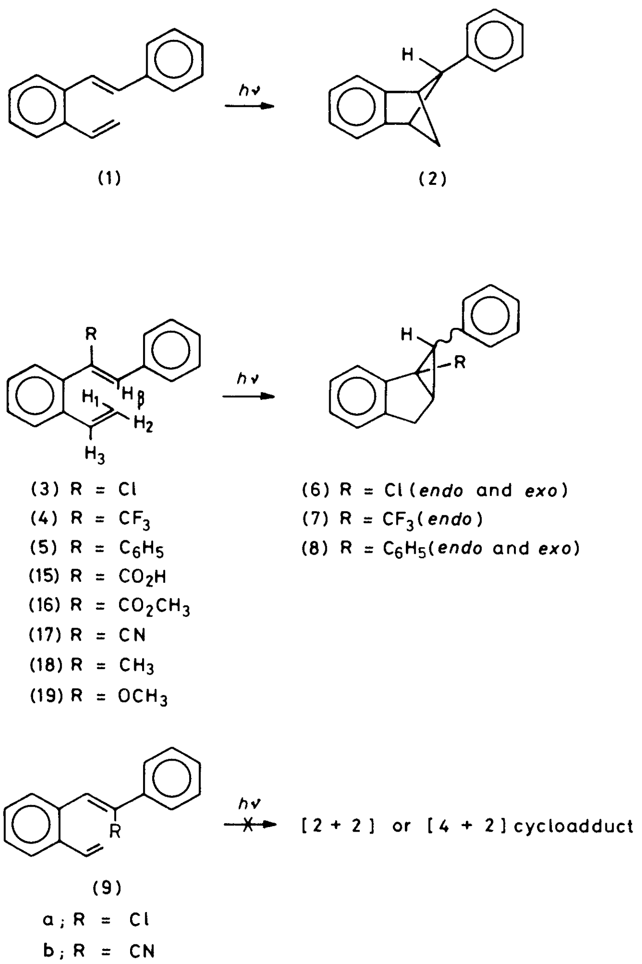
Previous studies on the photochemistry of 2-vinylstilbenes have revealed that the presence of a substituent at the stilbene double bond (α or β) exerts an influence on the route of the photoreaction under anaerobic conditions.[1-4] Steric crowding by an α-substituent can change the reaction mode from the [2 + 2]cycloaddition observed for the parent compound (1) to a [4 + 2]cycloaddition (Scheme 1). With the α-chloro derivative (3) of (1) photoelimination [3] is the main reaction besides the [4 + 2]cycloaddition. The β-substituted 2-vinylstilbenes examined thus far appeared to be unreactive with respect to the [2 + 2] as well as the [4 + 2]photocycloaddition [2,4] (Scheme 1).

It is still unknown whether substituents exert an electronic influence on the photoreactivity of (1). However, the photochemistry of 1,2-divinylbenzene derivatives has appeared to be largely dependent on the electronic nature of substituents.[5] Whereas 1,2-divinylbenzene itself forms tricyclo[4.4.0.0^{2,4}]-decatriene * by a photo[4 + 2]cycloaddition, substitution with electron-donating groups [as in (10)] causes [2 + 2]cycloaddition (Scheme 2). The push–pull system of ethoxycarbonyl-methoxydivinylbenzene (12) leads again mainly to a tricyclo[4.4.0.0^{2,4}]decatriene *viz.* (13), but the presence of two electron-withdrawing substituents [as in (14)] does not yield any cycloaddition product.

In this paper we report on the photochemical behaviour of 2-vinylstilbenes substituted at the α-position with different kinds of substituents.

Synthesis and Spectroscopic Properties.—The syntheses of α-chloro-, α-trifluoromethyl-, α-phenyl-, and α-methoxy-2-vinylstilbene (3)—(5) and (19), respectively, have been described earlier.[3,4] α-Cyano-2-vinylstilbene (17) and 2-vinylstilbene-α-carboxylic acid (15) were prepared according to Scheme 3. Esterification of (15) gave (16); α-methyl-2-vinylstilbene (18) was obtained from (15) by reduction with $LiAlH_4$, subsequent tosylation, and again reduction of the resulting tosylate with $LiAlH_4$.

