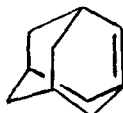


POSSIBLE PRECURSORS OF ADAMANTENE

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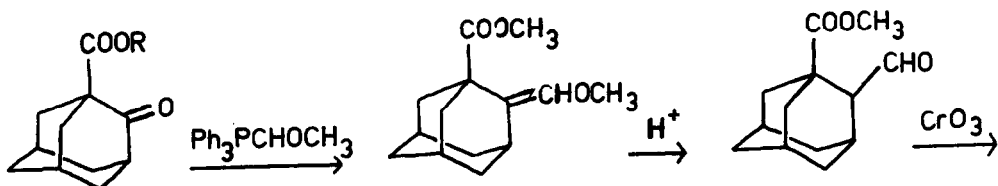
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The facile ring closure¹ of bicyclononane dicarboxylic acid to 2-oxo-adamantane carboxylic acid (I, R=H) opened a new route to 1,2-disubstituted adamantanes. We have used the ketoacid I as starting material for the preparation of precursors to the elusive² 1,2-dehydroadamantane or adamantene:

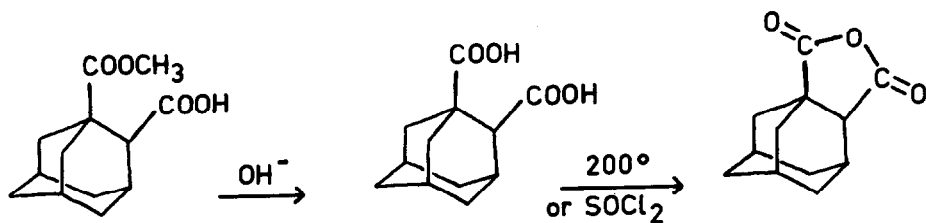


Treatment of the methyl ester¹ of I (R=CH₃), m.p. 86-87°, with the ylid of methoxymethylene phosphonium bromide in ether and subsequent hydrolysis and oxidation in a one pot procedure³ afforded the monomethyl ester of 1,2-adamantane dicarboxylic acid (II), m.p. 142-143°, in 55-60% yield. Hydrolysis gave the diacid III, m.p. 244-245°, which could easily be dehydrated by heating or stirring with thionylchloride to the corresponding anhydride IV, m.p. 208-210°. Diazomethane transformed II into the dimethyl ester V, a colourless liquid, purified by molecular distillation at 150-160°/12 mm.

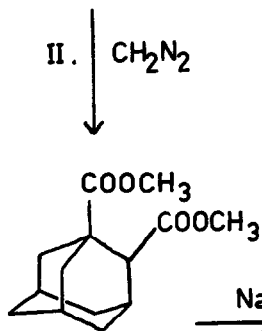
Satisfactory analytical and spectroscopic data were obtained for these new compounds, all dl-pairs. The mass spectra of III as well as IV show a strong peak at M⁺ = 133, pointing to the occurrence of the adamantene ion.



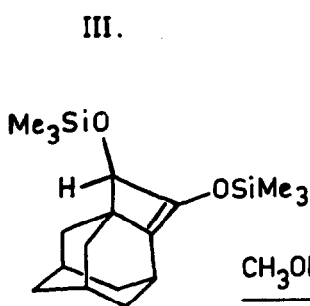
I. $\text{R} = \text{H}, \text{CH}_3$.



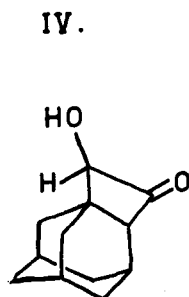
II. CH_2N_2



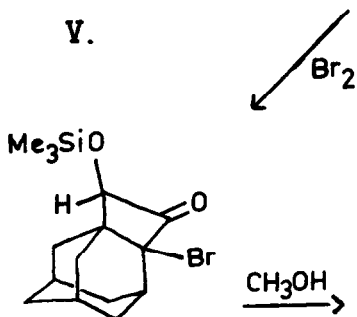
Na
 Me_3SiCl



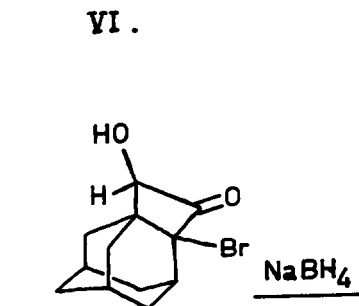
CH_3OH



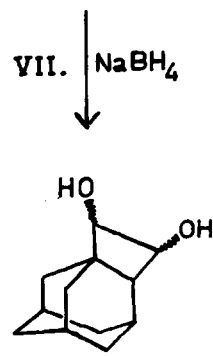
VII. NaBH_4



CH_3OH



NaBH_4



X.

