obtained in 38% yield (15 mg) as yellow crystals from CH_2Cl_2: mp 288–290 °C; NMR (Me_4Si, $CDCl_3$) δ 7.1–8.3 (m, 7 H), 6.2–6.9 (m, 3 H); MS, *m/e* 380 (M^+). Anal. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 94.65; H, 5.35.

The second, smaller band (presumed to be the cis isomer) gave 9 mg (23%) of yellow crystals (from $CHCl_3$): mp 280–285 °C; NMR (Me_4Si, $CDCl_3$) δ 7.6–8.2 (m, 10 H), 5.9–6.9 (m, 3 H); high-resolution mass spectrum calcd for $C_{30}H_{20}$ *m/e* 380.156 50, found *m/e* 380.154 30. Anal. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 94.65; H, 5.34.

Thermolysis of 20 in Cyclohexene. A mixture of 80 mg (0.201 mmol) of the tosylhydrazone salt **20** was heated in a sealed tube at 105 °C for 20 min. The workup yielded only dimers **23** and **24**. No other hydrocarbon product was detected.

Thermolysis of 20 in Benzene in the Presence of Dimethyl Fumarate 25. A mixture of 100 mg (0.252 mmol) of the tosylhydrazone salt **20** and 500 mg (3.47 mmol) of dimethyl fumarate in 10 mL of benzene was heated in a sealed tube at 105 °C for 20 min. A yellow precipitate formed. The benzene mixture was poured into 50 mL of CH_2Cl_2, washed twice with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed over an alumina column (activity grade III; neutral) eluting with 10% ether/pentane (1:3). This gave a fast-moving band (ca. 1 mg of dimer) followed by a second fraction which was dimethyl fumarate. A third fraction gave 38 mg (47%) of the spiro adduct **25** as a white crystalline solid: mp 124–125 °C (pentane/ether); NMR (Me_4Si, $CDCl_3$) δ 7.1–8.3 (m, 7 H), 6.8 (dd, 1 H), 6.3 (dd, 1 H), 5.1 (d, 1 H), 3.8 (s, 3 H), 3.25 (d, 1 H), 3.2 (s, 3 H), 2.25 (d, 1 H); high resolution mass spectrum calcd for $C_{21}H_{18}O_4$ *m/e* 334.120 51, found *m/e* 334.120 45. Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.42. Found: C, 75.45; H, 5.41.

Thermolysis of 20 in the Presence of Diphenylisobenzofuran 26. A mixture of 140 mg (0.35 mmol) of the tosylhydrazone salt **20** and 500 mg (1.2 mmol) of diphenylisobenzofuran in 10 mL of benzene was heated at 105 °C in a sealed tube for 20 min. After cooling, the tube was opened and 40 mL of CH_2Cl_2 added. To this was added 300 mg of maleic anhydride (to consume excess furan), and the solution was washed twice with water. The organic layer was dried over $MgSO_4$, and the solvent was removed at reduced pressure. The residue was chromatographed on activity grade III neutral alumina. Elution with 1:5 CH_2Cl_2/pentane gave two yellow bands. The first band yielded 70 mg (43%) of one of the isomers **26**: mp 160–164 °C (yellow crystals from benzene/pentane); NMR (Me_4Si, $CDCl_3$) δ 6.6–8.2 (m, 21 H), 6.5 (t, 1 H), 6.2 (d, 1 H), 5.8 (dd, 1 H); IR (CCl_4) 3080, 3040, 1670, 1605, 1500, 1450, 1320, 1290, 1260, 1220, 940 cm^{-1}; high-resolution mass spectrum calcd for $C_{34}H_{24}O$ *m/e* 460.182 72, found, *m/e* 460.182 65; ^{13}C NMR (Me_4Si, $CDCl_3$; 32 signals) δ 196.72 (CO), 140.79, 140.40, 140.26, 139.04, 137.53, 137.28, 136.46, 136.21, 132.39, 132.22, 131.95, 131.19, 131.09, 130.78, 130.63, 130.29, 130.10, 129.61, 129.12, 128.83, 128.73, 128.32, 128.24, 127.98, 127.29, 126.63, 126.34, 126.10, 125.76, 125.42, 123.98.