The configuration of the α-substituted 2-vinylstilbenes (*cis* or *trans*) was established by spectroscopic methods. In general, the u.v. absorption of the *trans*-isomers is at longer wavelengths and with higher extinction coefficients than that of the *cis*-isomers. The differences between $\lambda_{max.}$ of the *cis*- and *trans*-isomers of the substitution products are, however, much smaller than found for the *cis*- and *trans*-isomers of unsubstituted 2-vinylstilbenes, as a consequence of the increased torsion around the C_α–phenyl bond. In the ^1H n.m.r. spectra the aromatic protons of *cis*-isomers appear at higher field than those of *trans*-isomers (see Table 1). This is a better criterion than the chemical shift of H_β, because δH_β does not correlate very well with the value calculated by the method of Pascual as was argued before.[3]



(1) (2)

(3) R = Cl
(4) R = CF_3
(5) R = C_6H_5
(15) R = CO_2H
(16) R = CO_2CH_3
(17) R = CN
(18) R = CH_3
(19) R = OCH_3

(6) R = Cl (*endo* and *exo*)
(7) R = CF_3(*endo*)
(8) R = C_6H_5(*endo* and *exo*)

(9)
a; R = Cl
b; R = CN

Scheme 1.

Most of the substitution products [(3)—(5), (17), (19)] were obtained as *cis–trans*-mixtures, in which the *trans*-isomer was the main product. In the preparation of (3) the *trans* : *cis*-ratio was 5 : 1; in the preparation of (17) only the *trans*-isomer could be isolated; *cis*-(17) was obtained by irradiation of *trans*-(17) at 360 nm for 24 h. Only (15) and consequently compounds (16) and (18), which were prepared from (15),

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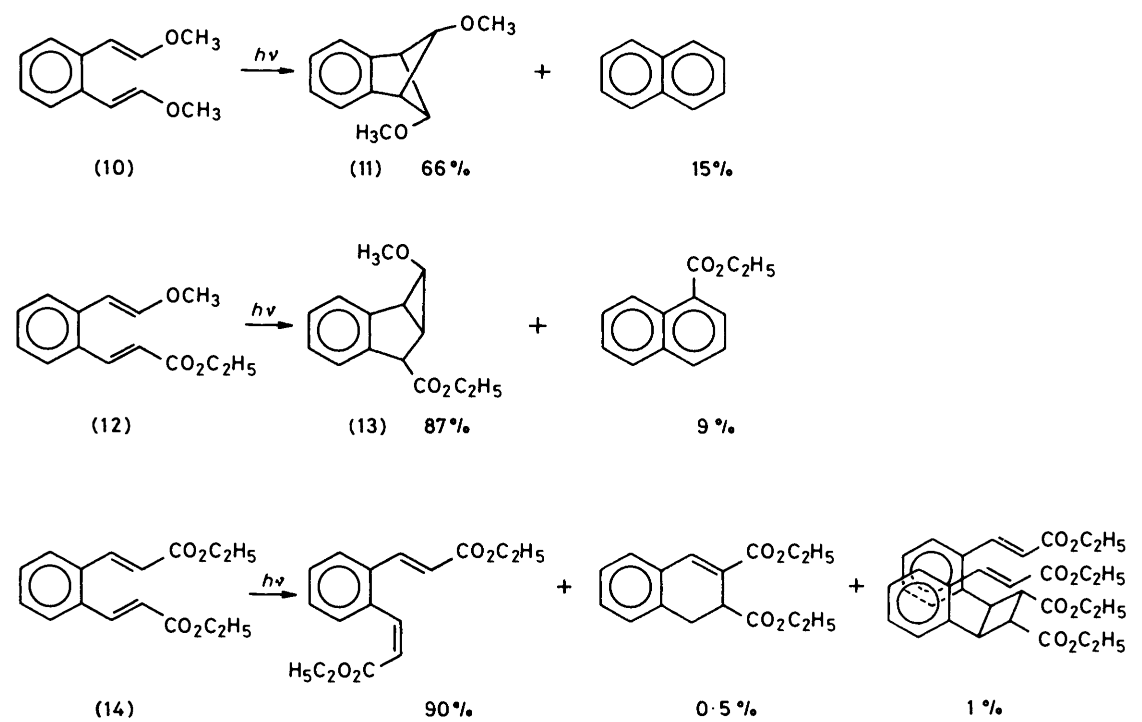
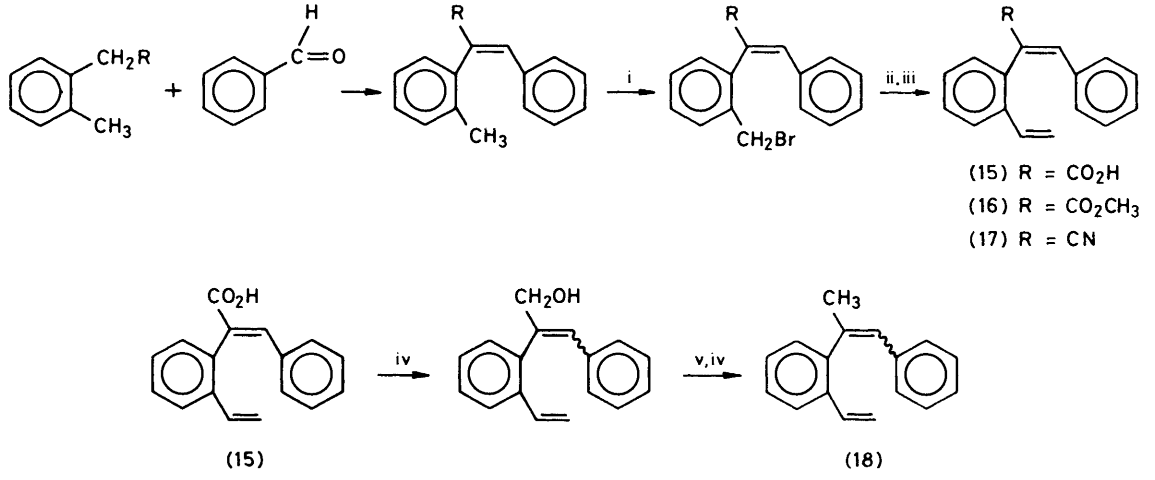
* In our previous papers [1-4] the name benzobicyclo[3.1.0]hex-2-ene was used for tricyclo[4.4.0.0^{2,4}]deca-1(10),6,8-triene.



