14 h at 20 °C, the product was partitioned between ether and saturated $CuSO_4$ solution (2×) and water (2×). After drying ($MgSO_4$) and ether evaporation (aspirator), a solid residue (14 mg) resulted which gave single spot on TLC (R_f 0.38; 2:1 hexane/ether, silica gel).

The crude solid acetate was dissolved in pyridine (1.1 mL) and cooled to 0 °C. Thionyl chloride (62 mg) and 4-(dimethylamino)pyridine (4 mg) were added in succession, and the mixture was stirred 1.5 h at 0 °C. The same workup as above gave a colorless oil. After preparative TLC (silica gel, 2:1 hexane/ether), 21 mg of pure **59** were obtained as a clear oil (82%) which crystallized from ether–hexane: mp 133.5–134 °C; 270-MHz NMR ($CDCl_3$) δ 7.2–7.6 (10 H, complex), 5.23 (1 H, d, J = 9.9 Hz), 5.21 (1 H, s), 5.00 (1 H, s), 4.51 (1 H, dd, J = 8.5, 3.3 Hz), 4.19 (1 H, dd, J = 9.9, 9.9 Hz), 3.50 (1 H, dd, J = 9.9, 4.6 Hz), 3.07 (1 H, dd, J = 13.5, 3.3 Hz), 2.97 (1 H, dd, J = 9.2, 3.7 Hz), 2.84 (1 H, dd, J = 13.5, 8.5 Hz), 2.60 (1 H, m), 2.47 (1 H, m), 2.21 (1 H, m), 1.92 (3 H, s), 0.83 (3 H, d, J = 6.6 Hz), 0.80 (9 H, s), −0.07 (3 H, s), −0.08 (3 H, s); IR ($CHCl_3$) 1740, 1674, 1659 cm^{-1}; mass spectrum, calcd for $C_{33}H_{43}NO_5Si$ m/e 561.291 02, obsd 561.2908.

Cytochalasin Functionality. Deprotection of 59 to 60. Acetate **59** (14.4 mg) was stirred in dry CH_2Cl_2 (1.5 mL) at −78 °C, and excess DIBAL in hexane (1 M, 0.25 mL) was added dropwise. After 5 h at −78 °C, CH_3OH (0.3 mL) was added dropwise, followed by aqueous H_2SO_4 (1 N, 0.4 mL). The dry ice bath was replaced by an ice bath, and the mixture was stirred 30 min. Solids were removed by filtration through a Celite plug ($CHCl_3$ rinse), and the organic phase was washed with water (3 × 10 mL). After the organic phase was dried ($MgSO_4$) and the solvent evaporated (aspirator), the residue was purified by preparative TLC over silica gel (5:1 ether/hexane) to give a major zone (R_f 0.31) containing 7.8 mg (74%) of **60** which crystallized from CH_2Cl_2–hexane: mp 122–123.5 °C; 270-MHz NMR δ 7.35–7.1 (5 H, complex), 5.29 (NH, br s), 5.23 (1 H, s) 5.01 (1 H, s), 4.47 (1 H, dd, J = 10.3, 10.0 Hz), 4.24 (1 H, d, J = 9.6 Hz), 3.99 (1 H, dd, J = 10.3, 4.0 Hz), 3.98 (OH, s), 3.40 (1 H, br dd, J = 5.1, 4.8 Hz), 2.81 (1 H, m, obscured), 2.76 (1 H, dd, J = 13.2, 4.8 Hz), 2.69 (1 H, dd, J = 10.3, 5.1 Hz), 2.59 (1 H, dd, J = 13.2, 8.8 Hz), 2.47 (1 H, ddd, J = 10.3, 6.2, 3.2 Hz), 2.20 (1 H, dddd, J = 10.0, 9.6, 5.1, 4.0 Hz), 1.00 (3 H, d, J = 7.0 Hz), 0.88 (9 H, s), 0.09 (3 H, s), 0.08 (3 H, s). IR ($CHCl_3$) 3425, 1690 cm^{-1}; mass spectrum, calcd for $C_{24}H_{37}NO_3Si$ m/e 415.254 25, obsd 415.2542.

Acknowledgment. This work was supported by the National Institutes of Health (Grant No. CA17918).

Registry No. (±)-**4a**, 80360-64-1; **4b**, 80360-65-2; (±)-**6a**, 80360-66-3; (±)-**11**, 80408-25-9; (±)-**12**, 80408-26-0; (±)-*cis*-**13**, 80360-67-4; (±)-*trans*-**13**, 80360-68-5; **15**, 39662-63-0; **16**, 14293-06-2; *cis*-**17**, 80360-69-6; *trans*-**17**, 80360-70-9; *cis*-**18**, 80360-71-0; *trans*-**18**, 80360-72-1; **21**, 17728-88-0; **22**, 80360-73-2; **22** 2,4-dinitrophenylhydrazone, 80360-74-3; (*E*)-**23**, 80360-75-4; **24**, 80360-76-5; **25**, 80360-77-6; **26**, 80360-78-7; **27**, 80360-79-8; **28**, 80360-80-1; **29**, 74457-20-8; **29** Mesylate, 80360-81-2; **30**, 80360-82-3; (*Z*)-**31**, 80360-83-4; (*E*,*E*)-**32a**, 80360-84-5; (*E*,*Z*)-**32a**, 80360-85-6; (*E*,*E*)-**32b**, 80360-86-7; (*E*,*Z*)-**32b**, 80360-87-8; (*E*,*E*)-**32c**, 80360-88-9; (*E*,*Z*)-**32c**, 80360-89-0; (*E*,*E*)-**32d**, 80360-90-3; (*E*,*Z*)-**32d**, 80360-91-4; **33**, 80360-92-5; **34**, 80360-93-6; **37**, 80360-94-7; (±)-**38**, 80360-95-8; (±)-**39**, 80360-96-9; **40**, 80360-97-0; (±)-41, 80360-98-1; (±)-**43**, 80360-99-2; (±)-**44**, 80361-00-8; **46**, 80361-01-9; **46** Acid, 80361-02-0; **47** (cis-fused), 80361-03-1; **47** (trans-fused), 80387-12-8; **48**, 80361-04-2; **49a**, 80361-05-3; **49b**, 80361-06-4; **50a**, 80361-07-5; **50b**, 80361-08-6; **51**, 80361-09-7; **52**, 80361-10-0; **53**, 80441-01-6; **54a**, 80361-11-1; **54b**, 80361-12-2; **55a**, 80361-13-3; **55b**, 80361-14-4; (±)-**57**, 80361-15-5; (±)-**58**, 80361-16-6; (±)-**58** diacetate, 80361-17-7; (±)-**59**, 80361-18-8; (±)-**60**, 80361-19-9; ethyl *N*-(3-ethoxy-1,3-dioxopropyl)-DL-phenylalanine, 80361-20-2; ethyl DL-phenylalanate, 1795-96-6; ethyl malonyl chloride, 36239-09-5; 1-benzoyl-5-benzyl-2-pyrrolidinone, 80361-21-3; (*E*,*E*)-4-Methyl-2,4-hexadien-1-ol, 57258-51-2; tiglaldehyde, 497-03-0; (*E*,*E*)-1-(*tert*-butyldimethylsiloxy)-4-methyl-2,4-hexadiene, 80361-22-4; ethyl 2-[(trimethylsilyl)methyl]-3-hydroxybutanoate, 80361-23-5; acetaldehyde, 75-07-0; ethyl 2-[(trimethylsilyl)methyl]-2-butenoate, 80361-24-6; 2-[(trimethylsilyl)methyl]-2-buten-1-ol, 80361-25-7; diphenyl [(*E*)-4-hydroxy-2-buten-1-yl]phosphine oxide, 80361-26-8; (*E*)-4-chloro-2-buten-1-ol, 1775-39-9; ethyl acrylate, 140-88-5; (*Z*)-2-[(phenylthio)methyl]but-2-en-1-ol, 80361-27-9; *N*-*tert*-butylethanimine, 7020-80-6; triethyl phosphonoacetate, 867-13-0; (*E*,*E*)-2,4-hexadiene, 5194-51-4; (*E*,*Z*)-2,4-hexadiene, 5194-50-3.

Photochemistry of 1,2-Distyrylbenzene Derivatives

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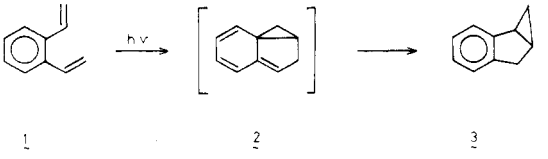
Photodimerization, accompanied by intramolecular, head to head [2 + 2] cycloaddition, which is observed with unsubstituted 1,2-distyrylbenzene (**12**), does not occur with derivatives containing an α or β substituent. α-Substituted 1,2-distyrylbenzenes yield benzobicyclo[2.1.1]hex-2-ene derivatives, at least when the substituent does not give rise to a new chromophoric system. Their photochemical behavior can be explained by assuming that such compounds (**22–24**) contain two formally conjugated but independently absorbing chromophores. The excitation energy is transferred to the chromophore with the lowest excitation energy, which determines the main route of the photoreaction. The formation of a photoelimination product as a second product from 1-(α-chlorostyryl)-2-(4-methylstyryl)benzene (**23**) but not from 1-(α-chloro-4-methylstyryl)-2-styrylbenzene (**24**) has been ascribed to the influence of the methyl substituent on the photocycloaddition. The concept used explains that the photoproduct of 1-(α-phenylstyryl)-2-styrylbenzene (**25**) arises via excitation of the triphenylethylene moiety. β-Substituted distyrylbenzene **26** is photostable due to steric hindrance.

About 15 years ago Pomerantz[1] and Meinwald[2] demonstrated that irradiation of 1,2-divinylbenzene (**1**) leads to benzobicyclo[3.1.0]hex-2-ene (**3**). The product arises via the initial formation of a [4 + 2] cycloaddition product (**2**), which undergoes a vinylcyclopropane–cyclopentene rearrangement (Scheme I). Several divinylbenzene derivatives, containing aliphatic substituents give similar results.[3,4] However, introduction of a phenyl group at the

Scheme I

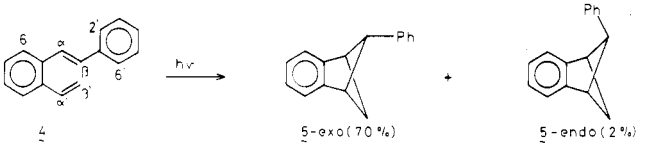


1 2 3

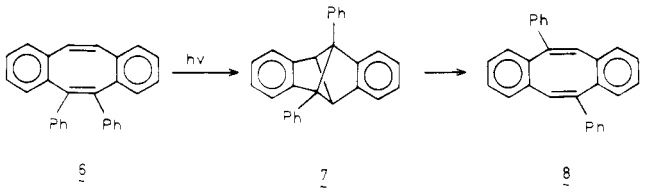
(1) M. Pomerantz, *J. Am. Chem. Soc.*, **89**, 694 (1967).
(2) J. Meinwald and P. H. Mazzocchi, *J. Am. Chem. Soc.*, **89**, 696 (1967).

