Synthesis and Chemistry of 9-Homonoradamantane (Tricyclo[3.3.2.0^{3,7}]decane)

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9-Homonoradamantane (tricyclo[3.3.2.0^{3,7}]decane) is one of the few unknown adamantane isomers. Two independent synthetic routes to this system were developed: the benzilic acid ring contraction of 10-homoprotoadamantane-4,5-dione leading to 2-substituted 9-homonoradamantanes and the diazomethane homologation of 9-noradamantanone to 9-homonoradamantan-9-one (**10**). The parent hydrocarbon, 9-homonoradamantane (**1**), and a number of its 9-substituted derivatives (9-homonoradamant-9-ene (**12**), 9-homonoradamantan-9-ol (**11a**), 9-chloro-9-homonoradamant-9-ene (**13**)) were, subsequently, prepared from ketone **10**. Hydrocarbons **1** and **12** rearranged readily to adamantane in the presence of $AlBr_3$, while alcohol **11a** rearranged to adamantane in concentrated sulfuric acid–pentane. Pyrolysis of the sodium salt of 9-homonoradamantan-2-one tosylhydrazone yielded a 5:1 mixture of 2,9- and 2,4-dehydro-9-homonoradamantane. Solvolysis of 9-homonoradamant-9-yl tosylate in 66.7% aqueous dioxane produced a 0.5:2:1 mixture of 9-homonoradamant-9-ene, 5-*endo*-protoadamantanol, and 9-homonoradamantan-9-ol, indicating a close relation between the 9-homonoradamant-9-yl cation and the 5-protoadamantyl cation.

Tricyclo[3.3.2.0^{3,7}]decane (**1**, 9-homonoradamantane) is one of the few adamantane isomers which has not been previously prepared.[1] It is by 13 kcal/mol more strained than adamantane[3] into which it can be transformed by just two 1,2-carbon shifts. In addition to adamantane, tricyclo[3.3.2.0^{3,7}]decane (**1**) is structurally related to both nor-

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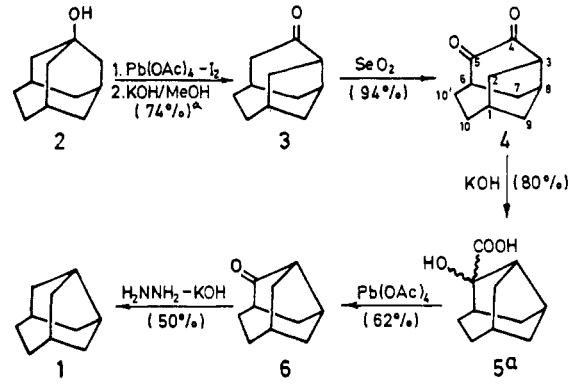
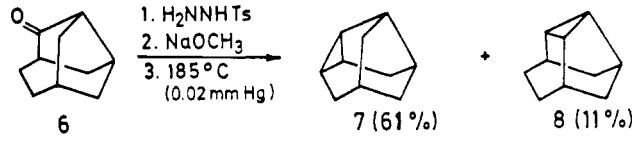
adamantane and homoadamantane, being a homo derivative of the former and a nor derivative of the latter. Consequently, it can be conveniently named 9-homonoradamantane, since the additional methylene group (9′) is adjacent to the carbon atom at position 9 in noradamantane.[5]

Scheme I

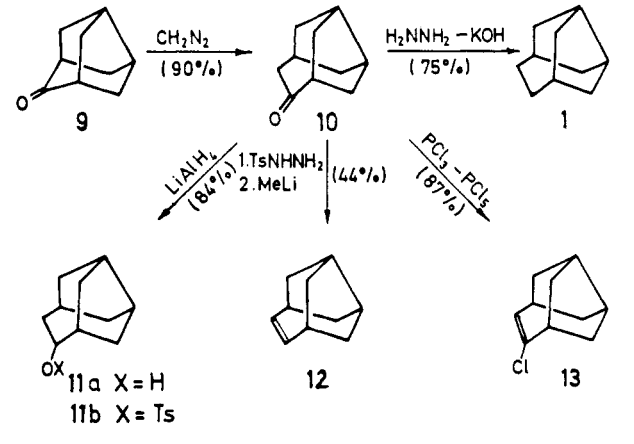


[a] Endo or exo isomer.

Scheme II



Scheme III



(1) According to the basic set of tricyclodecane structures[2,3] there are 18 reasonably stable isomers of adamantane with all carbons in rings other than three- or four-membered ones. Most of these isomers have been prepared: protoadamantane[4a] (tricyclo[4.3.1.0^{3,8}]decane), twistane[2,4b] [4.4.0.0^{3,8}], isotwistane[4c] [4.3.1.0^{3,7}], perhydrotriquinacene[4d] [5.2.1.0^{4,10}], *endo*- and *exo*-tetrahydrodicyclopentadiene[4e] [5.2.1.0^{2,6}], *exo*-1,2-trimethylenenorbornane[3,4f] [5.2.1.0^{1,5}], 1,7-trimethylenenorbornane[4g] [4.2.2.0^{1,5}], 2-homobrendane[4h] [5.2.1.0^{4,8}], 4-homobrendane[3,4f,4h-j] [5.2.1.0^{3,8}], 2-homobrexane[4k] [5.3.0.0^{4,8}], 4-homobrexane[4i,4l] [4.4.0.0^{3,7}], and *anti*- and *syn*-tricyclo[4.2.1.1^{2,5}]decane.[4m]

(2) H. W. Whitlock, Jr., and M. W. Siefken, *J. Am. Chem. Soc.*, **90**, 4929 (1968).

(3) E. M. Engler, M. Farcaşiu, A. Sevin, J. M. Cense, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 5769 (1973).