Scheme 2.



Scheme 3. *Reagents:* i, *N*-bromosuccinimide; ii, PPh_3; iii, CH_2O; iv, $LiAlH_4$; v, *p*-$CH_3C_6H_4SO_2Cl$

were initially obtained as *cis*-isomers: they could be isomerised partially by irradiation at 300 nm.

Results

Short irradiations at 300 nm under anaerobic conditions converted pure isomers of the α-substituted 2-vinylstilbenes into photostationary equilibrium mixtures of the *cis*- and *trans*-compounds (see Table 2). Upon prolonged irradiation at 300 or 360 nm in hexane the α-substituted 2-vinylstilbenes gave 1-substituted 10-phenyltricyclo[4.4.0.$0^{2,4}$]decatriene derivatives, with the exception of α-methoxy-2-vinylstilbene (19), which appeared to be photostable. Thorough analysis of the irradiated solutions did not give any indication of the presence of derivatives of phenyl-substituted tricyclo[6.1.1.$0^{2,7}$]decatrienes,* which arise by irradiation of the parent compound and of α-substituted distyrylbenzenes.[4]

Photocyclization of the substituted 2-vinylstilbenes, resulting in 1-vinylphenanthrenes and caused by traces of oxygen which remain in the solution after purging with argon, was only observed in the irradiation of α-cyano-2-vinylstilbene (17).

From the assignment of a configuration to the photoproducts, based on similar ^1H n.m.r. arguments as used previously [4] in the structure determination of *endo*-(7), it appeared that (15) and (16) like (4) had been converted solely into *endo*-tricyclo[4.4.0.$0^{2,4}$] decatrienes, whereas (17) and (18) like (3) had given an *endo–exo*-mixture of the photoproduct (see Scheme 4 and Table 2). Previously we reported [4] that *endo*-(7) and *endo*-(8) can be converted into the corresponding *exo*-compounds by short irradiation under anaerobic conditions at 250 nm. Such photoisomerizations are improbable at 300 or 360 nm, because of the low extinction of tricyclo[4.4.0.$0^{2,4}$]-

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* In our previous papers [1–4] the name benzobicyclo[2.1.1]hex-2-ene was used for tricyclo[6.1.1.$0^{2,7}$]dec-2,4,6-triene.