0022-3263/82/1947-1546$01.25/0

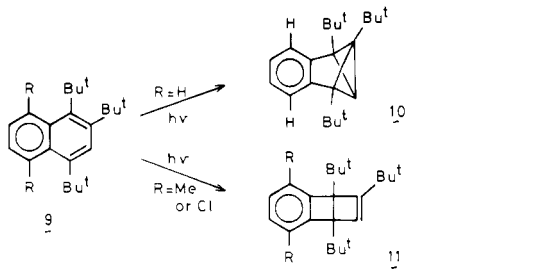
Scheme II



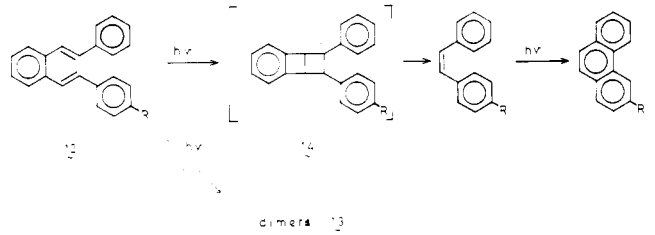
Scheme III



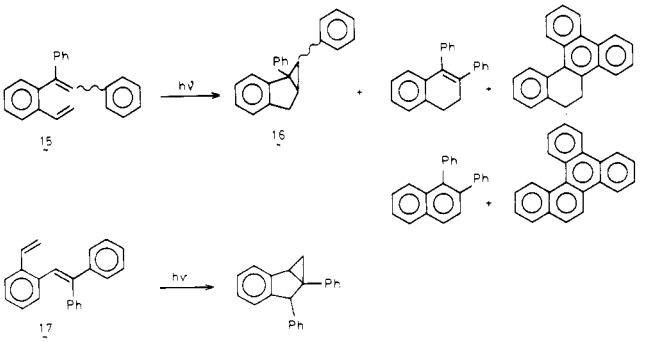
Scheme IV



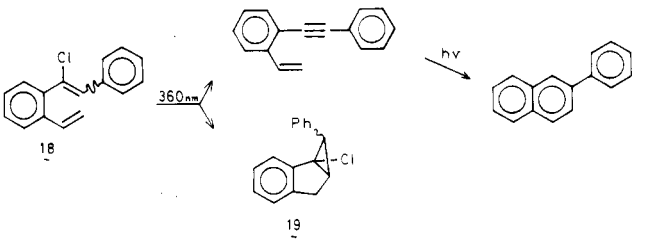
Scheme V



Scheme VI



Scheme VII



β-carbon atom of one of the vinyl groups, as in 2-vinylstilbene (**4**), leads to 5-phenylbenzobicyclo[2.1.1]hex-2-ene (**5**), which is isolated mainly as the exo isomer[5] (Scheme II).

The latter mode of photocyclization, formally a head to tail [2 + 2] cycloaddition, has also been proposed to explain the photoisomerization[6] of the diphenyldibenzocyclooctatetraene **6** (Scheme III). Furthermore, it is found in the photolysis of tri-*tert*-butylnaphthalene (**9**, R = H), which formally contains a 1,2-divinylbenzene moiety.[7] When additional substituents are present at C(5) and C(8), the reaction proceeds as a cyclization (Scheme IV). This cyclization has also been found as a photoreaction of 1,2-distyrylbenzenes (**12**), in which phenyl groups are present at the β-carbon atoms of both vinyl groups of the parent compound **1**. The main photoreaction of these compounds is a photodimerization, leading to a mixture of several isomers (**13**) and secondary products derived from them, but a stilbene and a phenanthrene are always isolated in small amounts as side product.[8] Their formation must be ascribed to a preceding head to head cycloaddition in **12**, giving the intermediate **14** (Scheme V).

In a study of the photochemistry of substitution products of **4** it has been found[9] that introduction of a single substituent at C(6) or C(β′) does not modify the photoreaction severely; the main photoreaction remains the formation of a benzobicyclo[2.1.1]hex-2-ene, but a benzobicyclo[3.1.0]hex-2-ene is formed as a side product. However, 2-vinylstilbenes substituted at C(2′) as well as C(6′) do not yield any cyclization product, and 2-vinylstilbenes having a phenyl substituent at C(α) (**15**) or C(β) (**17**) give benzobicyclo[3.1.0]hex-2-ene derivatives[10] (Scheme VI). With **15**, several other products are obtained, since the [4 + 2] photocycloaddition is accompanied by electrocyclization; with **17**, the photoproduct formation cannot well be ascribed to an initial [4 + 2] photocycloaddition as proposed in Scheme I, because it is accompanied by a phenyl migration, which points to a radical process.

α-Chloro-2-vinylstilbene (**18**), irradiated at 360 nm, yields small amounts of both an *exo*- and an *endo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (**19**), but other products arise from a photoelimination which is the main reaction[11] (Scheme VII). The influence of substituents on the nature of the photoproducts from 2-vinylstilbenes has been explained by the supposition that the different products originate from various conformations of the cis isomers.[9,12] Substituents affect the conformational equilibria and by this the course of the photoreaction, the rate of which depends on the concentration of the reactive conformer in its excited state. In a recent paper[11] arguments have been given, however, that photoreactions with this type of compounds may also proceed starting from the trans isomer.

(3) J. Meinwald and D. A. Seeley, *Tetrahedron Lett.*, **1970**, 3739.
(4) L. Ulrich, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **53**, 1323 (1970); H. Heimgartner, L. Ulrich, H. J. Jansen, and H. Schmid, *ibid*, **54**, 2313 (1971).
(5) M. Sindler-Kulyk and W. H. Laarhoven, *J. Am. Chem. Soc.*, **98**, 1052 (1976).
(6) L. E. Salisbury, *J. Org. Chem*, **43**, 4987 (1978); H. Simonson, Ph.D. Thesis, University of Michigan, 1970.
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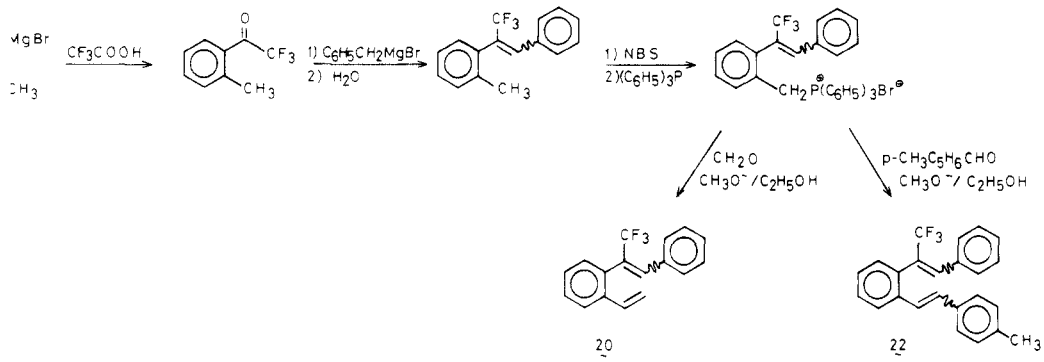
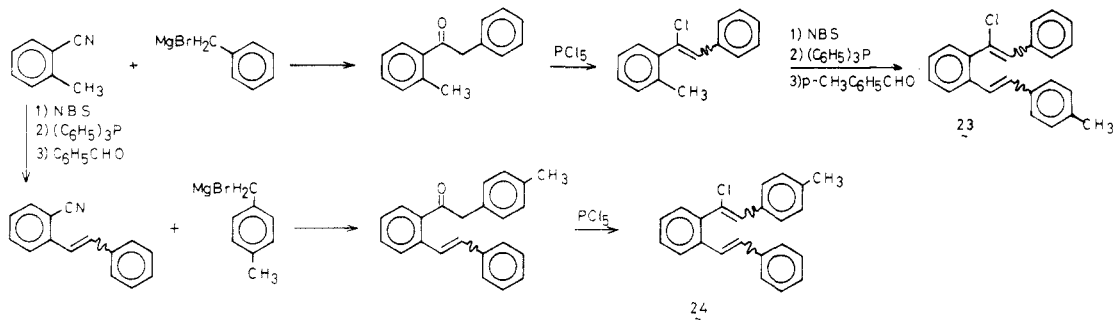
(8) W. H. Laarhoven, T. J. H. M. Cuppen, R. J. F. Nivard, *Tetrahedron*, **26**, 1069 (1970); T. E. M. van der Hark, P. T. Beurskens, and W. H. Laarhoven, *J. Cryst. Mol. Struct.*, **4**, 227 (1974); E. Müller, M. Meier, and M. Sauerbier, *Chem. Ber.*, **103**, 1356 (1970).
(9) M. Sindler-Kulyk, Thesis, Nijmegen University, 1976.
(10) M. Sindler-Kulyk and W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas*, **98**, 187, 452 (1979).
(11) P. M. op den Brouw and W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas*, *101*, 58 (1982).
(12) M. Sindler-Kulyk and W. H. Laarhoven, *J. Am. Chem. Soc.*, **100**, 3819 (1978).

