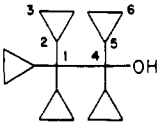
was refluxed for 10 h. 1,2,2,2-Tetracyclopylethanone (15, 4.5 g, 22 mmol) in 10 mL of hexane was added dropwise and refluxing was continued overnight. The excess lithium was destroyed with 10 mL of ethanol and the mixture was poured onto ice water. Extraction with ether, washing with water, drying ($MgSO_4$), and concentration resulted in a viscous oil which solidified upon distillation: bp 136–141 °C (1 mm); recrystallization from pentane gave 1.55 g (28%) of tetracyclopropylethanol: mp 33–34 °C; ^1H NMR ($CDCl_3$) δ 0.12–0.69 (m, 20 H), 0.71–0.98 (m, 3 H), 1.21–1.53 (m, 2 H), 1.89 (s, 1 H), NMR data is incorrectly reported in ref 5; ^{13}C NMR ($CDCl_3$) 0.0 (C-3), 1.5 (C-6), 10.5 (C-2), 15.0 (C-5), 43.0 (C-1), 77.1 (C-4); IR (CCl_4) 3590, 3475, 3075, and 2860 cm^{-1}.

Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.76; H, 10.65.



Pentacyclopropylethyl Carbocation (17). To a mixture of $HFSO_3$–SbF_5 (Aldrich) and FSO_2Cl (1:1 v/v) at −80 °C in a glovebag under nitrogen was added dropwise 150 mg of alcohol 16 in 0.5 mL of FSO_2Cl from a precooled pipet. The mixture was transferred to a 5-mm precooled NMR tube which was sealed and transferred to a 10-mm NMR tube containing 3 mL of acetone-d_6 for the lock signal: ^1H NMR (super acid) δ 0.3 (m, 20 H), 3.4 (bs, 5 H); ^{13}C NMR (super acid) δ 13.1 (2° C), 81.7 (3°), 125.6 (4°).

The calculation to determine nonclassical or classical nature was determined according to the Schleyer–Lenoir–Olah method.[16] $\Delta\Sigma\delta_{C^+,\delta CH}(ppm) = \Sigma\delta_{C^+}(ppm) - \Sigma\delta_{CH}(ppm) = 125.6 \times 2) + (81.3 \times 5) + (13.1 \times 10) - [(10.5 \times 3) + 43.0 + 77.1 + (15.0 \times 2) + (1.5 \times 4) + (40$, average correction for alcohol to hydrocarbon[19])]. For nonclassical ions the values are reported to be 270–325 ppm,[16] well below the value of 511 ppm calculated here.

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Registry No. 1, 7090-88-2; 2, 23534-93-2; 3, 15813-18-0; *cis*-4, 100515-65-9; *trans*-4, 100515-66-0; 5, 102652-65-3; 6, 37614-40-7; 7, 82701-08-4; 8, 4468-67-1; 9, 15813-19-1; 10, 52406-51-6; 11, 102652-66-4; 12, 102652-67-5; 15, 82701-09-5; 16, 82701-10-8; 17, 82701-11-9; dicyclopropyl ketone, 1121-37-5; 2,5-dimethyl-4,4-diisopropyl-3-hexanone, 54580-25-5; diisopropyl ketone, 565-80-0; cyclopropyl bromide, 4333-56-6.

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Photochemical Transformations. 43. Ionic and Di-π-methane Photochemistry of Some Benzylic Derivatives of Benzobicyclo[3.2.1]octadienes[1]

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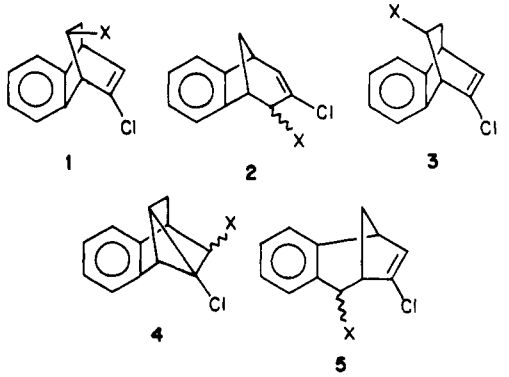
exo- and *endo*-7-chloro-3,4-benzobicyclo[3.2.1]octa-3,6-dien-2-ols (5-OH) give stereospecific di-π-methane rearrangements to *exo*- and *endo*-7-chloro-3,4-benzotricyclo[4.1.1.$0^{5,7}$]oct-3-en-2-ols (6-OH and 7-OH), respectively, under direct and triplet-senstized irradiations. *exo*-4,6-Dichloro-2,3-benzobicyclo[3.2.1]octa-2,6-diene (*exo*-5-Cl) gives an analogous di-π-methane rearrangement to 6-Cl under triplet-sensitized conditions. In addition, under both direct and sensitized irradiation, it gives ionic (solvolysis and epimerization) products. These include, in aqueous acetonitrile (direct), *endo*-5-Cl, *exo*-5-OH, and *exo*-5-$NHCOCH_3$, in aqueous acetonitrile (sensitized with benzophenone or acetone), *exo*-5-OH and *exo*-5-$NHCOCH_3$, and in aqueous acetone, *exo*-5-OH. The sensitized irradiations also lead to the homoallyl-to-cyclopropylcarbinyl rearrangement product, *exo*-6,7-dichloro-3,4-benzotricyclo[3.2.1.$0^{2,7}$]oct-3-ene (*anti*-4-Cl).

