dichloromethane–pentane, 2:5).

Reaction of Diphenyl Diselenide with 1-Hexyne (Aprotic). A solution of 1-hexyne (5 mmol), diphenyl diselenide (5 mmol), and sodium 2-methyl-2-butanolate (2 mmol) in 25 mL of benzene was heated under reflux for 24 h. Precipitated sodium benzeneselenolate was removed by filtration. The filtrate was diluted with 100 mL of water and extracted with toluene. The yellow oil (0.6 g) obtained by removal of the solvent under reduced pressure was subjected to ^{77}Se NMR spectroscopy without further purification. Apart from the products **8a** and **9h** mentioned in Table II it contained about 25% unreacted diphenyl diselenide.

Synthesis of *cis*-1-Phenyl-1,2-bis(phenylseleno)ethene. To a stirred solution of phenylacetylene (10 mmol) in 50 mL of dry THF was added sodium 2-methyl-2-butanolate (10 mmol) and 5 min later diphenyl diselenide (10 mmol). The solution became colorless and white crystals of sodium benzeneselenolate precipitated. At this stage the reaction mixture could be filtered and the filtrate worked up to give an almost quantitative yield of **9a**. In order to obtain **2a** 20 mL ethanol was added to the above reaction mixture, and it was refluxed overnight (16 h), diluted with 5 volumes of water, and extracted with toluene. The organic phase was washed with water, dried over $MgSO_4$, and evaporated under reduced pressure to yield **2a** as a slightly yellow oil 3.95 g (92%). ^{1}H NMR δ 7.0–7.8 (multiplet). ^{77}Se NMR data are given in Table III. The product contained no impurities judged from TLC and ^{77}Se NMR.

Phenyl 1-Hexynyl Selenide (9h). To a stirred solution of 1-hexyne (20 mmol) in 25 mL of dry toluene was added sodium 2-methyl-2-butanolate (20 mmole). After 5 min diphenyl diselenide (20 mmol) was added whereupon the reaction mixture was stirred for 15 min at room temperature, then poured out into 100 mL of deoxygenated water. The water phase was extracted with 50 mL of toluene, and the combined organic phase was washed with water, dried over $MgSO_4$, and evaporated. A slightly yellow oil (4.6 g) was obtained. It contained **9h** together with a little diphenyl diselenide (less than 5%) and was used without further purification in the addition reaction (^{77}Se NMR, δ 275 ppm ($CDCl_3$)). The water phase containing benzeneselenolate was acidified and air-oxidized to give an almost quantitative recovery of $^1/_2$ equiv of diphenyl diselenide.

Addition of Benzeneselenol to Seleno-Substituted Acetylenes (9b and 9h). The substituted alkyne **9b** or **9h** (10 mmol) was added to a THF solution of benzeneselenol prepared from phenyl trimethylsilyl selenide and slight excess of methanol or acetic acid.[24] The reaction mixture was refluxed overnight, whereupon the solvent was evaporated, and the crude product mixture was subjected to ^{77}Se NMR analysis. (Data given in Tables II and III.)

Summary

In this paper we give a general method for differentiation between isomeric alkenes substituted with two or more organo selenium groups. It is based on the homonuclear ^{77}Se coupling which gives rise to a satellite pattern at the foot of each selenium-77 line: 117–77 Hz coupling constants are found for cis $^3J_{\text{Se-Se}}$, 55–19 Hz for gem $^2J_{\text{Se-Se}}$, and 12–2 Hz for trans $^3J_{\text{Se-Se}}$.

Furthermore, an extended set of assigned $J_{\text{Se-H}}$ coupling constants is presented. These provide a basis for using ^{1}H–^{77}Se coupling constants to determine the stereochemistry of selenium-substituted alkenes including those with only one selenium group attached.

It is shown that the base-catalyzed reaction between diselenides and terminal acetylenes proceed via a substitution of the acetylenic proton followed by an addition of a selenolate ion. Under aprotic conditions the reaction may proceed to give a triseleno-substituted alkene. The addition of benzeneselenol to alkylseleno-substituted acetylenes gives rise to products with 1,2-migrated alkyl seleno groups probably via a selenirenium ion like intermediate.

