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$$C_6H_5CCH(C_6H_5)SR$$
7a, R = $C_6H_5CH_2$
10a, R = CH_3CH_2

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Sulfuric Acid Catalyzed Rearrangements of 1- and 3-Homoadamantanols

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Both 1- and 3-homoadamantanol yield homoadamantane, 1- and 2-methyladamantane, and 1-adamantylcarbinol in the reactions with 75% sulfuric acid (70°). The mechanism very likely involves formation of the 1- and 3-homoadamantyl cations, followed by hydride transfers and rearrangements of the resulting classical homoadamantyl cations into the corresponding bridged cations. A simple, good-yield preparation of 1-homoadamantanol is described.

Reactions with sulfuric acid leading to adamantane derivatives attracted considerable attention in the last few years.[1-8] *endo*-2,6-Trimethylene-*exo*-2-norbornanol in sulfuric acid was reported to rearrange smoothly into 1-adamantanol,[1] bicyclo[3.3.1]nonane-2,7-diol into 2-oxaadamantane,[2] while 3-hydroxymethylbicyclo[3.3.1]nonan-7-ol produced a mixture of 2-adamantanol, di(2-adamantyl) ether, and adamantane.[3] 2-Hydroxy-2-methyladamantane in 98% sulfuric acid gave various mixtures of methyladamantanones or methyladamantanes and hydroxymethyladamantanes depending on the temperature.[4] Synthetically useful reactions are also encountered. Treatment of deltacyclane with sulfuric acid gave either 1- or 2-noradamantanol or noradamantane, depending on conditions.[5] The reaction of adamantane or 1-adamantanol with 96% sulfuric acid (80°) resulted in a 50% yield of adamantanone,[6a] providing a very convenient method for the functionalization of the methylene position of adamantane. Both adamantanone oxime[7] and lactone 4-oxahomoadamantan-5-one[8] with sulfuric acid were reported to give fair yields of 4-hydroxyadamantan-2-one.[9]

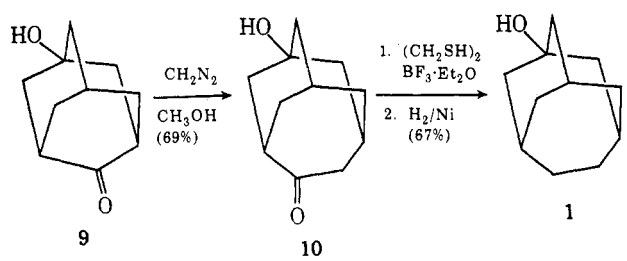
The reaction of adamantanols with sulfuric acid were extensively investigated by Geluk and Schlatmann.[6] 2-Adamantanol was shown to rearrange to 1-adamantanol (>98%) at 28° in concentrated sulfuric acid.[6a,10] An equilibrium mixture containing small amounts of 2-adamantanol was rapidly achieved from either direction. However, with 70% H_2SO_4 (90°) a mixture of 1,4-adamantanediol, adamantane, 1-hydroxy-4-adamantanone, and adamantanone was obtained.[6b] 1-Adamantanol, under essentially the same conditions, disproportionated into 1,3-adamantanediol and adamantane.[6b] The mechanism of these reactions appears to involve an intermolecular hydride transfer of a bridgehead hydrogen from one molecule of the starting alcohol to an adamantyl cation which is generated from another molecule of the alcohol and is transformed into adamantane.[11]

An analogous mechanism would be reasonably expected to operate in reactions of homoadamantyl alcohols with sulfuric acid. However, the 3- and 4-homoadamantyl cations, if formed, could rearrange into the corresponding nonclassical cations, which may lead to adamantane de-

rivatives. Such cations were reported to be involved as the intermediates in the acetolysis of chiral 1-adamantylcarbinyl-1′-*d* toxylate[12] and the $AlBr_3$-catalyzed rearrangement of homoadamantene.[13] Consequently, the product distribution in the sulfuric acid reaction of homoadamantyl alcohols should depend on the relative rates of the disproportionation reactions *vs.* the rearrangements of homoadamantyl cations.