Some years ago,[2] members of our research group began a study of the ground-state and excited-state interactions of the chlorobenzobicyclo[2.2.2]octadienyl and -[3.2.1]octadienyl systems and the chlorobenzotricyclo[3.2.1.$0^{2,7}$]-octene system. It was shown that ground-state reactions interconverted 1 and 2 species by anti (antarafacial) migrations. Similarly, species 3–5 were interconverted by ground-state reactions. No mixing of systems occurred. It was also shown that photolyses of 2-Cl and 2-OMs epimers in acetic acid or in acetonitrile–water led to 2-solvolysis products, to epimerization, and to rearrangement to 1-Cl (or 1-OMs) species. Irradiation of *anti*-4-Cl and *anti*-4-OMs led to 5 solvolysis products and 5 isomers,[3] while the *syn*-4 epimers were inert. Irradiation of 1-Cl also led[4] to 5 (syn migration) as principal products, although



about 30% of the anti migration products 2 were also produced. The syn [2.2.2] epimer 3 was photoinert.

While the direct irradiation of 2-OMs epimers led to "ionic" photochemistry (solvolysis and Wagner–Meerwein

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(3) Cristol, S. J.; Opitz, R. J.; Bindel, T. H.; Dickenson, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 7977.

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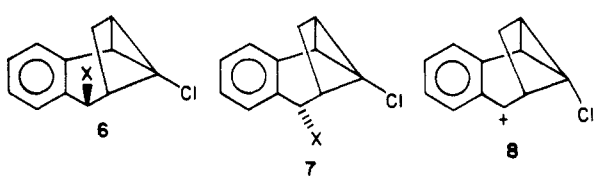
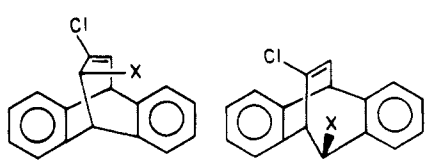
0022-3263/86/1951-2973$01.50/0

rearrangement), sensitized irradiations (acetone, 300 nm) gave only those isomers anticipated[5] for the di-π-methane rearrangement, as did the 2-OH and 2-OAc epimers.

Results

We were interested in looking at 5 species, which are different from the others in that the benzene ring is α to the C–X bond (benzylic) rather than β (homobenzylic). We have noted[6] that, in homobenzylic systems, photoreactivity to give (ultimately) carbocations and X^- depends upon electron transfer from the photoexcited aromatic ring to the σ^* orbital of the C–X bond. No requirement of this sort has been demonstrated for benzylic systems.[7] In addition, benzylic compounds give substantial amounts of radical products, derived, of course, from homolytic cleavage, in both sensitized and unsensitized reactions, while the corresponding homolyses in β-aryl compounds are less prevalent. As anticipated from work on a structurally related system, 9-OH,[13] the alcohol 5-OH epimers led only to the di-π-methane rearrangement products on either direct irradiation in aqueous acetonitrile or on sensitized irradiation (acetone). Following the general scenario[5] of di-π-methane rearrangements, *exo*-5-OH gave 6-OH (exo[14]) and *endo*-5-OH gave 7-OH (endo).





Experiments to determine the multiplicity of the direct irradiation processes were not conducted, but it seems reasonable to assume[5] that intersystem crossing to the triplet occurred.

Irradiation of *exo*-5-Cl in 2% D_2O in CD_3CN with 254-nm light led to quite different results. After about 50% of the starting exo chloride had reacted, the product mixture, after water wash, contained roughly 20% of *endo*-5-Cl, 50% of *exo*-5-OH, 10% of *exo*-5-$NHCOCD_3$, and 20% of 6-OH and perhaps a trace of *anti*-4-Cl. Thus, direct irradiation leads in part to epimerization by some recombination process and in large part to ionic photosolvolysis products. The 6-OH is undoubtedly a secondary product from *exo*-5-OH. These products accounted for about 50% of the loss of *exo*-5-Cl; presumably radical-derived products accounted for the remainder.

No endo solvolysis products could be detected, although ground-state solvolysis in an aqueous acetone of similar polarity gave a 3:1 exo–endo ratio of 5-OH.[15]

When a solution of *exo*-5-Cl in acetone-d_6 containing 3% of D_2O was irradiated with 300-nm light, the product mixture comprised about 55% of solvolysis products (5-OH and its di-π-methane isomer, 6-OH), 40% of 6-Cl and 5% of *anti*-4-Cl. No endo products were seen. Although *anti*-4-Cl is a normal product in the ferric chloride catalyzed equilibration rearrangement of 5-Cl,[4,15] photochemical transformations of homoallyl to cyclopropylcarbinyl systems have not previously been seen, although the reverse, in direct irradiation, is known.[3,16] It is of interest that solvolysis of *exo*-5-Cl competes with the di-π-methane rearrangement to 6-Cl in this triplet-sensitized system while it does not with the allylic isomers (2-OMs).[2] Clearly the ready capability[12] of benzylic chlorides to give ionic solvolysis products under triplet sensitization, and the reluctance of triplets of allylic chlorides or methanesulfonates[1,17] to photosolvolyze, are demonstrated with these isomers.

