4, olefinic), 2.87 (m, 2, doubly allylic hydrogens), and 2.27 (m, 2, allylic hydrogens).

Pyrolysis of 28. An nmr tube containing 6 mg (0.064 mmol) of **28** which had been sealed *in vacuo* at −196° was placed in an oven maintained at 173° for 15 min. After the tube had been removed from the oven and allowed to cool, it was opened, deuteriochloroform–TMS was added, and the nmr spectrum was immediately recorded. Only cycloheptadiene (**29**) and a small amount of unreacted tricycloheptane (**28**) were found to be present (ratio of approximately 8:1). Flame-ionization vpc confirmed that these were the only components of the mixture.

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Registry No. **6**, 34783-14-7; **7a**, 33995-51-6; **7b**, 49586-94-9; **8a**, 33995-52-7; **8b**, 49586-96-1; **9**, 33930-83-5; **12**, 34780-54-6; **13**, 33995-53-8; **14**, 33995-55-0; **15**, 33930-85-7; **16**, 49585-76-4; **17**, 49585-77-5; **18**, 34780-61-5; **19**, 33995-54-9; **20**, 33995-56-1; **21**, 4249-11-0; **22**, 33930-86-8; **23**, 33930-84-6; **24**, 49587-03-3; **25**, 49587-04-4; **26**, 49587-05-5; **27**, 22144-75-8; **28**, 28102-61-6; *N*-phenyltriazolinedione, 4233-33-4; cycloheptatriene, 544-25-2.

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Dissolving Metal Reduction of *anti*-Tricyclo[3.2.0.0^{2,4}]heptanes and *anti*-Tricyclo[3.3.0.0^{2,4}]octanes. Intramolecular Epoxide Cleavage as a Route to Highly Strained Tricyclic Alcohols

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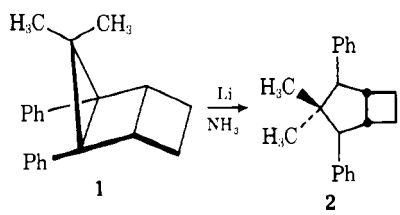
Reduction of epoxides derived from *anti*-tricyclo[3.2.0.0^{2,4}]hept-6-enes and *anti*-tricyclo[3.3.0.0^{2,4}]oct-6-enes with lithium in liquid ammonia affords exo tricyclic alcohols in high yield. The process involves initial reductive cleavage of the internal cyclopropane bond followed by back-side attack on the proximate C–O bond with formation of a new cyclopropane ring. The value of the synthetic method is revealed by the ready access which is gained to functionalized strained molecules inaccessible by other methods.

The relatively recent findings that phenyl substitution of cyclopropanes promotes their ready alkali metal cleavage and the intriguing stereoselectivity of these ring openings have stimulated considerable current interest.[2,3] Because the direction of cleavage of variously phenylated cyclopropane rings is minimally influenced by steric effects but markedly affected by electronic factors, a radical anion mechanism has been ascribed to the bond-breaking step. Subsequent events include addition of a second electron and ultimate protonation. In all likelihood, a range of mechanisms from purely radical anion to dianion is capable of operation depending upon the particular system

under study. Thus, when a more extensive π system as in cyclopropylnaphthalene is present, a dianion pathway comparable in nature to that which seemingly operates with cyclopropyl ketones[4] is perhaps favored. Further mechanistic work is required before these issues are fully resolved.

Irrespective of whether the rate-determining transition state occurs at the one- or two-electron transfer stage, reduction cleavage of a cyclopropane ring generates an intermediate species which is anionic in nature. To our knowledge, the latent chemical reactivity of radical anions or dianions produced under such conditions has not heretofore been investigated and, in particular, has not been put to synthetic use.[5] The major question studied to date has dealt with the regioselectivity of the reductive cleavage.[2,3] The present report describes a preparative application of this process which provides a convenient synthetic entry to otherwise difficultly accessible strained tricyclic alcohols.[6]

Since the synthesis of 1 is readily accomplished,[7] this hydrocarbon became the obvious example for testing the reducibility of phenyl-substituted *anti*-tricyclo[3.2.0.$0^{2,4}$]-heptanes. When 1 was allowed to react with 2 equiv of lithium metal in liquid ammonia, reduction proceeded readily to give 2 in 90% isolated yield, presumably as a mixture of isomers. In similar fashion, exo alcohol 3 was converted to 4. These results attested convincingly to the fact that the C_2–C_4 bond in these strained alicyclic molecules is particularly susceptible to reductive cleavage, at least when phenyl substituents are positioned at these sites.



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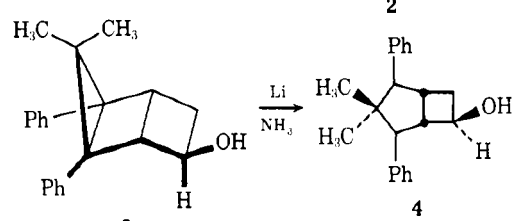
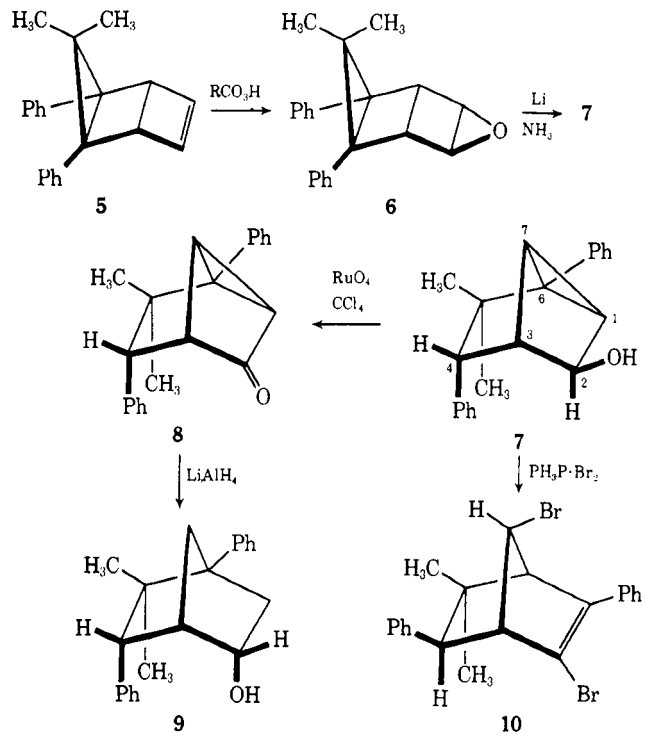
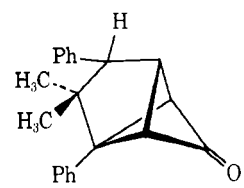


