

The 4-Homoadamantyl Cation. III.¹ Sulfuric Acid Catalyzed Rearrangement of 4-Homoadamantanol-5-¹³C

Katica Mlinarić-Majerski,^{2a,3} Zdenko Majerski,^{*2a} and Ernő Pretsch^{2b}

Rugjer Bošković Institute, 41001 Zagreb, Yugoslavia, and Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule, Zürich 8006, Switzerland

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The rearrangement-hydride transfer reduction of 4-homoadamantanol-5-¹³C in concentrated sulfuric acid-pentane gave homoadamantane (2), 2-methyladamantane (3), and 4-homoisotwistane (4). The label was equilibrated over all ring carbons in each of the products but there was a small excess of the label located at the methyl group of 3. The results are interpreted in terms of a rapid degenerate rearrangement of the 4-homoadamantyl cation accompanied by rearrangements of this cation to the 2-homoadamantyl cation and an unsymmetrically bridged 2-adamantylcarbinyl cation. Therefore, 1,2-carbon shifts, 1,2-hydride shifts, and 1,3-hydride shifts are all involved.

The course of the rearrangement of the 4-homoadamantyl cation is highly dependent on the reaction conditions. Acetolysis and formolysis of 4-homoadamantyl tosylate yielded mixtures of the corresponding 4-homoadamantyl esters in addition to homoadamantene.^{4,5} No product with the adamantane skeleton was formed. Experiments with isotopically labeled tosylate indicated the occurrence of both degenerate 1,2-carbon shifts and 1,2-hydride shifts. Thus, 4-homoadamantyl-4-²H tosylate produced 4-homoadamantyl acetate with 38–45% of the label at the α position. If only 1,2-carbon shifts had been involved 50% of the label should have been located at this position.⁵

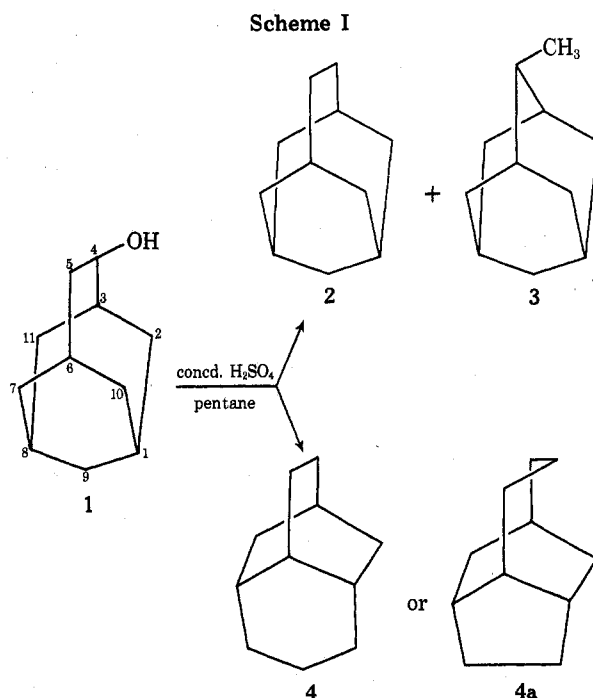
The reaction of homoadamantene with AlX₃ in carbon disulfide generated the 4-homoadamantyl cation, which yielded 20% of 2-methyladamantane.^{1,6} Homoadamantene-4-¹³C gave 2-methyladamantane with the majority of the label equally distributed between the α position and the methyl group, indicating that just the olefinic carbons were involved in this rearrangement.¹ Only a small amount of label was scrambled to the β and γ carbons relative to the methyl group. The degenerate homoadamantyl rearrangement (1,2-carbon shift) is retarded in such a low polar solvent as CS₂ presumably by intimate ion pairing. The suggested mechanism involves protonation of the olefinic bond by AlX₃-H₂O to form the classical 4-homoadamantyl cation. This cation rearranges rapidly to an unsymmetrically bridged 2-adamantylcarbinyl cation⁷ which then yields 2-methyladamantane by hydride abstraction.