The second yellow band yielded 25 mg (15%) of an isomeric adduct: mp 95–98 °C (benzene/pentane); NMR (Me_4Si, $CDCl_3$) δ 6.1–8 (m, 23 H), 5.8 (dd, 1 H). IR (CCl_4) 3080, 3045, 2980, 1670, 1270 cm^{-1}; high-resolution mass spectrum calcd for $C_{34}H_{24}O$ *m/e* 460.182 72, found *m/e* 460.182 35.

To gain more information about the structure of these products, we reduced 25 mg of the more abundant isomer in MeOH with H_2 in the presence of Pd/C. Following filtration and concentration, the residue was chromatographed on a short silica gel column eluted with CH_2Cl_2 to give 24 mg (95%) of the tetrahydro product: mp 160–162 (MeOH/CH_2Cl_2); NMR (Me_4Si, $CDCl_3$) δ 6.6–8.1 (m, 20 H), 1.2–2.6 (m, 10H); IR ($CHCl_3$) 3020, 2980, 2940, 1670, 1600 cm^{-1}; high resolution mass spectrum: Calcd for $C_{34}H_{28}O$: 464.21402; Found, 464.21351.

Synthesis of Mixture of Naphthobromocycloheptatrienes 21 and 22. A solution of 850 mg (4.13 mmol) of the ketone **19** in 20 mL of CH_2Cl_2 was cooled to 0 °C. A solution of 1 g (4.63 mmol) oxalyl bromide in 10 mL of CH_2Cl_2 was added over 15 min. After stirring for an additional 20 min at 0 °C, the mixture was permitted to warm to room temperature, and stirring was continued for 1.5 h. Solvent was removed, and the residue taken up in 10 mL of dry THF. This was cooled to 0 °C, and 250 mg of $LiAlH_4$ was added in small portions. The mixture was allowed to warm to room temperature and stirred for an additional 20 min. Excess $LiAlH_4$ was destroyed with water and the mixture extracted with CH_2Cl_2. After the mixture was washed and dried over $MgSO_4$, the oily residue was chromatographed over silica gel. Elution with 10:1 pentane/ether gave 750 mg (67%) of a mixture of two isomers: NMR (Me_4Si, $CDCl_3$) δ 7.0–8.3 (m), 6.3 (t, 1 H), 5.6–6.1 (m), 3.3 (br d, 2 H), 2.1 (t, 2 H); high-resolution mass spectrum calcd for $C_{15}H_{11}Br$ *m/E* 270.003 49, 272.001 04, found *m/e* 270.004 41, 272.002 37.

Reaction of Mixture of Bromonaphthocycloheptatrienes with Potassium *tert*-Butoxide in the Presence of Diphenylisobenzofuran. To a solution of 170 mg (0.62 mmol) of a mixture of bromonaphthocycloheptatrienes **21** and **22** in 15 mL of dry THF was added 500 mg (1.85 mmol) of diphenylisobenzofuran and 125 mg (1.11 mmol) of potassium *tert*-butoxide. The mixture was refluxed for 1.5 h. After the mixture cooled to room temperature, water was added and the mixture extracted with CH_2Cl_2. The organic layer was washed and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed over alumina, eluting with 1:4 CH_2Cl_2/pentane. This gave a fast moving yellow band (40 mg, 30%) of the dimers **23** and **24**, a fraction containing an unidentified hydrocarbon, and a yellow band that proved to be a mixture of **26** and its isomer (21.8%).

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation. We also acknowledge with warm appreciation MNDO results from Professor E. Waali prior to publication.

Registry No. **9**, 52783-97-8; **10**, 52783-93-4; **11**, 52783-98-9; **19**, 83477-24-1; **20**, 83477-33-2; **20**·Na, 83477-25-2; **21**, 83477-26-3; **22**, 83477-27-4; **23**, 83477-28-5; **24**, 83477-29-6; **25**, 83477-30-9; (*E*)-**26**, 83477-31-0; (*Z*)-**26**, 83477-32-1; H_4-**26**, 83477-37-6; **28**, 83477-35-4; **30**, 52783-96-7; **31**, 83477-34-3; **32**, 53247-52-2; **35**, 52784-03-9; dimethyl fumarate, 624-49-7; diphenylisobenzofuran, 5471-63-6.