3 4

Addition of lithium to a liquid ammonia solution of epoxide 6,[8] readily available from *m*-chloroperbenzoic acid oxidation of tricycloheptene 5, led to the formation of a configurationally pure dihydro alcohol, the *exo*-tricyclo[4.1.0.$0^{3,7}$]heptan-2-ol 7, in 90% yield. The definitive spectral data for 7 include an infrared peak at 3330 cm^{-1} arising from the secondary hydroxyl group and lanthanide shifting of its ^1H nmr signals. The pmr spectrum ($CDCl_3$, 60 MHz) includes singlets at δ 1.02 and 0.88 (3 H each, methyls), multiplets at δ 7.2 (10 H), 3.13 (2 H), 2.58 (2 H), and 1.88 (1 H), and a particularly revealing doublet (J = 3.7 Hz) for the >CHOH proton at δ 4.55. The overall multiplicity of this last absorption and the magnitude of the coupling constant is consistent only with exo substitution at C_2.[9] Were the hydroxyl group oriented endo, a doublet of doublets pattern ($J \cong$ 3–4 and 7 Hz) would be expected.[9,10] The spatial orientation of the OH substituent was further substantiated by the relative downfield shifting of the various signals upon incremental addition of Eu(fod)$_3$. In particular, the relevant ΔEu values[11] of the tertiary protons were seen to decrease in the order H_2 (−11.53), H_3 (−7.93), H_7 (−5.97), H_1 (−4.26), and H_4 (−2.37).



Oxidation of 7 with ruthenium tetroxide[12] proceeded in high (96%) yield to give ketone 8, which was readily differentiated from isomer 11[13] on the basis of its spectral



11

features. The carbonyl stretching frequency which appears at 1725 cm^{-1} is inconsistent with a cyclobutanone part structure but compatible with a strained conjugated cyclopropyl ketone formulation, particularly when geometrical factors are considered.[14] Furthermore, the ultraviolet maxima (CH_3CN) which are seen at 228 (ϵ 1740), 252 (350), 258 (435), and 265 (340) reflect not only the high ground state strain in 8 but also the geometrically enforced dihedral angle between the carbonyl group and the cyclopropane ring.[14]

Interestingly, when 8 was treated with lithium aluminum hydride in refluxing tetrahydrofuran, the cyclopropane ring was cleaved simultaneously with reduction of the carbonyl group and *endo*-norbornanol 9 was produced. That the C_1–C_7 and not the C_1–C_6 cyclopropyl bond had been severed was attested to by the presence of only one (H_4) benzylic proton in the nmr spectrum of 9 (see Experimental Section). This transformation is particularly reminiscent of those observed in the conversions of α,β-unsaturated ketones to fully saturated alcohols under comparable conditions.[15]

The endo stereochemistry of the 4-phenyl substituent in 7 was deduced from the coupling constant of H_4 with H_3 (J = 3.6 Hz) characteristic of an exo norbornyl proton.[16] This assignment received further support from the finding that 7 reacts with triphenylphosphine dibromide[17] to give dibromide 10, whose detailed stereochemistry and structure was established by three-dimensional X-ray analysis.

A well-formed crystal with the approximate dimensions 0.3 × 0.2 × 0.1 mm was mounted, and precession and Weissenberg photographs were used to determine cell constants and diffraction symmetry. The crystals were tri-

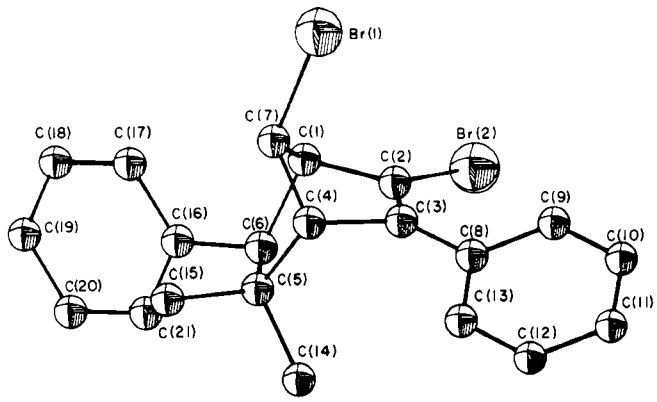


Figure 1. Computer-generated drawing of 2,*syn*-7-dibromo-5,5-dimethyl-3,*exo*-6-diphenylnorbornene (**10**).

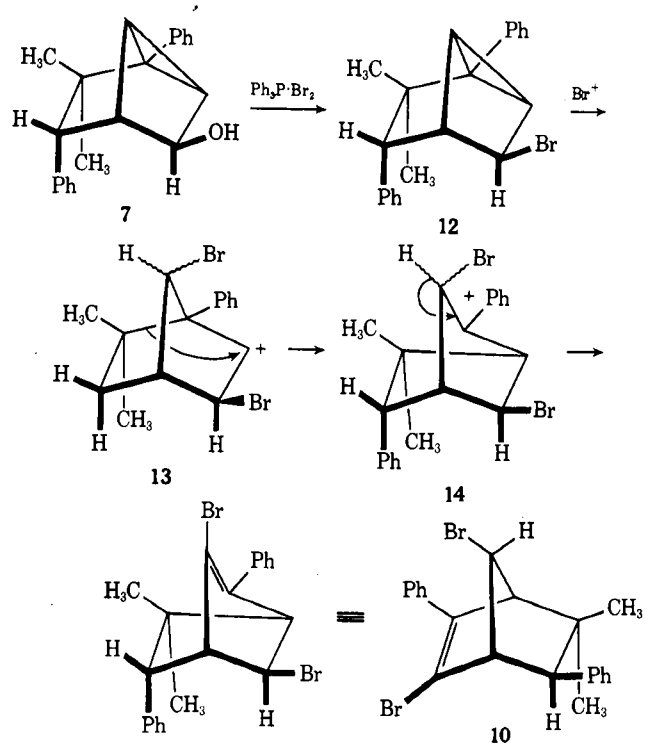
clinic with diffractometer-measured cell constants of a = 11.20 (1), b = 7.25 (1), c = 11.71 Å (1), α = 84.08 (5), β = 107.08 (6), γ = 90.00° (7). The calculated density for Z = 2 is 1.59 g/cm^3 and the observed density is 1.57 g/cm^3. The linear absorption coefficient is only 28 cm^{-1}; so no correction was made.