In this work we have studied the rearrangement of the 4-homoadamantyl cation in concentrated sulfuric acid¹⁰ using ¹³C labeling techniques. The 4-homoadamantyl cation was generated by protonation of 4-homoadamantanol-5-¹³C.

Results

4-Homoadamantanol-5-¹³C (1b) was obtained by LiAlH₄ reduction of 4-homoadamantanone-5-¹³C.¹¹ Comparison of ¹³C NMR spectra of the labeled (1b) and unlabeled (1a) 4-homoadamantanol, recorded under identical operating conditions, showed that no label scrambling had occurred during the synthesis of 1b; the label was located exclusively at position 5. (The ¹³C NMR spectrum of 4-homoadamantanol is discussed in detail in the Experimental Section.) Mass spectrometric analysis indicated a ¹³C enrichment as 7.5 ± 1%.

Alcohol 1 was stirred with concentrated sulfuric acid in the presence of pentane for a few minutes at room temperature. The pentane layer was separated and the solvent evaporated to yield 40% of a crude product mixture which was analyzed by GLC. GLC analysis indicated the presence

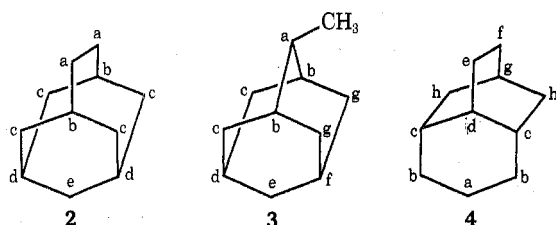


of three products in a ratio of 1:1:2 (Scheme I). The two minor products were identified as homoadamantane (2) and 2-methyladamantane (3) by ¹³C NMR, ¹H NMR, ir, and mass spectra, and GLC comparison with authentic samples. The major product was also a tricyclic undecane but turned out not to be a diamonoid hydrocarbon! Its mass spectrum showed a molecular ion peak at *m/e* 150. ¹H NMR and ir spectra indicated the absence of unsaturation, cyclopropane rings, and alkyl groups, while its melting point (56–58°) was considerably lower than typical for diamonoid hydrocarbons. The ¹³C NMR spectrum of this material showed eight signals (see Table I) corresponding to three different CH and five different CH₂ groups according to the proton off-resonance spectrum and the *T*₁ values. Such a ¹³C NMR spectrum is only compatible with the two tricyclic undecanes, 4 and 4a, among all possible 11-carbon tricyclic hydrocarbons possessing all of the carbons in rings and having no three- or four-membered rings.¹² According to empirical force-field calculations, 4 is 9.5 kcal/mol less strained than its isomer 4a.¹³ The more stable isomer, 4 (tricyclo[5.3.1.0^{3,8}]undecane), is known^{14,15} and has been conveniently named 4-homoisotwistane.¹⁰ Ir, ¹H NMR, and ¹³C NMR spectra of an authentic sample of this hydrocarbon were identical with those of the major

Table I
¹³C NMR Signal Intensities of the Rearrangement-Hydride Transfer Products of 4-Homoadamantanol (1a) and 4-Homoadamantanol-5-¹³C (1b) in Concentrated Sulfuric Acid at 22°

Product	Chemical shift ^a	Carbon ^b	T ₁ , ^c sec	Relative signal intensities ^d		x _i , % ^g
				1a ^e	1b ^f	
2	38.4	c	11.4	4.48	7.55	10
	36.5	e	11.5	1.14	1.66	7
	34.0	a	12.7	2.17	3.57	9
	32.1	b	19.7	2.16	3.55	9
	27.7	d	19.7	2.14	3.29	8
3	39.6	c	10.5	2.38	3.79	9
	39.2	a	19.5	1.10	1.73	8
	38.8	e	11.5	1.11	1.77	9
	34.0	b	17.5	2.19	3.37	8
	31.5	g	9.5	2.25	3.73	9
	28.7	d or f	16.5	1.06	1.67	8
	28.4	f or d	16.5	1.08	1.68	8
	19.0	CH ₃	10.0	0.92	1.86	15
	15.2	a	8.2	0.97	1.68	10
4	33.0	d	15.3	1.20	1.79	7
	32.2	b or h	8.9	2.39	3.81	9
	31.8	h or b	8.6	2.37	3.80	9
	30.8	c	15.3	2.15	3.53	9
	27.0	e or f	8.6	1.02	1.64	9
	26.2	f or e	9.0	1.06	1.73	9
	24.7	g	15.6	0.94	1.62	10
15.2	a	8.2	0.97	1.68	10	