(4) (a) B. R. Vogt, *Tetrahedron Lett.*, 1575 (1968); R. M. Black and G. B. Gill, *J. Chem. Soc., Chem. Commun.*, 972 (1970); W. H. W. Lunn, *J. Chem. Soc. C*, 2124 (1970); Z. Majerski and Z. Hameršak, *Org. Synth.*, in press; D. Lenoir, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 2138 (1974); C. A. Cupas, W. Schumann, and W. E. Heyd, *ibid.*, **92**, 3237 (1970); (b) H. W. Whitlock, Jr., *ibid.*, **84**, 3412 (1962); J. Gauthier and P. Deslongchamps, *Can. J. Chem.*, **45**, 297 (1967); A. Belanger, Y. Lambert, and P. Deslongchamps, *ibid.*, **47**, 795 (1969); (c) M. Tichy and J. Sicher, *Tetrahedron Lett.*, 4609 (1969); *Collect. Czech. Chem. Commun.*, **37**, 3106 (1972); A. Krantz and C. Y. Lin, *J. Am. Chem. Soc.*, **95**, 5662 (1973); (d) I. T. Jacobson, *Acta Chem. Scand.*, **21**, 2235 (1967); J. W. Baum and C. D. Gutsche, *J. Org. Chem.*, **33**, 4312 (1968); (e) J. F. Eijkman, *Chem. Weekbl.*, **1**, 7 (1903); P. v. R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960); P. v. R. Schleyer, M. M. Donaldson, R. D. Nicholas, and C. Cupas, "Organic Syntheses", Collect. Vol. V, Wiley, New York, 1973, p 16; (f) E. J. Corey and R. S. Glass, *J. Am. Chem. Soc.*, **89**, 2600 (1967); (g) W. Schröder, *Angew. Chem.*, **72**, 865 (1960); (h) Z. Majerski and J. Janjatović, *Tetrahedron Lett.*, in press; (i) J. G. Henkel and L. A. Spurlock, *J. Am. Chem. Soc.*, **95**, 8339 (1973); (j) B. Boyer, P. Dubreuil, G. Lamaty, J. P. Roque, and P. Geneste, *Tetrahedron Lett.*, 2919 (1974); N. Takaishi, Y. Fujikura, Y. Inamoto, and K. Aigami, *J. Org. Chem.*, **42**, 1737 (1977); (k) M. Jones, Jr., *J. Am. Chem. Soc.*, **89**, 4236 (1967); T. J. Katz and J. J. Cheung, *ibid.*, **91**, 7772 (1969); T. J. Katz, J. J. Cheung, and N. Acton, *ibid.*, **92**, 6643 (1970); K. Hojo, R. T. Seidner, and S. Masamune, *ibid.*, **92**, 6641 (1970); (l) C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *ibid.*, **89**, 4133 (1967); J. R. Scheffer, K. S. Bhandari, R. E. Gayler, and R. A. Wostradowski, *ibid.*, **97**, 2178 (1975); (m) L. A. Paquette, G. Klein, and C. W. Doecke, *ibid.*, **100**, 1595, 1596 (1978); B. Ernst and C. Ganter, *Helv. Chim. Acta*, **61**, 1107 (1978).

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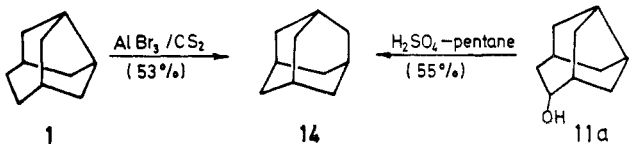
In this work, we report the synthesis and chemical studies of the hitherto unknown 9-homonoradamantane (1) and its 2- and 9-substituted derivatives.[6] Two independent synthetic approaches were used: the benzilic acid ring contraction of 10-homoprotoadamantane-4,5-dione, leading to 2-substituted 9-homonoradamantanes, and the diazomethane homologation of 9-noradamantanone to 9-homonoradamantan-9-one.

Results and Discussion

Syntheses. 9-Homonoradamantan-2-one (**6**) was prepared in 47% overall yield starting from 10-homoprotoadamantan-4-one (**3**, Scheme I). This ketone is readily available by thermolysis of 1-homoadamantyl hypoiodite (prepared in situ from 1-homoadamantanol, **2**) followed by the base-promoted intramolecular C-alkylation of the resulting iodo ketone.[9] Thus, 10-homoprotoadamantan-4-one (**3**) was oxidized by selenium dioxide to yield 94% of bright yellow 10-homoprotoadamantane-4,5-dione (**4**) which was converted (80%) on treatment with potassium hydroxide into 2-hydroxy-9-homonoradamantane-2-carboxylic acid (**5**). Interestingly, the ^{13}C NMR spectrum of acid **5** showed 11 signals indicating that just one isomer (endo or exo) was formed.[10] Decarboxylation of acid **5** by lead tetraacetate at room temperature yielded crude 9-homonoradamantan-2-one (**6**). Pure ketone **6** (≥98% by GLC; 62% based on **5**) was obtained by column chromatography on neutral alumina, using pentane–ether as eluent. Decarboxylation of α-hydroxy acid **5** to ketone **6** was also achieved by treatment with thionyl chloride in refluxing benzene,[11] although in a rather low yield (34%). In contrast to the lead tetraacetate decarboxylation, the thionyl chloride reaction produced, in addition to **6**, considerable amounts of tarry byproducts.

Scheme IV



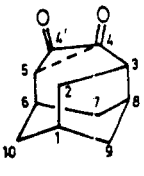
1 14 11a

Treatment of 9-homonoradamantan-2-one (**6**) with tosylhydrazine afforded the corresponding tosylhydrazone, which was readily converted into its sodium salt. Pyrolysis of the dry sodium salt produced 74% of a 5:1 mixture of two products (Scheme II). The major product was identified as 2,9-dehydro-9-homonoradamantane (**7**) by comparing the ^{13}C NMR, ^{1}H NMR, IR, and mass spectra of the product mixture with those of an authentic sample of **7**.[12] The ^{13}C NMR spectrum of the minor product showed six signals at 49.1 (2 C), 42.0 (1 C), 32.7 (1 C), 31.7 (2 C), 25.7 (2 C), and 23.5 (2 C) ppm, indicating that it was 2,4-dehydro-9-homonoradamantane (**8**).[13] In comparison, 2-noradamantylidene produced 2,4-dehydronoradamantane rather than the 2,9 isomer.[14] Positions 2 and 4 in the noradamantane system are closer to each other than those in the 9-homonoradamantane system, and the main bridge in the latter is almost certainly somewhat twisted, tilting the C_9–H bond toward position 2. Consequently, the carbene center in 9-homonoradamant-2-ylidene (contrary to 2-noradamantylidene) is more favorably situated for the insertion into the C_9–H bond than into the C_4–H bond.

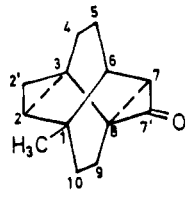
9-Homonoradamantan-9-one (**10**) was prepared in 90% yield by the diazomethane homologation of 9-noradamantanone[15] (**9**, Scheme III). The crude product contained 10% of the C_{11} homologue, 9-bishomonoradamantan-9(10)-one, which was separated by preparative GLC.

Starting from 9-homonoradamantan-9-one (**10**), a series of 9-substituted 9-homonoradamantanes was prepared (Scheme III). 9-Homonoradamantan-9-ol (**11a**) was ob-

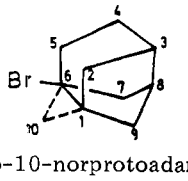
(5) This simple, semitrivial nomenclature can be used quite generally for the polycyclic systems derived from the parent system by adding or subtracting one (or more) methylene group(s). (IUPAC names of such compounds are frequently very complex.) The name of the system derived by the addition of a methylene group is formed from the name of the parent system preceded by prefix homo and the number of the lower numbered carbon adjacent to the inserted methylene group. (If necessary, the numbers of the two carbons flanking the inserted methylene group may be used to mark clearly its position.) When there is a choice, the methylene group is assumed to be inserted between the lowest numbered *bridge* carbon and the next higher numbered carbon. The name of the system derived by the subtraction of a methylene group is formed from the name of the parent system preceded by the prefix nor and the number of the subtracted carbon. For example



4-homoprotoadamantane-4,4′-dione



1-methyl-2,7-bishomotwistan-7′-one



6-bromo-10-norprotoadamantane

The inserted carbon in the homo systems is designed with the prime-marked number of the lower numbered carbon flanking it. All other carbons in both homo and nor systems are numbered as in the parent system. This nomenclature has been used in part by us and others since 1973: K. M. Majerski and Z. Majerski, *Tetrahedron Lett.*, 4915 (1973).