Photochemical Transformations. 31. Photorearrangements and Photoreactions of Some Benzobicyclooctadienyl Systems[1]

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Irradiations of esters of the *exo*- and *endo*-6,7-benzobicyclo[3.2.1]octa-3,6-dien-2-ols lead only to the di-π-methane rearrangement products, even under conditions where the 3-chloro derivatives lead to photosolvolysis and Wagner–Meerwein reaction products. A tentative rationalization of the chlorine-atom effect is offered.

Members of our research group have been interested for some time[2] in certain photochemically induced Wagner–Meerwein rearrangements and attendant photosolvolyses. Evidence is strong in these systems, all of which contain

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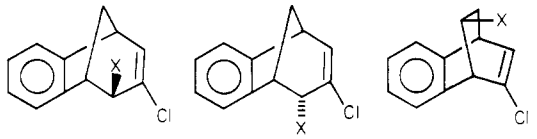
an aromatic ring that serves as light-absorbing chromophore and a carbon–nucleofuge bond, that excitation transfer (presumably electron transfer) occurs from the excited aromatic ring to the carbon–nucleofuge bond, resulting in the formation of an ion pair. This ion pair can undergo return to the original compound,[2e] return to an allylic isomer,[2e] return to a Wagner–Meerwein or other isomer,[2] or undergo dissociation leading to photosolvolysis.[2]

Particularly pertinent to the work described in this paper are the results on the 3-chlorobenzobicyclo[3.2.1]-octadienyl systems **1** and **2**. Direct irradiation of the *exo*-**1**



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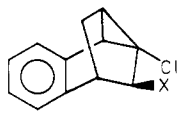

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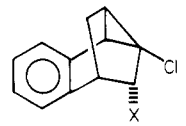

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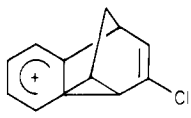
chloride, dichloroacetate or methanesulfonate or of the corresponding *endo*-**2** species in acetonitrile–water led to solvolysis products (largely 1-$NHCOCH_3$ and/or **1**-OH) and to Wagner-Meerwein rearrangements to **3**-X species, as well as to epimerization. The alcohols and the acetates did not show such reactions, but instead gave di-π-methane rearrangements (in much lower quantum yield[3]). Triplet-sensitized reactions of **1** and **2** species also gave **4** and **5** isomers via di-π-methane reactions, but none of the other isomerizations occurred. As with other systems,[2d] photoreaction of the acetate **1**-OAc was diverted from the di-π-methane path to the path leading to rearrangement to the [2.2.2] isomer **3**-OAc when the solvent was changed to acetic acid.[3]

These results were thus consistent with the idea that ion pairs were involved and that the reactivity of a photoactivated species to give the ion pair was related to the nucleofugacity of the leaving group. It also seemed reasonable to assume that there should be a correlation between photoreactivity and the stability of the cationic component of the ion pair.[4] The ion pair was initially perceived[2c] to contain as its cationic component the bridged ion **6**, although some bent, and therefore unsymmetrical, form of the allylic ion **7** might also be plausible. As electron-attracting substituents such as chlorine are known[6] to retard solvolysis rates in the ground state, if one assumed similar behavior in these photoreactions, removal of the β-chlorine atom in the ester derivatives of the allylic alcohols **1**-OH and **2**-OH would make the resulting compounds more photoreactive in forming ion pairs. As alcohols are readily



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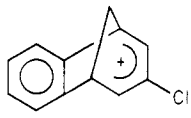

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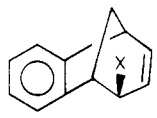

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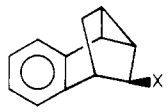

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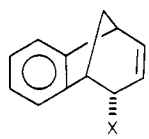
prepared in both exo and endo forms,[7] and as specific deuterium labeling was practical, such compounds seemed likely to be ideal substrates for mechanistic study.

Goldschmidt and Gutman[7b] irradiated the alcohol **8**-OH in cyclohexane, acetonitrile, and ether at 254 nm and in 20% acetone–hexane at 300 nm. They reported that only a single photoproduct was formed under all of these sets of conditions, and that this was the di-π-methane product **9**-OH. As it was known[2d] that related alcohols (with β-chlorine substituents) do not give ionic photoproducts even in acetic acid, but require mineral acid catalysis, their report did not dissuade us from study of esters of the alcohols **8**-OH and **10**-OH.