^a Relative to Me₄Si; solvent CDCl₃. ^b Description as indicated below.



^c Measured in undegassed solutions. ^d The standard deviation of a single signal intensity was found to be less than 5% of the measured value for each signal of unlabeled and labeled 3. Since the sample concentrations and operating conditions were virtually equal for 2, 3, and 4, the uncertainties in signal intensities can also be expected to be the same. ^e The sum of the signal intensities was taken as 12.1 (the number of carbons multiplied by the natural abundance of ¹³C); mean value of two measurements for 2 and 4, and five measurements for 3. ^f The sum of the signal intensities was taken as 19.6 (12.1 + 7.5, the percentage of the ¹³C enrichment); mean value of two measurements for 2 and 4, and four measurements for 3. Relative signal intensities of 4 obtained from 1b at 0° were essentially the same: 1.77, 3.86, 3.75, 3.51, 1.70, 1.74, 1.64, and 1.65. ^g The amount of label per carbon atom calculated by using eq 1.

product from the rearrangement-hydride transfer reduction of 4-homoadamantanol in sulfuric acid.

The conversion of 4-homoadamantanol to 4-homoisotwistane in sulfuric acid is the first example of a skeletal rearrangement of homoadamantane to a nonadamantanoid structure. 4-Homoisotwistane appears to be one of the most stable tricycloundecanes.¹³ Schleyer¹⁶ and Inamoto¹⁷ identified this hydrocarbon as an intermediate in the acid-catalyzed rearrangements of 2-hydroxymethyl-*exo*-2,3-trimethylenenorbornane, *exo*- and *endo*-2,3-tetramethylenenorbornane, and 2,3-trimethylenebicyclo[2.2.2]octane to methyladamantanes.

The products, homoadamantane (2), 2-methyladamantane (3), and 4-homoisotwistane (4), were stable under the used reaction conditions. Essentially no isomerization of 2

occurred in concentrated sulfuric acid-pentane even if an equivalent amount of 2-pentanol was present. Interestingly, the ratio of 2, 3, and 4 formed in the reaction of 4-homoadamantanol with sulfuric acid was found to depend on the reaction temperature. At room temperature (22°) the ratio 2:3:4 was 1:1:2, while at 0° it was 1:0.5:5.

The distribution of the ¹³C label in the products was determined by quantitative ¹³C NMR analysis. 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 filtering¹ which enhanced the signal-to-noise ratio and increased the signal width. By this procedure more than ten data points per signal were available. Nuclear Overhauser enhancements were not eliminated, since this would reduce the signal-to-noise ratio by a factor of up to three and the sample amounts were limited. The spectra of the labeled and unlabeled compounds were taken under precisely the same operating conditions. The relative signal intensities of homoadamantane (2), 2-methyladamantane (3), and 4-homoisotwistane (4) obtained from 4-homoadamantanol-5-¹³C (1b) and those of unlabeled 2, 3, and 4 are shown in Table I.