Table 1. ^1H N.m.r. shifts (δ) of α-substituted 2-vinylstilbene measured in $CDCl_3$ [a]

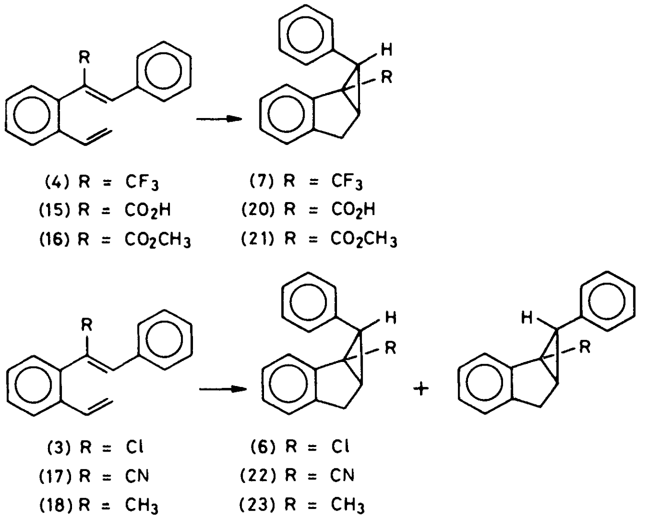
R	Compound	1-H	2-H	3-H	β-H	ArH	
CF_3	*cis* (4)	5.62	5.12	6.75	*b*	6.82—7.75	
	trans	5.70	5.26	6.88	6.84	7.16—7.70	
CO_2H	*cis* (15)	5.63	5.24	6.69	7.97	7.00—7.80	11.60 (H acid)
CO_2CH_3	*cis* (16)	5.64	5.15	6.69	7.89	6.93—7.72	3.75 (CH_3)
	trans	5.67	5.22	*b*	6.75	7.00—7.73	3.68 (CH_3)
CN	*cis* (17)	5.66	5.25	6.82	7.37	6.95—7.77	
	trans	5.73	5.35	6.97	7.11	7.00—7.68, 7.70—7.93	
Cl	*cis* (3)	5.72	5.25	6.84	7.00	6.84—7.71	
	trans	5.75	5.30	7.06	6.64	7.25—7.81	
Ph	*cis* [c] (5)	5.52	4.98	*b*	*b*	6.79—7.69	
	trans	5.56	5.08	*b*	6.51	6.74—7.70	
CH_3	*cis* (18)	5.62	5.13	6.80	6.47	6.80—7.37, 7.51—7.62	2.11 (CH_3)
	trans	5.69	5.23	*b*	6.37	6.80—7.60	2.18 (CH_3)
OCH_3	*cis* (19)	5.71	5.20	*b*	5.94	6.56—7.77	3.78 (CH_3)
	trans	5.77	5.30	7.06	5.59	7.00—7.75	3.44 (CH_3)

[a] $J_{1,2}$ 1.2, $J_{1,3}$ 17.0, $J_{2,3}$ 10.8 Hz for the *cis*- and *trans*-isomers. [b] Not observed, obscured by aromatic signals. [c] In CCl_4.

Table 2. Irradiation data of α-substituted 2-vinylstilbenes in hexane

R		Ratio *cis* : *trans*	Ratio *endo*/*exo* [4.4.0.0^{2,4}] decatriene	Van der Waals radius of R (nm)
CO_2H	(15)		∞	0.25 [b]
CN	(17)	3.0	0.5	0.21 [c]
CF_3	(4)	3.0	∞	0.22 [b]
CO_2CH_3	(16)	3.0	∞	0.25 [b]
Cl	(3)	3.0	0.5	0.18 [a]
H	(1)	2.0		0.12 [a]
CH_3	(18)	1.5	1.0	0.20 [a]
OCH_3	(19)	1.3		0.20 [b]

[a] 'Handbook of Chemistry and Physics,' The Chemical Rubber Co., Cleveland, 1979. [b] Calculated from values of Van der Waals radii and of bond lengths. [c] In length direction.


(4) R = CF_3 (7) R = CF_3
(15) R = CO_2H (20) R = CO_2H
(16) R = CO_2CH_3 (21) R = CO_2CH_3

(3) R = Cl (6) R = Cl
(17) R = CN (22) R = CN
(18) R = CH_3 (23) R = CH_3

Scheme 4.

decatrienes at these wavelengths; in fact, they were not observed on experimental control.

The ^1H n.m.r. data of the 2-substituted 3-phenyltricyclo-[4.4.0.0^{2,4}]decatrienes are given in Table 3.

