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(35) Enthalpy changes on hydrogenation (ΔH_{hyd}) are −27.1, −28.3, and −33 kcal/mol for cyclohexene, bicyclo[2.2.2]oct-2-ene, and norbornene, respectively.[28]
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The 4-Homoadamantyl Cation. II.[1] Mechanistic Studies on Lewis Acid Catalyzed Conversion of Homoadamantene to 2-Methyladamantane by Carbon-13 Labeling Techniques. Convenient Synthesis of 4-Homoadamantanone-*5*-^{13}C and Homoadamantene-*4*-^{13}C

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Received May 19, 1975

The Lewis acid catalyzed conversion of homoadamantene-*4*-^{13}C in CS_2 yielded 20% of 2-methyladamantane with the majority of the label equally distributed between the α position and the methyl group, indicating that only the olefinic carbons were involved in this rearrangement. The mechanism probably involves protonation of the olefinic bond by $AlX_3 \cdot H_2O$ to form the classical 4-homoadamantyl cation. This cation appears to rearrange rapidly to an unsymmetrically bridged 2-adamantylcarbinyl cation which yields 2-methyladamantane by hydride abstraction. The degenerate homoadamantyl rearrangement is retarded in such a low polar solvent as CS_2 presumably by intimate ion pairing. 4-Homoadamantanone-*5*-^{13}C was prepared in 46% overall yield by addition of $(CH_3)_3Si^{13}CN$ to adamantanone followed by $LiAlH_4$ reduction of the α-trimethylsilyloxy nitrile and Demjanow–Tiffeneau ring enlargement of the resulting α-aminomethyl alcohol [$(CH_3)_3Si^{13}CN$ was obtained in 88% yield from $(CH_3)_3SiCl$ and $Ag^{13}CN$]. This synthetic procedure appears to be a convenient general method for the preparation of ^{13}C-labeled ketones and their derivatives.

Lewis acid catalyzed rearrangements of polycyclic hydrocarbons are extremely useful methods for the preparation of adamantane and other diamonoid molecules.[4,5] The catalyst reacts with a promoter present in the reaction mixture to form carbonium ions which initiate intermolecular hydride transfers involving the hydrocarbon.[4a,f] The resulting carbonium ions then undergo a series of hydride transfers and 1,2-alkyl shifts leading to the thermodynamically most stable products, diamonoid hydrocarbons.[4a,f]

Although these processes have been known[4] for some time to involve carbonium ion intermediates, the first studies of these intermediates appeared in the literature only recently. Whitlock and Siefken constructed a rearrangement graph for tricyclodecane isomers showing the interrelationships among the isomers.[6] There are at least 2897 pathways between tetrahydrodicyclopentadiene and adamantane but no studies have yet succeeded in isolation and identification of intermediates during this isomerization.[4f] Most of the studies up to 1970 have only provided suggestive mechanistic information.[4,5a,6,7] Schleyer and co-workers[8] recently proposed a plausible pathway for the rearrangement of tetrahydrodicyclopentadiene to adamantane

on the basis of molecular mechanics calculations. The last part of this pathway was demonstrated experimentally. Thus, *exo*-1,2-trimethylenenorbornane was shown to rearrange to adamantane in the presence of AlX_3 through 2,6-trimethylenenorbornane and protoadamantane as it had been predicted.[8] Protoadamantane-*4*-^{13}C, under similar conditions, gave exclusively adamantane-*1*-^{13}C.[9] ^{14}C-Labeling techniques were used in mechanistic studies of the Lewis acid catalyzed isomerization of 1- and 2-methyladamantanes.[10a] 2-Methyladamantane-2-^{14}C yielded exclusively 1-methyladamantane-*1*-^{14}C. The methyl group thus remained attached to the same ring carbon throughout the isomerization indicating a skeletal rearrangement involving 2-adamantyl and 4-protoadamantyl cationic intermediates. An analogous mechanism was suggested for the degenerate isomerization of adamantane itself.[10b]

