A solution of the acid **16a** obtained above (0.36 g, 1.8 mmol) and *p*-toluenesulfonic acid (40 mg) in 10 mL of methanol was refluxed for 3 h. The solvent was removed under reduced pressure, and the residue was taken up in ether. The solution was washed with 10% aqueous sodium hydroxide, dried over anhydrous sodium sulfate, and evaporated. The residue was distilled [110–130 °C (2 mm), Kugelrohr] to give 0.27 g (70%) of methyl 2-(4-isobutylphenyl)propionate: $[\alpha]^{20}_D$ −49.0° (*c* 1.82, benzene); NMR (CCl_4) δ 0.92 (d, *J* = 7 Hz, 6 H), 1.45 (d, *J* = 8 Hz, 3 H), 1.85 (nonet, 1 H), 2.44 (d, *J* = 7 Hz, 2 H), 3.44–3.71 (m, 1 H), 3.67 (s, 3 H), 6.92–7.21 (AA'BB', 4 H). NMR spectroscopy with the chiral shift reagent Eu(dcm)$_3$ indicated that the ester is 80% ee.

2-(4-Biphenylyl)propionic Acid (16b). The cross-coupling of **14b** was carried out in a similar manner to that of **14b**. After hydrolysis and the workup, short silica gel column (benzene) treatment gave a mixture of 3-(4-biphenylyl)-1-butene (**15b**) and 4-ethylbiphenyl in a ratio of 1:1. NMR ($CDCl_3$) of **15b**: δ 1.37 (d, *J* = 7 Hz, 3 H), 3.48 (q, 1 H), 4.92–5.23 (m, 2 H), 5.81–6.24 (m, 1 H), 7.15–7.75 (m, 9 H). The mixture was subjected, without further purification, to oxidation with sodium periodate and potassium permanganate in a manner similar to the preparation of **16a**. Extraction of organic products with 10% aqueous sodium hydroxide followed by acidification with concentrated hydrochloric acid and ether extraction gave a ca. 60% yield of the acid **16b**:[21] NMR ($CDCl_3$) δ 1.59 (d, *J* = 8 Hz, 3 H), 3.83 (q, 1 H), 7.25–7.90 (m, 9 H), 9.50 (br s, 1 H).

Esterification (TsOH/MeOH) of the acid **16b** ($[\alpha]^{20}_D$ −24.4° (95% ethanol)) gave methyl 2-(4-biphenylyl)propionate: $[\alpha]^{20}_D$ −52.7° (*c* 2.06, benzene); NMR ($CDCl_3$) δ 1.54 (d, *J* = 7 Hz, 3 H), 3.68 (s, 3 H), 3.68–3.85 (q, 1 H), 7.29–7.75 (m, 9 H). NMR spectroscopy with Eu(dcm)$_3$ indicated that the ester is 82% ee.

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Registry No. **1a**, 74492-06-1; **1b**, 82821-95-2; **1c**, 74492-07-2; **1d**, 74492-09-4; **1e**, 85711-05-3; **1f**, 74492-08-3; **1g**, 82821-97-4; **1h**, 74492-10-7; **1i**, 60365-87-9; **2a**, 56-41-7; **2b**, 61-90-5; **2c**, 63-91-2; **2d**, 72-18-4; **2e**, 73-32-5; **2f**, 875-74-1; **2g**, 14328-52-0; (*S*)-**2h**, 20859-02-3; (*R*)-**2h**, 26782-71-8; **2i**, 147-85-3; **3a**, 2812-31-9; **3b**, 2439-37-4; **3d**, 2812-32-0; **3e**, 2439-38-5; **3f**, 29810-09-1; **4a**, 40916-65-2; **4b**, 69150-45-4; **4c**, 27720-03-2; **4c**·HCl, 85711-08-6; **4d**, 64584-88-9; **4e**, 85711-06-4; **4f**, 2202-65-5; **4f**·HCl, 1128-33-2; **4g**, 85711-07-5; **4h**, 74492-02-7; **4i**, 34381-71-0; **5a**, 74524-03-1; **5b**, 85711-09-7; **5c**, 74492-03-8; **5d**, 74492-04-9; **5e**, 85711-10-0; **5f**, 2202-63-3; **5g**, 85711-11-1; **5h**, 74492-05-0; **5i**, 67824-38-8; **6c**, 3182-95-4; **6f**, 56613-80-0; **6f**·HCl, 85711-12-2; **6g**, 85711-13-3; **6g**·HCl, 85711-14-4; **7**, 85711-15-5; **8**, 85711-16-6; (*R*)-**9**, 57496-01-2; **10**, 79186-17-7; (*S*)-**12a**, 58717-85-4; (*R*)-**12a**, 36617-88-6; (*S*)-**12b**, 77693-46-0; (*R*)-**12b**, 72782-48-0; (*S*)-**12c**, 77693-47-1; (*R*)-**12c**, 73335-32-7; (*S*)-**12d**, 54541-45-6; (*R*)-**12d**, 54541-44-5; (+)-**15a**, 85711-17-7; (−)-**15a**, 85711-18-8; **15b**, 85711-21-3; (*R*)-**16a**, 51146-57-7; (*S*)-**16a**, 51146-56-6; (*R*)-**16b**, 10516-54-8; (*S*)-**16b**, 10532-14-6; $PdCl_2$[(*S*)-Valphos], 85719-55-7; $PdCl_2$[(*S*)-Alaphos], 85719-56-8; $PdCl_2$[(*S*)-Phephos], 85719-57-9; $NiCl_2$, 7718-54-9; (*S*)-1-(dimethylamino)-2-(diphenylphosphinyl)propane, 85711-20-2; (*R*)-1-(dimethylamino)-2-(diphenylphosphinyl)propane, 74098-44-5; dichlorobis(acetonitrile)palladium(II), 14592-56-4; (*S*)-*N*,*N*-dimethylphenylalanine methyl ester, 27720-05-4; diphenylphosphine, 829-85-6; 1,4-dibromobutane, 110-52-1; (*S*)-2-(1-pyrrolidino)-3-phenylpropyl chloride hydrochloride, 85711-19-9; (*R*)-methyl 2-(4-isobutylphenyl)propionate, 81576-57-0; (*R*)-methyl 2-(4-biphenylyl)propionate, 85711-22-4; (1-chloroethyl)benzene, 672-65-1; 1-(1-chloroethyl)-4-methylbenzene, 2362-36-9; 2-(1-chloroethyl)naphthalene, 58464-06-5; 2-chlorooctane, 628-61-5; 1-(1-chloroethyl)-4-(2-methylpropyl)benzene, 62049-65-4; 4-(1-chloroethyl)-1,1'-biphenyl, 58114-03-7.

