New Synthesis of Triamantane Involving a Novel Rearrangement of a Polycyclic Olefin in the Gas Phase on Platinum

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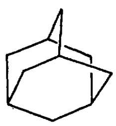
Summary Triamantane has been synthesised from diamantane-1-carboxylic acid, the key step involving multiple rearrangement of a polycyclic olefin in hydrogen in the gas phase on a platinum–silica catalyst.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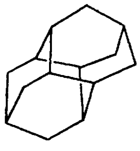
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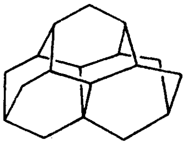
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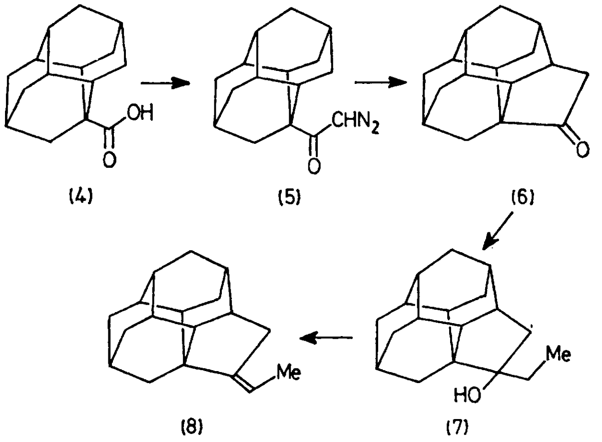

(4) (5) (6) (7) (8)

ADAMANTANE (**1**)[1] and diamantane (**2**),[2] the first two members of the regular diamondoid homologous series, are now readily accessible *via* aluminium halide-catalysed rearrangement of isomeric polycyclic hydrocarbons. The efficacy of this route depends on the selectivity of the rearrangement and on the availability of suitable precursors.[3] Although triamantane (**3**),[4] the third member of the series, has also been synthesised in this way, a three-step elaboration of cyclo-octatetraene is required to produce the isomeric precursor and the yield of the rearrangement step is very low, 2·0—5·2%. More elaborate precursors are required for higher members of the series; thus far none has been found.[3] We now propose an alternative synthetic approach to the larger diamondoid hydrocarbons. It involves the conversion of one member of the series into another and is illustrated here by a synthesis of triamantane from diamantane-1-carboxylic acid, involving in the key step an unusual rearrangement of an olefin in hydrogen in the gas phase on a supported platinum catalyst at elevated temperatures.

Diamantane-1-carboxylic acid (**4**)[5] was transformed into the acid chloride (oxalyl chloride in benzene at 20 °C) which with ethereal diazomethane furnished the crystalline diazo-ketone (**5**) in high yield. Slow addition of the diazo-ketone to a suspension of $CuSO_4$ in boiling toluene gave the cyclopentanone (**6**), 50%, m.p. 214—216 °C. Exposure of the ketone to EtMgBr produced the tertiary alcohol (**7**) (a mixture of epimers) and dehydration of this substance in boiling benzene containing iodine gave the crystalline olefin (**8**), m.p. 40—41 °C, in high yield. The catalyst for the final transformation was prepared by impregnating silica gel with $HPtCl_4$ (2% w/w in Pt) which was then reduced to the metal with hydrogen at 500 °C. When the olefin (**8**) was vapourised in a stream of hydrogen and passed through a horizontal bed of the catalyst at 430 °C a mixture of products was obtained, g.l.c. analysis of which revealed the presence of one major component and several minor components. Crystallisation of the mixture from acetone gave triamantane (**3**) 30%, m.p. 221 °C[4] with a premelting transition to a plastic crystal at 155 °C;† the spectral characteristics were in complete agreement with the published values.[4]

Although details of the mechanism are unknown, the overall change, involving expansion of the five-membered ring and transannular cyclisation of the methyl group on to a methylene group, is reminiscent of and was planned on the behaviour of simple n-alkanes under similar (catalytic reforming) conditions. n-Hexane, for example, is converted into a mixture of methylcyclopentane and cyclohexane with subsequent dehydrogenation of the latter to benzene.[6] With triamantane, however, the interlocking nature of the nucleus renders aromatisation less easy. The success of this route opens the way to larger diamondoid fragments.

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† Measured by differential scanning calorimetry by Dr. T. McO. Knox; for a general theory of plastic crystallinity in diamondoid hydrocarbons, see T. Clark, M. A. McKervey, H. Mackle, and J. J. Rooney, *J.C.S. Faraday I*, **1974**, **70**, 1279.

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[6] *Cf.* J. R. Anderson, *Adv. Catalysis*, 1973, **23**, 1.