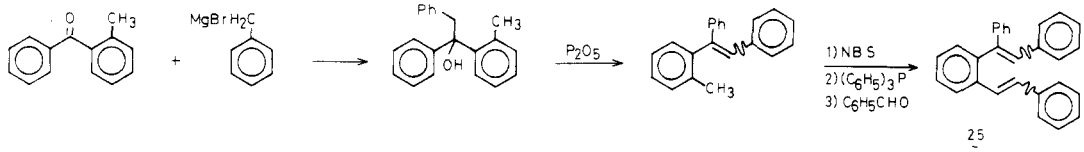
Scheme VIII



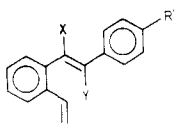
Scheme IX

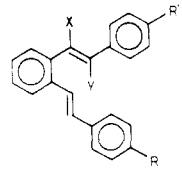


Scheme X



In this paper we present a study of the influence of substituents on the photochemistry of 1,2-distyrylbenzene. For that purpose the compounds **22–26** have been inves-





20 X=CF_3, Y=H, R'=H
21 X=H, Y=CN, R'=H
27 X=H, Y=H, R'=Me

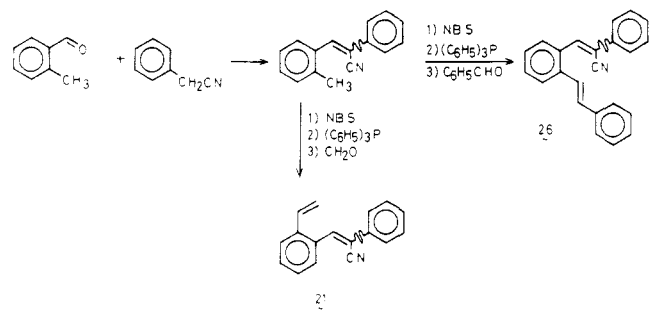
	X	Y	R	R'
22	CF_3	H	H	Me
23	Cl	H	H	Me
24	Cl	H	Me	H
25	Ph	H	H	H
26	H	CN	H	H

tigated. The effect of the noneliminating α-trifluoromethyl and β-cyano groups has also been studied in the 2-vinylstilbene system (compounds **20** and **21**). In the interpretation of the results **27** has been used for comparison.

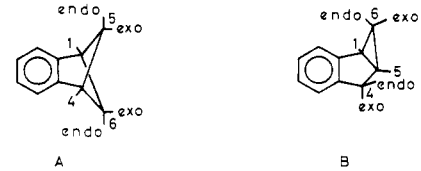
Synthesis. The compounds were prepared via known procedures as indicated in the Schemes VIII–XI. Details of the methods used will be given in the Experimental Section. The compound **27** was obtained in a way similar to that described[12] for the preparation of **4**.

Structure Determination of Photoproducts. The absence of a closely coupled multiplet in the NMR spectra of mixtures of photoproducts of **22–26** after irradiation, the absence of fragmentation peaks belonging to diarylethylenes in the mass spectra, and the absence of stilbenes or phenanthrenes as degradation products revealed that none of these compounds gave a head to head [2 + 2] cycloaddition product as was obtained from **12**.

Scheme XI



The identification of the photoproducts isolated was mainly based on their NMR data. In all cases the NMR spectra were analyzed by spin–spin decoupling and tickling and by comparison with spectra of known compounds. In some cases the spectra were simulated and iterated by the LAOCOON computer program.[13] NMR spectroscopy is very suited to distinguish between isomeric benzobicyclo[2.1.1]hex-2-ene derivatives (A) and benzobicyclo[3.1.0]-

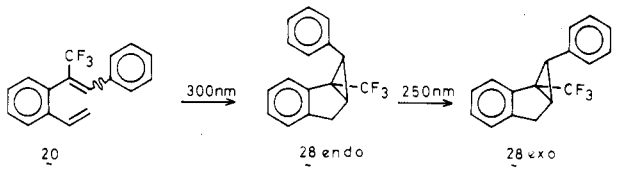


A B

hex-2-ene derivatives (B). The following information was

(13) LAOCOON-3 version by A. A. Bothner-By and S. M. Castellano with the plot routine by F. W. Pijpers and revised by J. W. Diesveld.

Scheme XII



obtained. δ values of the protons at C(5) and C(6) in B are at high field (δ <2.3) and in A at lower field (δ >2.3). Geminal coupling constants in A are different from those in B: $^2J_{5endo,5exo} = {}^2J_{6endo,6exo} = 5.5–6.5$ Hz in A; $^2J_{6endo,6exo} = 4.0–4.5$ Hz in B; $^2J_{4endo,4exo} = 16.5–17.5$ Hz in B. Vicinal coupling constants in A and B also show characteristic differences: in A $^3J_{1,5endo} = {}^3J_{1,6endo} = {}^3J_{4,5endo} = {}^3J_{4,6endo}$ = nearly zero and $^3J_{1,5exo} = {}^3J_{1,6exo} = {}^3J_{4,5exo} = {}^3J_{4,6exo} = 2.5–3.0$ Hz; in B $^3J_{1,6endo} = {}^3J_{5,6endo} = 3–4$ Hz, $^3J_{1,6exo} = {}^3J_{5,6exo} = 8–9$ Hz, $^3J_{5,4exo} = 6–7$ Hz, and $^3J_{5,4endo} = 0$ Hz. In A the long-range coupling constants $^4J_{5exo,6exo}$, $^4J_{5exo,6endo}$, and $^4J_{5endo,6exo}$ are nearly zero, but $^4J_{5endo,6endo}$ (= 7.0–7.5 Hz) is the largest coupling constant in this system. In B no long-range couplings are observed.

In Table I all relevant NMR data of the photocyclization products from the compounds investigated have been compiled, together with those of comparable photoproducts identified in previous investigations (**5**, **16**, and **19**).

Results

Compound 20. Irradiation of *trans*-α-(trifluoromethyl)-2-vinylstilbene (**20**) for a short time in hexane at 300 nm under anaerobic conditions resulted in a photostationary equilibrium of *cis*- and *trans*-**20**. Prolonged irradiation gave one novel product, which was separated by column chromatography and isolated in 67% yield. The occurrence of a large coupling (J = 17.5 Hz) in its NMR spectrum pointed to a benzobicyclo[3.1.0]hex-2-ene ($J_{4endo,4exo}$ = 17.5 Hz). The other coupling constants, 6.7 and 9.3 Hz (Table I), must be $J_{4exo,5}$ and $J_{5,6exo}$, respectively, so that substituents must be present at C(1) and C(6). The latter substituent must occupy the endo position and will be a phenyl group, because the δ value of H(6) is equal to that of H(6) in **16** (endo) and **19** (endo) (see Table I). Therefore, the product must be 1-(trifluoromethyl)-*endo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (*endo*-**28**).

Irradiation of *endo*-**28** for 3 h, at 254 nm yielded another benzobicyclo[3.1.0]hexene. In its NMR spectrum, H(4-endo) had been shifted downfield (δ 3.62) and H(6) upfield (δ 2.19), whereas $^3J_{5,6}$ was reduced to 5.7 Hz, and ^2J = 17.1 Hz was still present. Apparently, the product is the exo isomer (*exo*-**28**, Scheme XII).

Compound 22. Irradiation of **22** under the same conditions as used for **20** led after initial cis–trans isomerization again to one product (**29**), which was isolated in 60% yield. In its NMR spectrum all aliphatic proton signals with the exception of a CH_3 singlet were at relatively low field (δ 3.88, 4.16, and 5.13); this points to a benzobicyclo[2.1.1]hexene. The middle signal was a singlet, and the others were coupled (J = 2.5 Hz). This indicates that substituents are present at C(1), C(5), and C(6), whereas one of the substituents at C(5) and C(6) must occupy an exo the other an endo position. The Me protons were not deshielded by an opposing ring, as appeared from their δ value (2.32 ppm) which is equal to that in toluene (2.30 ppm). Therefore, the tolyl residue must be in the exo position. On similar grounds as given above the aryl groups must be at C(5) and (6); the product **29** is 1-(trifluoromethyl)-*endo*-5-phenyl-*exo*-6-tolylbenzobicyclo[2.1.1]hex-2-ene (Scheme XIII).

Table I. ^{1}H NMR Chemical Shifts (δ) and Coupling Constants (Hz [a]) of Substituted Benzobicyclo[3.1.0]hexenes, of Benzobicyclo[2.1.1]hexenes (5, 16, and 19) Previously Identified, and of the Photoproducts Studied in This Investigation

Benzobicyclo[3.1.0]hexenes

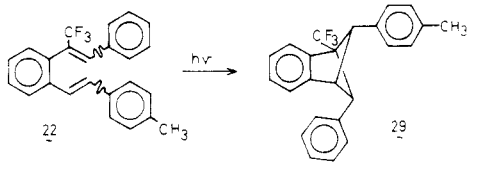
compd	shift H(4endo)	H(4exo)	H(5)	H(6endo)	H(6exo)	arom H	$J_{4endo,4exo}$	$J_{4exo,5}$	$J_{5,6endo}$	$J_{5,6exo}$
exo-**16** [b]	3.24	3.59	2.61	1.93		6.27-7.57	17.0	6.5		8.5
endo-**16** [b]	2.77	3.31	2.35		3.05	6.59-7.57	17.0	6.0	4.0	
exo-**19** [c]	3.05	3.55	2.60	2.00		6.5-7.6	16.5	6.0		8.0
endo-**19** [c]	2.62	3.28	2.60		3.09	6.5-7.6	17.0	6.0	5.0	
exo-**28**	3.62	3.04	2.86	2.19		6.6-7.8	17.1	6.3	5.7	
endo-**28**	2.77	3.25	2.61		3.03	6.6-7.8	17.5	6.7		9.3
33	4.33		2.82		3.51	6.84-7.63				8.0

Benzobicyclo[2.1.1]hexenes

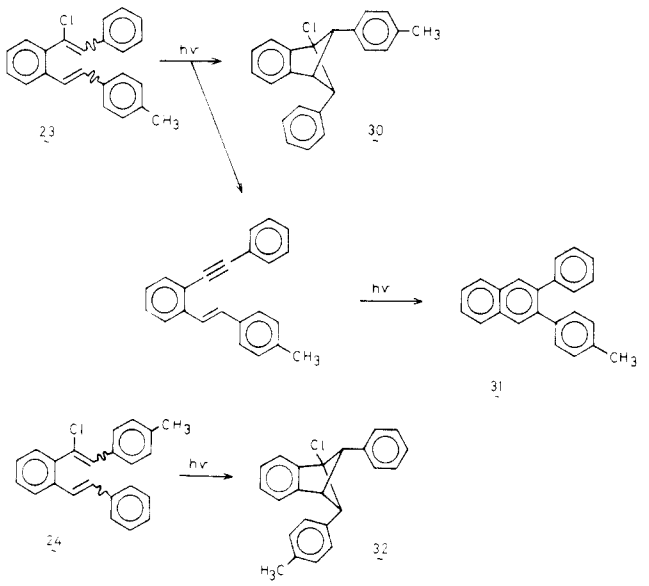
compd	shift H(1)	H(4)	H(5endo)	H(5exo)	H(6endo)	H(6exo)	arom H	CH_3	$J_{1,5exo}$	$J_{1,6exo}$	$J_{4,5exo}$	$J_{4,6exo}$	$J_{5endo,6endo}$	$J_{6endo,6exo}$
exo-**5**	3.44	3.44	3.95		2.40	3.14	6.8-7.3			2.5		2.5	7.5	6.3
endo-**5** [d]	3.44	3.44		4.26	2.35	2.66	6.6-7.2		2.5	2.5	2.5	2.5		5.5
29		3.88		4.16	5.13		6.69-7.39	2.32			2.5			
30		4.05		4.15	4.95		6.78-8.00	2.39			3.0			
32		4.05		4.17	4.90		6.84-8.00	2.17			3.0			

[a] Coupling constants not mentioned are nearly zero. [b] Reference 10 (in CCl_4). [c] Reference 11 (in $CDCl_3$). [d] Reference 5 (in CCl_4).

