Solvolysis of Brominated Neopentyl Derivatives in Super Acid: the Formation of Fluorosulphates

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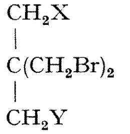
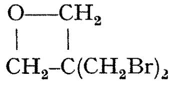
Summary The solvolysis of brominated neopentyl derivatives in antimony pentafluoride–fluorosulphonic acid–sulphur dioxide forms unrearranged fluorosulphate esters

THE extremely strong but weakly nucleophilic acid system, antimony pentafluoride–fluorosulphonic acid–sulphur dioxide† is commonly used to generate stable carbonium ions at low temperatures We now report that in this solvent system neopentyl derivatives (I), (IIa), (IIIa), and (IV) form fluorosulphate esters without the rearrangement commonly observed in neopentyl compounds [1,2]



CH_2X–$C(CH_2Br)_2$–CH_2Y



(IV)

(I) $X = Y = Br$
(IIa) $X = Br$ $Y = OH$
(IIb) $X = Br$, $Y = OSO_2F$
(IIIa) $X = Y = OH$
(IIIb) $X = Y = OSO_2F$
(IIIc) $X = OH$, $Y = OSO_2F$

The solvolyses were carried out by dissolving the compounds in the acid at −78° Temperatures at which reactions occurred were established by observing the temperature variation of the n m r spectra Quenching at −78° in methanol–potassium carbonate slurries allowed the isolation of products which were consistent with the n m r spectrum prior to quenching These products were identified by n m r , i r , mass spectrometry, and elemental analyses

Reaction conditions and products are summarized in the Table These brominated neopentyl derivatives, like the neopentyl glycol system,[3] are more stable in this solvent than neopentyl alcohol which readily dehydrates to the t-pentyl cation at −50° [2] Solvolysis occurs most readily with 2,2-bis(bromomethyl)-1,3-dibromopropane (I) with successive formation of 3-bromo-2,2 bis(bromomethyl)propanol fluorosulphate (IIb), 2,2-bis(bromomethyl)propane-1,3-diol difluorosulphate (IIIb), and 2-(bromomethyl)-2-(hydroxymethyl)propane-1,3-diol trifluorosulphate (V) Formation of trifluorosulphate is indicated in the n m r by

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† This acid system is composed of 1 ml of equimolar SbF_5–FSO_3H and 3 ml of liquid sulphur dioxide

TABLE

Solvolysis of neopentyl derivatives in SbF_5–FSO_3H–SO_2

	Conditions			Composition of products					
Reactant	Time	Temp.	% Yield	(IIa)	(IIb)	(IIIa)	(IIIb)	(IIIc)	(V)
$(BrCH_2)_4C$	5 min	−10 to −30°[a]	85	—	6	—	82	—	13
	5 h	−30°	71	—	3	—	41	—	56
$(BrCH_2)_3CCH_2OH$	20 h 45 min	at −30°, plus at −12°	70	24	5	—	8	56	6
(IV)	8 h	−12°	90	—	—	—	2	98	—
$(BrCH_2)_2C(CH_2OH)_2$	22 h	−12°	77	—	—	39	1	60	—

[a] Temperature required to effect solution.

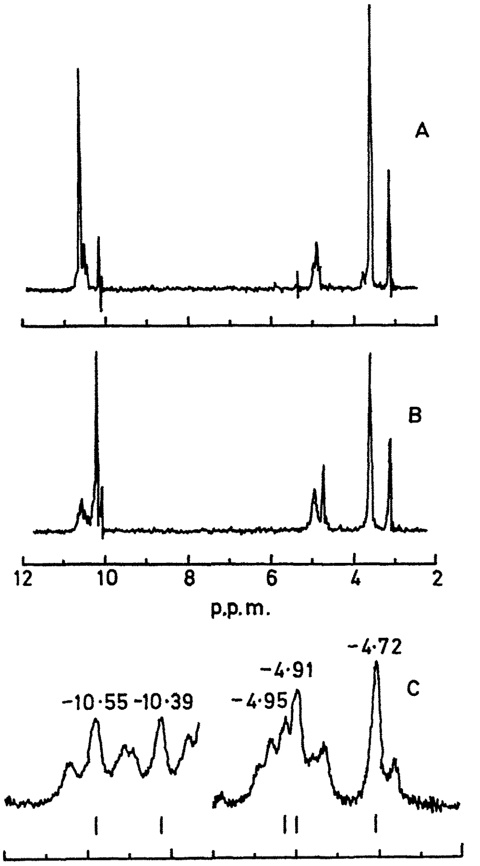

FIGURE. *N.m.r. spectra of compound* (IIa) *in* SbF_5–FSO_3H–SO_2: A. *at* −50°; B. *after* 100 *min. at* −15°; C. *Detail of figure B at* 100 *Hz sweep width.*

two singlets at δ 4·69 (CH_2OSO_2F) and 3·57 p.p.m. (CH_2Br). Compounds (IIa), (IIIa), and (IV), [3-bromo-2,2-bis(bromomethyl)propanol, 2,2-bis(bromomethyl)propane-1,3-diol, and 3,3-bis(bromomethyl)oxetan, respectively] exist in their protonated forms at low temperatures. Upon raising the temperature, the major isolable product from solvolysis of these three compounds is 2,2-bis(bromomethyl)propane-1,3-diol fluorosulphate (IIIc). For example, the Figure shows the change in the n.m.r. spectrum from the protonated alcohol at −50° with absorptions at δ 3·56 (s, 6, CH_2Br), 4·91 (t, 2, *J* 3·9 Hz, CH_2O), and 10·48 p.p.m. (t, 2, *J* 3·9 Hz, OH_2^+) to the spectrum at −15° which is consistent with the appearance of the protonated form of compound (IIIc) with absorptions at δ 3·57 (s, CH_2Br), 4·72 (s, CH_2OSO_2F), 4·95 (t, *J* 3·9 Hz, $CH_2OH_2^+$), and 10·55 p.p.m. (t, *J* 3·9 Hz, $CH_2OH_2^+$).

Formation of these fluorosulphates *via* an S_N2 displacement at these low temperatures seems unlikely in view of the slowness of these reactions in neopentyl systems.[1] Even neopentyl compounds with much better leaving groups[4] than bromine or protonated hydroxy require much stronger nucleophiles than fluorosulphonic acid in super acid. The tetrabrominated neopentane (I) is stable at 100° in water. The relative ease of formation of (IIIc) from the oxetan allows the protonated oxetonium ion as the solvolysis intermediate for both alcohols (IIa) and (IIIa). Similarly, we postulate a 1,3-bromonium ion intermediate, recently demonstrated in this system,[5] in the formation of the unrearranged fluorosulphonates from (I).

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