A total of 3305 independent reflections with θ less than 25° were measured on a Hilger-Watts four-cycle diffractometer. The intensity of each was measured by a θ–2θ step scan, and the backgrounds were measured by stationary front and back counts for each reflection independently. A total of 2230 reflections were found to have intensities at least three times their standard errors. These were taken to be observed and used in the solution and refinement of the structure.

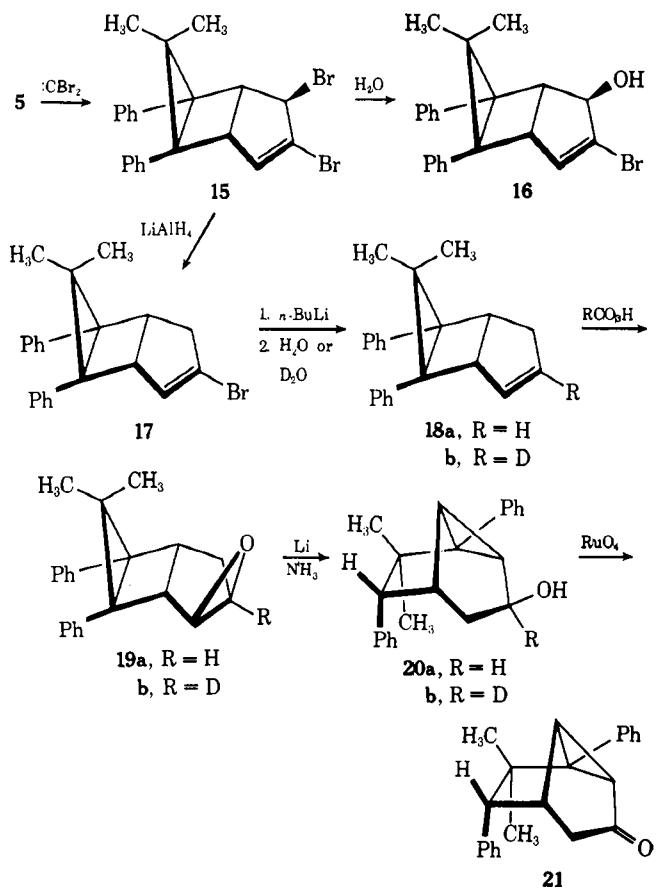
The structure was readily solved by use of a Patterson synthesis and subsequent Br-phased electron density syntheses. The structure was refined by full-matrix least-squares techniques. In the final refinement the correction for the real and imaginary parts of the anomalous dispersion for the bromine atoms was used, and the temperature factors of the bromine atoms and all the carbon atoms were allowed to vary anisotropically. The hydrogen atoms were seen in the final difference Fourier, but their positions would not refine well, and they were not included in the last least-squares cycles. The final crystallographic agreement parameter, R, is 0.079 and the final weighted R is 0.091.

Figure 1 shows a computer-generated drawing of the final X-ray model. All bond distances and angles agree well with generally accepted values.

The conversion of **7** to **10** is an unusual transformation involving not only the introduction of two bromine atoms but substantial C–C bond relocation as well. By analogy with the observation that *exo*-norbornanol reacts with triphenylphosphine dibromide to give chiefly exo bromide of retained structure,[18] we tentatively view the reaction as proceeding without significant stereochemical loss at C_2 (*cf.* **12**). Electrophilic ring opening by bromonium ion with formation of norbornyl cation **13** could serve to initiate 1,2 shift of C_5 with resultant formation of the more stable **14**. Deprotonation of **14** would then lead to the observed dibromide. It is, of course, not known rigorously whether the hydroxyl → bromine interchange at C_2 precedes cleavage of the adjoining three-membered ring. However, this would appear to be entirely plausible in view of the known reactivity of these tricyclic systems.[9,10] Additionally, were **10**-7-OH an intermediate in the formation of **10**, replacement of the 7-OH by bromine with retention of configuration would be rather unlikely because of the very probable intervention of the 7-norbornenyl cation in this instance.[18,19] Although this proposed mechanism remains but a working hypothesis, it does account reasonably for the apparent inversion at C_4 in **7**, the ultimate syn orientation of the 7-bromo substituent in **10**, and the positioning of both bromine and phenyl groups on the double bond.



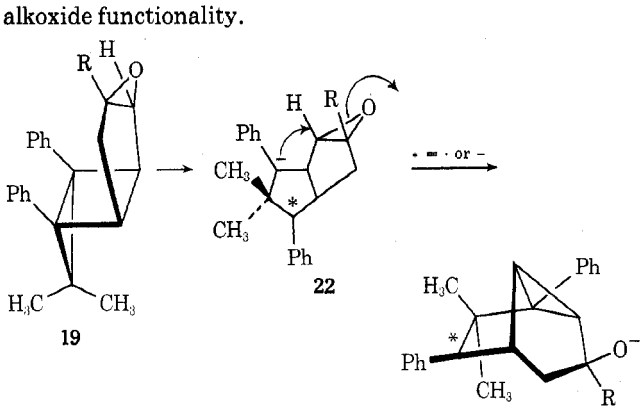
To gain further insight into the generality and mechanism of the title reaction, epoxides **19a** and **19b** were synthesized. These ring-expanded structures were derived by initial reaction of **5** with dibromocarbene followed by direct lithium aluminum hydride reduction of the rear-



ranged dibromide **15** so produced. All attempts to isolate **15** resulted in very rapid hydrolysis of the allylic bromine to give bromohydrin **16**. Halogen–metal interconversion in **17** (*n*-BuLi in ether) followed by addition of water or deuterium oxide furnished **18a** and **18b**, respectively. The pmr spectrum ($CDCl_3$, 60 MHz) of **18a** has methyl singlets at δ 1.57 and 0.73, a pseudo-singlet aryl absorption (10 H) at δ 7.22, multiplets of area 1 at δ 5.8, 5.55, 3.3, and 2.85, and a two-proton multiplet at δ 2.35. From the absence of the δ 5.8 signal in the spectrum of **18b**, unequivocal assignment of the two low-field multiplets to the pair of olefinic protons is possible.

