Synthesis and Reactivity Studies of 2,4-(Dimethylmethano)-2,4-didehydroadamantane: A Comparison with an Unsubstituted Analogue

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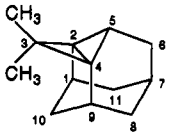
We prepared 2,4-(dimethylmethano)-2,4-didehydroadamantane (1), a *gem*-dimethyl[3.1.1]propellane, and systematically examined its chemical behavior in relation to its unsubstituted analogue 2,4-methano-2,4-didehydroadamantane (2). 2,4-(Dimethylmethano)-2,4-didehydroadamantane (1) was obtained in 70% yield by pyrolysis of the dry lithium salt of the tosylhydrazone derived from 4-isopropylidene-2-adamantanone (6) *in vacuo*. Propellane 1 is thermally more stable than 2, but its reactivity is considerably greater than that of 2. It is highly reactive toward electrophiles and free radicals. Propellane 1 also reacts with alcohols, dienes and oxygen but is less susceptible to polymerization than 2. Enhanced chemical reactivity of dimethyl[3.1.1]propellane 1, with respect to its unsubstituted analogue 2, is in accord with an increase in nucleophilicity of its central bond due to electron donation of the methyl groups.

Introduction

Small-ring propellanes are prone to a variety of interesting reactions[1] due to their molecular shape, variation of size, and presence of quaternary centers with "inverted" tetrahedral geometry. Because of their unusually reactive nature, small-ring propellanes have been the subjects of much theoretical interest,[2] X-ray and electron-diffraction analyses,[3] and vibrational[4] and photoelectron[5] spectroscopic studies.

Few propellanes substituted in the α-position to the central bond have been prepared so far, and there has been no systematic study of the effect of substituents on the nature and reactivity of the bond between the "inverted" carbon atoms. Szeimies et al. prepared alkyl- and aryl-substituted [1.1.1]propellanes[6a] as well as some [4.1.1]propellane derivatives.[6d] [4.1.1]Propellanone[7] was prepared in our laboratory. In continuation of our interest[7,8] on the effect of substituents on the central propellane bond, we have prepared 2,4-(dimethylmethano)-2,4-didehydroadamantane (1), a *gem*-dimethyl[3.1.1]-



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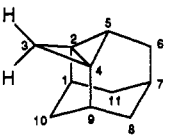

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propellane. One could expect that substituents with a positive inductive effect, such as methyl, would greatly enhance the reactivity in comparison to the unsubstituted propellane 2. Therefore, the properties and reactivity of 1 were compared with those of the parent propellane 2.

Results and Discussion

Synthesis. 2,4-(Dimethylmethano)-2,4-didehydroadamantane (1) was prepared by the intramolecular cycloaddition of 4-isopropylidene-2-adamantylidene to the exocyclic double bond. The carbene was generated by pyrolysis of the corresponding tosylhydrazone lithium salt *in vacuo*. This method has been previously used by us[7,9,10a-c] and also by Hamon and Trenerry[10d] in the synthesis of other [*n*.1.1]propellanes.

The synthesis of 1 originated with 4-hydroxy-2-ada-

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(1) (a) For reviews see: Ginsburg, D. *Propellanes: Structure and Reactions*; Verlag Chemie, GmbH: Weinheim, 1975. (b) Ginsburg, D. *Propellanes: Structure and Reactions*; Deparment of Chemistry: Technion, Haifa, 1980 and 1985; Sequels I and II. (c) Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379. (d) Ginsburg, D. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: Chichester, 1987; Chapter 19. (e) Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 975.

(2) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 773. Stother, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779. Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227. Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591. Zilberg, S. P.; Ioffe, A. I.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 358. Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 4133. Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985. Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001. Ushio, T.; Kato, T.; Ye, K.; Imamura, A. *Tetrahedron* **1989**, *45*, 7743.

(3) (a) Wiberg, K. B.; Burgmaier, G. J.; Sheu, K.; LaPlaca, S. J.; Hamilton, W. C.; Newton, M. D. *J. Am. Chem. Soc.* **1972**, *94*, 7402. (b) Szeimies-Seebach, U.; Harnisch, J.; Szeimies, G.; van Meersche, M.; Germain, G.; Declerq, J.-P. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 848. (c) Szeimies-Seebach, U.; Szeimies, G.; van Meersche, M.; Germain, G.; Declerq, J.-P. *Nouv. J. Chim.* **1979**, *3*, 357. (d) Chakrabarti, P.; Seiler, P.; Dunitz, J. D.; Schülter, A.-D.; Szeimies, G. *J. Am. Chem. Soc.* **1981**, *103*, 7378. (e) Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1985**, *107*, 7257. (f) Seiler, P.; Belzner, J.; Bunz, U.; Szeimies, G. *Helv. Chim. Acta* **1988**, *71*, 2100.

(4) Wiberg, K. B.; Dailey, W. P.; Walker, F. H.; Waddell, S. T.; Crocker, L. S.; Newton, M. *J. Am. Chem. Soc.* **1985**, *107*, 7247. Wiberg, K. B.; Waddell, S. T.; Rosenberg, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 2184.

(5) (a) Eckert-Maksić, M.; Mlinarić-Majerski, K.; Majerski, Z. *J. Org. Chem.* **1987**, *52*, 2098. (b) Gleiter, R.; Pfeifer, K.-H.; Szeimies, G.; Belzner, J.; Lehne, K. *J. Org. Chem.* **1990**, *55*, 636.

(6) (a) Szeimies-Seebach, U.; Schöffer, A.; Römer, R.; Szeimies, G. *Chem. Ber.* **1981**, *114*, 1767. (b) Kottirsch, G.; Polborn, K.; Szeimies, G. *J. Am. Chem. Soc.* **1988**, *110*, 5588. (c) Belzner, J.; Gareiss, B.; Polborn, K.; Schmid, W.; Semmler, K.; Szeimies, G. *Chem. Ber.* **1989**, *122*, 1509. (d) Baumgart, K.-D.; Harnisch, H.; Szeimies-Seebach, U.; Szeimies, G. *Chem. Ber.* **1985**, *118*, 2883.

(7) Majerski, Z.; Kostov, V.; Hibšer, M.; Mlinarić-Majerski, K. *Tetrahedron Lett.* **1990**, *31*, 915.

(8) Mlinarić-Majerski, K.; Šafar-Cvitaš, D.; Majerski, Z. *Tetrahedron Lett.* **1991**, *32*, 1655.

(9) (a) Mlinarić-Majerski, K.; Majerski, Z. *J. Am. Chem. Soc.* **1980**, *102*, 1418. (b) Mlinarić-Majerski, K.; Majerski, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7389.

(10) (a) Vinković, V.; Majerski, Z. *J. Am. Chem. Soc.* **1982**, *104*, 4027. (b) Majerski, Z.; Žuanić, M. *J. Am. Chem. Soc.* **1987**, *109*, 3496. (c) Majerski, Z.; Veljković, J.; Kaselj, M. *J. Org. Chem.* **1988**, *53*, 2662. (d) Hamon, P. D. G.; Trenerry, V. C. *J. Am. Chem. Soc.* **1981**, *103*, 4962.