Scheme XIII



Scheme XIV



Compounds 23 and 24. Irradiation experiments under the conditions described above gave different results for these isomeric compounds. After initial cis–trans isomerization, **24** yielded one photoproduct (**32**), but **23** gave an irradiation mixture from which two products (**30** and **31**) could be isolated by column chromatography. The NMR spectra of **30** and **32** were very similar (see Table I) and showed the same characteristics as the spectrum of **29**; the only difference was the position of the Me signal (δ 2.39 for **30** and δ 2.17 for **32**). Apparently, the tolyl group in **30** is in the exo position and in **32** in the endo position. The compounds must be 1-chloro-*endo*-5-phenyl-*exo*-6-tolyl- and 1-chloro-*exo*-5-phenyl-*endo*-6-tolylbenzobicyclo[2.1.1]hex-2-ene, respectively (Scheme XIV).

The second product (**31**) from **23** showed in the aliphatic region only a methyl singlet. The UV spectrum pointed to a naphthalene derivative. In view of the photoelimination, previously observed with **18**, the product might be 2-phenyl-3-(*p*-tolyl)naphthalene. This supposition was confirmed by the NMR spectrum, which consists of five well-separated aromatic signals at δ 7.07 (s, 4 H, tolyl), 7.24 (s, 5 H, phenyl), 7.48 (m, 2 H, H(6) and H(7)), 7.87 (m, 2 H, H(5) and H(8)), and 7.87 (s, 2 H, H(1) and H(4)).

Compound 25. Irradiation of **25** gave a rather complex mixture, from which four products (**33–36**) could be isolated by column chromatography and subsequent thin-layer chromatography. The yields varied between 5% and 15%. The NMR spectra of **34–36** showed only aromatic protons. The compound **36** was recognized as 9-phenylbenzo[*g*]chrysene by comparison with an authentic sample.[14] The NMR spectrum of **35** contains low-field signals (δ >8.0) which are characteristic for bay protons in phenanthrene derivatives. The eventual structure assignment as 9,10-dihydro-9-phenylbenzo[*g*]chrysene was based on a comparison of the NMR spectrum with those of 9,10-dihydrobenzo[*g*]chrysene[10] and 9-substituted 9,10-dihydrophenanthrenes.[15]

The third aromatic product (**34**) appeared to be a naphthalene derivative. In view of the analogy between the photoproducts **35** and **36** from **25** and the aromatic photoproducts from **15**, the compound **34** might be 1,2,3-triphenylnaphthalene. An identical product was obtained as the sole photoproduct on irradiation of 1,2,3,4-tetraphenylbutadiene.[16] This confirms the supposed structure.

The NMR spectrum of **33** contains three aromatic proton signals. One of them is at relatively high field (δ 2.82) and coupled with the signal having δ 3.51 (J = 8.0 Hz). These data point to a benzobicyclo[3.1.0]hexene structure containing three substituents (phenyl groups). Two of them must be at C(4) and C(6), respectively, because of the absence of geminal coupling constants ($^2J_{4exo,4endo} \approx 17$ Hz; $^2J_{6exo,6endo} \approx 4$ Hz in B). The third phenyl group will be at C(1) rather than at C(5); the high-field signal cannot belong to a benzylic proton, and H(5) is the sole, nonbenzylic position. ^3J = 8.0 Hz points to cis protons at the cyclopropane ring. The 6-phenyl substituent must therefore be in the endo-position (Scheme XV).

Compounds 21 and 26. Irradiation of these β-substituted compounds led to mixtures of cis–trans isomers. The ratio after reaching the photostationary state varied with the wavelength used. Long irradiation times (until 80 h) did not lead to photocyclization products.

Discussion

The result obtained with **22** is in agreement with previous observations that the presence of an α substituent in **4** causes photocycloaddition to a benzobicyclo[3.1.0]-hex-2-ene derivative instead of a benzobicyclo[2.1.1]hex-2-ene. The effect of an α substituent arises from its influence on the conformational equilibria. Unsubstituted 2-vinylstilbene (**4**) reacts mainly from conformation a (Scheme XVI), in which the distance between the ethylenic bonds is small enough to form rapidly a C(α)–C(β') bond after excitation. This leads to benzobicyclo[2.1.1]hex-2-ene. α substituents cause torsion around the C(α)–phenyl bond, diminish the overlap between the orbitals of C(α) and C(β'), and prevent the formation of this bond. Photocycloaddition proceeds then from conformation b, which leads initially to a [4 + 2] cycloaddition product and finally to a benzobicyclo[3.1.0]hex-2-ene, but generally at a lower rate.

A β substituent (**21**) has an effect similar to that of ortho substituents in the β-phenyl group. It causes torsion around the C(β)–phenyl bond, making conformations a and b less probable in the cis isomer. Moreover, the β substituent lowers the photoreactivity of these conformations in the trans isomer, because of reduced orbital overlap between relevant atoms in the excited state.

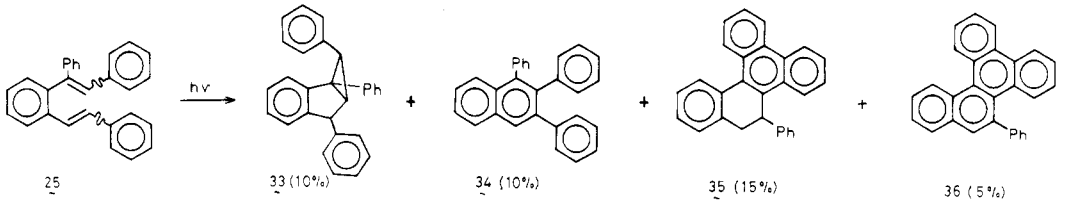
The most remarkable result from the experiments with the substituted 1,2-distyrylbenzenes **22–26** is the complete absence of dimers among the photoproducts, although their formation is the main photoreaction of **12**. Head to head [2 + 2] cycloaddition, which is a side reaction on irradiation of **12**, is also not observed with the substituted compounds. An explanation of the former observation may be that dimers are only formed from a rather planar parent compound (viz the trans,trans isomer), which tends to association, even at the low concentrations used in the irradiation experiments. α substituents reduce the planarity

(14) W. H. Laarhoven and T. J. H. M. Cuppen, *Recl. Trav. Chim. Pays-Bas*, **95**, 165 (1976).

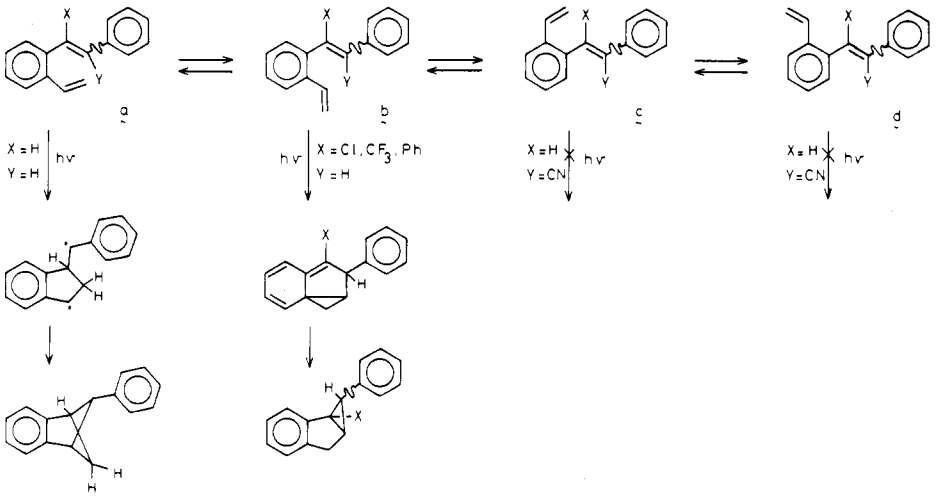
(15) R. G. Harvey, P. P. Fu, and P. W. Rabideau, *J. Org. Chem.*, **41**, 3722 (1976).

(16) T. J. H. M. Cuppen and W. H. Laarhoven, unpublished results.

Scheme XV



Scheme XVI



of the system as a consequence of torsion around the relevant C(α)–phenyl bond. This effect should also prevent the head to head [2 + 2] cycloaddition, because of the enlargement of the C(β)–C(β') distance.

The photochemical behavior of the α-substituted compounds **22–24** is very similar, but there is a small but significant difference between the very related compounds **23** and **24**: **23** undergoes photoelimination as a side reaction and **24** does not. The main photoproducts of all three compounds correspond to that of unsubstituted 2-vinylstilbene (**4**). For the explanation of this result the compounds can be viewed as containing two formally conjugated but independently absorbing chromophores, viz. an unsubstituted and an α-substituted stilbene moiety. This way of describing these molecules is in accordance with their UV spectra. The spectrum of *trans,trans*-**22** (Figure 1) has the longest wavelength absorption band at 300 nm, corresponding to that of *trans*-stilbene, but a second band is present at 256 nm, corresponding to that of α-substituted styrenes (250–260 nm) and α-substituted stilbenes. *trans,trans*-**12**, having two stilbene moieties without α-substituent, absorbs at longer wavelength than stilbene because of the more extended conjugation, but the spectrum shows a large second band at 280 nm.