Epoxide **19a**, when subjected to the action of lithium in liquid ammonia, gave alcohol **20a** in 95% yield. The pmr spectrum of the latter compound displays a ten-proton aryl singlet at δ 7.3, two methyl singlets at δ 1.19 and 0.73, and an endo α-hydroxyl proton adjacent to a methylene group (t, J = 5.5 Hz, 5.06). The methylene and methine protons appear together with the hydroxyl signal as two groups of multiplets centered at δ 2.85 (4 H) and 1.72 (3 H). In the pmr spectrum of **20b**, the α-hydroxyl absorption was lacking. Oxidation of **20a** with ruthenium tetroxide resulted in facile conversion to ketone **21**, which exhibited an anticipated carbonyl stretching frequency at 1695 cm^{-1}.

From these data, it is evident that opening of the epoxide ring in **6** and **19** is highly regiospecific. Recognizing that initial reduction of the epoxide ring in these molecules would not be expected to result in preferential C–O bond cleavage,[20] we conclude that the cyclopropyl bond common to the two phenyl substituents is ruptured (as in the case of **1** and **3**) with overwhelming kinetic preference. Once access is gained to radical anion **22** or its dianion equivalent,[2,3] rear-side attack on the proximate oxirane carbon atom occurs with formation of a cyclopropane ring. Protonation of anion **23** likely operates under kinetically controlled conditions[21] from the exo direction to place the phenyl substituent in an endo stereodisposition. Although **23** is also a phenyl-substituted cyclopropane derivative, it is presumably protected from further facile reduction because of electrostatic influences arising from the adjacent alkoxide functionality.



Thus, intramolecular epoxide cleavage which follows upon dissolving metal reduction of proximal cyclopropane rings makes possible the ready synthesis of functionalized strained-ring compounds. Although the work presented here relates to the preparation of tricyclic alcohols having exo stereochemistry, other synthetic applications of this reaction can be conceived and the likely generality of the method may prove to be of future importance.

Experimental Section

Melting points are corrected. Proton magnetic resonance spectra were obtained with Varian A-60A and HA-100 spectrometers and apparent splittings are cited. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

3,3-Dimethyl-2,4-diphenylbicyclo[3.2.0]heptane (2). To several 2-mm pieces of lithium wire dissolved in 50 ml of anhydrous liquid ammonia was added a solution containing 140 mg (0.530 mmol) of 1[7] in 2 ml of ether. The deep blue solution was stirred for 2 hr at −33°. Ethanol was added until the color was discharged, the ammonia was allowed to evaporate, and ether was added to the residue. The organic layer was washed with two 50-ml portions of water, dried, and evaporated *in vacuo*. Tlc analysis (silica gel–pentane) revealed one major spot and two very minor spots. The mixture was separated by preparative layer chromatography (silica gel–pentane). The product was purified by microdistillation and afforded 127 mg (90%) of colorless oil: obsd m/e 276; ir (KBr) 2915, 1610, 1495, 1471, 1431, 1389, 1364, 1238, 1160, 1117, 1078, 1031, 909, 900, 793, 754, and 694 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.3 (m, 10, aryl), 3.1–2.4 (m, 8), 1.25 (s, 3, CH_3), and 1.15 (s, 3, CH_3).

Anal. Calcd for $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 90.80; H, 8.76.

***anti*-3,3-Dimethyl-2,4-diphenyltricyclo[3.2.0.0^{2,4}]heptan-*exo*-6-ol (3).**[22] Into a magnetically stirred solution of 1.816 g (0.0066 mol) of 5[23] in 50 ml of tetrahydrofuran under nitrogen was introduced 7.3 ml of diborane solution (1.03 M in BH_3, 0.0075 mol) and the reaction mixture was stirred for 3 hr. Heating to 40° was followed by slow addition of 3 N sodium hydroxide solution (3.5 ml) and 30% hydrogen peroxide solution (3.5 ml). Addition of saturated sodium chloride solution (25 ml), removal of the organic layer, and extraction of the aqueous layer with ether (2 × 25 ml) was followed by drying of the combined organic layers. Filtration, solvent removal, and chromatography on silica gel with elution by hexane–ether (8:2) gave 1.78 g (92%) of the desired alcohol. Recrystallization from hexane furnished fine white needles: mp 114–117°; ir (KBr) 3268, 2907, 1603, 1488, 1441, 1319, 1224, 1080, 993, 819, 773, and 752 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.21 (m, 10, aryl), 4.31 (m, 1, H_6), 1.98–2.95 (envelope, 5, H_1, H_5, H_7, H_7, and hydroxyl), 1.28 and 0.77 (s, 3 each, methyls). This compound could not be obtained analytically pure and therefore the 3,5-dinitrobenzoate derivative was prepared.

To a solution of 0.871 g (0.003 mol) of 3 in 5 ml of anhydrous pyridine was added a solution of 1.384 g (0.006 mol) of 3,5-dinitrobenzoyl chloride in 20 ml of pyridine. The solution was stirred for 30 min at room temperature and placed in a freezer (−10°) for 48 hr. Upon removal, the yellow mixture was poured into 400 ml of ice water, stirred for 4 hr, and filtered to give the crude dinitrobenzoate. This was chromatographed on silica gel, eluted with benzene, decolorized with charcoal, and recrystallized from ether to give 1.13 g (78%)of the dinitrobenzoate: mp 145.5–147.5°; ir (KBr) 1724, 1541, 1340, 1277, 1171, 921, 774, 729, 719, and 697 cm^{-1}; δ_{TMS} ($CDCl_3$) 8.75 (s, 3, dinitrobenzoate aryl), 7.30 (br s, 10, aryl), 5.36 (m, 1, H_6), 2.33–3.33 (envelope, 4, H_1, H_5, H_7, H_7), 1.41 and 0.87 (s, 3 each, methyls).

Anal. Calcd for $C_{28}H_{24}N_2O_6$: C, 69.41; H, 4.99; N, 5.78. Found: C, 69.41; H, 4.99; N, 5.97.