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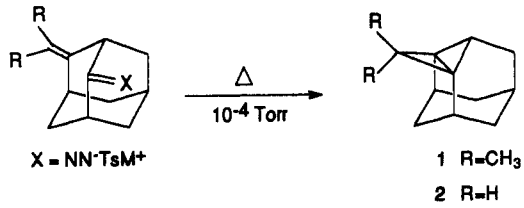
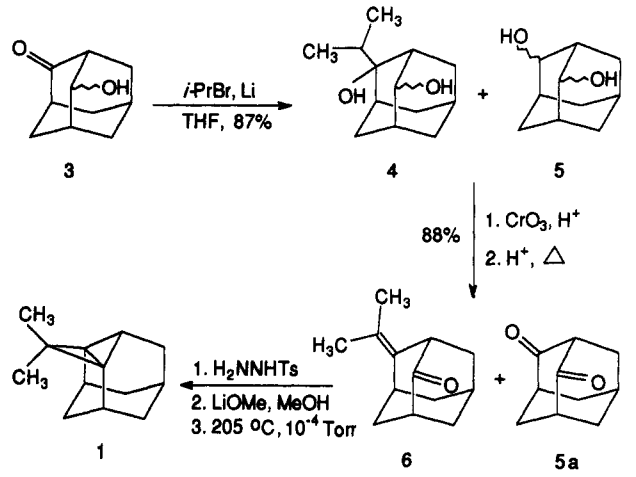


mantanone,[11] Scheme 1. A modification of the Barbieri reaction[12] was used for introduction of the isopropyl group to the adamantane skeleton. Isopropyllithium, formed from isopropyl bromide and lithium metal in THF under the action of ultrasound, adds to hydroxy ketone **3** to give a mixture of 2,4-dihydroxy-2-isopropyladamantane (**4**) and 2,4-dihydroxyadamantane (**5**) in the ratio of 5:1 and 87% yield. It was found that the optimum conditions of the reaction are at the temperatures between 0 and 4 °C and 0.01 M concentration of isopropyl bromide in THF. In more concentrated solutions and at higher temperatures the yield of the reduced diol **5** was increased, while at temperatures below 0 °C the overall yield of the reaction becomes lower. Jones oxidation of the mixture of diols **4** and **5**, followed by acid-catalyzed dehydration of the resulting 4-hydroxy-4-isopropyl-2-adamantanone, afforded a mixture of 2,4-adamantanedione (**5a**) and 4-isopropylidene-2-adamantanone (**6**) in 88% yield. After separation of ketone **6** by column chromatography on silica gel, it was transformed to the corresponding tosylhydrazone **7a** and then to its lithium salt **7b** with lithium methoxide in MeOH. Thermal decomposition of the dry lithium salt **7b** at 205 °C *in vacuo* afforded propellane **1**, 2,4-(dimethylmethano)-2,4-didehydroadamantane, 3,3-dimethylpentacyclo[5.3.1.$0^{2,4}$.$0^{2,5}$.$0^{4,9}$]undecane (IUPAC). This strained, pentacyclic hydrocarbon is at the same time a derivative of bicyclobutane with two carbon atoms of inverted geometry and a *gem*-dimethyl-substituted derivative of bridged [3.1.1]propellane.

The mass spectrum of **1** shows a molecular ion peak at *m/z* 174, in accord with molecular formula $C_{13}H_{18}$. In the ^{1}H NMR spectrum, two distinguished singlets at 1.28 (3 H) and 1.08 (3 H) correspond to the *exo*- and *endo*-methyl groups. In the ^{13}C NMR spectrum there are 10 signals for 10 nonequivalent carbon atoms. A quantitative ^{13}C NMR spectrum shows that three signals out of 10 are of double intensity, each for two equivalent C-atoms. From off-resonance decoupled spectra one can determine their multiplicity, singlets for C-2 and C-4, doublets for C-1 and C-9, and triplets for C-8 and C-11. The assignment of all other signals was based on the data of quantitative and off-resonance decoupled spectra, as well as the coupling constants J_{C-H} determined from NOE ^{13}C NMR spectra. A doublet at 26.0, J = 134 Hz, corresponds to C-7 and doublet at 59.4, J = 164 Hz, to cyclopropane carbon atom in position 5. Cyclopropane coupling constants (J_{C-H} = 160 Hz) are, because of enhanced s-character of its C–H bonds, higher than the coupling constants for sp^3-hybridized carbon atoms (125–135 Hz).[13] A triplet at 32.1 for C-6 with magnetically equivalent H-atoms and a doublet of doublets at 56.6 for C-10 with nonequivalent H-atoms were determined by the comparison with data obtained

Scheme 1



for the 2,4-methano-2,4-didehydroadamantane.[9b] The signal for the *endo*-CH_3-group was determined in the ^{13}C NMR spectrum to be at the lower field, 22.0, than the signal for the *exo*-CH_3 group, 19.8. This is in accord with the literature data for *exo*- and *endo*-shifts in position 2 of the bicyclobutane ring.[13] Two signals are quartets with J_{C-H} = 126 Hz. Characteristic vibrations of skeletal deformation in the IR spectrum of propellane **1** appear at 590 (s), 515 (m), and 435 (w) cm^{-1}. The IR spectrum of 2,4-methano-2,4-didehydroadamantane (**2**) shows characteristic skeletal deformation vibrations at 575 (s), 550 (w), 500 (w), 425 (w), and 353 (w) cm^{-1}. Intensive absorption in this region could be indicative of unusual charge distribution in small-ring propellanes.[14] IR spectral parameters of **1** and **2** are in accord with the literature data of Wiberg et al. for [2.2.1]-, [1.1.1]-, [2.1.1]-, and [3.2.1]propellanes[14,15] and Szeimies et al. for bridged and substituted [1.1.1.]propellanes.[6c] Intense low-frequency vibration bands are due to antisymmetric stretching vibrations of the propellane central bond with respect to the rest of the carbon skeleton. The Raman spectrum (Stokes region 100–1600 cm^{-1}) of *gem*-dimethyl-substituted propellane **1** shows a very intense vibrational band at 763 cm^{-1} due to symmetric stretching of the central propellane bond with respect to the symmetry plane and the rest of the hydrocarbon skeleton, and other vibrational bands at 1146 (m), 842 (m), and 645 (s) cm^{-1}. Unsubstituted propellane **2** absorbs at 1145 (m), 977 (m), 765 (vs), and 672 (s) cm^{-1}.

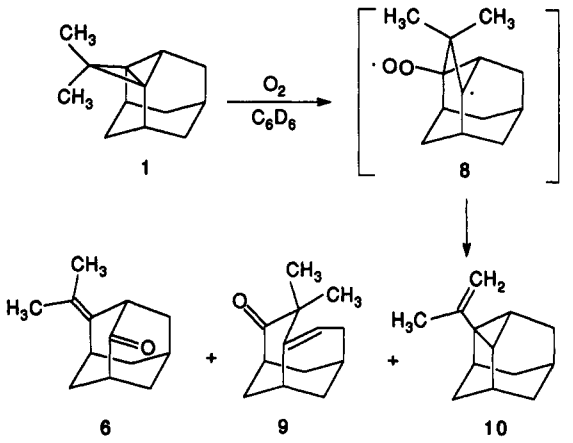
Reactivity Studies. 2,4-(Dimethylmethano)-2,4-didehydroadamantane (**1**) is thermally more stable than 2,4-methano-2,4-didehydroadamantane (**2**). The half-life of **1** at 62–65 °C in dry benzene-d_6 under a nitrogen atmosphere is approximately 38 h.[16] The competition experiment with the mixture of **1** and **2** showed that **2** decomposes three times faster than **1**. A *gem*-dimethyl effect is apparent in the stability of propellane **1**.[17]

Propellane **1** was entirely inert toward triethylamine, gaseous ammonia, and pyridine-d_5 at room temperature.

(11) Faulkner, D.; McKervey, M. A. *J. Chem. Soc. C* **1971**, 3906.
(12) (a) Luche, J.-L.; Damiano, J.-C. *J. Am. Chem. Soc.* **1980**, *102*, 7926. (b) Molle, G.; Bauer, P. *J. Am. Chem. Soc.* **1982**, *104*, 3481.
(13) (a) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; p 335. (b) Kalinowski, H. O.; Berger, S.; Braun, S. *^{13}C-NMR-Spectroskopie*; Georg Thieme Verlag: Stuttgart, 1984.
(14) Walker, F. H.; Wiberg, K. B.; Michl, J. *J. Am. Chem. Soc.* **1982**, *104*, 2056.
(15) Wiberg, K. B.; Walker, F. H. Pratt, W. E.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 3638.
(16) In the thermal rearrangement of **1** at 65 °C, in addition to polymeric material traces of 2-isopropenyl-2,4-didehydroadamantane (**10**) were also formed.
(17) For the general effect of strain upon reactivity and stability see: Stirling, C. J. M. *Tetrahedron* **1985**, *41*, 1613.