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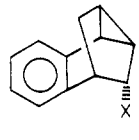

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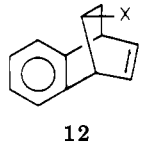

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exo-**1**-OH and *endo*-**2**-OH were prepared as described earlier.[7,8] Use of C_8K (potassium graphite)[9] to remove the chlorine atom in these alcohols to give **8**-OH and **10**-OH proved, in our hands, more efficacious than a literature procedure[7b] for the formation of **8**-OH, which utilizes sodium in liquid ammonia.

The exo alcohol **8**-OH was converted to its acetate, benzoate, and *p*-(trifluoromethyl)benzoate esters and the endo alcohol **10**-OH to its acetate and benzoate esters, using common procedures. Attempts to prepare and isolate the methanesulfonate ester of **8**-OH were unsuccessful as the compound decomposed rapidly. The [2.2.2] isomeric acetate **12**-OAc was prepared by treatment of **8**-OAc with perchloric acid in acetic acid, which gave a mixture containing about 80% of the [2.2.2] isomer. Methanolysis gave the known[7a] alcohol **12**-OH. In addition the chloride **8**-Cl was prepared.

When the esters of **8**-OH and of **10**-OH were irradiated at 300 nm in 25% acetone–75% acetonitrile sensitizer solvent, the di-π-methane products, as anticipated, were formed exclusively. The reactions were stereospecific, **8**-X species giving **9**-X and **10**-X giving **11**-X compounds.

The acetate, benzoate, and (trifluoromethyl)benzoate of **8**-OH and the acetate and benzoate of **10**-OH were irradiated in acetonitrile at 254 nm and, like the sensitized reactions, gave only the di-π-methane products. Even in acetic acid, where the chloro compound **1**-OAc gave substantial "ionic" rearrangement to **3**-OAc, the non-chloro derivatives **8**-OAc, **8**-OBz, and **10**-OAc gave only di-π-methane rearrangement products. The possibility that the

(1) Paper 30. Cristol, S. J.; Bindel, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 7287.

(2) For example, see: (a) Cristol, S. J.; Mayo, G. O.; Lee, G. A. *J. Am. Chem. Soc.* **1969**, *91*, 214. (b) Cristol, S. J.; Stull, D. P.; Daussin, R. D. *Ibid.* **1978**, *100*, 6674 and references therein. (c) Cristol, S. J.; Strom, R. M. *Ibid.* **1979**, *101*, 5707. (d) Cristol, S. J.; Daussin, R. D. *Ibid.* **1980**, *102*, 2866. (e) Cristol, S. J.; Strom, R. M. *Ibid.* **1980**, *102*, 5577. (f) Cristol, S. J.; Opitz, R. J.; Bindel, T. H.; Dickenson, W. A. *Ibid.* **1980**, *102*, 7977.

(3) Cristol, S. J.; Cruz, K. M., unpublished work.

(4) For example, triarylmethyl cyanides solvolyze quite readily[5] via the formation of triarylmethyl cations, while most nitriles are photoinert.

(5) Lifschitz, J. *Ber. Dtsch. Chem. Ges.* **1919**, *52*, 1919. Lifschitz, J.; Joffé, Ch. L. *Z. Physik. Chem.* **1921**, *97*, 426.

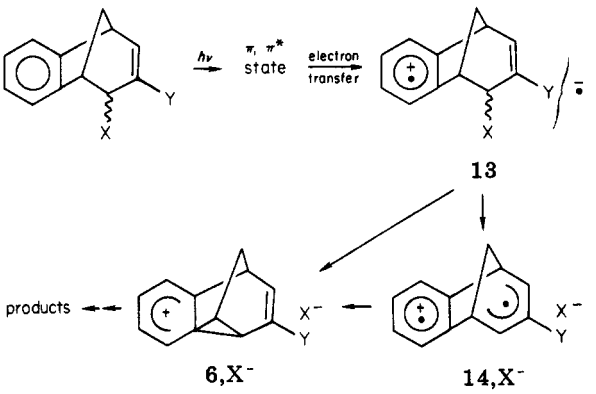
(6) See for example: Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; p 344 ff.

