# The Protoadamantane Route to 1,2- and 2,4-Disubstituted Adamantanes

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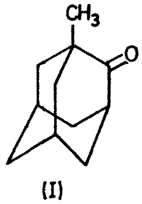
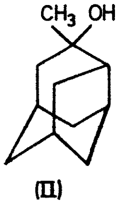
*Summary* Reaction sequences leading to 1,2- and 2,4-disubstituted adamantanes are described, the key step in each case involving a protoadamantane–adamantane rearrangement.

Protoadamantane (tricyclo[4,3,1,$0^{3,8}$]decane) and adamantane[1] are interconvertible *via* a single 1,2-alkyl shift and the strained protoadamantyl system can be isomerised to the more stable adamantyl system by aluminium bromide catalysis.[2] This change also occurs quantitatively on a 2% palladium–silica catalyst.[3] Earlier studies have demonstrated the efficacy of the $\pi$-route for the preparation of a variety of 2,4-disubstituted adamantanes.[4] We now report that the protoadamantane route is also readily adaptable to the synthesis of both 1,2- and 2,4-disubstituted adamantanes.[5]

Prior to the development of this method we relied on intramolecular insertion[6] and direct substitution reactions[7] to obtain 1,2-disubstituted adamantanes. For example oxidative rearrangement of either 2-methyl-2-adamantanol or 3-methyl-1-adamantanol or direct oxidation of 1-methyladamantane with 96% sulphuric acid gave 1-methyl-2-adamantanone (I) in < 5% yield.[7] This ketone has now been obtained in 82% yield by simply treating a mixture of the readily available 4-*endo*-methyl- and 4-*exo*-methyl-4-protoadamantanols (II)[2] with chromic acid in acetone.

The remarkable ease of the protoadamantane-adamantane rearrangement is illustrated by the reaction of 4-protoadamantanone (III)[8] with $PCl_5/PCl_3$ mixtures or with $PCl_5$ alone in carbon tetrachloride. These reagent combinations, customarily used for the conversion of ketones into *gem*-dichlorides,[9] afforded, instead of 4,4-dichloroprotoadamantane, a 1 : 1 mixture, separable by chromatography on silica gel, of 4-chloroprotoadamantene (IV) and 1,2-dichloroadamantane (V). Catalytic hydrogenation of the less polar component (IV) gave protoadamantane as the sole product and the assigned structure follows from the physical data: i.r. (film) 3060, 1640, and 825 cm$^{-1}$; 100 MHz n.m.r. ($CDCl_3$) $\tau$ 3·85 (m, 1H, C-5), 7·34 (m, 2H, C-3 and C-6), and 7·50—8·50 (m, 10H, skeletal); *m*/*e* ($M^+$) 168. The dichloride, m.p. 178—180° (dec.), was assigned structure (V) since hydrogenolytic dechlorination on palladium gave adamantane, the n.m.r. spectrum ($CDCl_3$) displayed a signal at $\tau$ 5·65 for the proton on C-2, and attempted hydrolysis with silver sulphate in 50% sulphuric acid regenerated 4-protoadamantanone (III) admixed with adamantanone. A mechanism for the formation of (V) is indicated by the arrows in (VI).


(I)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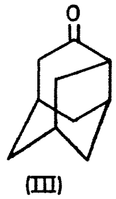
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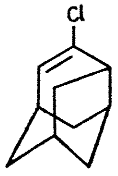
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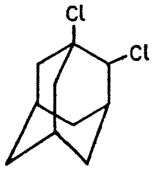
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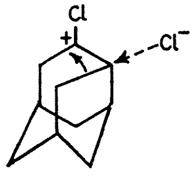
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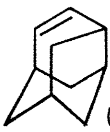
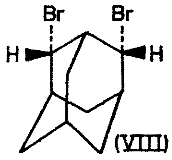
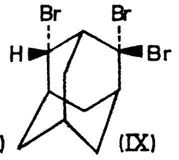
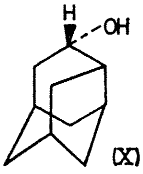

(VII)


(VIII)


(IX)


(X)

The route to 2,4-disubstituted derivatives is exemplified by the reaction of protoadamantene (VII)[8,10] with bromine in carbon tetrachloride. The product was a 3 : 2 mixture, separable by chromatography on silica gel, of the diaxial 2,4-dibromide (VIII), m.p. 171—172°, and the axial–equatorial dibromide (IX). Hydrogenolytic debromination of the mixture gave adamantane and the minor dibromide (IX) was identified by comparison (m.p. and n.m.r.) with one of the two dibromides produced in the bromination of 2,4-dehydroadamantane;[11] the *diaxial* isomer (VIII) is not formed in this reaction but the n.m.r. spectrum agrees closely with the calculated spectrum.[12]

In view of these extremely ready rearrangements it was of particular interest to examine the oxymercuration–demercuration of protoadamantene since the failure to observe either significant amounts of rearrangement or scrambling in the oxymercuration–demercuration of norbornene and related compounds has been associated by Brown[13] with the nonclassical ion question. However, even in this testing case, the reaction gave only a trace amount of rearrangement. Sequential treatment of (VII) with mercuric acetate and sodium borohydride gave a product containing predominantly *exo*-4-protoadamantanol (X). To facilitate closer examination the product was oxidised, yielding 4-protoadamantanone (III) (98%), an unidentified compound (1%), and adamantanone (1%).

We thank the Northern Ireland Ministry of Education for a postgraduate grant to B.D.C.

(*Received, November 9th*, 1970; *Com.* 1939.)

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