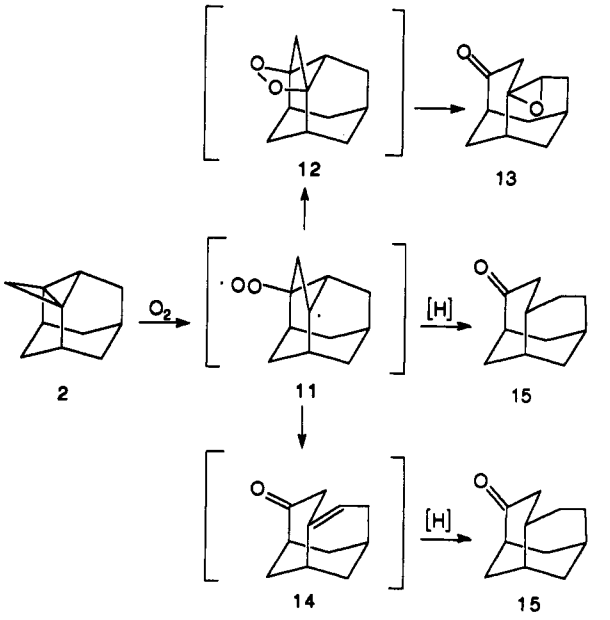
However, with electrophiles and free radicals 1 reacted readily. It reacted also with dienes and atmospheric oxygen.

Reaction with Oxygen. Small-ring propellanes are known to undergo facile addition of oxygen. For example, [3.2.1]propellane reacted with atmospheric oxygen to give a 1:1 copolymer.[18] It has been observed also that [3.1.1]-,[6d,9,10a,19] and [4.1.1]propellanes[3b,10b-d,20] are sensitive to oxygen and tend to polymerize. In contrast to these compounds, [2.2.2]propellane does not react with oxygen at a noticeable rate,[21] and it was suggested that the difference in reactivity probably results from the difference in bonding between cyclopropane and cyclobutane rings. However, it was found that [1.1.1]propellane also does not react with oxygen and is extremely stable.[22] 2,4-(Dimethylmethano)-2,4-didehydroadamantane (1) reacts rapidly with oxygen at room temperature to give a mixture of three low molecular weight products 6, 9, and 10 in a 4:3:1 ratio, respectively. The ratio of products depends on the concentration of oxygen. With a slow stream of oxygen 1 reacted slowly giving 6, 9, and 10 in a 2:1:1.5 ratio, respectively. The ratio of products was determined by GC (NPGS, 190 °C). The products were isolated in 72% yield by vacuum transfer, separated on a silica gel column, and identified by spectroscopic means (see Experimental Section).



The mechanism of this reaction most probably involves the initial interaction of an electron-rich outside lobe of the propellane central bond orbitals with oxygen and formation of adamantyl diradical 8 which then rearranges and closes to give 6, 9, and 10. However, we cannot rule out the possibility that formation of 2-isopropenyl-2,4-didehydroadamantane (10) is due to thermal rearrangement of 1.[16]

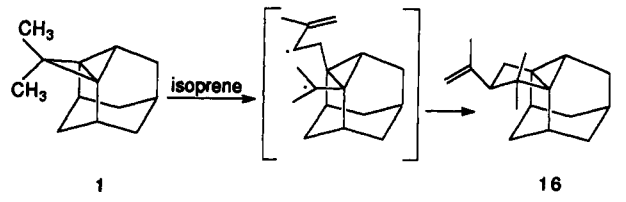
This is the first example of the formation of ketones as the products in the reaction of small-ring propellanes with oxygen. Due to the presence of methyl groups, the rearrangement of diradical 8 is much faster than polymerization. This result prompted us to reexamine the reaction of propellane 2 with oxygen. When a strong stream of oxygen was bubbled through the benzene-d_6 solution of 2 at room temperature, reaction was completed in 20 min. Major product 13[23] was isolated in 10% yield and identified by spectroscopic means. When the reaction was carried out in the presence of a proton source (1,4-cyclohexadiene) 15 was isolated as a major product in 22% yield. The formation of 15 and 13 could be explained by the formation of diradical 11 which can abstract protons to give 15 or close to peroxide 12 which then rearranges to epoxide 13. Since propellane 1 reacted with oxygen to give strained olefin 9 in a good yield, we have calculated[24] the heats of formation for 9 and 14 and found that 9 is more stable than 14, by approximately 7 kcal-mol^{-1}. Therefore, we cannot exclude the possibility of the formation of strained olefin 14 as an intermediate which abstracts protons to give 15.



Reaction with Isoprene. Small-ring propellanes react with electron-deficient alkenes and alkynes to give rearranged products through the intermediately formed diradicals.[25] In order to get further insight into this area of hydrocarbon chemistry we have studied the reaction of 1 with cyclopentadiene and isoprene. We chose to study these reactions because *gem*-dimethylsubstitution at [3.1.1]propellane should cause the central propellane bond to be more nucleophilic. [3.1.1]Propellane 1 does not react with cyclopentadiene, however, it reacts with isoprene to give a mixture of products. According to spectral data, molecular mass m/z 242, as well as IR, ^{1}H NMR, and ^{13}C NMR spectra, the major product is, most probably, 16.[26]

Radical Reactions. It is also known that the central C–C bonds in bicyclo[1.1.0]butane,[27a] bicyclo[2.1.0]-

(18) (a) Wiberg, K. B.; Burgmaier, G. J. *Tetrahedron Lett.* **1969**, 317. (b) Gassman, P. G.; Topp, A.; Keller, J. W. *Tetrahedron Lett.* **1969**, 1093.
(19) Gassman, P. G.; Proehl, G. S. *J. Am. Chem. Soc.* **1980**, *102*, 6862.
(20) Szeimies-Seebach, U.; Szeimies, G. *J. Am. Chem. Soc.* **1978**, *100*, 3966.
(21) Eaton, P. E.; Temme, G. H., III. *J. Am. Chem. Soc.* **1973**, *95*, 7508.
(22) Wiberg, K. B.; Waddell, S. T. *J. Am. Chem. Soc.* **1990**, *112*, 2194.
(23) 2-Oxo-4,5-epoxytricyclo[5.3.1.0^{4,9}]undecane.
(24) Molecular mechanics calculations were performed using the computer program PC MODEL 386 version 4.0.
(25) (a) Baumgärtel, O.; Harnisch, J.; Szeimies, G.; van Meersche, M.; Germain, G.; Declerq, J. P. *Chem. Ber.* **1983**, *116*, 2205. (b) Aue, D. H.; Reynolds, R. N. *J Org. Chem.* **1974**, *39*, 2315. (c) Wiberg, K. B.; Waddell, S. T.; Laidig, K. *Tetrahedron Lett.* **1987**, *27*, 1553.
(26) According to the ^{13}C NMR spectrum of the crude reaction mixture, the major product was present in a 70% yield. The IR spectrum exhibited the characteristic cyclopropane CH vibrational band at 3020, as well as characteristic =CH$_2$ and C=C vibrational bands at 3080 and 1640 cm^{-1}, respectively. The ^{1}H NMR spectrum showed a multiplet at 4.9–4.7 and the ^{13}C NMR spectrum had signals at 148 and 108 ppm, characteristic of exocyclic double bonds. Unfortunately, we were not able to get pure compound because of its decomposition during purification.
(27) (a) Moore, W. R.; Hall, S. S.; Largman, C. *Tetrahedron Lett.* **1969**, 4353. (b) Gassman, P. G.; Yamaguchi, R. *Tetrahedron* **1982**, *38*, 1123.



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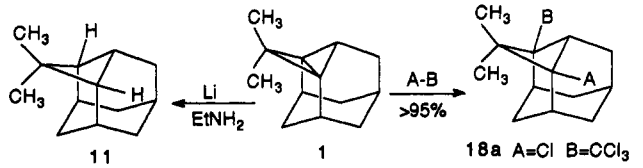
pentane[27b] derivatives, and small-ring propellanes[9,10ab,20,28] can easily be reduced by electron-transfer hydrogenation. Electron-transfer hydrogenation of **1** with lithium in refluxing ethylamine yielded exclusively 2,4-(dimethylmethano)adamantane (**17**). 2,4-Disubstituted 2,4-(dimethylmethano)adamantanes **18a-c** were, also, the only products of the free-radical reactions of propellane **1** with carbon tetrachloride, fluorotrichloromethane, and dimethyl disulfide.[29] The products **18a-c** were identified by IR, ^{1}H NMR, ^{13}C NMR, and mass spectra (see Experimental Section).