The amount of label per carbon atom cannot be calculated directly from the normalized signal intensities of the labeled and unlabeled compounds. In undegassed solutions the contribution of dissolved oxygen to the total relaxation rate of carbon atoms with relaxation times greater than 10 sec is significant,^{18a} so that nuclear Overhauser enhancements depend on the relaxation rates of the carbon atoms. A reduction of nuclear Overhauser effect is also expected for free rotating methyl groups.^{18b} Since such effects lead to multiplicative errors in the signal intensities we calculated the amount of label per carbon atom (x_i) by

$$x_i = \frac{100}{x_{\text{tot}}} \left[\frac{I_i^*/I_i(1.11N + x_{\text{tot}})}{\sum_i n_i I_i^*/I_i} - 1.11 \right] \quad (1)$$

where I_i* and I_i are the measured intensities of the *i*th signal in the labeled and reference compound, respectively, N is the total number of carbon atoms, n_i the number of equivalent carbons corresponding to the signal *i*, and x_{tot} the total amount of label (7.5%). The results indicate that the label is essentially equilibrated over all carbons in the nucleus in 2, 3, and 4, but there is a small, statistically significant, excess of label located at the methyl group of 3.

Discussion

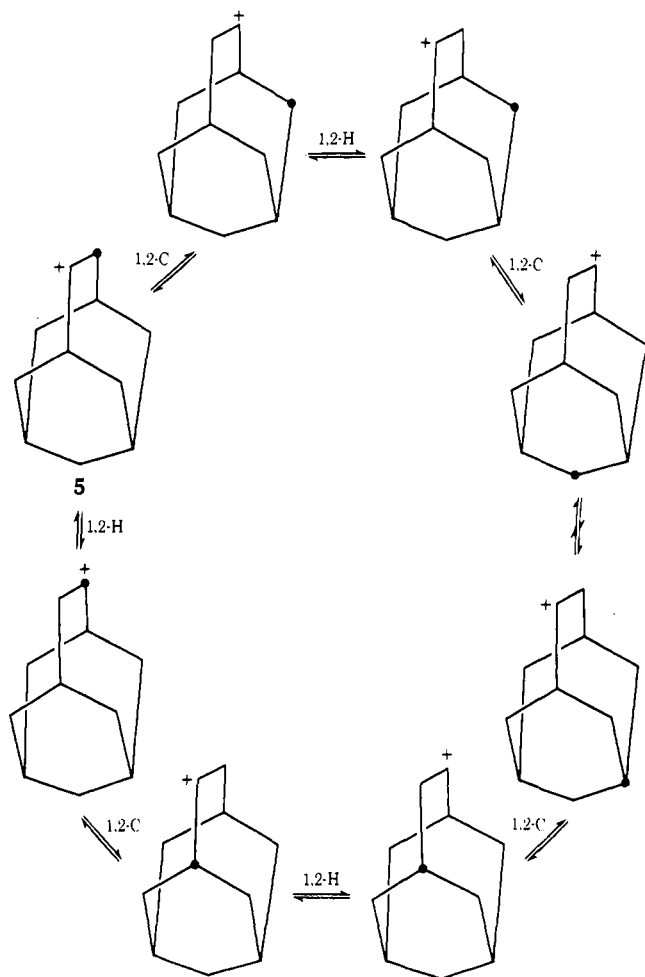
The sulfuric acid catalyzed conversion of 4-homoadamantanol to homoadamantane (2), 2-methyladamantane (3), and 4-homoisotwistane (4) undoubtedly involves protonation of the hydroxyl group followed by formation of the 4-homoadamantyl cation (5). This cation rearranges rapidly to other carbonium ions. The products 2, 3, and 4 are formed by the hydride-transfer reductions of the corresponding cations involving the solvent (pentane). The ¹³C label in 2, 3, and 4 obtained from 4-homoadamantanol-5-¹³C (1b) is completely scrambled over all ring carbons with experimental accuracy. However, there is a small but significant excess of label at the methyl group of 3.

The intermolecular hydride transfer from the products to pentyl cations (generated from the solvent) appears not to be an important process. If not, homoadamantane (2) should rearrange in the presence of pentyl cations, but essentially no rearrangement occurred when a mixture of 2 and 2-pentanol was subjected to the same reaction conditions as used for 4-homoadamantanol. A direct intermolec-

ular hydride transfer from one C₁₁ tricyclic molecule to another one is even less probable, since in the reaction mixture pentane was present in large excess. Moreover, hydride abstraction from 2 should preferably produce the 3-homoadamantyl cation, which is less strained than other bridgehead homoadamantyl cations.^{9b} This cation, under similar conditions, gives a considerable amount of 1-methyladamantane,⁸ which in the reaction of 4-homoadamantanol with sulfuric acid is formed just in traces.

