The Bond between Inverted Carbon Atoms. Synthesis and Chemistry of 2,4-Methano-2,4-didehydroadamantane: A Highly Reactive [3.1.1]Propellane[1]

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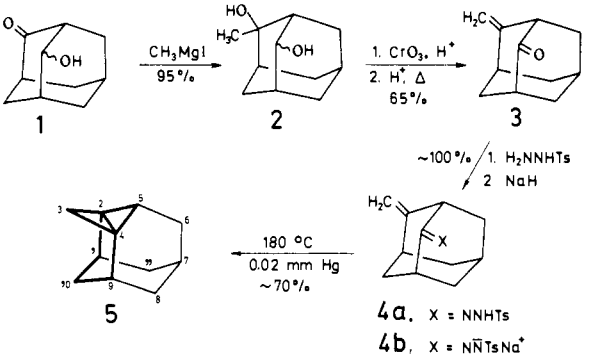
Abstract: In order to provide a better insight into the reactivity and nature of the bond between inverted carbon atoms, we prepared 2,4-methano-2,4-didehydroadamantane (**5**), a prototype small propellane, and systematically examined its chemical behavior. Propellane **5** was obtained in 70% yield by pyrolysis of the dry sodium salt of the tosylhydrazone derived from 4-methylene-2-adamantanone in vacuo. It was rather stable thermally and entirely inert toward nucleophiles but highly reactive toward electrophiles and free radicals. With acetic acid, hydrogen chloride, and methanol, **5** yielded mixtures of the corresponding 2-anti-substituted 4-methyleneadamantane (**7**), 2-substituted 2,4-methanoadamantane (**8**), and 2-(substituted-methyl) 2,4-didehydroadamantane (**9**), while carbon tetrachloride, tosyl chloride, and thiophenol gave exclusively the corresponding 2,4-disubstituted 2,4-methanoadamantanes (**10a–c**) through a free radical process. The electron-transfer hydrogenation yielded 2,4-methanoadamantane (**11**) as the only product. Both acids and free radicals attack the central bond producing the intermediary bridged 2,4-methano-2-adamantyl cation and the 4-substituted 2,4-methano-2-adamantyl free radicals, respectively. These results indicate a high electron density at the reaction site, i.e., at the back side of the inverted carbon atoms, and, consequently, a decrease in electron density between them. Such a bond appears to be a limiting form of the carbon–carbon single bond, while the other limiting form is the usual single bond between two carbon atoms in aliphatic compounds. All other carbon–carbon single bonds should necessarily lie between these two extremes.

The unusual chemical behavior of the bond between inverted carbon atoms has attracted attention since the first syntheses of small propellanes.[2a,b] Contrary to the usual carbon–carbon single bond, the central bond in small propellanes is highly reactive toward bromine as well as acids.[2-11] Large prepellanes, however, behave chemically like normal alicyclic hydrocarbons.[11]

Medium propellanes, such as [4.2.1],[12] [3.3.1],[13] [3.2.2],[14] [4.2.2],[14,15] and [3.3.2],[16] are generally reactive toward bromine and/or acids, although considerably less reactive than small propellanes. Small prepellane systems containing a total of six bridge carbons ([2.2.2],[3] [3.2.1],[2] and [4.1.1][4]) have been prepared in the last decade and were found to be very reactive. However, these prepellanes as well as the medium ones are rather stable thermally except the [2.2.2] homologue, which undergoes ring opening at a measurable rate even at room temperature.

Scheme I



Recently we prepared the first carbocyclic [3.1.1]propellane, the highly reactive 2,4-methano-2,4-didehydroadamantane,[5] and soon afterward Gassman and Proehl reported a synthesis of the parent [3.1.1]propellane.[6] Szeimies and co-workers obtained a complex carbocyclic spiro [3.1.1]propellane,[7a] as well as an oxa-[7b] and aza[3.1.1]propellane derivative.[7c] Last year we published a preparation of an exceptionally strained [3.1.1]propellane, 2,6-methano-2,6-didehydronorbornane,[8] and Wiberg et al. reported syntheses of [2.2.1]-[9] and [1.1.1]propellanes.[10] The former was isolated in a matrix, while the latter turned out to be rather stable thermally.

The main purpose of this investigation was to provide a better understanding of the reactivity and nature of the unusual bond between inverted carbon atoms. To this end we systematically examined the reactivity of 2,4-methano-2,4-didehydroadamantane (**5**), a prototype small propellane, toward nucleophiles, electrophiles, and free radicals, as well as its hydrogenolysis and thermal

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lability. In this paper we wish to report the results of our investigation and, by comparison with other propellanes and related systems, provide further insight into the nature of strained carbon–carbon single bonds.

Results

Synthesis. 2,4-Methano-2,4-didehydroadamantane[17] (**5**) was prepared by the intramolecular cycloaddition of 4-methylene-2-adamantylidene to the olefinic bond. The carbene was generated by pyrolysis of the corresponding tosylhydrazone alkali salt in vacuo. This methodology has been recently used by us[8] and also by Hamon and Trenerry[4b] for the preparation of other [*n*.1.1]-propellanes.

The synthesis of **5** originated with 4-hydroxy-2-adamantanone[18] (**1**) (Scheme I). Hydroxy ketone **1** was readily converted (95%) to 2-methyl-2,4-adamantanediol (**2**) by treatment with methyl Grignard reagent. Jones oxidation of diol **2** followed by acid-catalyzed dehydration of the resulting 4-hydroxy-4-methyl-2-adamantanone afforded 65% of 4-methylene-2-adamantanone (**3**). Tosylhydrazone **4a** and its sodium salt (**4b**) were prepared in almost quantitative yields from ketone **3** by standard procedures.[19] Pyrolysis of the dry tosylhydrazone sodium salt **4b** at 180 °C in vacuo produced 70% of propellane **5**, which was sublimed into a trap cooled by liquid nitrogen. It was more than 95% pure by quantitative ^{13}C NMR.

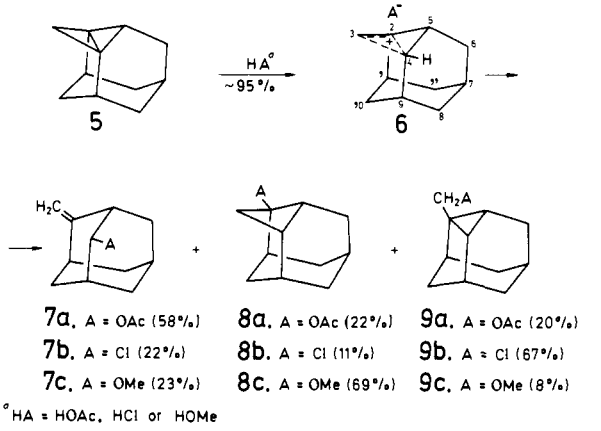
The structure of propellane **5** was established by spectral means. In particular, the mass spectrum showed a molecular ion peak at m/z 146 (65%), and the IR spectrum exhibited the characteristic cyclopropane C–H vibrational band at 3040 cm^{-1}. The ^1H NMR spectrum showed a complex multiplet at δ 2.36–1.06 and two distinctive doublets at δ 2.12 and 1.08 with a coupling constant of J = 4 Hz, typical of geminal cyclopropane protons.[20] These doublets were absent in the ^1H NMR spectrum of 2,4-(methano-d_2)-2,4-didehydroadamantane (**5a**), which was obtained by pyrolysis of the tosylhydrazone sodium salt of 4-(methylene-d_2)-2-adamantanone. The ^{13}C NMR spectrum unambiguously confirmed the structure of **5**: δ 64.4 (d, J = 166 Hz, 1 C, C-5), 50.1 (t, J = 129 Hz, 1 C, C-10), 40.9 (dd, J = 151, 169 Hz, 1 C, C-3), 44.0 (d, J = 138 Hz, 2 C, C-1, C-9), 34.2 (t, J = 128 Hz, 2 C, C-8, C-11), 30.8 (t, J = 129 Hz, 1 C, C-6), 26.6 (d, J = 133 Hz, 1 C, C-7), 24.2 (s, 2 C, C-2, C-4). The C-H coupling constants of the ^{13}C NMR dd signal at δ 40.9 are typical of the methylene carbon in the bicyclobutane system.[21] This signal was absent in the ^{13}C NMR spectrum of **5a**, which provided additional evidence for the structure of **5**. The other ^{13}C NMR signals were assigned by the relative signal intensities in the quantitative spectrum and their splitting patterns in the proton off-resonance decoupled spectra, as well as by the C–H coupling constants. The ^{13}C NMR signals corresponding to carbon atoms 6 and 10 were distinguished using the successive selective-decoupled technique.[22]

Reactivity Studies. The half-life of **5** at 65 °C is approximately 10 h in dry benzene-d_6 solution under a nitrogen atmosphere as determined by ^1H NMR.

