talline solid (mp 66–67 °C, hexane) and a clear oil, respectively. HRMS calcd for $C_{12}H_{20}O$: 180.1509. Found: **9**, 180.1509. **10**, 180.1513. IR **9** ($CDCl_3$): 3392, 3004, 2929, 2868, 1652, 1449, 1070, 969, 733 cm^{-1}. IR **10** (neat): 3450, 3002, 2927, 2863, 1652, 1447, 1070, 958, 728 cm^{-1}. NMR data: see text.

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Supplementary Material Available: MM2-derived conformations, calculated and experimental lanthanide-induced shifts for **9** and **10**, partial INADEQUATE spectrum, and slices from the HETCOR experiment for **10** (6 pages). Ordering information is given on any current masthead page.

Photochemistry of 1-Phenyl-1,2-dihydronaphthalene in Methanol

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The photochemistry of 1-phenyl-1,2-dihydronaphthalene (**1**) in methanol and hexane has been investigated. The lack of influence of solvent polarity and of the presence of sulfuric acid on the rate of formation of *exo*-4-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-**2**) from the primary, ring-opened photoproduct *cZt*-**3a** of **1** precludes a sudden-polarized, zwitterionic excited state from being involved in the intramolecular [4 + 2] photocycloaddition reaction leading to *exo*-**2**. The experimental results can be rationalized by assuming that this photoprocess involves a concerted $\pi_4a + \pi_2a$-type electrocyclic reaction. *cis*-Dibenzobicyclo[3.3.0]octa-2,7-diene (**8**) is proposed to arise by photocyclization of *cZc*-**3b**, followed by a thermal rearrangement. On irradiation of **1** with a broad-spectrum lamp, the ratio of the photoproducts *exo*-**2** and **8** is correlated with the ratio of the pe and pa conformers of **1**. The novel compound 1-(*o*-benzylphenyl)allene (**6**) is also formed under these conditions. Irradiation of **1** at 254 nm yields **8** as the only photoproduct. Photochemical addition of methanol was observed to compete with the photoprocess, leading to *exo*-**2**, though at a comparatively low level. A photodecomposition mode of *exo*-**2**, presumably involving heterolytic cleavage of the cyclopropane ring, presents the chief source of methoxylated photoproducts at low temperatures in methanol.

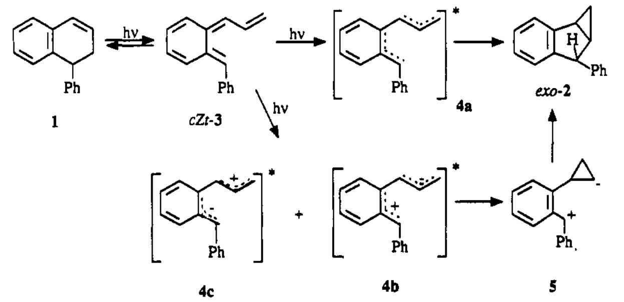
Introduction

Previously, it was reported[1,2] that irradiation of 1-phenyl-1,2-dihydronaphthalene (**1**) with a broad-spectrum lamp in hexane affords exclusively the exo isomer of 4-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-**2**). On the basis of these data, *exo*-**2** was supposed to arise from excitation of the pe conformer (**1**-pe, with the phenyl group occupying the pseudo-equatorial position) of **1**. Within this assumption two possible reaction pathways leading to *exo*-**2** were postulated,[1,2] i.e., a concerted, intramolecular [4 + 2] cycloaddition reaction involving an unpolarized excited singlet state of *cZt*-**3**, or a mechanism involving a sudden-polarized,[3] twisted, zwitterionic excited singlet state of *cZt*-**3** (Scheme I).

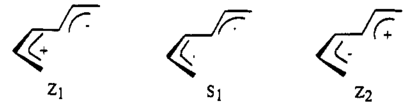
Considering the possibility of a concerted, intramolecular [4 + 2] photocycloaddition reaction of *cZt*-**3**, the structure of the end product *exo*-**2** requires the excited triene moiety in **4a** to cyclize in a $\pi_4a + \pi_2a$ fashion. Although this conclusion obviously violates the Woodward–Hoffman rules,[4] Tanaka et al.[5] emphasizes the possibility of photochemical, intramolecular $\pi_4a + \pi_2a$ cross-bicyclization in excited trienes of low symmetry.

A mechanism involving a sudden-polarized, zwitterionic state (**4b**) has been used to rationalize the observed stereochemistry of several bicyclo[3.1.0]hex-2-enes originating from apparently concerted, but symmetry-forbidden, intramolecular $\pi_4a + \pi_2a$ photocycloadditions of *cZt*-hexatrienes.[6-10] A two-step mechanism has been invoked[6] to explain the observation that the configuration of the asymmetric center resulting from the formation of the five-membered ring of the corresponding bicyclo[3.1.0]hex-2-ene is thermodynamically controlled. The photocycloaddition product of *exo*-**2** (Scheme I) can be rationalized as the thermodynamically favorable relaxation

Scheme I



Scheme II



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[1] Lamberts, J. J. M.; Laarhoven, W. H. *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 131.

[2] Lamberts, J. J. M. Thesis, Nijmegen, 1982.

[3] Bonacic-Koutecky, V.; Koutecky, J.; Michl, J. *Angew. Chem.* **1987**, *99*, 216.

[4] Woodward, R. B.; Hoffman, R. *The Condervation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.

[5] Tanaka, K.; Fukui, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2209.

[6] Dauben, W. G.; Kellog, M. S.; Seeman, J. I.; Vietmeyer, N. D.; Wendschuh, P. H. *Pure Appl. Chem.* **1973**, *33*, 197.

[7] Padwa, A.; Brodsky, L.; Clough, S. *J. Am. Chem. Soc.* **1972**, *94*, 6767.

[8] Courtot, P.; Rumin, R.; Salaun, J. I. *Pure Appl. Chem.* **1977**, *49*, 317.

[9] Courtot, P.; Rumin, R.; Salaun, J. I. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 192.

[10] Courtot, P.; Auffret, J. *J. Chem. Res., Synop.* **1981**, 304.

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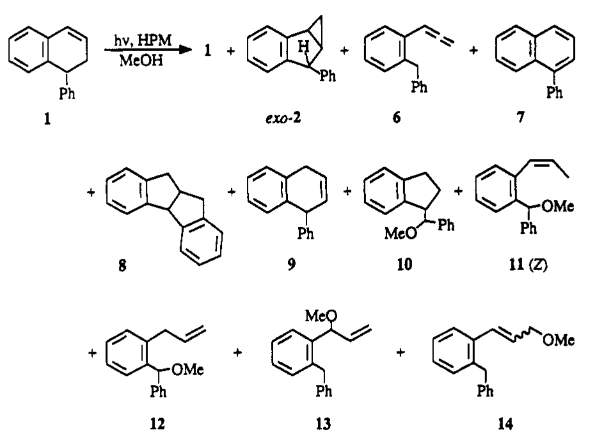
product of the sudden-polarized, zwitterionic excited state **4b**. On the other hand, a sudden-polarized, zwitterionic excited state of an s-trans 1,3-diene has been postulated[11] to give the corresponding [1.1.0]bicyclobutene via a concerted pathway.

Relative stabilities and electron configurations of unpolarized and of sudden-polarized, zwitterionic excited states have been the subject of extensive theoretical studies.[3,12-17] For unsubstituted *cZt*-1,3,5-hexatriene, the sudden-polarized, zwitterionic states Z_1 and Z_2 (Scheme II) were calculated to be of comparable stability and to lie 17 kcal mol^{-1} below the corresponding unpolarized excited state (S_1), at a twist angle of 90 degrees.[12] According to the authors, nearly full charge separation (ca. 0.8 e) between the two perpendicular allyl moieties of Z_1 and Z_2 should exist in this case. It is generally agreed that for twist angles θ outside the range $88° < \theta < 92°$ the zwitterionic character of the twisted excited singlet state of *cZt*-1,3,5-hexatriene is negligible.[13-16]

In contrast with the great theoretical interest summarized above, there is not much experimental support for the involvement of sudden-polarized excited states in the photochemistry of 1,3,5-hexatrienes and related polyenes.[18] In view of the fact that a comparatively small amount of evidence exists for the zwitterionic nature of these electronic states,[19] we embarked on a program to investigate the type of excited state involved in the photoreactions of 1,3,5-hexatrienes, generated by photochemical ring opening of substituted 1,2-dihydronaphthalenes. It was decided to use methanol as the solvent for the following reasons: First, stabilities of zwitterionic relative to nonpolar excited states are expected to be enhanced in polar solvents.[13-17,20] Second, zwitterionic intermediates might be trapped by polar solvents,[11,21,22] i.e., zwitterionic states might reveal themselves through formation of methanol adducts at a rate faster than that of the corresponding bicyclo[3.1.0]hex-2-ene. Furthermore, the addition of strong acid was considered as an important tool for trapping of zwitterionic excited states. Provided that their lifetimes exceed ca. 10^{-11} s,[22] such zwitterionic excited states might be trapped selectively by protonation, which might lead to enhanced rates of photoproduct formation in the presence of acid. Trapping of zwitterionic excited states by methanol might also give rise to the formation of cyclopropane derivatives[11,20,21] via polar intermediates such as **5** (Scheme I).