The high scrambling of the label in homoadamantane (2) can only be explained by essentially complete equilibration in the 4-homoadamantyl cation, i.e., by fast degenerate 1,2-carbon shifts accompanied by degenerate 1,2-hydride shifts. [If only 1,2-carbon shifts were involved the label in 2 would be located exclusively at positions a and c (see Table I, footnote b)]. In other words, the 4-homoadamantyl cation (5) formed directly from 4-homoadamantanol-5-¹³C is in a fast equilibrium with the 4-homoadamantyl cations labeled at other positions (Scheme II). Since degeneracy is

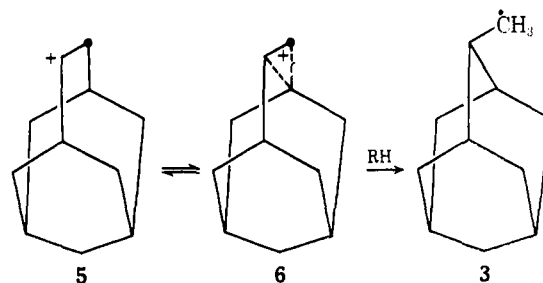
Scheme II



generally limited by bridging¹⁹ the 4-homoadamantyl cations in the equilibrium should be classical. Carbonium ions in concentrated sulfuric acid are essentially free. However, the 4-homoadamantyl cation (5) formed in the reaction of homoadamantene with AlX₃ in CS₂ is probably paired with a gegenion and, consequently, the degenerate rearrangement of 5 is retarded in this medium.¹

2-Methyladamantane (3) is probably formed by the hydride-transfer reduction of the unsymmetrically bridged 2-adamantylcarbiny cation (6, Scheme III) as proposed for its formation in the Lewis acid catalyzed conversion of homoadamantene.¹ This cation can arise from any of the clas-

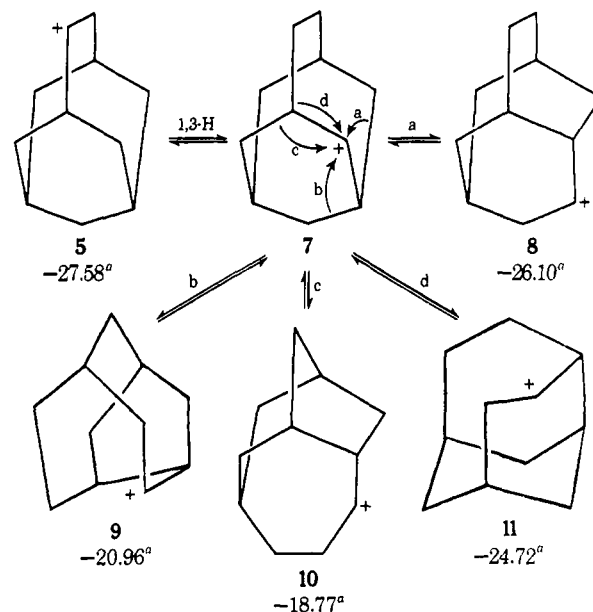
Scheme III



sical 4-homoadamantyl cations in the equilibrium. Since the ¹³C label is equilibrated over all carbons in the 4-homoadamantyl cation, the label could be expected to be scrambled over all carbons in the derived bridged 2-adamantylcarbiny cation and, therefore, 2-methyladamantane. The small excess of label found at the methyl group of 3 is consistent with the intermediacy of the bridged 2-adamantylcarbiny cation. The formation of this cation is probably slightly faster than the degenerate rearrangement of the 4-homoadamantyl cation.²⁰

The 1,2-carbon shifts and the 1,2-hydride shifts in the 4-homoadamantyl cation (5) lead either to another 4-homoadamantyl cation or to the bridged 2-adamantylcarbiny cation (6). The other skeletal rearrangements can only be explained as proceeding through the 2-homoadamantyl cation (7), which can be formed from the 4-homoadamantyl cation by a 1,3-hydride shift.^{21,22} Therefore, cation 7 is a precursor of 4-homoisotwistane. This cation can potentially rearrange by 1,2-carbon shifts to four different carbonium ions: 8, 9, 10, and 11 (Scheme IV). Dihedral angles between