Reactions of **5** with nucleophiles, electrophiles, and free radicals were systematically studied. Toward diethylamine (in benzene-d_6) and pyridine-d_5 as well as toward gaseous ammonia (in benzene-d_6) **5** was entirely inert at room temperature. However, with electrophiles and free radicals it reacted readily.

Glacial acetic acid reacted with **5** in benzene-d_6 solution instantaneously at room temperature yielding almost quantitatively a mixture of 2-*anti*-acetoxy-4-methyleneadamantane (**7a**), 2-acetoxy-2,4-methanoadamantane (**8a**), and 2-(acetoxymethyl)-2,4-didehydroadamantane (**9a**) in a ratio of 3:1:1 (Scheme II).

Scheme II



The reaction was exothermic. The product ratio was determined by quantitative ^{13}C NMR (see experimental section). Olefinic acetate **7a** was separated from saturated acetates **8a** and **9a** by column chromatography on $AgNO_3$-pretreated silica gel. Acetates **8a** and **9a** could not be separated from each other directly, and they were reduced with $LiAlH_4$ to the corresponding alcohols, **8**, A = OH and **9**, A = OH, which were separated by chromatography on a silica gel column. Olefinic acetate **7a** and the two alcohols **8**, A = OH and **9**, A = OH were identified by ^{13}C NMR, ^1H NMR, IR, and mass spectra (Table I).

The stereochemistry of the acetoxy substituent in 2-*anti*-acetoxy-4-methyleneadamantane (**7a**) was established by ^1H NMR spectroscopy. The ^1H NMR spectrum of **7a** (Table I) showed a sharp singlet at δ 4.63 corresponding to the olefinic protons. Such as singlet was also present in the spectra of 2-*anti*-hydroxy- and 2-*anti*-chloro-4-methyleneadamantane[23] and appears to be characteristic for the anti orientation of the substituent. The two olefinic protons in the corresponding syn epimers are very different and their ^1H NMR signals appear as two clear doublets. The anti orientation of the acetoxy substituent in **7a** was confirmed by $LiAlH_4$ reduction of 4-methylene-2-adamantanone (**3**) followed by separation and acetylation of the resulting epimeric alcohols. An examination of a molecular model of ketone **3** revealed that the carbonyl group was sterically more hindered at the anti than at the syn side. Consequently, to the major product of the $LiAlH_4$ reduction of **3** and the derived acetate were assigned the structures of 2-*anti*-hydroxy-4-methyleneadamantane and 2-*anti*-acetoxy-4-methyleneadamantane, respectively. Spectra of this acetate were identical with those of the major product (**7a**) formed in the reaction of propellane **5** with acetic acid.

Gaseous hydrogen chloride reacted with **5** in benzene-d_6 solution at room temperature very rapidly (1 min) to give a 1:0.5:3 mixture (by quantitative ^{13}C NMR) of 2-*anti*-chloro-4-methyleneadamantane (**7b**), 2-chloro-2,4-methanoadamantane (**8b**), and 2-(chloromethyl)-2,4-didehydroadamantane (**9b**) (Scheme II). Product distribution varied with reaction time and the amount of hydrogen chloride present in the reaction mixture. The original product mixture, upon standing in a refrigerator for 4 days in the presence of an excess of hydrogen chloride, was converted into a mixture of **7b**, **8b**, and **9b** in a ratio of 2:1:0.2, indicating that unstable cyclopropylcarbinyl chloride **9b** isomerized to the thermodynamically more stable chlorides **7b** and **8b**. Olefinic chloride **7b** was isolated by column chromatography on neutral alumina and identified by comparison of its ^{13}C NMR, ^1H NMR, IR, and mass spectra with the spectral data reported for 2-*anti*-chloro-4-methyleneadamantane.[23] The two saturated chlorides (**8b** and **9b**) rearranged during column chromatography and could not be isolated in pure forms. Positions and splitting patterns of their ^{13}C and ^1H NMR signals in the spectra of the product mixtures (Table I) indicated that these products were 2-chloro-2,4-

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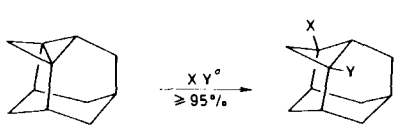
Table I. Spectral Data for the Reaction Products of Propellane 5 with Electrophiles and Free Radicals