3,3-Dimethyl-2,4-diphenylbicyclo[3.2.0]heptan-6-ol (4). To several 2-mm pieces of lithium wire dissolved in 50 ml of anhydrous liquid ammonia was added 290 mg (1.0 mmol) of 3 dissolved in 2 ml of dry tetrahydrofuran. The mixture was stirred at −33° for 2 hr and treated dropwise with ethanol until the blue color was discharged. The ammonia was allowed to evaporate and the residue was dissolved in chloroform, washed with water, dried, and evaporated *in vacuo*. Pentane was added to the remaining oil and the white precipitate that formed was removed by filtration. The product was crystallized from hexane to yield 140 mg (49%) of white crystals: mp 117–118°; δ_{TMS} ($CDCl_3$) 7.4 (m, 10, aryl), 4.9 (broad m, 1), 3.1 (broad m, 6), and 1.9 (broad s, 1, -OH).

7,7-Dimethyl-6,8-diphenyl-3-oxatetracyclo[3.3.0.0^{2,4}.0^{6,8}]octane (6). A mixture of 720 mg (2.62 mmol) of 5 and 500 mg (2.90 mmol) of *m*-chloroperbenzoic acid was stirred in 25 ml of chloroform at 25° for 8 hr. An additional 25 ml of chloroform was added and the solution was washed with two 50-ml portions of 10% sodium bicarbonate solution. The chloroform solution was dried, filtered, and evaporated *in vacuo*. The remaining oil was chromatographed (silica gel–benzene) and the benzene eluate was evaporated *in vacuo* to give an oil which soon crystallized. There was obtained 720 mg (94.5%) of white crystals: mp 71–72.5° from ethanol; ir (KBr) 2899, 1486, 1439, 1323, 1016, 1072, 1030, 945, 955, 792, 776, 731, 710, and 696 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.25 (s, 10, aromatic), 3.93 (d, J = 3 Hz, 2, >CHO–), 3.0 (d, J = 3 Hz, 2, methine), 1.29 (s, 3, CH_3), and 0.85 (s, 3, CH_3).

Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.57; H, 7.01.

5,5-Dimethyl-*endo*-4,6-diphenyltricyclo[4.1.0.0^{3,7}]heptan-*exo*-2-ol (7). To 20 ml of anhydrous ammonia containing 28.0 mg (4 mg-atoms) of lithium wire was added 576 mg (2 mmol) of epoxide dissolved in 3 ml of ether. The mixture was stirred for 1 hr at −33° and ethanol was added until the blue color faded. The ammonia was allowed to evaporate and the residue was taken up in ether. The ether layer was washed with water (2 × 50 ml), dried, and evaporated *in vacuo*. The remaining oil soon crystallized from hexane to give 522 mg (90%) of colorless crystals: mp 121–123°; ir (KBr) 3300, 2924, 1613, 1500, 1443, 1431, 1362, 1220, 1136, 1089, 1069, 1047, 1032, 826.4, 789.3, 757, 729, and 700 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.2 (s, 10, aryl), 4.55 (d, J = 3.7 Hz, 1), 3.13 (m, 2), 2.58 (m, 2), 1.88 (m, 1), 1.02 (s, 3, CH_3), 0.88 (s, 3, CH_3).

Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.85; H, 7.52.

5,5-Dimethyl-*endo*-4,6-diphenyltricyclo[4.1.0.0^{3,7}]heptan-2-one (8). Alcohol 7 was oxidized with a ruthenium tetroxide solution prepared as follows.[12] To 50 mg of black ruthenium dioxide (Englehardt) in 10 ml of carbon tetrachloride at 0° was added 10 ml of a 10% aqueous sodium periodate solution. The two-phase mixture was stirred vigorously at 0° until the black ruthenium dioxide was transformed into the characteristically yellow soluble ruthenium tetroxide. The carbon tetrachloride layer was separated from the aqueous layer and used immediately.

To 100 mg (0.345 mmol) of alcohol 7 in 10 ml of carbon tetrachloride cooled to 0° was added the above ruthenium tetroxide solution. The mixture, which immediately turned black, was stirred for 0.5 hr at 0°. The solution was filtered and the filtrate was treated with a small portion of activated carbon and filtered through Celite. After evaporation of solvent, the remaining oil soon crystallized (in those runs where crystallization did not take place, the oil was triturated with pentane) and was recrystallized from hexane. There was obtained 95 mg (95.6%) of colorless crystals: mp 117–118°; ir (KBr) 2900, 1725, 1510, 1450, 1350, 1125, 880, 820, 790, 775, 750, 735, and 700 cm^{-1}; λ_{max} (CH_3CN) 227.7 nm (ϵ 1740), 252.5 (356), 258.5 (436), and 265.0 (343); δ_{TMS} ($CDCl_3$) 7.32 (s, 10, aryl), 3.42 (m, 3), 3.15 (m, 1), 0.94 (s, 3, CH_3), 0.70 (s, 3, CH_3).

Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.34; H, 7.02.

5,5-Dimethyl-4,*endo*-6-diphenylnorbornan-*endo*-2-ol (9). A mixture of 100 mg (0.347 mmol) of ketone 8 and 200 mg of lithium aluminum hydride in 25 ml of tetrahydrofuran was refluxed for 15 hr. Water was cautiously added, followed by anhydrous magnesium sulfate. The mixture was filtered and evaporated *in vacuo*. Pentane was added to the remaining oil and the white, crystalline precipitate was removed by filtration. The product was recrystallized once from acetone and once from hexane to give 60 mg (61.3%) of colorless crystals: mp 142.5–144.5°; δ_{TMS} ($CDCl_3$) 7.6–7.2 (m, 10, aryl), 4.48 (m, 1), 3.27 (d, J = 4.0 Hz, 1), 2.9 (m, 1), 2.2–1.6 (m, 5), 1.1 (s, 3, CH_3), and 0.8 (s, 3, CH_3); m/e 292.1822 (calcd m/e, 292.1827).

Anal. Calcd for $C_{21}H_{24}O$: C, 86.25; H, 8.27. Found: C, 86.25; H, 8.20.