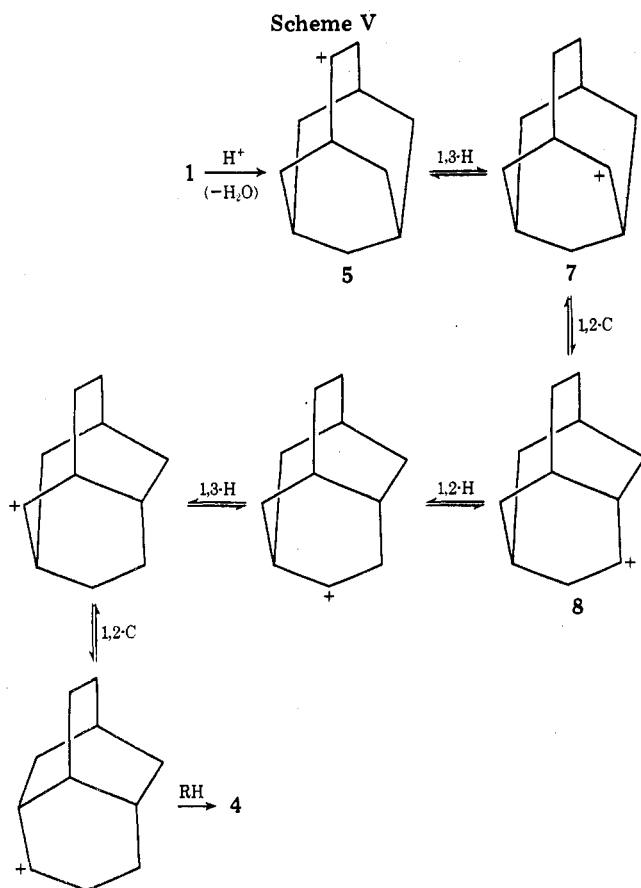
Scheme IV



^a Calculated heats of formation (kcal/mol) of the corresponding hydrocarbons.¹³

the 2-homoadamantyl cation empty p orbital and the migrating C-C bonds are similar in all four cases (20–40°). However, the calculated heats of formation (as well as strain energies) of the hydrocarbons corresponding to cations 8, 9, 10, and 11 are significantly different.¹³ Since all four cations (8–11) are secondary, the relative stabilities of these cations should roughly parallel to the relative stabilities of the corresponding hydrocarbons. Cation 8 appears to be the most stable, whereas cations 9 and 10 are considera-

bly less stable. For a similar reaction, isomerization of *exo*-1,2-trimethylenenorbornane to adamantane, it has been shown that the course of the reaction is governed by the relative thermodynamic stabilities of the possible products.²³ This indicates that the product-determining steps involve transition states closer to the products than to the initial cations. Using the same approach it can be predicted that rearrangement pathways b and c of the 2-homoadamantyl cation probably cannot compete successfully with pathways a and d (see Scheme IV). A reasonable mechanism of the conversion of the 4-homoadamantyl cation to 4-homoisotwistane via 8 is outlined in Scheme V. However, cation 11 is only about 2 kcal/mol less stable than cation 8 and cannot be excluded as a possible intermediate in the conversion of the 4-homoadamantyl cation to 4-homoisotwistane. There are a number of possible pathways for this conversion via cation 11 several of which involve only cationic intermediates with stabilities comparable to that of 8 and 11. However, these pathways are longer than that shown in Scheme V.