(7) (a) Tanida, H.; Tori, K.; Kitahonoki, K. *J. Am. Chem. Soc.* **1967**, *89*, 3212. (b) Goldschmidt, Z.; Gutman, U. *Tetrahedron* **1974**, *30*, 3327.

(8) Cristol, S. J.; Strom, R. M.; Stull, D. P. *J. Org. Chem.* **1978**, *43*, 1150.

(9) (a) Bergbreiter, D. E.; Killough, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 2126. (b) Lalancette, J. M.; Rollin, G.; Dumas, P. *Can. J. Chem.* **1972**, *50*, 3058.

Scheme I



Wagner–Meerwein rearrangement could not be detected because the photostationary state might be completely on the side of the [3.2.1] isomers was explored by irradiation of the [2.2.2] anti-acetate 12-OAc at 254 nm in acetonitrile. No rearrangement to the [3.2.1] acetate was observed.

The effect of removal of chlorine on the reaction is clearly opposite to that predicted from ground-state reactivity concepts, and we offer a tentative rationalization of our results.

It has been shown[2f] that many electron transfers from excited benzene rings to carbon–halogen or carbon–oxygen bonds to give ionic products seem to involve a geometric anti arrangement and are presumed to require a π^* to σ^* transfer. Those cases all involve *saturated* (i.e., nonallylic) systems. This requirement is not seen in the allylic systems 1 and 2, where both anti (exo isomer) and syn (endo isomer) transfers occur readily. The reason for this is not yet clarified, but the allylic double bond (π or π^*) and carbon–nucleofuge (σ or σ^*) orbitals must provide enough interaction such that geometric constraints are not seen. Electron transfer must be directed into a hybrid molecular orbital that has availability either syn or anti to the carbon–nucleofuge bond, that is, which uses both lobes of the π or π^* orbital of the double bond rather than simply into the σ^* orbital of the carbon–nucleofuge bond.[10] This is represented in Scheme I, in which the transferred electron is indicated (structure 13) as being delocalized into the hybrid molecular orbital. This excited state zwitterionic biradical may decay to an ion pair involving cation 6 or to the cation biradical 14, as discussed earlier.[2e] Clearly it is difficult to rationalize the effect of the chlorine substituent in the steps leading either to 6 or to 14. On the other hand, electron transfer from the benzene ring to the allylic system would undoubtedly occur more readily when strongly electron attracting groups are present on the double bond, and we tentatively propose this explanation for the chlorine-atom effect.

Experimental Section

General Procedures. Commercially available reagents and solvents were used without purification unless otherwise noted. Melting points were determined on a Thomas-Hoover Unimelt apparatus and are corrected. Carbon–hydrogen analyses were performed by Galbraith Laboratories. ^{1}H NMR spectra were obtained with a Varian Associates EM-390 spectrometer. Chemical shifts are relative to internal Me_4Si.

High-pressure liquid chromatography separations were carried out with a Waters Associates Model 6000A pump. A Beckman Model 25 ultraviolet spectrometer equipped with a Waters Associates microcell unit was used for UV detection (254 nm). Analytical separations were conducted with two Waters Associates 30 cm by 4 mm μ-Porasil columns connected in series, and preparative separations were carried out with a Whatman 50 cm by 9 mm Partisil M9 column. Tetrahydrofuran (distilled from $LiAlH_4$)–hexanes mixed solvent systems were used as eluants.

Photochemical Studies. Rayonet–Srinivasan–Griffin photochemical reactors equipped with either twelve 300-nm lamps or sixteen 254-nm lamps and a merry-go-round apparatus were used in this study.

***exo*-6,7-Benzobicyclo[3.2.1]octa-3,6-dien-2-ol (8-OH).** Twenty-one grams (1.75 mol) of graphite was placed in a three-neck, predried flask with an overhead stirrer and heated to 125 °C under argon. Finely chopped potassium 9.6 g (0.25 mol), washed in pentanes, was added over a period of 15 min. The powdery potassium graphite (C_8K)[9] was suspended immediately after cooling to room temperature in 100 ml of dry THF.