Registry No. **1a**, 32847-07-7; **1b**, 32847-15-7; **1c**, 32846-96-1; **1d**, 32847-03-3; **1e**, 32847-12-4; **1f**, 32846-91-6; **2a**, 7392-13-4; **2b**, 7392-17-8; **2c**, 101316-22-7; **2d**, 101316-23-8; **2e**, 101349-67-1; **3a**, 101316-24-9; **3b**, 101349-68-2; **3c**, 101316-25-0; **4a**, 101316-26-1; **4b**, 101316-27-2; **4c**, 101316-28-3; **4d**, 101316-29-4; **4e**, 101316-30-7; **5a**, 60466-30-0; **5b**, 101316-31-8; **5c**, 101316-32-9; **5d**, 94848-67-6; **5e**, 101316-33-0; **6a**, 94848-68-7; **6b**, 101316-34-1; **6c**, 101316-35-2; **8a**, 101316-36-3; **9a**, 30665-96-4; **9b**, 19859-24-6; **9c**, 101349-66-0; **9d**, 101349-69-3; **9e**, 81699-91-4; **9f**, 101316-37-4; **9g**, 101316-38-5; **9h**, 68001-64-9; ^{77}Se, 14681-72-2; PhSeH, 645-96-5; PhC≡CH, 536-74-3; EtOCOC≡CH, 623-47-2; $CH_3(CH_2)_3C$≡CH, 693-02-7; PhSeSePh, 1666-13-3; $PhCH_2SeSeCH_2Ph$, 1482-82-2; AcESeSeAcE, 101316-39-6; $CH_3SeSeCH_3$, 7101-31-7.

Photochemistry of 2-Vinylstilbene, 1,2-Distyrylbenzene, and 2,2′-Distyrylbiphenyl Absorbed on Silica Gel. Influence of Ground-State Conformers on Formation of Photoproducts

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Irradiation of 2-vinylstilbene (**1**) absorbed on silica gel gives rise to several products. In addition to *exo*- and *endo*-5-phenylbenzobicyclo[2.1.1]hex-2-enes (**2** and **3**) (the sole products formed in solution) derivatives of naphthalene and of indene are formed. The formation of these products has been ascribed to variation in the photoreactivities of the distinct conformers of **1** and to the reduced mobility of the intermediate biradicals leading to **2** (and **3**) when they are absorbed on silica gel. 1,2-Distyrylbenzene (**22**) absorbed on silica gel forms upon irradiation not only dimers (nearly the sole photoproducts in solution) but also *exo*-5,*endo*-6-diphenylbenzobicyclo[2.1.1]hexene (**25**), a product analogous to **2**, and an indene derivative (**26**). Irradiation of 2,2′-distyrylbiphenyl (**28**) absorbed on silica gel and in solution gives the two photoproducts **29** and **30** in the same ratio. The results are discussed in terms of the NEER principle and the absorption of parts of the molecules to the silica gel surface.

The photochemistry of compounds absorbed on silica gel is still a rather unexploited field.[1] In the course of our photochemical studies we became familiar with several compounds for which different ground-state conformers seemed to lead to different photoproducts. According to the NEER principle[2] (nonequilibration of excited rotamers) the photoproduct composition of such compounds should depend on the rotamer equilibrium in the ground

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[1] For literature see ref 1 in: Bauer, R. K.; de Mayo, P.; Okada, K.; Ware, W. R.; Wu, K. C. *J. Phys. Chem.* **1983**, *87*, 460.

[2] Jacobs, H. J. C.; Havinga, E. *Adv. Photochem.* **1979**, *11*, 305.

0022-3263/86/1951-1663$01.50/0

state and/or the photoreactivity of the various conformers. Both might be different for dissolved and absorbed molecules. Irradiation of such compounds absorbed on silica gel might then lead to a product composition different from that in solution.

At the moment the absorption of compounds on silica gel can only be described in rather general terms. Silica gel comprises two types of functional groups, viz., siloxane and silanol residues, inhomogeneously distributed over the surface.[3] Absorption occurs mainly at "preferred sites", where several silanol groups are present in vicinal or geminal positions. At those sites binding is possible not only by dispersion forces, but also by electrostatic interaction and hydrogen bridges,[3-6] depending on the polarity of the compound and the way of activation of the absorbent. Although molecules absorbed on the surface can be displaced by using their thermal energy and by shaking,[7] their mobility is always strongly reduced in comparison with molecules in solution. de Mayo deduced[7] from Stern–Volmer plots that the mean displacement of acenaphthylene within the lifetime of the excited state (1 ns) is only 0.2 nm, and Selivanovskii[8] estimated the rate of internal rotation of the iminoxy radical on a silica gel surface 500 times lower than in solution.

In this paper we present the results of irradiation experiments of three compounds absorbed on silica gel, viz., 2-vinylstilbene (**1**), 1,2-distyrylbenzene (**22**), and 2,2′-distyrylbiphenyl (**28**), and compare the product compositions with those on irradiation in solution.