Our results demonstrate that the mechanism and, consequently, the product composition of the rearrangement-hydride transfer reduction of the 4-homoadamantyl cation depends highly on the reaction medium. The rearrangement in concentrated sulfuric acid involves 1,2-carbon shifts and both 1,2- and 1,3-hydride shifts, while the Lewis acid catalyzed rearrangement in nonpolar carbon disulfide¹ involves mainly the 1,2-carbon shift leading to the bridged 2-adamantylcarbanyl cation and 2-methyladamantane. The degenerate homoadamantyl rearrangement of the 4-homoadamantyl cation in the presence of AlX_3 in carbon disulfide is retarded by ion pairing.¹ However, this rearrangement is very rapid in concentrated sulfuric acid, where cat-

ionic intermediates are essentially free and probably live longer.

Experimental Section

¹³C 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 $CDCl_3$ solutions (ca. 160 μ l) were measured using a 5-mm cylindrical microcell. The deuterium signal of the solvent was used as the internal lock. The free induction decay spectra were accumulated in 8192 data points. Chemical shifts are given in parts per million relative to internal Me_4Si . Relaxation times (T_1) were measured in undegassed solutions. ¹H NMR spectra were recorded on a Varian A-60A spectrometer, 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.

4-Homoadamantanol-5-¹³C (**1b**) was obtained in 92% yield by $LiAlH_4$ reduction of 4-homoadamantanone-5-¹³C¹ using the standard procedure.

The proton decoupled ¹³C NMR spectrum of 4-homoadamantanol shows 11 signals at 76.5 (6.6, d), 44.4 (4.0, t), 40.7 (t), 40.6 (d), 36.7 (3.5, t), 36.3 (3.8, t), 35.6 (3.7, t), 29.6 (d), 29.5 (t), 27.5 (6.3, d), and 27.1 ppm (6.8, d) (the data in parentheses indicate T_1 values in seconds and the multiplicity as determined by proton off-resonance decoupling). The T_1 values of the seven well-resolved signals are in accord with the results of the off-resonance decoupling. The signals at 29.5, 40.6, 76.5, 44.4, 29.6, and 35.6 ppm are assigned to carbons 2, 3, 4, 5, 6, and 11 (see Scheme I), respectively, on the basis of the proton off-resonance decoupling and estimated chemical shift values (28.2, 36.4, 76.0, 44.5, 28.4, and 34.7 ppm, respectively). These values were calculated using the chemical shifts of homoadamantane (see Table I) and the correction increments²⁴ for the introduction of the hydroxyl group. This procedure could not be used successfully to assign the signals of the δ carbons relative to the hydroxyl group. The estimated chemical shift values were identical for carbons 7 and 10 (38.4 ppm) and 1 and 8 (27.7 ppm).

Reaction of 4-Homoadamantanol-5-¹³C (1b**) with Sulfuric Acid.** To a mixture of 1 ml of concentrated H_2SO_4 and 2.5 ml of pentane vigorously stirred at room temperature (22°) 250 mg (1.5 mmol) of **1b** was added all at once. After 3 min 5 ml of pentane was added and the resulting mixture was poured on 100 ml of ice-water. The layers were separated and the aqueous one was extracted with pentane. The combined pentane extracts were washed with water and dried. The solvent was carefully removed through a Vigreux column to give 88 mg (39%) of the crude product. GLC analysis (SE-30, 80°) indicated the presence of three major products in a ratio of 1:1:2 and less than 1% of 1-methyladamantane. The major products were isolated by preparative GLC (SE-30, 120°) and identified as homoadamantane (2), 2-methyladamantane (3), and 4-homoisotwistane (4) by comparison of ¹³C NMR, ¹H NMR, ir, and mass spectra with those of authentic samples.

The reaction of **1b** with concentrated H_2SO_4 in the presence of pentane was also carried out at 0° for 4 min. The work-up as described above gave 2, 3, and 4 in a ratio of 1:0.5:5, respectively.

Homoadamantane (2), 2-methyladamantane (3), and 4-homoisotwistane (4) were subjected to the same reaction conditions as used for 4-homoadamantanol (1). After 24 hr only traces of rearranged products were detected by GLC. A mixture of 2 (1.5 mmol) and 2-pentanol (1.5 mmol) was also subjected to the same reaction conditions as 1 and the mixture was worked up as described above. GLC analysis indicated the absence of 2-pentanol and essentially no isomerization of 2.