A solution of 6 g (29 mmol) of the alcohol 1-OH[7,8] in 100 mL of dry THF was added slowly to the freshly prepared suspension of C_8K in THF, kept at 0 °C. After an additional 2 h of stirring at 25 °C, the remaining C_8K was destroyed with ethanol. The suspension was filtered, the solvents were removed by distillation, and the residual oil was dissolved in ether. The ether phase was washed with water, 10% HCl, and water and dried ($MgSO_4$). Evaporation of the solvent left 4.5 g of crude oil, which, after distillation [118–121 °C (1.5 torr)], yielded 3.7 g (21.5 mmol, 74%) of 8-OH, whose ^{1}H NMR spectrum was consistent with that reported.[12]

***exo*-6,7-Benzobicyclo[3.2.1]octa-3,6-dien-2-ol benzoate (8-OBz)** was prepared from alcohol 8-OH with benzoyl chloride and pyridine: ^{1}H NMR ($CDCl_3$) δ 7.7 (m, 9 H, aromatic H), 6.6 (dd, 1 H, H-4, $J_{4,3}$ = 9 Hz, $J_{4,5}$ = 7 Hz), 5.4 (d, 1 H, H-2, $J_{2,1}$ = 2 Hz), 5.4 (m, 1 H, H-3, $J_{3,4}$ = 9 Hz), 3.5 (m, 2 H, H-1 and H-5), 2.4 (m, 2 H, H-8_{syn} and H-8_{anti}). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.57; H, 5.85. Found: C, 82.76; H, 6.03.

***exo*-6,7-Benzobicyclo[3.2.1]octa-3,6-dien-2-ol *p*-(trifluoromethyl)benzoate (8-OTfb)** was prepared from 8-OH, *p*-(trifluoromethyl)benzoyl chloride and pyridine in ether. The ester was chromatographed through silica gel and recrystallized from ethanol: mp 75–75.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.0 (m, 4 H, benzoate H), 7.3 (m, 4, aromatic H), 6.5 (m, 1 H, H-4), 5.4 (d, 1 H, H-2, $J_{2,1}$ = 2 Hz), 5.3 (m, 1 H, H-3), 3.4 (m, 2 H, H-1 and H-5), 2.3 (m, 2 H, H-8_{syn} and H-8_{anti}). Anal. Calcd for $C_{20}H_{15}O_2F_3$: C, 69.75; H, 4.40. Found: C, 69.97; H, 4.34.

***exo*-6,7-Benzobicyclo[3.2.1]octa-3,6-dien-2-ol acetate (8-OAc)** was prepared by acetylation of 8-OH with acetyl chloride and pyridine and had properties similar to those described earlier.[7a,12]

***endo*-6,7-Benzobicyclo[3.2.1]octa-3,6-dien-2-ol (10-OH)** was prepared from 2-OH by removal of chlorine with C_8K substantially as described above for 8-OH. It and its acetate (10-OAc) had properties similar to those described earlier.[7a,12]

***endo*-6,7-Benzobicyclo[3.2.1]octa-3,6-dien-2-ol benzoate (10-OBz)** was prepared from 10-OH with benzoyl chloride in pyridine: mp ca. 10 °C; ^{1}H NMR ($CDCl_3$) δ 7.6 (m, 9 H, aromatic and benzoate H), 6.5 (ddd, 1 H, H-4, $J_{4,3}$ = 9 Hz, $J_{4,5}$ = 7 Hz, $J_{4,2}$ = 2 Hz), 6.0 (m, 1 H, H-2), 5.3 (ddd, 1 H, H-3, $J_{3,4}$ = 9 Hz, $J_{3,5}$ = $J_{3,2}$ = 2 Hz), 3.8 (m, 1 H, H-1), 3.4 (dd, 1 H, H-5, $J_{5,4}$ = 7 Hz, $J_{5,8_{anti}}$ = 4 Hz), 2.4 (m, 2 H, H-8_{syn} and H-8_{anti}). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.57; H, 5.85. Found: C, 82.54; H, 5.98.

