tion and with water, and dried and evaporated to a gum, which was chromatographed over alumina (30 g). Elution with hexane gave unidentified oily material (0.049 g). Elution with hexane–ether (199:1, 99:1) gave oily ketonic material (ν 1720, 1680 cm^{-1}) and further hexane–ether (97:3, 20:1) elution gave a mixture of hydroxy compounds (0.488 g), $[\alpha]D$ +27° (*c* 5.45). Most of this mixture (0.434 g) was rechromatographed over alumina (20 g). Elution with hexane–ether (97:3) gave 13 fractions (0.342 g) composed of mixtures of 2-methylene-5α-cholestan-3α-ol (**24**) and alcohol **11** identified by infrared and nmr measurements. Recrystallization of this material from acetone afforded 2-methylene-5α-cholestan-3α-ol (**24**) (0.076 g): mp 116–120°, raised by further recrystallization to 127–128° (0.033 g); $[\alpha]D$ +35° (*c* 0.7); ν 3560 (OH), 1647 (C=C), 902, and 705 cm^{-1}; δ 4.90 and 4.75 (=CH_2), 4.23 (C-3 H), and 2.08 ppm (OH).

Anal. Calcd for $C_{28}H_{48}O$ (400.66): C, 83.93; H, 12.08. Found: C, 84.10; H, 12.01.

Further elution with hexane–ether (24:1 and 20:1) gave mixtures of alcohols **24**, **11**, and **2a**. These combined fractions were recrystallized from methanol and gave a sharp-melting compound, mp 150.5–151.5°, $[\alpha]D$ +11° (*c* 1.30). Infrared analysis indicated that this compound was a complex (*ca.* 1:1) of **24** and **2a**.

Anal. Calcd for $C_{28}H_{48}O$ (400.66): C, 83.93; H, 12.08. Found: C, 83.90; H, 12.12.

Final elution with hexane–ether (47:3 and 9:1) gave alcohol **2a** (0.015 g) identified by melting point (132–133°), mixture melting point, and infrared spectrum.

Assay of the alcohol mixtures by quantitative infrared, nmr, and optical rotation indicated that the alcohols **24**, **2a**, and **11** were formed in the ratio of 57:13:30, respectively. The corrected total yield was 60%.

Photosensitized Oxygenation of 3-Methyl-5α-cholest-2-ene (13).—A pyridine solution (180 ml) of olefin **13** (3.00 g) was irradiated and oxygenated in the presence of hematoporphyrin (0.050 g). After 32 hr, the starting olefin was completely consumed and the reaction mixture was worked up as in the preceding experiment to give a light brown gum (3.1 g), which was chromatographed over alumina (90 g).[27] Elution with hexane and hexane–ether (99:1 to 97:1) afforded several oily fractions (0.170 g). Further elution with hexane–ether (9:1 to 7:3) gave a mixture of alcohols **15a** and **21**, 2.40 g, $[\alpha]D$ +18.6° (*c* 4.806). Rechromatography of most (2.18 g) of this material over alumina followed by several crystallizations from acetone afforded **21**: mp 107–108°; $[\alpha]D$ +9° (*c* 3.34); ν 3571 (OH), 1642 (C=C), 1034 (C—O), 898, and 762 cm^{-1}. This sample was identical with authentic **21** (infrared, mixture melting point). For analysis the sample was dried *in vacuo* for 2 days at room temperature.

Anal. Calcd for $C_{28}H_{48}O$ (400.66): C, 83.93; H, 12.08. Found: C, 84.02; H, 11.72.

Assay of the alcohol mixture by quantitative infrared and comparison with synthetic mixtures established that **21** and **15a** were formed in the ratio of *ca.* 70:30, respectively, and in a corrected total yield of 77%.

Attempted Photosensitized Oxygenations of 2-Methylene- and 3-Methylene-5α-cholestane.—Pyridine solutions (40 ml) of each olefin (0.1 g) were separately irradiated and oxygenated in the presence of hematoporphyrin (0.008 g) with additional dye (0.004 g) being added after 75 hr. Infrared examination of aliquots showed no evidence of hydroperoxide formation and work-up at the end of 100 hr gave only the starting olefins.