On excitation of compounds containing independently absorbing chromophores, the lowest excited state will be determined by the chromophore having the lowest excitation energy.[17] In **22–24** this is the unsubstituted stilbene moiety, at least when it has the trans configuration. In that case the compound will show similar behavior to that of 2-vinylstilbenes without an α-substituent and give a benzobicyclo[2.1.1]hex-2-ene, as is found. When the unsubstituted stilbene moiety is in the cis configuration, the excitation energy of this moiety will not differ much from that of the α-substituted stilbene moiety; UV spectra of *cis*-stilbene and α-substituted *cis*- or *trans*-stilbenes are

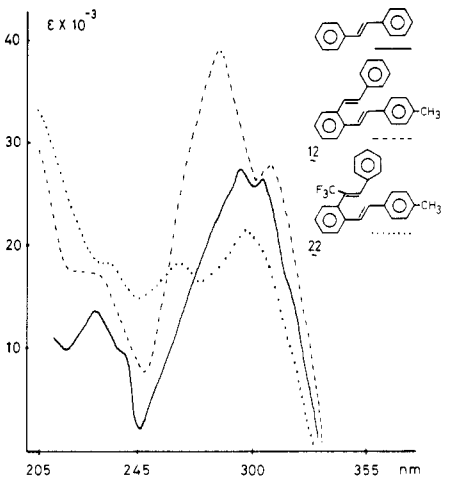


Figure 1. UV spectra of *trans*-stilbene, 1-(4-methylstyryl)-2-styrylbenzene (**12**) and 1-[α-(trifluoromethyl)-4-methylstyryl]-2-styrylbenzene (**22**) in methanol.

very similar! The excited states of rather equal energies, originating from excitation of both chromophores, might lead to a benzobicyclo[2.1.1]- and a benzobicyclo[3.1.0]-hex-2-ene. The latter product will not be formed, however, because the formation of a benzobicyclo[2.1.1]hexene from a vinylstilbene, in which the conformational equilibria have not been disturbed by steric factors, is generally faster than the formation of a benzobicyclo[3.1.0]hexene, as appears from the photoreactivity of **4** (see also Table II, **20** and **27**).

The occurrence of photoelimination on irradiation of **23** must be due to the excitation of the α-chloro-substituted stilbene moiety. With **18** this is the main reaction, which proceeds apparently faster than the competitive [4 + 2] cycloaddition.[11] The other product (**30**) from **23** must arise via excitation of the unsubstituted stilbene moiety. The difference between **23** and **24** must be due to the effect of the position of the *p*-methyl substituent on the rate of the photocycloaddition. As appears from Table II, the introduction of a *p*-methyl group in **4**, giving **27**, reduces the

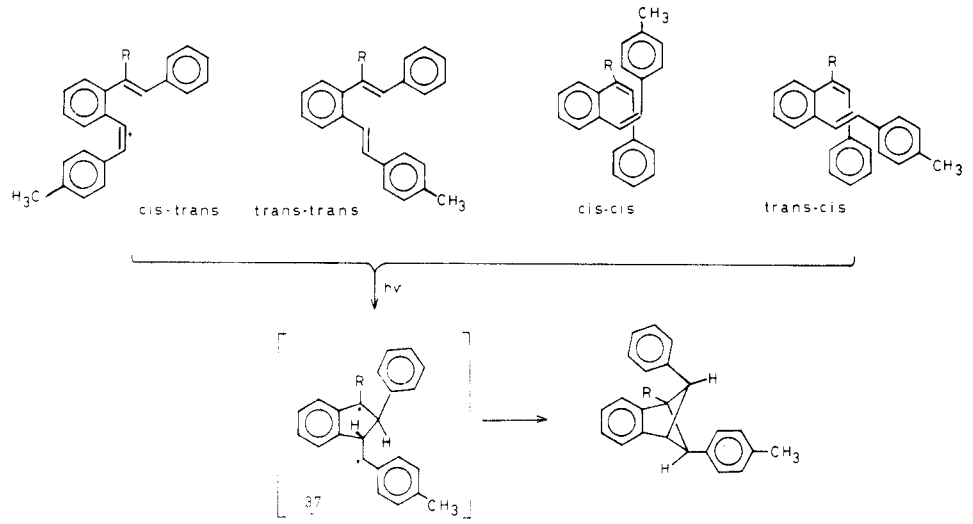
(17) N. J. Turro, "Modern Molecular Photochemistry", Benjamin/Cummings Publishing Co., Inc., Menlo Park, CA, 1978, p 340.

Table II. Percentages of Photoproducts from Irradiation under Similar Conditions at 300 nm for Equal Time Intervals ($c = 1.4 \times 10^{-3}$ mol/dm^3)

	composition of the irradiation mixture, %					
	starting compd					
compd	cis	trans	benzobicyclo-[2.1.1]hexene	benzobicyclo-[3.1.0]hexene	naphthalene deriv	polymer
4	35		53			12
27	59	8	25			5
20	68	13		10		9
22	81		19			
23	59 [a]		24 [b]		17	
24	35		18 [b]			47

[a] Including a tolane derivative. [b] The percentage decreases on irradiation at 300 nm because of the photolability of this product.

Scheme XVII

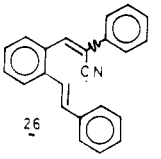


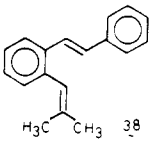
[2 + 2] photocycloaddition rate by about 50%. This enhances the preference of **24** to react via excitation of the unsubstituted stilbene moiety, so that elimination is not observed. The effect in **23** is opposite.

The results with the compounds **22–24** show that the formation of the photocyclization products **29**, **30**, and **32** proceeds quite stereospecifically: the aryl group originating from the excited stilbene moiety is always in the exo position, and the aryl group from the α-substituted moiety is in the endo position. It can be assumed that the photocyclization proceeds via a biradical intermediate, as has been proven for the photocyclization of **4**. Apparently, the primary cyclization step of α-substituted distyrylbenzenes leads only to a biradical having the aryl residues in trans position (**37** in Scheme XVII), independent of the type of isomer from which the reaction starts. In the second ring closure the phenyl group chooses the more stable exo position as was previously found with **4**.

On irradiation of **25**, the compound will be excited in the triphenylethylene moiety, which has the lower excitation energy[18] according to its UV spectrum. Therefore, the photochemical behavior should correspond to that of **15**. Indeed, **25** yields a benzobicyclo[3.1.0]hexene and several products resulting from an initial electrocyclization, quite similar to **15**.

The presence of the β substituent in **26** will cause strong torsion over the C(β)–phenyl bond. Therefore, the compound will be excited in the unsubstituted stilbene moiety. It should behave as a vinylstilbene having two substituents at C(β'). Apparently, the substituents prevent easy orbital overlap which should lead to either a [2 + 2] or a [4 + 2] photocycloaddition product. In this context it is of interest that 2-isobutylenestilbene (**38**) is also photostabile.





In summary it can be stated that the special photochemical behavior of unsubstituted 1,2-distyrylbenzene (**12**) must be ascribed to the rather planar conformation of the whole molecule in the excited state, which leads to a head to head [2 + 2] photocyclization product. Introduction of an α-substituent reduces the planarity and disturbs full conjugation. Such compounds are excited in the stilbene moiety having the lower excitation energy and give photocyclization products similar to those of corresponding 2-vinylstilbenes. Introduction of an α-phenyl substituent in **12** leads to a compound in which the triphenylethylene moiety has the lowest excitation energy and photocyclized analogues to those of α-phenyl-2-vinylstilbene. Introduction of a β substituent in **12** leads to compounds which do not undergo photocyclization because of insufficient overlap between the relevant orbitals after excitation.

Experimental Section

NMR spectra were recorded on a Varian T-60 or a Bruker WH-90 NMR instrument in CCl_4 or $CDCl_3$ solution and with tetramethylsilane (δ 0) as an internal standard.

UV spectra were measured with a Cary 15 UV or a Perkin-Elmer 555 spectrometer; the wavelength is given in nanometers. Mass spectra were obtained by using a Varian SM2B or a Finnigan 2000 mass spectrometer. Masses (m/e values) are given along

(18) H. Suzuki, *Bull. Chem. Soc. Jpn*, **33**, 389 (1960).

with relative intensities in parentheses. The irradiations were performed in a Rayonet RPR-100 or RPR-200 photoreactor. The anaerobic irradiations were carried out under an argon atmosphere. The argon was purified from oxygen through a BTS catalyst and dried over phosphorous pentoxide, silica, and potassium hydroxide. Alumina (Baker) or silica (Merck, 0.063–0.200 mm) preparative thin layer chromatography (TLC) was used for the chromatographic separations.

α-(Trifluoromethyl)-2-methylstilbene. A 17.5-g (0.05 mol) sample of benzyltriphenylphosphonium bromide and 9.5 g (0.05 m) of 2-methyl-α,α,α-trifluoroacetophenone[19] were dissolved in 200 mL of methanol. After addition of 2.8 g (0.05 mol) of sodium methoxide the solution was refluxed for 20 h. The solvent was evaporated and the residue dissolved in a mixture of chloroform and water. The chloroform layer was extracted with water, separated, and dried over $MgSO_4$. The solvent was evaporated again and the residue dissolved in hexane. Triphenylphosphine oxide precipitated as a white solid and was filtered off. The filtrate was evaporated, and the residue was purified by column chromatography on silica with hexane as the eluent. The total yield of *cis*- and *trans*-α-(trifluoromethyl)-2-methylstilbene was 60%.

Trans isomer: ^1H NMR ($CDCl_3$) δ 2.39 (s, CH_3, 3 H), 6.86 (s, H(β), 1 H), 7.03–7.30 (m, arom H, 4 H), 7.30–7.67 (m, arom H, 5 H); UV (methanol) λ_{max} (log ε) 203 (4.52), 250 (4.30); mass spectrum, 263 (40), 262 (M^+, 100), 261 (12), 248 (19), 247 (58), 227 (34), 193 (64), 192 (14), 191 (16), 184 (36), 179 (24), 178 (71), 165 (11).

Cis isomer: ^1H NMR ($CDCl_3$) δ 2.13 (s, CH_3, 3 H), 6.82–7.44 (m, arom H + H(β), 10 H); UV (methanol) λ_{max} (log ε) 208 (4.59), 252 (4.09); mass spectrum, 263 (36), 262 (M^+, 100), 261 (12), 247 (49), 227 (30), 193 (56), 192 (14), 191 (15), 184 (33), 197 (17).