6-Cl was identified by its ^1H NMR spectrum compared with that of 6-OH. When the reaction mixture was heated with 35% water in acetone, signals (^1H NMR) for 5-Cl and 6-Cl disappeared and were replaced by those for *exo*-5-OH (from 5-Cl) and 7-OH (from 6-Cl) with corresponding intensities. A small amount of 6-OH could have been formed and not noted, as it was present in substantial amount in the photoproduct mixture. Molecular models of the 6 and 7 compounds suggest that endo substituents are more axial-like than exo substituents, and therefore 7 species are more likely to be produced from cation 8 by stereoelectronic control.[18]

Discussion of Results

To summarize, then, the exo and endo alcohols in both the allylic (2) and benzylic (5) systems show only di-π-methane chemistry under both direct and sensitized conditions in aqueous acetonitrile or acetone. This is consistent with previous experience with 9-OH where it was shown[13] that a compound analogous to 2-OH photoreacts in a solvolytic fashion, that is, to give 10-$NHCOCH_3$, only under strongly acidic conditions.

The photoreactions of 5-Cl, which, in the singlet state, give photoheterolysis and photohomolysis products and, in the triplet state, give photoheterolysis and di-π-methane products, may be contrasted with those of 2 species[2] and with those of 9 species.[17] With 2-Cl, 2-OMs, and 9-Cl, direct irradiation gave photoheterolysis products, while triplet sensitization led not to solvolysis and radical products but only to di-π-methane rearrangements. We perceive that the choice of reactions of these allylic systems derived from the requirement that the β-aryl (allylic) systems suffer transfer of the π^* electron initially produced from the π,π^* state to the σ^* orbital of the carbon–nucleofuge bond for loss of nucleofuge and that their triplet π,π^* states do not have enough energy to consummate this

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(6) See ref 1 and previous papers in series.
(7) In this regard, benzylic quarternary ammonium salts are photoactive,[8-10] while 7-dibenzobicyclo[2.2.2]octa-2,5-dienyltrimethylammonium salts are not.[11] Further, benzyl systems lead to much radical fragmentation, even in polar solvents, not seen in the other systems.[12]
(8) Ratcliff, M. A., Jr.; Kochi, J. K. *J. Org. Chem.* **1971**, *36*, 3112.
(9) (a) Appleton, D. C.; Bull, D. C.; Givens, R. S.; Lillis, V.; McKenna, J.; McKenna, J. M.; Thackeray, S.; Walley, A. R. *J. Chem. Soc. Perkin Trans. 2* **1980**, 77. (b) Appleton, D. C.; Bull, D. C.; Givens, R. S.; Lillis, V.; McKenna, J.; McKenna, J. M.; Walley, A. R. *J. Chem. Soc., Chem. Commun.* **1974**, 473. (c) Lillis, V.; McKenna, J.; McKenna, J. M.; Taylor, P. S.; Williams, I. H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 83. (d) Lillis, V.; McKenna, J.; McKenna, J. M.; Smith, M. J.; Williams, I. H. *J. Chem. Soc., Chem. Commun.* **1974**, 474.
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(12) Cristol, S. J.; Bindel, T. H. *Org. Photochem.* **1983**, *6*, 327.
(13) Cristol, S. J.; Daussin, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 2866.
(14) We extend the use of the term "exo" to denote the position syn to the less substituted carbon atom of the parent system and "endo" to the anti position.
(15) Dickenson, W. A. Ph.D. Dissertation, University of Colorado—Boulder, 1981.
(16) Hixson, S. S.; Franke, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 3677 and references therein.
(17) Cristol, S. J.; Stull, D. P.; Daussin, R. D. *J. Am. Chem. Soc.* **1978**, *100*, 6674.
(18) Goering, H. L.; Towns, D. L. *J. Am. Chem. Soc.* **1963**, *85*, 2295.

transfer within their lifetimes.[19] Accordingly, the lower energy-requiring di-π-methane interactions leading to di-π-methane rearrangement products occur, in preference to either electron or energy transfer[20] to the remote carbon–X bond. On the other hand, benzylic systems have their C–X bonds certainly closer to the excited aromatic rings (and probably conjugated with them as well). Thus the fates of their excited states are more closely related to heterolytic and homolytic bond dissociation energies, both of which are lower than triplet energies of aromatic rings.

It is of some interest that the 5^+Cl^- ion pair produced in the direct irradiation gives substantial epimerization, while that from the triplet sensitization does not. The possibility that this is a solvent effect was tested by running sensitized reactions in acetonitrile-d_3 containing 2% D_2O and either benzophenone or acetone as sensitizer. The benzophenone experiment gave about 25% of *exo*-**5**-OH and **6**-OH, 15% of *exo*-**5**-$NDCOCD_3$, 25% of *anti*-**4**-Cl, and 35% of **6**-Cl, while the acetone-sensitized reaction gave 35% of *exo*-**5**-OH and **6**-OH, 15% of *exo*-**5**-$NDCOCD_3$, 20% of *anti*-**4**-Cl, and 30% of **6**-Cl. Within experimental error, these are not significantly different. Two curious differences (other than the di-π-methane rearrangement) are apparent between the direct irradiations and the triplet-sensitized reactions in acetonitrile. First, the ratio of alcohol (*exo*-**5**-OH and **6**-OH) to amide (*exo*-**5**-$NDCOCD_3$) is reduced from about 7:1 to about 2:1. Second, no *endo*-**5**-Cl is produced in the triplet reaction; its formation is replaced by a roughly equivalent production of *anti*-**4**-Cl. Clearly the 5^+Cl^- pairs produced in the singlet and triplet reaction are not identical and recombine or are captured, at least in part, before relaxing to identical species. The precise nature of the differences between the two is not clear to us.