Registry No.—**2a**, 22599-96-8; **2b**, 37392-80-6; **2c**, 22599-97-9; **2d**, 37392-82-8; **4a**, 20997-60-8; **4b**, 37163-88-5; **4** (R = COPh), 37163-89-6; **4** (R = 3′,5′-dinitrobenzoate), 37406-79-4; **5**, 14528-10-0; **6**, 2097-78-1; **10**, 22599-98-0; **11**, 22599-94-6; **12**, 37392-87-3; **15a**, 37392-88-4; **15b**, 37392-89-5; **15c**, 37392-90-8; **15d**, 37413-07-3; **16a**, 37392-91-9; **16b**, 37392-92-0; **16c**, 37392-93-1; **18**, 37392-94-2; **18** acetate, 37392-95-3; **18** 3,5-dinitrobenzoate, 37392-96-4; **20**, 37392-97-5; **21**, 37392-98-6; **22**, 21152-07-8; **24**, 22599-92-4.

(27) Chromatography over activated silica gel gave diene **22** along with unidentified material.

Syntheses in the Noradamantane Series

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Preparations of several derivatives of noradamantane, including 1- and 2-noradamantanols, 1-bromonoradamantane, and noradamantane-1-carboxylic acid, are described. The reaction of deltacyclane (tetracyclo[4.3.0.$0^{2,4}$.$0^{8,7}$]nonane) with sulfuric acid is shown to lead to either 1- or 2-noradamantanol or noradamantane, depending on conditions. Other compounds, such as *exo*-2-brendanol and oxaadamantane, are also found in the reaction mixtures. Reaction pathways leading to the various products are discussed.

Investigations of the chemistry of adamantane (**1**) have been abetted considerably by the ease and simplicity of direct functionalization of the parent hydrocarbon.[1] Ionic substitutions, *e.g.*, bromination[2] and Koch–Haaf carboxylation,[3] give bridgehead products cleanly.[1] Adamantanone and several disubstituted adamantanes can be obtained by sulfuric acid oxidation of **1** under a variety of conditions.[4] Even nonselective substitution reactions, such as free-radical halogenations,[1] can be synthetically useful because of the high symmetry of adamantane, which limits the number of monosubstituted isomers to two.

Noradamantane (**2**),[5] only a single methylene removed from adamantane (**1**), behaves quite differently. Ring contraction decreases bridgehead reactivity at

(1) Reviews: (a) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); (b) R. C. Bingham and P. von R. Schleyer, *Fortschr. Chem. Forsch.*, **18**, 1 (1971); (c) E. M. Engler and P. von R. Schleyer, *MTP Rev. Sci.*, in press.

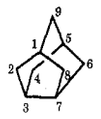
(2) S. Landa, S. Kriebel, and E. Knobloch, *Chem. Listy*, **48**, 61 (1954).

(3) H. Koch and H. Haaf, *Org. Syn.*, **44**, 1 (1964).

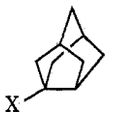
(4) H. W. Geluck and J. L. M. A. Schlatmann, *Tetrahedron*, **24**, 5361, 5369 (1968); *Recl. Trav. Chim. Pays-Bas*, **90**, 516 (1971).

(5) (a) B. R. Vogt and J. R. E. Hoover, *Tetrahedron Lett.*, 2841 (1967); (b) P. v. R. Schleyer and E. Wiskott, *ibid.*, 2845 (1967); (c) A. Nickon, G. D. Pandit, and R. O. Williams, *ibid.*, 2851 (1967).

1



2



3, X = COOH
4, X = $COCH_3$
5, X = OH

both the 1 and 3 positions of **2** substantially,[6] and, as will be shown here, ionic substitutions of **2** are not useful synthetic methods. Furthermore, because of the lower symmetry, five monosubstituted noradamantane isomers are possible; photohalogenation of **2** gives complex mixtures.[7]

Most of the known noradamantane derivatives have been prepared by synthetic sequences starting from adamantane precursors.[1b,c] Vogt and Hoover[5a] obtained 3-noradamantanecarboxylic acid (**3**) by Favorskii ring contraction. An ingenious two-step oxidative cleavage–cyclization sequence makes 3-noradamantyl methyl ketone (**4**) readily available from 2-methyl-1-adamantanol.[8] Baeyer–Villiger oxidation of **4** gives 3-noradamantanol (**5**) *via* its acetate.[9,10]