product[a]	^{13}C NMR (C_6D_6), δ	^{1}H NMR (C_6D_6), δ	IR (film), cm^{-1}	MS, *m/z* (%)
7a	169.1 (s), 154.2 (s), 104.5 (t), 76.6 (d), 43.1 (d), 39.3 (t), 38.1 (d), 36.7 (t), 33.8 (t), 32.0 (d), 31.6 (t), 27.7 (d), 20.9 (q)	4.96 (br s, 1 H), 4.63 (s, 2 H), 2.63 (br s, 1 H), 2.4–1.2 (m, CH_3 at δ 1.79, 14 H)	3070 (w), 2920 (s), 2860 (m), 1740 (s), 1655 (m), 1450 (m), 1365 (m), 1235 (s), 1020 (m), 885 (m)	206 (M$^+$, 24), 164 (26), 146 (100), 131 (41), 105 (37), 104 (76), 93 (46), 92 (37), 91 (83), 79 (50), 78 (58), 77 (38)
7c	155.7 (s), 103.4 (t), 83.6 (d), 55.3 (q), 42.9 (d), 39.5 (t), 38.6 (d), 36.9 (t), 33.5 (t), 31.8 (d), 31.4 (t), 28.0 (d)	4.66 (s, 2 H), 3.24 (br s, 1 H), 3.14 (s, 3 H), 2.68 (br s, 1 H), 2.5–1.2 (m, 11 H)	3070 (w), 2915 (s), 2850 (m), 1655 (w), 1455 (m), 1445 (m), 1100 (s), 880 (m)	178 (M$^+$, 40), 148 (67), 105 (36), 93 (32), 92 (38), 91 (100), 85 (44), 79 (49), 77 (55)
8, A = OH	74.3 (s), 47.2 (d), 37.86 (dd), 37.82 (d), 34.8 (t), 34.6 (t), 32.1 (t), 30.3 (t), 29.7 (d), 28.0 (d), 25.7 (d)[b]	2.4–1.1 (m)[b]	3280 (s), 2900 (s), 2840 (m), 1450 (m), 1340 (m), 1280 (m), 1225 (m), 1180 (m), 1135 (s), 975 (m)[c]	164 (M$^+$, 100), 121 (56), 95 (64), 94 (39), 93 (35), 91 (35), 79 (91), 77 (37)
8b	67.2 (s), 49.7 (d), 40.7 (d), 40.0 (t), 35.0 (t+d), 34.6 (t), 31.7 (t), 30.2 (t), 27.6 (d), 25.3 (d)	~2.5–1.1 (m)		
8c	79.2 (s), 50.1 (q), 42.7 (d), 35.4 (d), 35.1 (t), 34.8 (t), 32.7 (t), 31.7 (t), 31.1 (t), 30.1 (d), 29.0 (d), 26.3 (d)	3.07 (s, 3 H), 2.3–1.0 (m, 15 H)	2920 (s), 2855 (m), 1460 (m), 1350 (m), 1230 (m), 1190 (m), 1132 (s)	178 (M$^+$, 100), 135 (27), 109 (59), 105 (30), 91 (70), 79 (78), 77 (65)
9, A = OH	70.0 (t), 51.0 (t), 37.8 (s), 35.5 (d), 33.3 (t), 32.66 (t), 32.57 (d), 28.7 (t), 28.1 (d), 26.2 (d), 26.1 (d)[b]	3.51 (AB system, 2 H), 2.5–1.2 (m, 14 H)[b]	3280 (s), 3020 (w), 2920 (s), 2850 (m), 1455 (m), 1340 (m), 1200 (m), 1185 (m), 1140 (m), 1020 (s)[c]	164 (M$^+$, 53), 146 (13), 135 (72), 133 (14), 105 (33), 93 (31), 92 (33), 91 (67), 79 (100), 78 (48), 77 (39)
9b	54.3 (t), 50.4 (t), 36.9 (s), 36.4 (d), 33.22 (d), 33.15 (t), 32.6 (t), 31.7 (d), 29.3 (d), 28.7 (t), 26.3 (d)	3.23 (AB system), 2.4–1.0 (m)	3020 (w) (see text)	
10a	105.1 (s), 62.4 (s), 57.3 (s), 51.4 (d), 43.0 (dd),[d] 39.2 (d), 35.8 (t), 34.0 (t), 31.3 (d), 31.0 (t), 27.2 (t), 24.9 (d)	2.96 (br s, 1 H), 2.46–0.78 (multiplet with a distinctive AB system at δ 2.31,[d] 13 H)	3010 (m),[d] 2920 (s), 2855 (m), 1465 (m), 1450 (m), 1157 (s), 920 (m), 890 (s), 783 (s), 760 (s)	302 (M$^+$, 3), 300 (M$^+$, 6), 298 (M$^+$, 5), 264 (100), 262 (100), 229 (45), 227 (70), 181 (41), 115 (50), 91 (79), 79 (73), 77 (83)
10b	144.5 (s), 134.7 (s), 129.8 (d), 129.5 (d), 63.3 (s), 61.9 (s), 50.1 (d), 42.1 (t), 39.6 (d), 35.0 (t), 32.4 (t), 30.9 (t), 28.4 (d), 27.7 (t), 24.5 (d), 21.3 (q)	7.65 (d, 2 H), 6.81 (d, 2 H), 3.20 (br s, 1 H), 2.34 (AB system + br s, 3 H), 2.05 (br s, 1 H), 1.90 (s, 3 H), 1.8–1.2 (m, 9 H)	3090 (w), 3070 (w), 2920 (s), 2860 (m), 1595 (m), 1460 (m), 1445 (m), 1290 (s), 1140 (s), 810 (s), 680 (s)[c]	183 (M$^+$-Ts, 33), 181 (M$^+$-Ts, 100), 145 (35), 139 (18), 125 (17), 117 (20), 105 (17), 91 (67), 79 (18), 77 (21)
10c	135.9 (d), 133.9 (s), 128.7 (d), 127.8 (d), 54.6 (s), 43.8 (d), 36.9 (t), 36.2 (d), 36.0 (d), 34.9 (t), 34.6 (t), 32.5 (t), 30.7 (t), 28.8 (d), 25.9 (d)	7.6–7.3 (m, 2 H), 7.1–6.9 (m, 3 H), 2.5–0.9 (m, 15 H)	3070 (w), 3050 (w), 2910 (s), 2850 (m), 1470 (m), 1455 (m), 1440 (m), 750 (m), 695 (m)	256 (M$^+$, 53), 164 (36), 147 (100), 119 (55), 105 (59), 93 (43), 91 (91), 84 (38), 79 (79), 77 (38)

[a] Elemental analyses were determined for all products, except 8b and 9b, and found to be correct. Chlorides 8b and 9b could not be isolated in a pure form (see text). [b] Recorded in $CDCl_3$. [c] In KBr disc. [d] This signal(s) is absent in the spectrum of **10a**-d_2 (obtained from 2,4-(methano-d_2)-2,4-didehydroadamantane (**5a**)).

Scheme III

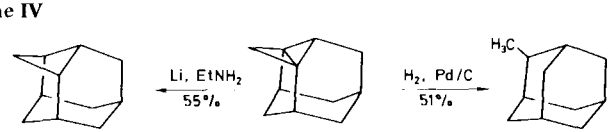


5

10a, X = Cl; Y = CCl_3
10b, X = Cl, Y = Ts
10c, X = PhS; Y = H

°XY = CCl_4, TsCl or PhSH

Scheme IV



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methanoadamantane (**8b**) and 2-(chloromethyl)-2,4-didehydroadamantane (**9b**). The structure of **9b** was confirmed by the presence of the cyclopropane IR band (3020 cm^{-1}) in the spectrum of a product mixture containing **9b** as the major component.

Methanol (freshly distilled from KOH) reacted with **5** in benzene-d_6 solution at room temperature rather slowly ($t_{1/2} \simeq$ 1 h) yielding a 1:3 mixture (by quantitative ^{13}C NMR) of 2-*anti*-methoxy-4-methyleneadamantane (**7c**) and 2-methoxy-2,4-methanoadamantane (**8c**) (Scheme II). A minor product (8%), probably 2-(methoxymethyl)-2,4-didehydroadamantane (**9c**),[24a] as well as a small amount of a white insoluble material were also produced.[24b] The two major products, **7c** and **8c**, were separated by column chromatography on $AgNO_3$-pretreated silica gel and identified by ^{13}C NMR, ^1H NMR, IR, and mass spectra (Table I). The anti orientation of the methoxy substituent in olefinic ether **7c** was established by its ^1H NMR spectrum (Table I), which showed a sharp singlet at δ 4.65, typical of 2-anti-substituted 4-methyleneadamantanes (vide supra).

Propellane **5** also reacted readily with other electrophiles such as silver ion ($AgBF_4$) and bromine to give complex mixtures of products.

With neat carbon tetrachloride as well as with tosyl chloride and thiophenol in benzene-d_6 solution **5** reacted instantaneously at room temperature under an oridinary fluorescent light yielding almost exclusively (by ^{13}C NMR) the corresponding 2,4-disubstituted 2,4-methanoadamantanes [2-chloro-4-(trichloromethyl)-2,4-methanoadamantane (**10a**), 2-chloro-4-tosyl-2,4-methanoadamantane (**10b**), and 2-(phenylthio)-2,4-methanoadamantane (**10c**); Scheme III]. The products were identified by ^{13}C NMR, ^1H NMR, IR, and mass spectra (Table I). The structure of **10c** was confirmed by Raney nickel desulfurization to the known hydrocarbon 2,4-methanoadamantane (**11**).[25]