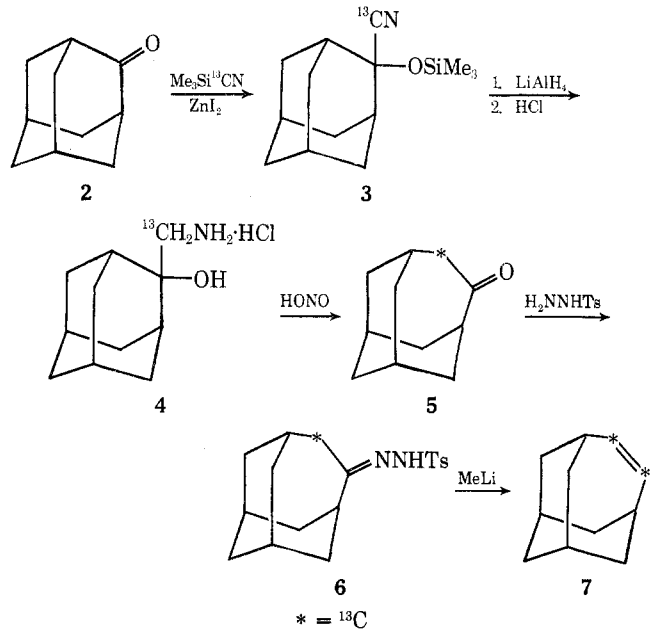
Recently we reported[11] the Lewis acid catalyzed conversion of homoadamantene to 2-methyladamantane. Homoadamantane, under similar conditions, yielded a 2:1 mixture of 2- and 1-methyladamantane.[11] Since no 1-methyladamantane was formed from homoadamantene, 1- and 2-methyladamantane presumably arise through different intermediates which interconvert very slowly, if at all. We now report mechanistic studies on the Lewis acid catalyzed conversion of homoadamantene to 2-methyladamantane using ^{13}C labeling techniques and homoadamantene-*4*-^{13}C as the starting material.

Synthesis of 4-Homoadamantanone-*5*-^{13}C (5) and Homoadamantene-*4*-^{13}C (7). Homoadamantene can be obtained readily by the reaction of an alkyllithium with the tosylhydrazone of 4-homoadamantanone.[11] However, the reported procedures for the preparation of 4-homoadamantanone[12-14] are not convenient for the introduction of ^{13}C isotope into the homoadamantane nucleus.

The key step in our synthesis of 4-homoadamantanone-*5*-^{13}C (5) and homoadamantene-*4*-^{13}C (7) was a modification of Evans–Sundermeyer's reaction. Evans[15] and Sundermeyer[16] found recently that ketones and aldehydes react readily with trimethylsilyl cyanide in the presence of a Lewis acid catalyst to give α-trimethylsilyloxy nitriles which can be reduced readily to the corresponding α-aminomethyl alcohols. No excess of either reactant was necessary. However, the reported preparation of trimethylsilyl cyanide required stirring of AgCN with a large excess of trimethylsilyl chloride followed by fractional distillation of the resulting mixture of trimethylsilyl cyanide and trimethylsilyl chloride.[15,17] This procedure is inconvenient for small-scale preparations of expensive trimethylsilyl cyanide-^{13}C (1). We found, however, that the separation of trimethylsilyl cyanide and trimethylsilyl chloride was unnecessary; the crude mixture can be used just as well. The complete synthetic sequence is outlined in Scheme I. The reaction of adamantanone (2) with an equimolar amount of trimethylsilyl cyanide-^{13}C (1), in trimethylsilyl chloride at 25° in the presence of zinc iodide as catalyst, gave 2-cyano-^{13}C-2-trimethylsilyloxyadamantane (3) smoothly in 98% yield. Reduction of 3 by $LiAlH_4$ followed by introduction of gaseous HCl yielded 2-aminomethyl-^{13}C-2-hydroxyadamantane hydrochloride (4). 4-Homoadamantanone-*5*-^{13}C (5) was obtained by Demjanow–Tiffeneau ring enlargement[13b] of 4 in 46% yield based on 1. The ketone 5 was converted to the corresponding tosylhydrazone which gave homoadamantene-*4*-^{13}C (7) upon treatment[11] with an excess of methyllithium in an overall yield of 56%. The described synthesis of 4-homoadamantanone-*5*-^{13}C and homoadamantene-*4*-^{13}C should be a convenient general method for the preparation of ^{13}C-labeled ketones and olefins.