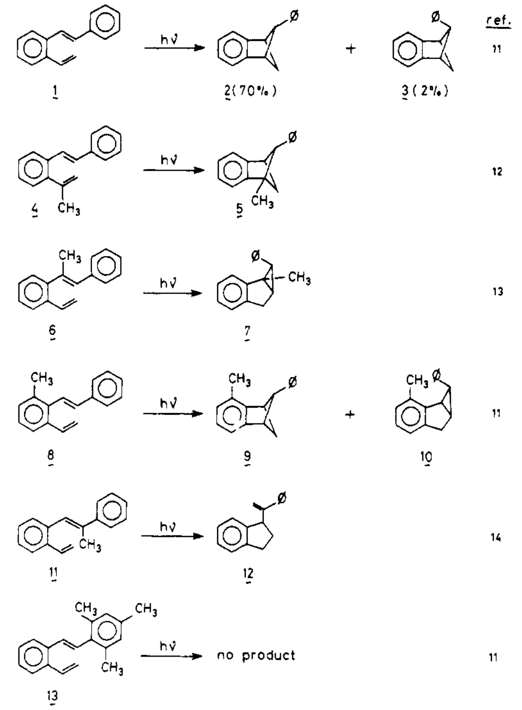
Methods

Activation of silica gel and absorption of substrates were done as described in ref 7. Silica gel (5–25 g, Merck 35–70 mesh, the same batch for all experiments) was heated at 200–210 °C (0.3 mmHg) for 16 h in a tube, immersed in a bath of Woods metal. A solution of the substrate in hexane was added in vacuo and under cooling in liquid nitrogen to prevent turbulation. The solvent was then removed from the slurry by carefully increasing the vacuum up to 0.3 mmHg while shaking the tube. After 1 h the last trace of the solvent was evaporated by heating on a waterbath.

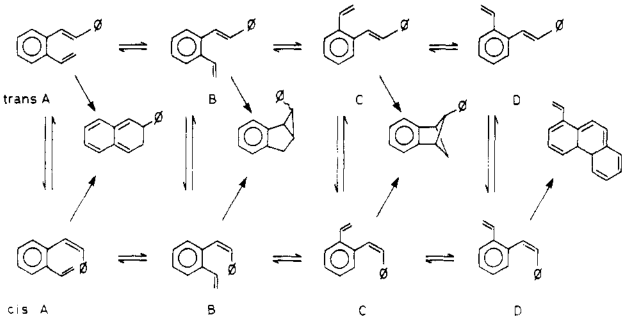
The silica gel with the absorbed substrate was transfered to an irradiation tube under vacuum, and the tube was filled with argon, held at 10^{-5}–10^{-6} mmHg for 2 h, filled again with argon, and irradiated in a Rayonet reactor at 300 or 360 nm while rotating the tube. After the irradiation, the absorbent was extracted with a mixture of methanol and chloroform and the product mixture was analyzed.

To exclude the occurrence of thermal reactions a sample of all three substrates, treated in the same way but without irradiation was analyzed. The samples had remained unchanged. Coverage of the absorbent (surface of substrate molecules/surface of silica gel)[7-10] varied from 0.7–3.5%. The surface of the silica gel was 560 $m^2 \cdot g^{-1}$. The surface of substrate molecules was calculated from known molecular parameters (2-vinylstilbene 0.8 nm^2).

Scheme I



Scheme II



Results and Discussion

A. 2-Vinylstilbene (1). Previously we demonstrated that the photochemical behaviour of **1** (in solution) alters on introduction of substituents, as is illustrated for several methyl-substituted vinylstilbenes (**4**, **6**, **8**, **11**, **13**) in Scheme I.

As the electronic effect of the methyl group is very small, we supposed that the substituent effects had to be ascribed to steric factors. From the correlation between δ-values of the vinyl protons (a ground-state parameter) of a large number of vinylstilbenes and their photoproducts, we deduced[14] that the distinct photoproducts originate from different ground state conformers (Scheme II).

The preferred photoreaction of **1** is the formation of a benzobicyclo[2.1.1]hexene (**2** and **3**) via a biradical intermediate,[11] because this cyclization is a very fast trapping of the twisted stilbene biradical by the vinyl group.[12] The subsequent ring closure of this 1-benzylindan biradical

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(3) Kisielev, A. V. "Structure and Properties of Porous Materials"; Academic Press: New York, 1958.

(4) Kisielev, A. V.; Lygin, V. I. "Infrared Spectra of Surface Compounds"; Wiley: New York, 1975.

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(13) Op den Brouw, P. M.; Laarhoven, W. H. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1015.

(14) Op den Brouw, P. M.; De Zeeuw, P.; Laarhoven, W. H. *J. Photochem.* **1984**, *27*, 327.

Scheme III

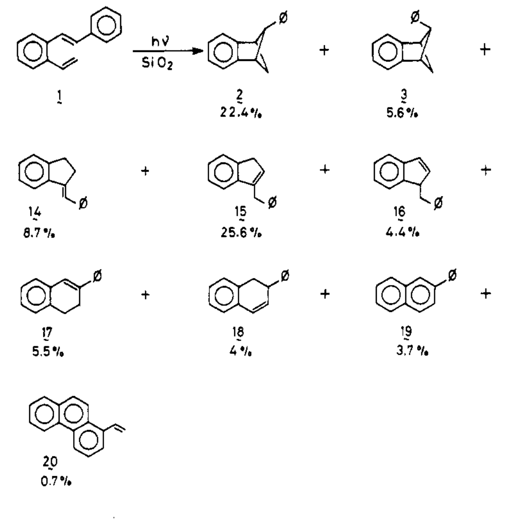

Table I. Product Yield and Product Composition of Irradiations of 2-Vinylstilbene (1) on Silica Gel for 6 h at Different Coverage Percentages