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18a A=Cl B=CCl_3
18b A=Cl B=$CFCl_2$
18c A=B=SCH_3

It was shown that unsubstituted propellane **2** possesses free-radical character to a certain extent.[30] Similarly, an excess of carbon tetrachloride in the reaction mixture of propellane **1** in C_6D_6 caused a strong ESR signal to appear (Figure 1). The splitting constants of approximately 12.56 G are consistent with the structure of the 2,4-(dimethylmethano)-2-adamantyl free radical **19**.

Reactions with Electrophiles. In contrast to the free-radical reactions of **1**, its reaction with electrophiles yielded mixtures of rearranged products. Dimethyl[3.1.1]propellane **1** reacted instantaneously at room temperature with glacial acetic acid and methanol and slowly with water, ethanol, and isopropyl and *tert*-butyl alcohols, yielding mixtures of at least two products (Table 1). According to the GC–mass analysis in the reaction of **1** with acetic acid besides **21a** four unidentified products were obtained, less than 1% of each. In the presence of water propellane **1** reacted slowly (18 days)[31] yielding a mixture of **6**, **10**, and **21b** in a 1:1.2:2.8 ratio, respectively. Methanol (freshly distilled from KOH) reacted with **1** instantaneously and exothermally, yielding a 1:1.5:1.5 mixture of 2-isopropenyl-2,4-didehydroadamantane (**10**), 2,4-(dimethylmethano)-2-methoxyadamantane (**20c**), and 4-isopropylidene-2-methoxyadamantane (**21c**), respectively. In the presence of triethylamine, dimethyl[3.1.1]propellane **1** reacted with methanol slowly and gave **10** as the major product. Compound **10** was also the major product in the reactions of **1** with ethanol, *i*-PrOH, and *t*-BuOH (Table 1). With *t*-BuOH, **1** gave **10** in addition to two products in a ratio of 1:1. These products were identified as **6** and **9**, the products obtained in the reaction of **1** with oxygen. With degassed *t*-BuOH **1** reacted in 1 month to give **10** as a sole volatile product.

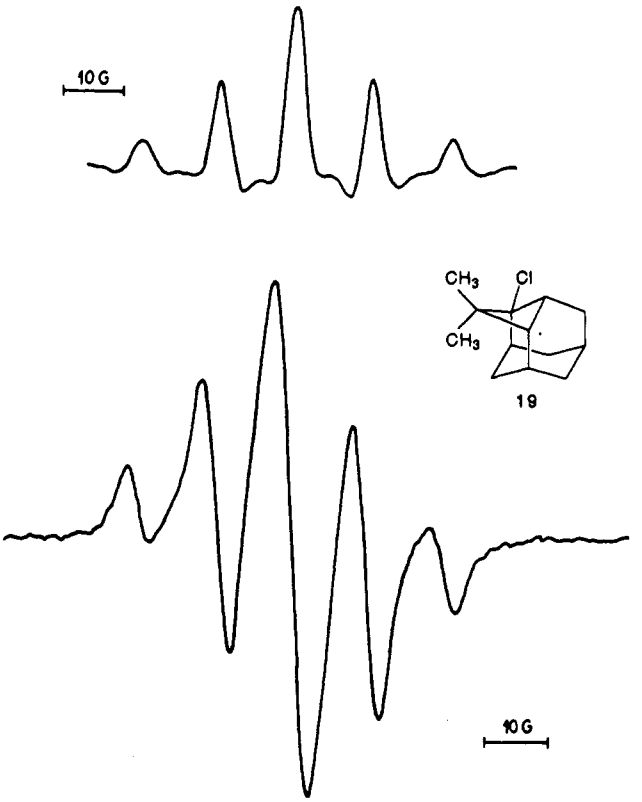


Figure 1. ESR spectrum of the 2,4-(dimethylmethano)-2-adamantyl radical **19**.

Table 1. Product Distribution in the Reaction of Propellane 1 with Electrophiles

electrophiles HA	pK_a[a]	product ratio[b] 10	20	21	reaction time
AcOH	4–5			96	<1 min
H_2O		25		55	18 days[31]
MeOH	16	26	35	39	<1 min
MeOH/Et_3N		43	26	31	3 hours
EtOH	18	70		30	3 hours
i-PrOH	18	75		25	3 days
t-BuOH	19	75			1 week

[a] Measured in benzene: McEwen, W. K. *J. Am. Chem. Soc.* **1963**, *58*, 1124. [b] Product ratio was determined from ^{13}C NMR spectra of the crude mixtures.

Propellane **2** reacted instantaneously with acetic acid and methanol yielding mixtures of the corresponding 2-*anti*-substituted 4-methyleneadamantane, 2-substituted 2,4-methanoadamantane, and 2-(methyl-substituted) 2,4-didehydroadamantane[9b] but did not react with ethanol, *i*-PrOH, or *t*-BuOH. No products were detected (by ^{13}C NMR) after 48 h at room temperature in benzene-d_6. After 1 week polymerization took place due to thermal decomposition.

Comparative investigations of the relative reactivities of **1** and **2** showed that **1** is much more reactive although its central bond is more sterically hindered. The reaction rates of propellanes **1** and **2** with acetic acid are approximately the same, **1** being slightly faster. Acetic acid is a much stronger acid than an alcohol, and the attacking species in this case is most probably a proton. A proton is highly electrophilic, and both propellanes **1** and **2** react

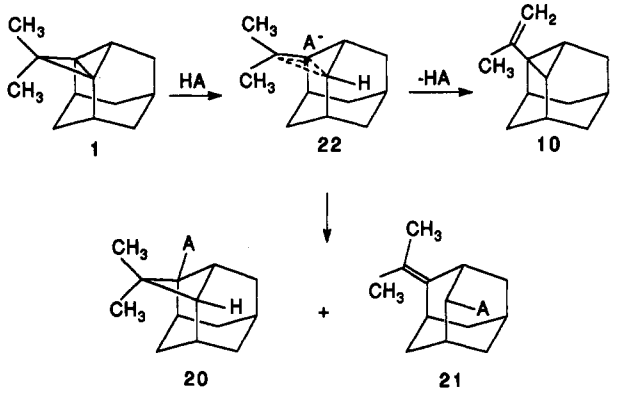
(28) (a) Semmler, K.; Szeimies, G.; Belzner, J. *J. Am. Chem. Soc.* **1985**, *107*, 6410. (b) Wiberg, K. B.; Waddell, S. T.; Laidig, K. *Tetrahedron Lett.* **1986**, *27*, 1553. (c) Belzner, J.; Szeimies, G. *Tetrahedron Lett.* **1987**, *28*, 3099.

(29) Because of the instantaneous reaction of **1** and **2** with these reagents, we were not able to perform competition experiments.

(30) Mlinarić-Majerski, K.; Majerski, Z.; Rakvin, B.; Veksli, Z. *J. Org. Chem.* **1989**, *54*, 545.

(31) In the reaction with water at 4 °C both propellanes **1** and **2** reacted very slowly, most probably due to the formation of a two-phase system.