The structure assignment to the products of propellane **5** in the reactions with acetic acid, hydrogen chloride, and methanol, as well as with carbon tetrachloride, tosyl chloride, and thiophenol, relies on the ^1H NMR, ^{13}C NMR, IR, and mass spectra (Table I). The products having the same structure show some common characteristics. All 2-*anti*-substituted 4-methyleneadamantanes (**7a–c**) exhibit the characteristic ^1H NMR sharp methylene singlet at $\delta \sim 4.6$ and the broad singlet of the hydrogen geminal to the polar substituent (δ 3.24–4.96), as well as the three low-field ^{13}C NMR signals corresponding to the two olefinic carbon atoms (singlet at $\delta \sim 155$ and triplet at $\delta \sim 104$) and the carbon bearing the polar substituent (doublet between δ 67.2[23] and 83.6). 2-Monosubstituted and 2,4-disubstituted 2,4-methanoadamantanes (**8**, A = OH, **8b**, **8c**, and **10a–c**) display the characteristic one and two low-field ^{13}C NMR singlets, respectively, between δ 54.4 and 79.2. The ^1H NMR spectra of 2-(substituted-methyl) 2,4-didehydroadamantanes (**9**, A = OH, and **9b**) show the characteristic low-field signals of an AB system corresponding to the CH_AH_BX group; their ^{13}C NMR spectra exhibit the clearly distinguishable signals of this group (triplet at δ 70.0 and 54.3, respectively) and the adjacent quarternary carbon atom as well as the low-field signal (triplet at $\delta \sim 51$) corresponding to the carbon situated across from the cyclopropane ring in the chair bycyclo[3.1.0]hexane system.[22] The IR spectra of the olefinic (**7a–c**) and cyclopropane products (**9**, A = OH and **9b**) show C–H vibrational bands at 3070 and 3020 cm^{-1}, respectively, typical of olefins and cyclopropanes. The mass of the molecular ions were determined for all products, except **8b** and **9b**, which could not be isolated in a pure form, and found to be correct.

With oxygen, propellane **5** reacted at 0 °C spontaneously producing a white solid, which was scarcely soluble in benzene-d_6. Its ^{13}C NMR spectrum indicated that this was a polymeric material.

The central bond in propellane **5** can easily be hydrogenated (Scheme IV). Electron-transfer hydrogenation[26] of **5** with lithium in refluxing ethylamine yielded exclusively 2,4-methanoadamantane (**11**). However, catalytic hydrogenolysis of **5** with Pd/C in benzene-d_6 solution produced 2-methyladamantane (**12**). Cleavage of the central bond in the first step would lead to stable hydrocarbon **11**. The central bond is strongly sterically hindered; hence, close contact of this bond with a catalyst surface is virtually impossible, and one of the external cyclopropane bonds is therefore cleaved first. Products **11** and **12** were identified by comparison of their spectra with the spectral data reported for these hydrocarbons.[25,27]

Discussion

2,4-Methano-2,4-didehydroadamantane (**5**) is thermally rather stable, indicating that a homolytic cleavage of the central bond leading to the diradical 2,4-methanoadamantane-2,4-diyl cannot be a favorable process.

Reactions of propellane **5** with acids, AcOH, HCl, and MeOH, yield mixtures of the corresponding homoallyl (**7**), cyclobutyl (**8**), and cyclopropylcarbinyl (**9**) products (Scheme II). The mechanism of these reactions presumably involves addition of a proton to the central bond leading to the intermediary 2,4-methano-2-adamantyl cation (**6**). The product structures as well as exclusive formation of the anti homoallyl epimers indicate that this cation is bridged. The positive charge in cation **6** is delocalized over three carbon atoms, 2, 3, and 4, and consequently, the products arise by nucleophilic attack at these three carbons. The syn side of carbon 4 in the bicyclobutonium ion **6** is heavily hindered due to bridging, and the nucleophile can attack only from the anti side. The methoxy ethers **7c**, **8c**, and **9c** are probably formed by a slow proton transfer from methanol (or traces of an acid) to **5** followed by the preferential attack of another methanol molecule at the tertiary carbon 2 in cation **6**. Since acetic acid and hydrogen chloride are much stronger acids and less nucleophilic than methanol, the acetates **7a**, **8a**, and **9a** and chlorides **7b**, **8b**, and **9b** arise preferably through a collapse of the intermediary ion pair and only to a small extent by a nucleophilic attack of the acid at this ion pair. The difference in the product distributions can be explained by the different nature and location of the counter ion in the intermediary ion pair.[28]

Contrary to the carbenium ion reactions of **5**, its reactions with carbon tetrachloride, tosyl chloride, and thiophenol yield no rearranged product. The only products are the corresponding 2,4-disubstituted 2,4-methanoadamantanes (**10a–c**) (Scheme III), which arise from the apparent additions to the central bond, indicating that these reactions are free radical processes. Generally, free radical migrations of alkyl groups do not occur at ordinary temperatures, while the related carbenium ions undergo facile rearrangements.[29] Moreover, similar additions of carbon tetrachloride,[30] tosyl chloride,[31] and thiophenol[32] to olefinic bonds have been shown to involve free radical intermediates.

Similarly as an olefinic bond, the central bond in **5** can be easily hydrogenated. The mechanism of the electron-transfer hydrogenation[26] of **5** to 2,4-methanoadamantane (**11**) (Scheme IV) presumably involves an electron addition to the central bond leading to a radical anion. Proton transfer from ethylamine to this radical anion yields 2,4-methano-2-adamantyl free radical, which is hydrogenated to **11** by another electron addition followed by protonation.

Hence, propellane **5** is completely inert toward nucleophiles but highly sensitive toward acids as well as free radicals and electrons, which attack the central bond yielding the intermediary 2,4-methano-2-adamantyl cation and the corresponding 2,4-methano-2-adamantyl free radicals, respectively. This indicates

(24) (a) ^{13}C NMR ($CDCl_3$) δ 79.7, 58.2, 50.5, 35.5, 33.1, 32.8, 32.5, 28.5, 27.9, 27.0, 26.3; the twelfth signal, corresponding probably to the quarternary carbon, was not detected. (b) Analogous products were obtained on exposure of the parent [3.1.1]propellane to methanol.[6]

(25) Sasaki, T.; Eguchi, S.; Hirako, Y. *J. Org. Chem.* **1977**, *42*, 2981.

(26) Moore, W. R.; Hall, S. S.; Largman, C. *Tetrahedron Lett.* **1969**, 4353.

(27) Mlinarič-Majerski, K.; Majerski, Z.; Pretsch, E. *J. Org. Chem.* **1976**, *41*, 686.

(28) The acetate ion is not only larger than the chloride ion but possesses also two equivalent nucleophilic centers.

(29) March, J. "Advanced Organic Chemistry"; McGraw-Hill: New York, 1977; p 975.

(30) (a) Greene, F. D.; Rees, W. W. *J. Am. Chem. Soc.* **1960**, *82*, 890. (b) Walling, C.; Huyser, E. S. *Org. React.* **1963**, *13*, 91–149.

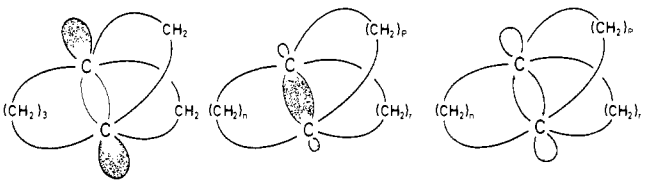
(31) Cristol, S. J.; Reeder, J. A. *J. Org. Chem.* **1961**, *26*, 2182.

(32) (a) Cristol, S. J.; Brindell, G. D. *J. Am. Chem. Soc.* **1954**, *76*, 5699. (b) Pryor, W. A. "Mechanisms of sulfur Reactions"; McGraw-Hill: New York, 1962; pp 71–93.

a high electron density at the reaction site, i.e., at the back side of the inverted carbon atoms and, consequently, a decrease in electron density between them as represented by **13**. The central bond of **5** appears, therefore, to be formed from two weakly bonding orbitals. Such an electron-density distribution in the central bond is in accord with the results of theoretical calculations for other small propellanes[2e,33-35] as well as with the electron-density difference maps obtained by the X-ray analysis of an aza[3.1.1]propellane derivative.[36] The ab initio molecular orbital[34] and maximum overlap[35] calculations for [1.1.1]propellane predicted that the central bond was formed from sp^4 hybrids directed away from each other and sp^{44} hybrid orbitals, respectively. According to the latter calculations the central bond of the parent [3.1.1]propellane should be formed from sp^{11} hybrids.