Due to annelation within the s-cis moiety, the energy separation between **4b** and **4c** (Scheme I) is expected to be greater[14] than that for the corresponding Z_1 and Z_2 states (Scheme II) of *cZt*-1,3,5-hexatriene. According to the theory of the sudden-polarization effect,[16] the fraction of the charge exchanged between the two allyl moieties in **4b** or **4c** would then be relatively small, suggesting that the zwitterionic excited state **4b** of *cZt*-**3** might be relatively stable and possess a large dipole moment. Thus, zwitterionic states of *s-cis* and *s-trans*-1,3,5-hexatrienes deriving from 1,2-dihydronaphthalenes appear to be particularly promising candidates for selective trapping by methanol or strong acid.

Scheme III



Considering other arguments for the choice of substituted 1,2-dihydronaphthalenes as the experimental probe, it can be stated that the photochemistry of these compounds in hexane is well established.[1,2,23] Furthermore, these compounds provide the advantage of in situ generation of 1,3,5-hexatrienes[24] at low concentrations, thereby avoiding undesirable side reactions such as polymerization.

Results

Irradiation of 1 in Methanol. Photoproduct analyses were performed with 100-mg samples obtained from broad-spectrum irradiations of **1** (2×10^{-3} M) at room temperature and at −60 °C. The photoproducts were separated into a hydrocarbon fraction and a fraction containing methanol adducts by elution from a 10-cm silica gel column with carbon tetrachloride. All photoproducts were stable to column chromatography and to temperature-programmed GC at 150 °C.

NMR and GCMS of the hydrocarbon fraction indicated the presence of two major photoproducts, both having m/e 206. One of these was recognized as *exo*-**2** (Schemes I and III) by the characteristic NMR absorptions[2,25] of its aliphatic protons. Its presence was confirmed by running an authentic sample of *exo*-**2**[25] along with the hydrocarbon fraction in GC.

The NMR characteristics of the major photoproduct comprised a singlet at δ 4.02 (2 H) and a triplet at δ 6.30 (1 H), coupled (J = 6.82 Hz) to doublet at δ 5.03 (2 H). This suggested the presence of an $ArCH_2Ar$ group (Ar = aryl) and a singlet olefinic proton, coupled to apparently equivalent protons of a terminal olefinic methylene group. The only $C_{16}H_{14}$ isomer uniting these structural elements, is (*o*-benzylphenyl)allene (**6**), the formation of which could be envisaged via a 1,5-H shift from *cZc*- or *cZt*-**3**. In accord with this assignment, the IR spectrum of the hydrocarbon fraction displayed characteristic absorptions at 1945 and 1075 cm^{-1} due to the antisymmetrical and symmetrical stretching vibrations[26] of the cumulated olefinic bonds in **6** (Scheme II). The identity of **6** was confirmed by chem-

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[11] Dauben, W. G.; Ritscher, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 2925.

[12] Bonacic-Koutecky, V. *J. Am. Chem. Soc.* **1978**, *100*, 396.

[13] Bonacic-Koutecky, V.; Bruckmann, P.; Hiberty, P.; Koutecky, J.; Leforestier, C.; Salem, L. *Angew. Chem.* **1976**, *87*, 599.

[14] Meerman-van Benthum, C. M.; Jacobs, H. J. C.; Mulder, J. J. C. *Nouv. J. Chim.* **1978**, *2*, 123.

[15] Bonacic-Koutecky, V.; Cizek, J.; Dohnert, D.; Koutecky, J. *J. Chem. Phys.* **1978**, *69*, 1168.

[16] Salem, L. *Acc. Chem. Res.* **1979**, *12*, 87.

[17] Bruni, M. C.; Daudley, J. P.; Langlet, J.; Malrieu, J. P.; Momucchioli, F. *J. Am. Chem. Soc.* **1977**, *99*, 3587.

[18] Squillacote, M.; Semple, T. C. *J. Am. Chem. Soc.* **1987**, *109*, 892.

[19] Schilling, C. L.; Hilinski, E. F. *J. Am. Chem. Soc.* **1988**, *110*, 2296.

[20] Salem, L.; Stoehrer, W. D. *J. Chem. Soc., Chem. Commun.* **1975**, 140.

[21] Barltrop, J. A.; Browning, H. E. *J. Chem. Soc., Chem. Commun.* **1968**, 1481.

[22] Turro, N. J. *Modern Molecular Photochemistry*; Benjamin: Menlo Park, 1978; pp 398–401, 505–508.

[23] Salisbury, K. *Tetrahedron Lett.* **1971**, 737.

[24] Lamberts, J. J. M.; Laarhoven, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 1736.

[25] Lamberts, J. J. M.; Laarhoven, W. H. *J. Org. Chem.* **1983**, *48*, 2202.

[26] Fischer, H. In *The Chemistry of Alkenes*; Patai, S., Ed.; Interscience: London, 1964; p 1127.

ical synthesis. The NMR and IR data of **6** compare favorably to those reported[27-29] for 1-phenylallene. Contrary to *exo*-**2**, **6** has not been observed previously[1,2] as a photoproduct from **1** in hexane.

Apart from *exo*-**2** and **6**, the hydrocarbon fraction contained four minor products. 1-Phenylnaphthalene (**7**, Scheme III) was identified by its mass spectrum (m/e 204), low-field NMR absorptions at δ 7.75–7.94, and UV absorption at λ_{max} 294 nm. *cis*-Dibenzobicyclo[3.3.0]octa-2,7-diene (**8**, Scheme III) was recognized by the mass spectrum (m/e 206),[30] which displays little fragmentation as compared to the mass spectra of its isomers **1**, *exo*-**2**, and **6**. These assignments were verified by comparing the NMR and GCMS data of the hydrocarbon fraction with those of authentic samples of **7**[2] and **8**.[30,31] The presence of 1-phenyl-1,4-dihydronaphthalene (**9**)[32] among the photoproducts of **1** in methanol was established similarly.[1,33] The identity of the remaining component (m/e 206) could not be established with certainty. The retention time in GC and a set of NMR absorptions not addressable to hydrocarbons **1**, *exo*-**2**, or **6–9** suggest it to be *endo*-**2** (NMR ($CDCl_3$): δ 0.79 (dd, $J_{6\text{-endo},6\text{-exo}} = J_{5,6\text{-exo}} = 4.5$ Hz, $J_{1,6\text{-endo}} = 8.0$ Hz, $H_{6\text{-endo}}$); cf.[2,19] *exo*-**2**). In contrast with **7** and **8**, which occurred in yields up to 10%, only traces of *endo*-**2** and **9** were present in the hydrocarbon fraction.

The composition of the fraction containing the methanol adducts showed a marked dependence on the irradiation time. Irradiation of **1** (2×10^{-3} M) for short periods of time (<40 min) yielded four methanol adducts, as indicated by the strong, sharp NMR absorptions at δ 3.14, 3.18, 3.35, and 3.37, due to methoxy groups. Application of TLC afforded three fractions: The first fraction consisted of two similar components, inseparable by TLC or GC. The major component displayed the NMR characteristics of an aromatic functionality (δ 6.54 (d, J = 7 Hz, 1 H)); δ 6.83–7.26 (m, 8 H)), a sterically crowded methoxy group (δ 3.18 (s, 3 H)), two coupled methylene groups (δ 2.03–2.31 (m, 2 H) and δ 2.58–2.88 (m, 2 H)), and an ArCHOMe group (δ 4.19 (d, J = 7.0 Hz, 1 H)) adjacent to a tertiary CH fragment (δ 3.36–3.63 (m, 1 H)). By the results of spin-decoupling, these NMR absorptions were assigned to 1-(α-methoxybenzyl)indan (**10**, Scheme III). In accord with this assignment, the EI mass spectrum (EIMS) displayed a parent peak at m/e 238 (M^+, 0.4) and fragmentation peaks at m/e 222 ($C_9H_9COPh^+$, 1.1), 121 ($PhCHOMe^+$, 100), 117 ($C_9H_9^+$, 11), and 115 ($C_9H_7^+$, 14). Obviously, **10** exists as a pair of diastereomers, ($1R,\alpha S;1S,\alpha R$)-**10** and ($1S,\alpha S;1R,\alpha R$)-**10**, which explains the occurrence of satellites at δ 1.52–1.82 (m, 2 H), δ 3.22 (s, 1 H), and δ 4.11 (d, J = 7.0 Hz, 1 H) in the NMR spectrum of this fraction. These assignments were confirmed by chemical synthesis of a diastereomeric mixture of **10**. Considering that minimal steric interaction in **10** requires the α-CH fragment to be located either below or above the plane of the indanyl moiety, it emerges that only in ($1R,\alpha S;1S,\alpha R$)-**10** can the methylene protons at C(2) be in the proximity of the shielding zone of the α-phenyl group. Hence, the NMR absorptions at δ 1.52–1.82 and δ 2.03–2.31 were assigned to, respectively, the $1R,\alpha S;1S,\alpha R$ and $1S,\alpha S;1R,\alpha R$ diastereomers of **10**. It should further be mentioned that the predominance of the $1S,\alpha S;1R,\alpha R$ diastereomer in chemically synthesized samples of **10** is much less (($1S,\alpha S$;$1R,\alpha R$)-**10**/($1R,\alpha S;1S,\alpha R$)-**10** = 2) than in samples derived from irradiations of **1** (($1S,\alpha S;1R,\alpha R$)-**10**/($1R,\alpha S;1S,\alpha R$)-**10** = 5).

