

THE DEHYDRATION PRODUCTS FROM 2-METHYL-2-ADAMANTOL

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The anomalous dehydration product obtained upon prolonged heating at modest temperature of 2-methyl-2-adamantanol in 85% phosphoric acid is shown to have the dimeric structure *V* instead of the 5-methyl-4-protoadamantene structure *III* previously proposed.

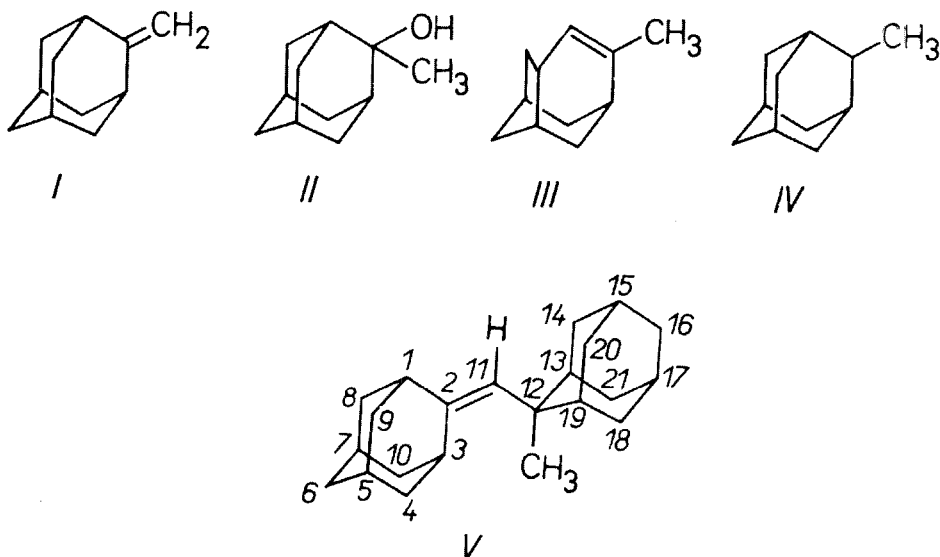
In 1961, Schleyer and Nicholas reported that methyleneadamantane (*I*) could be sublimed in good yield from a hot solution of 2-methyl-2-adamantanol (*II*) in 85% phosphoric acid¹. Recently, Kuthan, Paleček and Musil reported² that they were able to obtain methyleneadamantane by this dehydration procedure only if the acidic solution of 2-methyl-2-adamantanol was rapidly brought to a temperature of 180 to 240°C. When the reaction temperature was increased slowly over a prolonged period, a different reaction product was obtained to which the skeletally rearranged 5-methyl-4-protoadamantene structure *III* was assigned on the basis of microanalysis and spectral properties². This latter report has prompted us to communicate the results of our own of this reaction.

When a mixture of *II* and 85% phosphoric acid was stirred at 120–150°C for six h, a white, crystalline sublimate was obtained which consisted of *I* and 2-methyladamantane (*IV*) in a 2 : 1 ratio. Quenching of the non-volatile acidic reaction residue on ice, followed by extraction with ether, yielded a waxy solid. Recrystallization of this solid from benzene-methanol (5 : 1) followed by repeated recrystallization from pentane at –78°C gave a white, crystalline solid of m.p. 89.2–91.0°C. With the exception of its mass spectrum, this compound exhibited properties virtually identical with those which Kuthan, Paleček, and Musil have ascribed² to structure *III*.**

We assign the dimeric structure *V* to this compound on the basis of its spectral properties and the thermodynamically feasible pathway by which it may be formed

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** The identity of the two samples has now been confirmed by direct comparison. We thank Prof. J. Kuthan for his courtesy in this regard.



under the given reaction conditions. The mass spectrum of *V* shows a molecular ion at $m/e = 296$, corresponding to the molecular formula $C_{22}H_{32}$. Additional structural information is obtained from the prominent peak at $m/e = 281$, formed by loss of the methyl group from the molecular ion to give the resonance-stabilized allylic fraction product. The expected broad metastable peak at $m/e = 266.8$ resulting from this fragmentation is clearly observed.

Both the 1H and ^{13}C NMR spectra are consistent with structure *V*. Compound *V* shares several structural features with the known compounds neopentylideneadamantane³ and ethylideneadamantane³ which are reflected in similarities in their 1H -NMR spectra (Table I). Most notable in this regard are the sharp singlet signal at $\delta 5.10$ (1 H) and the broad singlet at $\delta 2.95$ (1 H) which are attributed, respectively, to the vinyl proton and, most probably, the bridgehead proton *syn* to the 2-methyl-2-adamantyl residue which is attached to the exocyclic double bond of *V*. Corresponding signals in neopentylideneadamantane are found at $\delta 5.01$ and 3.01 and in ethylideneadamantane at $\delta 5.01$ and $\delta 2.82$ (ref.³).

