

The Resolution of 3-Methyl-5-bromoadamantanecarboxylic Acid

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Summary The preparation of a novel chiral adamantane and its conversion into an optically active bicyclo[3,3,1]nonane derivative are described.

A DERIVATIVE of adamantane, *e.g.* (I), in which the four bridgehead positions are substituted each with a different group has been used¹ to illustrate models of chemical topology. One can visualise such a molecule as a formal analogue of lactic acid (II) in which the centre of chirality (denoted by the dot) lies at the 'unoccupied' centre of the adamantane nucleus. We report here the first resolution of a substituted adamantane of this type.

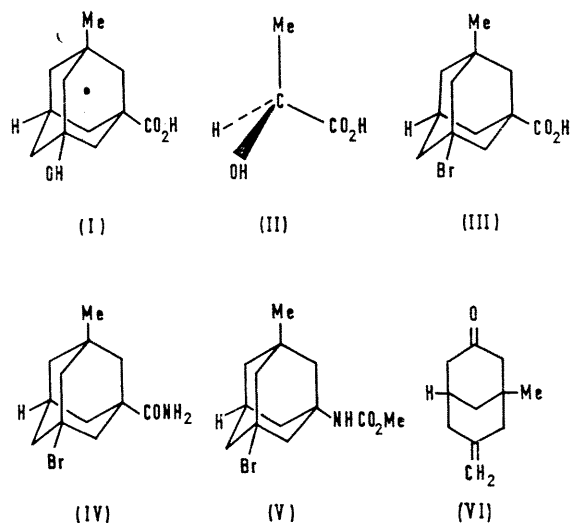
3-Methyl-5-bromoadamantanecarboxylic acid (III), prepared by aluminium bromide-catalysed bromination of

3-methyladamantanecarboxylic acid² at 0°, was treated with dehydroabietylamine³ in aqueous methanol. After 24 hr., the crystalline dehydroabietylammmonium salt was isolated and fractionally crystallised from ethanol affording material, m.p. 140.5–141°, $[\alpha]_D^{23} + 18.9^\circ$. Decomposition of this salt with sodium hydroxide in water–ether gave, after acidification, the crystalline bromoacid (III), m.p. 128–130°, which had an immeasurably small optical rotation at the sodium D-line. Nevertheless, it was possible to show that resolution had occurred to a measurable extent. The bromoacid was transformed by conventional reactions, *via* the bromoamide (IV), m.p. 111–112°, into the bromo-urethane (V), m.p. 112–113°. This latter compound, on treatment with sodium hydroxide in boiling water, underwent a fragmentation reaction of the type described by Stetter and Tacke⁴ giving optically active 1-methyl-7-methylenebicyclo[3,3,1]nonan-3-one (VI), b.p. 118–119°/8.5 mm., $[\alpha]_D^{23} - 10.4^\circ$ (48% yield from III). This structural assignment is based on the i.r. spectrum of (VI) which showed significant absorptions at 3070, 1720, 1660, and 890 cm^{-1} , and on the n.m.r. spectrum (CDCl_3): τ 8.96 (s, 3H, CH_3), 5.23 (s, 2H, vinylic), 8.27 (s, 2H, 9-H), and the remaining protons 7.7, unresolved.

The fact that (VI) was obtained in optically active form clearly establishes that the bromoacid (III) obtained from the dehydroabietylammmonium salt contained a preponderance of one of the enantiomers although the optical purity is not yet known. Hydrolysis of resolved (III) with hot aqueous sodium hydroxide gave 3-methyl-5-hydroxyadamantanecarboxylic acid (I), m.p. 163–164°, which was also optically inactive at the sodium D-line.

Experiments designed to reveal the absolute configurations of this new series of compounds are in progress.

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¹ V. Prelog, Robert Robinson Lecture, 1968, delivered before The Chemical Society, The Institute of Chemistry of Ireland, and The Royal Institute of Chemistry in Dublin on 3 April 1968; *cf. Chem. in Britain*, 1968, 4, 382; see also R. C. Fort, jun. and P. von R. Schleyer, *Chem. Rev.*, 1964, 277.

² H. Koch and J. Franken, *Chem. Ber.*, 1963, 96, 213.

³ W. J. Gottstein and L. C. Cheney, *J. Org. Chem.*, 1965, 30, 2070.

⁴ H. Stetter and P. Tacke, *Angew. Chem.*, 1962, 74, 354; H. Stetter and P. Tacke, *Chem. Ber.*, 1963, 96, 694.