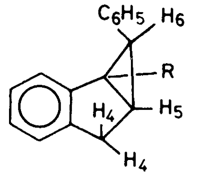
Discussion

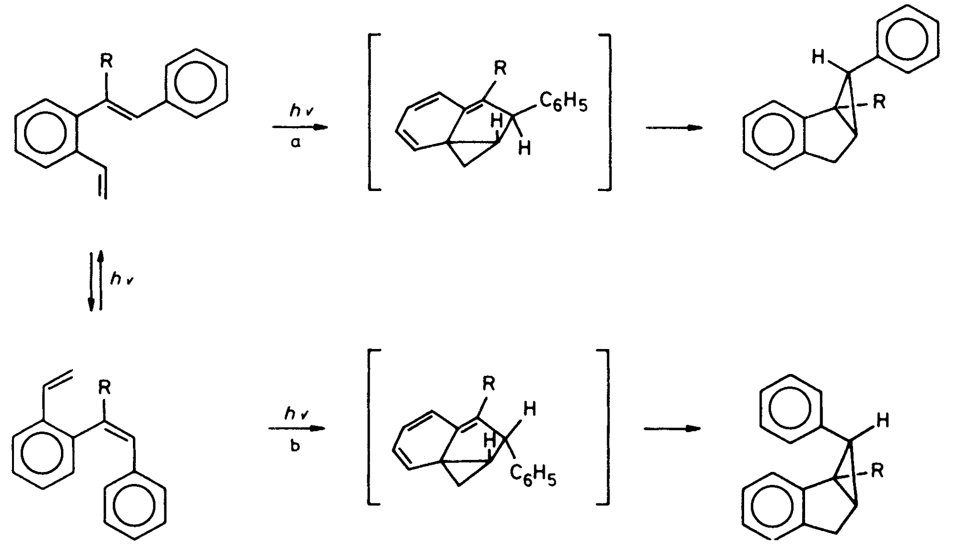
The results clearly indicate that the electronic effect of substituents cannot be an important factor in determining the direction of the photoconversion of α-substituted 2-vinylstilbenes. Although the electronic effects of the substituents, present in the compounds investigated, are quite different, as appeared from the large differences between the chemical shifts of β-H (Table 1), α-substituted 2-vinylstilbenes gave generally (4 + 2)photoaddition products with only one exception [*viz.* (19)]. On the other hand the mere presence of any α-substituent is of decisive influence on the photoreaction; the unsubstituted 2-vinylstilbene (1) gives only the [2 + 2]-photoaddition product (2). Moreover, the nature of the α-substituent is of influence on the stereoselectivity of the photoreaction; (15) and (16) give pure *endo*-isomers of a tricyclo[4.4.0.0^{2,4}]decatriene, as was previously found with (4); (17) and (18) give a mixture of *endo*- and *exo*-isomers, similarly to (3).

The formation of an isomer mixture in several cases necessitates an extension of the originally proposed mechanism,[1] in which the [4 + 2]photoaddition of an α-substituted 2-vinylstilbene was ascribed to the photoreactivity only of the *cis*-isomer of the starting compound, reacting in a special conformation (Scheme 5, reaction b). Apparently a similar reaction is possible starting from the *trans*-isomer, yielding the *exo*-product (Scheme 5, reaction a). The ratio between *endo*- and *exo*-isomer in the product is not simply related, however, to the ratio between the *cis*- and *trans*-isomer in the 2-vinylstilbene used; the latter ratio is nearly constant in the photostationary state for various α-substituted 2-vinylstilbenes (see Table 2). Therefore, it must be accepted that the efficiencies of the photoreactions a and b for *trans*- and *cis*-isomers, respectively, are influenced independently by the α-substituent R. Our results suggest that in the presence of small substituents (Cl, CN, CH_3) relatively large amounts of the *exo*-product are formed; in these cases the [4 + 2]photoaddition of the *trans*-isomer must be fast. 2-Vinylstilbenes containing larger substituents (CF_3, CO_2H, CO_2CH_3) yield only the *endo*-product; the photoreactivity of the *trans*-isomer must then be low. This steric influence might occur in both steps of the formation of the tricyclo[4.4.0.0^{2,4}]decatriene: in the primary photo-Diels–Alder cycloaddition and in the vinyl-cyclopropane rearrangement. In the latter reaction it is necessary for the formation of the 6-*exo*-phenyl isomers (Scheme 5a) as the end product that the phenyl group moves through the plane

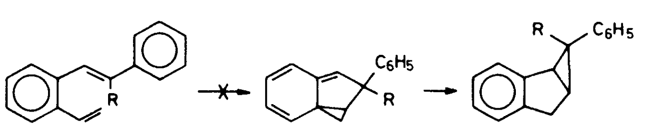
Table 3. ^{1}H N.m.r. shifts (δ) and coupling constants (Hz) of the protons of tricyclo[4.4.0.0^{2,4}]decatriene derivatives in $CDCl_3$ solutions