Photochemistry of Phenyl-Substituted Benzobicyclo[3.1.0]hex-2-enes. A Reverse Di-π-methane Rearrangement

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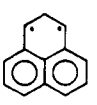
The photochemical rearrangements of phenyl-substituted benzobicyclo[3.1.0]hex-2-enes can generally be explained by assuming that homolytic fission of that cyclopropane bond which leads to the most stable diradical is the primary step. The final products are formed by 1,2 hydrogen shifts in the intermediate. An exception to this general pattern was observed with 5-phenylbenzobicyclo[3.1.0]hex-2-ene (**5**). The photoproducts of **5** could only be explained by assuming reverse di-π-methane rearrangements followed by 1,3 hydrogen shifts. It is argued that this reaction path is followed because of the high rate to the back-reaction of the homolytic bond fission of **5**.

Substituted cyclopropanes undergo two major photochemical reactions, viz., cis–trans isomerization and rearrangement to propenes. As a special class of cyclopropanes, bicyclo[3.1.0]hex-2-enes show epimerization at C(6) as their prominent photoreaction upon direct as well as sensitized irradiation[1,2] (Scheme I). Recently, a trimethylene diradical (**2**) has been shown to play a role in the photorearrangement of naphthobicyclo[3.1.0]hexane.[3] This study is aimed at the investigation of the influence of the position of the phenyl substitutent in the photorearrangement of



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(1) (a) H. E. Zimmerman and G. A. Epling, *J. Am. Chem. Soc.*, **94**, 8749 (1972), and references cited therein; (b) J. S. Swenton, J. A. Hyatt, T. J. Walker, and A. L. Crumrine, *ibid.*, **93**, 4808 (1971).

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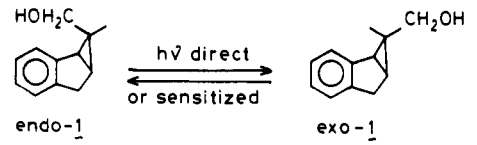
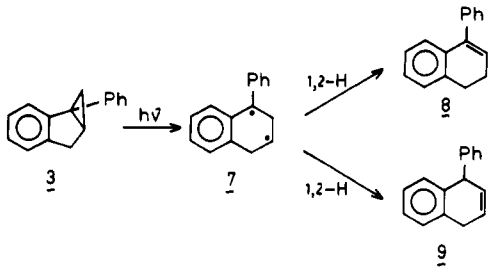
Scheme I

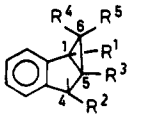


Scheme II



phenyl-substituted benzobicyclo[3.1.0]hex-2-enes.