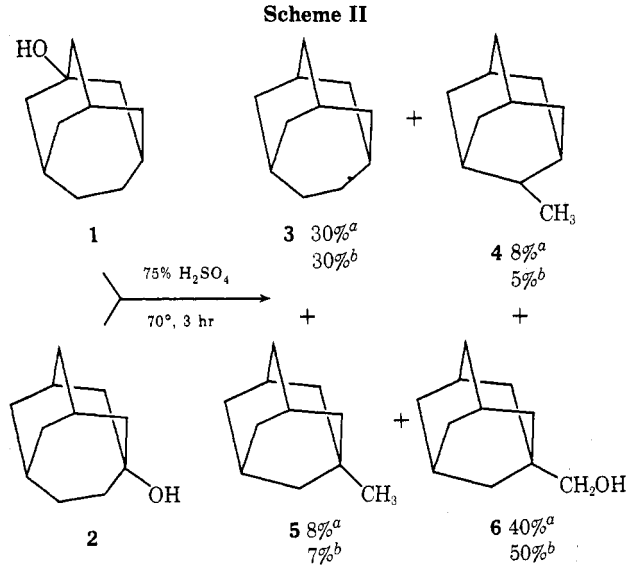
We wished to compare the reactions of bridgehead adamantanol and homoadamantanols with sulfuric acid under essentially the same conditions. 3-Homoadamantanol (**2**) can easily be prepared,[14] but a convenient synthesis[15] of 1-homoadamantanol (**1**) has not been reported according to our knowledge. As the starting material we chose readily available 1-hydroxy-4-adamantanone (**9**).[6c] Diazomethane homologation of **9** gave 1-hydroxy-4-homoadamantanone (**10**) in a 69% yield (Scheme I). However, the Clemmensen and the Wolff–Kishner reductions failed to give **1** in satisfactory yields. 1-Homoadamantanol (**1**) was obtained in a 67% overall yield from **10** by Raney nickel desulfurization of the corresponding ethylene thioketal (**11**).[16]

Scheme I



1-Homoadamantanol (**1**) or 3-homoadamantanol (**2**) was stirred vigorously in 75% sulfuric acid at 70° for 3 hr. In definite time intervals small samples were taken out from the reaction mixture and analyzed by glc. The final product distributions from **1** and **2** were quite similar (Scheme II).

Scheme II



[a] The main products of **1**.[17] [b] The main products of **2**.[17] An amount of polymer was also formed. The relative amounts of homoadamantane (**3**), 2-methyladamantane (**4**), and 1-methyladamantane (**5**) were found to increase with time at the expense of 1-adamantylcarbinol (**6**).

The methyladamantanes (**4** and **5**) were identified by glc using the internal standards; homoadamantane (**3**) and 1-adamantylcarbinol (**6**) were isolated by preparative glc and identified by comparison of their ^1H nmr, ir, and mass spectra with those of the authentic samples. Homoadamantane (**3**) and the methyladamantanes (**4** and **5**) were proved to be stable under the above conditions. 1-Adamantylcarbinol (**6**) was found to be the *only* alcohol present in both reaction mixtures on quenching the reaction after 10 min. Upon treatment of **6** with H_2SO_4 under the same conditions as used for **1** and **2** the following final product distribution was obtained: **3**, 23%; **4**, 3%; **5**, 8%; and unreacted **6**, 45%.[17]

Isomerization of **1** and **2** into **6** is not surprising. The homoadamantyl skeleton is known to be about 10 kcal/mol more strained than the adamantyl skeleton[18] and, therefore, **6** should be thermodynamically more stable than **1** and **2**. This is in accord with complete isomerization of 3-homoadamantyl acetate into 1-adamantylcarbinyl acetate in acetic acid containing *p*-toluenesulfonic acid.[14] However, under kinetically controlled conditions homoadamantyl products may be favored. Hydrolysis of 1-adamantylcarbinyl tosylate in aqueous diglyme in the presence of sodium carbonate produced virtually quantitatively 3-homoadamantanol.[14] The mechanism of the isomerization of **1** and **2** into **6** very likely involves the initial formation of the 1- and 3-homoadamantyl cations (Scheme III). This is probably followed by hydride transfers resulting in the isomerization of the 1 and 3 cations into each other and into the 2-, 4-, and 9-homoadamantyl cations. The 1,2-intramolecular hydride transfers are highly improbable to occur on the homoadamantyl skeleton.[19] As in the case of the adamantyl nucleus[20] the relationship between the vacant p orbital and the migrating hydride is very unfavorable.