The ¹³C NMR spectrum of 2-methyladamantane (3) has been described in detail previously.^{1,25} The spectrum of homoadamantane (2) shows five signals (Table I). The signals at 38.4 and 36.5 ppm are assigned to carbons c and e, respectively, on the basis of their relative intensities (see Table I, footnote b). The relaxation time T_1 corresponding to the signal at 34.0 ppm is considerably shorter than those corresponding to the signals at 32.1 and 27.7 ppm. Since relaxation times of CH_2 groups are generally shorter than those of CH groups, the signal at 34.0 ppm is assigned to the ethylene-bridge carbons (a). The chemical shift of the ethylene-bridge carbons in 2,6-bishomoadamantane is exactly the same.²⁶ In both homoadamantane and 2,6-bishomoadamantane the "ethylene" carbons are more shielded than the methylene ones. This is consistent with Grant's additivity rule for polycyclic hydrocarbons.²⁷ The bridgehead carbons in 2,6-bishomoadamantane, flanked by an "ethylene" group and two methylene groups, are less

shielded than those in adamantane which are flanked by three methylene groups. Consequently, the signals at 32.1 and 27.7 ppm in the spectrum of **2** are assigned to bridgehead carbons b and d, respectively.

The ^{13}C NMR spectrum of 4-homoisotwistane (**4**) is assigned by comparison of experimental and calculated chemical shifts. The spectrum shows eight signals (Table I). According to the proton off-resonance decoupling and the T_1 values the signals at 33.0, 30.8, and 24.7 ppm correspond to CH groups while those at 32.2, 31.8, 27.0, 26.2, and 15.2 ppm correspond to CH_2 groups. Grant's additivity rule²⁷ was used to calculate the shifts of carbons a and b (16.2 and 32.7, respectively). To calculate the chemical shifts of the other carbons the shifts of bicyclo[2.2.2]octane²⁸ were taken as the basis and the influence of the trimethylene bridge was estimated using the additivity increments. For carbons c, d, e, f, g, and h (see Table I, footnote b) the following values were obtained: 32.1, 33.9, 26.7, 26.7, 24.6, and 29.2 ppm, respectively. Therefore, the signals at 15.2, 30.8, 33.0, and 24.7 ppm are assigned to carbons a, c, d, and g, respectively, whereas the signals at 32.2 and 31.8 ppm, as well as the signals at 27.0 and 26.2 ppm, could not be assigned in this way.

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Registry No.—**1a**, 25763-45-5; **1b**, 57443-88-6; **2**, 281-46-9; **3**, 700-56-1; **4**, 43000-53-9.

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Tetrabutylammonium Borohydride. Borohydride Reductions in Dichloromethane

Douglas J. Raber* and Wayne C. Guida

Department of Chemistry, University of South Florida, Tampa, Florida 33620

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The utility of tetrabutylammonium borohydride as a reducing agent has been investigated. The high solubility of this reagent in dichloromethane permits reductions to be carried out in high yields in the absence of protic solvents. The selectivity of tetrabutylammonium borohydride in dichloromethane toward organic carbonyl compounds is similar to that exhibited by sodium borohydride in aqueous or alcoholic media. At room temperature acid chlorides are reduced extremely rapidly, aldehydes and ketones are reduced at convenient rates, and esters are reduced quite slowly. Synthetic procedures and results are reported for the reduction of a variety of aldehydes and ketones.

The preparation of quaternary ammonium borohydrides (tetramethylammonium, tetraethylammonium, and benzyltrimethylammonium borohydride) was reported by Banus, Bragdon, and Gibb in 1952.¹ The tetramethyl derivative exhibited solubilities similar to those of the alkali metal borohydrides, and consequently the quaternary am-

monium derivatives did not appear to offer any advantages as synthetic reagents. Subsequently, Sullivan and Hinckley reported² the preparation of quaternary ammonium borohydrides which contained long chain alkyl groups: cetyltrimethylammonium borohydride and tricaprilmethylammonium borohydride. These compounds are soluble in