(6) Recently, synthesis and ^{13}C NMR studies of 9,9′-benzo-9-homonoradamant-9-ene[7] and 9,9′-benzo-9-homonoradamanta-3,9-diene[8] were reported. The chemistry of the parent system 9-homonoradamantane, should be, however, fairly different from that of the benzo derivatives in which carbon atoms 9 and 9′ of the 9-homonoradamantane skeleton are incorporated into a benzene ring.

(7) H. Duddeck and H. Klein, *Tetrahedron Lett.*, 1917 (1976); *Tetrahedron*, **33**, 1971 (1977).

(8) R. Greenhouse, W. T. Borden, H. Hirotsu, and J. Clardy, *J. Am. Chem. Soc.*, **99**, 1664 (1977).

(9) Z. Majerski, Z. Hameršak, and D. Škare, *Tetrahedron Lett.*, 3943 (1977).

(10) The stereospecific rearrangement of 10-homoprotoadamantane-4,5-dione (**4**) into α-hydroxy acid **5** can be explained by the specific geometry of the 10-homoprotoadamantane skeleton. Attack of the base at the carbonyl group in position 5 (more likely) would lead to cleavage of the C_5–C_6 bond followed by the formation of the C_6–C_4 bond, while attack at position 4 would result in C_4–C_3 bond cleavage and formation of the C_3–C_5 bond. Inspection of molecular models indicated that the C_6–C_4 bond would be formed preferably at the exo side and the C_3–C_5 bond at the endo side. In the former case, the endo acid would arise, while in the latter, the exo acid would be produced.

(11) S. H. Liggero, Z. Majerski, P. v. R. Schleyer, A. P. Wolf, C. S. Redvanly, H. Wynberg, J. A. Boerma, and J. Strating, *J. Labelled Compds.*, **7**, 3 (1971).

(12) 2,9-Dehydro-9-homonoradamantane (**7**) is structurally identical with 5,7-dehydroprotoadamantane. This hydrocarbon was obtained previously by pyrolysis of the 5-protoadamantanone tosylhydrazone sodium salt (D. Škare and Z. Majerski, *J. Chem. Soc., Chem. Commun.*, 1000 (1974)).

(13) The ^{13}C NMR spectrum of the third possible isomer, 2,8-dehydro-9-homonoradamantane, would show 7 signals (3 × 2 C and 4 × 1 C).

(14) A. Nickon and G. D. Pandit, *Tetrahedron Lett.*, 3663 (1968).

(15) For synthesis of 9-noradamantanone, see: (a) M. R. Vegar and R. J. Wells, *Tetrahedron Lett.*, 2565 (1969); (b) D. Gravel and S. Rahal, *Can. J. Chem.*, **53**, 2671 (1975).

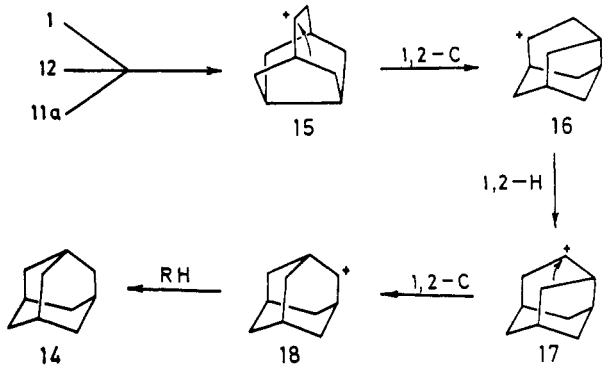
tained in 84% yield by $LiAlH_4$ reduction. Treatment of the tosylhydrazone derived from **10** with methyllithium produced 44% of the strained olefin 9-homonoradamant-9-ene (**12**), while treatment of **10** with PCl_3–PCl_5 yielded 87% of 9-chloro-9-homonoradamant-9-ene (**13**, 95% pure by GLC). Olefins **12** and **13** were identified by IR, ^1H NMR, ^{13}C NMR, and mass spectrometry (see Experimental Section). The reaction with PCl_3–PCl_5 proceeds, presumably, via the 9-chloro-9-homonoradamant-9-yl cation. This cation could rearrange to the 6-chloro-5-protoadamantyl cation by just one 1,2-carbon shift. In comparison, 4-protoadamantanone will react with PCl_3–PCl_5 via the 4-chloro-4-protoadamantyl cation to give a 1:1 mixture of 4-chloro-4-protoadamantene and 1,2-dichloroadamantane.[16] This is in good agreement with the calculated heats of formation of 9-homonoradamantane (−19.4 kcal/mol), protoadamantane (−21.1 kcal/mol), and adamantane (−32.6 kcal/mol).[3] Both the 9-chloro-9-homonoradamant-9-yl and 4-chloro-4-protoadamantyl cations are stabilized by the α-chloro atom.[17] The relative stabilities of these cations should roughly parallel the relative stabilities of the corresponding hydrocarbons. The stabilizing effect of the α-chloro atom can easily prevail over the small stability difference between the protoadamantane and the 9-homonoradamantane system, but it cannot overcome the large difference in stabilities of the adamantane and the protoadamantane system.

The parent hydrocarbon, 9-homonoradamantane (**1**), was obtained by the Wolff–Kishner reduction of either 9-homonoradamantan-2-one (**6**) or 9-homonoradamantan-9-one (**10**). Its structure was unambiguously confirmed by mass (M^+, m/e 136) and ^{13}C NMR spectrometry (four signals: δ 42.4 (t, 4 C), 41.8 (d, 2 C), 37.0 (d, 2 C), 30.5 (t, 2 C)). In addition, IR, ^1H NMR, ^{13}C NMR, and mass spectra, as well as GLC retention times of 9-homonoradamantane samples prepared from ketones **6** and **10**, were identical.

Ionic bromination of 9-homonoradamantane (**1**) with bromine at room temperature, at reflux, or in the presence of boron tribromide yielded no bromo derivative; the starting hydrocarbon was recovered exclusively. Formation of the bridgehead 1- or 3-(9-homonoradamantyl) cations would require more vigorous conditions, since these cations cannot achieve planarity without serious distortions of the rigid 9-homonoradamantane skeleton. Bromination of **1** in the presence of $AlBr_3$, however, produced a complex mixture of products.