Experimental Section

General. ^1H NMR spectra were recorded on a Varian Associates EM-390 spectrometer and were taken in $CDCl_3$ solvent (with 1–5% Me_4Si) unless otherwise noted. Mass spectra were obtained on a Varian MAT CH-5 or MAT CH-7 spectrometer. Melting points were determined with a Thomas-Hoover Unimelt apparatus and are corrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Certain compounds were difficult to purify and decomposed rapidly so that elemental analyses of such materials were not attempted. Low-resolution mass spectral data for these compounds are presented.

Irradiations were performed in a Rayonet Srinivasan-Griffin Photochemical Reactor (Southern New England Ultraviolet Co.), referred to as the "Rayonet", with either RPR-2537 Å (254 nm) or RPR-3000 Å (300 nm) lamps. Samples were sealed with rubber septa and deoxygenated by bubbling nitrogen gas through the solutions (10 min for NMR-tube irradiations, 30 min for larger samples) before irradiation. NMR-tube irradiations were performed by using a merry-go-round apparatus, Model MGR-100 (Southern New England Ultraviolet Co.). Generally water (or D_2O) was added to the principal solvent to insure hydrolysis of reaction intermediates to amides (from CH_3CN) or to alcohols (from acetone). Quantitative values for loss of starting material and formation of various products in NMR-tube irradiations were determined by integration of the signal in the ^1H NMR spectrum for the proton geminal to an electronegative functional group (H-2 for **5**-OH, **6**-OH, and **7**-OH, H-4 for **5**-Cl and **6**-Cl, and H-7 for **4**-Cl) with the total integration of the spectrum for δ 0–9 (excluding residual protons on solvent) being used as an internal standard.

Preparation of *exo*-7-Chloro-3,4-benzobicyclo[3.2.1]octa-3,6-dien-2-ol (*exo*-5-OH).[21] A mixture of *exo*- and *endo*-**5**-OAc, weighing 647 mg (3.1 mmol), prepared by acetolysis of *syn*-**4**-OMs, in 25 mL of 0.1 M NaOMe in MeOH, was heated at reflux for 5 min. Addition of water was followed by extraction with ether. The ether extracts were combined, washed with brine and dried ($MgSO_4$). Evaporation of solvent left 480 mg (97%) of an oil, which crystallized from ether–hexane solvent. Repeated recrystallization from the same solvent gave 260 mg (52%) of *exo*-**5**-OH: mp 115–116 °C; ^1H NMR δ 7.3 (m, 4, Ar H), 6.40 (d, 1 H, H-6, $J_{6,5}$ = 3 Hz), 4.80 (dd, 1 H, H-2, $J_{2,1}$ = 2 Hz, $J_{2,OH}$ = 5 Hz), 3.40 (t, 1 H, H-5, $J_{5,8_{anti}} = J_{5,6}$ = 3 Hz), 3.00 (dd, 1 H, H-1, $J_{1,8_{anti}}$ = 5 Hz, $J_{1,2}$ = 2 Hz), 2.4 (m, 2 H, H-8_{syn}, H-8_{anti}), 2.1 (d, 1 H, OH, $J_{OH,2}$ = 5 Hz). Anal. Calcd for $C_{12}H_{11}ClO$: C, 69.74; H, 5.76. Found: C, 69.87; H, 5.44.

Preparation of 7-Chloro-3,4-benzobicyclo[3.2.1]octa-3,6-dien-2-one (5-k).[21] A solution of 209 mg (1.0 mmol) of a 2.6:1 mixture of *exo*-**5**-OH and *endo*-**5**-OH (prepared as described above) in 4 mL of acetone was treated with 2.7 M Jones reagent[22] in the usual fashion. The reaction mixture was diluted with brine and extracted with ether. The combined ether extracts were washed with aqueous $NaHCO_3$ and H_2O and dried ($MgSO_4$). Solvent evaporation left 211 mg of a red oil, which was placed on a thick-layer silica gel plate. Elution with 10% ether in hexane gave a band (R_f = 0.22), whose extraction gave a colorless oil, which was distilled [~80 °C (0.8 torr)]: ^1H NMR δ 7.5 (br m, 4 H, Ar H), 6.60 (d, 1 H, H-6, $J_{6,5}$ = 3 Hz), 3.70 (t, 1 H, H-5, $J_{5,6} = J_{5,8_{anti}}$ = 3 Hz), 3.40 (d, 1 H, H-1, $J_{1,8_{anti}}$ = 3 Hz), 2.9 (m, 2 H, H-8_{syn} and H-8_{anti}). Anal. Calcd for $C_{12}H_9ClO$: C, 70.43; H, 4.43. Found: C, 70.39; H, 4.58.

Preparation of *endo*-7-Chloro-3,4-benzobicyclo[3.2.1]-octa-3,6-dien-2-ol (*endo*-5-OH). To a solution of 134 mg (0.66 mmol) of **5**-k in 10 mL of anhydrous ethyl ether was added 32 mg of $LiAlH_4$. After 2 h, the excess $LiAlH_4$ was quenched with 0.7 mL of saturated sodium potassium tartrate solution. After filtration, the solution was washed with water and dried ($MgSO_4$). Filtration and evaporation of solvent gave 115 mg (87%) of clear oil, which was shown by ^1H NMR analysis to be almost pure *endo*-**5**-OH. After chromatography on silica gel, two recrystallizations from dichloromethane/hexane solvent gave mp 54–56 °C: ^1H NMR δ 7.3 (m, 4 H, Ar H), 6.30 (d, 1 H, H-6, $J_{6,5}$ = 3 Hz), 4.90 (dd, 1 H, H-2, $J_{2,1}$ = 5 Hz, $J_{2,OH}$ = 10 Hz), 3.3 (t, 1 H, H-5, $J_{5,6}$ = 3 Hz, $J_{5,8_{anti}}$ = 4 Hz), 3.2 (t, 1 H, H-1, $J_{1,2} = J_{1,8_{anti}}$ = 5 Hz), 2.60 (ddd, 1 H, H-8_{anti}, $J_{8_{anti},1}$ = 5 Hz, $J_{8_{anti},5}$ = 4 Hz, $J_{8_{anti},8_{syn}}$ = 11 Hz), 2.0 (d, 1 H, H-8_{syn}, $J_{8_{syn},8_{anti}}$ = 11 Hz), 1.9 (d, 1 H, OH, $J_{OH,2}$ = 10 Hz). Anal. Calcd for $C_{12}H_{11}ClO$: C, 69.74; H, 5.37. Found: C, 69.87; H, 5.55.