According to GC and NMR, the second fraction consisted again of two similar compounds. The chemical shifts of the methoxy substituents (δ 3.35 and 3.37) indicated considerably less steric crowding of these groups, as compared to **10**. The NMR spectrum displayed olefinic multiplets (δ 4.86–5.14, 5.63–6.12, and 6.41–6.59) and an aliphatic doublet (δ 1.60) split by allylic couplings, as well as singlets (δ 5.43 and 5.47) indicative of the presence of an Ar_2CHOMe group[34] in both compounds. From the results of integration and spin-decoupling, the constituents of the second fraction were identified at (Z)-1-(α-methoxybenzyl)-2-propen-1-ylbenzene (**11**) and 1-(α-methoxybenzyl)-2-propen-2-ylbenzene (**12**, Scheme III). Both CI- and EIMS of **11** and **12** gave weak parent peaks at the correct mass. These compounds were easily discriminated by the presence of a strong peak at m/e 121 in the CI and EI mass spectra of **11**, but not of **12**. Similarly, **11** and **12** could be discriminated from **10** by EIMS.

In addition to **11** and **12**, the third fraction contained still another compound, the NMR spectrum of which revealed the presence of a methoxy group (δ 3.14 (s)), an $ArCH_2Ar$ group (δ 4.04 (s)), and a vinyl group (δ 5.15 and 5.87 (m)) similar to that in **12**. In accord with the results of spin-decoupling, these NMR data were assigned to 1-(methoxyprop-2-enyl)-2-benylbenzene (**13**, Scheme III). Unfortunately, insufficient separability of **13** from **11** and **12** prevented further characterization of this compound by GCMS.

Prolonged (>90 min) irradiation of **1** (10^{-3} M) in methanol containing sulfuric acid (10^{-2} M) afforded two additional methanol adducts, along with a diminished yield of **10**. The new adducts were separated from compounds **10–13** by TLC and collected as a mixture, which proved to be inseparable by GC. Contrary to compounds **10–13**, the EIMS of this mixture displayed a parent peak (m/e 238) of substantial intensity (18), as well as a relatively weak fragmentation peak at m/e 121 (18), pointing to the absence of an α-methoxybenzyl group. The NMR spectrum of the mixture displayed absorptions characteristic of two slightly different methoxy groups (δ 3.23 and 3.26 (s)) as well as cis (δ 6.56 (d), δ 5.80 (dt, J_{cis} = 11.4 Hz)) and a trans (δ 6.80 (d), 6.09 (dt, J_{trans} = 16.0 Hz)) olefinic bond, both conjugated with an aryl group. From the results of spin-decoupling experiments, the new adducts were concluded to be (Z)- and (E)-1-(3-methoxyprop-1-enyl)-2-benzylbenzene (**14**, Scheme III), being present in a 4:1 ratio.

From the yield vs time plots of the photoreaction of **1** evaluated at various temperatures or in the presence of sulfuric acid, it was concluded that *exo*-**2**, **6**, **8**, and **11–13** are primary photoproducts. Compound **10**, on the other hand, clearly emerged as a secondary photoproduct. A typical result supporting this conclusion is presented in Figure 1, in which it can be seen that the conversion of **1** into *exo*-**2**, **6**, **8**, **11**, and **13** begins at t = 0, whereas the production of **10** starts when the yield of *exo*-**2** approaches its maximum value (t = 10 min). Beyond this maximum, **10** is formed at a rate comparable to the rate of decomposition of *exo*-**2**. This points to decomposition of *exo*-**2** into **10** as the chief secondary photoreaction in broad-

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(27) Bestmann, H. J. Seng, F. *Tetrahedron* **1965**, *21*, 1373.

(28) Runge, W. *Z. Naturforsch.* **1977**, *32B*, 1296.

(29) Runge, W. *Z. Naturforsch.* **1978**, *33B*, 932.

(30) Laarhoven, W. H.; Lijten, F. A. T.; Smits, J. M. M. *J. Org. Chem.* **1985**, *50*, 320.

(31) Smits, J. M. M.; Noordik, J. H.; Beurskens, P. T.; Laarhoven, W. H.; Lijten F. A. T. *J. Cryst. Spect. Res.* **1986**, *16*, 23.

(32) Carruthers, W.; Hall, G. E. *J. Chem. Soc. B* **1966**, 862.

(33) Lamberts, J. J. M.; Haasnoot, C. A. G.; Laarhoven, W. H. *J. Org. Chem.* **1984**, *49*, 2490.

(34) In the similar compound 1-methoxy-1-phenyl-1-(*o*-tolyl)methane, the NMR absorption of the benzylic proton was found at δ 5.36 ppm; cf. 15.

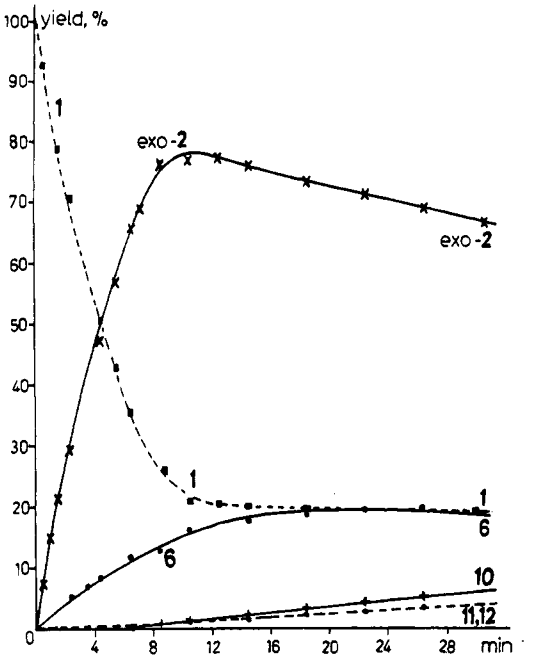

Figure 1. Broad-spectrum irradiation (HPM) of 1-phenyl-1,2-dihydronaphthalene (**1**, 2 × 10^{-3} M) in methanol at −72 °C: yield vs time plots for the conversion of **1** and the formation of *exo*-4-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-**2**), 1-(*o*-benzylphenyl)allene (**6**), 1-(α-methoxybenzyl)indane (**10**), and 1-(α-methoxybenzyl)-2-prop-1-enylbenzene (**12**).

spectrum irradiation of **1** in methanol. The occurrence of this reaction was confirmed by irradiation of an authentic sample of *exo*-**2** under similar conditions: In this experiment, **10** was formed as the major photoproduct, along with small yields of **9** and polymeric compounds. By evaluating the yield vs time curves of **10** in neat and in acidified (2 × 10^{-2} M H_2SO_4) methanol under otherwise identical experimental conditions, it was verified that the photochemical decomposition reaction *exo*-**2** is not subject to acid catalysis. Since **6** proved to be photostable upon broad-spectrum irradiation in methanol for 2 h, formation of the methanol adducts **13** and **14** through secondary photoreactions of **6** can be ruled out.

Due to the low abundances in the irradiation mixture, the yield vs time curves obtained for *endo*-**2**, **7**, and **9** were too inaccurate to decide whether these products originate from primary photoreactions. Assuming *endo*-**2** to be a secondary photoproduct, its formation can only be envisaged from *exo*-**2** by a nonconcerted photoisomerization reaction of this compound.[2,24] In view of the greater thermodynamic stability of *exo*-**2**, *endo*-**2** is not likely to be formed via this route. Hence, *endo*-**2** is most probably a primary photoproduct of **1**. The observed traces of **7** presumably originate from aromatization of **1** by residual oxygen. As previously discussed,[25] **9** is a minor secondary photoproduct, formed by decomposition of *exo*-**2**.

Under the irradiation conditions stated in Figure 1, **14** could not be detected among the photoproducts of **1**. Both (*Z*)- and (*E*)-**14** are secondary photoproducts occurring exclusively upon prolonged irradiation of **1** in methanol, containing sulfuric acid.

Initial, relative quantum yields (ψ_0) of primary photoproduct formation were evaluated from the slopes of the yield vs time curves at zero irradiation time (Figure 1). The results concerning the influence of the temperature and sulfuric acid in the initial, relative quantum yields are collected in Table I.

Table I. Influence of the Temperature (*T*) and the Concentration of Sulfuric Acid ([H_2SO_4]) on the Initial, Relative Quantum Yields (Ψ_0, ±20%) of Primary Photoproduct Formation from 1-Phenyl-1,2-dihydronaphthalene (1, 2 × 10^{-3} M) in Methanol

		Ψ_0				
T, °C	[H_2SO_4], M	**1**[a]	**2**	**6**	**8**	**12** + **13**
−72	0	300	270	43	<1	2
−30	0	270	220	38	<1	3
15	0	50	42	10	2.4	3
15	2.5 × 10^{-2}	40	30	7	3	3
15	2 × 10^{-1}	50	37	10	5	3
15[b]	0	75	76	2.6	1.6	−

[a] Initial relative quantum yield of disappearance. [b] Solvent: hexane.

Irradiation of 1 in *n*-Hexane. For investigation of the influence of the solvent polarity on the primary photoreactions of **1**, the irradiation experiment outlined in Figure 1 was repeated with **1** in hexane. GCMS and NMR analysis of a 100-mg sample irradiated at 15 °C for 75 min revealed the presence of **1** (11%), *exo*-**2** (54%), **6** (4%), **8** (3%), **9** (14%), five unknown $C_{16}H_{14}$ isomers (8%), and *endo*-**2** (6%). According to the observed initial, relative quantum yield vs time curves, *exo*-**2**, **6**, and **8** are primary photoproducts, whereas the five unidentified unknown $C_{16}H_{14}$ isomers are secondary photoproducts. In accord with previous reports,[1,2] decomposition of *exo*-**2** into **9** was identified as the chief secondary photoreaction. Though all photoproducts were unstable toward prolonged irradiation (>30 min), the expected polymerization reaction could be suppressed completely by employing highest purity hexane.