	coverage percentage	
	0.7	3.5
percentage of **1** converted	100	50
(**2** + **3** + **14** + **15** + **16**)/(**17** + **18** + **19**)	5.0	5.0
(**14** + **15** + **16**)/(**2** + **3**)	1.3	1.3
2/**3**	4.0	4.0

yields mainly the thermodynamically more stable *exo*-isomer **2**. Formation of this type of photoproduct will be suppressed when the stability (occurrence) of the relevant conformers C is reduced (e.g., in α-substituted vinylstilbenes, **6**) or when the required orbital overlap in that conformer becomes insufficient for steric reasons (e.g., with **13**). In the former case reaction via conformer B appears, in the latter case all conformers appear to be photostabile (under anaerobic conditions to prevent oxidation of the primary 4a,4b-dihydrophenanthrene cyclization product from conformers *cis*-C and *cis*-D).

Irradiations of **1** absorbed on silica gel were performed with samples, covered with the substrate for 0.7 and 3.5%. After irradiation (6 h, 300 nm) the photoproducts were extracted from the absorbent with methanol/chloroform; about 65% of the originally used amount was recovered. The mixture was analysed by NMR, TLC, and capillary GLC. The latter method showed the presence of 16 compounds; 10 of them, representing more than 80% of the product mixture could be identified (see Scheme III).

Variation of the coverage percentage showed that the photoconversion of **1** is delayed when the coverage is enlarged, but the product composition remains unchanged (Table I).

The identification is based on the NMR spectrum of the mixture, NMR and MS data of individual compounds, and comparison of retention time and NMR data of isolated products with those of authentic samples. The absence of the characteristic patterns of the vinyl protons of *cis*-**1** and *trans*-**1** in the spectrum of the mixture showed that **1** had been converted completely (coverage 0.7%). On the other hand the presence of **2** and **3** was indicated by absorptions at δ 3.97 (d, J = 7.5 Hz), 3.30 (d, J = 2.5 Hz), 3.17 (dd, J = 6.25 and 2.25 Hz) and 2.3 (dd, J = 7.5 and 6.25 Hz, belonging to **2**, and at δ 4.3 (t, J 2.5 Hz) and 3.4 (t, J v 2.5 Hz), pointing to **3**. The other signals, characteristic for **3**[11] were partly overlapped by other signals but could clearly be observed in double resonance experiments (δ 2.66, dt and δ 2.35, d, J = 2.5 Hz). Compounds **2** and **3** were not found, however, among the products obtained by GLC separation. This is due to their instability at 200 °C. The thermolysis products expected from **2** and **3**,[11] viz., *cis*- and *trans*-**1** could be detected on GLC and their amounts were used as the amounts of **2** and **3**, formed on irradiation. The ratio of **2** and **3** was calculated from the NMR data.

Low-field absorptions in the NMR spectrum of the mixture at 8.0 and 8.5 ppm, the former having a much higher intensity, suggested the presence of a phenanthrene and a naphthalene derivative. They could be identified as 1-vinylphenanthrene (**20**) and 2-phenylnaphthalene (**19**) by comparison of their retention times (9.16 and 8.78 min, respectively) and mass spectra with those of samples prepared by direct synthesis. Because the presence of **19** had probably to be ascribed to dehydrogenation of one or more dihydronaphthalenes we looked for the presence of **17** and **18**. Both products were found via similar ways as **19** and **20** (comparison of NMR, MS, and GLC data).

Finally, three signals which did not originate from previously recognized products, were observed in the NMR spectrum of the mixture, viz., a broad triplet (δ 6.15) and two doublets (δ 3.85 and 3.28). They appeared to belong to the same compound; decoupling of the signal at δ 3.85 sharpened the other signals, with what appeared to be coupled directly. The pattern is identical with that of 3-benzyl-1*H*-indene (**15**), the presence of which was assured by comparison of the retention time (7.7 min) and mass spectrum of the relevant fraction and a synthesized sample. Its formation did suppose that the isomeric compounds **14** and **16** might also occur in the mixture. The latter product (**16**) could easily be detected because of the equal retention time (7.24 min) and mass spectrum of one of the fractions and a sample obtained by synthesis. The presence of **14** could not be established in this way, because some attempts to prepare **14** led only to **15**. Because it is known that 2-benzylindene yields 2-benzylideneindan on irradiation,[15] we irradiated **15**, directly at 254 nm and at 300 nm using acetone as a sensitizer. In both cases we got a mixture of products. Separation by GLC revealed that **15** was still present; one of the other compounds had the same retention time as one of the unidentified components in the irradiation mixture of **1**. Its mass spectrum showed a parent peak at 206 ($C_{16}H_{14}$) and a strong peak at 178 (loss of C_2H_4), just as should be expected for **14**.