Scheme 2



HA = (a) AcOH; (b) H_2O; (c) MeOH; (d) EtOH; (e) *i*-PrOH; (f) *t*-BuOH

equally fast. Propellane **2** reacted with water slowly to give polymeric material. However, when ultrasound was applied during the reaction, after 50 min no presence of **2** was detected and two alcohols were isolated in a 58% yield and identified as *anti*-2-hydroxy-4-methyleneadamantane and 2-hydroxy-2,4-methanoadamantane. IR, ^{1}H NMR, and ^{13}C NMR spectra of these compounds are in accord with published data.[9b] In contrast to the reactions of dimethylpropellane **1** with acetic acid and water, **1** reacts considerably faster with methanol than the unsubstituted propellane **2**. This raises the question of whether, in this reaction, the attacking species is the proton or whether there is a heterolytic cleavage of the O–H bond of alcohols caused by the increased nucleophilicity of the central bond of **1** with methyl substitution at C_3. The difference in the product distribution in the reaction of **1** with methanol in the presence of triethylamine as well as in the reactions with other alcohols implies that the reaction of **1** with alcohols most likely involves two processes: the heterolytic cleavage of the O–H bond as well as the electrophilic attack by a proton followed by the attack of another molecule of methanol via the cation **22** (Scheme 2). Since propellane **2** reacted with neither ethanol, *i*-PrOH, nor *t*-BuOH, these results could be best explained by the higher nucleophilicity of the central bond in propellane **1** compared to propellane **2** due to the electron donation of the methyl groups in **1**.

Conclusions

We may conclude that reactivity of dimethyl[3.1.1]propellane **1** is considerably greater than that of **2**, due to the higher nucleophilicity of its central bond. The enhanced chemical reactivity of propellane **1** with respect to its unsubstituted analogue **2** is in accord with the increase in electron density on the outer side of the "inverted" carbon atoms and an increase of the HOMO energy of propellane **1** due to the electron donation of the methyl groups.

Experimental Section

General. The purity of all compounds was determined by GC and/or ^{13}C NMR. ^{1}H and ^{13}C NMR spectra were taken on JEOL FX 90Q or Varian Gemini 300 spectrometers. IR spectra were recorded on a Perkin-Elmer M-297 or Perkin-Elmer 580 B, and Raman spectra were obtained with Dilor Z 24 spectrometer using the green line at 514.5 nm of an Ar ion laser Coherent Innova 100–15, "single mode". GC analyses were carried out on a Varian Aerograph 1800 or 3300 gas chromatographs on stainless steel and capillary columns, respectively, and GC–mass analyses on a Perkin-Elmer Sigma 3 gas chromatograph connected to a Kratos MS-125 spectrometer. The mass spectra were recorded on Varian CH-7 or Extrel FTMS 2001 spectrometers. Benzene-d_6 (99% *d*, Merck) was dried over molecular sieves prior to use. Other solvents and chemicals, if not stated otherwise, were of commercial reagent grade and were used without further purification.

2,4-Dihydroxy-2-isopropyladamantane (4). Li granula (0.17 g, 24 mmol, Merck) were added to a solution of 4-hydroxy-2-adamantanone (**3**)[11] (1.0 g, 6 mmol) and of *i*-PrBr (1.48 g, 12 mmol) in 120 mL of absolute THF (0.1 M solution of *i*-PrBr in THF) at 0–4 °C in a nitrogen atmosphere. The mixture was exposed to ultrasonic waves (30 kHz, 120 W) for 3 h. The unreacted Li was removed by vacuum filtration and the solvent evaporated. To the crude residue was added 30 mL of water, and the suspension was neutralized with 10% HCl. The neutral reaction mixture was extracted with ether (3 × 40 mL), and the combined extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent yielded a mixture of diols **4** and **5** (1.08 g, 87%) in the ratio of 5:1 (GC, FS 130 °C): IR (KBr) 3250, 2920, 2860, 1460, 1060, 915 cm^{-1}. The mixture of diols **4** and **5** was used in the next step of the synthesis without further purification.

4-Isopropylidene-2-adamantanone (6). To a stirred solution of the mixture of diols **4** and **5** (1.5 g, 7 mmol) in 25 mL of acetone, at room temperature, was added Jones reagent dropwise until a permanent red color appeared. The reaction mixture was stirred for an additional hour at the same temperature. The inorganic salts were removed by filtration, the filtrate was evaporated, and the crude residue was dehydrated in a vacuum sublimator at 120 °C (~20 Torr). The wet mixture of sublimed products was dissolved in ether (50 mL), washed with saturated $NaHCO_3$ solution, and dried over $MgSO_4$. Evaporation of ether yielded ketones **5a** and **6** (1.23 g, 94%) in the ratio of 1:8 (GC, FS 130 °C). Pure 4-isopropylidene-2-adamantanone (**6**) (1.1 g, 83%) was obtained by column chromatography on silica gel (elution with 0 → 50% ether in pentane): IR (KBr) 2930, 2860, 1720, 1455, 1375, 1230, 1060 cm^{-1}; ^{1}H NMR (C_6D_6) 3.58 (br s, 1 H), 2.79 (br s, 1 H), 2.50 (br s, 1 H), 1.94–1.42 (m, 15 H, with distinguished singlet at 1.53 corresponding to the CH_3 groups); ^{13}C NMR (C_6D_6) 212.2 (s), 136.2 (s), 120.9 (s), 53.2 (d), 46.4 (d), 40.9 (t), 38.8 (t), 37.7 (t), 37.4 (t), 32.2 (d), 27.8 (d), 19.9 (q), 19.3 (q); MS *m/z* (rel intensity) 190 (M^+, 100), 162 (42), 147 (49), 121 (47), 120 (32), 119 (45), 106 (25), 105 (19), 104 (55), 93 (34), 92 (33), 91 (60). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53, found C, 82.12; H, 9.26.

4-Isopropylidene-2-adamantanone Tosylhydrazone Lithium Salt (7b). 4-Isopropylidene-2-adamantanone (**6**) (1.0 g, 5.3 mmol) was dissolved stepwise in a warm (50 °C), stirred solution of (*p*-toluenesulfonyl)hydrazine (1.008 g, 5.4 mmol, 2% excess) in 4 mL of absolute EtOH. The mixture was stirred for 1 h at the same temperature. After the mixture was cooled in the refrigerator, 4-isopropylidene-2-adamantanone tosylhydrazone (**7a**) crystallized out, the mother liquor was pipetted off, and the product was washed several times with pentane and dried *in vacuo*. There was obtained 1.61 g (85%) of white solid material: IR (KBr) 3220, 2920, 2850, 1650, 1600, 1450, 1390, 1330, 1160, 915 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.9–7.7 (m), 7.4–7.1 (m), 4.0 (br s), 3.6 (br s), 3.2–1.2 (m), 2.4 (s), 1.55 (s); ^{13}C NMR ($CDCl_3$) 169.98, 169.87, 143.57, 143.46, 136.35, 135.61, 134.93, 129.35, 129.24, 127.99, 120.83, 120.04, 44.47, 40.46, 39.45, 38.99, 38.83, 38.43, 37.53, 37.30, 36.91, 32.22, 31.99, 31.15, 27.54, 21.50, 19.98, 19.87, 19.75, 19.30; NMR data indicate that tosylhydrazone **7a** is a mixture of *syn*- and *anti*-isomers; HRMS calcd for $C_{20}H_{28}N_2SO_2$ 358.1709, found 358.1615.

Tosylhydrazone **7a** was added gradually to the solution of LiOMe (0.190 g, 5.0 mmol) in 7 mL of absolute MeOH with stirring at 0 °C. The reaction mixture was stirred for another hour at 0 °C and for half an hour at ~30 °C. The solvent was evaporated, and the residual salt **7b** was dried *in vacuo* (10^{-3} Torr): IR (KBr) 2920, 2850, 1670, 1450, 1230, 1125, 1080, 1030, 1010, 980, 810 cm^{-1}.

LiOMe was prepared by a modified method of Brown et al.[32]

(32) Brown, L.; Dickerhoof, D. W.; Bafus, D. A. *J. Am. Chem. Soc.* **1962**, *84*, 1371.

Absolute MeOH, 10.6 mL (8.42 g, 263 mmol), was added dropwise over 0.5 h, with cooling and in a N_2 atmosphere, to Li granula (1.84 g, 263 mmol, Merck) in 100 mL of dry benzene. The reaction mixture was kept in an ultrasound bath (30 kHz, 120 W) for 3 h. Unreacted Li was removed by filtration *in vacuo*. Evaporation of benzene afforded white, powdered LiOMe (7.50 g, 75%).