The relative, initial quantum yields of formation of the primary photoproducts *exo*-**2**, **6**, and **8** in this solvent, at 15 °C, have been collected in the last row of Table I. The results can be compared directly to those obtained in methanol, at 15 °C. From this comparison, it emerges that replacement of methanol by the nonpolar solvent hexane enhances the initial quantum yield of formation of *exo*-**2** from **1** to a greater extend (2.3 times) than the initial quantum yield of disappearance of starting material (1.6 times). Though deriving from primary photoreactions, **9** and *endo*-**2** are formed at initial, relative quantum yields negligible to that of *exo*-**2**. The yield of allene **6** in hexane is much lower than in methanol, which explains that previously this compound was overlooked.[1]

Irradiation of 1 at 254 nm. Changing from broad-spectrum to monochromatic irradiation has been reported[30] to alter the photochemistry of **1** dramatically. On prolonged irradiation of **1** at 254 nm in hexane or methanol, *cis*-dibenzobicyclo[3.3.0]-octa-2,7-diene (**8**) has been obtained[30,31] in nearly quantitative yield. The present results indicate that the initial quantum yield of formation of **8** from **1** in methanol at 254 nm is hardly affected by the presence of acid. After 5 h of irradiation of **1** (10^{-3} M) in methanol, the yield of **8** is 25% in the absence of H_2SO_4 and 20% in the presence of a 20-fold excess (2 × 10^{-2} M) of H_2SO_4. Under identical irradiation conditions (merry-go-round) the yield of **8** is 25%, after a 5-h irradiation period in hexane. This demonstrates that the initial, relative quantum yield of formation of **8** from **1** is independent of the solvent polarity.

These results suggest that formation of **8** neither occurs via a nonconcerted radical or ionic pathway nor involves assistance by the solvent. This suggestion is in accord with an earlier observation,[30] viz. that irradiation of **1** in CD_3OD gave no detectable deuterium incorporation into **8**.

Influence of the Conformer Equilibrium on the Photochemistry of 1 in Methanol and in Hexane. In

Table II. ^1H NMR (500 MHz) Spectral Data of 3,4-Dideuterio-1-phenyl-1,2-dihydronaphthalene in CD_3OD and C_6D_{12}: Trans Couplings ($J_{1,2}$, Hz), Ratio (χ_{pe}/χ_{pa}) of the Conformers 1-pe and 1-pa, and Upfield Shifts (Hz) of H_8, Relative to H_5 ($\Delta\delta_{5,8}$), H_6 ($\Delta\delta_{6,8}$), and H_7 ($\Delta\delta_{7,8}$)

	CD_3OD						C_6D_{12}				
T, °C	$J_{1,2}$	χ_{pe}/χ_{pa}	$\Delta\delta_{5,8}$	$\Delta\delta_{6,8}$	$\Delta\delta_{7,8}$	T, °C	$J_{1,2}$	χ_{pe}/χ_{pa}	$\Delta\delta_{5,8}$	$\Delta\delta_{6,8}$	$\Delta\delta_{7,8}$
−10	9.71	1.23	170.7	199.1	146.5	10	11.50	2.5	134.5	168.5	120.6
20	9.49	1.15	159.5	188.5	137.7	30	11.47	2.1	129.2	163.2	116.0
50	9.16	1.05	151.3	180.7	131.7	50	12.10	2.1	124.1	157.9	111.8

Table III. Chemical Shifts ($\delta(^{13}C)$, in ppm, Relative to Internal TMS, 24 °C) and Temperature Dependence ($\delta(^{13}C, T) - (^{13}C, 24\ °C)$) Thereof for 1-Phenyl-1,2-dihydronaphthalene (1) (Compiled from Proton Noise-Decoupled 100-MHz ^{13}C NMR Spectra in CD_3OD)

	$\delta(^{13}C)$	$\delta(^{13}C, T) - \delta(^{13}C, 24\ °C)$				$\delta(^{13}C)$	$\delta(^{13}C, T) - \delta(^{13}C, 24\ °C)$		
position	24 °C	−40 °C	−60 °C	−80 °C	position	24 °C	−40 °C	−60 °C	−80 °C
C(1)	44.98	−0.07	−0.11	−0.16	C(7)	128.20	0.10	0.12	0.16
C(2)	33.05	0.08	0.10	0.11	C(8)	128.81	0.00	0.00	0.00
C(3)	127.92	0.16	0.22	0.29	C(8a)	139.16	−0.06	−0.09	−0.12
C(4)	129.08	0.04	0.03	0.03	C(9)	145.96	−0.11	−0.14	−0.17
C(4a)	135.41	0.05	0.06	0.07	C(10,14)	129.35	0.11	0.14	0.18
C(5)	127.18	0.02	0.01	0.01	C(11,13)	129.41	0.15	0.20	0.25
C(6)	127.78	0.12	0.16	0.20	C(12)	127.40	0.13	0.18	0.22

the literature, the role of the principles of least motion (PLM)[9,10] and nonequilibration of excited rotamers (NEER)[35] in controlling the stereochemistry of the end products obtained from hexatrienes, generated by photochemical ring opening of different cyclohexadiene conformers, has been emphasized. Since photochemical conversion of 1 via the pentaene intermediates *cZc*- and *cZt*-**3** belongs to this class of reactions, it is important to establish whether these principles apply here. If PLM would apply to the photochemical ring opening of the pseudoequatorial (1-pe) and pseudoaxial (1-pa) conformers of 1 and, simultaneously, the NEER principle would be valid for the resulting pentaene intermediates **3**, the ratios of initial, relative quantum yields (ψ_0, Table I) for different end products would be expected to correlate with the ratios χ_{pe}/χ_{pa} of 1-pe and 1-pa in hexane and methanol.

These ratios were determined from 500-MHz ^1H NMR spectra of 3,4-dideuterio-1,2-dihydronaphthalene (1-*3,4-d_2*) in C_6D_{12} and CD_3OD, according to the procedure described by Lamberts et al.[1,2] The required trans couplings ($^3J_{1,2}$) of the protons at C(1) and C(2) were obtained from a computer simulation of the ABX pattern displayed by their NMR signals. In order to trace the most stable conformer of 1 and to extrapolate χ_{pe}/χ_{pa} ratios to low temperatures, the ratio was monitored at various temperatures. The data obtained in methanol (Table II) are the most accurate, deriving from very reliable (rms error <0.1) computer simulations of the double AB pattern (Figure 2a) due to H_2 and $H_{2'}$. In this case the χ_{pe}/χ_{pa} ratio decreases smoothly with increasing temperature, indicating 1-pe to be thermodynamically more stable conformer. As can be seen in Table II, the χ_{pe}/χ_{pa} ratio also correlates with the difference in chemical shift of H_8 and the other aromatic protons (H_5–H_7) of the dihydronaphthalene moiety. This can be ascribed to greater shielding of H_8 by the phenyl substituent in the 1-pe than in the 1-pa conformer. A similar correlation was observed for the chemical shifts ($\delta(^{13}C)$, Table III) of the carbon nuclei in 1. As can be seen in Table III, the largest variations in $\delta(^{13}C)$ concern the carbons C(9)–C(14) of the phenyl substituent and C(3), i.e., the positions were a change of conformation is expected to result into a major alteration of the chemical environment.

In C_6D_{12} the protons H_2 and $H_{2'}$ provide a deceptively simple NMR pattern (Figure 2b) due to an extremely small difference (0.002 ppm) of their chemical shifts. Consequently, computer simulations were less accurate (rms errors between 0.1 and 0.25) than in the previous case. This is reflected in that the χ_{pe}/χ_{pa} ratios (Table II) do not decrease smoothly with increasing temperature in this solvent. However, the observation that in C_6D_{12} the chemical shift differences between H_8 and the other aromatic protons of the dihydronaphthalene moiety display a smooth temperature dependence similar to that in CD_3OD suggests the χ_{pe}/χ_{pa} ratio to be a smooth function of temperature in C_6D_{12} as well. These results indicate that both in hexane and in methanol, 1-pe is the thermodynamically more stable conformer of 1. From a comparison of the χ_{pe}/χ_{pa} values in methanol and in hexane, the stability difference between 1-pe and 1-pa is concluded to be largest in nonpolar solvents.

The correlations between the ratios of initial, relative quantum yields and χ_{pe}/χ_{pa} are given in Table IV. The results are compatible with the assumption of PLM and the NEER principle as the factors controlling the stereochemistry of the photoreactions of 1-pe and 1-pa to *exo*-**2**,

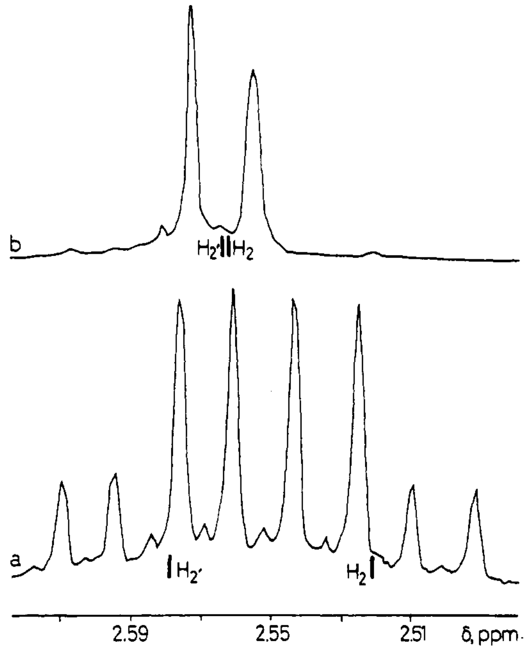

Figure 2. Aliphatic part (H_2 and $H_{2'}$) of the 500-MHz ^1H NMR spectrum of 3,4-dideuterio-1-phenyl-1,2-dihydronaphthalene in CD_3OD (a) and C_6D_{12} (b).