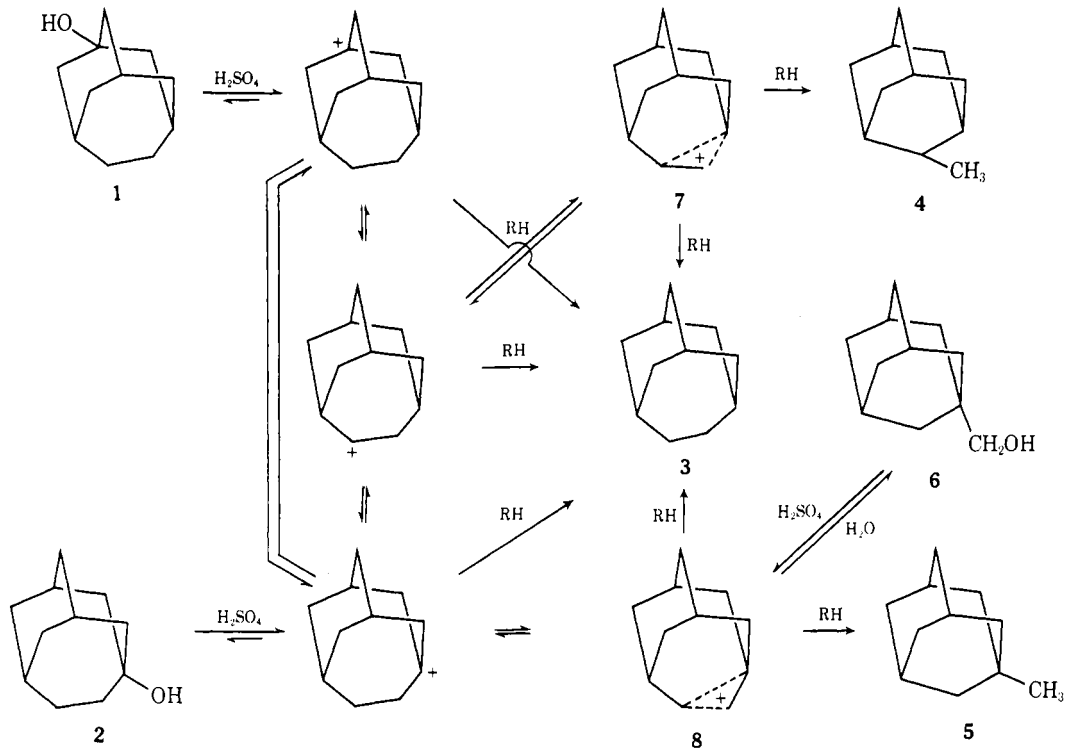
Total amounts of the hydrocarbons **3**–**5** are quite high regardless of the starting alcohol. Homoadamantane (**3**) can be formed from *any* homoadamantyl cation by a hydrogen abstraction from the products, polymer, or the starting alcohol. 1-Adamantylcarbinol (**6**), 1-methyladamantane (**5**), and 2-methyladamantane (**4**) could be formed either from the bridged homoadamantyl cations[12-14] **8** and **7** or from the primary 1- and 2-adamantylcarbinyl cations. Since simple primary carbonium ions appear to be energetically inaccessible under usual reaction conditions,[12,21] we suggest the nonclassical homoadamantyl cations **7** and **8** as the more plausible intermediates (Scheme III).[22]