Carbonium Ion Rearrangements. 9-Homonoradamantane (**1**) isomerized readily to adamantane (**14**) in the presence of a Lewis acid (Scheme IV). The isomerization induced by $AlBr_3$ in carbon disulfide was complete within 4 h at room temperature, indicating the close relationship of these two systems. Treatment of 9-homonoradamant-9-ene (**12**) with $AlBr_3$ in carbon disulfide as well as the hydride-transfer reduction of 9-homonoradamantan-9-ol (**11a**) in concentrated sulfuric acid–pentane at room temperature or 0 °C produced adamantane (**14**) as the sole definable product. These reactions proceed, presumably, through the initially formed 9-homonoradamant-9-yl cation (**15**), which subsequently rearranges via the 5- and 4-protoadamantyl cations (**16** and **17**) to the more stable 2-adamantyl cation (**18**) and yields adamantane (**14**) by hydride abstraction (Scheme V).

Scheme V



Cation **15** arises by the Lewis acid-promoted hydride abstraction[18] from **1** by protonation of the olefinic bond in **12** by $AlX_3{\cdot}H_2O$,[19] or by dehydration of protonated alcohol **11a**.[20]

The close relationship between the 9-homonoradamant-9-yl cation and the 5-protoadamantyl cation is also demonstrated by solvolytic studies. 9-Homonoradamant-9-yl tosylate (**11b**) was solvolyzed in 66.7% aqueous dioxane at 50 °C for 10 half-lives in the presence of 2,6-lutidine; the reaction mixture was extracted with ether, and the extracts were concentrated and analyzed. GLC analysis revealed the presence of three products in a ratio of 0.5:2:1. The products were stable under the reaction conditions used. The first component was identified as 9-homonoradamant-9-ene (**12**) and the third one as 9-homonoradamantan-9-ol (**11a**) by comparison of their IR, ^1H NMR, and mass spectra as well as their GLC retention times with those of authentic samples. The IR and mass spectra of the major product indicated that it was an alcohol isomeric with **11a**. This alcohol was identified as 5-*endo*-protoadamantanol by comparison of its GLC retention time and its ^1H NMR, IR, and mass spectra with those of authentic samples of 5-*endo*- and/or 5-*exo*-protoadamantanol.[21,22]

Position 5 in the protoadamantane system is sterically less hindered at the exo side. Nevertheless, the solvolysis of 9-homonoradamant-9-yl tosylate (**11b**) produced 5-*endo*-protoadamantanol rather than the exo isomer. This can be interpreted by postulating either σ bridging in the intermediary cation or a rapid equilibrium between the classical 9-homonoradamant-9-yl cation (**15**) and the 5-protoadamantyl cation (**16**). The C_9–OTs bond in **11b** is antiperiplanar relative to the C_1–C_2 bond and, therefore, well situated for σ participation. This participation would lead to the bridged 9-homonoradamant-9-yl cation **19**, an intermediate between the 9-homonoradamant-9-yl "cation" **19a** and the 5-protoadamantyl "cation" **19b**. The exo side of position 1 in cation **19** is protected by the bridging and the nucleophile would attack preferably from the endo side. The leaving group, departing from the endo side, would protect the endo rather than the exo side.

Kinetic results, however, provide no evidence for anchimeric assistance to ionization of 9-homonoradamant-

(16) B. D. Cuddy, D. Grant, and M. A. McKervey, *J. Chem. Soc. C*, 3173 (1971); D. Lenoir, R. Glaser, P. Mison, and P. v. R. Schleyer, *J. Org. Chem.*, **36**, 1821 (1971).

(17) J. March, "Advanced Organic Chemistry", McGraw-Hill, New York, 1977, p 156, and references therein.

(18) R. C. Bingham and P. v. R. Schleyer, *Fortschr. Chem. Forsch.*, 18, 14 (1971), and references therein.

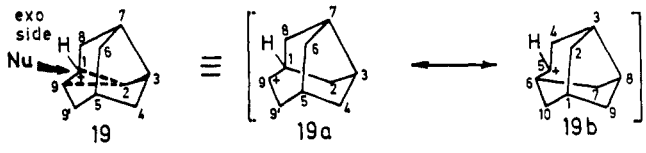
(19) K. Mlinarić-Majerski, Z. Majerski, and E. Pretsch, *J. Org. Chem.*, 40, 3772 (1975).

(20) For example, see K. Mlinarić-Majerski, Z. Majerski, and E. Pretsch, *J. Org. Chem.*, 41, 686 (1976).

(21) J. Boyd and K. H. Overton, *J. Chem. Soc., Perkin Trans. 1*, 2533 (1972). We are grateful to Professor Overton for providing us with copies of ^1H NMR spectra of 5-*endo*- and 5-*exo*-protoadamantanol.

(22) An authentic sample of 5-*endo*-protoadamantanol was prepared by $LiAlH_4$ reduction[21] of 5-protoadamantanone.[23]

(23) M. Fărcaşiu, D. Fărcaşiu, J. Slutsky, and P. v. R. Schleyer, *Tetrahedron Lett.*, 4059 (1974).



9-yl tosylate (**11b**). Tosylate **11b**, like 2-adamantyl tosylate (**20**),[24] should receive meager nucleophilic solvent assistance owing to steric limitations in backside accessibility. The relative solvolysis rate of **11b** as compared to that of **20** can be estimated from carbonyl stretching frequencies of the corresponding ketones and the torsional and nonbonded interaction energy changes on ionization.[25,26] 2-Adamantyl tosylate (**20**), owing to its similarity with the 9-homonoradamant-9-yl structure, appears to be a good standard. In the preferred conformation of **11b** the tosyl group is very probably equatorial. Models of **11b** reveal the torsional angles (ϕ), around the C–C bonds adjacent to the tosyl group, to be 30° (H–C_1–C_9–H) and 60° (H–C_9–C_9–H). Nonbonded interaction energy changes on ionization of **11b** can be reasonably assumed to be about equal to those of **20**. From these considerations and the experimentally determined carbonyl frequencies of 9-homonoradamantan-9-one (1690 cm^{-1}) and 2-adamantanone (1720 cm^{-1}), the relative solvolysis rate (k_{rel}) of **11b** to **20** was estimated, using a modified version of Schleyer's[26] expression (eq 1) to be 1.2×10^5. Experimen-

$$\log k_{rel} = (1720 - \nu_{CO})/8 + 1.32\sum_i(1 + \cos 3\phi_i) \quad (1)$$

tally, the solvolysis rate of **11b** ($k = 3.6 \times 10^{-4}$ s^{-1}, 60% aqueous EtOH, 25 °C) is 1.4×10^3 times greater than that of **20** ($k = 2.5 \times 10^{-7}$ s^{-1});[24b] i.e., it is slower than predicted, indicating the importance of factors other than those included in expression 1. In any event, the kinetic results provide no evidence for anchimeric assistance to solvolysis of 9-homonoradamant-9-yl tosylate (**11b**). Consequently, the rapid equilibrium between the classical 9-homonoradamant-9-yl cation (**15**) and the 5-protoadamantyl cation (**16**) appears to be the more plausible alternative.