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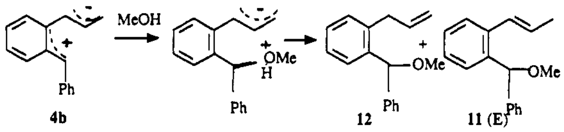
(35) Jacobs, H. J. C.; Havinga, E. *Adv. Photochem.* **1979**, *2*, 305.

Table IV Comparison of the 1-pe/1-pa Conformers Ratio (χ_{pe}/χ_{pa}) of 1-Phenyl-1,2-dihydronaphthalene (1) with the Ratios of Initial Rates of *exo*-4-Phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-2) and 1-(*o*-Tolylphenyl)allene (Ψ_0(*exo*-2)/Ψ_0(6)) and of *exo*-2 and *cis*-Dibenzobicyclo[3.1.0]octadiene (Ψ_0(*exo*-2)/Ψ_0(8)) in Methanol and Hexane at 15 °C

solvent	χ_{pe}/χ_{pa}	Ψ_0(*exo*-2)/Ψ_0(6)	Ψ_0(*exo*-2)/Ψ_0(8)
CH_3OH	1.17	4.2	17.5
C_6H_{12}	2.1	29	47.5

Scheme IV

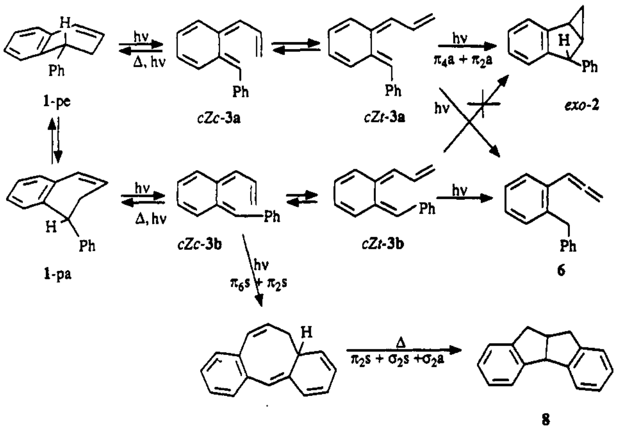


6, and 8, in both hexane and methanol.

Discussion

The absence of a significant effect of the solvent polarity and of the concentration of sulfuric acid on the initial, relative quantum yields of the primary photoproducts from 1 (Table I) indicates that selective trapping of the excited state of the pentaene intermediates *cZc*- and *cZt*-3 (Scheme I) does not occur. The simplest way to rationalize this result is by proposing that the excited states of *cZc*- and *cZt*-3 are not zwitterionic in nature. Evidence against the involvement of zwitterionic excited states in the photochemical methanol addition to stilbene has been published recently.[36] The possibility that the zwitterionic excited states 4b or 4c of pentaene intermediate *cZt*-3 (Scheme I) are nevertheless involved in the photochemistry of *cZt*-3 cannot, however, be ruled out by the failure to trap the excited state with methanol or sulfuric acid.[19] If the energy separation of the zwitterionic excited states 4b and 4c would be in the order of the exchange integral K_{ab} between the positively and negatively charged centers, the theory of the sudden polarization effect[16] predicts these charges to exchange at a rate $k = 2K_{ab}/\pi$ = ca. 5×10^{13} s^{-1}. This is much faster than the diffusion-controlled rate of proton transfer ($k = 10^{11}$–10^{12} s^{-1}). The effective dipole moment of the zwitterionic state would then average zero on the time scale of the scavenging reactions and selective trapping by protons indeed should not be expected. However, because of annelation of the s-cis allyl moiety with the diene system in zwitterionic states 4a and 4b, it is conceivable that the energy separation between these states exceeds the exchange integral K_{ab} (ca. 7 kcal mol^{-1} in the case of the twisted excited singlet state of ethylene).[16] Within this assumption only a fraction of the positive and negative charges on 4a would be involved in the exchange process,[16] so that, in contrast with the case of the parent, unsubstituted *cZt*-1,3,5-hexatriene,[12] the zwitterionic excited state of *cZt*-3, might have an appreciable dipole moment. Whether such a highly polarized excited state could be scavenged efficiently by protons remains a matter of speculation, since this process may be notoriously slow, in particular for free carbanions.[37] However, trapping of the highly polar, zwitterionic states 4a and 4b by methanol might alternatively involve nucleophilic attack (Scheme IV) of methanol in the rate-determining step, which may take place[38,39] with rate constants close to the diffusion-controlled limit (ca. 5×10^9 s^{-1} in methanol).[40]

Scheme V



A mechanism rationalizing the formation of the primary photoproducts is given in Scheme V. The validity of the NEER principle governs that photochemical interconversion between 1-pe and 1-pa does not occur, whereas PLM assures that photochemical conrotary ring opening of 1-pe and 1-pe leads stereospecifically to *cZc*-3a and *cZc*-3b, respectively. Though photochemical interconversion of *cZc*(or *cZt*)-3a and -3b cannot be ruled out, the rates of these processes are assumed to be lower than the rates of equilibration of 1-pe and 1-pa and of thermal reversion of *cZt*-3a or *cZt*-3b to 1. The photostationary 3a/3b ratio should then be correlated to the conformer ratio χ_{pe}/χ_{pa}. From Table IV, the following relations between χ_{pe}/χ_{pa} and the ratios ψ_0(*exo*-2)/ψ_0(6) and ψ_0(*exo*-2)/ψ_0(8) of photoproduct formation in hexane and methanol are obtained:

$$\left(\frac{\chi_{pe}}{\chi_{pa}}\right)_{hexane} : \left(\frac{\chi_{pe}}{\chi_{pa}}\right)_{MeOH} = 1.8 \pm 0.5 \quad (1a)$$

$$\left(\frac{\psi_0(exo\text{-}2)}{\psi_0(8)}\right)_{hexane} : \left(\frac{\psi_0(exo\text{-}2)}{\psi_0(8)}\right)_{MeOH} = 2.7 \pm 0.5 \quad (1b)$$

$$\left(\frac{\psi_0(exo\text{-}2)}{\psi_0(6)}\right)_{hexane} : \left(\frac{\psi_0(exo\text{-}2)}{\psi_0(6)}\right)_{MeOH} = 7 \pm 2 \quad (1c)$$

According to eqs 1a and 1b the ratio ψ_0(*exo*-2)/ψ_0(8) of the initial, relative quantum yields of formation of *exo*-2 and 8 changes by approximately the same factor as the conformer ratio χ_{pe}/χ_{pa}, on going from methanol to hexane. This is compatible with the hypothesis put forward in the introduction that *exo*-2 arises from 1-pe by an intramolecular $\pi_4a + \pi_2a$ photocycloaddition reaction of *cZt*-3a and that 8 evolves from 1-pa via an intramolecular $\pi_6s + \pi_2s$ photocyclization reaction of *cZt*-3b.

The validity of this interpretation is subjected to the condition that the relative quantum yields of the reaction steps indicated in Scheme V are not affected by the solvent polarity. Formation of *exo*-2, 6, and 8 involves only concerted, unimolecular (thermal and photochemical) reaction steps.

As far as 8 is concerned, this proposition is supported by the results of monochromatic irradiations of 1 in hex-

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[36] Woning, J.; Laarhoven, W. H. *J. Chem. Soc., Perkin Trans. II* **1989**, 2147.

[37] Dorfman, L. M.; Sujdak, R. J.; Bockrath, B. *Acc. Chem. Res.* **1976**, *9*, 352.

[38] Richard, J. P.; Rothenberg, M. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1361.

[39] Chiang, Y.; Kresge, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 6363.

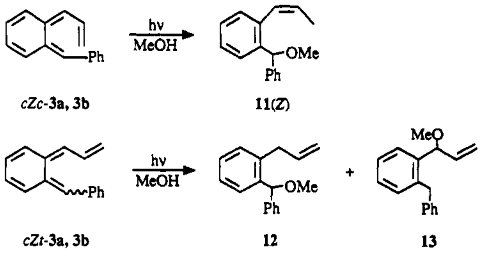
[40] Cowan, O. D.; Drisco, R. L. *Elements of Organic Photochemistry*; Plenum: New York, 1968; p 67.

ane, MeOH, and CD_3OD,[30] which indicate the absence of interaction between the solvent and the transition state involved in thermal $\pi_2s + \pi_2a + \sigma_2a$ rearrangement[30] (Scheme V) leading to **8**. As far as *exo*-**2** and **6** are concerned, the experimental results in Table I suggest that the formation of these compounds does not involve sudden-polarized, zwitterionic excited states of *cZc*-**3** or *cZt*-**3**.