Decatriene	*endo*-4-H	*exo*-4-H	5-H	*endo*-6-H	*exo*-6-H	ArH	$J_{4endo,-4exo}$/Hz	$J_{4exo,5}$	$J_{5.6exo}$	$J_{5.6endo}$	$J_{4endo,5}$
endo-(22)	2.80	3.19	2.93		3.18	6.67—7.67	17.4	6.6	7.5		0
exo-(22)	3.13	3.53	3.04	2.15		6.7—7.7	17.1	6.6		5.4	0
endo-(21)	2.72	3.20	2.78		3.41	6.62—7.31	17.7	6.9	9.0		0, 9
endo-(23)	2.57	3.11	1.98		2.34	6.66—7.88	17.1	6.8	7.8		0
exo-(23)	2.26	2.69	2.1	2.1		6.99—7.40	15.0	7.0			
endo-(6)	2.62	3.28	2.60		3.09	6.5—7.6	16.5	6.0	8.0		0
exo-(6)	3.05	3.55	2.60	2.00		6.5—7.6	16.5	6.0		5.0	0
endo-(7)	2.76	3.24	2.62		3.03	6.60—7.80	17.5	6.7	9.3		0
exo-(7)	3.04	3.62	2.19	2.86		6.7—7.7	17.1	6.3		5.7	0





Scheme 5.



of the five-membered ring. This process can be hampered by a bulky R group that either prevents the rearrangement, giving back the starting stilbene, or leads to the 6-*endo*-phenyl isomer *via* a non-concerted process. Such a steric influence of bulky groups is known in cyclization reactions.[6]

In the present case it is remarkable, however, that quite small increases in the radius of the R group prohibit the formation of the *exo*-product so rigorously. Moreover, previously [3,4] we observed that β-substituted 2-vinylstilbenes does not form any tricyclodecane derivative. In this type of compound the vinyl–cyclopropane rearrangement of the primary cyclization product is not hindered by a bulky group at C(2), so that it had to be concluded that the photo-Diels–Alder reaction does not take place. It is well known that conformational differences between α-substituted *trans*-stilbenes and unsubstituted *trans*-stilbene are larger than those between α-substituted *cis*-stilbenes and unsubstituted *cis*-stilbene.[7] Therefore, we assume that the origin of the observed steric influence is the interaction between a bulky R group at C_α and the β-phenyl group of the *trans*-vinylstilbene. This steric strain is partly released by a torsion over the stilbene double bond by which the required orbital overlap for bond formation between the double bond is prohibited.

A similar kind of steric influence is reflected in the higher thermodynamic stability of *cis*-α-trifluoromethylstilbene in comparison with the corresponding *trans*-isomer.[8]

Experimental

^{1}H N.m.r. spectra were recorded on a Varian T 60 or a Bruker WH90 spectrometer in $CDCl_3$ solution and with tetramethylsilane (δ 0) as an internal standard (see Tables 1 and 3). U.v. spectra were measured with a Cary 15 or a Perkin 555 spectrometer for methanol solutions. Mass spectra were obtained using a Varian SM2B or a Finnigan 2000 spectrometer. Elemental analyses of the compounds were in agreement with theoretical values. Irradiations were performed in a Rayonet RPR 100 or 200 photoreactor under anaerobic conditions. To that aim a stream of nitrogen or argon, previously purified and dried through a BTS catalyst, phosphorus pentaoxide, silica, and potassium hydroxide, was led through the solutions.

Reaction mixtures were separated by column chromatography or t.l.c. over alumina (Baker) or silica (Merck 0.063—0.200 mm). In general, hexane was used as the eluant, but sometimes the polarity of the eluant was increased by the addition of increasing amounts of chloroform.

The synthesis of α-chloro-2-vinylstilbene (3), α-trifluoromethyl-2-vinylstilbene (4), and α-methoxy-2-vinylstilbene (19), as well as the irradiation products of (3) and (5), have been described previously.[3,4]

Synthesis of the Starting Materials.—*α-Cyano-*2*-vinylstilbene* (17). According to the method of Wawzonek[9] α-cyano-2-methylstilbene was synthesized starting from 2-methylbenzyl cyanide and benzaldehyde in 50% yield. Then the stilbene was brominated by 1 mol. equiv. of *N*-bromosuccinimide in carbon tetrachloride with stirring and light from a 250 W Philips lamp during 4—6 h. After cooling the succinimide was filtered off and the remaining CCl_4 solution was evaporated *in vacuo*. The crude bromide was dissolved in toluene and 1 mol. equiv. of triphenylphosphine was added and the solution was refluxed for 16 h. After cooling the phosphonium salt precipitated as a solid and was filtered off. In a Wittig reaction the phosphonium salt dissolved in ethanol with 1 mol. equiv of sodium ethanolate was dissolved with formaldehyde in ethanol at room temperature and converted into (17). After evaporation of the solvent equal amounts of chloroform and water were added. After extraction and separation of the layers, the chloroform was evaporated and the crude stilbene was chromatographed on silica with hexane as eluant. In a yield of 60% mainly the *trans*-isomer was isolated. The *trans*-isomer was an oil, $\lambda_{max.}$ 295 (log ε 4.15), 272 (4.04), and 250 nm (4.03); *m*/*e* 231 (31%), 230 (15), 206 (100), and 191 (30). (Found: M^+, 231.106. Calc. for $C_{17}H_{13}N$: *M*, 231.105.)