The intermediacy of the bridged 9-homonoradamant-9-yl cation (**19**), however, cannot be excluded completely. The solvolysis results could be interpreted by the initial formation of an essentially classical cationic intermediate (tight ion pair). This intermediate could turn, subsequently, into the bridged cation **19** (solvent-separated ion pair), from which all products arise. The vicinity of the leaving group in the tight ion pair should influence the positive charge location favoring the original, classical structure of the intermediate. This influence should be less pronounced in the solvent-separated ion pair in which charge delocalization may be favored.

Experimental Section

^{13}C NMR spectra were taken on a JEOL FX-100 spectrometer, ^1H NMR spectra were obtained on a Varian A-60A spectrometer, IR spectra were recorded with a Perkin-Elmer 257 spectrophotometer, and mass spectra were taken on a Varian CH-7 mass spectrometer. GLC analyses were carried out on a Varian Aerograph 1800 gas chromatograph. Melting points were determined, using a Thiele apparatus, in sealed capillary tubes completely immersed in oil and are uncorrected. $AlBr_3$ (Fluka) was taken out from a freshly opened ampule and kept in a tightly closed flask. The drying agent employed was magnesium sulfate unless otherwise specified.

10-Homoprotoadamantane-4,5-dione (4). A mixture of 10-homoprotoadamantan-4-one[9] (**3**; 820 mg, 5 mmol), selenium dioxide (670 mg, 6.04 mmol), dioxane (3 mL), and 4–5 drops of water was stirred at 70–75 °C for 24 h. The reaction mixture was then allowed to cool down, diluted with ether (25 mL), filtered, washed with water (3 × 10 mL), and dried. The solvent was evaporated without heating and the crude product recrystallized from heptane to give 837 mg (4.7 mmol, 94%) of bright yellow diketone **4** (≥96% pure by GLC, QF-1, 170 °C): mp 229–231 °C; ^{13}C NMR ($CDCl_3$) δ 203.7, 201.5, 50.5, 47.5, 41.4, 39.8, 37.7, 36.4, 31.8, 30.1, 29.2; ^1H NMR ($CDCl_3$) δ 3.5–0.9 (complex m); IR (KBr) 2930 (s), 2860 (m), 1715 (s), 1455 (m), 1255 (m), 1120 (m), 1015 (m), 910 (m) cm^{-1}; MS *m/e* (relative intensity) 178 (M^+, 51), 150 (43), 94 (69), 81 (100), 80 (95), 68 (55), 67 (53).

2-Hydroxy-9-homonoradamantane-2-carboxylic Acid (5). Freshly recrystallized diketone **4** (800 mg, 4.5 mmol) and potassium hydroxide (4.2 g, 75 mmol) were dissolved in a mixture of dioxane (22 mL) and water (20 mL). The solution was refluxed for 2.5 h. After the solution was cooled, most of the dioxane was evaporated, water (25 mL) was added to the residue, and the resulting aqueous alkaline solution was extracted with ether (3 × 25 mL) and then acidified with concentrated HCl to pH 1–2. The precipitated product was extracted with plenty of ether, and the combined extracts were dried. Removal of solvent left 706 mg (3.6 mmol, 80%) of off-white α-hydroxy acid **5**: mp 111–114 °C; ^{13}C NMR (Me_2SO-d_6) δ 177.1, 83.1, 46.7, 43.9, 42.4, 40.0, 36.0, 34.7, 30.9, 29.4, 21.8; ^1H NMR (Me_2SO-d_6) δ 3–1 (complex m), and 5 (br s); IR (KBr) 3360 (s), 2925 (s), 2850 (m), 1720 (s), 1100 (m) cm^{-1}; MS *m/e* (relative intensity) 196 (M^+, 2), 178 (2), 151 (100), 95 (14), 93 (15), 91 (18), 79 (97).

9-Homonoradamantan-2-one (6). (a) A suspension of α-hydroxy acid **5** (590 mg, 3 mmol) and freshly recrystallized lead tetraacetate (1.46 g, 3.3 mmol) in a mixture of dry benzene (8 mL) and pyridine (0.25 mL) was stirred at room temperature for 48 h. Ethylene glycol (0.2 mL) was then added, and the reaction mixture was stirred for an additional 30 min, diluted with benzene (20 mL), and filtered. The filtrate was washed with 5% HCl (10 mL) and water (10 mL) and dried. The solvent was evaporated and the crude product was purified by column chromatography on Al_2O_3 (neutral, activity III/IV), using 0 → 100% ether–pentane mixture as eluent, followed by sublimation in vacuo. Pure ketone **6** (≥98% by GLC, QF-1, 130 °C) was obtained in 62% yield (280 mg, 1.87 mmol): mp 218–220 °C; ^{13}C NMR ($CDCl_3$) δ 224.2, 50.9, 46.6, 39.7, 39.6, 37.8, 37.5, 35.7, 30.0, 25.5; ^1H NMR ($CDCl_3$) δ 3.2–1.2 (complex m, maximum at 1.67 ppm); IR (KBr) 2935 (s), 2860 (m), 1737 (s), 1450 (m), 1180 (m), 1053 (m) cm^{-1}; MS *m/e* (relative intensity) 150 (M^+, 79), 93 (49), 80 (100), 79 (84), 67 (53), 66 (46).

(b) To a suspension of 196 mg (1 mmol) of α-hydroxy acid **5** in dry benzene (3 mL) was carefully added 80 μL (1.1 mmol) of thionyl chloride. The reaction mixture was refluxed with stirring for 3 h and then allowed to cool down. The solvent was evaporated and the product was purified as described under (a) to yield 51 mg (0.34 mmol, 34%) of pure ketone **6** (≥99% by GLC).

9-Homonoradamantan-2-one Tosylhydrazone Sodium Salt. A solution of 9-homonoradamantan-2-one (**6**, 300 mg, 2 mmol) and *p*-toluenesulfonylhydrazine (400 mg, 2.15 mmol) in absolute ethanol (3 mL) was stirred at 50–60 °C for 30 min and then allowed to stand overnight in a refrigerator. The crystallized product was collected and dried in vacuo. The crude tosylhydrazone was dissolved in dry tetrahydrofuran (3 mL), sodium methoxide ($CH_3ONa \cdot 2CH_3OH$, 260 mg, 2 mmol) was added, and the resulting thick suspension was stirred at room temperature for 1 h. The solvent was evaporated and the salt was dried in vacuo.