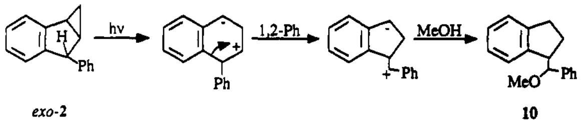
The attractiveness of the present hypothesis is that it complies with other experimental results and theoretical considerations. Considering the geometries of the four pentaene intermediates *cZc*-**3a**, *cZt*-**3a**, *cZc*-**3b**, and *cZt*-**3b** (Scheme V), it is noted that only *cZc*-**3b** exhibits the appropriate geometry for an allowed $\pi_6s + \pi_2s$ photocyclization reaction, leading to **8**. Moreover, the present hypothesis associates the chief photoreaction, i.e., the formation of *exo*-**2**, with the most abundant pentaene intermediate (*cZt*-**3a**). As noted in the introduction, a photocyclization of the $\pi_4a + \pi_2a$-type is not rigorously forbidden in 1,3,5-hexatrienes of low symmetry.[5] The present hypothesis is also consistent with the observed temperature effect (Table I) on the initial, relative quantum yields of *exo*-**2** and **8** in methanol. A decrease in temperature will cause the equilibrium between **1**-pe and **1**-pa to shift toward the more stable **1**-pe conformer. In accord with this expectation, $\psi_0(exo\text{-}2)$ and $\psi_0(8)$ (Table I) were found to increase and decrease, respectively, with decreasing temperature. Obviously, the lowering of the initial, relative quantum yield of the allowed, thermal $\pi_2s + \pi_2a + \sigma_2a$ rearrangement[30] (Scheme V) provides an additional contribution to the decrease of $\psi_0(8)$ with decreasing temperature.

In an attempt to shed more light on the underlying cause of the dramatic wavelength effect on the photochemistry of **1**, some kinetic experiments have been performed.[41] The results of these experiments prove that, in accord with previous reports on related 1,2-dihydronaphthalenes,[42,43] a brief, broad-spectrum irradiation of **1** in quartz produces the intermediate pentaenes **3** in appreciable steady-state concentrations. According to the results obtained in hexane and in neat as well as in acidic methanol at 254 nm, the reactivity of these species is low at this wavelength. This may be attributed [23] to the fact that the pentaenes **3** will compete strongly with **1** for the absorption of incident light at 254 nm, but not at longer wavelengths, where only the pentaenes exhibit appreciable UV-vis absorption. By this argument, the highly selective photoreaction of pentaene *cZc*-**3b** to **8** can, however, not be accounted for. The formation of **8** might involve a higher excited state of *cZc*-**3b** with appreciable excitation of the phenyl group. The photocycloaddition reaction to *exo*-**2** requires excitation of *cZt*-**3a** in its long wavelength absorption band, into the lowest excited singlet state. It is not known if ring closure of *cZt*-**3b** also occurs at 435 nm. Independent of this, the ratio *exo*-**2**:**8** should be determined by the intensity ratio of the 435- and 254-nm output of the broad-spectrum lamp. With use of the same lamp, light intensity, substrate concentrations, and highly UV-transparent solvents, the ratio *exo*-**2**:**8** will be constant, unless the conformer ratio χ_{pe}/χ_{pa} and, consequently, the ratio of the pentaenes **3a** and **3b** is changed.

Scheme VI



Scheme VII



Along with the intramolecular photocycloaddition reacttion leading to *exo*-**2**, the formation of **6** in both hexane and methanol is seen to be suppressed completely on changing from broad-spectrum to monochromatic (254 nm) irradiation of **1**. This indicates a photochemical 1,5-H shift to be responsible for the formation of **6** from the pentaene precursor **3**. Apart from this argument, the assumption of a thermal pathway to **6** would be in conflict with the absence of a temperature effect on $\psi_0(6)$ (Table I), as well as with the observation[41] that on warming of a cold solution containing an appreciable concentration of the pentaenes **3**, **6** appeared not to have formed. According to eqs 1a and 1c, **6** derives presumably from both **1**-pe and **1**-pa. This is consistent with the consideration that both *cZt*-**3a** and *cZt*-**3b** possess the appropriate geometry for a symmetry-allowed, photochemical 1,5-H shift.

The primary photoproducts **11**–**13** can be rationalized as methanol adducts of the pentaene intermediates **3** (Scheme VI). In analogy with **6**, a thermal pathway from *cZc*- and *cZt*-**3** to these products can be ruled out.[41] In accord with this rationalization, **11**–**13**, like *exo*-**2** and **6**, were not observed on irradiation of **1** at 254 nm.

As far as the secondary photoreactions are concerned, the mode of decomposition of *exo*-**2** is quite unusual for a benzobicyclo[3.1.0]hex-2-ene. The usual decomposition pathway for these compounds involves homolytic cleavage of the C(1)–C(5) cyclopropane bond and subsequent 1,2-H shifts, yielding 1,2- or 1,4-dihydronaphthalenes.[1,2,25,44] This reaction was observed with *exo*-**2** in hexane.[25] The formation of **10** from *exo*-**2** in methanol can be rationalized, when heterolytic fission of the C(1)–C(5) cyclopropane bond[45] is invoked in the reaction mechanism (Scheme VII). The lack of influence of sulfuric acid on the decomposition rate might be explained by assuming the sequence of the above reactions to take place in a more or less concerted fashion. Alternatively, it could be speculated that, in analogy with the cases of ethylene[16] and *cZt*-1,3,5-hexatriene,[12,16] the zwitterionic excited state depicted in Scheme VII possesses no net dipole moment due to a rapid exchange of the positive and negative charges. Examples of

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(41) Upon broad-spectrum irradiation of **1** (2×10^{-3} M, in methanol or hexane) for 5 min, at temperatures of 191–223 K, a broad long-wavelength UV-vis absorption (λ_{max} 435 nm, ϵ ca. 0.2) due to the pentaene intermediates **3** was observed. After switching off the light, the kinetic parameters for the overall thermal reversion of **3** into **1**-pe and **1**-pa were determined from the decay of the 435-nm absorption as a function of time, at three different temperatures. This gave $\Delta E_{act} = 13 \pm 1$ kcal mol^{-1}, $\Delta G^{\ddagger} = 14.6 \pm 0.5$ kcal mol^{-1}, $\Delta H^{\ddagger} = 13 \pm 2$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -8 \pm 3$ eu, in the temperature range 191–223 K. These data compare favorably to those reported for thermal, concerted electrocyclic ring closure reactions of simple 1,3,5-hexatrienes. After warming the cold solutions to room temperature, only **1** was found to be present, indicating that none of the compounds listed in Scheme III arises by thermal reactions of the pentaenes **3**.

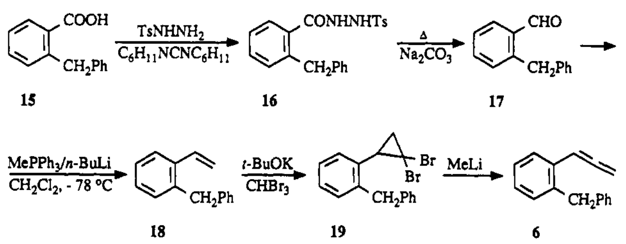
(42) Kleinhuis, H.; Wijting, R. L. C.; Havinga, E. *Tetrahedron Lett.* **1971**, 255.

(43) Widmer, U.; Heimgartner, H.; Schmid, H. *Helv. Chim. Acta* **1975**, *58*, 2210.

(44) Laarhoven, W. H.; Berendsen, N. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 10.

(45) Hixson, S. S. *Org. Photochem.* **1979**, *4*, 191.

Scheme VIII



analogous photochemical methanol addition reactions not subject to acid catalysis, but nevertheless involving heterolytic cleavage of a cyclopropane bond, have been reported.[46]

Experimental Section

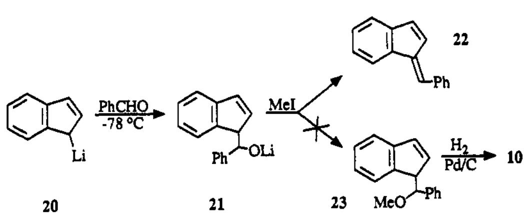
Apparatus and Procedures. Irradiations were performed with nitrogen-purged, 2 × 10^{-3} M solutions of **1**, using a Philips 125 W high-pressure mercury (HPM) lamp or Philips TUV G15T8 (254 nm) tubes. Spectrograde methanol (Merck) and hexane (Baker) were used throughout. For the evaluation of the initial, relative quantum yields vs time plots (Figure 1), **1** was irradiated with a HPM lamp in a 200-mL irradiation vessel, equipped with a nitrogen inlet, a methanol-cooled (–90 to 25 °C) quartz finger, and a sampling outlet. During the irradiation experiment, the vessel was purged continuously with nitrogen and 0.2-mL aliquots were taken at 2–4-min time intervals. The composition of these samples was determined by GC. Mass balances exceeding 98% for samples taken after short periods of irradiation (<20 min), and 95% for samples taken after 20–120 min, were reproducibly obtained. Relative quantum yields were measured on an Aberchrome 540 actinometer[47] to verify that the light intensity and the emission spectrum of the lamp did not change in the course of several weeks of experimentation.

Separation of the photoproducts was accomplished by TLC or column chromatography on silica gel (Merck 60, 70–230 mesh), using carbon tetrachloride or hexane–toluene mixtures as the eluant. Mixtures of photoproducts were analyzed by GC, employing a HP 5790 gas chromatograph, equipped with HP or Chrompack fused-silica capillary columns, a HP 3390A integrator, and a flame ionization detector. The response of the detector was assumed to be proportional to the number of carbon atoms present in the compound detected. Samples originating from irradiations in methanol containing sulfuric acid were neutralized with OH^--exchanged Dowex IRA-400 ion-exchange resin prior to GC or GCMS.