2,4-(Dimethylmethano)-2,4-didehydroadamantane (1). A flask containing dry tosylhydrazone lithium salt **7b** (0.36 g, 1 mmol) was connected to a high vacuum pump (10^{-4} Torr) *via* a "U" trap cooled by liquid nitrogen. When the flask was immersed in a hot oil bath (205 °C) the pyrolysis product distilled into the trap. After 15 min the oil bath was removed, dry nitrogen was allowed to fill the apparatus, the flask was disconnected, and a stream of dry nitrogen was allowed to pass through the trap. The trap was closed at both ends and weighed. The propellane 1 was obtained as a dense, colorless liquid (0.122 g, 70%). For the IR spectra 1 was put neat between two KBr pellets in a drybox filled with nitrogen and the spectrum recorded immediately. For ^1H and ^{13}C NMR spectra (*vide supra*) and the reactivity studies 1 was dissolved under dry nitrogen in anhydrous benzene-d_6 (0.35 mL), and the resulting solution was transferred *via* syringe into an NMR tube which was flushed previously with dry nitrogen: IR (film KBr) 3035, 3010, 2930, 2860, 1470, 1175, 590, 515, 435 cm^{-1}; Raman (neat) 1146 (m), 842 (m), 763 (vs), 645 (m) cm^{-1}; ^1H NMR (C_6D_6) 2.93–2.33 (m, 3 H), 1.99–1.46 (m, 9 H), 1.28 (s, *exo* CH_3), 1.08 (s, *endo* CH_3); ^{13}C NMR (C_6D_6) 59.4 (d, J_{C-H} = 165 Hz, C-5), 56.6 (dd, J_{C-H} = 128 and 131 Hz, C-10), 56.0 (s, C-3), 36.2 (t, J_{C-H} = 129 Hz, C-8 and C-11), 35.8 (d, J_{C-H} = 136 Hz, C-1 and C-9), 34.1 (s, C-2 and C-4), 32.1 (t, J_{C-H} = 128 Hz, C-6), 26.0 (d, J_{C-H} = 134 Hz, C-7), 22.0 (q, J_{C-H} = 126 Hz, C-12), 19.8 (q, J_{C-H} = 126 Hz, C-13); MS *m/z* (rel intensity) 174 (M^+, 100), 159 (27), 145 (22), 133 (28), 119 (43), 117 (38), 105 (54), 91 (89), 79 (50), 77 (35).

Thermolysis of 1. The NMR tube containing propellane 1 in benzene-d_6 under dry nitrogen was tightly closed and immersed in an oil bath at 62–63 °C. Thermal decomposition of 1 was followed by ^1H NMR spectroscopy. The intensity of signals at 1.06 and 1.28 which correspond to the protons of two methyl groups were measured periodically, and the half-life of thermal decomposition for 1 was determined using the usual procedure. The competition experiments with the mixture of propellanes 1 and 2 were performed in the same way.

Reaction of Propellane 1 with Oxygen. Propellane 1 (0.139 g, 0.8 mmol) was dissolved in 0.4 mL of benzene-d_6 under a nitrogen atmosphere. The solution was transferred to an NMR tube, and a fast stream of oxygen was bubbled through the solution for 20 min at 22 °C. Completion of the reaction was determined by ^1H NMR. Vacuum transfer of the crude reaction mixture (10^{-2} Torr, 190 °C) afforded 0.108 g (72%) of three products in a 1:3:4 ratio (GC, NPGS, 190 °C). The products were separated by silica gel column chromatography. Elution with pentane afforded 0.011 g of 2-isopropenyl-2,4-didehydroadamantane (**10**): IR (film KBr) 3090, 3020, 2930, 2850, 1640, 1625, 1455, 1445, 1375, 885 cm^{-1}; ^1H NMR (C_6D_6) 4.82 (s, 1 H), 4.77 (s, 1 H), 2.40–2.1 (m, 3 H), 1.9–1.2 (m, 13 H, with a singlet at 1.68 corresponding to the CH_3 group); ^{13}C NMR (C_6D_6) 148.6 (s), 108.2 (t), 50.5 (dd), 41.3 (s), 36.6 (d), 33.4 (t), 33.1 (t), 32.8 (d), 30.3 (d), 28.9 (t), 27.8 (d), 26.5 (d), 20.9 (q); MS *m/z* (rel intensity) 174 (M^+, 46), 159 (30), 145 (35), 131 (66), 117 (47), 105 (74), 91 (100), 79 (37); HRMS calcd for $C_{13}H_{18}$ 174.1403, found 174.1404.

Elution with pentane:ether (95:5) gave 0.023 g of 2-oxo-3,3-dimethyltricyclo[5.3.1.$0^{4,9}$]undec-4-ene (**9**), followed by 0.037 g of methylene ketone **6**.

Spectral data of **9**: IR (film KBr) 2900, 1700, 1620, 1490, 1470, 1455, 1440, 1385, 1365, 1110, 1060, 1010 cm^{-1}; ^1H NMR (C_6D_6) 5.83 (m, 1 H), 2.54–0.70 (m, 17 H, with two distinct singlets at 1.35, and 1.16 corresponding to CH_3 groups); ^{13}C NMR (C_6D_6) 213.79 (s), 144.61 (s), 127.26 (d), 52.85 (t), 47.72 (d), 39.10 (t), 37.59 (t), 33.80 (d), 32.49 (t), 30.32 (t), 29.63 (d), 24.34 (q), 23.07 (q); MS *m/z* (rel intensity) 190 (M^+, 58), 162 (40), 147 (66), 133 (13), 121 (56), 120 (34), 119 (60), 107 (30), 105 (92), 93 (58), 92 (31), 91 (100), 79 (73), 77 (60).

Reaction of Propellane 2 with Oxygen. Propellane 2 (0.131 g, 0.9 mmol) was dissolved in 0.4 mL of benzene-d_6 under a nitrogen atmosphere. The solution was transferred to an NMR tube, and a fast stream of oxygen was bubbled through at room temperature. Completion of the reaction was determined by ^1H NMR. After 20 min no propellane 2 was observed. GC analysis of the crude product showed a very complex mixture. The main product was isolated by column chromatography on Al_2O_3 activity II/III. Elution with ether in petroleum–ether (0 → 100%) afforded 0.016 g (10%) of 2-oxo-4,5-epoxytricyclo[5.3.1.$0^{4,9}$]-undecane (**13**): IR (KBr) 2900, 1720, 1460, 1435, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) 3.2 (d, 1 H, J_{C-H} = 12.9 Hz), 2.8–1.2 (m, 13 H, with distinguished doublet at 1.8, J_{C-H} = 12.9 Hz); ^{13}C NMR ($CDCl_3$) 212.4 (s), 57.9 (d), 55.1 (s), 46.1 (t), 44.9 (d), 33.2 (t), 32.1 (t), 31.5 (t), 31.4 (t), 29.3 (d), 27.1 (d); MS *m/z* (rel intensity) 178 (M^+, 23), 164 (27), 150 (74), 135 (54), 117 (36), 108 (87), 91 (68), 80 (91), 79 (100); HRMS calcd for $C_{11}H_{14}O_2$ 178.0988, found 178.0993.

Reaction of Propellane 2 with Oxygen in the Presence of 1,4-Cyclohexadiene. To the solution of propellane 2 (0.117 g, 0.8 mmol) in 0.4 mL of benzene-d_6 was added 0.094 mL (1 mmol) of 1,4-cyclohexadiene. A fast stream of oxygen was bubbled through the reaction solution for 25 min. The reaction was followed by ^1H NMR. GC analysis of the crude mixture indicated the presence of **13** and **15** in a 1:3.5 ratio, respectively, plus one unidentified product and a significant quantity of polymeric material. Major product **15** was isolated by column chromatography on neutral alumina using ether in pentane (0 → 100%) as eluent, followed by sublimation at 80 °C and 20 Torr. There was obtained 0.013 g (9.9%) of tricyclo[5.3.1.$0^{4,9}$]undecan-2-one (**15**). IR, ^1H, ^{13}C, and MS spectra are identical with those of an authentic sample prepared from 2-protoadamantanone with CH_2N_2: IR (KBr) 2910, 2880, 1720, 1460, 1445, 1410, 1350, 1260, 1220, 1145 cm^{-1}; ^1H NMR ($CDCl_3$) 2.8–1.0 (br complex m, 16 H). ^{13}C NMR ($CDCl_3$) 220.82 (s), 44.07 (d), 43.79 (t), 39.44 (t), 31.66 (t), 30.19 (t), 28.49 (d), 26.40 (t), 25.67 (d), 25.16 (t), 24.32 (d); MS *m/z* (rel intensity) 164 (M^+, 100), 122 (13), 104 (25), 91 (32), 80 (45), 79 (84); HRMS calcd for $C_{11}H_{16}O$ 164.1195, found 164.1168.