The phenyl-substituted benzobicyclo[3.1.0]hex-2-enes **3–5** were prepared from the corresponding indenes by way



	R^1	R^2	R^3	R^4	R^5
3	Ph	H	H	H	H
exo-**4**	H	Ph	H	H	H
5	H	H	Ph	H	H
endo-**6**	H	H	H	Ph	H
exo-**6**	H	H	H	H	Ph

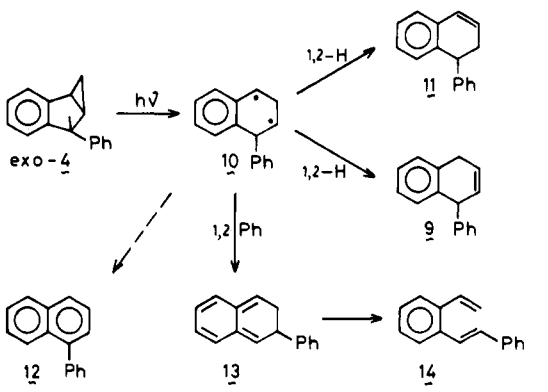
of a Simmons–Smith reaction[4] using a zinc–copper couple according to Rawson and Harrison.[5] Use of a zinc–silver couple[6,7] turned out to be unsuccessful. *endo*- and *exo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (*endo*- and *exo*-**6**) were isolated from irradiation mixtures of 2-phenyl-1,2-dihydronaphthalene.[8] All compounds were irradiated in hexane by using 254-nm light, and the product mixtures were analyzed by NMR spectroscopy and gas chromatography.

Results and Discussion

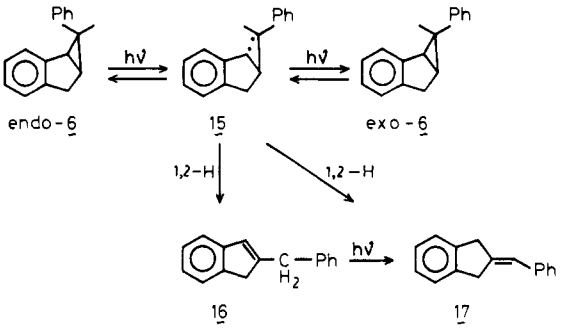
Irradiation of 1-phenylbenzobicyclo[3.1.0]hex-2-ene (3) yielded two products. The main product was 4-phenyl-1,2-dihydronaphthalene (**8**), identified by its NMR spectrum and by comparison with an authentic sample (Aldrich). The NMR spectrum of the second product pointed to 1-phenyl-1,4-dihydronaphthalene (**9**). This suggestion was verified by the independent synthesis of **9** as described in the Experimental Section and by comparison with the NMR spectrum reported by Carruthers et al.[9] (see Scheme II). The formation of both products can be explained by homolytic fission of the internal C(1)–C(5) cyclopropane bond of **3**, leading to the most stable diradical (**7**) followed by 1,2 hydrogen shifts.

Irradiation of *exo*-4-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-4) for 4 h led to four products: 1-phenyl-1,4-dihydronaphthalene (**9**, 18%), 1-phenyl-1,2-dihydronaphthalene (**11**, 44%), 1-phenylnaphthalene (**12**, 15%), and a very small amount of 2-vinylstilbene (**14**); about 23% of *exo*-**4** remained. Compounds **9**, **11**, and **12** were identified by their NMR spectra and comparison with authentic samples. Compound **14** shows the characteristic pattern of a vinyl group in its NMR spectrum and was easily identified by comparison with the well-known 2-vinylstilbene.[10]

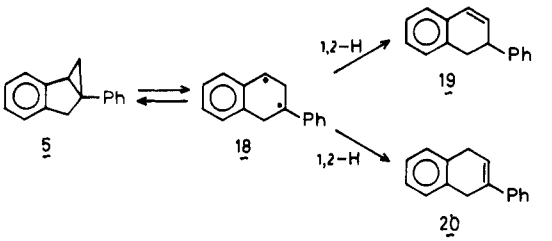
Scheme III



Scheme IV



Scheme V



Compounds **9** and **11** can be formed via a similar mechanism as given for **3**: homolytic fission of the C(1)–C(5) bond leading to diradical **10** (Scheme III) followed by 1,2 hydrogen shifts. However, a 1,2 phenyl shift in **10** leading to 2-phenyl-2,3-dihydronaphthalene (**13**) followed by ring opening must be involved in the formation of **14**. As may be expected, the ring opening of **13** into **14** is more efficient than the photochemically not allowed suprafacial 1,5 hydrogen shift into stable dihydronaphthalenes.

The photochemistry of 6-phenylbenzobicyclo[3.1.0]hex-2-ene (6) is related to that of 1,2-diphenylcyclopropane: *endo*- and *exo*-**6** interconvert upon irradiation, and this process is accompanied by a structural rearrangement to 2-benzylideneindan (**17**, Scheme IV). This compound was identified from its NRM spectrum. The identification of **17** by NMR was supported by its