VIII.

IX.

The acyloin condensation of the dimethyl ester V using dispersed sodium in boiling toluene (0.01M) in the presence of excess trimethylchlorosilane gave an unusual product. Instead of the expected disilylether we found the bond isomer VI⁴, 3,4-bis-[trimethylsilyloxy]-tetracyclo[5.3.1.1^{5.9}0^{1.4}]dodecene, b.p. 128-132°/0.8 mm in a yield of 50-60%. Upon addition of bromine in chloroform to the acyloin product VI one equivalent of trimethylbromosilane was eliminated. The intermediate VIII -not isolated- was treated with methanol giving rise to a crystalline solid, 3-oxo-2-hydroxy-4-bromotetracyclo[5.3.1.1^{5.9}0^{1.4}]dodecane (IX)⁵, m.p. 190-191°, purified by recrystallization from hexane/benzene, C₁₂H₁₅O₂Br, M⁺ = 272, in a yield of 65%. IR frequencies: C=C in VI at 1710 cm⁻¹, C=O in VIII and IX at 1780-1790 cm⁻¹. This reaction V — IX was first monitored by PMR spectroscopy. Compounds VI, VIII and IX show a multiplet of adamantyl protons at $\delta = 1.4-2.8$ with slight variation while the C₂ proton exhibited a sharp singlet at $\delta = 4.2$ in VI, $\delta = 5.3$ in VIII and $\delta = 5.5$ in IX. The hydroxyl proton in IX is situated at $\delta = 3.6$ (CCl₄) and rapidly exchanges with deuterium oxide. Further structural assignments were made on the basis of ¹³CMR spectroscopy of VI and VIII. The observed shifts were interpreted using the tables collected by Levy and Nelson⁶ and the results obtained by Lipman et.al. on adamantane compounds⁷. We then find

for VI: $\delta = 133.7$ and 130.4 (C₃ and C₄), $\delta = 83.8$ (C₂), $\delta = 43.9 - 32.3$ (9 peaks due to adamantane carbons), $\delta = 3.3$ (methylcarbons of the silyl ether).

for VIII: $\delta = 198.5$ (C₃), $\delta = 92.1$ (C₄), $\delta = 91.1$ (C₂), $\delta = 42.2 - 30.1$ (9 peaks due to adamantane carbons), $\delta = 3.0$ (methylcarbons of the silyl ether).

The mass spectrum of VI gives in addition to the M⁺ at 336 in its fragmentation pattern, a peak at 148 instead of at 133 indicating the 3,4-double bond position. The acyloin VII, m.p. 130-145°, a mixture of diastereoisomers, was obtained from VI by reaction with methanol. Reduction of IX with NaBH₄ produced the same diol mixture as was obtained from the acyloin VII. Oxidative cleavage (lead tetraacetate, followed by chromic acid) of X gave the diacid III, characterized as the diester V.

The formation of VI can be rationalized by assuming that the rigidity of the adamantane skeleton does not allow the C₂ and C₃ carbons to become sp² hybridized simultaneously. Isomerization of the double bond occurs to relief strain. Unsuccessful attempts to oxidize the acyloin VII to the 2,3-dione support this hypothesis. This is in full accord with the experiments of Turro⁸ and coworkers.

Properties and reactions of the new 1,2-adamantane derivatives are being studied at the moment.

Acknowledgements: We thank Dr. J. de Wit and Drs. J. Runsink for the C_{13} NMR experiments and Prof. P. von R. Schleyer and Dr. J. Lugtenburg for a helpful discussion.

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1. J.A. Peters, J.D. Remijnse, A. van de Wiele and H. Bekkum, Tetrahedron Letters 1971, 3065.
We thank Prof. Van Bekkum for extensive experimental details concerning the synthesis of I
2. Recently one of the dimers of adamantene, the accepted intermediate in the reaction of 1,2 diiodoamantane and butyllithium, was isolated.
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(b) D. Lenoir, Tetrahedron Letters, 1972, 4049.
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4. A concerted 1,3-hydrogen shift is not allowed according to molecular orbital theory (R.B. Woodward, R. Hoffmann, "The Conservation of Orbital Symmetry"). If this theory applies to this strained, fused system, the isomerization of the double bond may be caused by traces of acid.
5. The reaction product did not appear to be a mixture of diastereoisomers. One pure compound was isolated. On steric grounds we assume that this is the isomer having the hydroxylgroup trans to the bromine.
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