Preparation of *exo*-4,6-Dichloro-2,3-benzobicyclo[3.2.1]-octa-2,6-diene (*exo*-5-Cl). To a solution of 532 mg (2.58 mmol) of *syn*-**4**-OH[2] in 11 mL of tetrahydrofuran (freshly distilled from $LiAlH_4$) was added 2.5 mL of thionyl chloride. The solution was heated at 62 °C for 4 days. The excess $SOCl_2$ was decomposed with 80 mL of H_2O, and this was extracted with two 60-mL portions of ether. The combined ether layers were washed several times with water, aqueous $NaHCO_3$, and brine and dried ($MgSO_4$). Filtration and evaporation of solvent gave a yellow oil, the ^1H NMR analysis of which showed about 70% conversion from starting material to benzylic chlorides. (The benzylic chlorides were present in an exo–endo ratio of 3:1 in this experiment although a similar experiment gave a 7:1 ratio of benzylic chlorides, again with the exo predominating.) In addition, the ^1H NMR spectrum showed another product with properties of a polymer of THF. Separation of this mixture on silica gel column resulted in isolation of 222 mg (38%) of *exo*-**5**-Cl which was relatively free of contamination from its epimer. The nearly colorless oil which was obtained in this manner had ^1H NMR and mass spectra consistent with the assigned structure: mass spectrum, *m/e* (relative intensities) 224 (9, M^+), 226 (6, $M^+ + 2$), 189 (100, $M^+ - 35$), 153 (86, $M^+ - 71$); ^1H NMR δ 7.2 (m, 4 H, Ar H), 6.40 (d, 1 H, H-7, $J_{7,1}$ = 3 Hz), 5.20 (d, 1 H, H-4, $J_{4,5}$ = 2 Hz), 3.40 (m, 1 H, H-1), 3.10 (m, 1 H, H-5), 2.50 (m, 2 H, H-8_{syn} and H-8_{anti}). A crystalline sample[23] had mp 59–62 °C. Anal. Calcd for $C_{12}H_{10}Cl_2$: C, 64.03; H, 4.48. Found: C, 64.13; H, 4.52.

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(23) Prepared by Dr. M. S. Fleming.

^{1}H NMR Spectrum of *endo*-4,7-Dichloro-2,3-benzobicyclo[3.2.1]octa-2,6-diene (*endo*-5-Cl). Column chromatography of mixtures of *exo*- and *endo*-5-Cl did not permit separation of pure endo chloride. However, samples were obtained which were sufficiently enriched in the endo epimer that a ^{1}H NMR spectrum could be obtained: δ 7.4 (m, 4 H, Ar H), 6.40 (d, 1 H, H-7, $J_{7,1}$ = 3 Hz), 5.40 (d, 1 H, H-4, $J_{4,5}$ = 5 Hz), 3.3 (m, 2 H, H-1 and H-5), 2.7 (ddd, 1 H, H-8$_{anti}$, $J_{8_{anti},1}$ = 4 Hz, $J_{8_{anti},5}$ = 5 Hz, $J_{8_{anti},8_{syn}}$ = 11 Hz), 2.1 (d, 1 H, H-8$_{syn}$, $J_{8_{syn}8_{anti}}$ = 11 Hz).

Preparation of 7-Chloro-*exo*-2-acetamido-3,4-benzobicyclo[3.2.1]octa-3,6-diene (*exo*-5-NHCOCH$_3$). To an ice-cold solution of 100 mg of *exo*-5-OH in 5 mL of dry CH_3CN was added 40 μL of concentrated H_2SO_4. The solution was allowed to warm to room temperature and to stand for 3 h. Extraction with three 30-mL portions of ether followed addition of 50 mL of water. The combined ether layers were washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl and dried ($MgSO_4$). Filtration and evaporation of solvent gave 110 mg of white crystals. ^{1}H NMR analysis showed that approximately 65% of the starting material had been converted to benzylic amides (*exo*- and *endo*-5-NHCOCH$_3$) and that the exo–endo ratio of these amides was about 7:1. The exo benzylic amide was obtained by recrystallization from ether: mp 192.5–193.5 °C; ^{1}H NMR δ 7.0 (m, 4 H, Ar H), 6.10 (d, 1 H, H-6, $J_{6,5}$ = 3 Hz), 5.90 (m, 1 H, NH), 5.20 (dd, 1 H, H-2, $J_{2,1}$ = 2 Hz, $J_{2,NH}$ = 7 Hz), 3.2 (t, 1 H, H-5, $J_{5,6}$ = 3 Hz, $J_{5,8_{anti}}$ = 4 Hz), 2.80 (dd, 1 H, H-1, $J_{1,2}$ = 2 Hz, $J_{1,8_{anti}}$ = 5 Hz), 2.30 (ddd, 1 H, H-8$_{anti}$, $J_{8_{anti},1}$ = 5 Hz, $J_{8_{anti},5}$ = 4 Hz, $J_{8_{anti},8_{syn}}$ = 11 Hz), 1.8 (m, 4 H, H-8$_{syn}$ and CH$_3$). Anal. Calcd for $C_{14}H_{14}ClON$: C, 67.88; H, 5.70. Found: C, 67.52; H, 5.90.