α-(Trifluoromethyl)-2-vinylstilbene (20). A 3-g (0.017 mol) sample of *N*-bromosuccinimide (NBS) was added to 4.5 g (0.017 mol) of 2-methyl-α-(trifluoromethyl)stilbene dissolved in CCl_4. After the mixture was refluxed for 5 h under irradiation with a 250 W-Philips IR lamp, the benzylic bromide was formed in 90% yield. Without further purification the bromide was dissolved in chloroform and stirred with an equivalent amount of triphenylphosphine for 20 h. After evaporation of most of the solvent the solution was poured into ether. The phosphonium salt precipitated as a white solid, which was filtered, dissolved in ethanol, and supplied with an equivalent amount of sodium methoxide. After 0.5 h, 10 equiv of a formaldehyde–ethanol solution (10%) was added dropwise. The mixture was stirred for 20 h and refluxed for 2 h. The solvent was evaporated and the residue dissolved in a mixture of chloroform and water. The chloroform layer was extracted with water, separated, and evaporated, and the residue was purified by column chromatography on silica with hexane as the eluent. A 67% yield of *cis*- and *trans*-**20** as colorless oils was obtained.

trans-**20**: ^1H NMR ($CDCl_3$) δ 5.26 (dd, *trans*-ArC=CH^2, 1 H), 5.70 (dd, ArC=CH^1, 1 H), 6.84 (s, H(β), 1 H), 6.88 (dd, ArH^3C=C, 1 H), 7.16–7.70 (m, arom H, 9 H), $J_{1,2}$ = 1.2 Hz, $J_{1,3}$ = 17.2 Hz, $J_{2,3}$ = 10.8 Hz; UV (methanol) λ_{max} (log ε) 290 (3.25, sh), 246 (4.42).

cis-**20**: ^1H NMR ($CDCl_3$) δ 5.12 (dd, H^2, 1 H), 5.62 (dd, H^1, 1 H), 6.75 (dd, H^3, 1 H), 6.82–7.75 (m, arom H + H(β), 10 H, $J_{1,2}$ = 1.2 Hz, $J_{1,3}$ = 17.2 Hz, $J_{2,3}$ = 10.8 Hz); UV (methanol) λ_{max} (log ε) 244 (4.32); mass spectrum (mixture of isomers), 274 (M^+, 6), 265 (5), 101 (9), 91 (100), 77 (13).

α-(Trifluoromethyl)-2-(4-methylstyryl)stilbene (22). A similar procedure as given in the previous prescriptions but with 4-methylbenzaldehyde instead of the formaldehyde gave **22**: yield 56% (mixture of isomers which could not be completely separated); ^1H NMR ($CDCl_3$) δ 2.07 (s, CH_3, 3 H), 6.75–7.70 (m, all other protons, 16 H); UV (methanol) λ 324 (sh), 314 (max), 301 (max), 255 (max); mass spectrum, 364 (M^+, 100), 295 (11), 274 (15), 273 (15), calcd for $C_{24}H_{14}F_3$ *m/e* 364.313, found *m/e* 364.311 ± 0.003.

α-Chloro-2-(4-methylstyryl)stilbene (23). A procedure similar to that applied in the synthesis of α-chloro-2-vinylstilbene (**18**)[11] with *p*-methylbenzaldehyde instead of formaldehyde gave **23** as a mixture of cis–trans isomers: 88% yield; ^1H NMR ($CDCl_3$) δ 2.2–2.3 (s, CH_3, 3 H), 6.5–7.8 (m, all other protons, 16 H); UV (methanol) λ_{max} 300, 255; mass spectrum, 332, 330 (M^+, 4, 9), 295 (50), 203 (41), 204 (61), 205 (37), 206 (36), 193 (37), 192 (94), 191 (100), 189 (57); cald for $C_{23}H_{19}Cl$ *m/e* 330.235, found *m/e* 330.235 ± 0.003.

2-Cyanostilbene. This compound was obtained by known methods,[12] starting from 2-methylbenzonitrile. The nitrile was treated with NBS and triphenylphosphine and the phosphonium salt was converted into the product via a Wittig-reaction with benzaldehyde. After distillation at 50–65 °C (1–7 mmHg) 2-cyanostilbene was obtained: ^1H NMR ($CDCl_3$) δ 6.70 (s, H(α) and H(β), 2 H), 7.06–773 (m, arom H, 9 H).

4'-Methyl-2-stilbenyl Benzyl Ketone. 2-Cyanostilbene was converted into the ketone by treatment with (*p*-methylbenzyl)-magnesium bromide via a known method:[10] ^1H NMR (CCl_4) δ 2.27 (s, CH_3, 3 H), 2.77 (s, CH_2, 2 H), 6.87 (br s, arom H, 13 H).

α-Chloro-2-styryl-4'-methylstilbene (24). The previous compound was treated with PCl_5 in benzene.[11] A total yield of 31% of *cis*- and *trans*-**24** was obtained. By column chromatography a small amount of 1-chloro-2-(*p*-tolyl)-3-phenylnaphthalene was also isolated.

For the mixture of isomers (**24**): ^1H NMR (CCl_4) δ 2.1–2.3 (2 s, CH_3, 3 H), 6.4–7.6 (m, all other protons, 16 H); UV (methanol) λ_{max} 306 (sh), 254 (max); mass spectrum, 332, 330 (M^+, 14, 40), 295 (100), 279 (20), 262 (16), 239 (38), 202 (27), 190 (54); calcd for $C_{23}H_{19}Cl$ *m/e* 330.235, found *m/e* 330.234 ± 0.003.

For 1-chloro-2-(*p*-tolyl)-3-phenylnaphthalene: ^1H NMR ($CDCl_3$) δ 2.32 (s, CH_3, 3 H), 7.05 (s, arom H, 4 H), 7.13 (s, arom H, 5 H), 7.51–7.96 (m, arom H_{napht}, 4 H), 8.28–8.42 (m, arom H(8), 1 H; UV (methanol) λ_{max} 298, 250, 238; mass spectrum, 330, 328 (M^+, 37, 100), 329 (28), 293 (17), 292 (19), 278 (35), 248 (28), 246 (28).

α-Phenyl-2-styrylstilbene (25). A modification of the synthesis of α-phenyl-2-vinylstilbene (**15**),[9] with benzaldehyde instead of formaldehyde, gave **25** as a mixture of isomers in a yield of 25% (colorless oil): ^1H NMR ($CDCl_3$) δ 6.0–6.8 (m, 2 H), 6.8–7.4 (m, 19 H), 7.6–7.8 (m, 1 H); UV (methanol) λ_{max} 294, 226; mass spectrum, 358 (M^+, 74), 359 (22), 281 (20), 268 (62), 267 (100), 265 (62), 252 (34), calcd for $C_{28}H_{22}N$ *m/e* 358.172, found *m/e* 358.171 ± 0.003.

β-Cyano-2-methylstilbene. According to the method of Wawzonek[20] this stilbene was obtained in a yield of 75%: mp 95.5–96.5 °C; ^1H NMR ($CDCl_3$) δ 2.36 (s, CH_3, 3 H), 7.56 (s, H(α), 1 H), 7.09–7.93 (m, arom H, 9 H); UV (ethanol) λ_{max} (log ε) 306 (4.27), 226 (4.09), λ_{min} (log ε) 216 (4.01).

β-Cyano-2-vinylstilbene (21). β-Cyano-2-methylstilbene was converted into **21** in a manner similar to that described for **20** (yield 72%). The isomers were separated by TLC.

cis-**21**: ^1H NMR ($CDCl_3$) δ 5.40 (dd, H(2), 1 H), 5.65 (dd, H(1), 1 H), 6.85 (dd, H(3), 1 H), 6.95–7.90 (m, arom protons + H(α), 10 H, $J_{1,2}$ = 1.2 Hz, $J_{1,3}$ = 17.1 Hz, $J_{2,3}$ = 10.8 Hz).

trans-**21**: mp 57–59 °C; ^1H NMR ($CDCl_3$) δ 5.44 (dd, H(2), 1 H), 5.62 (dd, H(1), 1 H), 6.91 (dd, H(3), 1 H), 7.82 (s, H(α), 1 H), 7.31–8.01 (m, arom protons, 9 H, $J_{1,2}$ = 1.2 Hz, $J_{1,3}$ = 17.1 Hz, $J_{2,3}$ = 10.8 Hz); UV (methanol) λ_{max} (log ε) 306 (4.26), 251 (4.17), 229 (4.21), λ_{min} (log ε) 272 (3.95), 244 (4.16), 215 (4.14); mass spectrum (mixtures of isomers), 231 (M^+, 100), 230 (56), 216 (10), 204 (14), 203 (21), 202 (22), 191 (6), 190 (6), 189 (5), 178 (6), 175 (5), 154 (12), 153 (19).

β-Cyano-2-styrylstilbene (26). β-Cyano-2-methylstilbene was converted into **26** as described for **25** (yield 54%). The mixture of isomers was not separated: ^1H NMR ($CDCl_3$) δ 6.67 (s, $H_{ethylene}$), 6.53–7.78 and 7.84–8.10 (m, arom protons + $H_{ethylene}$); UV (methanol) λ_{max} 303, 276, 269; mass spectrum, 307 (M^+, 4), 220 (4), 210 (32), 209 (64), 208 (65), 207 (57), 205 (35), 204 (100), 203 (60), calcd for $C_{23}H_{17}N$ *m/e* 307.136, found *m/e* 307.134 ± 0.003.

4'-Methyl-2-vinylstilbene (27). A 44.5-g (0.1 mol) sample of *p*-xylyltriphenylphosphonium bromide was dissolved in dry ethanol. The solution was supplied with 1.1 equiv of CH_3ONa, added in small amounts under stirring. After the mixture was stirred for 15 min, 13.2 g (0.1 m) of 2-vinylbenzaldehyde[21] was added dropwise. The stirring was continued for 18 h after which

(19) K. T. Dishart and R. Levine, *J. Am. Chem. Soc.*, 78, 2268 (1956).

(20) S. Wawzonek and E. M. Sanolin, "Organic Syntheses", Collect. Vol. II, 5th ed., Wiley, New York, 1965, p 715.

(21) W. J. Dale, L. Stan, and C. W. Strobel, *J. Org. Chem.*, 26, 2225 (1961).

the solvent was evaporated. The residue was purified as described for **20**. A 78% yield of *cis*- and *trans*-**27** (colorless oils) was obtained.

cis-**27**: ^{1}H NMR ($CDCl_3$) δ 2.24 (s, CH_3, 3 H), 5.22 (dd, H(2), 1 H), 5.66 (dd, H(1), 1H), 6.61 (br s, H(α) **H**(β), 2 H), 6.95 (dd, H(3), 1 H), 6.70–7.60 (m, arom protons, 8 H, $J_{1,2}$ = 1.5 Hz, $J_{1,3}$ = 17.6 Hz, $J_{2,3}$ = 10.9 Hz); UV (methanol) λ_{max} (log ϵ) 294 (3.83, sh), 274 (3.96, sh), 250 (4.17), 237 (4.10, sh).

trans-**27**: ^{1}H NMR ($CDCl_3$) δ 2.30 (s, CH_3, 3 H), 5.31 (dd, H(2), 1 H), 5.59 (dd, H(1), 1 H), 6.93 (d, H(β), 1 H), 7.03 (dd, H(3), 1 H), 7.33 (d, H(α), 1 H), 6.90–7.80 (m, arom protons, 8 H); UV (methanol) λ_{max} (log ϵ) 301 (4.30), 268 (3.85, sh), 258 (4.17, sh), 225 (4.12); mass spectrum (mixture of isomers), 221 (36), 220 (M^+, 100), 219 (26), 215 (11), 206 (15), 205 (70), 204 (29), 203 (33), 202 (34), 189 (16), 178 (19), 129 (16), 128 (43), 119 (13), 115 (15).