Pyrolysis of the 9-Homonoradamantan-2-one Tosylhydrazone Sodium Salt. The dry salt was pyrolyzed at 180–190 °C (0.02 mmHg) for 30 min, and the sublimable products were collected in a trap cooled by liquid nitrogen. Purification by column chromatography (Al_2O_3, activity I, pentane eluent) followed by sublimation afforded 198 mg (74% based on **6**) of a mixture of two major products (82 and 15% by GLC) and three minor products (≤3% total). The GLC analysis was performed

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on a capillary Carbowax 20M column at 75 °C. The ^{13}C NMR ($CDCl_3$) spectrum of the product mixture showed the presence of two components, **7** (δ 42.6, (t, 1 C), 41.2 (d, 1 C), 40.4 (d, 1 C), 37.7 (t, 1 C), 34.8 (t, 1 C), 32.5 (d, 1 C), 28.7 (t, 1 C), 26.3 (d, 1 C), 23.4 (d, 1 C), 12.2 (d, 1 C) (83%)) and **8** (δ 49.1 (2 C), 42.0 (1 C), 32.7 (1 C), 31.7 (2 C), 25.7 (2 C), 23.5 (2 C) (17%)); [**7** + **8**: ^1H NMR ($CDCl_3$) δ 2.8–0.5 (complex m); IR (KBr) 3020 (w), 2930 (s), 2855 (m), 1455 (w), 755 (w) cm^{-1}; MS *m/e* (relative intensity) 134 (M^+, 73), 119 (26), 105 (22), 92 (100), 91 (66), 80 (54), 79 (94)].

9-Noradamantanone (9) was prepared starting from bicyclo[3.3.1]non-2-en-9-ethylene ketal following the procedure outlined by Vegar and Wells.[15a] Bicyclo[3.3.1]non-2-en-9-ethylene ketal[27] (27 g, 0.15 mol) was converted to a 2:1 mixture (24.8 g, 0.125 mol, 83.5%) of *exo*-bicyclo[3.3.1]nonan-3-ol-9-ethylene ketal and the corresponding *exo*-2 alcohol by the hydroboration in tetrahydrofuran at 0 °C followed by oxidation with alkaline hydrogen peroxide.[21,28] The pure *exo*-3 alcohol (≥98% by GLC, SE-30, 140 °C; 13.8 g, 0.07 mol; mp 62–64 °C; ^1H NMR ($CDCl_3$) δ 4.58–4.22 (m, 1 H), 3.9 (s, 4 H), 2.1–1.4 (m, 13 H); IR (KBr) 3260 (s), 2920 (s), 2890 (s), 1445 (m), 1388 (m), 1125 (s), 1052 (s), 832 (m) cm^{-1}) was separated by column chromatography on alumina (neutral, activity II/III), using 3:1 cyclohexane–ethyl acetate as eluent, and oxidized[29] with Jones' reagent at 0 °C to bicyclo[3.3.1]nonan-3-on-9-ethylene ketal (11.8 g, 0.06 mol, 86%; mp 45–49 °C; ^1H NMR ($CDCl_3$) δ 3.98 (s, 4 H), 3.12–1.25 (complex m, 12 H); IR (KBr) 2940 (s), 2920 (s), 1712 (s), 1122 (s), 1030 (s), 947 (m), 823 (m) cm^{-1}). The ketone (9.8 g, 0.05 mol) was converted to the corresponding tosylhydrazone by treatment with tosylhydrazine (9.8 g, 0.053 mol) in methanol (15 mL) for 5 h under gentle reflux. The resulting solution was allowed to stand overnight at 0 °C, and the precipitated tosylhydrazone was isolated by filtration (16.0 g, 0.044 mol, 88%). Treatment of the tosylhydrazone (14.5 g, 0.04 mol) with sodium methoxide ($CH_3ONa{\cdot}2CH_3OH$, 5.2 g, 0.044 mol) in dry tetrahydrofuran (15 mL) for 24 h at 20 °C afforded bicyclo[3.3.1]nonan-3-on-9-ethylene ketal tosylhydrazone sodium salt in 88% yield (13.5 g, 0.035 mol). Pyrolysis of the dry sodium salt (13.5 g, 35 mmol) at 12–14 mmHg and 200–220 °C yielded 43% (2.7 g, 15 mmol) of a 1.5:1 mixture of noradamantan-9-ethylene ketal and bicyclo[3.3.1]non-2-en-9-ethylene ketal. Noradamantan-9-ethylene ketal (≥98% pure by GLC, QF-1, 130 °C; 1.64 g, 9.1 mmol; mp 48–50 °C; ^1H NMR ($CDCl_3$) δ 3.89 (s, 4 H), 2.5–1.45 (m, 12 H); IR (KBr) 2955 (s), 2920 (s), 2860 (s), 1360 (m), 1220 (m), 1135 (s), 1080 (s), 955 (s), 830 (m) cm^{-1}) was separated by column chromatography on silica gel with 9:1 cyclohexane–ethyl acetate as eluent. Treatment[27] of noradamantan-9-ethylene ketal (0.9 g, 5 mmol) with concentrated HCl (1 mL) in 70% aqueous methanol (10 mL) at 40–45 °C for 6 h afforded 9-noradamantanone (≥99% pure by GLC, SE-30, 110 °C; 0.63 g, 4.63 mmol, 93%): mp 192–194 °C; ^1H NMR ($CDCl_3$) δ 2.65 (br s, 4 H), 1.8 (br s, 8 H); IR (KBr) 2860 (m), 1720 (s), 1460 (m), 1215 (m), 1040 (m), 967 (m), 892 (m) cm^{-1}; MS *m/e* (relative intensity) 136 (M^+, 46), 118 (13), 117 (10), 80 (63), 79 (50), 70 (27), 67 (100), 66 (37).

9-Homonoradamantan-9-one (10). To a mixture of 9-noradamantanone (9, 205 g, 15 mmol), potassium hydroxide (10.0 g, 178 mmol), methanol (22 mL), and water (4 mL) stirred at 0–5 °C was added dropwise over 2 h a solution of *p*-toluenesulfonylmethylnitrosamide ("Diazald", 5.6 g, 26.2 mmol) in methanol (45 mL).[30] After the addition of the Diazald solution was completed, the reaction mixture was stirred at 0–5 °C for an additional 2 h and at room temperature overnight. Most of methanol was evaporated in vacuo, and water (40 mL) and ether (30 mL) were added to the residue. The layers were separated and the aqueous one was extracted with ether (3 × 30 mL). The combined extracts were dried. Evaporation of the solvent yielded crude 9-homonoradamantan-9-one (2.03 g, 13.5 mmol, 90%) which contained 10% of the C_{11} homologue, 9-bishomonoradamantan-9(10)-one. Pure 9-homonoradamantan-9-one (**10**) was obtained by preparative GLC (5% SE-30, 130 °C): mp 209–210 °C; ^{13}C NMR ($CDCl_3$) δ 218.2, 54.5, 48.7, 43.6, 41.7, 39.8, 34.2; ^1H NMR ($CDCl_3$) δ 2.9–1.3 (complex m, maximums at 2.43, 1.74, and 1.53 ppm); IR (KBr) 2920 (s), 2850 (m), 1690 (s), 1450 (m), 1330 (m), 1252 (m), 1060 (m), 895 (m) cm^{-1}; MS *m/e* (relative intensity) 150 (M^+, 87), 121 (22), 107 (100), 106 (70), 95 (49), 81 (62), 80 (53), 79 (76), 67 (74).

