Regioselective Functionalisation of Triamantane

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Summary The $C_{18}H_{24}$ diamondoid hydrocarbon triamantane reacts with bromine largely at the 2-position and with lead tetrabenzoate largely at the 3-position; 2-bromotriamantane can be isomerised to 9-bromotriamantane and the 9-methyl derivative can be obtained directly from a $C_{19}H_{26}$ precursor by aluminium chloride-catalysed rearrangement.

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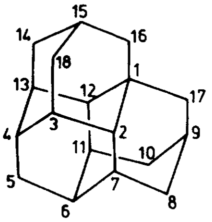
Triamantane (**1**), a $C_{18}H_{24}$ heptacyclic hydrocarbon of the diamondoid family, is now readily accessible from norbornadiene.[1] We have explored ways of functionalising the molecule using reactions which reveal large differences in reactivity at the various positions. Triamantane possesses four non-equivalent bridgehead positions, at carbon atoms 2, 3, 4, and 9, and three non-equivalent methylene positions, at carbon atoms 5, 8, and 17. For a saturated hydrocarbon composed exclusively of cyclohexane rings, triamantane is exceedingly reactive in substitution reactions, much more so than adamantane and diamantane under comparable conditions.[2]

Brief exposure (*ca.* 5—10 min) of triamantane to bromine at 0 °C led to complete conversion into a mixture of monobromides; longer times and/or higher temperatures produced dibromides. The monobromides were not analysed or isolated as such but were hydrolysed in hot aqueous dimethylformamide. Separation of the alcohols using the 'short column' chromatographic technique[3] furnished triamantan-2-ol (**2**) (73%), m.p. 293—294 °C, triamantan-3-ol (**3**) (23%), m.p. 247—248 °C, triamantan-9-ol (**4**) (*ca.* 3%), m.p. 173—174 °C, and a trace of impure triamantan-4-ol (**5**) (*ca.* 1%). The alcohols were individually converted into bromides with hot hydrobromic acid. Differences in internal symmetry facilitated analysis of the ^{13}C n.m.r. spectra of the two sets of isomers, leading unequivocally to the structural assignments.

Bridgehead bromination of diamondoid hydrocarbons is thought to proceed *via* electrophilic attack at a C–H bond with the intermediate formation of carbocations.[2] The product distribution observed with triamantane suggests that the 2-position forms the most stable cation and the 4- and 9-positions the least stable cations. The relative stabilities of these cations may depend on differences in inductive and hyperconjugative effects arising from the degree of chain branching at the β-carbon atoms of each cation.[4] Diamantane brominates at the 1-position rather than at the 4-position;[4] the 1-diamantyl cation has two β-branches while the 4-cation has none. In triamantane, the 2-cation has three β-branches, the 9-cation has none, and the 3- and 4-cations have two each; qualitatively, bromination favours the 2-position.‡ Although the 3- and 4-cations have the same degree of β-branching, the 3-position is favoured statistically by a factor of two. Nevertheless, the 4-position appears to be unusually unreactive.

The topology of triamantane is such that a substituent at the 2-position has four unfavourable 1,3-interactions with *syn* axial hydrogen atoms while a 3- or 4-substituent has only two such interactions, and a 9-substituent, the least encumbered, has none. Accordingly, although bromination shows a kinetic preference for the 2-position, 2-bromotriamantane should be the least stable of the tertiary isomers. Treatment of the 2-bromide with $AlBr_3$ in CH_2Br_2 resulted in isomerisation–disproportionation, giving triamantane and equal amounts of the 9-bromide and a mixture of the 3- and 4-bromides. Similarly, when the 2-alcohol was dissolved in H_2SO_4–$MeCO_2H$ (2:3) at 50 °C triamantane and the 9-alcohol were the major products.