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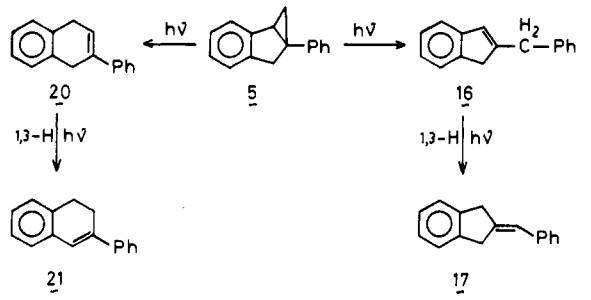
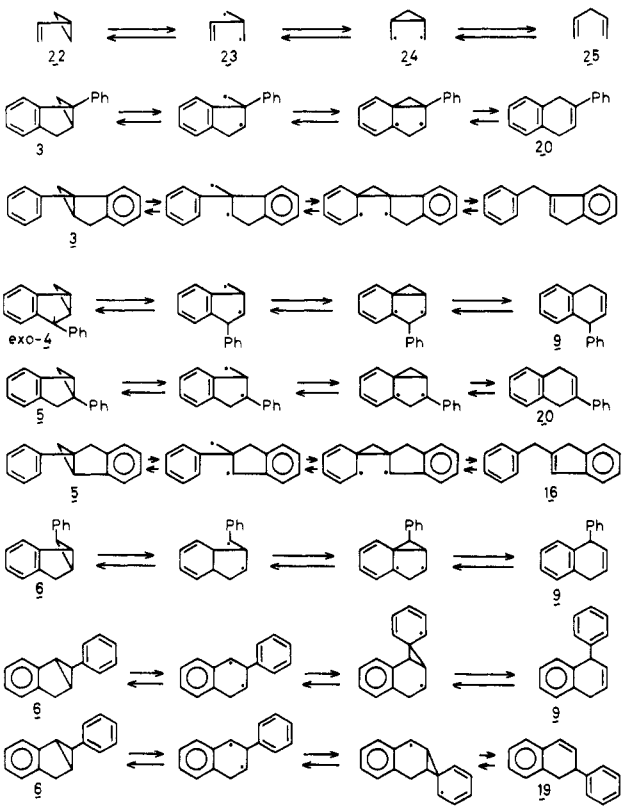
Scheme VI



Scheme VII



synthesis from 2-benzyl-1*H*-indene (**16**). Irradiation of **16**, dissolved in hexane at 254 nm through quartz for 1 h gave **17** in 81% yield, leaving 17% of unchanged starting material; the irradiation causes a fast 1,3 hydrogen shift in **16**. The synthesis of **16** is described in the Experimental Section. The remarkably fast 1,3 hydrogen H shift leading to **17** might explain why **17** is the only observed rearrangement product from **6**, whereas 1,2 hydrogen shifts in the intermediate diradical **15** should lead to **16** as well as **17**. Compound **6** provides the third example where product formation is governed by the most stable diradical that can be formed by homolytic fission of one of the cyclopropane bonds in the starting compounds. In this case it is the external C(1)–C(6) cyclopropane bond (see Scheme IV).

Photochemistry of 5-Phenylbenzobicyclo[3.1.0]-hex-2-ene. Retro-di-π-methane Rearrangements. On the basis of the foregoing experiments, formation of 2-phenyl-1,2-dihydronaphthalene (**19**) and 2-phenyl-1,4-dihydronaphthalene (**20**) via biradical **18** was expected in the irradiation of 5-phenylbenzobicyclo[3.1.0]hex-2-ene (**5**, Scheme V). When **5** was irradiated for 4 h at 254 nm, three products were isolated, and 42% of unchanged **5** remained. The main product, present in 44%, was easily identified by its NMR spectrum as 3-phenyl-1,2-dihydronaphthalene (**21**). The second product (8%) showed in its NMR spectrum two multiplets of two protons each at 3.5–3.7 and 3.7–3.9 ppm. Their position at relatively low field suggests that both correspond to methylene groups with neighboring phenyl and olefinic moieties according to the Shoolery rules. One of the methylene groups experiences some additional deshielding relative to the other. In addition, a multiplet of one proton was observed at 6.3 ppm, pointing to an olefinic proton, and a nine-proton multiplet in the aromatic region at 7.1–7.6 ppm. The data point to 2-phenyl-1,4-dihydronapthalene (**20**). This was checked by comparing the NMR spectrum with a spectrum reported in the literature[11] and by comparison with a sample isolated from a pyrolysis mixture of **5**.[8] The methylene group closer to the phenyl substituent will experience more deshielding than the other methylene group.

The third compound (18%) was easily identified as 2-benzylideneindan (**17**), which has been synthesized independently as described above.

No trace of **19** or of its photoproducts could be detected in the irradiation mixture.

To explain the presence of **20**, one might envisage a ring opening of the internal C(1)–C(5) cyclopropane bond leading to diradical **18** (Scheme V) followed by a 1,2 hydrogen shift leading to **20**. However, if this should be the mechanism, the absence of the equally stable **19** cannot be explained; moreover, an intermediate like **18** does not explain the presence of **17**. Therefore, the primary formation of the diradical **18** was rejected.