*α-Methoxycarbonyl-*2*-vinylstilbene* (16). After a Perkin condensation[10] of 2-methylphenylacetic acid and benzaldehyde, 2-methylstilbene-α-carboxylic acid was obtained in 60% yield. This compound was converted into 2-vinylstilbene-α-carboxylic acid by subsequent bromination, formation of the phosphonium salt, and a Wittig reaction as described above. The acid was esterificated by refluxing it in benzene, methanol, and sulphuric acid during 3 h. After neutralization and evaporation of the solvents the ester was chromatographed on silica with hexane as the eluant and yielded 40% *cis*-(16), $\lambda_{max.}$ 276 (log ε 3.89), 260 (3.89), 252 (3.88), and 202 nm (4.21); *m*/*e* (mixture of isomers) 264 (49%), 233 (17), 232 (24), 231 (19), 220 (13), 205 (53), 204 (10), 203 (77), 202 (15), and 201 (28).

*α-Methyl-*2*-vinylstilbene* (18). 2-Vinylstilbene-α-carboxylic acid (5 g, 0.02 mol) was dissolved in ether (100 ml). Then $LiAlH_4$ (2.76 g, 0.07 mol) was added and the mixture was refluxed. After extraction with water the ether layer was separated from the water layer and dried. After isolation of the product, crude α-hydroxymethyl-2-vinylstilbene (1 g), tosyl chloride (0.7 g, 0.004 mol), and pyridine (0.47 g, 0.06 mol) were dissolved in chloroform (25 ml). This solution was stirred for 16 h. Then water was added and the chloroform layer was extracted and separated from the water layer and finally dried and evaporated *in vacuo*. The remaining oil which contained the crude tosylate was dissolved in THF (25 ml) and stirred with $LiAlH_4$ (1.02 g) during 16 h. After the same work-up as described above the oil was chromatographed on silica with hexane as eluant and yielded *cis*-α-methyl-2-vinylstilbene (350 mg, 39%) as an oil, $\lambda_{max.}$ 248 nm (log ε 4.19), λ_{min} 227 nm (log ε 4.08); *m*/*e* (mixture of isomers) 220 (100%), 208 (54), 207 (68), 206 (48), 205 (41), 204 (45), and 203 (42) (Found: M^+, 220.125. Calc. for $C_{17}H_{16}$: *M*, 220.125).

Irradiations.—trans-*α-Cyano-*2*-vinylstilbene* (17). Compound (17) (750 mg) dissolved in hexane (2 l), degassed with nitrogen, was irradiated at 300 nm in a RPR 200-photoreactor during 8 h. The *cis*/*trans*-mixture of isomers obtained in this way was purified by column chromatography on silica with hexane as eluant and separated by t.l.c. with chloroform–hexane as eluant. The *cis*-isomer (17) could also be obtained by irradiation of *trans*-(17) at 360 nm during 24 h giving a mixture of *cis*–*trans*-isomers containing 80—90% of *cis*-(17), $\lambda_{max.}$ 275 (log ε 4.15), 249 (4.12), 224 (4.18), and 218 nm (4.17), λ_{min} 260 (log ε 4.12), 236 (4.08), and 2.01 nm (4.17). Irradiation of (17) (330 mg) dissolved in hexane (500 ml) under the same conditions during 40 h at 300 nm in a RPR-100 photoreactor yielded 40% of *endo*- and *exo*-2-cyano-3-phenytricyclo-[4.4.0.0^{2,4}]deca-1(10),6,8-triene (22) (ratio 1 : 2) and 10% 10-cyano-1-vinylphenanthrene together with polymer and a small quantity of unidentified products. Separation of this mixture of photo-products by column chromatography, t.l.c., and h.p.l.c. yielded in the following order: *endo*-(22), *exo*-(22), and the phenanthrene. Compound *endo*-(22) was not completely free from *exo*-(22) and was identified by its n.m.r. spectrum. 10-Cyano-1-vinylphenanthrene had $\lambda_{max.}$ 320 (log ε 4.11), 308 (4.12), and 252 nm (4.74). The *exo*-isomer of (22) $\lambda_{max.}$ 276 (log 3.36), 266 (3.56), 259 (3.63), and 229 nm (4.06).