2,*syn*-7-Dibromo-5,5-dimethyl-3,*exo*-6-diphenylnorbornene (10). To 262 mg (1 mmol) of triphenylphosphine in 5 ml of anhydrous dimethylformamide was added 0.1 ml (1.82 mmol) of bromine. The mixture was stirred for 10 min and 290 ml (1 mmol) of alcohol 7 was introduced. The mixture was stirred at 45–50° for 12 hr, poured into 100 ml of water, and extracted with ether (2 × 50 ml). The combined ether layers were washed with water 2 × 50 ml), dried, and evaporated *in vacuo*. The remaining yellow residue was triturated with pentane and filtered. The filtrate was evaporated *in vacuo* and the remaining yellow oil was chromatographed (silica gel–hexane). After evaporation of the solvent, there remained a colorless oil that soon crystallized. The product was recrystallized from pentane to furnish 148 mg (34.4%) of colorless crystals: mp 142.5–143.5°; δ_{TMS} ($CDCl_3$) 7.0–7.8 (m, 10, aryl), 4.77 (t, J = 1.8 Hz, 1), 3.35 (m, 1), 3.13 (m, 1), 2.88 (s, 1), 1.15 (s, 3, CH_3), and 0.73 (s, 3, CH_3).

Anal. Calcd for $C_{21}H_{20}Br_2$: C, 58.65; H, 4.69. Found: C, 58.24; H, 4.68.

Collection and Reduction of Intensity Data. Clear crystals of $C_{21}H_{20}Br_2$ were grown by slow evaporation of a CH_2Cl_2–heptane solution. Preliminary Weissenberg photography of the *h*0*l* and *h*1*l* and the precession photography of the 0*kl* and 1*kl* zones showed that the crystals belonged to the triclinic system with space groups P_1 or $P\bar{1}$. The crystal selected for data collection had approximate dimensions 0.30 × 0.15 × 0.08 mm with the b^* axis colinear with the spindle axis. θ values for 20 strong reflections were accurately measured on a Hilger-Watts four-circle diffractometer and least-squares analysis gave the following cell constants: a = 11.20 (1), b = 7.25 (1), c = 11.76Å (1), α = 84.08 (1), β = 107.08 (2), and γ = 90.00° (2). The calculated density of 1.60 g cm^{-3} for two formula weights per unit cell agreed with values measured by flotation in aqueous $ZnCl_2$ solution. All reflections in the *hkl*, $\bar{h}$*kl*, *hk*$\bar{l}$, and $\bar{h}$*k*$\bar{l}$ octants with $\theta \leq 25°$ were measured using Zr-filtered Mo Kα (0.71069 Å) radiation. Reflections were measured using the θ–2θ scan mode with stationary crystal-stationary counter backgrounds measured at $\theta_{hkl} \pm (0.25° + 0.01\theta_{hkl})$ for half of the net time as the peak was measured. Periodically checked standard reflections revealed no decrease in intensity. The adsorption coefficient for this material is 6 cm^{-1} and no correction was deemed necessary. A total of 3305 reflections were measured and after correction for Lorentz, polarization, and background effects 2230 were judged to have $I \geq 3\sigma(i)$ and were considered observed.

Solution and Refinement. The three-dimensional Patterson synthesis was deconvoluted assuming space group $P\bar{1}$ to yield two independent Br positions.[24] The Br-phased electron density synthesis revealed all nonhydrogen atoms. Full-matrix, least-squares refinement in which all atoms had anisotropic thermal motions smoothly converged to a final crystallographic discrepancy index of R = 0.079 and wR = 0.091. The scattering factors were those of Cromer and Waber.[25] In Table III we give final fractional coordinates for all nonhydrogen atoms and their temperature factors; in Table I we give selected bond distances and Table II contains bond angles.[26] Finally, in Figure 1 we give a computer-generated, perspective drawing of the final X-ray model.

7-Bromo-3,3-dimethyl-2,4-diphenyltricyclo[3.3.0.0^{2,4}]oct-6-en-*exo*-8-ol (16). To 272 mg (1 mmol) of 5 and 450 mg of potassium *tert*-butoxide in 10 ml of olefin-free pentane at 0° was added dropwise 600 mg of bromoform in 5 ml of pentane during 5 min. The mixture was allowed to stir for 0.5 hr at 0° and for 1 hr at 25°. Pentane (25 ml) was added and the solution was washed once with water (50 ml), dried, filtered, and evaporated *in vacuo*. Tlc (silica gel–pentane) showed starting material to be present (25% by nmr). The mixture was separated by preparative layer chromatography (silica gel–pentane) and the fraction with the lowest R_f was collected. The oil so obtained soon crystallized and was recrystallized from hexane: 165 mg (43.4%); mp 133–135°; m/e 380.0770 (calcd m/e, 380.0776); ir (KBr) 3226 (broad), 2899, 1613, 1502, 1449, 1070, 1042, 1031, 1000, 859, 836, 809, 765, 738, and 699 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.26 (m, 10, aryl), 5.95 (d, J = 2.8 Hz, 1, vinyl), 4.90 (d, J ' 3.0 Hz, 1), 3.50 (m, 3), 1.60 (s, 3, CH_3), and 0.80 (s, 3, CH_3).

Anal. Calcd for $C_{22}H_{21}BrO$: C, 69.30; H, 5.55. Found: C, 69.55; H, 6.00.

7-Bromo-3,3-dimethyl-2,4-diphenyltricyclo[3.3.0.0^{2,4}]oct-6-ene (17). To a mixture of 272 mg (1 mmol) of 5 and 500 mg (4.46 mmol) of potassium *tert*-butoxide in 10 ml of pentane at 0° was added dropwise 600 mg (240 mmol) of bromoform dissolved in 5 ml of pentane. The mixture was stirred at 0° for 1 hr and at 25° for 2 hr, at which point it was filtered through Celite. To the filtrate was added 200 mg of lithium aluminum hydride and the mixture was refluxed for 10 hr. Water was cautiously added and the organic layer was decanted from the aqueous layer, dried, filtered, and evaporated *in vacuo*. The remaining oil was chromatographed on silica gel impregnated with 15% (by weight) of silver nitrate using hexane as the eluent. The white solid was recrystallized from methanol to give 200 mg (54.8%) of the bromide: mp 128–129°; δ_{TMS} ($CDCl_3$) 7.2 (s, 10, aryl), 5.65 (m, 1, vinyl), 3.25–D.2 (m, 4), 1.5 (s, 3, CH_3), and 0.75 (s, 3, CH_3).

Anal. Calcd for $C_{22}H_{21}Br$: C, 72.33; H, 5.79. Found: C, 72.32; H, 5.80.