9-Homonoradamantane (1) was prepared by the Huang-Minlon modification of the Wolff–Kishner reduction[11] of both 9-homonoradamantan-2-one (**6**) and 9-homonoradamantan-9-one (**10**). Starting materials of 120 mg (0.8 mmol) of ketone **6** and 1.36 g (9 mmol) of ketone **10** were used to obtain 9-homonoradamantane (≥99% pure by GLC, SE-30, 90 °C) in 50% (55 mg, 0.4 mmol) and 75% (920 mg, 6.76 mmol) yield, respectively: mp 197–199 °C; ^{13}C NMR ($CDCl_3$) δ 42.4 (t, 4 C), 41.8 (d, 2 C), 37.0 (d, 2 C), 30.5 (t, 2 C); ^1H NMR ($CDCl_3$) δ 2.7–1.0 (complex m, maximums at 1.7, 1.66, and 1.42 ppm); IR (KBr) 2930 (s), 2855 (m), 1450 (m), 1330 (w), 1314 (w), 1170 (w), 1012 (w), 795 (w), 785 (w), 760 (w) cm^{-1}; MS *m/e* (relative intensity) 136 (M^+, 100), 121 (29), 107 (27), 94 (70), 93 (54), 80 (55), 79 (76), 67 (63).

9-Homonoradamantan-9-one Tosylhydrazone. A solution of 9-homonoradamantan-9-one (**10**, 1.1 g, 7.3 mmol) and *p*-toluenesulfonylhydrazine (1.45 g, 7.8 mmol) in methanol (6 mL) was stirred under gentle reflux for 3 h. The reaction mixture was allowed to stand overnight in a refrigerator and the crystallized product was collected (2.26 g, 7.1 mmol, 97%).

9-Homonoradamant-9-ene (12). Methyllithium (20 mL of a 2 M solution in hexane) was added dropwise over 30 min to a suspension of 2.5 g (7.85 mmol) of 9-homonoradamantan-9-one tosylhydrazone in dry ether (10 mL) stirred at 0 °C in a nitrogen atmosphere. The stirring was continued for 24 h at 0 °C, and ether (20 mL) was added followed by dropwise addition of water until the two layers separated. (The color of the reaction mixture changed gradually during the addition of water from brown-red through yellow to white.) The reaction mixture was neutralized with 10% aqueous hydrochloric acid, and the aqueous layer was extracted with ether (5 × 20 mL). The combined extracts were dried, the solvent was removed through a Vigreaux column, and the residue was sublimed in vacuo to give 480 mg (3.58 mmol, 45.6%) of **12** (≥97% pure by GLC, Carbowax 20M, 95 °C): mp 141–143 °C; ^{13}C NMR ($CDCl_3$) δ 137.1 (d, 2 C), 43.4 (d, 2 C), 43.1 (t, 4 C), 39.1 (d, 2 C); ^1H NMR ($CDCl_3$) δ 5.95 (dd, J_1 = 5 Hz, J_2 = 3 Hz, 2 H), 3.0–1.35 (complex m, maximum at 1.57 ppm, 12 H); IR (KBr) 3020 (m), 2930 (s), 2855 (s), 1640 (w), 1445 (m), 1030 (m), 695 (m) cm^{-1}; MS *m/e* (relative intensity) 134 (M^+, 70), 119 (29), 106 (19), 105 (26), 92 (100), 91 (74), 79 (80), 67 (54).

Reaction of 9-Homonoradamantane (1) and 9-Homonoradamant-9-ene (12) with $AlBr_3$. A solution of hydrocarbon **1** or **12** (2 mmol, 272 mg of **1**, 268 mg of **12**) and dry $AlBr_3$ (400 mg, 1.5 mmol) in carbon disulfide (8 mL) was stirred at room temperature for 4 h and for 10 min, respectively. Substantial amounts of tar were formed during the reactions. The reaction mixture was diluted with carbon disulfide (10 mL) and 20 mL of ice–water was added. The layers were separated, and the carbon disulfide solution was washed with water and dried over anhydrous K_2CO_3. The solvent was carefully removed through a Vigreaux column and the residue sublimed in vacuo. The product was identified as adamantane by ^1H NMR, IR, and mass spectra and GLC comparison with an authentic sample. The yield was 53% (144 mg, 1.06 mmol) based on **1** and 48% (131 mg, 0.96 mmol) based on **12**.

9-Chloro-9-homonoradamant-9-ene (13). To a mixture of 9-homonoradamantan-9-one (**10**, 450 mg, 3 mmol) and phosphorus trichloride (1.1 mL, 12.5 mmol) stirred at 0 °C was added phosphorus pentachloride (1.6 g, 7.7 mmol) in three portions over 30 min. The reaction mixture was stirred at 0 °C for an additional 4 h and then allowed to warm slowly to room temperature and poured on ice–water (30 mL). The resulting emulsion was extracted with ether (4 × 20 mL). The combined ether extracts were washed with a 2% $NaHCO_3$ solution (40 mL) and water (40 mL) and dried. The solvent was evaporated through a Vigreaux column and the residue distilled in vacuo to give **13** (95% pure by GLC, SE-30, 130 °C; 443 mg, 2.62 mmol, 87.3%): ^{13}C NMR ($CDCl_3$) δ 141.1 (s, 1 C), 132.9 (d, 1 C), 49.7 (d, 1 C), 42.8 (d, 2 C), 42.7 (t, 2 C), 42.0 (t, 2 C), 38.8 (d, 1 C); ^1H NMR ($CDCl_3$) δ 6.04 (dd, J_1 = 9 Hz, J_2 = 2 Hz, 1 H), 3.0–1.4 (m, maximums at 1.75 and 1.67 ppm, 12 H); IR (film) 3020 (w), 2930 (s), 2850 (m),

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1623 (w), 1442 (m), 1025 (m), 970 (m), 873 (m) cm^{-1}; MS *m/e* (relative intensity) 170 (13), 168 (M^+, 35), 133 (41), 91 (100), 80 (42), 67 (51).

9-Homonoradamantan-9-ol (11a) was prepared in 84% yield by $LiAlH_4$ reduction of ketone **10**. **11a**: mp 219–220 °C; ^1H NMR ($CDCl_3$) δ 4.0 (dt, 1 H), 2.7–1.1 (m, 15 H); IR (KBr) 3310 (s), 2915 (s), 2825 (m), 1450 (m), 1048 (m), 1030 (m), 1000 (m) cm^{-1}; MS *m/e* (relative intensity) 152 (M^+, 14), 134 (100), 119 (24), 108 (25), 105 (25), 92 (46), 79 (67), 67 (56).