Deltacyclene (tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]non-8-ene, **6**)[11] or, more specifically its hydrogenation products, deltacyclane (**7**)[5c,12] and brexane (**8**),[5b,12] serve as alternative starting materials. With aluminum halide catalysts, **8** gives noradamantane (**2**).[5b] Deltacyclane (**7**) has been reported to react with sulfuric acid to yield the equatorial 2-noradamantanol (**9**).[5c] We have now found that this deltacyclane–sulfuric acid system, which is in fact quite complex, can also be used to prepare 1-noradamantanol (**10**) and even noradamantane itself in satisfactory yields by appropriate modification of the reaction conditions. As by-products, two alcohols, 2-exobrendanol (**11**)[12] and *epi*-2-noradamantanol (the epimer of **9**),[5c] are formed in very small amounts. The major side-product (up to 10% yield), oxaadamantane (**12**),[13] was quite unexpected. In addition, if formic acid is added to the deltacyclane–sulfuric acid system, 1-noradamantanecarboxylic acid (**13**) can be obtained, but the yield is poor. (Attempts to prepare **13** *via* a Koch–Haaf reaction[3] directly on noradamantane (**2**) were unsuccessful.) Scheme I summarizes these reactions.

The procedure originally reported[5c] involved the addition of a dilute pentane solution of **7** to 96% sulfuric acid at about −3°, followed rapidly by a hydrolytic work-up to give **9** in 80% yield. We have now found that longer reaction times, increased initial concentration of deltacyclane, higher temperatures, or stronger acid favor the formation of tertiary alcohol **10** and diminish the proportion of **9**. Table I illustrates the course of a reaction in which **7** was added to 96% H_2SO_4 kept at about −3°. Under these conditions 2-noradamantanol (**9**), probably present as its sulfate ester, rearranges moderately rapidly to the more stable 1-noradamantanol (**10**) or its sulfate. If deltacyclane is added at 25° to 99% sulfuric acid and the mixture is hydrolyzed after only 3 min, 1-noradamantanol (**10**) is the major component (80%) of the product. If an excess of pentane is used as a hydride transfer agent, up to 50% of noradamantane (**2**) can be isolated in pure form. Carbon monoxide (from the dehydration of formic acid) can also trap the 1-noradamantyl cation (**16**) to give **13**, but this is less efficient.

Resistance to oxidation and the lack of CHOH pmr absorption reveal the tertiary nature of 1-noradamantanol (**10**). The spectral and physical properties of **10** (mp 224.5–225°, tosylate mp 65.8–66.4°) differ from those of 3-noradamantanol (mp 250–251°, tosylate mp 45–46.7°).[9] Phosphorus tribromide converted **10** to 1-bromonoradamantane (**14**), and the

SCHEME I

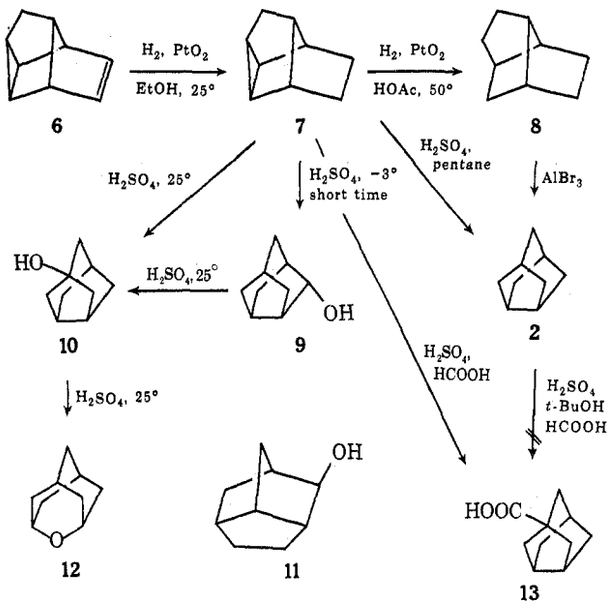


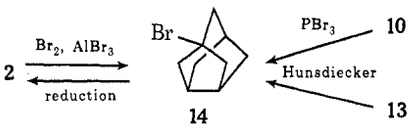
TABLE I

SULFURIC ACID TREATMENT OF DELTACYCLANE (7)[a]

Aliquot	Time, min	Noradamantanols,[b] relative % 9	10
1	0	87	13
2	1	77	23
3	5	64	36
4	11	49	51
5	20	35	65
6	40	23	77
7	60	21	79
8	90	16	84
9	600	12	88

[a] Deltacyclane (0.18 ml) added to 5 ml of 96% H_2SO_4 and kept at about −3°. [b] Relative percentages were determined by glpc. The two noradamantanols **9** and **10** constituted *ca.* 90% of the product extractable with ether. The other components and their ratios varied with time and included noradamantane (**2**), 2-*exo*-brendanol (**11**), 2-*epi*-noradamantanol (*epi*-**9**), and oxaadamantane (**12**), as well as some unreacted deltacyclane.