^{1}H NMR Spectrum of 7-Chloro-*exo*-2-acetamido-3,4-benzobicyclo[3.2.1]octa-3,6-diene (*endo*-5-NHCOCH$_3$). From samples enriched in *endo*-5-NHCOCH$_3$, produced by equilibration of the exo isomer preparation at 150 °C, the following ^{1}H NMR spectrum could be deduced: δ 7.2 (m, 4 H, Ar H), 6.30 (d, 1 H, H-6, $J_{6,5}$ = 3 Hz), 5.90 (m, 1 H, N-H), 5.4 (dd, 1 H, H-2, $J_{2,1}$ = 5 Hz, $J_{2,NH}$ = 9 Hz), 3.3 (m, 2 H, H-1 and H-5), 2.60 (ddd, 1 H, H-8$_{anti}$, $J_{8_{anti},1}$ = 5 Hz, $J_{8_{anti},5}$ = 4 Hz, $J_{8_{anti},8_{syn}}$ = 11 Hz), 2.1 (m, 4 H, H-8$_{syn}$ and CH$_3$).

Direct Irradiation of 7-Chloro-3,4-benzobicyclo[3.2.1]octa-3,6-dien-*exo*-2-ol (*exo*-5-OH): Preparation of 7-Chloro-3,4-benzotricyclo[4.1.1.0^{5,7}]oct-3-en-*exo*-2-ol (6-OH). A solution of 400 mg of *exo*-5-OH in 400 mL of dry CH_3CN in a large quartz tube was irradiated with 12 254-nm lamps in the Rayonet for 3.0 h. The solvent was evaporated to give 432 mg of a brown oil. ^{1}H NMR analysis indicated that approximately equal amounts of *exo*-5-OH and 6-OH were present (on a smaller scale, it was noted that the formation of 6-OH accounted for substantially all of the loss of 5-OH). Partial separation of the two alcohols resulted from thick-layer silica gel chromatography and repeated elution with hexanes containing 30% ether. The faster moving band was predominantly starting material, while 126 mg of slightly yellow solid (which was more than 90% 6-OH) was obtained from the slower moving material. Pure 6-OH was obtained by recrystallization from ether/hexane solvent: mp 103–104 °C; ^{1}H NMR δ 7.4 (m, 4 H, Ar H), 5.0 (d, 1 H, H-2, $J_{2,1}$ = 3 Hz), 3.0 (dm, 1 H, H-1, $J_{1,8_{anti}}$ = 8 Hz), 2.4 (m, 3 H, H-5, H-6, and H-8$_{anti}$), 1.8 (s, 1 H, OH), 1.2 (dd, 1 H, H-8$_{syn}$, $J_{8_{syn},1}$ = 2 Hz, $J_{8_{syn},8_{anti}}$ = 10 Hz). Anal. Calcd for $C_{12}H_{11}OCl$: C, 69.74; H, 5.37. Found: C, 69.80; H, 5.50.

Sensitized Irradiation of 7-Chloro-3,4-benzobicyclo[3.2.1]octa-3,6-dien-*exo*-2-ol (*exo*-5-OH). A solution of 32 mg of *exo*-5-OH in 0.5 mL of acetone-d_6 containing 3% D_2O in a Pyrex NMR tube was irradiated with five 300-nm lamps in the Rayonet. After 6.4 h of irradiation, 25–30% of the starting material had been converted to 6-OH. The observed product accounted for all of the loss of starting material. After 67.5 h of irradiation, 75–80% of the starting material had reacted. 6-OH still accounted for more than 90% of the loss of starting material. A small resonance was observed at δ 5.2 in the ^{1}H NMR spectrum which may represent formation of a trace of another, unidentified, product.

Preparation of 7-Chloro-3,4-benzotricyclo[4.1.1.0^{5,7}]oct-3-en-2-one (6-k). To a solution of 45 mg of 6-OH in 5 mL of acetone was added 0.15 mL of Jones' reagent[22] dropwise. After 0.5 h, 0.25 mL of isopropyl alcohol was added to react with the remaining oxidant. Water (30 mL) was added, and the solution was extracted with three 20-mL portions of ether. The combined ether layers were washed with saturated aqueous $NaHCO_3$ and water and dried ($MgSO_4$). Filtration and removal of the solvent gave 39 mg (88%) of light yellow oil whose properties were consistent with those expected for 6-k: ^{1}H NMR δ 8.0 (dd, 1 H, Ar H ortho to carbonyl, J_{meta} = 1 Hz, J_{ortho} = 8 Hz), 7.6 (m, 3 H, Ar H), 3.4 (dd, 1 H, H-1, $J_{1,8_{syn}}$ = 2 Hz, $J_{1,8_{anti}}$ = 10 Hz), 2.8 (m, 3 H, H-5, H-6 and H-8$_{anti}$), 1.4 (dd, 1H, H-8$_{syn}$, $J_{8_{syn},1}$ = 2 Hz, $J_{8_{syn},8_{anti}}$ = 11 Hz); mass spectrum, *m/e* (relative intensity) 204 (52, M$^+$), 206 (16, M$^+$ + 2), 169 (91, M$^+$ - 35), 141 (100, M$^+$ - 63).