Electron Transfer Hydrogenation of Propellane 1. To a stirred solution of $EtNH_2$ (0.06 mL, 0.0415 g, 0.92 mmol) in *n*-pentane (2 mL) at −80 °C and in a dry nitrogen atmosphere was added Li metal (0.020 g) in small pieces. After the addition of Li the solution became intensely dark blue colored. Stirring was continued for another 0.5 h, and then a solution of propellane 1 (0.160 g, 0.92 mmol) in 0.5 mL of *n*-pentane was added *via* a syringe through the serum cap. The mixture was stirred additionaly 1.5 h at −80 °C, 1.5 h at −4 °C, and 45 min at the reflux temperature of $EtNH_2$ (17 °C) and then poured onto ice. The product was extracted with pentane (3 × 30 mL), and the combined extracts were washed with 5% HCl and dried over $MgSO_4$. The evaporation of solvent afforded 0.104 g (64%) of colorless oily 2,4-(dimethylmethano)adamantane (**17**). An analytical sample of **17** was obtained by chromatography on silica gel: IR (KBr) 3025, 3000, 2910, 2860, 1460, 1380, 1370, 1345, 1250, 1105, 950, 815 cm^{-1}; ^1H NMR (C_6D_6) 2.9–0.7 (m, 20 H, with two distinct singlets at 1.3 and 1.2 corresponding to the CH_3 groups); ^{13}C NMR (C_6D_6) 47.9 (d, C-2, C-4), 39.9 (s, C-3), 36.8 (t, C-8, C-11), 36.1 (dd, C-10), 35.0 (t, C-6), 34.5 (d, C-5), 31.0 (d, C-1, C-9), 30.2 (d, C-7), 25.6 (q, C-12), 25.2 (q, C-13); MS *m/z* (rel intensity), 176 (M^+, 100), 161 (32), 133 (40), 119 (23), 105 (27), 96 (22), 93 (26), 91 (48).

2-Chloro-4-(trichloromethyl)-2,4-(dimethylmethano)adamantane (18a). Carbon tetrachloride (0.10 mL, 0.160 g, 1.04 mmol) was added *via* syringe to a solution of 1 (0.080 g, 0.46 mmol) in 0.3 mL of benzene-d_6 in an atmosphere of dry nitrogen. Excess solvent was evaporated, and the 0.148 g (98%) of oily product (purity 95% according to ^{13}C NMR) was purified by column chromatography on Al_2O_3 (activity II/III elution with pentane). An analytical sample of **18a** was obtained by distillation (110 °C, 10^{-2} Torr) using a Kugelrohr apparatus: IR (KBr) 3075, 3020, 2930, 2880, 1465, 1450, 1385, 1370, 1115, 1090, 960, 925, 895, 865, 770, 750, 740, cm^{-1}; ^1H NMR (C_6D_6) 3.3–0.7 (m, 18 H, with two singlets at 1.5 and 1.2 corresponding to CH_3 groups); ^{13}C NMR (C_6D_6) 104.7 (s, C-14), 72.6 (s, C-2), 61.3 (s, C-4), 55.8 (s, C-3), 48.3 (d), 40.3 (d), 37.0 (t), 35.7 (dd, C-10), 34.3 (d), 32.9 (t), 28.6 (d), 27.8 (t), 25.1 and 25.0 (q's, C-12 and C-13); MS *m/z* (rel intensity) 330 (M^+ + 4, 0.8), 328 (M^+ + 2, 1.8), 326 (M^+, 1.2), 295 (21), 293 (67), 291 (65), 257 (66), 256 (21), 255 (100), 251 (44), 249 (43), 219 (31), 211 (15), 209 (44), 173 (23), 131 (25), 105 (32), 91 (54).

2-Chloro-4-(dichlorofluoromethyl)-2,4-(dimethylmethano)adamantane (18b). Freshly distilled fluorotrichloromethane (0.050 mL, 0.075 g, 0.55 mmol) was added *via* syringe at room temperature to a stirred solution of 1 (0.080 g, 0.46 mmol) in 0.3 mL of benzene-d_6 in an atmosphere of dry nitrogen. Solvent and excess $CFCl_3$ were evaporated, and the crude product (0.142 g, 100%) was purified by column chromatography (Al_2O_3), activity II/III, elution with pentane) to afford white, waxy product **18b** (0.131 g, 92%): IR (KBr) 3065, 3020, 2980, 2930, 2860, 1475, 1470, 1460, 1385, 1370, 1225, 1210, 1140, 1100, 1080, 1050, 1000, 960, 895, 875, 795, 765 cm^{-1}; ^1H NMR (C_6D_6) 3.03 (s, 1 H), 2.5 (m, 1 H), 2.22 (s, 1 H), 2.11 (s, 1 H), 2.01 (d, 1H), 1,83 (d, 1 H), 1.62–1.3 (m, 8 H, with distinguished doublet at 1.47 corresponding to the CH_3 group), 1.16 (s, CH_3 group), 0.89 (d, 1 H); ^{13}C NMR (C_6D_6)[33] 124.7 (1 C, d, J_{C-F} = 304.2 Hz), 72.5 (1 C), 59.2 (1 C, d, J_{C-F} = 18.6 Hz), 53.9 (1 C), 46.7 (1 C), 40.7 (1 C), 36.1 (1 C, d, J_{C-F} = 3.7 Hz), 35.5 (1 C), 33.2 (1 C), 32.47 (1 C, d, J_{C-F} = 3.7 Hz), 28.2 (1C), 27.36 (1 C, d, J_{C-F} = 5.7 Hz), 24.8 (1 C), 24.15 (1 C). MS *m/z* (rel intensity) 312 (M^+ + 2, 2), 310 (M^+, 2), 277 (60) 275 (100), 239 (35) 203 (23) 183 (23); HRMS calcd for $C_{14}H_{18}FCl_2$ (M^+ - Cl) 275.0764, found 275.0778.

2,4-Bis(methylthio)-2,4-(dimethylmethano)adamantane (18c). Freshly distilled dimethyl disulfide (0.085 mL, 0.089 g, 0.95 mmol) was added *via* syringe at room temperature to a stirred solution of 1 (0.160 g, 0.92 mmol) in 0.3 mL of benzene-d_6 in an atmosphere of dry nitrogen. Evaporation of solvent and excess of CH_3SSCH_3 afforded the crude product **18c** (0.246 g, 100%, purity 95% according to ^{13}C NMR). The product **18c** was purified by silica gel column chromatography (elution with 0 → 100% benzene in pentane): IR (KBr) 3060, 3010, 2930, 2865, 1440, 1385, 1370, 1260, 1215, 1110, 970, 950, 880, 855 cm^{-1}; ^1H NMR (C_6D_6) 2.57–2.44 (m, 2 H), 2.18–2.02 (m, 4 H), 1.8–1.46 (m, 14 H with two distinct singlets at 1.74 and 1.49 which correspond to the SCH_3 and CH_3 groups, respectively), 1.23 (d, 1 H), 1.12 (s, 3 H); ^{13}C NMR (C_6D_6) 56.4 (s, C-2 and C-4), 52.9 (s, C-3), 44.1 (d), 35.7 (dd, C-10), 35.3 (d, C-1 and C-9), 34.7 (t, C-8 and C-11), 30.3 (t), 26.9 and 25.9 (q's C-12 and C-13), 25.4 and 11.7 (t and q, respectively, C-14 and C-15); MS *m/z* (rel intensity) 221 (M^+ - SCH_3, 100), 173 (14), 145 (13), 131 (40), 117 (13), 105 (17), 91 (18); HRMS calcd for $C_{14}H_{21}S$ (M^+- SCH_3) 221.1358, found 221.1364.