Under essentially the same conditions 1- and 2-adamantanol are known to disproportionate quite easily.[6a] However, 1- and 3-homoadamantanol produced neither homoadamantanediols nor homoadamantanones in appreciable quantities. Therefore, the isomerization of the homoadamantyl cations leading to the adamantyl derivatives seems either to be considerably faster than the disproportionation reactions or the disproportionation products are highly unstable. These products, if formed, would generate again the homoadamantyl cations. The bridged 3- and 4-homoadamantyl cations appear to be favored over the corresponding classical cations under the used reaction conditions. However, the 3-homoadamantyl cation obtained in superacid solutions at −78° is stable and does not rearrange.[23] Both ^1H and ^{13}C nmr spectroscopic studies indicate the classical nature of this cation. Therefore, the equilibrium between the classical and the nonclassical 3-homoadamantyl cation should depend strongly upon the reaction conditions. A similar dependence would be expected for the 4-homoadamantyl cation.

Experimental Section

Melting points were determined in sealed capillary tubes using a Thiele apparatus. Infrared spectra were recorded on a Perkin-

Scheme III



Elmer M-257 spectrophotometer, ^1H nmr spectra on a Varian A-60A spectrometer, and mass spectra on a Varian CH-7 mass spectrometer. Purity of compounds was controlled by a Varian Aerograph M-1800 gas chromatograph.

Authentic samples of 1-methyladamantane,[24a] 2-methyladamantane,[24b] 3-homoadamantanol,[14] and 1-adamantylcarbinol[14] were prepared according to the published procedures. Homoadamantane was obtained by catalytic reduction of homoadamantene.[13]

1-Hydroxy-4-homoadamantanone (10).[25] To a stirred mixture of 1-hydroxy-4-adamantanone[6c] (16.6 g, 0.1 mol), KOH (60.0 g, 1.07 mol), water (25 ml), and CH_3OH (150 ml), a solution of "Diazald" (45.0 g, 0.21 mol) in CH_3OH (360 ml) was added dropwise at 0° over a period of 4.5 hr. Stirring was continued overnight at room temperature. The resulting white-gray suspension was evaporated to dryness *in vacuo*, ether (350 ml) and water (250 ml) were added, the layers were separated, and the aqueous one was extracted with ether (7 × 100 ml). Combined ether extracts were dried over $MgSO_4$. The solvent was evaporated to yield 12.4 g (68%) of **10** (≥96% pure by glc): mp 263–265°; ir (KBr) 3400, 2920, 1690 cm^{-1}; mass spectrum m/e (rel intensity) 180 (M^+, 52), 162 (25), 95 (100); tosylhydrazone, mp 156–158°; ir (KBr) 3420, 3230, 2910, 1330, 1170 cm^{-1}.

1-Hydroxy-4-homoadamantanone Ethylene Thioketal (11).[26] To a solution of **10** (3.6 g, 0.02 mol) in ethanedithiol (3 ml) stirred at 0° was added boron trifluoride etherate (1.5 ml). The reaction flask was immediately taken out from the cooling bath and left to stand for about 10 min at room temperature with occasional shaking. Methanol (2–3 ml) was added and the reaction mixture was left overnight in a refrigerator. The precipitate was filtered by suction, washed with cold CH_3OH, and dried: yield 3.9 g (78%); mp 105–107° (recrystallized from CH_3OH); ir (KBr) 3260, 2920, 1445, 1095, 1040 cm^{-1}; mass spectrum *m/e* (rel intensity) 256 (M^+, 100), 196 (77), 105 (43), 95 (43).

1-Homoadamantanol (1). To a solution of **11** (2.7 g, 0.01 mol) in absolute ethanol (60 ml) was added 24 g of Raney nickel (W-2). The mixture was stirred and refluxed for 18 hr. Separated nickel was filtered off and washed with absolute ethanol. The filtrate was concentrated to a small volume, diluted with water (300 ml), and extracted with ether (4 × 80 ml). The extracts were dried and the solvent was evaporated to yield 1.5 g (86%) of 1-homoadamantanol (≥98% pure by glc): mp 266–268° (lit.[15] mp 269–270°); ir (KBr) 3300, 2920, 1450, 1080, 1040, 880 cm^{-1}; mass spectrum *m/e* (rel intensity) 166 (M^+, 33), 95 (100).