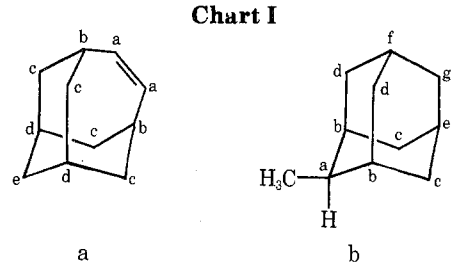
The proton-decoupled ^{13}C NMR spectrum of homoadamantene shows signals at 138.1 (d), 37.2 (t), 34.1 (t), 32.5

Scheme I



(d), and 30.0 ppm (d) (the multiplicity, indicated in parentheses, was determined by proton off-resonance decoupling). The CH_2 signals at 37.2 and 34.1 ppm were assigned on the basis of their relative line intensities to carbons e and c, respectively (Chart I, a). The assignment of the CH

Chart I



signals (32.5 and 30.0 ppm) was based on selective ^1H-decoupling experiments. The lower field signal (32.5 ppm) was assigned to carbons b which are coupled with the lower field protons. The chemical shift of olefinic carbons a is in good agreement with the value (135.8 ppm) of the chemical shift of the olefinic carbons in cycloheptene when corrected for substituents.[18]

Comparison of the ^{13}C NMR spectra of labeled and unlabeled homoadamantene, recorded under identical operating conditions, shows that no label scrambling occurred during the synthesis. The label was located exclusively at the olefinic carbons. Mass spectrometric analysis indicated the ^{13}C enrichment as 10 ± 1%.

Results and Discussion

Homoadamantene-*4*-^{13}C (7) was stirred with an excess of $AlBr_3$ in carbon disulfide for 5 min at room temperature. Substantial amounts of tar (almost insoluble in CS_2) were formed during the reaction. The carbon disulfide solution was decanted from the tar, the solvent was evaporated, and the residue was sublimed to yield 20% of a crude product which was analyzed by GLC. The major product (80–85%) was isolated by preparative GLC and identified as 2-methyladamantane (8) by ^{13}C NMR, ^1H NMR, ir, and mass spectra, and GLC comparison with an authentic sample. Less than 0.5% of 1-methyladamantane was present.[19] The

Table I
^{13}C NMR Signal Intensities of Unlabeled 2-Methyladamantane (8a) and 2-Methyladamantane-^{13}C (8b) Obtained from Homoadamantene-4-^{13}C (7)

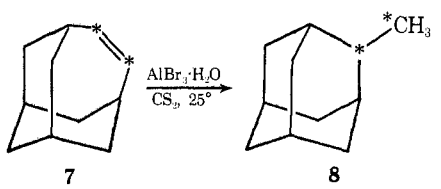
Carbon[a]	Chemical shift[b]	T_1, sec[c]	Relative signal intensities[d] 8a[e]	8b[f]
a	39.2	19.5	1.10 ± 0.05	5.27 ± 0.05
b	34.0	17.5	2.19 ± 0.01	2.62 ± 0.05
c	39.6	10.5	2.38 ± 0.04	2.72 ± 0.16
d	31.5	9.5	2.25 ± 0.02	2.67 ± 0.07
e	28.7	16.5	1.08 ± 0.02	1.08 ± 0.05
f	28.4	16.5	1.06 ± 0.01	1.07 ± 0.04
g	38.8	11.5	1.11 ± 0.03	1.15 ± 0.12
CH_3	19.0	10.0	0.92 ± 0.06	5.52 ± 0.06