The identical ketone was obtained by similar oxidation of the endo alcohol 7-OH.

Sensitized Irradiation of 7-Chloro-3,4-benzobicyclo[3.2.1]octa-3,6-dien-*endo*-2-ol (*endo*-5-OH): Preparation of 7-Chloro-3,4-benzotricyclo[4.1.1.0^{5,7}]oct-3-en-*endo*-2-ol (7-OH). A solution of 72 mg of *endo*-5-OH in 15 mL of acetone containing 3% water in a Pyrex test tube was irradiated in the Rayonet with six 300-nm lamps. After 12 h, the solvent was evaporated, leaving 73 mg of a light yellow oil. ^{1}H NMR analysis showed that 35–40% of the starting material had been converted to 7-OH. No other product could be detected. The two alcohols were separated by column chromatography on silica gel. In this manner a sample of 25 mg of 7-OH was obtained as an oil. The ^{1}H NMR spectrum of this sample was consistent with that expected: δ 7.4 (m, 4 H, Ar H), 4.4 (dd, 1 H, H-2, $J_{2,1}$ = 4 Hz, $J_{2,OH}$ = 7 Hz), 3.2 (m, 1 H, H-1), 2.6 (m, 3 H, H-5, H-6, and H-8$_{anti}$), 1.8 (d, 1 H, OH, $J_{OH,2}$ = 7 Hz), 0.9 (dd, 1 H, H-8$_{syn}$, $J_{8_{syn},1}$ = 2 Hz, $J_{8_{syn},8_{anti}}$ = 11 Hz); mass spectrum, *m/e* (relative intensity) 206 (6, M$^+$), 208 (2, M$^+$ + 2), 171 (68, M$^+$ - 35), 153 (100, M$^+$ - 53). Further support for the identification of this compound was given by the fact that it was oxidized with Jones' reagent in acetone to give 6-k, the same ketone which was obtained upon oxidation of the epimeric alcohol, 6-OH.

Direct Irradiation of 7-Chloro-3,4-benzobicyclo[3.2.1]octa-3,6-dien-*endo*-2-ol (*endo*-5-OH). A solution of 31 mg of *endo*-5-OH in 0.5 mL of CD_3CN containing 2% D_2O in a quartz NMR tube was irradiated with 13 254-nm lamps in the Rayonet and monitored periodically by ^{1}H NMR. After 3.0 h of irradiation, 35% of the starting material had reacted. The only product which was observed was the 7-OH. This product accounted for about 65% of the loss of starting material. At longer irradiation times, continued conversion to 7-OH was observed. The reaction slowed considerably, perhaps because of the accumulation of light-absorbing byproducts.

Sensitized Irradiation of *exo*-4,6-Dichloro-2,3-benzobicyclo[3.2.1]octa-2,6-diene (*exo*-5-Cl) in Acetone-d_6 Containing 3% D_2O. Identification of *exo*-5,7-Dichloro-3,4-benzotricyclo[4.1.1.0^{2,7}]oct-3-ene (6-Cl). A solution of 40 mg (0.18 mmol) of *exo*-5-Cl in 0.5 mL of acetone-d_6 containing 3% D_2O in a Pyrex NMR tube was examined by ^{1}H NMR and was observed to contain about 2–3% of *endo*-5-Cl. The solution was irradiated with six 300-nm lamps in the Rayonet and monitored periodically by ^{1}H NMR. After 10 h of irradiation, 50% of starting material had reacted. Four products were observed which in total accounted for three-fourths of the loss of starting material. These products (and their relative proportions among the identified products) were *exo*-5-OH (38%), 6-OH (19%) (believed to arise from *exo*-5-OH), *anti*-4-Cl[4] (5%), and a compound assumed to be 6-Cl (38%). The assignment of structure of 6-Cl was based on the chemical shift of its carbinyl proton (0.3 ppm downfield of the signal for the carbinyl proton of *exo*-5-Cl, just as the H-2 signal for 6-OH is 0.3 ppm downfield of that for *exo*-5-OH) and its multiplicity (a 3 Hz doublet) and its solvolysis (see below). After 100 h of irradiation only 5–10% of the starting material remained. The product ratios were similar to those observed after 10 h (with the expected increase in the relative proportion of 6-OH) except that one additional product, 7-OH, now comprised approximately 5% of the product mixture. This compound could arise as the (ground- or excited-state) solvolysis product of 6-Cl. To provide additional support for the identification of 6-Cl as a product in this irradiation, the solution was diluted with D_2O (injected by syringe) to give a solution of approximately 35% D_2O/65% acetone-d_6. the still-sealed NMR tube was heated at 54–60 °C for 12 h. (Under these conditions benzylic chlorides would be expected to solvolyze to give alcohols of the same carbon skeleton while the other compounds in the mixture should not

react.) ^{1}H NMR showed that the presumed 6-Cl had hydrolyzed to give (at least predominantly) 7-OH (and the starting material which had remained after the irradiation had hydrolyzed to give *exo*-5-OH).