As a mechanism more suitable to explain the formation of the photoproducts **17**, **20**, and **21**, reverse di-π-methane rearrangements were considered (Scheme VI). (Until now, photochemical, reverse di-π-methane rearrangements have been rather seldom observed.[12,13,16] Some more examples of the closely related bicycle rearrangement have been published.[14] Thermal reverse di-π-methane rearrangements are also known.[13,15,16]) The primary products should then be **16** and **20**, from which **17** and **21** might arise via photochemical 1,3 hydrogen shifts. The absence of **16** among the photoproducts of **5** might be due to the high rate of the 1,3 hydrogen shift of **16** onto **17** as was found previously (see above).

Comparison of the Photochemistry of the Phenyl-Substituted Benzobicyclo[3.1.0]hex-2-enes. The results of the irradiations of the phenyl-substituted benzobicyclo[3.1.0]hex-2-enes show that only 5-phenylbenzobicyclo[3.1.0]hex-2-ene (**5**) leads to products that must be derived from a retro-di-π-methane rearrangement (**16** and **20**). This can be understood by comparing the schemes of formal retro-di-π-methane pathways for all phenyl-substituted benzobicyclo[3.1.0]hex-2-enes (**3–6**). They are shown (Scheme VII) according to the biradical model of the di-π-methane rearrangement which is given in reverse on the top line.

In the *observed* reactions **5** → **20** and **5** → **16** both formal, intermediate biradicals contain a benzylic radical site.

(11) E. J. Eisenbraun, R. G. Melton, P. W. Flanagan, M. C. Hamming, and G. W. Keen, *Prepr. Div. Petrol. Chem., Am. Chem. Soc.*, **16**, B43–50 (1971).

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(16) W. Adam and D. DeLucchi, *J. Org. Chem.*, **46**, 4133 (1981).

In the schemes given for **3** and **4** none of the formal intermediates show benzylic radical stabilization, and in both schemes leading from **6** to **9** a benzylic radical site is only present in one of the intermediates. This might explain why these reactions do not occur; energetically they are less favorable in comparison to the paths given in the Schemes II–IV.

The absence of the photoconversion **6** → **19** seems less clear, because this reaction should proceed via formal biradical intermediates, which are both benzylic radicals as in the photoreaction observed with **5**.

Both **5** and **6** are 1,2-diphenylcyclopropanes in which an ortho position of a phenyl group is linked to a C atom of the cyclopropane unit via a methylene bridge. The difference in reaction pattern may be explained by assuming that for both **5** and **6** the bond fission to biradicals with two benzylic radicals (**15** and **18** respectively) is the preferred reaction. The 1,2 hydrogen shift has a rather slow reaction rate, compared to the rate of the reclosure of the bond, as is demonstrated by the rapid *endo*-**6** ⇌ *exo*-**6** epimerization. For biradical **15** an escape to stable end products may be possible by the less fixed position of the two benzyl radicals.

For biradical **18** the rate of bond reclosure will be much higher leading to **5**. An escape to other products will then take place by the di-π-methane rearrangement.

It may therefore be concluded that the occurrence of a reverse di-π-methane rearrangement in phenyl-substituted benzobicyclo[3.1.0]hex-2-enes is connected with the presence of a benzylic radical in both diradical structures of the reverse di-π-methane mechanism but that, in general, the reaction by a bond fission is the preferred reaction.

Experimental Section

^{1}H NMR spectra were recorded on a Bruker WM90 or WM200 spectrometer in $CDCl_3$; δ values are given in parts per million relative to Me_4Si as an internal standard, and J values are expressed in hertz. Mass spectra were recorded on a Varian MAT SM-28 or a Finnigan 2200 quadruple mass spectrometer and UV spectra on a Perkin-Elmer 555 instrument. Melting points were determined by using a Leitz melting point microscope and are uncorrected.

Gas chromatography (GLC) was performed by using either a Varian Aerography Series 1200 or a Hewlett-Packard 5710 A instrument fitted with a 10% w/w SE-30 on Chromosorb SHP column and a flame-ionization detector.

For column chromatography silica (Merck, Kieselgel 60) or alumina (Baker, aluminium oxide, neutral) was used; HPLC separations (Merck, Kieselgel 60H) were carried out on a Jobin-Yvon S.A. Miniprep LC fitted with a Waters Associates R404 differential refractometer and a Pye Unicam LC-UV detector.

Direct irradiations were carried out under anaerobic conditions with 254-nm light (4 Philips TUV germicidal 15-W lamps) and 10^{-3} M solutions in hexane in a quartz container. The photoreactions were followed by GLC and NMR spectroscopy from samples taken from the solutions at several times intervals. In all cases a rapid ingrow of the products was observed in the first hour.