The remaining components in the product mixture of **1** could not be identified. Some of them had retention times, nearly equal to those of benzobicyclo[3.1.0]hexenes, which might arise from conformer B of **1** (see Scheme II). Their presence could not be secured, however, by NMR or MS. The mass spectra of two other unidentified components (m/e 222, 204 and m/e 248, 233, 202, 189, respectively) point to derivatization of **1** during the irradiation, e.g., introduction of an OH function or an SiO group (m/e 44).

In the formation of a much larger variety of photoproducts from **1** on silica gel than in solution three remarkable trends can be observed: (i) In solution photoproducts (**2** and **3**) arise only from conformer C, because the primary formation of a biradical from C is much faster than possible photoreactions of other conformers. When this process is suppressed (e.g., by the introduction of substituents, the main alternative is the formation of benzobicyclo[3.1.0]hexenes (**7** and **10** in Scheme I) from con-

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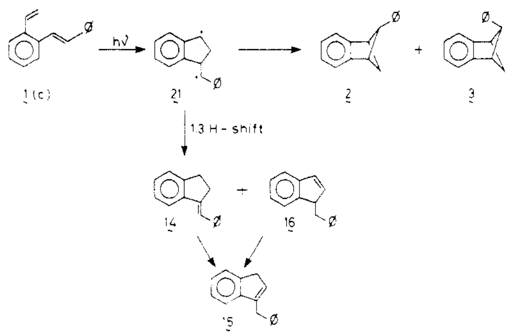
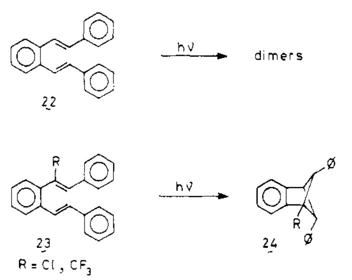
(15) Lamberts, J. J. M.; Laarhoven, W. H. *J. Org. Chem.* **1983**, *48*, 2202.

(16) Laarhoven, W. H.; Cuppen, Th. J. H. M.; Nivard, R. J. F. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 187, 452.

Scheme IV



Scheme V



former B. This is ascribed to a [4 + 2] photo Diels–Alder reaction, followed by a vinyl–cyclopropane rearrangement.[11,13] This alternative seems not to be available for 1 on silica. Instead of benzobicyclo[3.1.0]hexenes (from B) photoproducts of A (**17**, **18**, **19**) and possibly from D (**20**) are found. In view of the low yield of **20** it has to be considered possible that its formation requires the presence of an oxidant to convert the primarily formed dihydrophenanthrene derivative into the end product.

This modification in photochemical behaviour might be explained by accepting that all conformers (A–D) are nearly equally well absorbed, mainly by dispersion forces involving all parts of the molecule (vinyl group, phenyl rings, central double band), but not necessarily all parts continuously at the same time or with the same strength. The conformers A and B are in equilibrium when only the stilbene part is absorbed; the conformations A and C are in equilibrium when only the β-ring is absorbed and so on. During tumbling over the silica gel surface noncomplexed parts of the molecule can be reabsorbed; absorbed parts, released.

Distinct photoreactions of the absorbed molecules occur when the lifetime of the absorbed conformer is long enough to be excited and when the excited absorbed conformer leads to a photoproduct. Absorbed conformer A having immobilized double bonds, is converted into the products **17**–**19**. No conversion of conformer B into a benzobicyclo[3.1.0]hexene is observed. This may be explained by absorptions on silica gel of conformer B in an unfavourable orbital orientation for the [4 + 2] cycloaddition reaction. It is known that for a photo-Diels–Alder reaction the orientation of the vinyl group had to be nearly perpendicular to the diene system.[14] It may be that on absorption the conformation B is too planar to react in a [4 + 2] cycloaddition.

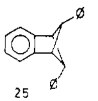
(ii) In solution the biradical (**21**) arising from the conformer C is completely converted into **2** (and **3**). Indan or indene derivatives which might arise from **21** via H-shifts (see Scheme IV) are not formed in solution. Evidently the H-shifts proceed musch more slowly than the conversion **21** → **2** (or **3**).

When **1** is absorbed in silica gel, considerable amounts of **14**–**16** are formed. The explanation might be similar to that given under i. Conversion of **21** into **2** or **3** requires that the benzyl group in **21** is released from the surface. This is not necessary for the hydrogen shifts leading to **14**, **15**, and **16**. Again a necessary condition for the formation of these products is that the lifetime of **21** on the surface is sufficiently long. The formation of the indene derivatives is, therefore, in accordance with the observations that the rotation (mobility) of radicals is decreased.[8-10] It seems that within the lifetime of **21**, the 1,3-hydrogen shifts are silica gel mediated, because in solution such shifts in radicals are not usual. (iii) In solution the ring closure of **21** leads mainly to the thermodynamically more stable *exo* product **2**; the ratio **2**/**3** is about 35. Apparently the internal rotation of the benzyl group in **21** is much faster than ring closure. On silica the ratio **2**/**3** is much smaller (ca. 4). This effect can be ascribed to the restricted rotation of the benzyl group on the surface.