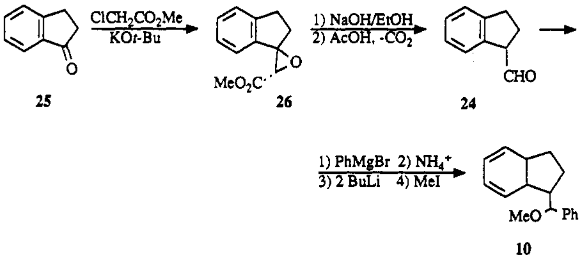
The photoproducts were characterized by ^1H NMR (Hitachi/Perkin-Elmer R-24B and Bruker WH-90 spectrometers, internal standard TMS), GCMS (VG 70-70), IR (Perkin-Elmer 379) and UV-vis (Perkin-Elmer 555) spectroscopy, as well as by chemical synthesis.

The 500-MHz ^1H NMR spectra of **1**-*3,4*-d_2 were recorded on a Bruker AM-500 spectrometer. The procedure for obtaining the ratios χ_{pe}/χ_{pa} (Table II) of the 1-pe and 1-pa conformers is described in refs 1 and 2. The 100-MHz ^{13}C and two-dimensional, ^{13}C–^1H correlated NMR spectra of **1** were recorded on a Bruker AM-400 spectrometer, using a VST probe. The low-field ^{13}C resonances due to the quaternary carbon atoms in **1** were assigned by comparison with $\delta(^{13}C)$ values for alkyl-substituted 1,2-dihydronaphthalenes,[48] which were corrected for the presence of the phenyl substituent in **1** with the aid of an empirical increment system.[49]

Scheme IX



Scheme X



Preparations. The starting materials 1-phenyl-1,2-dihydronaphthalene (**1**), 3,4-dideuterio-1,2-dihydronaphthalene (**1**-*3,4*-d_2) and 4-phenylbenzobicyclo[3.1.0]hex-2-ene (mixture of *endo*- and, predominantly, *exo*-**2**) were prepared as previously described.[1,2]

1-(*o*-Benzylphenyl)allene (6). This compound was prepared from *o*-benzylbenzoic acid (**15**) according to the procedure described for 1-phenylallene (Scheme VIII).[50,51]

Hydrazide **16** was prepared[50] by stirring a solution of **15** (10.6 g, 50 mmol), dicyclohexylcarbodiimide (11.3 g, 55 mmol), and *p*-toluenesulfonohydrazide (9.3 g, 50 mmol) in dry THF (130 mL) overnight, at ambient temperature. Removal of the dicyclohexylurea precipitate, followed by evaporation of the solvent, afforded crude **16**, which was recrystallized from hexane and then from ethanol. Extrusion of N_2 from **16** was initiated by the addition of anhydrous sodium carbonate to a hot (160 °C) solution of **16** in ethylene glycol.[50] The extrusion reaction was allowed to proceed for 75 s and then quenched by pouring the reaction mixture into water. Crude **17** was isolated by extraction with hexane, drying of the organic phase, and evaporation of the solvent. Purification by flash chromatography (silica gel, eluant $CHCl_3$) afforded **17** as a colorless oil in 80% yield. This compound was converted into *o*-benzylstyrene (**18**) by a Wittig reaction with methyltriphenylphosphonium bromide and *n*-BuLi in CH_2Cl_2, at –78 °C:[50] 60-MHz ^1H NMR ($CDCl_3$) δ 4.0 (s, 2 H), $ArCH_2Ar$), 5.0 and 5.3 (both dd, J_{cis} = 11 Hz, J_{trans} = 17 Hz, 1 H, $CH{=}CH_2$), 6.3–7.4 (m, 10 H, Ar H, $CH = CH_2$); EIMS *m/e* (rel intensity) 195 (4), 194 (M^+, 26), 180 (12), 179 (100), 178 (33), 165 (9), 152 (4), 115 (16), 91 (9).

Compound **19** was prepared[51] by dropwise addition of a solution of *t*-BuOK (7.1 g, 63 mmol) in *t*-BuOH (50 mL) to a solution of **18** (5.6 g, 29 mmol) and $CHBr_3$ (14.7 g, 58 mmol) in pentane at ca. –10 °C. The reaction mixture was allowed to warm to room temperature, diluted with diethyl ether (250 mL), and extracted with water. Drying of the organic layer, followed by filtration, evaporation of the solvent, and purification by column chromatography afforded **19** as a colorless oil: 60-MHz ^1H NMR ($CDCl_3$) δ 1.7 (d, 2 H, $J_{2,3}$ = 9 Hz, H_3, $H_{3'}$), 2.5 (t, 1 H, H_2), 3.8 (s, 2 H, $ArCH_2Ar$), 6.8 (s, 9 H, Ar H); EIMS *m/e* (rel intensity) 368 (1.3), 366 (M^+, 2.7), 364 (1.2), 287 (3.6), 285 (3.9), 206 (48), 205 (31), 181 (11), 180 (84), 179 (100), 178 (23), 165 (18), 128 (29), 115 (18), 91 (89).

For the preparation of **6**, a solutionn of **19** in diethyl ether, cooled to –78 °C, was treated with a slight excess of MeLi in hexane, followed by dilute hydrochloric acid.[51] The reaction mixture was allowed to warm to room temperature and extracted with water. Drying of the organic phase ($MgSO_4$), followed by filtration and evaporation of the solvent, afforded crude **6**, which was purified by column chromatography: IR (film) ν 3080, 3060, 3020, 2910, 2855, 1940 (C=C=C), 1602, 1493, 1453, 1075 cm^{-1}; 90-MHz ^1H NMR ($CDCl_3$) δ 4.04 (s, 2 H, $ArCH_2Ar$), 5.03 (d, $^4J_{1,3}$ = 6.9 Hz, 1 H, H_3), 6.30 (t, 1 H, H_1), 7.0–7.3 (m, 9 H, Ar H); EIMS

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(46) Irving, C. S.; Petterson, R. C.; Sarkar, I.; Kristinnson, H.; Aaron, C. S.; Griffin, G. W.; Boudreau, G. J. *J. Am. Chem. Soc.* **1965**, *88*, 5675.

(47) Heller, H. G.; Langlan, J. R. *J. Chem. Soc., Perkin Trans. II* 1981, 343.

(48) Adamczyk, M.; Watt, S. D.; Netzel, D. A. *J. Org. Chem.* **1984**, *49*, 4226.

(49) Hesse, M.; Meier, H.; Zeeh, B. *Spectrokopische Methoden in der Organischen Chemie*; Thieme: Stuttgart, 1984; pp 228–229.

(50) Crow, W. D.; McNab, H. *Austr. J. Chem.* **1981**, *34*, 1037.

(51) Chen, T.-Y. R.; Anderson, M. R.; Grossman, S.; Peters, D. G. *J. Org. Chem.* **1987**, *52*, 1231.

m/*e* (rel intensity) 207 (16), 206 (M^+, 100), 205 (41), 191 (38), 178 (25), 165 (17), 152 (6), 129 (24), 128 (41), 115 (17), 101 (12), 91 (84).

1-(α-Methoxybenzyl)indan (10). This compound proved to be inaccessible by strategies based on 1-metalated indan or indene. Reaction of the readily accessible 1-lithio-1*H*-indene (**20**)[52] with benzaldehyde in THF at −78 °C afforded **21** (Scheme IX). Attempts to methylate this product with MeI at −25 °C resulted in elimination of LiOH to yield 1-benylidene-1*H*-indene (**22**, lit.[53] mp 87–88 °C, yield ca. 50%) instead of the desired compound **23**. Attempts to synthesize **10** via 1-indanylmagnesium chloride failed. Heating 1-chloroindan[54] with Mg in THF yielded indene and $MgCl_2$, instead of the Grignard reagent. Attempts to prepare 1-lithioindan from Li and 1-methoxyindan[55] in THF at −15 °C[56] were also unsuccessful.

Fortunately, the reversed approach, viz. synthesis of **10** via the reaction of 1-formylindan (**24**) and phenylmagnesium bromide (Scheme X) proved to be effective.

The compound (±)-1-formylindan (**24**) was prepared according to a known method[57] with some modifications. A Darzens condensation of **25** with methyl chloroacetate yielded crude methyl indan-1-spiro-2′-oxirane-3′-carboxylate (**26**) as a thick brown syrup, which crystallized upon the addition of absolute ethanol (1 mL g^{-1}). Recrystallization from absolute ethanol (10 mL g^{-1}) afforded pure **26** (mp 85.5–86.0 °C): IR (KBr) ν 1747 ($C{=}O$), 1205 ($C{-}O$) cm^{-1}; 90-MHz ^1H NMR ($CDCl_3$) δ 2.28–2.45 (m, 2 H, H_2), 2.96–3.18 (m, 2 H, H_3), 3.82 (s, 3 H, OCH_3), 3.92 (s, 1 H, $H_{3'}$), 6.97–7.06 (m, 1 H, H_7), 7.06–7.34 (m, 3 H, H_4, H_5, H_6); EIMS *m*/*e* (rel intensity) 204 (M^+, 9), 186 (1), 173 (3), 147 (100), 133 (14), 117 (31), 116 (25), 115 (60), 91 (9). Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.56; H, 5.97.