[a] See Chart I, b. [b] Relative to Me_4Si; solvent $CDCl_3$. [c] Measured in undegassed solutions. [d] Uncertainties are standard deviations. [e] The sum of the signal intensities was taken as 12.1 (the number of carbons multiplied by the natural abundance of ^{13}C); mean value of five measurements. [f] The sum of the signal intensities was taken as 22.1 ± 1 (12.1 + 10, the percentage of the ^{13}C enrichment); mean value of three measurements.

proton-decoupled ^{13}C NMR spectrum of 2-methyladamantane shows eight signals which were assigned according to Maciel et al.[20] (see Table I and Chart I, b). The assignment of carbons e and f remains tentative.

The signal intensities in routine ^{13}C NMR spectra are generally not proportional to the number of equivalent carbons owing to the saturation effect, different nuclear Overhauser effect (NOE) enhancement for different carbons, the dependence of the digital spectrum signal intensities on their positions, and systematic errors of the spectrometer. To eliminate the influence of the saturation effect a waiting time between successive pulses five times as long as the longest relaxation time was used. Dependence of signal intensities on their positions in the digital spectrum was avoided by using the narrowest possible sweep width (1250 Hz) and a mathematical filtering[21] which enhanced the signal to noise ratio and increased the signal width. By this procedure more than ten data points per signal were available. The NOE enhancements were not eliminated, since the sample amounts were limited. The spectra of the labeled and the unlabeled compounds were taken under precisely the same operating conditions. Comparison of the corresponding relative signal intensities gave intensity enhancements proportional to the amounts of the label at the particular positions. The results are shown in Table I.

The relative signal intensities of all corresponding carbons except for a and CH_3 in labeled and unlabeled 2-methyladamantane are almost the same. There is a small increase in the signal intensities of carbon atoms b, c, and d in 2-methyladamantane obtained from homoadamantene-4-^{13}C. However, the signal intensities of carbons a and CH_3 are significantly and equally enhanced. In other words, the majority of the label (~90%) in 2-methyladamantane obtained by $AlBr_3$ catalyzed conversion of homoadamantene-4-^{13}C is equally distributed between positions a and CH_3.

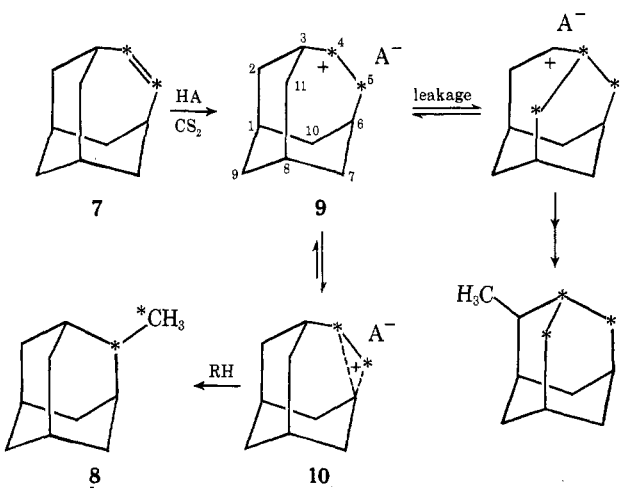


7 8

* = ^{13}C

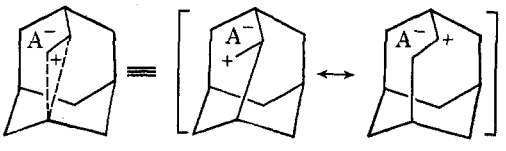
The mechanism of this reaction almost certainly involves protonation of the olefinic bond in the initial step to form a carbonium ion. An analogous mechanism has been suggested and is generally accepted for the Lewis acid catalyzed alkylations of alkenes by alkanes.[22] Lewis acids readily react with moisture (e.g., from air) to form a strongly acidic complex.[23,24] Such an acid can easily protonate olefinic bonds. Protonation of homoadamantene (7) presumably leads first to the classical 4-homoadamantyl cation (9) (Scheme II). Homoadamantene does not have the required