In order to confirm the absence of 5-methyl-4-protoadamantene (*III*) as a product of this reaction, an authentic sample was synthesized through dehydration of 5-methyl-5-protoadamantanol. As expected, its properties are quite different from those of *V*.

The reasonable mechanism shown below, analogous to the well known acidic dimerization of isobutylene⁴, explains the observed behaviour of *II* under these reaction conditions. Lower reaction temperatures allow the concentration of *I* to increase, thereby favoring bimolecular addition to the 2-methyl-2-adamantyl cation

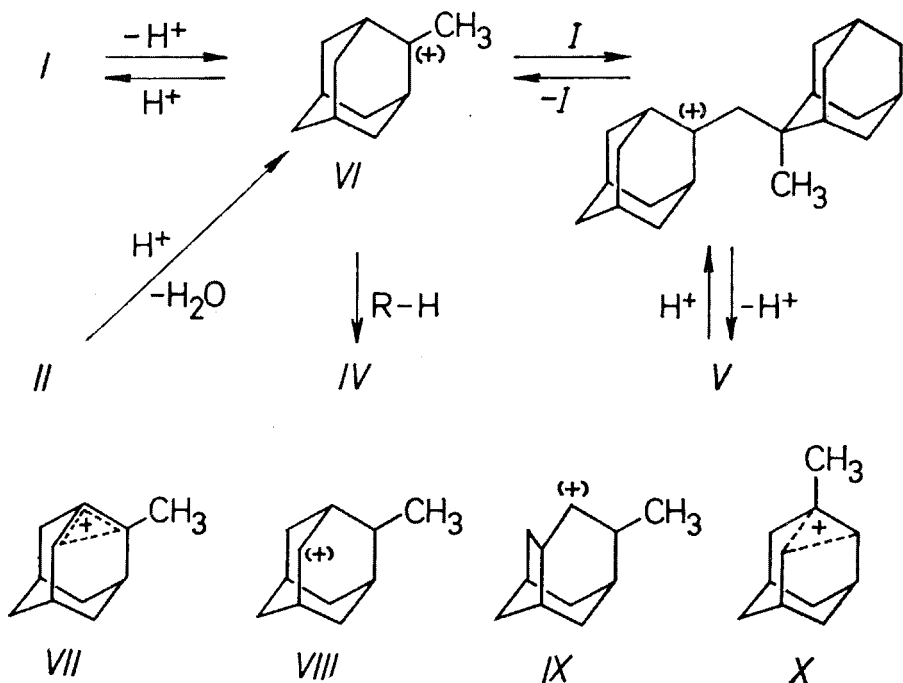
TABLE I
 ^{13}C NMR Spectrum of Compound *V*

Carbon	$\delta^{13}\text{C}$, p.p.m. ^a	Carbon	$\delta^{13}\text{C}$, p.p.m. ^a	Carbon	$\delta^{13}\text{C}$, p.p.m. ^a
2	146.4	4, 10 (or 8, 9)	39.3	18, 21 (or 14, 20)	34.1
11	129.4	5, 7 (or 13, 19)	38.7	15 (or 17)	29.6
1, 3	43.1	13, 19 (or 5, 7)	38.5	17 (or 15)	28.8
8, 9 (or 4, 10) and 12	41.2	14, 20 (or 18, 21)	35.8	CH ₃	26.4
6	40.1	16	34.4		

^a Capillary tetramethylsilane, deuteriochloroform.

it to form the cation precursor to *V*. In fact, when *II* is stirred with 85% phosphoric acid at 25°C for twelve h, *V* is the only reaction product obtained.

Mention must be made regarding the rationale put forth by the previous workers² to explain the formation of presumed structure *III*. It was stated that "the formation