*cis-α-Methoxycarbonyl-*2*-vinylstilbene* (16). Compound (16) (30 mg) dissolved in hexane (50 ml) was irradiated for 2 h at 300 nm under argon atmosphere and yielded a 3 : 1 *cis*/*trans*-mixture of isomers. After enrichment of the fraction containing the *trans*-isomer by column chromatography on silica with hexane–chloroform as eluant the reported (Table 1) n.m.r. spectrum was obtained. Irradiation of (16) (500 mg) in hexane (1.5 l) during 24 h at 300 nm under argon atmosphere resulted in *endo*-2-methoxycarbonyl-3-phenyltricyclo[4.4.0.0^{2,4}]deca-1(10),6,8-triene (21) in 90% yield according to the n.m.r. spectrum. After careful column chromatography on silica with hexane as eluant (21) was isolated and crystallized, m.p. 80—81 °C, $\lambda_{max.}$ 304 (log ε 3.07), 275 (3.42), 268 (3.59), 259 (3.55), and 254 nm (2.48); *m*/*e* 265 (41), 264 (74), 233 (36), 232 (100), 206 (37), 205 (75), 204 (62), 203 (64), and 202 (57) (Found: M^+, 264.117. Calc. for $C_{18}H_{16}O_2$: *M*, 264.115).

cis-2-*Vinylstilbene-α-carboxylic acid* (15). Compound (15) (500 mg) were irradiated under the conditions mentioned above for (16) in hexane with 5% ethanol at 360 nm during 8 h. According to the n.m.r. spectrum *ca.* 15% of *endo*-3-phenyltricyclo[4.4.0.0^{2,4}]deca-1(10),6,8-triene-2-carboxylic acid (20) was formed.

*α-Methyl-*2*-vinylstilbene* (18). After irradiation of (18) (26 mg) dissolved in hexane (50 ml) under argon atmosphere during 1.5 h, 90% of the starting compound appeared to be converted into *endo*- and *exo*-2-methyl-3-phenyltricyclo-[4.4.0.0^{2,4}]deca-1(10),6,8-triene (23). After purification by column chromatography on silica with hexane and separation by t.l.c. with hexane as the eluant the band with the larger R_F value contained the *exo*-isomer and the following band with a lower R_F value contained the *endo*-isomer. The isomers were not completely separated. A third band contained *trans*- and *cis*-(18).

*α-Trifluoromethyl-*2*-vinylstilbene* (4). Solutions of (4) in hexane (10^{-3}M) were irradiated under different dehydrogenating conditions to observe a competition between [4 + 2]cycloaddition and photocyclization. Addition of 1 mol. equiv. of tetracyanoethylene to a degassed solution led to 28% of (7) and 22% of phenanthrene derivatives. Irradiation of the solution without degassing yielded 14% of (7) and 6% phenanthrene. Addition of several equivalents of iodine yielded 2% of (7) and 70% of phenanthrene. In none of these cases could a precursor of (7) be detected as was found when (1) is irradiated under these conditions.[1]

References

1 M. Sindler-Kulyk and W. H. Laarhoven, *J. Am. Chem. Soc.*, 1978, **100**, 3819.

2 M. Sindler-Kulyk and W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas*, 1979, **98**, 187, 452.

3 P. M. op den Brouw and W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 58.

4 P. M. op den Brouw and W. H. Laarhoven, *J. Org. Chem.*, 1982, **47**, 1546.

5 C. V. Maher, Ph.D. Thesis, Cornell University, 1975.

6 T. R. Rodgers and H. Hart, *Tetrahedron Lett.*, 1969, 4845.

7 H. Suzuki, *Bull. Chem. Soc. Jpn.*, 1960, **33**, 389.

8 G. Ruban, P. Zobel, G. Kossmehl, and R. Nuch, *Chem. Ber.*, 1980, **113**, 3384.

9 S. Wawzonek and E. M. Sanolin, *Org. Synth.*, 1965, Coll. Vol. 3, 715.

10 A. I. Vogel, ' Practical Organic Chemistry,' Longmans, London, 1979, 4th edn., p. 801.

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