Acid-Catalyzed Rearrangement of 8-OAc to *anti*-5,6-Benzobicyclo[2.2.2]octa-5,7-dien-2-ol Acetate (12-OAc). A solution of 428 mg (2.00 mmol) of 8-OAc in 10 mL of glacial acetic acid containing 0.1 M $HClO_4$ was heated at 75 °C for 3 h. The solution was diluted with water and extracted with ether. The ethereal extracts were washed with water, aqueous sodium bicarbonate, and water and dried ($MgSO_4$). Removal of the solvent left 410 mg of oil whose ^{1}H NMR spectrum indicated about 80% rearrangement to 12-OAc. Pure 12-OAc was separated by preparative HPLC, using hexanes/4% THF as eluent. It was eluted after the [3.2.1] isomer(s): ^{1}H NMR ($CDCl_3$) δ 7.2 (m, 4 H, aromatic H), 6.7 (ddd, 1 H, H-8, $J_{8,7}$ = 8 Hz, $J_{8,4}$ = 7 Hz, $J_{8,1}$ = 2 Hz), 6.4 (dd, 1 H, H-7, $J_{7,8}$ = 8 Hz, $J_{7,1}$ = 6 Hz), 4.9 (ddd, 1 H, H-2, $J_{2,3_{syn}}$ = 8 Hz, $J_{2,1}$ = $J_{2,3_{anti}}$ = 3 Hz), 4.2 (m, 1 H, H-1), 3.9 (m,

(10) In the saturated (non-allylic, non-benzylic, and non-cyclopropylcarbinylic) systems, electron transfer to carbon–halogen bonds is much favored over that to carbon–oxygen bonds.[11]

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1 H, H-4), 2.1 (m, 1 H, H-3_{syn}), 2.0 (s, 3 H, CH_3), 1.4 (ddd, 1 H, H-3_{anti}, $J_{3_{syn},3_{anti}}$ = 13 Hz, $J_{3_{anti},2} = J_{3_{anti},4}$ = 3 Hz). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.47; H, 6.60. Found: C, 78.59; H, 6.75.

Irradiations. The procedures for irradiation of all of the substrates were substantially identical. For the direct irradiation, approximately 50 mg of substrate was dissolved in 2.0 mL of acetonitrile-d_3 or acetic acid in a quartz NMR tube (5-mm i.d.). The solutions were purged with argon for 10 min. Irradiations were carried out in Rayonet–Srinivasin–Griffin photoreactors equipped with 254-nm lamps. The process and extent of photoreaction were monitored by ^1H NMR and the photoproducts isolated by preparative HPLC.

The procedure for sensitized irradiation was similar to that in acetonitrile, except that one-third of the solvent was acetone-d_6 used as a sensitizer, Pyrex NMR tubes were used, and 300-nm lamps were used in the photoreactor.

In all cases (except the chloride 8-Cl), starting with esters of 8-OH or 10-OH, only tricyclic isomers **9** and **11** were produced, even though reactions in some cases were carried out to complete disappearance of starting material. The properties of new compounds are given below.

***anti*-3,4-Benzotricyclo[3.2.1.$0^{2,7}$]oct-3-en-6-ol benzoate (9-OBz)**: mp 58–59 °C; ^1H NMR ($CDCl_3$) δ 7.7 (m, 9 H, aromatic and benzoate H), 4.8 (s, 1 H, H-6), 3.2 (d, 1 H, H-5, $J_{5,8_{anti}}$ = 5 Hz), 2.4 (ddd, 1 H, H-8_{anti}, $J_{8_{anti},8_{syn}}$ = 12 Hz, $J_{8_{anti},5}$ = 5 Hz, $J_{8_{anti},1}$ = 3 Hz), 2.3 (dd, 1 H, H-2, $J_{2,1} = J_{2,7}$ = 7 Hz), 1.9 (m, 2 H, H-1 and H-7), 1.1 (d, 1 H, H-8_{syn}, $J_{8_{syn},8_{anti}}$ = 12 Hz).

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.57; H, 5.85. Found: C, 82.53, H, 5.73.

***anti*-3,4-Benzotricyclo[3.2.1.$0^{2,7}$]oct-3-en-6-ol *p*-(trifluoromethyl)benzoate (9-OTfb)**: ^1H NMR ($CDCl_3$) δ 7.9 (m, 4 H, benzoate H), 7.1 (m, 4 H, aromatic H), 4.8 (s, 1 H, H-6), 3.2 (d, 1 H, H-5, $J_{5,8_{anti}}$ = 5 Hz), 2.3 (ddd, 1 H, H-8_{anti}, $J_{H\text{-}8_{anti},H\text{-}8_{syn}}$ = 12 Hz, $J_{8_{anti},5}$ = 5 Hz, $J_{8_{anti},1}$ = 3 Hz), 2.3 (dd, 1 H, H-2, $J_{2,1} = J_{2,7}$ = 7 Hz), 1.9 (m, 2 H, H-1 and H-7), 1.1 (d, 1 H, H-8_{syn}, $J_{8_{syn},8_{anti}}$ = 12 Hz). Anal. Calcd for $C_{20}H_{15}O_2F_3$: C, 69.75; H, 4.40. Found: C, 69.77; H, 4.64.