Benzophenone-Sensitized Irradiation of *exo*-5-Cl in Wet CD_3CN. A solution of 43 mg (0.19 mmol) of *exo*-5-Cl and 13 mg (0.07 mmol) of benzophenone in 0.5 mL of CD_3CN containing 2% D_2O in a Pyrex NMR tube was irradiated with 16 300-nm lamps in the Rayonet. It was monitored during the irradiation by ^{1}H NMR. After 6 h of irradiation, approximately 70% of the starting material had reacted. Five products (which accounted for about 60% of the lost starting material) were observed. These products (along with the percentage of the identified product which they represented) were *exo*-5-OH (18%), 6-OH (9%), *exo*-5-$NDCOCD_3$ (15%), *anti*-4-Cl (25%), and 6-Cl (33%). A trace of 7-OH, the solvolysis product of 6-Cl, was also present. Some small, unidentified ^{1}H NMR resonance were also observed.

Acetone-Sensitized Irradiation of *exo*-5-Cl in Wet CD_3CN. A solution of 34 mg (0.15 mmol) of *exo*-5-Cl in 0.5 mL of CD_3CN containing 10% acetone-d_6 and 3% D_2O in a Pyrex NMR tube was irradiated with 16 300-nm lamps in the Rayonet. The experiment was monitored periodically by ^{1}H NMR. After 6.0 h of irradiation, approximately 55% of the starting material had reacted. Five products were observed (which appeared to represent more than 90% of the reacted starting material). These products (along with the percentages of the observed product which they represented) were *exo*-5-OH (25%), 6-OH (12%), *exo*-5-$NDCOCD_3$ (13%), *anti*-4-Cl (22%), and 6-Cl (29%).

Direct Irradiation of *exo*-5-Cl. A solution of 28 mg (0.12 mmol) of *exo*-5-Cl in 0.5 mL of CD_3CN containing 2% D_2O in a quartz NMR tube was examined by ^{1}H NMR both before and after 21 h in the dark. No change during this period was observed. The solution was then irradiated with 12 254-nm lamps in the Rayonet and examined periodically by ^{1}H NMR. After 1.5 h of irradiation 50% of the starting material had reacted. Four products (which in total accounted for only 50% of the loss of starting material) were observed. These products were *exo*-5-OD (53%), *endo*-5-Cl (21%), 6-OD (16%) (believed to be a secondary product arising from the *exo*-5-OD), and *exo*-5-$NDCOCD_3$ (10%). No other products could be identified; however, the ^{1}H NMR spectrum was consistent with the speculation that any other specific products must be minor relative to those which were identified. After 8 h of irradiation over 70% of starting material had been lost. Little change in the relative proportions of the products was seen (except that the relative amount of 6-OH had increased). A trace of *anti*-4-Cl was detected at this time; however, it is not possible to state that this could not have been present in the starting material. Irradiation was continued to 100 h. Little additional change occurred (probably because of the development of a brown film on the inside walls of the NMR tube).

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Registry No. *syn*-4-OH, 72204-35-4; *anti*-4-Cl, 75947-49-8; 5-K, 102306-40-1; *exo*-5-OAc, 102306-38-7; *endo*-5-OAc, 102418-45-1; *exo*-5-OH, 102306-39-8; *endo*-5-OH, 102418-46-2; *exo*-5-Cl, 102306-41-2; *endo*-5-Cl, 102418-47-3; *exo*-5-$NHCOCH_3$, 102306-42-3; *endo*-5-$NHCOCH_3$, 102418-48-4; *exo*-5-$NDCOCD_3$, 102306-46-7; 6-OH, 102306-43-4; 6-K, 102306-44-5; 6-Cl, 102306-45-6; 7-OH, 102418-49-5.

Carbonylation of β-Aminoethanols, Diols, and Diol Amines†

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Oxazolidinones are prepared from the palladium-catalyzed carbonylation of β-aminoethanols under mild conditions. With *N*-alkyl-substituted substrates, conditions for double carbon monoxide incorporation to give morpholinediones have been discovered. Cyclic carbonates can be prepared from the carbonylation of diols. The carbonylation of *N*-phenyl-1-aminopropane-2,3-diol can give either the carbonate or oxazolidinone as the major product depending on the reaction conditions.

Oxazolidinones are an important class of heterocyclic compounds which have many biological uses.[1] Their preparation normally involves the use of dangerous phosgene or phosgene-based reagents. An attractive alternative to phosgene is carbon monoxide; recently, several groups have reported on the use of carbon monoxide to prepare carbamates and carbonates.[2,3] We report that oxazolidinones can be readily prepared from the palladium-catalyzed carbonylation of β-amino alcohols under mild conditions. We have also discovered conditions for double carbonylation of β-aminoethanols containing *N*-alkyl substituents to give morpholine-2,3-diones.

Results

The reaction of *N*-alkyl-β-amino alcohols with carbon monoxide in the presence of 4–10 mol % of $PdCl_2$ with $CuCl_2$ as oxidant and NaOAc as based in ethylene glycol dimethyl ether (DME) gives 75–95% yields of the oxazolidinone (Table I). The reaction conditions are mild; only

Table I. Catalytic Reactions[a]

β-amino alcohols			oxazolidinone yield, %
R_1	R_2		
n-Bu	Ph		94[c]
t-Bu	Ph		83[c]
n-Bu	CH_3		95[b]
Me	H		77[b]
$CH_3C{=}O$	H		34[c]
Ph	H	$PdCl_2/CuCl_2/NEt_3$/room temp	48[c]

[a] 4–10 mol % of $PdCl_2$ was used with 2 equiv of base and oxidant. Mixture was heated at 80 °C overnight except for the last example. [b] Isolated yield. [c] GC yield based on added internal standard.

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