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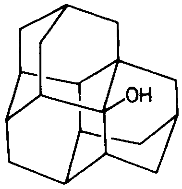

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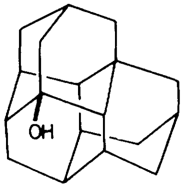

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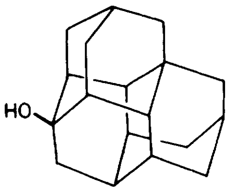

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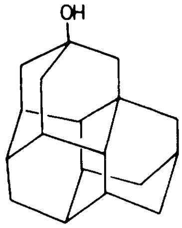

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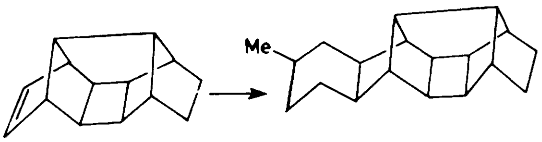

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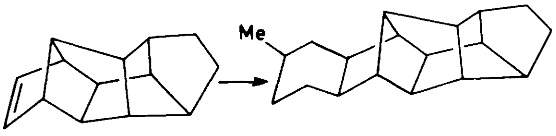

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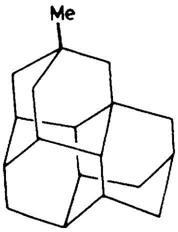

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Thermodynamic control was also observed in the $AlBr_3$-catalysed rearrangement of the polycycles (**6**) and (**7**). These precursors, prepared from the olefins (**8**) and (**9**),[1] respectively, and isoprene, with subsequent hydrogenation, gave 9-methyltriamantane (**10**) as the major rearrangement product. These isomerisations provide the most convenient route to 9-substituted derivatives.

Selective attack at the 3-position was achieved with $Pb(OAc)_4$ in acetic acid but the reaction was complicated by further functionalisation of the initially formed acetates.§

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‡ In superacid media triamantane gives the 2-triamantyl cation exclusively; unpublished results of G. A. Olah.

§ The functionalisation of adamantane and diamantane with $Pb(OAc)_4$ has been described by S. R. Jones and J. M. Mellor, *J.C.S. Perkin I*, 1976, 2576, who found that the addition of CF_3CO_2H prevented further reaction. The use of $Pb(OAc)_4$ for functionalising diamondoid hydrocarbons has also been studied by Schleyer and his co-workers; personal communication.

This problem was overcome using Pb(OCOPh)$_4$ in molten benzoic acid as solvent under which conditions triamantane gave, after saponification of the benzoates, the 3-alcohol (**3**) as the major product; minor amounts of the other isomers were also obtained, the 2-isomer being the least abundant. Recent work suggests that the mechanism of oxidation of saturated hydrocarbons with Pb^{IV} salts involves electrophilic attack at a C–H bond.[5] With triamantane, however, there is clearly a substantial difference in detail between attack on a C–H bond by bromine and by Pb^{IV}. In particular, the low reactivity of the 2-position in the latter reaction may reflect the relative inaccessibility of the C-H bond and the rather bulky nature of the reagent.

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[1] R. Hamilton, M. A. McKervey, J. J. Rooney, and J. F. Malone, *J.C.S. Chem. Comm.*, 1976, 1027; for earlier less efficient syntheses of triamantane see V. Z. Williams, jun., P. von R. Schleyer, G. J. Gleicher, and L. B. Rodewald, *J. Amer. Chem. Soc.*, 1966, **88**, 2862, and W. Burns, M. A. McKervey, and J. J. Rooney, *J.C.S. Chem. Comm.*, 1975, 965.

[2] For a discussion of bridgehead reactivity in adamantane and diamantane see R. C. Fort, jun., 'Adamantane, The Chemistry of Diomondoid Molecules,' Marcel Dekker, New York, 1976.

[3] B. J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 4.

[4] T. M. Gund, P. von R. Schleyer, G. D. Unruh, and G. J. Gleicher, *J. Org. Chem.*, 1974, **39**, 2995.

[5] S. R. Jones and J. M. Mellor, *J.C.S. Perkin II*, 1977, 511.