Benzobicyclo[3.1.0]hex-2-ene was synthesized by cyclopropanation of indene (general procedure). A mixture of zinc dust (7.3 g, 0.112 mol) and CuCl (1.5 g, 0.113 mol) in 30 mL of dry ether was stirred and refluxed for 30 min under nitrogen. Indene (5 g, 0.043 mol) was added, followed by diiodomethane (15 g, 0.056 mol), and the reaction mixture was refluxed overnight. The solvent was then allowed to evaporate completely. This concentration of the solutes proved to enhance the yield considerably. The reaction was quenched by careful addition of water (20 mL). Ether (20 mL) was added to dissolve the organic components, and the resulting mixture was filtered through Hyflo to remove the insoluble material. The organic layer was washed consecutively with saturated solutions of NH_4Cl, $NaHCO_3$, and NaCl. The solution was dried over $MgSO_4$, filtered, and evaporated in vacuo. After chromatography on silica with hexane as the eluent 2.5 g (0.019 mol) of benzobicyclo[3.1.0]hex-2-ene was obtained as a colorless oil: yield 44%; ^{1}H NMR as reported.[17]

1-Phenylbenzobicyclo[3.1.0]hex-2-ene (3). 3-Phenyl-1*H*-indene was prepared by the Grignard reaction of phenylmagnesium bromide with 1-indanone followed by dehydration with TsOH in toluene: yield 56.3%; NMR as reported.[18]

3-Phenyl-1*H*-indene (8.26 g, 0.043 mol) was subjected to cyclopropanation as described above for indene. After chromatography on silica with hexane/toluene (9.1) as the eluent and purification on HPLC (silica, hexane) 3.23 g (37% yield) of **3** was obtained as a colorless oil which solidified upon standing: mp 38–40 °C; NMR ($CDCl_3$) δ 0.54 (t, H(5-endo), 1 H, $J_{6\text{-endo},6\text{-exo}}$ = 4.2, $J_{5,6\text{-endo}}$ = 4.2), 1.72 (dd, H(6-exo), 1 H, $J_{5,6\text{-exo}}$ = 8.3), 1.95 (m, H(5), 1 H, $J_{4\text{-exo},5}$ = 6.0, $J_{4\text{-endo},5}$ = 1.0), 3.00 (d, H(4-endo), 1 H, $J_{4\text{-endo},4\text{-exo}}$ = 17.0), 3.39 (dd, H(4-exo), 1 H), 7.0–7.5 (d, arom H, 9 H); UV (MeOH) λ_{max} 276 nm (log ϵ 3.04, sh), 269 (3.24, sh), 228 (3,97, sh), 218 (4.05, sh), 209 (4.12); mass spectrum, *m/e* (relative intensity) 206 (M^+, 100), 191 (38), 178 (12), 165 (12), 128 (18), 115 (12), 91 (18). Anal. Calcd for $C_{16}H_{14}$: C, 93.18; H, 6.48. Found: C, 93.10; H, 6.90; exact mass 106.108 ± 0.003, theory 206.110.

***exo*-4-Phenylbenzobicyclo[3.1.0]hex-2-ene (4).** 3,3-Diphenylpropionic acid (Aldrich) was converted into 3-phenyl-1-indanone by treatment with $SOCl_2$ and cyclization of the acid chloride with $AlCl_3$ in benzne.[19] After distillation under reduced pressure and recrystallization from ethanol, 3-phenyl-1-indanone was obtained as white crystals: mp 78 °C (lit. mp 76.5–77.5 °C,[19] 82.0–82.5 °C[20]); NMR as reported.[20]

3-Phenyl-1*H*-indene (5.8 g, 0.03 mol) was subjected to cyclopropanation as described for indene. After chromtography on silica with hexane as the eluent 2.9 g (0.014 mol, 46% yield of *exo*-4-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-**4**) was obtained: mp 75–77 °C; NMR ($CDCl_3$) δ 0.25 (q, H(6-endo), 1 H, $J_{6\text{-endo},6\text{-exo}}$ = 4.2, $J_{5,6\text{-endo}}$ = 4.0, $J_{1,6\text{-endo}}$ = 3.3), 1.15 (m, H(6-exo), 1 H, $J_{5,6\text{-exo}}$ = 8.0, $J_{1,6\text{-exo}}$ = 8.0), 1.91 (m, H(5), 1 H, $J_{1,5}$ = 6.0, $J_{4\text{-endo},5}$ = 0.6), 2.52 (m, H(1), 1 H, $J_{1,4\text{-endo}}$ = 1.3), 4.21 (brs, H(4-endo), 1 H), 6.8–7.5 (m, arom H, 9 H); UV (MeOH) λ_{max} 276 nm (log ϵ 3.15), 268 (3.18, sh), 214 (4.09); mass spectrum, *m/e* (relative intensity) 206 (m^+, 100), 191 (46), 178 (13), 165 (11), 128 (29), 115 (11), 91 (35). Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found C, 93.08; H, 6.92; exact mass 206.108 ± 0.003, theory 206.110.

