The Isolation of a Stabilized Bromonium Ion

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Summary A reasonably stable bromonium bromide (II) is formed when a solution of adamantylideneadamantane (I) in carbon tetrachloride is treated with bromine in carbon tetrachloride.

WE report that a reasonably stable yellowish solid (II) is obtained when a solution of adamantylideneadamantane m.p. 181—182° (I)† in carbon tetrachloride is treated with bromine in the same solvent at room temperature (slightly more than two molecules of bromine are used). Attempts to recrystallize this material (II) from polar solvents (acetone, Me_2SO) resulted in recovery only of starting material (I) and the reappearance of molecular bromine.

When the new substance (II) was stirred for about 5 min.

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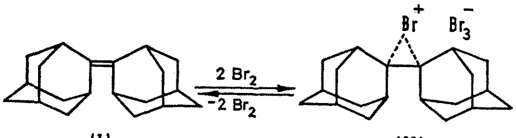
† We thank Mr. H. W. Geluk and Drs. J. G. Korsloot of Philips-Duphar, Weesp, Holland, for a gift of adamantylideneadamantane. Its preparation and chemistry will be the subject of a joint publication shortly.

with carbon tetrachloride and potassium iodide solution at 40° the quantity of bromine liberated was 94·5%, as determined by titration of the iodine formed. Furthermore, 94% of adamantylideneadamantane (I) could be isolated. The yellowish solid (II), washed with hexane and subsequently with ether was obtained in a yield of 96%. It has the composition $C_{20}H_{28}Br_4$ as shown by microanalysis (carried out 6 hr. after the preparation). The insolubility‡ of the compound in carbon tetrachloride, hexane, and ether strongly indicates that the product is a salt. This is supported by the mass spectrum of the solid (II) which shows a strong peak at *m/e* 268. The molecular weight of the starting material (I) is 268. In addition intense peaks of Br^+ (79, 81; doublet (1 : 1) and Br_2^+ (158, 160, 162; triplet 1 : 2 : 1) are observed.



(I) (II)

These observations point to the conclusions:

(1) The empirical formula of the new compound must be $C_{20}H_{28}Br_4$.

(2) The bond which connects the two adamantane skeletons has remained intact.

(3) The bromine atoms present in the molecule are not covalently bound. A bromine substitution product can be excluded (value of *m/e*; *no* absorption in the i.r. spectrum indicating a C–Br bond; reversibility of the reaction under mild conditions).

We suggest that the reasonably stable solid (II) is in fact the first example of a bromonium bromide whose existence in electrophilic bromine addition reactions has until now been to our knowledge a mere postulate.[1]

(*Received, June 23rd*, 1969; *Com.* 905.)

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‡ This insolubility is the reason that no n.m.r. and u.v. spectra could be obtained.

[1] *cf.* J. Hine, "Physical Organic Chemistry," 2nd Edn., 1962, McGraw-Hill Inc., p. 217.