2-(1-Isobutenyl)stilbene (37). 2-Stilbenecarbaldehyde, synthesized from 2-(bromomethyl)stilbene and nitropropane with sodium,[22] was converted into **37** with isopropyltriphenylphosphonium bromide in a yield of 27%. For *trans*-**37**: ^{1}H NMR ($CDCl_3$) δ 2.50 and 2.70 (2 s, 2 CH_3, 6 H), 6.73 (m, H(3), 1 H), 7.10–7.90 (m, arom protons + H(α) + H(β), 11 H); UV (methanol) λ_{max} (log ϵ) 299 (4.34), 2.50 (4.11), 2.17 (4.23).

Irradiations. α-(Trifluoromethyl)-2-vinylstilbene (20). A stream of argon was led through a solution of **20** (10^{-3} mol/dm^3) in hexane during 0.5 h. Then the solution was irradiated in a quartz tube at 300 nm for 25 h. After evaporation of the solvent, the product was isolated and purified by column chromatography on silica with hexane as the eluent. The colorless oil was identified as *endo*-6-phenyl-1-(trifluoromethyl)benzobicyclo[3.1.0]hex-2-ene (**28**) by spectroscopy: ^{1}H NMR ($CDCl_3$) δ 2.61 (dd, H(5), 1 H), 2.77 (dd, H(4endo), 1 H), 3.03 (d, H(6exo), 1 H), 3.25 (dd, H(4exo), 1 H), 6.60–7.80 (m, arom protons, 9 H, $J_{4exo,5}$ = 6.7 Hz, $J_{4exo,4endo}$ = 17.5 Hz, $J_{4endo,5}$ = $J_{4endo,6exo}$ = $J_{4exo,6exo}$ = 0, $J_{5,6exo}$ = 9.3 Hz; after iteration of the stimulated spectrum, δ 2.62, 2.76, 3.02, and 3.23, respectively, give $J_{4exo,5}$ = 6.5 Hz, $J_{4endo,4exo}$ = −16.2 Hz, $J_{4endo,5}$ = 1.5 Hz, $J_{4endo,6exo}$ = 1.5 Hz, $J_{4exo,6exo}$ = 0, $J_{5,6exo}$ = 9.6 Hz; UV (methanol) λ_{max} (log ϵ) 294 (2.74), 2.83 (2.79), sh), 274 (3.13), 266 (3.15), 258 (3.21, sh), 251 (3.37); mass spectrum, 274 (M^+, 6), 205 (3), 118 (4), 105 (3), 91 (100).

***endo*-6-Phenyl-1-(trifluoromethyl)benzobicyclo[3.1.0]-hex-2-ene (28).** Compound *endo*-**28** (5 mg in 50 mL of hexane) was irradiated for 3 h at 254 nm under the same conditions as described above. Besides polymers, an endo–exo mixture of **28** had been formed according to NMR. *exo*-6-Phenyl-1-(trifluoromethyl)benzobicyclo[3.1.0]hex-2-ene (*exo*-**28**) was not isolated. NMR data of *exo*-**28** are given in Table I.

α-(Trifluoromethyl)-2-(4-methylstyryl)stilbene (22). A stream of argon was led through a solution of 600 mg of **22** in 1.5 L of hexane. The solution was irradiated in a quartz tube at 300 nm for 40 h. The NMR spectrum revealed the presence of *exo*-5-(*p*-tolyl)-*endo*-6-phenylbenzobicyclo[2.1.1]hex-2-ene (**29**). After the usual workup, column chromatography of the residue yielded **29** as a colorless oil: 60% yield; ^{1}H NMR (see Table I): UV (methanol) λ_{max} (log ϵ) 303 (2.82), 271 (3.19), 264 (3.34), 257 (3.36); mass spectrum, 364 (M^+, 2), 349 (3), 295 (5), 273 (7), 181 (25), 105 (100), calcd for $C_{24}H_{19}F_3$ m/e 364.313, found m/e 364.312 ± 0.003.

α-Chloro-2-(4-methylstyryl)stilbene (23). Irradiation of a 10^{-3} mol/dm^3 solution of **23** in hexane under argon atmosphere at 300 nm gave after short irradiation 2-(4-methylstyryl)tolane. After 3 h of irradiation 24% and after 8 h 35% of *exo*-5-(*p*-tolyl)-*endo*-6-phenyl-1-chlorobenzobicyclo[2.1.1]hex-2-ene (**30**) together with 2-phenyl-3-(*p*-tolyl)naphthalene (**31**) appeared to be present. (After 26 h of irradiation at 360 nm, 42% of **30** was obtained.) The photoproducts were separated and purified by column chromatography on silica with hexane as the eluent and by TLC. The photoproducts were eluted in following order: tolane derivative, **30**, and **31**.

2-(4-Methylstyryl)tolane. Cis isomer: ^{1}H NMR ($CDCl_3$) δ 2.29 (s, CH_3, 3 H), 6.65 (d, H(3), 1 H), 6.86 (d, H(3), 1 H), 7.02–7.67 (m, arom H, 14 H, $J_{2,3}$ = 12.3 Hz); UV (methanol) λ_{max} (log ϵ) 298 (4.25, sh), 279 (4.35), 274 (4.35); UV λ_{min} (log ϵ) 241 (4.13). Trans isomer: mp 96–97 °C; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, CH_3, 3 H), 7.06–7.76 (m, all other protons, 16 H); UV (methanol) λ_{max} (log ϵ) 3.17 (4.35), 280 (4.57), 276 (4.56, sh); UV λ_{min} (log ϵ) 296 (4.26), 244 (4.10); mass spectrum, (mixture of isomers) 295 (23), 294 (M^+, 100), 293 (27), 279 (59), 278 (23), calculated for $C_{23}H_{18}$ m/e 294.141, found m/e 294.141 ± 0.03.

1-Chloro-*exo*-5-(*p*-tolyl)-*endo*-6-phenylbenzobicyclo-[2.1.1]hex-2-ene (30): colorless oil; ^{1}H NMR (see Table I); UV (methanol) λ_{max} (log ϵ) 273 (3.25), 2.66 (3.28), 258 (3.25), 254 (3.22, sh); mass spectrum 352 (4), 330 (M^+, 11), 196 (16), 295 (50), 294 (16), 280 (7), 279 (10), 278 (9), 239 (12), 225 (11), 217 (10), 205 (39), 204 (61), 203 (36), 202 (35), 193 (38), 192 (94), 191 (100).

2-Phenyl-3-(*p*-tolyl)naphthalene (31): mp 70.5–71.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.33 (s, CH_3, 3 H), 7.07 (s, arom H, *p*-tolyl, 4 H), 7.24 (s, arom H, phenyl, 5 H), 7.48 (m, H(6) and H(7), 2 H), 7.87 (2, H(1) and H(4), 2 H), 7.87 (m, H(5) and H(8), 2 H); UV (methanol) λ_{max} (log ϵ) 3.17 (4.35), 280 (4.57), 276 (4.56, sh), λ_{min} (log ϵ) 296 (4.26), 244 (4.10); mass spectrum, 295 (23), 294 (M^+, 100), 293 (27), 279 (59), 278 (23), calculated for $C_{23}H_{18}$ m/e 294.141, found m/e 294.142 ± 0.003.

α-Chloro-4′-methyl-2-styrylstilbene (24). Irradiation of 25 mg of **24** dissolved in 50 mL of hexane in a quartz tube at 300 nm under an argon atmosphere for 6 h yielded according to the NMR spectrum, besides 29% **24**, 21% *exo*-5-phenyl-*endo*-6-(*p*-tolyl)-1-chlorobenzobicyclo[2.1.1]hex-2-ene (**32**) and 50% polymer (at 360 nm after 43 h of irradiation, 30% **32** and 70% polymer). After the usual workup **32** was isolated from the first elution fractions: ^{1}H NMR (see Table I); UV (methanol) λ_{max} (log ϵ) 273 (3.24), 264 (3.30), 259 (3.29), 252 (3.27); mass spectrum, 332 (2), 330 (M^+, 6), 296 (5), 295 (14), 272 (5), 239 (6), 219 (37), 218 (20), 217 (100), calculated for $C_{23}H_{19}Cl$ m/e 330.235, found m/e 330.235 ± 0.003.

1-Chlorobenzobicyclo[2.1.1]hex-2-ene Derivatives. Irradiation of 10^{-3} mol/dm^3 solutions of **30** and **32** in hexane under argon atmosphere at 254 nm for 5 h led to the disappearance of these compounds. The resulting products were not identified.

α-Phenyl-2-styrylstilbene (25). After 10 h of irradiation of a 1.5×10^{-3} M solution of **25** in hexane under an argon atmosphere at 360 nm, the NMR spectrum showed the presence of ~10% 1,2,3-triphenylnaphthalene (**34**), ~10% 1, *exo*-4,*endo*-6-triphenylbenzobicyclo[3.1.0]hex-2-ene (**33**), ~5% 9-phenylbenzo[*g*]chrysene (**36**), ~15% 9,10-dihydro-9-phenylbenzo[*g*]chrysene (**35**), 5% of an unidentified phenanthrene derivative, ~2% an unidentified benzobicyclo[3.1.0]hex-2-ene derivative, ~53% **25** and polymers. After the usual workup, column chromatography on alumina with hexane as the eluent followed by TLC gave the photoproducts in the following order.