A final conclusion from the experiments is that the conformational equilibria of **1** in solution and on silica gel are disturbed in the same way on irradiation, viz., by the predominating disappearance of C. As the total amount of material recovered from silica gel is considerable, it is very probable that continuous restoration of the equilibria (A, B, D → C) occurs also in samples of **1** absorbed on silica gel, since more than 67% of the products originate from C when **1** is completely converted.

B. 1,2-Distyrylbenzene (22). Irradiation of **22** in solution yielded only dimers, even at concentrations as low as 10^{-5}–10^{-6} mol·L^{-1}, apparently because of strong association of the compound.[16] Introduction of an α-substituent leads to less planar compounds and interferes with the association. Compounds like **23** give benzobicyclo[2.1.1]hexenes (**24**) on irradiation[17] (Scheme V).

Irradiation of **22** on silica gel (coverage 1%) at 300 nm gave a mixture of products. After extraction from silica gel the products were separated by preparative TLC. Eight fractions became visible under UV light. They were scratched from the plate and extracted with a mixture of methanol and chloroform. The 5 slower moving bands (together 18%) were dimers according to their mass spectra. The next fraction appeared to be nearly pure *endo*-5,*exo*-6-benzobicyclo[2.1.1]hexene (**25**, 6.6%), identified by its NMR spectrum and the analogy of the spectrum with that of **24** (R = Cl, CF$_3$). The seventh fraction consisted mainly of 3-benzyl-2-phenyl-1*H*-indene (**26**), recognized by comparison of NMR data with those of an independently prepared sample. The last fraction was a mixture, which was further analyzed by GLC-MS. It consisted of 5 products, together with starting material (overall conversion 90%). These products have not been identified. The main compound (20%) might be 5,6-diphenylbenzobicyclo[2.2.0]hex-2-ene (**27**) because of the occurrence of two broadened singlets in the NMR spectrum (δ 1.6 and 2.4) and a parent peak at 282 and a strong peak at 178 (M − benzocyclobutane) in the mass spectrum. Though this compound could not be isolated because of its instability and because its structure is not completely elucidated, the suggested structure is in accordance with the isolation of stilbene and phenanthrene as minor side products from the photoreaction of **22** in solution.[16] An-



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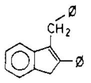

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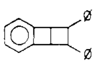

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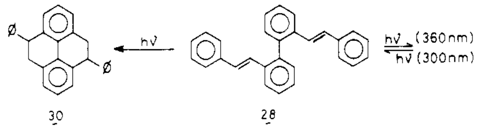
(17) Op den Brouw, P. M.; Laarhoven, W. H. *J. Org. Chem.* **1982**, *47*, 1546.

Scheme VI



yhow dihydronaphthalene derivatives did not occur in the mixture. As expected, the dominating bimolecular dimerization of **22** in solution is largely suppressed on silica gel, but not excluded. Instead **22** a phenyl-substituted vinylstilbene yields both types of photoproducts of the conformer C as found with **1**, viz., a benzobicyclo[2.1.1]hexene derivative (**25**) and an indene derivative (**26**). Notwithstanding the fact that the photochemical behavior of **22** on silica gel could not be elucidated completely, the overall picture is that silica gel influences the photochemistry of **22** drastically and that it is now comparable to the results found with 2-vinylstilbene.

C. 2,2′-Distyrylbiphenyl (28). Irradiation of **28** in solution at 360 nm gives mainly the intramolecular cycloaddition product **29**. A second product is tetrahydropyrene **30**. At lower wavelengths **30** is the sole product because the formation of **29** is reversible under these conditions[18] (Scheme VI). When the phenyl groups in **28** are changed for cyano or carboxyl groups, the formation of the corresponding tetrahydropyrenes is the only photoreaction.[19] This is due to the different UV absorption properties of these compounds. The cyano and carboxyl group containing compounds absorb at wavelengths which are equal to those of the [2 + 2] cycloaddition product, which possesses however a larger extinction. Therefore, the equilibrium will be shifted to the starting compound, and so to the irreversible tetrahydropyrene formation.[18] Nevertheless, it might be that on silica gel **28** has a different preferential conformation which might lead to a different ratio of **29**/**30**. In solution the preferential conformation of **28** is the one in which the mean dihedral angle of the biphenyl moiety in **28** is 90°.[20]

Therefore, the preferential formation of **29** (at 350 nm) has to be ascribed to a much higher rate of this reaction (ϕ = 0,3) in comparison with the formation of **30** (ϕ = 0.003[18]). The quantum yield of the former reaction is equal to that of the intermolecular formation of a tetraphenylcyclobutane from stilbene in concentrated (0.55 M) solutions.[21] The high quantum yield (ϕ = 0.33) of the latter reaction is ascribed to excimer formation.[22-23]

In Table II results of the irradiation of **28**, absorbed on silica gel at 360 nm for various time intervals, are compared with those in solution. On the whole the results are very similar. Analysis of the product mixtures after extraction of the absorbent with methanol/chloroform shows that the same compounds (**29** and **30**) are formed on silica gel, and that the amount of **30** slowly increases with the irradiation time just as found in solution. The increase of **30** must be due to a shorter wavelength emission of the lamps used.