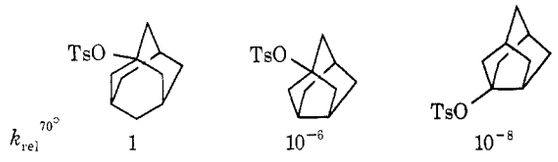
(6) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971).
(7) J. S. Wishnok, unpublished observations.
(8) R. M. Black and G. B. Gill, *Chem. Commun.*, 972 (1970).
(9) E. M. Engler, unpublished observations, Princeton University. See ref 10.
(10) W. D. Graham and P. v. R. Schleyer, *Tetrahedron Lett.*, 1179 (1972).
(11) L. G. Cannell, *ibid.*, 5967 (1966); J. J. Mrowca and T. J. Katz, *J. Amer. Chem. Soc.*, **88**, 4012 (1966); T. J. Katz, J. C. Carnahan, Jr., and R. Boeke, *J. Org. Chem.*, **32**, 1301 (1967).
(12) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. Digiorgio, *J. Amer. Chem. Soc.*, **87**, 1613, 1615 (1965).
(13) (a) H. Stetter and P. Tacke, *Ber.*, **96**, 694 (1963); (b) M. Fisch, S. Smallcombe, J. C. Gramain, M. A. McKervey, and J. E. Anderson, *J. Org. Chem.*, **35**, 1886 (1970); (c) R. M. Black, G. B. Gill, and D. Hands, *Chem. Commun.*, 311 (1972).



same bromide was obtained by the Hunsdiecker reaction of 1-noradamantanecarboxylic acid (**13**) (mp 94–96°); the reported melting points for the isomer **3** are 106–107°[5a] and 107–108°[8]). Reduction of **14** with either sodium and *tert*-butyl alcohol in tetrahydrofuran or by tributyltin hydride gave noradamantane (**2**). These reactions constitute structure proofs for **10**, **13**, and **14**. Spectral evidence provided support.

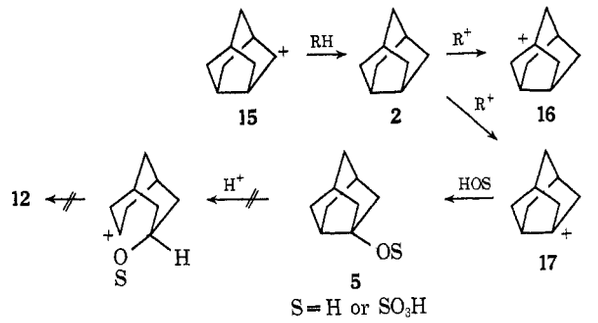
Direct ionic substitutions of noradamantane do not appear to be useful methods for the preparation of noradamantane derivatives. Sulfuric acid does not attack the hydrocarbon at room temperature, and only decomposition products result from the treatment of noradamantane with sulfuric acid at 80–90°. The failure of Koch–Haaf carboxylation of **2** has already been noted. Direct ionic bromination occurred only in the presence of the strong catalyst $AlBr_3$. At least three products were formed, and the major product, 1-noradamantyl bromide (**14**, less than 20% yield), required purification by preparative glpc. Noradamantane does not behave like adamantane.

This difference can be understood when one considers that the reactivity of both of the bridgehead positions of noradamantane are very much reduced relative to that of adamantane.[6] The acetolysis of 1-noradamantyl tosylate was studied here: k_1 (100.0°) $= 8.14 \times 10^{-6}$ sec^{-1}, k_1 (125.0°) $= 8.5 \times 10^{-5}$ sec^{-1}; $\Delta H^{\pm} = 27.0$ kcal/mol, $\Delta S^{\pm} = 10$ eu. Relative acetolysis rates at 70° are shown below, and provide quantitative comparison.[6,9,14]