1,2,3-Triphenylnaphthalene (34), mp 153 °C. This compound gave the following spectroscopical data, in agreement with those of an authentic sample: ^{1}H NMR ($CDCl_3$) δ 6.66–7.25 (m, arom H_{phenyl}, 15 H), 7.25–7.66 (m, H(5–7), 3 H), 7.87–7.96 (s and m, H(4) and H(8), 2 H); UV (methanol) λ_{max} (log ϵ) 301 (3.76, sh), 287.5 (3.96, sh), 245 (4.30); UV λ_{min} (log ϵ) 228 (3.98); mass spectrum, 356 (M^+, 100), 279 (23), 278 (18), 277 (12), 276 (13).

1,*exo*-4,*endo*-6-Triphenylbenzobicyclo[3.1.0]hex-2-ene (33): ^{1}H NMR (see Table I); UV (methanol) λ_{max} (log ϵ) 298 (3.03, sh), 280 (3.27), 270 (3.32); mass spectrum, 358 (M^+, 20), 280 (10), 268 (20), 267 (100), 269 (18), 252 (9), 202 (5), 192 (6), 167 (24).

Unidentified benzobicyclo[3.1.0]hex-2-ene derivative: ^{1}H NMR ($CDCl_3$) δ 2.95–3.45 (m, H(1–6), 4 H), 6.71–7.95 (m, arom H, 19 H).

9-Phenylbenzo[*g*]chrysene (36), mp 167 °C. The spectroscopical data were in agreement with literature data.[13]

Unidentified phenanthrene derivative: ^{1}H NMR ($CDCl_3$) δ 7.0–8.0 (m, arom H), 8.7–8.9 (m, arom H).

9,10-Dihydro-9-phenylbenzo[*g*]chrysene (35): ^{1}H NMR ($CDCl_3$) δ 3.12 (B of ABX, H(10), 1 H), 3.51 (A of ABX, H(10′), 1 H), 4.91 (X of ABX, H(9), 1 H), 6.80–8.00 (m, arom H, 15 H), 8.53–8.82 (m, arom H, 2 H, $J_{9,10'}$ = 5.1 Hz, $J_{9,10}$ = 2.9 Hz, $J_{10,10'}$ = −14.2 Hz, UV (methanol) λ_{max} (log ϵ) 330 (3.93), 317 (4.00), 3.05 (3.28, sh), 279 (4.12), 268 (4.29), 260 (4.35), 251 (4.34), 243 (4.34).

4′-Methyl-2-vinylstilbene (27). A 2×10^{-3} M solution of **27** in methanol degassed with argon was irradiated for 9 h at 360 nm and yielded 52% *exo*-5-(*p*-tolyl)benzobicyclo[2.1.1]hex-2-ene, 38% polymers, and 10% **27**. After the usual workup the first elution fractions contained the bicyclohexene (colorless oil): ^{1}H NMR ($CDCl_3$) δ 2.36 (s, CH_3, 3 H), 2.39 (dd, H(6endo), 1 H), 3.14

(22) H. B. Hass and M. L. Bender, "Organic Syntheses", Collect. Vol. II, 5th ed., Wiley, New York, 1965, p 932.

(d of t, H(6exo), 1 H), 3.40 (d, H(1) and H(4), 2 H), 3.92 (d, H(5), 1 H), 6.80–7.40 (m, arom H, 8 H, $J_{1,5} = J_{1,6endo} = 0$, $J_{1,6exo} = 2.5$ Hz, $J_{6exo,6endo} = 6.3$ Hz, $J_{5endo,6endo} = 7.5$ Hz); UV (methanol) λ_{max} (log ϵ) 273 (3.24), 265 (3.24), 259 (3.17), 252 (3.10, sh), 220 (4.10); mass spectrum 220 (M^+, 4), 205 (2), 204 (2), 203 (2), 202 (1), 128 (6), 121 (2), 115 (5), 105 (100).

Registry No. *cis*-**4**, 59154-50-6; *exo*-**5**, 58719-66-7; **12**, 27685-27-4; **15**, 80663-29-2; **18**, 80663-30-5; *cis*-**20**, 80663-31-6; *trans*-**20**, 80663-32-7; *cis*-**21**, 80663-33-8; *trans*-**21**, 80663-34-9; **22**, 80663-35-0; **23**, 80663-36-1; **24**, 80663-37-2; **25**, 80663-38-3; **26**, 80663-39-4; *cis*-**27**, 80663-40-7; *trans*-**27**, 80663-41-8; *endo*-**28**, 80663-42-9; *exo*-**28**, 80734-35-6; **29**, 80663-43-0; **30**, 80663-44-1; **31**, 80663-45-2; **32**, 80734-36-7; **33**, 80679-17-0; **34**, 1942-39-8; **35**, 80679-18-1; **36**, 60300-71-2; *trans*-**38**, 80663-46-3; benzyltriphenylphosphonium bromide, 1449-46-3; 2-methyl-α,α,α-trifluoroacetophenone, 341-39-9; *trans*-α-(trifluoromethyl)-2-methylstilbene, 80663-47-4; *cis*-α-(trifluoromethyl)-2-methylstilbene, 80679-19-2; (*E*)-α-(trifluoromethyl)-2-(bromomethyl)stilbene, 80663-48-5; (*Z*)-α-(trifluoromethyl)-2-(bromomethyl)stilbene, 80663-49-6; 4-methylbenzaldehyde, 104-87-0; 2-methylbenzonitrile, 529-19-1; 2-cyanostilbene, 80663-50-9; 4′-methyl-2-stilbenyl benzyl ketone, 80663-51-0; *p*-methylbenzyl bromide, 104-81-4; 1-chloro-2-(*p*-tolyl)-3-phenylnaphthalene, 80663-52-1; β-cyano-2-methylstilbene, 80663-53-2; *p*-xylyltriphenylphosphonium bromide, 2378-86-1; 2-vinylbenzaldehyde, 28272-96-0; 2-stilbenecarbaldehyde, 63104-89-2; *cis*-2-(4-methylstyryl)tolane, 80663-54-3; *trans*-2-(4-methylstyryl)tolane, 80663-55-4; *exo*-5-(*p*-tolyl)benzobicyclo[2.1.1]hex-2-ene, 80663-56-5; *trans*-stilbene, 103-30-0.

New Approach to Lythraceae Alkaloids: Total Synthesis of (±)-Vertaline

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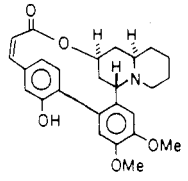
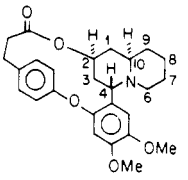
A new approach to Lythraceae alkaloids is described within the context of a total synthesis of (±)-vertaline (**2**). The use of *N*-silyl imines in the preparation of benzylic amines as well as a stereoselective bicycloannelation approach to the synthesis of quinolizidinones is discussed.

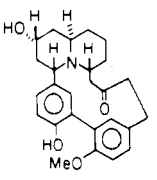
Macrocyclic quinolizidine alkaloids isolated from members of the Lythraceae plant family can be classified according to three structural types. These are represented below by the biphenyl lactone cryogenine (**1**), the diphenyl



1



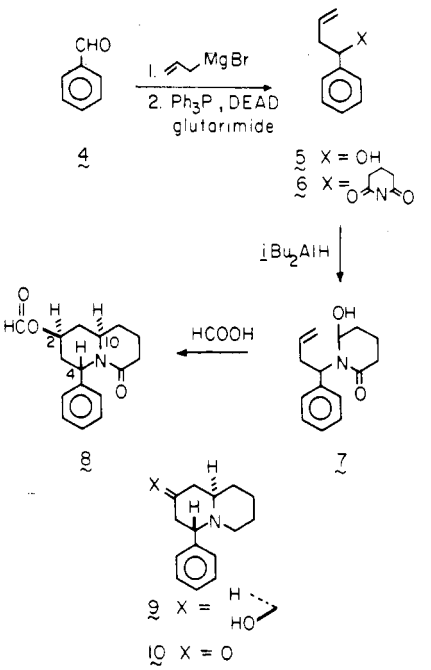
2



3

ether lactone vertaline (**2**), and the carbocyclic biphenyl lythrumine (**3**).[1] Several total syntheses of lactonic Lythraceae alkaloids have been reported, all of which use Mannich reactions of pelletierine with substituted benzaldehydes, biaryls, or diaryl ethers to assemble the quinolizidine moiety.[2-5] We recently reported a highly stereoselective quinolizidinone synthesis which suggested an efficient alternative to the pelletierine route to Lythraceae alkaloids.[6] This report outlines the development of this method within the context of a total synthesis of (±)-vertaline (**2**).

Scheme I



Our approach to vertaline was based on the model studies[6] shown in Scheme I. Treatment of benzaldehyde (**4**) with allylmagnesium bromide gave carbinol **5** (91%) which was converted to glutarimide **6** (55%) by using the conditions of Mitsunobu.[7] Imide **6** was reduced with diisobutylaluminum hydride[8] to afford carbinol amide **7**

(1) For a review see: Fujita, E.; Fuji, K. "International Review of Science, Organic Chemistry Series Two"; Wiesner, K., Ed.; Butterworths: London, 1976, 119.

(2) For syntheses of diphenyl ether lactones see the following. Vertaline: Hanaoka, M.; Ogawa, N.; Arata, Y. *Chem. Pharm. Bull.* **1974**, *22*, 973. Hanaoka, M.; Ogawa, N.; Arata, Y. *Ibid.* **1976**, *24*, 1045. Lagerine: Hanaoka, M.; Kamei, M.; Arata, Y. *Ibid.* **1975**, *23*, 2191. Decaline: Hanaoka, M.; Ogawa, N.; Arata, Y. *Ibid.* **1975**, *23*, 2140. Hanoaka, M.; Ogawa, N.; Arata, Y. *Tetrahedron Lett.* **1973**, 2355. Wróbel, J. T.; Golebiewski, W. M. *Ibid.* **1973**, 4293.

(3) For syntheses of biphenyl lactones see the following: Decinine: Lantos, I.; Loev, B. *Tetrahedron Lett.* **1975**, 2011. Decamine: Lantos, I.; Razgaitis, C.; VanHoeven, H.; Loev, B. *J. Org. Chem.* **1977**, *42*, 228.

(4) No syntheses of the macrocarbocyclic quinolizidines (e.g., **3**) have been reported.

(5) For other relevant reports see: Fuji, K.; Ichikawa, K.; Fujita, E. *Tetrahedron Lett.* **1979**, 361. Horhammer, R. B.; Schwarting, A. E.; Edwards, J. M. *J. Org. Chem.* **1975**, *40*, 656.

(6) Hart, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 397.

(7) Mitsunobu, O.; Wada, M.; Sano, T. *J. Am. Chem. Soc.* **1972**, *94*, 679.

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