The literature data on reactions of other propellanes are rather scarce but all are consistent with a gradual decrease in reactivity with an increase in ring sizes. [4.1.1]Propellane reacts with formic acid instantaneously at room temperature[4b] and [3.2.1]propellane with acetic acid "very rapidly" at the same temperature.[2c,d] However, medium propellanes [4.2.1][12] and [3.3.1][13a] react with acetic acid rather slowly: the half-life of the former is 1.6 h at 50 °C and that of the latter 8 h at 100 °C. Large propellanes, such as [4.3.2],[37] [3.3.3],[38a] [4.4.2],[38b] and [4.3.3],[38a] are inert even toward 2 M (or more concentrated) hydrochloric or sulfuric acid. The reactivity of propellanes toward bromine exhibits a similar dependence on ring sizes. Propellanes [3.2.1],[2b,c] [2.2.2],[3a] [4.2.1],[12,39] and [3.3.1][13] react instantaneously between −50 and −78 °C, the reactions of [3.2.2][14] and [4.2.2]propellanes[14] are complete in 10–20 min at room temperature, and the bromonolysis of [3.3.2]propellane[16] requires at the same temperature 3 days under a fluorescent light, while [4.4.2][38b,40] and [4.4.3]propellanes[41] are entirely inert.[42] Both the acids and bromine add to the propellane central bonds.[43]

The electron-density distributions in the central bond of large propellanes and in the usual carbon–carbon single bond in aliphatic compounds should be essentially the same, as represented by **14**. However, the electron density in the central bond of small propellanes appears to be considerably higher at the back side of the inverted carbon atoms than between them (**13**). The electron-density distribution in the central bond of medium propellanes is probably between that of small and large propellanes as represented by **15**. A ring enlargement in small propellanes should, therefore, follow a decrease in electron density at the back side

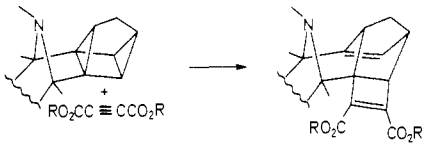


13 14 15

of the inverted carbon atoms and an increase in electron density between these atoms.[46] This is in good agreement with the experimental results on the reactivity of propellanes (vide supra).

We may conclude that *the central bond in small propellanes is actually a limiting form of the carbon–carbon single bond, while the other limiting form is the usual single bond between two carbon atoms in aliphatic compounds. All other carbon–carbon single bonds necessarily lie between these two extremes*,[47] and their reactivity should be higher the closer they are to the central bond in small propellanes. The decreasing reactivity order in electrophilic additions,[33,34,48] bicyclobutane > bicyclopentane > bicyclo[2.2.0]hexane ≃ cyclopropane > cyclobutane, as well as the relative reactivities of the propellanes are in accord with this prediction.

Note Added in Proof. Subsequent to the submission of this paper, Szeimies et al. reported that a [3.2.1]propellane, sharing the cyclobutane ring with a bicyclopentane unit, reacted spontaneously with an acetylenedicarboxylate to form an olefinic cyclobutene adduct by cleaving the propellane and bicyclopentane central bonds (Baumgärtel, O.; Harnisch, J.; Szeimies, G.; Van Meerssche, M.; Germain, G.; Declercq, J.-P. *Chem. Ber.* **1983**, *116*, 2205). The two electron-rich back lobes of the propellane



and bicyclopentane central bonds apparently produced the cyclobutene ring with the electron-poor acetylene, while the other two formed the olefinic bond.

Experimental Section

The purity of all compounds was controlled by GC and/or ^{13}C NMR. ^{13}C and ^1H NMR spectra were taken on a JEOL FX100 and/or a JEOL FX90Q spectrometer, IR spectra were recorded with a Perkin-Elmer 297 spectrophotometer, and mass spectra were obtained on a Varian CH-7 mass spectrometer. The quantitative analyses with ^{13}C NMR were performed by a combination of long-pulse intervals (120 s) to assure complete relaxation of all ^{13}C nuclei and a gated decoupling, which eliminated the nuclear Overhauser enhancement.[49] GC analyses were carried out on a Varian Aerograph 940 or 1800 gas chromatograph on stainless-steel analytical or capillary columns. Melting points were determined in sealed capillary tubes completely immersed in oil by using a Thiele apparatus and were uncorrected. Benzene-d_6 (≥99% *d*, Merck) was dried over molecular sieves prior to use. All other chemicals, if not specified otherwise, were of commercial reagent grade and were used without further purification.

2-Methyl-2,4-adamantanediol (2). A solution of methyl iodide (4.7 g, 33 mmol) in anhydrous ether (25 mL) was added dropwise to a stirred suspension of dry magnesium turnings (0.85 g, 35 mmol) in anhydrous ether (5 mL). The resulting mixture was stirred under reflux for 1 h and a solution of 4-hydroxy-2-adamantanone[18] (**1**) (1.85 g, 11 mmol) in anhydrous ether (70 mL) was added dropwise. The reaction mixture was stirred under reflux for additional 4 h and then allowed to cool. A

(33) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779.
(34) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 773.
(35) Herr, M. L. *Tetrahedron* **1977**, *33*, 1897.
(36) Chakrabarti, P.; Seiler, P.; Dunitz, J. D.; Schlüter, A.-D.; Szeimies, G. *J. Am. Chem. Soc.* **1981**, *103*, 7378.
(37) Cargill, R. L.; Pond, D. M.; LeGrand, S. O. *J. Org. Chem.* **1970**, *35*, 359.
(38) (a) Altman, J.; Cohen, E.; Maymon, T.; Petersen, J. B.; Reshef, N.; Ginsburg, D. *Tetrahedron* **1969**, *25*, 5115. Weiss, U.; Edwards, J. M. *Tetrahedron Lett.* **1968**, 4885. (b) Altman, J.; Babad, E.; Itzchaki, J.; Ginsburg, D. *Tetrahedron, Suppl.* **1966**, *No. 8*, pt 1, 279.
(39) The central bond in [4.2.1]propell-3-ene is more reactive toward bromine than the olefinic bond.[12]
(40) Bloomfield, J. J.; Irelan, J. R. S. *Tetrahedron Lett.* **1966**, 2971.
(41) Paquette, L. A.; Meisinger, R. H.; Wingard, R. E., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 2230.
(42) It should be noted that [2.2.2]-, [3.2.2]-, [4.2.2]-, and [3.3.2]propellanes react with bromine, although none of them contains a cyclopropane ring.
(43) In addition to the ring sizes, the reactivity of propellanes should depend on other factors such as the extent to which the central bond is bent as well as on strain relief by its cleavage. The central bond orbitals of a propellane are straight only if all three rings are equal, and in all other cases they are bent. The higher reactivity of 1,3-didehydroadamantane compared to that of the parent [3.3.1]propellane[13] can be attributed to a larger strain-energy difference between the former propellane[13a] and adamantane[44] than between the latter one[45] and bicyclo[3.3.1]nonane.[44] The *relatively* high thermal stability of [1.1.1]propellane appears to be based on the relatively small strain-energy difference between this propellane and the corresponding bicycloalkane.[10] In small propellanes all bonds are strained and, consequently, other bonds beside the central one may be involved in the reactions of these propellanes.
(44) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005.
(45) The strain-energy of the parent [3.3.1]propellane was estimated to be 35 kcal/mol (Gasteiger, J.; Dammer, O. *Tetrahedron* **1978**, *34*, 2939).
(46) The nature of the central bond in propellanes containing two small rings and a large one should be essentially equal to that in the related small-ring bicycloalkanes.
(47) Chemical behavior of olefins could be explained by two bonds with electron-density distribution similar to that in the bent central bond of a medium propellane. Such bonds would be similar to well-known banana bonds.
(48) Wiberg, K. B.; Bishop, K. C., III; Davidson, R. B. *Tetrahedron Lett.* **1973**, 3169. Wiberg, K. B.; Ellison, G. B. *Tetrahedron* **1974**, *30*, 1573. Wiberg, K. B.; Lampman, G. M.; Ciula, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Ibid.* **1965**, *21*, 2749.
(49) Shoolery, J. N. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 79.