The acid-catalyzed opening of the three-membered ring of deltacyclane (**7**) in carboxylic acid solution gives brexyl and brendyl products.[5c] In sulfuric acid, however, further rearrangement to the 2-noradamantyl cation (**15**) occurs. As in the adamantyl series,[15] the rearrangement of **15** to the 1-noradamantyl cation (**16**) is undoubtedly intramolecular and proceeds *via* noradamantane (**2**) which is always found as a by-product in these reactions. When an additional hydride source, such as pentane, is present, reduction becomes the predominant reaction course. Despite the modest yields, this is an attractive method for the preparation of noradamantane because of the experimental simplicity.[16]

The greater stability of the 1-noradamantyl (**16**) over the 3-noradamantyl cation (**17**), as revealed by the 100-fold difference in the tosylate solvolysis rates, helps explain why 1-noradamantyl and not 3-noradamantyl products are found in the reactions described. The interesting possibility also exists that 3-noradamantanol (**5**) or its sulfate ester is not stable in concentrated sulfuric acid, but suffers "wrong way" C_3–C_7 protolytic cleavage (*i.e.*, carbon protonation rather than oxygen protonation) with eventual production of oxaadamantane (**13**) as shown above. Recent experiments, however, indicate that 3-noradamantanol (**5**, S = H) is not converted readily to **12**, although partial conversion of **10** to **12** has been achieved in reaction in 96% H_2SO_4 at room temperature (Scheme I). The scope and mechanism of oxaadamantane formation are under investigation.



Experimental Section

Deltacyclane (**7**).—Twenty-five grams of tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (**6**)[11] in 60 ml of 95% EtOH was hydrogenated at 25° in a Parr apparatus with PtO_2 catalyst. Initial H_2 pressure was 57 psi. The yield of deltacyclane[12] was quantitative.

1-Noradamantanol (**10**).—Deltacyclane (1.2 g) was added dropwise to a mixture of sulfuric acid (Baker analyzed, 97%, 36 ml) and fuming sulfuric acid (15% oleum, Baker Analar, 4 ml) at room temperature over a period of 1 min. The mixture was stirred at room temperature for 3 min and then poured over crushed ice (200 g). When the ice had melted, the solution was extracted with ether (2 × 50 ml) and the ether solution was washed with sodium bicarbonate and water. The acidic water phase together with the washings were refluxed and stirred for 4 hr to ensure hydrolysis of all sulfate esters. The mixture was reextracted with ether and the ether extracts were washed as before and dried over $MgSO_4$. Gas chromatographic analysis (SE-30) showed the presence of **10** (80%), **9** (~7%), oxaadamantane (**12**)[13] (~10%), and other minor components (~3%). The ether solution was evaporated carefully and the residue was sublimed to give 1.06 g of crude product, which was purified by chromatography on alumina (50 g of Woelm neutral; grade III made by addition of 5% w/w water). The elution was carried out with pentane and pentane–ether. Oxaadamantane was eluted with 5% ether, **9** was eluted with 15–20% ether, and **10** was eluted with 30% ether. Pure **10** was obtained after rechromatography on alumina, followed by two recrystallizations from pentane, and sublimation: mp (sealed capillary) 224.5–225°; ir (CCl_4) ν 3581, 1155, 1116, 1072, 1024 cm^{-1}; nmr ($CDCl_3$) δ 1.5 (6 H, s with shoulder), 1.76 (4 H, s, broad shoulder), 2.37 (3 H, broad peak, $W_{1/2} = 14$ Hz, 2.9 (1 H, s).

Anal. Calcd for $C_9H_{14}O$ (138.20): C, 78.21; H, 10.21. Found: C, 78.50; H, 10.33.

1-Noradamantanol (**10**) could not be oxidized with chromic acid in pyridine, in acetic acid, or in acetone. This alcohol (10 mg) in ether (0.5 ml) was added to 96% H_2SO_4 (10 ml) and the pale yellow solution was stirred for 3 hr at room temperature. After pouring onto ice and conventional work-up, glpc analysis of the product mixture showed starting alcohol **10** and *ca.* 10% of a component with the same retention time as that of oxaadamantane (**12**).

1-Noradamantyl Tosylate.—Tosylation of **10** was achieved by the usual pyridine method.[17] Acetolysis rates were determined

(14) Solvolysis rates of 1-noradamantyl triflate: R. C. Bingham, W. F. Sliwinski, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 3471 (1970).