of compound *III* may be explained by a prototropic isomerization of the non-classical carbonium ion *VII* which is facilitated by its longer presence in the reaction mixture on slower dehydration"². Not only is the relevance of ion *VII* to the formation of *III* obscure (a pathway such as *VI* → *VIII* → *IX* → *III* would have to be involved), but also such an argument runs counter to the known facts regarding the relationships between adamantyl and protoadamantyl compounds⁵⁻⁷. Although bridged ("non-classical") species intermediate in structure between adamantyl and protoadamantyl cations are known, available evidence indicates that they are formed from 2-adamantyl cations or precursors only when the ring strain incurred in assuming a more protoadamantyl-like structure is more than offset by charge stabilization due to appropriately situated substituents⁵⁻⁷. This is the case with 1-methyl-2-adamantyl cation precursors which yield the bridged structure *X*. In cation *X*, although ring strain is increased relative to the classical 1-methyl-2-adamantyl cation, electronic stabilization due to charge delocalization onto a tertiary carbon more than makes up for this in the bridged ion⁶. The relationship between cations *VI* and *VII*, on the other hand, is just the opposite in terms of substituent stabilization. Not only does *VI* contain less ring strain than *VII*, but the charge also resides on a tertiary carbon in *VI*. In order for *VI* to be transformed into *VII*, not only must ring strain increase, but also electronic stabilization must decrease as charge is dispersed from a tertiary carbon onto a secondary. This does not seem a reasonable event under these conditions. A recent study of the 2-methyl-2-adamantyl cation through its direct observation by NMR in strong acid solutions bears out its classical, tertiary structure⁸. Furthermore, in the alternative formulation, both steps *VI* → *VIII* and *VIII* → *IX* would be highly unfavorable thermodynamically.

It is interesting to note that upon standing at -60°C or higher, a solution of *V* in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ gives a $^1\text{H-NMR}$ spectrum identical with that reported for the 2-methyl-2-adamantyl cation⁸. Clearly, this is the result of protonation and cleavage of the dimeric olefin and suggests that a dynamic equilibrium may exist in 85% phosphoric acid solution as well. Verification of the reversibility of the dimer formation was obtained upon heating a solution of *V* in 85% phosphoric acid at 190 to 250°C . Under these conditions a mixture of hydrocarbons rapidly sublimed from the reaction mixture. Analysis of the mixture showed it to consist of 41% *I*, 29% *IV*, 22% 1-methyladamantane, and 8% adamantane. The formation of 1-methyladamantane, although unexpected, is not without precedent⁹.

EXPERIMENTAL

Melting points were determined in sealed capillaries on a Thomas Hoover melting point apparatus and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee and Spang Microanalytical Laboratory, Ann Arbor, Michigan. Infrared spectra were determined in tetrachloromethane solutions on either a Perkin-Elmer 237 or 621 spectrophotometer. $^1\text{H-NMR}$ spectra were determined on either JEOLCO JNM-4H-100,

Varian A-60A, T-60A, A56/60A, or HA-100 spectrometers. ^{13}C -NMR spectra were determined on a Varian VFT, XL-100-15 spectrometer equipped with a broad-band proton noise decoupler and a variable temperature probe as previously described⁸. Chemical shifts are reported in units of δ (parts per million) relative to internal tetramethylsilane for ^1H -NMR and capillary tetramethylsilane for ^{13}C -NMR. Gas chromatographic analyses and separations were performed on either a Varian-Aerograph 90-P instrument with a 0.25 in \times 5 ft or 0.25 in \times 20 ft 20% Carbowax 20M on 60-80 Chromosorb W column or a Perkin-Elmer 810 instrument equipped with a 100 ft capillary Carbowax 20M column. Mass spectra were recorded on a Nuclide 12-90 G Mass Spectrometer at 40 eV using mercury and 1,3,5-tribromobenzene as standards.

Dehydration of 2-Methyl-2-adamantanol (II)

A) At moderate temperature: To 50 ml of 85% phosphoric acid (in a flask fitted with a reflux condenser) 5.0 g (30 mmol) of alcohol *II* (ref.³) was added under stirring. The mixture was maintained at 120-150°C for six h, during which time a white solid collected in the condenser. The sublimate was dissolved in ether and the solution was washed twice with a saturated aqueous solution of sodium hydrogen carbonate, twice with water, and dried over magnesium sulfate. Removal of the ether gave 1.2 g of a solid. Sublimation of this material (90°C/15 Torr) gave 1.0 g of a solid which was shown by gas-liquid chromatography and ^1H -NMR analysis to consist of a mixture of methyleneadamantane¹ and 2-methyladamantane¹ in a 2 : 1 ratio.