Reaction of 1- and 3-Homoadamantanol and 1-Adamantylcarbinol with 75% Sulfuric Acid. General Procedure. A solution of the corresponding alcohol in 75% H_2SO_4 (0.332 g, 0.002 mol in 2.4 ml) was stirred vigorously at 70° for 3 hr. The reaction mixture was shaken occasionally to introduce sublimed hydrocarbons into the solution. In definite time intervals small samples of the reaction mixture were taken out, poured onto plenty of crushed ice, and extracted with ether. The extracts were dried over anhydrous K_2CO_3 and analyzed by glc (SE-30, 90°). After 3 hr the remaining reaction mixture was worked up as described above. The solvent was evaporated to give 0.169 g of the crude product mixture. The main products (**3** and **6**) were isolated by preparative glc (SE-30, 135°) and identified by comparison of their ^1H nmr, ir, and mass spectra with those of authentic samples. The methyladamantanes (**4** and **5**) were identified by glc (SE-30, 90° and FFAP, 100°) using the internal standards. Ir spectra of the crude product mixture showed a very weak absorption corresponding to a carbonyl group (~1700 cm^{-1}); glc analyses indicated no presence of a diol.

A sample of **3**, **4**, and **5** was treated with 75% H_2SO_4 under the same conditions as used in the reactions of **1** and **2**. The glc analyses indicated no reaction.

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Registry No. 1, 31061-64-0; **2**, 14504-80-4; **6**, 770-71-8; **9**, 20098-14-0; **10**, 49701-73-7; **10** tosylhydrazone, 49664-60-0; **11**, 49664-61-1; **12**, 49664-62-2.

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(9) 1-Hydroxyadamantan-4-one can be obtained (in a mixture with adamantane-2,6-dione and 1,3-adamantanediol) by the fuming sulfuric acid (20% SO_3) reaction of adamantane followed by chromic acid oxidation.[6c]
(10) At 80° 2-adamantanol undergoes a disproportionation reaction to give adamantanone and adamantane.[6a]
(11) Adamantanone and 1-hydroxy-4-adamantanone are probably formed by disproportionation reactions of the corresponding 2-hydroxyadamantyl derivatives with an adamantyl cation which acts as the hydride acceptor and is converted into adamantane.[6b]

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(16) 1-Homoadamantanol was also prepared by catalytic reduction of 1-hydroxy-4-homoadamantene (**12**) formed in a poor yield by the reaction of 1-hydroxy-4-homoadamantanone tosylhydrazone with *n*-butyllithium. **12** had mp 250–252°; mass spectrum *m/e* (rel intensity) 164 (M^+, 100), 106 (46), 95 (62); ir (KBr) 3300, 1060, 890, 755, 720 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.4–1.8 (11 H, m), 2.47 (3 H, broad s), 6.03 (2 H, dd, J = 6.1, 3.5 Hz).
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(22) This mechanism is supported by an increase of the ratio **5**:**4** with reaction time observed with all three alcohols (**1**, **2**, and **6**). In the very beginning of the reaction this ratio was found to be lower than one in the case of **1** but higher than one in the cases of **2** and **6**.
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(25) *Cf.* P. v. R. Schleyer, E. Funke, and S. H. Liggero, *J. Amer. Chem. Soc.*, **91**, 3965 (1969).
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Synthesis of Unsaturated Azlactones from *N*-Acylamino Acids