***endo*-6-Phenylbenzobicyclo[3.1.0]hex-2-ene (*endo*-6).** This compound was isolated from irradiation mixtures of 2-phenyl-1,2-dihydronaphthalene (**14**):[8] NMR (90 MHz, $CDCl_3$) similar to the reported one in CCl_4;[10] NMR (200 MHz, $CDCl_3$) δ 2.25 (m, H(5), 1 H, $J_{1,5}$ = 6.2 Hz, $J_{4\text{-endo},5}$ = 1.0, $J_{4\text{-exo},5}$ = 6.4, $J_{5,6\text{-exo}}$ = 8.0), 2.43 (t, H(6-exo), 1 H, $J_{1,6\text{-exo}}$ = 8.0), 2.68 (br d, H(4-endo), 1 H, $J_{1,4\text{-endo}}$ = 1.3, $J_{4\text{-endo},4\text{-exo}}$ = 17.4, $J_{4\text{-endo},5}$ = 1.0), 2.91 (m, H(1), 1 H), 3.10 (dd, H(4-exo), 1 H), 6.6–7.45 (m, arom H, 9 H).

***exo*-6-Phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-6).** This compound was isolated from irradiation mixtures of **14**: NMR (90 MHz, $CDCl_3$) similar to that reported in CCl_4;[10] NMR (200 MHz, $CDCl_3$) δ 1.49 (t, H(6-endo), 1 H, $J_{1,6\text{-endo}}$ = 3.0 Hz, $J_{5,6\text{-endo}}$ = 3.4), 2.20 (m, H(5), 1 H, $J_{1,5}$ = 6.2, $J_{4\text{-endo},5}$ = 1.2 $J_{4\text{-exo},5}$ = 6.0), 2.65 (m, H(1), 1 H, $J_{1,4\text{-endo}}$ = 1.3), 3.12 (br d, H(4-endo), 1 H, $J_{4\text{-endo},4\text{-exo}}$ = 17.4), 3.33 (dd, H(4-exo), 1 H, 6.9–7.4 (m, arom H, 9 H).

5-Phenylbenzobicyclo[3.1.0]hex-2-ene (5). 2-Phenyl-1*H*-indene was prepared through the Grignard reaction of phenylmagnesium bromide with 2-indanone followed by dehydration with TsOH in toluene: yield 34% mp 167 °C (lit.[21,22] mp 167–168 °C); NMR as reported.[21]

2-Phenyl-1*H*-indene (4.0 g, 0.021 mol) was subjected to cyclopropanation as described for indene. After the workup and purification on silica with hexane as the eluent 1.2 g (5.8 mmol,

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28% yield) of 5-phenylbenzobicyclo[3.1.0]hex-2-ene (5) was obtained as a white solid: mp 59–61 °C; NMR ($CDCl_3$) δ 0.68 (t, H(6-endo), 1 H, $J_{1,6\text{-endo}}$ = 3.8, $J_{6\text{-endo},6\text{-exo}}$ = 4.2), 1.51 (dd, H(6-exo), 1 H, $J_{1,6\text{-exo}}$ = 8.0 Hz), 2.71 (ddd, H(1), 1 H, $J_{1,4\text{-endo}}$ = 1.3), 3.37 (br d, H(4-endo), 1 H, $J_{4\text{-endo},4\text{-exo}}$ = 17.0), 3.47 (d, H(4-exo), 1 H), 7.0–7.4 (m, arom H, 9 H); UV (MeOH) λ_{max} 230 nm (log ε 4.04, sh), 204 (4.58); mass spectrum, *m/e* (relative intensity) 206 (M^+, 100), 191 (15), 178 (14), 165 (24), 128 (18), 92 (33). Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.18; H, 6.82; exact mass 206.111 ± 0.003, theory 206.110.

1-Phenyl-1,4-dihydronaphthalene (9). This compound was obtained by reduction of 4-phenyl-2-tetralone[23] to the corresponding alcohol and subsequent dehydration. A mixture (1.4 g) of 1-phenyl-1,2-dihydronaphthalene (11) and 9 was obtained. Chromatography on silica with hexane as the eluent followed by an additional purification on HPLC (silica/hexane) yielded 9 as a clear oil: yield 196 mg, corresponding to 14% of the mixture; NMR as reported;[9] mass spectrum, *m/e* (relative intensity) 206 (M^+, 100), 191 (20), 178 (6), 165 (5), 128 (21), 115 (5), 102 (5), 91 (9); exact mass 206.112 ± 0.003, theory 206.110. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.18; H, 6.82.