Reaction of 9-Homonoradamantan-9-ol (11a) with Sulfuric Acid.[20] To a mixture of concentrated sulfuric acid (3 mL) and pentane (15 mL) vigorously stirred at room temperature was added 304 mg (2 mmol) of **11a** all at once. After 30 min 10 mL of pentane was added and the resulting mixture was poured on 50 mL of ice–water. The layers were separated and the aqueous one was extracted with pentane (5 × 20 mL) followed by ether (5 × 20 mL). The combined pentane extracts were washed with water (2 × 20 mL) and dried. The solvent was carefully removed through a Vigreaux column and the residue sublimed in vacuo to give 152 mg (1.1 mmol, 55%) of adamantane (≥98% pure by GLC, SE-30, 90 °C). From the ether extracts only adamantane (ca. 10 mg) was isolated.

9-Homonoradamant-9-yl tosylate (11b) was prepared by the standard pyridine method.[31] The crude tosylate was recrystallized from 9:1 pentane–ether at −15 °C. Pure **11b** was obtained in 77% yield (mp 41–43 °C).

Kinetic Measurements. The solvolysis rate of **11b** was determined by continuous potentiometric titration by using a Radiometer Copenhagen SBR 2/TTT 11 pH-stat, maintaining the pH of the reaction solution at 6.8. The initial concentration of the tosylate was ca. 0.002 M (10 mg in 15 mL of solvent). The rate constant was calculated from the standard integrated first-order law and is an average value of five individual rate constants; k_{11b} (60% aqueous EtOH, 25 °C) = (3.59 ± 0.01) × 10^{-4} s^{-1} (the uncertainty is one standard error).

Attempts of Bromination of 9-Homonoradamantane (1). A mixture of **1** (204 mg, 1.5 mmol) and bromine (5 mL, 91 mmol) was stirred for 5 h at room temperature and then dissolved in CCl_4 (20 mL) and poured onto ice–water (50 mL). The layers were separated and the aqueous one was extracted with carbon tetrachloride (3 × 20 mL). Combined carbon tetrachloride extracts were shaken with 50-mL portions of saturated aqueous sodium bisulfite until colorless, washed with water (2 × 20 mL), and dried over $CaCl_2$. The solvent was evaporated in vacuo and the residue (130 mg) analyzed by GLC (SE-30, 90 and 150 °C). Only unchanged **1** was detected. Sublimation in vacuo yielded pure **1** (110 mg). The reactions under gentle reflux of bromine for 2.5 h without catalyst and in the presence of boron tribromide (0.8 mL, 8.5 mmol) yielded also exclusively unchanged **1**. However, stirring of **1** (120 mg, 0.88 mmol) in carbon disulfide (6 mL) with bromine (3 mL, 58 mmol), in the presence of $AlBr_3$ (150 mg) for 4 h at room temperature, gave a complex mixture of products (170 mg) containing, in addition to **1**, material insoluble in $CHCl_3$ (78 mg) and two major products with GLC retention times close to that of 1-bromoadamantane.

Solvolysis Product Studies. A solution of **11b** (460 mg, 1.5 mmol) and 2,6-lutidine (177 mg, 1.65 mmol) in 5 mL of 66.7% aqueous dioxane was stirred for 2.5 h at 50 °C. The reaction mixture was allowed to cool down, water (20 mL) was added, and the resulting mixture was extracted with ether (55 × 20 mL). Combined ether extracts were washed with 1% aqueous HCl (20 mL) and 1% aqueous $NaHCO_3$ solution (20 mL) and dried. The solvent was carefully evaporated and the residue (ca. 200 mg) was analyzed by GLC (QF-1, 110 °C). The analysis revealed the presence of three products in the ratio of 0.5:2:1. The products were separated by preparative GLC (QF-1, 110 °C) and identified by IR, ^1H NMR, and mass spectra as well as by GLC comparison with authentic samples to be 9-homonoradamant-9-ene, 5-*endo*-protoadamantanol, 9-homonoradamantan-9-ol, respectively.

Essentially the same product ratio (0.5:2:1) was obtained after 2.5 and 8 h, indicating the products were stable under the reaction conditions used.

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Registry No. 1, 49700-60-9; 3, 65989-65-3; 4, 71382-25-7; 5, 71382-26-8; 6, 71382-27-9; 6 tosylhydrazone, 71382-28-0; 6 tosylhydrazone sodium salt, 71382-29-1; 7, 31517-39-2; 8, 71382-30-4; 9, 23691-62-5; 9 ethylene ketal, 23691-63-6; 10, 71382-31-5; 10 tosylhydrazone, 71382-32-6; 11a, 63923-71-7; 11b, 71382-33-7; 12, 63923-70-6; 13, 71382-34-8; sodium methoxide, 124-41-4; bicyclo[3.3.1]non-2-ene 9-ethylene ketal, 71382-35-9; *exo*-bicyclo[3.3.1]nonan-3-ol 9-ethylene ketal, 70260-42-3; *exo*-bicyclo[3.3.1]nonan-2-ol 9-ethylene detal, 40540-94-1; bicyclo[3.3.1]nonan-3-one 9-ethylene ketal, 54283-54-4; bicyclo[3.3.1]nonan-3-one 9-ethylene ketal tosylhydrazone, 71382-36-0; bicyclo[3.3.1]nonan-3-one 9-ethylene ketal tosylhydrazone sodium salt, 71382-37-1; adamantane, 281-23-2; phosphorus trichloride, 7719-12-2; phosphorus pentachloride, 10026-13-8; 5-*endo*-protoadamantol, 31503-22-7.

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Ion Radicals. 45. Reactions of Zinc Tetraphenylporphyrin Cation Radical Perchlorate with Nucleophiles[1,2]

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Details are given of the reactions of zinc tetraphenylporphyrin cation radical perchlorate ($ZnTPP^{+\cdot}$, ClO_4^-) with pyridine, triphenylphosphine, triphenylarsine, nitrite ion, thiocyanate ion, methanol, water, ammonia, methylamine, and dimethylamine. Reaction with the first five of these nuclophiles gave ZnTPP and a β-substituted ZnTPP according to the usual stoichiometry of reactions of aromatic cation radicals with nucleophilies. From the reaction with nitrite ion a bilitriene was also obtained, identical with that reported earlier by Evans and Smith. The bilitriene was also obtained from reaction with water in tetrahydrofuran. Reaction with methanol gave a meso-substituted methoxyisoporphyrin, previously isolated by Dolphin et al. from reaction of $ZnTPP^{2+}$ with methanol. Reaction with ammonia and the amines gave large yields of ZnTPP. The way in which the bilitriene is formed, the problem of electron exchange with nitrite ion, and the reaction with methanol are discussed.

Four years ago we reported briefly that zinc tetraphenylporphyrin cation radical perchlorate ($ZnTPP^{+\cdot}$, ClO_4^-) reacted with pyridine in acetonitrile solution and gave the β-substituted pyridinium derivative (1).[3] The

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