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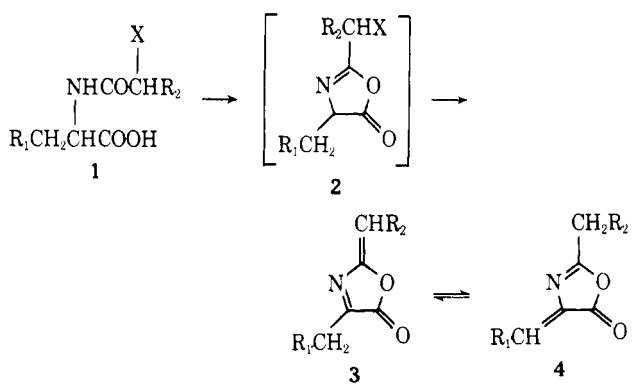
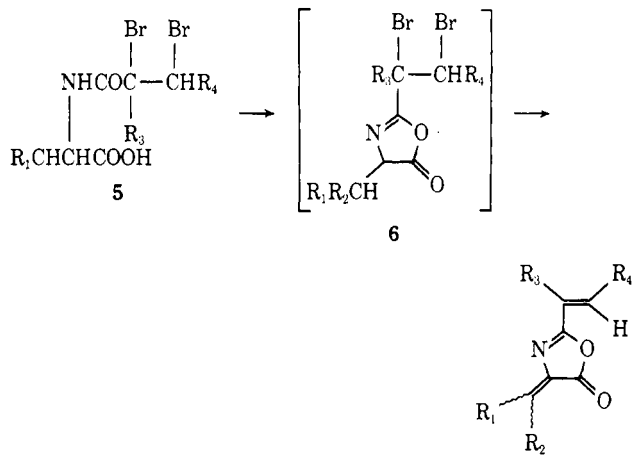
Received August 3, 1973

Phenylalanine, tyrosine, valine, leucine, and isoleucine have been converted to their *N*-(α-methylcinnamoyl) derivatives (**8**). Azlactonization followed by bromine oxidation gave the corresponding unsaturated azlactones (**7**). The configuration about the newly formed double bond was established by nmr correlations, the *Z* configuration being predominant. The mechanism of the double dehydrobromination steps is discussed.

The Bergmann reaction,[1] in which an *N*-(α-haloacyl)-amino acid (**1**) is converted by an acetic anhydride–pyridine mixture into a pseudo-azlactone (**3**), has been known for many years. Several workers[2] have shown that an equilibrium between **3** and the "unsaturated" azlactone **4** can be established and that the position of this equilibrium is determined by the structures of R_1 and R_2 and the conditions[2c,3] under which the reaction is carried out. Our recent communication[4] outlined a procedure making use of an extension of the Bergmann reaction to produce "dehydro" amino acid derivatives without the necessity for equilibration. Treatment of an *N*-α,β-dibromoacylamino acid (**5**) in acetic anhydride at room temperature gave, presumably, the saturated azlactone **6** which was *doubly* dehydrobrominated upon the addition of pyridine to give the unsaturated azlactone **7**. It is the purpose of this paper to describe this work more completely.



Our initial experiments were carried out on the *N*-(DL-*erythro*-2,3-dibromo-2-methylbutanoyl)-L-phenylalanine (**5a**), which was prepared by a Schotten–Baumann acylation of L-phenylalanine with the dibromoacyl chloride. The derivative, **5a**, was, surprisingly, a sharply melting crystalline solid, even though it was necessarily a mixture of diastereomers. We chose this acyl group because it was readily obtained by bromination of commercially available tiglic acid and we envisioned a necessity for the α-methyl group (R_3 = CH_3) to prevent a possible dehydrobromination of the 2-dibromoalkyl group in **6** since this would, of course, disallow the formation of **7**. A 93% yield[5] of crystalline **7a** was isolated when **5a** was dissolved in acetic anhydride and treated with somewhat more than 2 molar equiv of pyridine. In order to confirm the structure of **7a**, it was prepared by Erlenmeyer[6] condensation of benzalde-



	R_1	R_2	R_3	R_4
a	C_6H_5	H	CH_3	CH_3
b	C_6H_5	H	CH_3	C_6H_5
c	*p*-$AcOC_6H_4$	H	CH_3	C_6H_5
d	CH_3	CH_3	CH_3	C_6H_5
e	CH_3	CH_3CH_2	CH_3	C_6H_5
f	$(CH_3)_2CH$	H	CH_3	C_6H_5
g	C_6H_5	H	H	C_6H_5
h	CH_3	CH_3	H	C_6H_5