2-Benzyl-1*H*-indene (16). This compound was synthesized from 2-indanone through a Grignard reaction with benzylmagnesium chloride followed by dehydration using TsOH in toluene in a yield of 30%. After purification on silica with hexane as the eluent a clear oil was obtained which solidified spontaneously into a white solid: mp 47–48.5 °C (lit. mp 46.5–48,[23] 48–49.5,[24] 48 °C[25]); ^1H NMR ($CDCl_3$) δ 3.3 (br s, indene methylenic H, 2 H), 3.8 (br s, benzylic H, 2 H), 6.5 (br s, indene olefinic H, 1 H), 6.9–7.4 (m, arom H, 9 H) [the assignment of the protons at 3.3 and 3.8 ppm might be inverted (cf. literature data[24])]; UV (MeOH) λ_{max} 257 nm (log ε 4.17), 206 (4.42); λ_{min} 232 nm (log ε 3.60); mass spectrum (Finnigan), *m/e* (relative intensity) 206 (M^+, 18), 128 (13), 115 (16), 81 (100). Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.09; H, 6.91.

2-Benzylideneindan (17). This compound was obtained in 81% yield as an oil by irradiation of 16 for 1 h at 254 nm: ^1H NMR ($CDCl_3$) δ 3.9 (vbr, methylene H, 4 H), 6.6 (quintet, olefinic H, 1 H), 6.9–7.5 (m, arom H, 9 H); mass spectrum, *m/e* (relative intensity) 208 (M^+, 100), 191 (10), 128 (13), 91 (17). Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.05; H, 6.95.

2-Phenyl-1,4-dihydronaphthalene (20). This compound was isolated as a clear oil from a product mixture obtained after flash vacuum pyrolysis of 5-phenylbenzobicyclo[3.1.0]hex-2-ene (5) at 700 °C:[8] ^1H NMR ($CDCl_3$) δ 3.5–3.7 (m, methylene H at C(4), 2 H), 3.7–3.9 (m, methylene H at C(1), 2 H), 6.3 (m, olefinic H, 1 H), 7.1–7.6 (m, arom H, 9 H); NMR spectrum similar to reported one in CCl_4;[11] mass spectrum (Finnigan), *m/e* (relative intensity) 206 (M^+, 35), 128 (30), 115 (20), 91 (100).

Registry No. 3, 82645-20-3; *exo*-4, 85803-90-3; 5, 85803-91-4; *endo*-6, 67504-58-9; *exo*-6, 67504-57-8; 9, 13387-49-0; 16, 16274-93-4; 17, 23114-34-3; 20, 40650-73-5.

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Steric and Electronic Effects in S_N2 Reactions of 9-Substituted Fluorenyl and α-Cyano Carbanions with Benzyl Chloride in Dimethyl Sulfoxide Solution

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Rates of reactions of $PhCH_2Cl$ with carbanions derived from six α-cyano carbon acids of varied structure with pK_a values ranging over 16 units have been measured. When placed on a log *k* vs. pK_a plot the points fit near to the extended Brønsted line obtained earlier for the 9-(methoxycarbonyl)fluorenyl ion family, 9-CO_2MeFl^-, reacting with $PhCH_2Cl$. It is concluded that differences in shape, size, charge concentration, solvation, or aromaticity play no obvious part in determining the reactivity of these carbanions, all of these effects being incorporated into a single parameter, basicity. Substitution of H by Me in 9-R-Fl^- ions causes no steric effect on reactivity, even toward *i*-PrBr, despite the fact that Me is attached directly to the donor site. Alkyl functions of the type RCH_2 or related functions such as RS, which protrude on one side only of the flat fluorenyl anion, cause only small rate retardations, relative to Me (at the same basicity). Alkyl groups such as *i*-Pr, *t*-Bu, *o*-MeC_6H_4, and 2,4,6-$Me_3C_6H_2$ (Mes) which protrude on both sides of the fluorenyl ion cause sizable steric rate retardations. An equation is derived that allows a reactivity factor, *r*, to be calculated for 9-G-Fl^- ions reacting with $PhCH_2Cl$ in Me_2SO solution. The *r* values relative to a 9-$MeFl^-$ ion of comparable basicity are as follows: CN, 0.45; CO_2Me, 0.45; Me, (0.0); *t*-$BuCH_2$, −0.10; PrS, −0.15; Et, −0.17; *i*-PrS, −0.18; *t*-BuS, −0.18; $PhSO_2$, −0.25; PhO, −0.49; MesS, −0.54; Ph, −0.58; Me_3Si, −1.2; *i*-Pr, −1.5; *o*-MeC_6H_4, −2.2; *t*-Bu, −2.6; Mes, −3.1. Comparison of *r* values with *S*° steric parameters derived for 2-alkylpyridines[5c] shows some marked differences. These are due in part to the utilization of an electron pair in a p orbital by the carbanion as contrasted with an electron pair in an sp^2 orbital by the pyridine.

There have been many studies of steric effects in S_N2 reaction caused by increasing the size and branching in the alkyl halide but relatively few quantitative studies where steric effects in the nucleophile have been examined. The retardation of alkylation rates caused by *o*-alkyl groups in pyridines were among the first effects of this type to be observed, and these have received most subsequent attention.[1-5] In their pioneering studies of steric effects on equilibria and rates,[3] Brown and his students found that rates of reactions of 2-alkylpyridines with CH_3I in nitro-

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