3,3-Dimethyl-2,4-diphenyltricyclo[3.3.0.0^{2,4}]oct-6-ene (18a). All glassware was thoroughly flame dried before proceeding. To a solution of 100 mg (0.274 mmol) of 17 in 10 ml of anhydrous ether under a nitrogen blanket at 0° was added 2.44 ml (5.48 mmol) of *n*-butyllithium in ether. The mixture was stirred under dry nitrogen for a period of 24 hr at 25°. Water was cautiously added until the evolution of gas ceased. The ether layer was decanted, dried, and evaporated *in vacuo*. The remaining oil was chromatographed on silica gel using pentane as the eluent. The oil so obtained was molecularly distilled to give 60 mg (76.5%) of a crystalline distillate: mp 63–64.5°; m/e 286.1725 (calcd m/e, 286.1721); δ_{TMS} ($CDCl_3$) 7.22 (s, 10, aryl), 5.8 (m, 1, vinyl), 5.5 (m, 1, vinyl), 3.3 (broad m, 1), 2.85 (broad m, 1), 2.35 (broad m, 2), 1.57 (s, 3, CH_3), and 0.73 (s, 3, CH_3).

Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.21; H, 7.91.

3,3-Dimethyl-2,4-diphenyltricyclo[3.3.0.0^{2,4}]oct-6-ene-7-*d* (18b). All glassware was thoroughly flame dried before proceeding. A solution of 100 mg (0.274 mmol) of **17** in 10 ml of anhydrous ether under a nitrogen blanket at 0° was added 2.44 ml (5.48 mmol) of *n*-butyllithium in ether. The mixture was stirred under dry nitrogen at 25° for a period of 24 hr. Deuterium oxide was cautiously added until the evolution of gas ceased. The ether layer was decanted, dried, and evaporated *in vacuo*. The remaining oil was chromatographed on silica gel using pentane as the eluent to give 60 mg (76.5%) of hydrocarbon. This product was used without further purification: δ_{TMS} ($CDCl_3$) 7.22 (s, 10, aryl), 5.5 (m, 1), 3.3 (m, 1), 2.85 (m, 1), 2.35 (m, 2), 1.57 (s, 3, CH_3), and 0.73 (s, 3, CH_3).

8,8-Dimethyl-7,9-diphenyl-3-oxatetracyclo[4.3.0.0^{2,4}.0^{7,9}]nonane (19a). To a solution of 60 mg (0.210 mmol) of **18a** in 10 ml of chloroform at 25° was added 40 mg (0.233 mmol) of *m*-chloroperbenzoic acid. The mixture was stirred at 25° for 3 hr, washed with saturated bicarbonate solution (1 × 25 ml), dried, and evaporated *in vacuo*. The remaining oil was chromatographed on silica gel using benzene as the eluent. The resulting clear oil soon crystallized and was recrystallized from methanol to give 62 mg (97.5%) of white solid: mp 95–97°; δ_{TMS} ($CDCl_3$) 7.2 (m, 10, aryl), 3.5 (d, J = 3.0 Hz, 1), 3.2 (d, J = 3.0 Hz, 1), 2.8 (d, J = 4.0 Hz, 1), 2.57 (m, 1), 1.9 (m, 2), 1.4 (s, 3, CH_3), and 0.70 (s, 3, CH_3).

Anal. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33. Found: C, 87.14; H, 7.33.

8,8-Dimethyl-7,9-diphenyl-3-oxatetracyclo[4.3.0.0^{2,4}.0^{7,8}]nonane-4-*d* (19b). To a solution of 60 mg (0.210 mmol) of **18b** in 10 ml of chloroform at 25° was added 40 mg (0.233 mmol) of *m*-chloroperbenzoic acid. The mixture was stirred at 25° for 3 hr, washed with saturated sodium bicarbonate solution (25 ml), dried over $MgSO_4$, and evaporated *in vacuo*. The remaining oil was chromatographed on silica gel using benzene as the eluent. The resulting clear oil crystallized and was recrystallized from methanol to give 62 mg (97.5%) of white solid: mp 95–97°; *m/e* 303.1736 (calcd *m/e*, 303.1733); δ_{TMS} ($CDCl_3$) 7.2 (m, 10, aryl), 3.28 (s, 1), 2.88 (d, J = 3.8 Hz, 1), 2.63 (m, 1), 1.98 (m, 2), 1.48 (s, 3, CH_3), and 0.73 (s, 3, CH_3).

6,6-Dimethyl-*endo*-5,7-diphenyltricyclo[5.1.0.0^{4,8}]octan-*exo*-2-ol (20a). To 20 ml of anhydrous liquid ammonia containing 28.0 mg (4 mg-atoms) of lithium wire was added 100 mg (0.331 mmol) of epoxide **19a** dissolved in 3 ml of anhydrous ether. The mixture was stirred at −33° for 2 hr and ethanol was added until the blue color was discharged. The ammonia was allowed to evaporate and the residue was taken up in ether. The ether was washed with water (2 × 20 ml), dried, and evaporated *in vacuo*. Pentane was added to the remaining oil and the white precipitate that formed was removed by filtration. Nmr analysis of the crude material revealed only one product. This material was recrystallized from hexane to give 95 mg (94.5%) of white crystals: mp 131–132°; δ_{TMS} ($CDCl_3$) 7.3 (s, 10, aryl), 4.9 (t, J = 5.5 Hz, 1), 3.3–2.6 (m, 4), 1.60 (m, 3), 1.19 (s, 3, CH_3), and 0.73 (s, 3, CH_3); ir (KBr) 3279 (broad), 2924, 1590, 1475, 1449, 1429, 1368, 1250, 1205, 1134, 1070, 1058, 1031, 1021, 1001, 760, 740, and 699 cm^{-1}.

Anal. Calcd for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 87.03; H, 8.03.

6,6-Dimethyl-*endo*-5,7-diphenyltricyclo[5.1.0.0^{4,8}]octan-*exo*-2-ol-*d* (20b). To 20 ml of liquid ammonia containing 28.0 mg (4 mg-atoms) of lithium wire was added 100 mg (0.331 mmol) of epoxide **19b** dissolved in 3 ml of anhydrous ether. The mixture was stirred at −33° for 2 hr and ethanol was added until the blue color was discharged. The ammonia was allowed to evaporate and the residue was taken up in ether. The ether was washed with water (2 × 20 ml), dried, and evaporated *in vacuo*. Pentane was added to the remaining oil and the white precipitate that formed was removed by filtration and recrystallized from hexane to give 95 mg (94.5%) of colorless crystals: mp 131–132.5°; δ_{TMS} ($CDCl_3$) 7.3 (s, 10, aryl), 3.3–2.6 (m, 4), 2.0 (s, 1, -OH), 1.70 (m, 2), 1.2 (s, 3, CH_3), and 0.70 (s, 3, CH_3); *m/e* 305.1891 (calcd *m/e*, 305.1889.

