Brominolysis of Bridgehead-substituted Adamantane Derivatives

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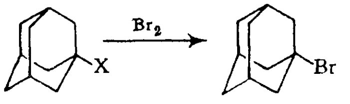
BECAUSE of recent interest shown in bridgehead reactivity[1] we report our finding of a simple technique for the displacement of bridgehead substituents on the adamantane skeleton.

1-Fluoroadamantane (I)[2] was dissolved in anhydrous bromine and heated under reflux for four hours. A standard work-up procedure[3] gave 1-bromoadamantane (V)[3] (80—90%) as the only isolable product.[†] Similar yields were obtained simply by stirring the solution at room temperature overnight. Identical results were also obtained when untreated reagent-grade bromine was used directly with no special drying procedure.



(I) X=F
(II) X=Cl
(III) X=OH
(IV) X=H

(V)

Similar treatment of (II), (III), and (IV)[3] also produced high yields of (V).[†] Several compounds containing nitrogen attached to the bridgehead reacted vigorously to give unidentified products. No brominolysis of the bridgehead substituent was observed for X = CN, CO_2H, Me,[3] or p-$NO_2C_6H_4$.[4]

Other workers have accomplished displacement of groups at the adamantyl bridgehead but, in general, these reactions require either exotic reagents not commonly available[5] or unusually drastic conditions and equipment.[1b]

It has been demonstrated that in solutions of

[†] The product was identified by comparison of its n.m.r. spectrum and v.p.c. behaviour with that of authentic 1-bromoadamantane.[2,3]

(I) or (II) in SbF_5–SO_2, a potent Lewis acid solvent, the bridgehead substituent departs with the bonding pair of electrons, thus generating a carbonium ion,[5] and we suggest a similar explanation for our results since bromine is known to act as a formal Lewis acid in olefin brominations and on reaction with nucleophiles.

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