saturated aqueous solution of NH_4Cl (25 mL) was added dropwise, the resulting layers were separated, and the aqueous one was extracted with ether (3 × 50 mL). The combined extracts were washed with brine (100 mL) and dried ($MgSO_4$). Evaporation of the solvent yielded diol **2** (1.9 g, 95%), which was used without purification. Pure diol **2** (a mixture of two isomers in a ratio of 10:1) was obtained by sublimation: mp 242–245 °C; ^{13}C NMR ($CDCl_3$) δ 77.2 (d), 75.8 (s), 43.0 (d), 39.0 (d), 37.2 (t), 34.9 (t), 34.3 (d), 33.6 (t), 27.5 (t), 27.3 (q), 26.2 (d); ^1H NMR ($CDCl_3$) δ 4.4 (br s, 2 H), 3.93 (br s, 1 H), 2.6–1.4 (m, 12 H), 1.30 (s, 3 H); IR (KBr) 3310 (s), 2900 (s), 2860 (s), 1470 (m), 1455 (m), 1440 (m), 1135 (s), 1120 (s) 1080 (s), 1045 (s), 1023 (s), 910 (s) cm^{-1}; MS, m/z 164 ($M^+ - 18$, 100%), 121 (40), 93 (29), 80 (21), 79 (46). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.48; H, 9.95. Found: C, 72.24; H, 10.00.

2-(Methyl-d_3)-2,4-adamantanediol was obtained by following the procedure described for the protio analogue and using methyl-d_3 iodide (99% d, Merck).

4-Methylene-2-adamantanone (3). To a solution of diol **2** (1.0 g, 5.5 mmol) in acetone (15 mL) stirred at room temperature was added Jones reagent dropwise until a permanent red color appeared. The reaction mixture was stirred for an additional 30 min at the same temperature. The inorganic salts were removed by filtration, the filtrate was evaporated in vacuo, and the resulting crude 4-hydroxy-4-methyl-2-adamantanone was dehydrated at 110 °C (20 mmHg) in a sublimator. The sublimed wet ketone **3** was dissolved in pentane, the solution was dried ($MgSO_4$), pentane was evaporated, and the residue was resublimed to yield **3** (0.58 g, 65%; ≥98% pure by GC, QF-1, 160 °C): mp 135–138 °C; ^{13}C NMR (C_6D_6) δ 211.1 (s), 153.3 (s), 104.7 (t), 58.8 (d), 46.4 (d), 42.1 (t), 38.9 (t), 38.12 (t or d), 38.08 (d or t), 37.6 (t), 27.9 (d); ^1H NMR (C_6D_6) δ 4.52 (s, 2 H), 3.13 (br s, 1 H), 2.47 (br s, 1 H), 2.31 (br s, 1 H), 1.9–1.5 (m, 9 H); IR (KBr) 3075 (w), 2920 (s), 2855 (m), 1725 (s), 1652 (m), 1450 (m), 1225 (m), 1065 (m) cm^{-1}; MS, m/z 162 (M^+, 57%), 93 (100), 92 (100), 91 (95), 79 (55), 77 (51). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.52; H, 8.89.

4-(Methylene-d_2)-2-adamantanone was obtained in the same manner as the protio analogue by using D_2O and D_2SO_4 for the preparation of Jones reagent.

4-Methylene-2-adamantanone Tosylhydrazone (4a) and Its Sodium Salt (4b). Tosylhydrazine (195 mg, 1.05 mmol) and ketone **3** (162 mg, 1.0 mmol) were dissolved in warm absolute ethanol (2.5 mL).[19] The resulting homogeneous mixture was left overnight in a refrigerator; water (30 mL) was then added, and the product was extracted with ether (3 × 25 mL). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated. The resulting tosylhydrazone **4a** (330 mg, 100%) was used without purification. The NMR data indicated that it was a 1:1 mixture of the syn and anti isomer: ^{13}C NMR ($CDCl_3$) δ 169.1 (s), 167.8 (s), 153.6 (s), 152.1 (s), 143.6 (s, 2 C), 135.5 (s, 2 C), 129.4 (d, 2 C), 127.9 (d, 2 C), 104.9 (t), 104.0 (t), 49.9 (d), 42.2, 41.8, 40.4, 39.0, 38.9, 38.7, 38.1 (2 C), 37.8, 37.4, 31.2 (d), 27.7 (d, 2 C), 21.5 (q, 2 C), two signals could not be located; ^1H NMR ($CDCl_3$) δ 7.83 (d, J = 8 Hz, 4 H), 7.27 (d, J = 8 Hz, 4 H), 4.64 (d, J = 1.7 Hz, 1 H), 4.53 (d + s, 3 H), 3.64 (br s), 3.12 (br s), 2.7–1.6 (m, CH_3 at δ 2.39); IR (KBr) 3220 (m), 3060 (w), 2920 (s), 2850 (m), 1640 (m), 1598 (m), 1338 (m), 1325 (m), 1165 (s), 1090 (m), 815 (m), 710 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{22}N_2O_2S$: C, 65.42; H, 6.71; N, 8.48. Found: C, 65.24; H, 6.93; N, 8.47.

4-Methylene-2-adamantanone Tosylhydrazone Sodium Salt (4b). Sodium hydride (50% suspension in mineral oil, 55 mg, 1.15 mmol) was added in small portions to a solution of tosylhydrazone **4a** (330 mg, 1.0 mmol) in dry tetrahydrofuran (2.5 mL) stirred at room temperature. (Tetrahydrofuran was dried with CaH_2, distilled from $LiAlH_4$, and kept over this reagent.) The resulting thick suspension was stirred at the same temperature for an additional hour, the solvent was evaporated, and the salt was dried for at least 1 h in vacuo (0.02 mmHg, ~40 °C): IR (KBr) 3065 (w), 2915 (s), 2845 (m), 1650 (m), 1445 (m), 1240 (s), 1130 (s), 1095 (s), 810 (s) cm^{-1}.

4-(Methylene-d_2)-2-adamantanone tosylhydrazone and its sodium salt were prepared in the same manner as the protio analogues.

2,4-Methano-2,4-didehydroadamantane (5). A flask containing dry tosylhydrazone sodium salt **4b** (prepared from 162 mg, 1.0 mmol, of ketone **3**) was connected to a high-vacuum pump via an "U" trap cooled by liquid nitrogen. The flask and the trap were evacuated (≤0.02 mmHg), and then the flask was immersed in a hot-oil bath (180–190 °C). A transparent waxy product sublimed into the trap. After 20 min the oil bath was removed, dry N_2 gas was allowed to fill the apparatus, the flask was disconnected, and a stream of dry N_2 gas was allowed to pass through the trap. The trap was closed at both ends and weighed to determine the yield of **5** (103 mg, 70.5%; ≥95% pure by ^{13}C NMR): IR (KBr) 3040 (w), 2905 (s), 2850 (m), 1462 (m), 1450 (m), 1330 (m), 1190 (m), 1070 (m), 1020 (w) cm^{-1} (the KBr disc was prepared in a dry box); MS, m/z 146 (M^+, 65%), 131 (85), 117 (60), 105 (91), 104 (83), 92 (46), 91 (100), 79 (46), 77 (40).

For the ^{13}C NMR and ^1H NMR spectra (vide supra) and the reactivity studies **5** was dissolved under dry N_2 gas in anhydrous benzene-d_6 (0.4 mL) and the resulting solution was transferred via a syringe into an NMR tube, which was flushed previously with dry N_2 gas.

2,4-(Methano-d_2)-2,4-didehydroadamantane (**5a**) was obtained in the same manner as the protio analogue.