6,6-Dimethyl-*endo*-5,7-diphenyltricyclo[5.1.0.0^{4,8}]octan-2-one (21). To 100 mg (0.329 mmol) of **20a** dissolved in 10 ml of carbon tetrachloride at 0° was added a solution of ruthenium tetroxide prepared as above. The mixture, which turned black immediately, was stirred for 0° for 1 hr, filtered through Celite, and evaporated *in vacuo*. The remaining oil soon crystallized and was recrystallized from hexane to give 94 mg (95.5%): mp 151–152.5°; ir (KBr) 2985, 1695, 1481, 1429, 1399, 1370, 1351, 1250, 1183, 1170, 1124, 1006, 926, 865, 751, and 698 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.2 (s, 10, aryl), 3.4 (m, 1), 3.2 (m, 1), 2.5–2.1 (m, 4), 3.1 (s, 3, CH_3), and 0.70 (s, 3, CH_3).

Anal. Calcd for $C_{22}H_{22}O$: C, 87.37; H, 7.33. Found: C, 87.63; H, 7.34.

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Registry No. 1, 33995-52-7; **2,** 49644-54-4; **3,** 49587-09-9; **4,** 49587-10-2; **5,** 34783-15-8; **6,** 39781-90-3; **7,** 39781-91-4; **8,** 39781-92-5; **9,** 39781-93-6; **10,** 39781-94-7; **16,** 49587-17-9; **17,** 49587-18-0; **18a,** 39781-96-9; **18b,** 49587-20-4; **19a,** 39781-95-8; **19b,** 49644-56-6; **20a,** 39781-97-0; **20b,** 49587-22-6; **21,** 39781-98-1; dinitrobenzoate of **3,** 49587-24-8.

Supplementary Material Available. Tables I–III will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-467.

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The Reduction of 2-Substituted 2-Halonorbornanes by Tri-*n*-butyltin Hydride[1]

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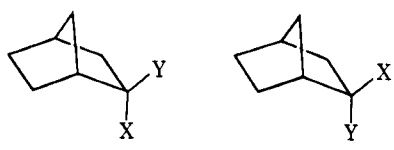
The reduction of a series of 2-substituted 2-halonorbornanes by tri-*n*-butyltin hydride has been carried out. Product analysis revealed that complete loss of stereochemistry had taken place, demonstrating that, unlike similarly substituted vinyl and cyclopropyl radicals, the presence of an electronegative substituent is not sufficient to permit a monosubstituted alkyl radical to retain configurational integrity on the time scale of most nongeminate reactions. The moderate stereoselectivity of the 2-norbornyl radical in atom abstraction reactions is contrasted by the only slight selectivity (k_{exo}/k_{endo} = 1.4) which 2-chloronorbornane exhibits as a halogen donor toward tri-*n*-butyltin radical.

There is considerable spectroscopic evidence in support of the contention[2-4] that the configuration of free radicals is strongly influenced by the difference in electronegativity between the radical center and its substituents. Thus, studies of tri- and difluoromethyl radicals by esr[5] and of trifluoromethyl radicals by infrared spectroscopy[6] and photoionization[7] indicate that these intermediates have a distinctly nonplanar geometry, while the balance of evidence from electronic[8] and electron spin resonance spectra[9] favors a planar structure for the methyl and unsubstituted alkyl radicals. Fluoro- and hydroxymethyl radicals may also persist in a nonplanar configuration.[10] In contrast to the weight of spectroscopic evidence, there exists only scattered chemical information about the nature and, in particular, the configurational integrity of α-substituted alkyl radicals.[11]

We have explored the relationship between substituent electronegativity and the configurational stability of α-substituted alkyl radicals by examining the stereochemistry of the 2-substituted norbornanes obtained from the tri-*n*-butyltin hydride reduction of 2-substituted 2-halonorbornanes of known stereochemistry. In each of the reductions studied the result was that, within our limits of detection, the reduction proceeded with complete *loss* of configuration at the 2 position. A summary of these stereochemical results is presented in Table I.



1 2

X = Cl, Br
Y = F, OCH_3, Cl, CH_3, H

The stereoselectivity of the 2-norbornyl radical in atom-capture reactions has been examined extensively;[15] however, the degree of stereoselectivity involved in atom transfer from a norbornyl ring remains unknown. In an effort to determine the relative selectivity of atom transfer from the 2 position of the norbornyl ring we have examined the competitive reduction of *exo*- and *endo*-2-chloronorbornane using a limiting amount of tri-*n*-butyltin hydride.[16] The observed relative rate constant[17] (k_{exo}/k_{endo} = 1.4 ± 0.1) reveals that only a slight preference exists for exo chlorine abstraction.

The stereospecific synthesis of 1 and 2 (X = Br; Y = F) was achieved by treating 2-bromonorborn-2-ene and 2-fluoronorborn-2-ene with, respectively, anhydrous hydrogen fluoride and anhydrous hydrogen bromide in methylene chloride at −78°. *exo*-2-Chloro-*endo*-2-methoxynorbornane was prepared by treating 2-methoxynorborn-2-ene with anhydrous hydrogen chloride in pentane at −120°. The absence of CHX (X = F, Cl, Br) resonances in the nmr spectra of these compounds, taken together with their other spectral characteristics and their method of preparation,[18] provides convincing evidence for the assigned stereochemistries. The remaining compounds were synthesized using unexceptional adaptations of literature procedures.

Discussion

Organotin hydrides are among the most active of all hydrogen atom donors known.[19] Thus, if the difference in electronegativity between an alkyl carbon and its α substituents is important in determining the configuration of the carbon radical, it is apparent from these stereochemical results that electronegativity differences alone are not sufficient to permit monosubstituted alkyl radicals to retain configurational integrity on the time scale of most nongeminate reactions.

These stereochemical results do not provide an adequate basis for conclusions concerning the geometry of the intermediate radicals; in particular they do not indicate whether the 2-fluoronorborn-2-yl radical has a planar or a shallow or rapidly inverting pyramidal configuration. It is noteworthy in this regard that the reduction of 2-bromo-2-fluoronorbornane proceeds with loss of stereochemistry