Reaction of Propellane 1 with Acetic Acid. Acetic acid (0.095 g, 1.58 mmol) was added *via* syringe under a nitrogen atmosphere at 15 °C to a solution of 1 (0.187 g, 1.1 mmol) in 0.3 mL of benzene-d_6. The reaction was instantaneous. After evaporation of solvent and filtration through silica gel to remove unreacted acetic acid, 0.208 g (82%) of reaction products was obtained. The mixture was 96% pure of one component (by ^{13}C NMR spectrum). Pure product **21a** (0.162 g) was isolated by repeated silica gel column chromatography (pentane:ether, 8.5:1.5) in 64% yield: IR (KBr) 2920, 2860, 1780, 1465, 1445, 1370, 1240, 1195, 1090, 1025, 995 cm^{-1}; ^1H NMR (C_6D_6) 4.85 (br s, 1 H), 3.07 (br s, 1 H), 2.76 (br s, 1 H), 2.31–1.91 (m, 3 H), 1.91–1.25 (m, 16 H with distinct singlets at 1.84, 1.62 and 1.58 corresponding to the CH_3 groups); ^{13}C NMR (C_6D_6) 169.24 (s), 136.69 (s), 119.98 (s), 76.41 (d), 38.60 (t), 37.08 (d), 36.46 (t), 32.90 (t), 32.11 (d), 32.00 (d), 31.60 (t), 27.65 (d), 20.99 (q), 19.70 (q); MS *m/z* (rel intensity) 234 (M^+, 95), 174 (100), 159 (41), 145 (22), 133 (68), 131 (76), 119 (79), 105 (56), 91 (90), 79 (68).

Reaction of Propellane 1 with Water. Distilled water (0.01 mL) was added *via* syringe to an NMR tube containing 0.080 g (0.46 mmol) of propellane 1 in 0.3 mL of dry C_6D_6 at room temperature and in an atmosphere of dry nitrogen. The mixture was reacted 1 h at room temperature and then at 4 °C to completion. The progress of the reaction was monitored by ^{13}C NMR. The beginning of the reaction was visible from the spectrum after 24 h, and completion occurred after 18 days. The ^{13}C NMR spectrum of the crude reaction mixture indicated the formation of three major components in the ratio of 25:55:20. They were identified as compounds **10**, **21b**, and **6** by comparison with the ^{13}C NMR spectra of authentic samples of **10** and **6** and of independently synthesized **21b**.

***anti*- and *syn*-4-Isopropylidene-2-adamantanol (21b and 22).** A solution of 4-isopropylidene-2-adamantanone (0.45 g, 2.4 mmol) in 40 mL of dry ether was added dropwise over 10 min and with stirring to a suspension of $LiAlH_4$ (0.098 g, 2.6 mmol) in 40 mL of dry ether. Stirring was continued at reflux for 14 h. Excess $LiAlH_4$ was destroyed with water. The organic layer was separated and the water layer extracted with ether (2 × 50 mL). Combined ether extracts were dried over $MgSO_4$. Evaporation of solvent gave a mixture of *anti*- and *syn*-4-isopropylidene-2-adamantanol (**21b** and **22**) (0.44 g, 96%): ^1H NMR (C_6D_6) 3.9–0.8 (m, 40 H, with distinct singlets at 1.66 and 1.62 for 6 H each); ^{13}C NMR (C_6D_6) 138.21, 135.27, 121.79, 118.40, 75.74, 74.10, 40.46, 40.18, 38.99, 38.71, 37.66, 36.68, 36.46, 35.09, 34.65, 33.07, 32.73, 32.28, 30.98, 28.10, 27.37, 19.75, 19.64. *anti*-Alcohol **21b** was separated from the mixture by repeated column chromatography (Al_2O_3 II/III, elution with 20 → 100% ether in pentane): IR (KBr) 3290, 2990, 2960, 2950, 2850, 1467, 1450, 1375, 1065, 1035, 1020, 965 cm^{-1}; ^1H NMR ($CDCl_3$) 3.73 (m, 1 H), 2.83 (m,2 H), 2.28–0.75 (m, 17 H with dinstinct singlet at 1.64 corresponding to the CH_3 groups); ^{13}C NMR ($CDCl_3$) 137.14 (s), 118.51 (s), 74.04 (d), 39.28 (d), 38.26 (t), 35.06 (d), 33.97 (t), 31.60 (d), 31.38 (t), 30.36 (t), 27.20 (d), 19.61 (q), 19.31 (q). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H 10.48. Found: C, 81.41; H, 10.48.

Reaction of Propellane 1 with Methanol. Absolute methanol (0.032 g, 1 mmol) freshly distilled from KOH was added *via* syringe under a dry nitrogen atmosphere and at room temperature to the solution of 1 (0.160 g, 0.92 mmol) in 0.3 mL of benzene-d_6. The reaction took place instantaneously. Evaporation of solvent and excess methanol gave a mixture of three products (0.179 g, 100%) in a ratio of 2:3:1 (GC, FS 120 °C). Products were isolated by column chromatography on silica gel in a 55% overall yield. Elution with pentane:ether (95:5) yielded first 2-isopropenyl-2,4-didehydroadamantane (**10**), (0.331 g, 34%). Further elution afforded 2-*anti*-methoxy-4-isopropylideneadamantane (**21c**), (0.502 g, 51%) and 2-methoxy-2,4-(dimethylmethano)adamantane (**20c**) (0.151 g, 15%).

Spectral data of **21c**: IR (KBr) 2920, 2850, 2820, 1465, 1450, 1375, 1195, 1100, 980, 965, 915, cm^{-1}; ^1H NMR (C_6D_6) 3.25–3.10 (m, 4 H, with distinct singlet at 3.20), 2.81 (br s, 1 H), 2.3–2.45 (m, 2 H), 2.08 (br s, 1 H), 1.86–1.44 (m, 14 H with two singlets at 1.63 and 1.62 corresponding to the CH_3 groups); ^{13}C NMR (C_6D_6) 137.93 (s), 118.45 (s), 83.19 (d), 55.36 (q), 38.83 (t), 36.85 (d), 36.51 (t), 32.68 (t), 32.45 (d), 31.43 (t), 31.32 (d), 27.82 (d), 19.75 (q), 19.53 (q); MS, *m/z* (rel intensity) 206 (M^+, 48), 174 (100), 159 (35), 145 (39), 131 (60), 117 (34), 105 (51), 91 (63); HRMS calcd for $C_{14}H_{22}O$ 206.1665, found 206.1663.

Spectral data of **20c**: IR (KBr) 3020, 2980, 2920, 2860, 2820, 1470, 1380, 1360, 1240, 1175, 1100, 1080, 1070, 865, 855, 830, 805 cm^{-1}; ^1H NMR (C_6D_6) 3.10 (s, 3 H), 2.48 (m, 1 H), 2.35–2.00 (m, 2 H), 2.0–1.04 (m, 13 H with singlet at 1.11 corresponding to the CH_3 group), 0.87 (s, 3 H); ^{13}C NMR (C_6D_6) 75.89 (s), 50.98 (dd), 49.79 (q), 41.14 (s), 34.41 (d), 33.78 (t), 33.23 (t), 33.17 (d), 28.78 (t), 27.08 (d), 26.59 (d), 24.36 (q), 23.57 (d), 20.87 (q); MS *m/z* (rel intensity) 206 (M^+,19), 191 (100), 174 (32), 131 (46), 117 (35), 105 (52), 91 (70), 79 (32), 73 (53); HRMS calcd for $C_{14}H_{22}O$ 206.1665, found 206.1642.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of 1, **10**, **17**, **18a-c**, and **21a** and ^1H NMR spectra of **9**, **13**, **15**, **20c**, and **21c** (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(33) It is interesting to note that this compound exhibits a fluorine effect through several bonds. Total interpretation of the spectra of compound **18b**, as well as the long-range effect studies, will be published elsewhere.