Reaction of 5 with Acetic Acid. Glacial acetic acid (45 μL) was added via a syringe to an NMR tube containing the solution of **5** in benzene-d_6.[50] The reaction was exothermic. The quantitative ^{13}C NMR spectrum indicated the presence of three products[51] in a ratio of 3:1:1. The product mixtures of three experiments were combined, the solvent was evaporated, and olefinic acetate **7a** was isolated by column chromatography on $AgNO_3$-pretreated silica gel using pentane–ether (9:1) as eluent. Fractions containing the mixture of saturated acetates **8a** and **9a** were combined, and the solvent was removed in vacuo. ^{13}C NMR (C_6D_6) δ 170.3 (s), 169.0 (s), 79.2 (s), 71.1 (t), 50.8 (t), 44.9 (d), 36.9, 36.0, 35.3, 34.8, 34.7, 34.6, 33.2, 32.9, 32.8, 32.3, 32.1, 30.7, 29.0, 28.6, 28.4, 26.9, 26.5, 25.8, 21.3 (q), 20.6 (q). Acetates **8a** and **9a** could not be separated from each other and they were reduced to the corresponding alcohols with $LiAlH_4$ in dry ether at reflux. The usual work-up procedure gave a mixture of alcohols **8**, A = OH, and **9**, A = OH, which were separated on a silica gel column using cyclohexane–ether (9:1 to 7:3) as eluent and then sublimed. Spectral data of olefinic acetate **7a** and alcohols **8**, A = OH and **9**, A = OH are given in Table I. **7a**: Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.73; H, 9.03. **8, A = OH**: mp 259–262 °C; Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.33; H, 9.84. **9, A = OH**: mp 192–197 °C; Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.68; H, 9.93.

Reaction of 5 with Hydrogen Chloride. Dry hydrogen chloride was bubbled through the solution of **5** in benzene-d_6[50] for 1 min at room temperature. The excess of hydrogen chloride was then blown out from the product mixture by a stream of dry N_2 gas, which was bubbled through the mixture until a litmus paper showed no reaction on acid. Another sample of **5**, treated with hydrogen chloride as described above, was left in a refrigerator for 4 days before the excess of hydrogen chloride was removed. The quantitative ^{13}C NMR spectra of both product mixtures showed the presence of three products.[51] Olefinic chloride **7b** was isolated from the latter mixture by column chromatography on neutral alumina (activity I) using pentane as eluent. Chloride **7b** was identified by comparison of its spectra with the spectral data reported for this compound.[23] The cyclobutyl and cyclopropylcarbinyl chlorides (**8b** and **9b**) rearranged during the column chromatography and could not be isolated. Their ^{13}C NMR and ^1H NMR spectral data are shown in Table I.

Reaction of 5 with Methanol. Absolute methanol (35 μL, freshly distilled from KOH) was added via a syringe to the solution of **5** in benzene-d_6.[50] The reaction was monitored by comparing intensity of the methoxy ^1H NMR signals of **7c** and **8c** with that of Me_4Si. The ^1H NMR and quantitative ^{13}C NMR spectra taken after completion of the reaction indicated the presence of two major products. In addition to the methoxy ethers, a small amount of a white material, insoluble in benzene-d_6, was also formed. When methanol was not freshly distilled from KOH this material became the major product. The product mixtures of three experiments were combined, the solvent was evaporated, and olefinic ether **7c** was separated from saturated ether **8c** by column chromatography on $AgNO_3$-pretreated silica gel using pentane–ether (9:1 to 1:1) as eluent. According to the quantitative ^{13}C NMR spectrum the saturated ether fraction contained, in addition to **8c**, up to 10% of another product, presumably **9c**.[24] The spectral data of the products are given in Table I. **7c**: Anal. Calcd for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 80.63; H, 10.03. **8c**: Anal. Calcd for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 80.97; H, 10.34.

Reaction of 5 with Other Electrophiles. Bromine (70 μL) and a catalytic amount of $AgBF_4$, respectively, were added to the solution of **5** in benzene-d_6.[50] The latter reaction was strongly exothermic. Both reactions produced complex mixtures of products according to the ^{13}C NMR spectra.

Reaction of 5 with Carbon Tetrachloride. Carbon tetrachloride (80 μL) was added via a syringe to the solution of **5** and **5a**, respectively, in benzene-d_6.[50] The ^{13}C NMR spectrum indicated the presence of only one product. The solvent was evaporated, and the residue (173 mg, 58% based on **3**) was distilled (110 °C/0.01 mmHg) by using a Kugelrohr apparatus to yield pure **10a**. The spectral data of **10a** and **10a**-d_2 are shown in Table I. Anal. Calcd for $C_{12}H_{14}Cl_4$: C, 48.03; H, 4.70; Cl,

(50) The solution of **5** was prepared as described in the paragraph: 2,4-methano-2,4-didehydroadamantane. Purity of **5** was checked by ^{13}C NMR before the reaction.

(51) The total amount of byproducts was approximatively 5%.

47.26. Found: C, 48.38; H, 4.95; Cl, 46.94. The same product was obtained when neat **5** was dissolved in carbon tetrachloride.

Reaction of 5 with Tosyl Chloride. Tosyl chloride (140 mg, freshly recrystallized from pentane) was added to the solution of **5** in benzene-d_6.[50] The ^{13}C NMR spectrum showed the presence of one product.[51] The solvent was evaporated, and the product was purified of the excess of tosyl chloride by column chromatography on neutral alumina (activity II/III) using pentane–ether (1:0 to 0:1) as eluent. The spectral data of the product (**10b**) are given in Table I. Mp 154–157 °C. Anal. Calcd for $C_{18}H_{21}SO_2Cl$: C, 64.17; H, 6.28; Cl, 10.52. Found: C, 63.94; H, 6.57; Cl, 10.23.

Reaction of 5 with Thiophenol. Freshly distilled thiophenol (70 μL) was added via a syringe to the solution of **5** in benzene-d_6.[50] The ^{13}C NMR spectrum indicated the presence of one product[51] and virtually no **5**. The spectral data of the product (**10c**) are shown in Table I. Anal. Calcd for $C_{17}H_{20}S$: C, 79.63; H, 7.86; S, 12.51. Found: C, 79.90; H, 8.04; S, 12.70.

A crude sample of **10c** was desulfurated with Raney nickel (W2, 2 g) in absolute ethanol (20 mL). The reaction mixture was vigorously stirred for 1.5 h at reflux, then allowed to cool, and filtered. The filtrate was diluted with water (100 mL), and the resulting mixture was extracted with pentane (3 × 30 mL). The combined extracts were dried ($MgSO_4$) and the solvent was evaporated to yield 2,4-methanoadamantane (**11**) and two minor products, 2-methyladamantane (**12**) and 2-methyleneadamantane, in a ratio of 3:1:1 (by GC, Carbowax 20M, 110 °C). The products were separated by preparative GC (QF-1, 120 °C) and identified by comparison of their ^{13}C NMR, ^1H NMR, IR, and mass spectra with the spectra of authentic samples.

Reaction of 5 with Oxygen. The trap containing sublimed **5** (vide supra) was immersed in an ice water bath and allowed to fill with dry oxygen. After 10 min the oxygen atmosphere was replaced with dry N_2 gas. In another experiment, dry oxygen was bubbled through the solution of **5** in benzene-d_6[50] for 5 min at room temperature. In both cases a white solid, scarcely soluble in benzene-d_6, was obtained.

Thermal Decomposition of 5. An NMR tube containing the solution of **5** in benzene-d_6[50] under dry N_2 gas was tightly closed and immersed in a water bath heated at 65 °C. After 13 h the tube was cooled to room temperature, and the ^1H NMR spectrum was recorded. The area ratio below the doublet at δ 1.08 (which belongs to **5**) and all other signals indicated that 62% of **5** decomposed. To check this result the tube was opened, and the remaining **5** was converted to **10a** by treatment with carbon tetrachloride (vide supra). Integration of the signal at δ 2.96 (which belongs to **10a**) against all other signals in the ^1H NMR spectrum of the product mixture showed that 57% of **5** decomposed. The half-life of **5** was estimated from the mean value of the decomposition by using the usual procedure.