Saponification of **26** with NaOH in ethanol,[57] followed by evaporation of the solvent, addition of diethyl ether, filtration, and washing with a little cold ethanol afforded crude sodium indan-1-spiro-2′-oxirane-3′-carboxylate as a light-brown solid. Decarboxylation in concentrated acetic acid and subsequent workup afforded (±)-**24** (bp 65–70 °C/0.3 mm, n^{20}_D 1.5534) in 25% overall yield: 90-MHz ^1H NMR ($CDCl_3$) δ 2.15–2.49 (m, 2 H, H_2), 3.00 (t, $J_{2,3}$ = 7.40 Hz, 2 H, H_3), 3.94 (dt, $J_{1,2}$ = 7.17 Hz, $J_{1,HCHO}$ = 2.74 Hz, 1 H, H_1), 7.23 (s, 4 H, Ar H), 9.63 (d, 1 H, CHO); EIMS *m*/*e* (rel intensity) 147 (M + 1, 48), 146 (M^+, 12), 145 (11), 129 (21), 118 (16), 117 (100), 116 (24), 115 (33), 91 (14).

For the preparation of **10**, a solution of (±)-**24** (1.59 g, 10.8 mmol) in dry diethyl ether (5 mL) was added dropwise to an ice-cold etheral solution (10 mL) of phenylmagnesium bromide (ca. 20 mmol). The reaction mixture was kept at 0 °C for 15 min, diluted with diethyl ether (10 mL), and extracted with saturated, aqueous NH_4Cl (10 mL). Drying ($MgSO_4$) of the organic phase, followed by filtration and evaporation of the solvent, afforded 1.80 g (74%) of 1-indanylphenylcarbinol as a brown oil. The latter was dissolved in THF (25 mL), and the resulting solution was reacted with excess of *n*-BuLi (20 mmol). This was followed by the addition of a large excess of MeI (5 mL, 80 mmol) and refluxing of the reaction mixture for 3 h. Evaporation of the solvent and purification of the residue by column chromatography (silica gel, eluant CCl_4) afforded 1.25 g (49%, based on the quantity of **24** used) of **10** as a colorless oil: 90-MHz ^1H NMR of (1*S*,α*S*; 1*R*,α*R*)-**10** ($CDCl_3$) δ 2.03–2.31 (m, 2 H, H_2), 2.58–2.88 (m, 2 H, H_3), 3.18 (s, 3 H), OCH_3), 3.36–3.63 (m, 1 H, H_1), 4.19 (d, $J_{1,\alpha}$ = 7.2 Hz, 1 H, H_α), 6.54 (d, $J_{6,7}$ = 7.0 Hz, 1 H, H_7), 6.83–7.26 (m, 8 H, Ar H); 90-MHz ^1H NMR of (1*R*,α*S*;1*S*,α*R*)-**10** ($CDCl_3$) δ 1.52–1.82 (m, 2 H, H_2), 2.6–3.0 (m, 2 H, H_3), 3.22 (s, 3 H, OCH_3), 3.3–3.6 (m, 1 H, H_1), 4.11 (d, $J_{1,\alpha}$ = 7.0 Hz, 1 H, H_α), 6.8–7.3 (m, 9 H, Ar H); EIMS (diastereomeric mixture) *m*/*e* (rel intensity) 238 (M^+, 0.42), 223 (0.56), 222 (1.1), 221 (0.4), 207 (3.8), 122 (18), 121 (100), 117 (11), 116 (5), 115 (11), 105 (5), 91 (16), 77 (17). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 84.71; H, 7.41.

(*Z*)-1-(α-Methoxybenzyl)-2-propen-1-ylbenzene (11): 90-MHz ^1H NMR ($CDCl_3$) δ 1.60 (dd, $J_{1,3}$ = 1.5 Hz, $J_{2,3}$ = 6.8 Hz, 3 H, $CH{=}CHC\mathit{H}_3$), 3.35 (s, 3 H, OCH_3), 5.42 (s, 1 H, $Ar_2C\mathit{H}OMe$), 5.81 (dq, $J_{1,2}$ = 11.4 Hz, 1 H, $CH{=}C\mathit{H}CH_3$), 6.50 (dq, 1 H, $C\mathit{H}{=}CHCH_3$), 7.0–7.4 (m, 9 H, Ar H); GC-EIMS (CH_4) *m*/*e* (rel intensity) 238 (M^+, 0.56), 223 (0.26), 207 (58), 206 (100), 191 (27), 179 (41), 178 (28), 165 (22), 161 (30), 152 (7), 129 (47), 128 (32), 121 (25), 115 (21), 105 (12), 91 (89), 77 (31); GC-CIMS (CH_4) *m*/*e* (rel intensity) 239 (M + 1, 6), 208 (17), 207 (100), 206 (21), 179 (6), 161 (40), 129 (67), 128 (32), 121 (93), 91 (28).

1-(α-Methoxybenzyl)-2-propen-2-ylbenzene (12): 90-MHz ^1H NMR ($CDCl_3$) δ 3.3–3.5 (m, $J_{1,2}$ = 6.3 Hz, $J_{1,3}$ = 3.3 Hz, $J_{1,3'}$ = 3.1 Hz, 2 H, $C\mathit{H}_2CH{=}CH_2$), 3.36 (s, 3 H, OCH_3), 4.97 (m, $J_{2,3}$ = J_{trans} = 16.5 Hz, $J_{3,3'}$ = 2.0 Hz, 1 H, $CH_2CH{=}C\mathit{H}_2$), 5.04 (m $J_{2,3'}$ = J_{cis} = 10.5 Hz, 1 H, $CH_2CH{=}C\mathit{H}_2$), 5.47 (s, 1 H, $Ar_2C\mathit{H}OMe$), 5.91 (m, 1 H, $CH_2C\mathit{H}{=}CH_2$), 7.0–7.4 (m, 9 H, Ar H); GC-EIMS *m*/*e* (rel intensity) 238 (M^+, 0.52), 223 (1.7), 206 (100), 191 (31), 179 (37), 178 (26), 165 (20), 152 (7), 128 (19), 121 (31), 115 (17), 91 (87); GC-CIMS (CH_4) *m*/*e* (rel intensity) 239 (M + 1, 3.5), 208 (14), 207 (100), 206 (30), 179 (11), 128 (25), 119 (16), 117 (20), 91 (100).

1-(1-Methoxyprop-2-enyl)-2-benzylbenzene (13): 90-MHz ^1H NMR ($CDCl_3$) δ 3.14 (s, 3 H, OCH_3), 4.04 (s, 2 H, $ArCH_2Ar$), 4.81 (d, $J_{1,2}$ = 6.3 Hz, 1 H, $C\mathit{H}CH{=}CH_2$), 5.14 (m, $J_{2,3}$ = J_{cis} = 9.3 Hz, 1 H, $CHCH{=}C\mathit{H}_2$), 5.15 (m, $J_{2,3'}$ = J_{trans} = 18.0 Hz, 1 H, $CHCH{=}C\mathit{H}_2$), 5.87 (m, 1 H, $CH_2C\mathit{H}{=}CH_2$), 6.8–7.4 (m, 9 H, Ar H); EIMS of a mixture of **11**, **12**, and **13**; highest mass at *m*/*e* 238 (M^+, 0.5).

1-(3-Methoxyprop-1-enyl)-2-benzylbenzene (14, *Z*/*E* = 4): 90-MHz ^1H NMR of (*Z*)-**14** ($CDCl_3$) δ 3.23 (s, 3 H, OCH_3), 4.00 (d, $J_{2,3}$ = 6.0 Hz, 2 H, $CH{=}CHC\mathit{H}_2OMe$), 4.03 (s, 2 H, $ArCH_2Ar$), 5.80 (dt, $J_{1,2}$ = J_{cis} = 11.4 Hz, 1 H, $CH{=}C\mathit{H}CH_2OMe$), 6.56 (d, 1 H, $C\mathit{H}{=}CHCH_2OMe$), 7.0–7.4 (m, 9 H, Ar H); 90-MHz ^1H NMR of (*E*)-**14** ($CDCl_3$) δ 3.26 (s, 3 H, OCH_3), 4.00 (dd, $J_{1,3}$ = 1.2 Hz, $J_{2,3}$ = 5.7 Hz, 2 H, $CH{=}CHC\mathit{H}_2OMe$), 4.03 (s, 2 H, $ArCH_2Ar$), 6.09 (dt, $J_{1,2}$ = J_{trans} = 16.0 Hz, 1 H, $CH{=}C\mathit{H}CH_2OMe$), 6.80 (d, 1 H, $C\mathit{H}{=}CHCH_2OMe$), 7.0–7.4 (m, 9 H, Ar H); EIMS (4:1 mixture of (*Z*)-**14** and (*E*)-**14** *m*/*e* (rel intensity) 238 (M^+, 18), 207 (23), 206 (95), 205 (3), 193 (12), 192 (13), 191 (30), 180 (50), 179 (100), 178 (67), 165 (37), 152 (10), 129 (17), 128 (20), 121 (17), 117 (18), 115 (44), 105 (10), 91 (88).

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(52) Wakefield, B. J. *The Chemistry of Organolithium Compounds*: Pergamon, Oxford, 1974; pp 26–27.

(53) *DMS UV Atlas of Organic Compounds*; Butterworths, Verlag Chemie: London, 1967; Vol. III, F4/9.

(54) *Organic Syntheses*; Blatt, A. H., Ed.; Wiley: New York, 1963; Collect. Vol. II, 336.

(55) Weissgerber, R. *Chem. Ber.* **1911**, *44*, 1436.

(56) *Houben-Weyl Methoden der Organischen Chemie*, 4th ed.; Mueller, E., Ed., Thieme: Stuttgart, 1970; Vol. 13/1, 161.

(57) Kavadias, G.; Velkof, S. *Can. J. Chem.* **1978**, *56*, 730.