Table II. Irradiation of 2,2′-Distyrylbiphenyl (28) in Hexane and on Silica Gel at 360 nm

solvent/silica gel	irradiation time	tetrahydropyrene **30**, %	total conversion, %
hexane	5 min	0	30
hexane	11 min	1.1	44
hexane	15 min	1.2	39
hexane	30 min	3.0	88
hexane	60 (1 h)	4.3	87
hexane	3 h	5.4	91
hexane	6 h	10.4	92
hexane	22 h	20.0	95
silica gel	1 h	4.1	73
silica gel	1.5 h	5.2	68
silica gel	2 h	6.1	83
silica gel	2.5 h	3.8	73
silica gel	22 h	16.3	86

From the results no arguments are available for any preferred absorption of a conformer of **28**. As for vinylstilbene it seems likely that parts of the molecule **28** are absorbed, whereas either the absorbed or the "free" part can be excited. The identical ratio of the photoproducts obtained by irradiation in a solvent or on silica gel show that the product formation in both cases is determined only by the relative quantum yields.

Conclusion

From the results obtained from the irradiation experiments of the three compounds under investigation the following conclusions can be drawn.

Irradiation of vinylstilbene (**1**) absorbed on silica gel gives more extended information for the fact that (1) the photochemistry of **1** is determined by the equilibrium of its conformers in the ground state and (2) the silicagel surface interacts on different places of the photochemical process: on the lifetime of the conformers and on the mobility of the radicals. The same conclusion can be drawn from the experiments with 1,2-distyrylbenzene.

The results obtained with 2,2′-distyrylbiphenyl points to the conclusion that in this case the NEER principle is not important for the photoproduct formation.

Experimental Section

^{1}H NMR spectra were recorded on a Hitachi Perkin-Elmer R24 or a Bruker WH90 spectrometer in $CDCl_3$. δ-Values are given in ppm relative to tetramethylsilane as internal standard and J values are expressed in Hz.

Mass spectra were recorded on a VG-7070E instrument coupled with a Carlo Erba gaschromatograph. UV spectra were measured with a Perkin-Elmer 555 instrument. Gas chromatography was performed by using a Hewlett-Packard 5790A instrument fitted with a cross-linked silicone column length 25 m, diameter 0.31 mm and a flame ionization detector.

Synthesis. The synthesis of the starting compounds and most of the photoproducts have been published previously: compounds **1**, **2**, **3**, and **20** in ref 11; **15** and **16** in ref 24; **17** in ref 25; **18** in ref 26; **22** in ref 16; and **28** in ref 18.

3-benzyl-2-phenyl-1*H*-indene (**26**) was prepared by epoxidation of **15** followed by Grignard reaction with phenylmagnesium bromide and dehydration. To 2.1 g (0.01 mol) of **15** in 40 mL of dry CH_2Cl_2 was added 2.1 g (0.01 mol) of *m*-chloroperbenzoic acid (85%). The mixture was stirred overnight at room temperature, extracted with $NaHCO_3$ solution, and washed with water. The organic layer was dried with $MgSO_4$. After evaporation of the solvent the crude oil was added to an ice-cooled solution of phenylmagnesium bromide, prepared from 21.3 g of bromobenzene and 0.34 g of Mg in 25 mL of ether.

The resulting mixture was stirred for 1 h and worked up in the usual way. The obtained crude alcohol was dissolved in 150 mL of toluene, 0.5 g of *p*-toluene sulfonic acid was added, and the water was removed by azeotropic destillation in 17 h. The re-

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[20] In the UV spectrum of **28** no conjugation between two stilbene moieties can be observed. Examination of 2-(4-methoxystyryl)-2′-styrylbiphenyl with shift reagents by NMR spectroscopy reveals that there is no preference for either the syn or the anti conformer.

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sulting reaction mixture was then shaken with bicarbonate solution and water and the organic layer dried on $CaCl_2$. After evaporation of the toluene the residue was purified by chromatography on Al_2O_3 with hexane-toluene mixtures as eluents.