(15) P. v. R. Schleyer, L. K. M. Lam, D. J. Raber, J. L. Fry, M. A. McKervey, J. R. Alford, B. D. Cuddy, V. G. Keizer, H. W. Geluck, and J. L. M. A. Schlatmann, *ibid.*, **92**, 5246 (1970). Also see P. Vogel, M. Saunders, W. Thielecke, and P. v. R. Schleyer, *Tetrahedron Lett.*, 1429 (1971).

(16) This method has also been found useful for the preparation of other cage hydrocarbons such as homoadamantane and substituted adamantanes: J. S. Wishnok, S. H. Liggero, and W. D. Graham, unpublished results, Princeton University. For a published example, see ref 10.

(17) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 1179f.

by standard techniques.[6] The analytical sample had mp 65.8–66.4°.

Anal. Calcd for $C_{16}H_{20}O_3S$ (292.397): C, 65.72; H, 6.89; S, 10.97. Found: C, 65.87; H, 6.90; S, 10.76.

Oxaadamantane (12).—The material isolated from the column chromatography described above had mp 231–232° after one sublimation and was more than 99% pure by glpc. An analytical sample, mp 232–233° (lit. mp 232.5°,[13a] 225–230°[13b]), was obtained by preparative glpc: ir (CCl_4) ν 1448, 1314, 1190, 1054, 1014, 893 cm^{-1}; nmr (CCl_4) broad maxima centered around δ 1.58, 1.74, 2.04, and a broad, symmetrical two-proton singlet at 4.0 due to the bridgehead CH's adjacent to oxygen.

Anal. Calcd for $C_9H_{14}O$ (138.20): C, 78.21; H, 10.21. Found: C, 77.94; H, 10.17; mass spectrum (molecular ion), *m/e* 138.

Reaction of Noradamantane with Sulfuric Acid.—Noradamantane (0.6 g) suspended in sulfuric acid (25 ml) was recovered unchanged after stirring for 9 hr at room temperature. In a separate experiment, 0.4 g of noradamantane and 9 ml of sulfuric acid were heated at 80–90° for 9 hr in a sealed tube. Following work-up (quenching with ice–water, extracting with ether, drying with $CaCl_2$, and evaporating the ether), only a few milligrams of material was recovered. Nmr and ir spectra showed this material to be mostly noradamantane, although there were some very weak absorptions in the infrared spectra corresponding to carbonyl groups (~1735 cm^{-1}). Reaction at 80–90° for shorter periods of time simply resulted in higher recoveries of noradamantane.

1-Bromonoradamantane (14). **A. Direct Bromination.**—A stirred mixture of noradamantane (1.5 g) and $AlBr_3$ (2.2 g) in CS_2 (20 ml) was cooled to 0°. Bromine (1.4 g) was added over a period of 45 min and the mixture was allowed to warm to room temperature and was stirred for 18 hr. At the end of this period considerable tar had formed on the walls of the flask. The CS_2 solution was decanted, washed with saturated $NaHCO_3$, and dried over $MgSO_4$. The solution was concentrated, and the major product was isolated by preparative gas chromatography (20 ft × 0.375 in., 30% SE-52 on 45/60 Chromosorb W). Yields of pure, waxy white **14** were less than 20%: mp 49–50° (sealed tube); *m/e* (molecular ion) 201 (with the characteristic bromine isotope distribution); nmr (CCl_4) δ 1.65 (4 H, s), 2.03, 2.18 (6 H, poorly resolved singlet), 2.41 (3 H, broad peak); ir (CS_2) ν_{max} 1311, 1271, 1138, 994, 870, 786, 686 cm^{-1}.

Anal. Calcd for $C_9H_{13}Br$ (201.19): C, 53.72; H, 6.51; Br, 39.76. Found: C, 53.73; H, 6.67; Br, 39.69.

Two other products (with retention times of 0.65 and 1.2 relative to **14** and relative concentrations of 3 and 8%, respectively) were also observed in this reaction mixture (glpc analysis on 5 ft × 0.25 in. 20% SE-30 on 60/80 Chromosorb W, 120°). These compounds have not been identified.

B. Action of PBr_3 on Tertiary Alcohol 10.—Alcohol **10** (1 g) was dissolved ln benzene (4 ml) at room temperature, and a solution of distilled PBr_3 (0.7 ml) in benzene (1 ml) was added dropwise over a 5-min period. The pale yellow mixture was stirred at room temperature for 3 hr and then at 50° for 5.5 hr. The mixture was then poured into ice water, and the aqueous phase was extracted with pentane (3 × 10 ml). The combined organic layer and pentane extracts were washed with water, saturated $NaHCO_3$, and again with water, and then dried over $MgSO_4$. The solution was concentrated to a small volume, and the major product was isolated by preparative gas chromatography (20 ft × 0.375 in., 30% Carbowax 20M on 40/60 Chromosorb W). This compound (mp 49–50°, yield 36%) was identical in all respects (mass, ir, and nmr spectra) with compound **14** obtained by procedure A above.