Scheme II



7 9 8 10

geometry for a concerted one-step transformation to a bridged ion, since the olefinic and two adjacent bridgehead carbons lie in the same plane and, therefore, the incipient empty p orbital at carbon C_4 is perpendicular to the C_5–C_6 bond. However, the classical cation **9** cannot give 2-methyladamantane (**8**) directly and probably rearranges rapidly to another intermediate which yields **8** by hydride abstraction. The classical primary 2-adamantylcarbinyl cation may be ruled out as the intermediate because such carbonium ions appear to be energetically inaccessible under normal reaction conditions.[26] Since the majority of the label in 2-methyladamantane-^{13}C (**8b**) is equally distributed between carbons a and CH_3, only the olefinic carbons of homoadamantene-4-^{13}C (**7**) are involved in the rearrangement. Any rearrangement involving other carbons would lead to extensive label scrambling. The unsymmetrically bridged 2-adamantylcarbinyl (4-homoadamantyl) cation[27] (**10**) appears to be the most plausible intermediate to account for the experimental results. This structure is a hybrid between the primary 2-adamantylcarbinyl cation (**10a**) and the more strained but secondary 4-homoadamantyl cation (**10b**).



10 10a 10b

Protonation of homoadamantene in a nonpolar solvent like carbon disulfide presumably leads to intimate ion pairs. Stability differences between secondary and primary intimate ion pairs should be significantly reduced relative to those between the corresponding free ions. In addition, the adamantane skeleton is about 10 kcal/mol less strained than the homoadamantane skeleton.[29] Consequently, the contribution of structure **10a** should be predominant and hydride abstraction by the "primary" center leading to 2-methyladamantane (**8**) is highly favored.

The small amount of label scrambling over carbons b, c,

and d indicates a limited extent of the degenerate homoadamantyl rearrangement (Scheme II). This leakage provides additional evidence for the intermediacy of the 4-homoadamantyl cation. Since degeneracy is generally limited by ion pairing,[13a,30] the small extent of degenerate homoadamantyl rearrangement observed in CS_2 is consistent with the formation of intimate ion pairs in this nonpolar solvent. In other media the degenerate homoadamantyl rearrangement is well known to occur to a large extent. For example, the 4-homoadamantyl cation formed in acetolysis and formolysis of the specifically deuterated 4-homoadamantyl tosylate was reported to undergo extensive label scrambling and degenerate rearrangement.[12a,13a] In concentrated sulfuric acid the degenerate rearrangement of the 4-homoadamantyl cation is essentially complete.[31]

Experimental Section

The labeled $K^{13}CN$ was purchased from Merck Sharp and Dohme, Canada Ltd. and contained 90% of ^{13}C. $AlBr_3$ (Fluka) was kept in a tightly closed flask; no special protection from air moisture was used during its handling. Other chemicals were analytical grade. All melting points were taken on a Kofler hot stage and are uncorrected. The ^{13}C NMR spectra were taken at 22.628 MHz on a Bruker-Spectrospin HFX-90 spectrometer equipped with a B-SC-FFT-12 Fourier transform unit. Samples (40–50 mg) in deuteriochloroform solutions (ca. 160 μl) were measured using a 5-mm cylindrical microcell. The deuterium signal of the solvent was used as the internal lock. The free induction decay signals were accumulated in 8192 data points. Chemical shifts are given in parts per million relative to internal Me_4Si. The ^1H NMR spectra were recorded on a Varian A-60A spectrometer using $CDCl_3$ as solvent, ir spectra were taken on a Perkin-Elmer M-257 spectrophotometer, and mass spectra on a Varian CH-7 mass spectrometer. GLC analyses were carried out on a Varian Aerograph M-1800 gas chromatograph with a M-480 integrator. All new compounds gave satisfactory elemental analyses.