Pure **26** was isolated as an oil: mass spectrum,[27] *m/e* 282 (M^+, 36%), 191 (100), 165 (8), 91 (24); UV (EtOH) λ max (log ϵ), 283 nm (4.37); NMR ($CDCl_3$) δ 7.6-6.9 (m, 14 H, aromatic), 4.15 (br s, 2 H, H_{benzyl}, $J_{homoallyl}$ = 1 Hz), 3.87 ppm (br s, 2 H H(1)).

Registry No. (*E*)-**1**, 58719-65-6; *exo*-**2**, 58719-66-7; *endo*-**3**, 58769-73-6; **14**, 16275-02-8; **15**, 22495-71-2; **16**, 16275-01-7; **17**, 20669-52-7; **18**, 62019-39-0; **19**, 612-94-2; (*E,E*)-**22**, 27164-48-3; **25**, 100994-76-1; **26**, 18888-79-4; (*E,E*)-**28**, 33510-35-9; **29**, 38385-44-3; **30**, 38385-45-4.

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[27] The peak at *m/e* 165 may be an indication that a small amount of 1-benzyl-1-phenyl-1*H*-indene is present as a side product. In the NMR spectrum and GLC no indication of this product could be observed.

Linear Free-Energy Relationship in the Pyridinolysis of 2,4-Dinitrophenyl *p*-Chlorobenzoate in Ethanol Aqueous Solution

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The title reactions are kinetically studied in 44 wt % aqueous ethanol at 25 °C, ionic strength 0.2 M (KCl). A linear Brönsted-type plot (log k_N against basicity of the substituted pyridine, where k_N is the second-order rate constant for the reactions) is found. The reactions are nucleophilic as shown by both the inhibition of the rate constant observed in the presence of added excess of 2,4-dinitrophenoxide ion and the value of the Brönsted-type slope (β 0.94). Comparison of the Brönsted-type obtained with those found in the pyridinolyses of 2,4-dinitrophenyl benzoate (curved, with the center of curvature at pK_a 9.5) and 2,4-dinitrophenyl *p*-nitrobenzoate (linear) under the same experimental conditions indicates that electron withdrawal from the remaining aryl group of the tetrahedral intermediate ($T^{\pm}$) formed in these reactions shifts the center of the Brönsted-type curvature toward higher pK_a values and hence favors amine expulsion from $T^{\pm}$ relative to 2,4-dinitrophenoxide ion. Activation parameters for the reactions of the title substrate with 3-methyl- and 4-(dimethylamino)pyridines are reported and their values discussed in comparison with the ones found for similar reactions.

Among the many types of free-energy relationships that have been applied to nucleophilic reactions of reactive carbonyl compounds the Brönsted-type equation is one which has received a good deal of attention.[1-9] When this equation applies to the reactions of a common substrate with a series of structurally homogeneous nucleophiles it takes the form log k_N = log G_N + βpK_a, where k_N is the rate constant for the nucleophilic reaction, K_a is the ionization constant of the conjugate acid of the nucleophile, and G_N and β are coefficients which depend on the substrate, the nucleophilic series, and the solvent.

In the reactions of a series of quinuclidines with aryl phenyl carbonates it has been found that the above equation is linear for the substrates with relatively poor leaving groups but becomes nonlinear as the leaving ability of these groups increases.[2a] Quantification of the Brönsted-type plots obtained shows that the value of the position of the center of the curvature on the pK_a axis (pK_a°) is smaller the larger the nucleofugality of the leaving group of the substrate.[2a] The same effect has been found in the reactions of a series of 3- and 4-monosubstituted pyridines with methoxycarbonyl and acetyl derivatives. The value of pK_a° for the former reactions increases as the leaving group of the substrate changes from chloride (pK_a° = 3.6)[3] to 2,4-dinitrophenoxide (pK_a° = 7.8)[4] to *p*-nitrophenoxide,[5] and to phenoxide ions,[6] the two latter Brönsted-type plots being straight (pK_a° > 10). Likewise, in the pyridinolysis of the acetyl substrates pK_a° increases in the following series: acetyl chloride (pK_a° = 3.6),[7] 2,4-dinitrophenyl acetate (pK_a° = 7.3),[6] and *p*-nitrophenyl acetate (pK_a° > 10).[3]

The effect of the nature of the nonleaving group of the substrate on the pK_a° value has received less attention. Gresser and Jencks found that in the reactions of quinuclidines with aryl 3,4-dinitrophenyl carbonates the pK_a° value increases as the "nonleaving" substituted phenoxy group becomes less basic (more electron-withdrawing).[2b] Similarly, in the pyridinolysis of 2,4-dinitrophenyl benzoates in aqueous ethanol the Brönsted-type plot found for the reactions of the *p*-nitrobenzoate derivative is straight,[8] whereas the same plot is curved for the unsubstituted substrate,[9] indicating that the pK_a° value increases as the nonleaving group of the substrate is more electron-withdrawing.

In order to shed more light on the influence of the nature of the nonleaving group of the substrate on the pK_a° value we continue in the present work our previous studies on

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