The phosphoric acid solution was poured over ice and extracted with ether. The ether extract was washed twice with a saturated aqueous solution of sodium hydrogen carbonate, twice with water, and dried over magnesium sulfate. Removal of the ether gave a yellow, waxy solid which would not easily sublime. Recrystallization of this material produced 1.54 g of crystals, m.p. 74-76°C. Repeated recrystallization of a portion of this product from pentane at -78°C gave crystals of m.p. 89.2-91.0°C. This compound rapidly decolorized a solution of bromine in tetrachloromethane and had the following spectral properties: IR 3050, 2980, 1650, 1375, 848 cm^{-1} ; Raman (solid, laser excitation 514.5 nm) 2979, 1655, 845 cm^{-1} ; ^1H -NMR (CCl_4) δ 1.20; (s, 3 H), 1.46 (br s, 2 H), 1.52-2.15 (br m, 23 H), 2.25 (br s, 2 H), 2.95 (br s 1 H), 5.10 (s, 1 H) mass spectrum *m/e* (relative intensity 297 (29), 296 (100, M^+), 281 (124), 266.8 (broad metastable), 148 (10). For $\text{C}_{22}\text{H}_{32}$ (296.2) calculated: 89.12% C, 10.88% H; found: 89.23% C, 10.76% H.

B) At room temperature: A mixture of 1.65 g (9.9 mmol) of *II* in 25 ml of 85% phosphoric acid was stirred at room temperature for twelve h. The reaction mixture was then poured onto ice and the resulting crude solid product was collected, then taken up in ether, washed, and dried. Removal of the ether and recrystallization of the solid from light petroleum at low temperature yielded 0.85 g at *V*, m.p. 88-89°C, identical with that obtained at higher temperatures. An additional 0.25 g of product, m.p. 84-88°C, was obtained by ether extraction of the original aqueous acid solution.

High-Temperature Cleavage of Dimer *V*

In a flask equipped with reflux condenser, 3.5 ml of 85% phosphoric acid and 0.320 g (1.08 mmol) of *V* were rapidly warmed to 195°C with the aid of a hot bath. At this temperature, the dimer immediately dissolved to give a colorless solution and water and a white, crystalline sublimate quickly formed on the condenser. The bath temperature was allowed to rise to 250°C, then returned to 215°C where it was kept for one hour and then further reduced to 195°C for two hours. The major portion of sublimate was formed within the first fifteen minutes of heating. Gas-liquid chromatography, IR and NMR analysis of this crude sublimate (0.307 g) showed it to contain 41% *I*, 29% *IV*, 22% 1-methyladamantane, and 8% adamantane.

Synthesis of 5-Methyl-4-protoadamantene (*III*) and 5-Methyleneprotoadamantane

To an ether solution containing 6.7 mmol of methylmagnesium iodide was added over an 0.25 h period 0.502 g (3.35 mmol) of 5-protoadamantanone¹⁰ in ether. The mixture was stirred under nitrogen for 2.5 g at room temperature and was then held at reflux for an additional 0.5 h. It was then cooled to ice-bath temperature, hydrolyzed by addition of saturated ammonium chloride solution, and extracted with ether. The combined ether extracts were washed and dried over sodium sulfate. Removal of solvent gave 0.58 g of crude alcohol. A small portion was purified by preparative gas-liquid chromatography to give a solid; m.p. 54.5–56.0°C; IR broad OH band centered at 3360 cm⁻¹; ¹H-NMR (CCl₄) δ 1.18 (s, 1 hydroxyl H), 1.22 (s, 3 methyl H), 1.25 to 2.50, most prominent at 1.55 (multiplets, 14 H). If the preferred attack of nucleophiles upon 5-protoadamantanone is from the exo side, then the likely structure of this product is 5-methyl-5-*endo*-protoadamantanol¹¹.

Treatment of the crude alcohol with POCl₃ in pyridine according to the method of Sauers^{12,13} gave, after work-up, an equimolar mixture of two olefins. These were purified by preparative gas-liquid chromatography (20 ft Carbowax, 145°C). The first compound to come off the column was an oil, identical as 5-methyl-4-protoadamantene (*III*) on the basis of its spectral properties: IR 3028, 2872, 1673, 1379 and 825 cm⁻¹; ¹H-NMR (CCl₄) δ 1.10–1.75, prominent doublet at 1.63 (*J* = 1.8 Hz, 11 H, multiplets), 1.75–2.82 (4 H, multiplets), 5.72 (1 vinyl H, br d, apparent *J* = 7 Hz). Double-resonance irradiation at δ 5.72 caused collapse of the doublet at δ 1.63 to a singlet. For C₁₁H₁₆ (148.1) calculated: 89.12% C, 10.88% H; found: 89.20% C, 10.90% H.

The second compound, m.p. 52.5–53.5°C, was identified as 5-methyleneprotoadamantane: IR 3076, 1643 and 887 cm⁻¹; ¹H-NMR (CCl₄) δ 1.10–2.70, most prominent at 1.50 and 2.25 (14 H, multiplets), 4.68 (2 vinyl H, br s). For C₁₁H₁₆ (148.1) calculated: 89.12% C, 10.88% H; found: 89.17% C, 10.84% H.

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