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ON THE BROMINATION OF 1-BROMO-1-(ADAMANTYL-1)ETHANE

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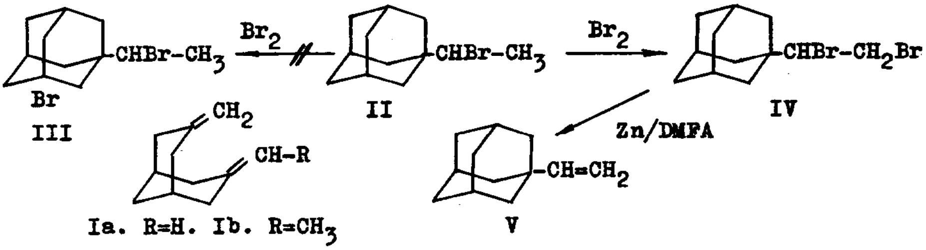
In our previous paper (1) we have reported debromination conditions for 1-bromo-3-bromomethyladamantane accompanied by fragmentation of the adamantane nucleus and formation of 3,7-dimethylenebicyclo [3,3.1] nonane (1a). The next homolog of 1a, 3-methylene-7-ethylidenebicyclo [3.3.1] nonane (1b), we have intended to synthesise by the similar sequence of reactions.



The starting 1-hydroxy-1-(adamantyl-1)ethane (2) under heating in a sealed tube with saturated solution of hydrogen bromide in glacial acetic acid forms 1-bromo-1-(adamantyl-1)ethane II [yield,57%; b.p.133-134°/5 mm; δ1,63(3H, methyl, doublet, J=7 cps), δ1,64 (12H, methylene, partially resolved doublet, J=2,5 cps), δ2,00 (3H, bridgehead, broad singlet), δ3,83(1H, quartet, J=7 cps)].

Quite unexpectedly the bromination of the bromide II with bromine without solvent (2 hours, 100°) instead of 1-bromo-1-(3-bromoadamantyl-1)ethane (III) yielded1,2-dibromo-1-(adamantyl-1)ethane (IV) [yield, 84%; m.p. 61-62°; δ1,70 (12H, partially resolved doublet, J= 2,5 cps), δ2,05 (3H, bridgehead, broad singlet), δ3,20-4,15 (3H, side chain ABC system)].

The structure of dibromide IV was supported by its conversion into 1-vinyladamantane V under debromination by zinc dust in boiling dimethylformamide. The olefin V [yield, 84%; b.p. 66-67°/4mm; δ 1,57 (6H, triplet, J=2,5 cps), δ 1,71 (6H, doublet, J=2,5 cps), δ 1,98 (3H, bridgehead, broad singlet), δ 4,80 (2H, methylene) AB and δ 5,65 (1H, methine) C parts of ABC system, J_{AB}=2,1 cps, J_{AC}=10,1 cps, J_{BC}=18,3 cps] was identical with authentic sample (3) and after addition of two bromine atoms at room temperature in CCl_4 gave dibromide IV.

The bromination of the compound II into the methyl group is unique enough, especially in the presence of three bridgehead hydrogens, capable to be substituted for bromine in the same conditions. The presence of the bromine atom in the α-position of the substituent does not prevent the bromination of the adamantane nucleus, 1-bromomethyladamantane being the example of this (4). We consider it possible to explain such an unusual bromination pathway by the following. The bromine atom was split off with bromine molecule as the known Br_3^- anion, and carbonium ion thus formed simultaneously lost the proton in β-position. The addition of bromine molecule to the double bond gave the dibromide IV. The formation of complex mixture of polybromides, possibly containing bridgehead bromines also, under the prolonged refluxing of II with bromine should be noted, though this ought to be subjected to further studies (5).

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4. F.N.Stepanov, V.F.Baklan, S.D.Isaev, Zhur.Org.Khim.(USSR),**1**,280(1965).
5. All new compounds gave satisfactory elemental analyses. NMR spectra were taken on the Varian A-60A spectrometer in CCl_4 solutions with TMS as internal standard.