Four-membered Ring Bromonium Ions

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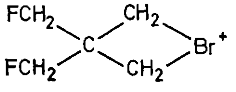
Summary Dissolution of 1-bromo-3-fluoro-2,2-bis(fluoromethyl)propane (I) in antimony pentafluoride-sulphuryl chloride fluoride solution yields a stable, four-membered ring bromonium ion.

The generation, identification, and stability of four-membered ring halogenonium ions is of theoretical interest.[1] The intermediacy of four-membered ring bromonium ions in deamination[2] and solvolysis[3] reactions of halogenated neopentyl derivatives has been deduced. We report the direct observation of four-membered ring bromonium ions by examination of the low-temperature n.m.r. behaviour and of the products derived from ionization of the propane derivatives (I)—(III).

Dissolution of compound (I) in SbF_5–SO_2ClF yields a pale yellow solution which becomes dark and decomposes when heated above $-50°$. The ^1H n.m.r. spectrum at $-55°$, relative to internal Me_4NBF_4 at δ 3·10, consists of a singlet at δ 5·28 and a doublet at δ 4·68 (J_{HF} 47 Hz, CH_2F). The downfield shift of the bromomethyl absorption of compound (I) in SbF_5–SO_2ClF, δ 5·28 *vs.* 3·49 (CCl_4), indicates significant positive charge formation. This chemical shift is consistent with methylene absorptions at δ 5·5 and 5·2 in three- and five-membered ring bromonium ions[4] respectively. The two absorptions at δ 5·28 and 4·68 are of equal intensity and have line widths of 2·5 Hz that are broadened only slightly upon cooling of the solution to −96°. These spectra are consistent with four-membered ring bromonium ion (V), in which the fluorine atoms do not participate in the delocalization of the positive charge. Quenching of the solution at −78° in MeOH–K_2CO_3 gave as the major product the methyl ether (VI) (54%), δ ($CDCl_3$) 4·51 (4H, d, J_{HF} 46 Hz, CH_2F), 3·45 (4H, m, CH_2Br + CH_2OMe), and 3·36 (3H, s, OMe).

$R^1CH_2{\cdot}C(CH_2R^2)_2CH_2Br$

(I) $R^1 = R^2 = F$
(II) $R^1 = R^2 = Br$
(III) $R^1 = F$, $R^2 = Br$
(IV) $R^1 = OMe$, $R^2 = Br$


(V)

$BrCH_2C(CH_2F)_2CH_2{\cdot}OMe$

(VI)

Quenching of solutions of the analogous compounds (II) or (III) in SbF_5–SO_2ClF at −78° yielded the propane (IV) (60%). The ^1H n.m.r. spectra of these solutions show a single absorption at δ 5·17. The line width of this absorption varies reversibly with temperature. This observation suggests that all three bromine atoms can participate in delocalization of the positive charge.

The absence of starting material in the products from ionization of compounds (I)—(III) and their low concentrations in SbF_5 (0·1—0·2 M) argue against a linear dialkylhalogenonium ion.[5] The formation of the four-membered ring bromonium ion (V) probably reflects the unfavourable energetic alternatives such as halogenomethyl rearrangement or hydride transfer in these halogenated neopentyl derivatives.

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[1] G. A. Olah, J. M. Bollinger, Y. K. Mo, and J. M. Brinich, *J. Amer. Chem. Soc.*, 1972, **94**, 1164; J. W. Larsen and A. V. Metzner, *ibid.*, p. 1614.

[2] C. E. Reineke and J. R. McCarthy, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 6376.

[3] J. H. Exner, L. D. Kershner, and E. R. Larsen, *Chem. Comm.*, 1971, 1174.

[4] G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, 1968, **90**, 2587; G. A. Olah and P. E. Peterson, *ibid.*, p. 4675.

[5] G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, 1969, **91**, 2113.