Silver cyanide-^{13}C was obtained in quantitative yield by mixing aqueous solutions of $K^{13}CN$ ($K^{13}CN/KCN$ = 1:9) and $AgNO_3$ in equimolar amounts. The product was collected by filtration, washed with water, alcohol, and ether, and dried in vacuo.

Trimethylsilyl Cyanide-^{13}C (1). A modification of the reported[15,17] procedures was used. A suspension of dry $Ag^{13}CN$ (7.5 g, 56 mmol) in trimethylsilyl chloride (18.5 g, 170.5 mmol) was stirred vigorously for 3 days at room temperature in a tightly closed flask protected from light. The volatile liquid was then carefully filtered from AgCl and unreacted $Ag^{13}CN$. A fresh amount of trimethylsilyl chloride (21.0 g, 193.5 mmol) was added to the mixture of silver salts, the suspension was stirred for 3 more days, and the liquid was filtered off. The combined filtrates (37.5 g), which contained 13% of 1 and 87% of trimethylsilyl chloride, were used directly in the following reaction step. The content of 1 was determined by GLC (SE-30, 55°) or by integration of the methyl signals in the ^1H NMR spectrum [δ 1 0.73 ppm, $(CH_3)_3SiCl$: 0.85 ppm]. The overall yield of 1 was 88% (based on $Ag^{13}CN$).

2-Cyano-^{13}C-2-trimethylsilyloxyadamantane (3) was prepared by a modification of Evans–Sundermeyer's synthesis[15,16] for trimethylsilyl cyanohydrin ethers. To a mixture of 5.0 g (33.3 mmol) of adamantanone (2) and a catalytic amount of dry ZnI_2, stirred in a flask closed with a rubber serum cap, 34.2 mmol of 1 (26.0 g of a 13% solution of 1 in trimethylsilyl chloride) was added via syringe. The flask was previously flushed with dry nitrogen. The reaction is exothermic, but external cooling is unnecessary for small scale preparations. The resulting clear solution was stirred for 2 hr at room temperature and filtered. The flask and the filter were rinsed with dry ether and combined filtrates were evaporated in vacuo without heating to give 8.15 g (98%) of 3: mp 92–95°; ir (KBr) 2900 s, 2850 w, 2230 w, 1450 s, 1250 s, 1115 s, 1080 s, 887 s, 835 s, 755 cm^{-1} s; ^1H NMR δ 0.22 (9 H, s), 1.3–2.7 (14 H, m, maximums at 2.0 and 1.7 ppm); mass spectrum *m/e* (rel intensity) 249 (M^+, 2.13), 234 (100), 207 (11.7).

2-Aminomethyl-^{13}C-2-hydroxyadamantane Hydrochloride (4). A solution of 8.1 g (32.3 mmol) of crude 3 in 10 ml of dry ether was added dropwise within 20 min to a stirred mixture of 1.4 g (37.0 mmol) of $LiAlH_4$ in 30 ml of dry ether. The reaction mixture was stirred under gentle reflux for an additional 2 hr, cooled to room temperature, and diluted with 30 ml of ether. Water (20 ml) and 15% NaOH (2 ml) were added dropwise, followed by more water until two layers separated. The aqueous layer was extracted five times with 50 ml of ether. (2-Methylamino-2-hydroxyadamantane[32] is only moderately soluble in ether). The combined ether extracts were dried overnight and filtered. Dry gaseous HCl was introduced until no more solid precipitated (2–3 hr). The product was collected by filtration and air dried to yield 4.6 g (65%) of 4, mp 287–290° dec (lit.[13b] mp 288–290° dec.).