***syn*-3,4-Benzotricyclo[3.2.1.$0^{2,7}$]oct-3-en-6-ol benzoate 11-OBz**: mp 108–109 °C; ^1H NMR (CD_3CN) δ 7.4 (m, 9 H, aromatic and benzoate H), 5.5 (dd, H-6, $J_{6,5}$ = 5 Hz, $J_{6,7}$ = 3 Hz), 3.6 (dd, 1 H, H-5, $J_{5,6} = J_{5,8}$ = 5 Hz), 2.4 (dd, 1 H, H-2, $J_{2,7} = J_{2,1}$ = 7 Hz), 2.0 (m, 3 H, H-1, H-7 and H-8_{anti}), 1.1 (d, 1 H, H-8_{syn}, $J_{8_{syn},8_{anti}}$ = 12 Hz). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.57; H, 5.85. Found: C, 82.42; H, 6.00.

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Registry No. 1-OH, 54647-01-7; 2-OH, 64626-01-3; 8-OH, 54647-02-8; 8-OBz, 83511-40-4; 8-OTfb, 83511-41-5; 8-OAc, 16938-95-7; 9-OBz, 83511-43-7; 9-OTfb, 83527-58-6; 10-OH, 57089-48-2; 10-OBz, 83542-14-7; 11-OBz, 83542-15-8; 12-OAc, 83511-42-6.

New Synthesis of Azabufalin from C-17 Steroidal Ketones

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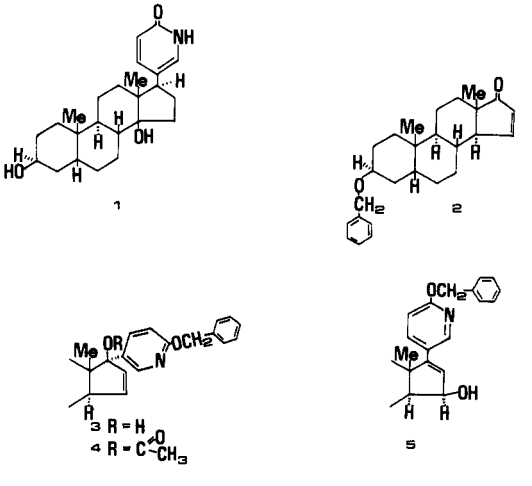
A new and superior method for the conversion of the appropriate steroidal pyridyl derivatives into azabufalin by using the known 2-(benzyloxy)pyridyl bromide at the 17-ketone is reported.

Recent studies[1,2] on synthetic cardioactive steroid analogues have shown that azabufalin (**1**) may have important use pharmacological activity. In previous work,[2,3] we demonstrated that azabufalin can be synthesized by a method which features the reaction of a steroidal ketone with 2-methoxypyridyllithium and the conversion of the pyridyl ring into a pyridone derivative. By using Wiesner's synthetic strategy[4] one can obtain the substitution and natural configuration at C-14. Our previous method[2] used 2-methoxy-5-bromopyridine in the reaction at the 17-ketone. However, the transformation of a methoxypyridyl derivative into an *N*-benzylpyridone derivative by using benzyl bromide gave only a 52% yield, with 40% of the starting material recovered. Even after recycling several times, this troublesome step gave a total yield of only 70%. The risk of formation of a 14,15-unsaturated elimination product, due to the formation of hydrogen bromide in the reaction, further complicated this synthetic route. In this paper a new and superior method for the conversion of the appropriate steroidal pyridyl derivative to azabufalin, using the known 2-(benzyloxy)pyridyl bromide,[5] is reported.

Results and Discussion

The α,β-unsaturated ketone **2**, synthesized by Wiesner's group,[4] has been successfully used for the total synthesis of cardenolide and isocardenolide compounds. Condensation of compound **2** with 5-bromo-2-(benzyloxy)pyridine



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