Electron-Transfer Hydrogenation of 5. A three-neck flask containing ethylamine (3 mL) was fitted with a dry ice reflux condenser and a rubber serum cap. A gentle stream of dry N_2 gas was allowed to pass through the apparatus, the flask was immersed into a dry ice/acetone bath, stirring was started, and lithium metal was added in small pieces until an intensive blue color appeared.[26] The open neck of the flask was then closed, the dry ice/acetone bath was removed, and a solution of **5** in pentane (0.5 mL) was added via a syringe through the serum cap. The reaction mixture was stirred at reflux (~17 °C) in a dry nitrogen atmosphere for 4 h and then poured onto ice. The product was extracted with pentane (3 × 25 mL), and the combined extracts were dried ($MgSO_4$). The solvent was evaporated and the residue sublimed yielding 2,4-methanoadamantane (**11**) (57 mg, 55.5% based on **5**; ≥99% pure by GC, Carbowax 20M, 130 °C).

Catalytic Hydrogenation of 5. A two-neck flask containing 10% Pd/C (~35 mg) and benzene-d_6 (0.5 mL) was connected via one neck to a hydrogen source and a vacuum pump. The other neck was closed with a rubber serum cap. The flask was cooled by liquid nitrogen, evacuated, then filled with hydrogen, and allowed to gain room temperature. The solution of **5** in benzene-d_6[50] was added via a syringe through the serum cap. The resulting suspension was stirred at room temperature under hydrogen at atmospheric pressure for 3 h and then filtered. The solvent was evaporated and the residue sublimed to yield 2-methyladamantane (**12**) (52.6 mg, 51% based on **5**), which contained up to 10% in total of two byproducts (by GC, QF-1, 90 °C). The ^{13}C NMR spectrum indicated that neither of them was 2-homoprotoadamantane (tricyclo-[5.3.1.$0^{4,9}$]undecane).[52]

2-*syn*-Hydroxy-4-methyleneadamantane and 2-*anti*-Hydroxy-4-methyleneadamantane. A solution of ketone **3** (250 mg, 1.54 mmol) in dry ether (5 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (70 mg, 1.8 mmol) in dry ether (5 mL). The reaction mixture was stirred at reflux for 3 h, and then wet ether (10 mL) was added dropwise followed by careful addition of water. The usual workup procedure yielded a mixture of 2-*syn*-hydroxy-4-methyleneadamantane (*syn*-**7**, A = OH) and 2-*anti*-hydroxy-4-methyleneadamantane (*anti*-**7**, A = OH), in a ratio of 3:2 (by GC, DEGS, 150 °C; 210 mg, 83%). Alcohols *syn*-**7**, A = OH, and *anti*-**7**, A = OH, were separated by column chromatography on neutral alumina (activity II/III) using pentane–ether (1:1) as eluent. *syn*-**7**, A = OH: mp 162–165 °C; ^{13}C NMR ($CDCl_3$) δ 153.4 (s), 106.0 (t), 75.2 (d), 46.1 (d), 38.8 (t), 38.3 (d), 37.9 (t), 36.0 (t), 34.5 (d), 33.8 (t), 26.8 (d); ^1H NMR ($CDCl_3$) δ 4.72 (AB system, 2 H), 3.87 (br s, 1 H), 2.45 (br s, 2 H), 2.1–1.5 (m, 11 H); IR (KBr) 3300 (s), 3080 (w), 2910 (s), 2855 (s), 1665 (m), 1450 (m), 1090 (m), 1050 (m), 1000 (m), 880 (s) cm^{-1}; MS, *m/z* 164 (M^+, 100%), 146 (5), 95 (32), 94 (77), 93 (98), 92 (48), 91 (50), 79 (46), 77 (29). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.48; H, 10.02. *anti*-**7**, A = OH: mp 168–171 °C; ^{13}C NMR ($CDCl_3$) δ 155.3 (s), 103.2 (t), 74.7 (d), 45.6 (d), 39.1 (t), 37.7 (d), 36.7 (t), 34.3 (d), 32.7 (t), 30.6 (t), 27.5 (d); ^1H NMR ($CDCl_3$) δ 4.60 (s, 2 H), 3.84 (br s, 1 H), 2.6–1.4 (m, 13 H); IR (KBr) 3280 (s), 3075 (w), 2910 (s), 2855 (s), 1660 (m), 1450 (m), 1060 (m), 1015 (m), 880 (m) cm^{-1}; MS, *m/z* 164 (M^+, 100%), 146 (5), 95 (31), 94 (74), 93 (91), 92 (46), 91 (50), 79 (44), 77 (26). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.58; H, 10.03.

2-*syn*-Acetoxy-4-methyleneadamantane (*syn*-7, A = OAc) and 2-*anti*-acetoxy-4-methyleneadamantane (7a) were prepared in 67% and 73% yield, respectively, from the corresponding alcohols (*syn*-**7**, A = OH, and *anti*-**7**, A = OH) by the usual procedure with acetic anhydride in dry pyridine.[53] *syn*-**7**, A = OAc: ^{13}C NMR (C_6D_6) δ 169.3 (s), 153.2 (s), 104.5 (t), 77.8 (d), 42.9 (d), 39.4 (t), 38.5 (d), 38.3 (t), 36.1 (t), 33.9 (t), 32.2 (d), 27.4 (d), 20.9 (q); ^1H NMR (C_6D_6) δ 4.98 (br s, 1 H), 4.64 (AB system, 2 H), 2.65 (br s, 1 H), 2.5–1.4 (m, CH_3 at δ 1.78, 14 H); IR (film) 3060 (w), 2910 (s), 2850 (s), 1735 (s), 1655 (w), 1450 (m), 1365 (m), 1250 (s), 1235 (s), 1040 (m) cm^{-1}; MS, *m/z* 206 (M^+, 37%), 164 (19), 146 (52), 131 (29), 105 (34), 104 (52), 93 (51), 92 (40), 91 (100), 79 (65), 77 (52). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.53; H, 8.80.

The spectra of the anti epimer were identical with those of olefinic acetate **7a** (Table I) obtained in the reaction of **5** with acetic acid.

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Registry No. 1, 26278-43-3; **2**, 87433-41-8; **2** 2-methyl-d_3, 87433-42-9; **3**, 73586-29-5; **3** 4-methylene-d_2, 87433-43-0; **4a** (isomer 1), 87433-44-1; **4a** (isomer 2), 87433-45-2; **4a** 4-methylene-d_2, 87433-46-3; **4b** (isomer 1), 87433-47-4; **4b** (isomer 2), 87433-48-5; **4b** 4-methylene-d_2, 87433-49-6; **5**, 73586-31-9; **5a**, 87433-50-9; *anti*-**7a**, 87433-51-0; *syn*-**7a**, 87480-68-0; *anti*-**7b**, 74381-15-0; *anti*-**7c**, 87433-52-1; *anti*-**7** (A = OH), 87480-69-1; *syn*-**7** (A = OH), 81831-71-2; **8a**, 87433-53-2; **8b**, 87433-54-3; **8c**, 87433-55-4; **8** (A = OH), 87433-56-5; **9a**, 87433-57-6; **9b**, 87433-58-7; **9c**, 87450-37-1; **9** (A = OH), 87433-59-8; **10a**, 73586-32-0; **10a**-d_2, 87433-60-1; **10b**, 87433-61-2; **10c**, 86831-64-3; **11**, 59014-95-8; **12**, 700-56-1; 2-methyleneadamantane, 875-72-9; 4-hydroxy-4-methyl-2-adamantanone, 87433-62-3.

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