4-Homoadamantanone-5-^{13}C (5) was prepared in 71% yield starting from 4.5 g (20.7 mmol) of 4 following Schlatmann's procedure,[13b] except that the precipitate formed in the reaction was not collected by filtration but extracted five times with 20-ml portions of ether. The combined extracts were washed three times with saturated $NaHCO_3$ solution, dried, and evaporated. The crude product was sublimed to give 2.4 g (71%) of 5 (~95% pure by GLC). If necessary, 5 can be purified by column chromatography on Al_2O_3 (neutral, activity II) using ether as the eluent.

4-Homoadamantanone-5-^{13}C Tosylhydrazone (6). To a solution of 2.7 g (14.5 mmol) of *p*-toluenesulfonylhydrazide in 7 ml of warm methanol was added 2.3 g (14 mmol) of 5 in small portions. The reaction mixture was allowed to stand overnight in a refrigerator and the crystallized product (4.1 g) was collected. Additional 0.3 g of the product was obtained from the mother liquor. The overall yield was 4.4 g (95%), mp 169–172°.

Homoadamantene-4-^{13}C (7). Methyllithium (20 ml of a 2 *M* solution in ether) was added dropwise over 30 min to a suspension of 3 g (9.0 mmol) of 6 in 15 ml of dry ether stirred at 0° in a nitrogen atmosphere. The stirring was continued for 2–3 hr at 0° and overnight at room temperature. The reaction mixture was diluted with 10 ml of ether and water was added dropwise until two layers separated. (The color of the reaction mixture changed gradually during the addition of water from brown-red through yellow to white.) The reaction mixture was neutralized with dilute HCl and the aqueous layer was extracted four times with ether. The combined extracts were dried, the solvent was removed through a Vigreux column, and the residue was sublimed in vacuo to give 0.8 g (60%) of 7 (99% pure by GLC), mp 236–238°.

Reaction of Homoadamantene-4-^{13}C (7) with $AlBr_3$. A solution of 250 mg (1.7 mmol) of 7 and 750 mg (2.8 mmol) of $AlBr_3$ in 5 ml of CS_2 was stirred for 5 min at room temperature. A substantial amount of tar was formed during the reaction. The reaction mixture was diluted with 5 ml of CS_2 and 100 ml of ice–water was added. The layers were separated, and the carbon disulfide solution was washed with water and dried. The solvent was carefully removed through a Vigreux column to give 51.4 mg (20.3%) of crude product. GLC analysis (SE-30, 80°) indicated a single major product and four minor products (15–20% in total) with considerably longer retention times. The major product was isolated by preparative GLC (30% SE-30, 120°) and identified as 2-methyladamantane by ^{13}C NMR, ^1H NMR, ir, and mass spectra and GLC comparison with an authentic sample.

A partly reacted sample of 7 was isolated from the reaction mixture as described for the product. The ^{13}C NMR spectrum indicated no label scrambling.

Acknowledgments. This work was supported by a grant from the Research Council of the Republic of Croatia (Yugoslavia) and by the Schweizerischer Nationalfonds zur Förderung der Wissenschaftlichen Forschung. We thank Professors P. v. R. Schleyer for helpful discussions and D. E. Sunko for the use of equipment. We are also thankful to Professor D. A. Evans, who kindly sent to us the manuscript of his work prior to publication.

Registry No.—1, 56804-58-1; 2, 700-58-3; 3, 56804-59-2; 4, 56804-60-5; 5, 56804-61-6; 6, 56804-62-7; 7, 56804-63-8; 8a, 700-56-1; 8b isomer A, 56804-64-9; 8b isomer B, 56804-65-0; 9, 56804-66-1; ^{13}C-cyanic acid, silver salt, 56804-67-2; trimethylsilyl chloride, 75-77-4; *p*-toluenesulfonyl hydrazide, 1576-35-8; homoadamantane, 24669-57-6.

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