Reduction of 14 to Noradamantane (2),—The bromo compound **14** (0.29 g) and *tert*-butyl alcohol (0.30 g) were dissolved in dry tetrahydrofuran (3 ml). Sodium (0.15 g) was added, and the mixture was stirred at room temperature for 3 hr. Additional *tert*-butyl alcohol (0.5 ml) was added to dissolve some remaining sodium, and the mixture was refluxed for 3 hr. Methanol was added, and the yellow reaction mixture was poured into 20 ml of ice water, which was extracted with pentane (3 × 15 ml). The pentane extracts were washed with water and dried over $MgSO_4$. Analysis by glpc (20 ft × 0.375 in., 30% SE-30 on 30/60 mesh Chromosorb W) showed only a single product which, after isolation by preparative gas chromotography, was identified as noradamantane (ir and nmr spectra identical with those of an authentic sample).[5]

The bromide **14** (*ca.* 0.01 g) was also converted smoothly to noradamantane by treatment with (n-Bu)$_3$SnH (*ca.* 0.20 g) for 5 hr at room temperature. During this period glpc analysis revealed a steady decrease ln the starting material accompanied by the appearance and increase of the noradamantane peak.

Noradamantane (2).—Deltacyclane (10 g) in pentane (50 ml) was added to 60 ml of 96% sulfuric acid at room temperature, and the mixture was stirred mechanically at high speed for 2 hr. The layers were allowed to separate, and the pentane layer was taken up with a pipette and then evaporated, leaving 3.9 g of virtually pure **2**. An additional 50 ml of pentane was added to the acid layer and stirring was continued for several hours, after which the layers were separated again. This procedure was repeated several times over a 10-hr period, and led ultimately to a total yield of **2** of about 50%. A single sublimation gave material (mp 203–204°) that showed only one peak on flame-ionization gas chromatography and that was identical in all respects with noradamantane obtained *via* established methods.[5]

Noradamantane-1-carboxylic Acid (13),—Deltacyclane (0.5 g) was added dropwise to 96% sulfuric acid (200 ml), and the mixture was stirred at room temperature for 2.5 hr. The solution was cooled to 0°, ice-cold formic acid (75 ml) was added, and stirring was continued at 0° for 30 min. The reaction mixture was poured onto ice (300 g) and extracted with CCl_4 (3 × 20 ml). The combined extracts were washed with dilute NaOH and the combined basic solutions were neutralized with HCl to precipitate the organic acid. The precipitate was taken up in ether, and the aqueous solution was extracted with ether. The combined ether extracts were washed once with water and dried over $MgSO_4$. The ether was evaporated and the residue was sublimed to yield *ca.* 0.09 g of a white solid: mp 94–96°; *m/e* (molecular ion) 166; nmr (CCl_4) δ 1.6 (6 H, s), 1.82 (unresolved singlet), 12.2 (1 H, s). The signals at δ 1.82, 2.00, and 2.24 could not be integrated individually, but the total signal amounted to 4 H. The general appearance of this spectrum, except for the downfield acid proton, was very similar to that of **10** and was markedly different from that of 3-noradamantanecarboxylic acid[5a,b] (nmr spectrum kindly supplied by Dr. B. R. Vogt). The ir spectrum had prominent peaks at ν_{max} (CCl_4) 1700, 1415, 1280, and 1155 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}O_2$ (166.21): C, 72.26; H, 8.49. Found: C, 72.2; H, 8.3.

A Hunsdiecker reaction[18] was carried out on this acid, and glpc analysis (Carbowax 20M and SE-30) revealed that the major product had retention times identical with those of **14**. Direct nmr analysis of the washed and dried $BrCCl_3$ solution from this reaction confirmed the identity of **14** as the major product.

Registry No.—**2**, 7075-86-7; **7**, 6567-11-9; **10**, 37392-59-9; **10** tosylate, 33305-61-2; **12**, 281-24-3; **13**, 37392-60-2; **14**, 37392-61-3.

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