

Short Communication

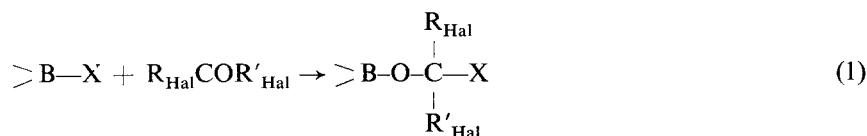
Some new polyhalogenoketones and the temperature variable NMR spectrum of 1-dimethylamino-1,1,3-trichloro-3,3-difluoroacetone

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The interaction of perhalogenoketones and boron halides has been extensively investigated¹⁻⁵ and has been shown to be a good route to perhalogenoborate esters.



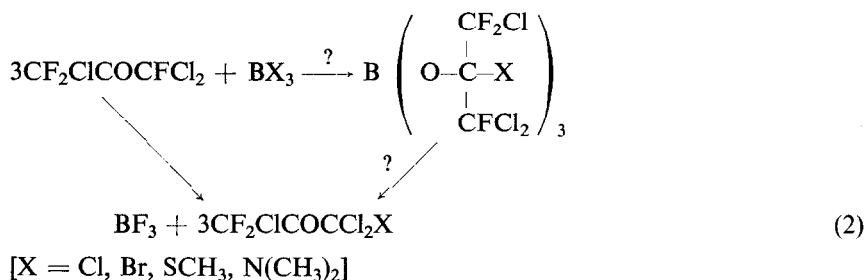
Such perhalogenoborate esters are often otherwise inaccessible due to the non-availability of the corresponding alcohol, which would be the conventional precursor^{6,7}.

In an investigation of the interaction of the fluorochloroacetones with boron halides we reported the synthesis of a wide range of perhalogenoborate esters⁵.

For one of these ketones, however, the reaction was anomalous, and no perhalogenoborate esters could be isolated. It was decided to investigate this failure of borate formation more fully.

Results and discussion

When 1,1,3-trichloro-1,3,3-trifluoroacetone reacted with boron halides and with alkylthio- and dialkylamino-borons, boron trifluoride was invariably formed, along with the corresponding ketone. It is possible that the reaction did proceed through the conventional insertion reaction to form a perhalogenoborate ester, which underwent decomposition by the elimination of boron trifluoride. Such a scheme is outlined in equation (2), but it must be noted that at no stage was the proposed intermediary borate observed. Thus it is also possible that the boron trifluoride is formed by a direct metathesis between the ketone and the boron compound.



All of the other fluorochloroketones studied formed stable borate esters, which were not decomposed even upon heating. It would therefore appear that this particular activity is associated with the unique fluorine atom in 1,1,3-trichloro-1,3,3-trifluoroacetone.

Recent studies of the action of aluminium halides upon polyhalogenoketones have also resulted in the formation of some new polyhalogenoketones by halogen exchange⁸. In these reactions, however, a range of ketones appears capable of halogen exchange, unlike the uniqueness of 1,1,3-trichloro-1,3,3-trifluoroacetone in our reaction.

The four ketones isolated from our reactions are characterised in Table 1.

Of particular interest is the product 1-dimethylamino-1,1,3-trichloro-3,3-difluoroacetone, [(CH₃)₂N]Cl₂CCOCF₂Cl. In a routine measurement of the proton magnetic resonance spectrum of this compound, the two methyl groups were found to be non-equivalent. The spectrum, however, was temperature-dependant and at 120° the two methyl resonances had completely coalesced. The details of the temperature variation are illustrated in Figure 1, and the spectra are reproducible through heating and cooling cycles.

At 40°, one of the two methyl resonances is a sharp singlet but the other is a triplet. After heating to 100°, the coalescence appears to be to a singlet, but on further heating to 120° the spectrum sharpens to what appears to be a triplet, but with a very small splitting of only about one half of that of the triplet at 40°.

Construction of a model of [(CH₃)₂N]Cl₂CCOCF₂Cl shows the molecule to be very sterically hindered and Figure 2 illustrates the configuration most favoured from considerations of the model. Rotation about the (CH₃)₂N-C bond is extremely hindered and herein probably lies the cause of the non-equivalence of the two methyl groups. One methyl group CH₃^(A) fits closely between the two fluorine atoms and the other methyl group CH₃^(B) fits closely between the two chlorine atoms.

One of the methyl groups is obviously coupling with the two fluorine atoms of the CF₂Cl group, but it is difficult to assign the triplet of the 40° ¹H NMR spectrum categorically to either CH₃^(A) or CH₃^(B). If the origin of the coupling is "through space", it is probable that the protons of CH₃^(A) are those coupled to the CF₂Cl group. If, however, from the model one methyl group is selected as a

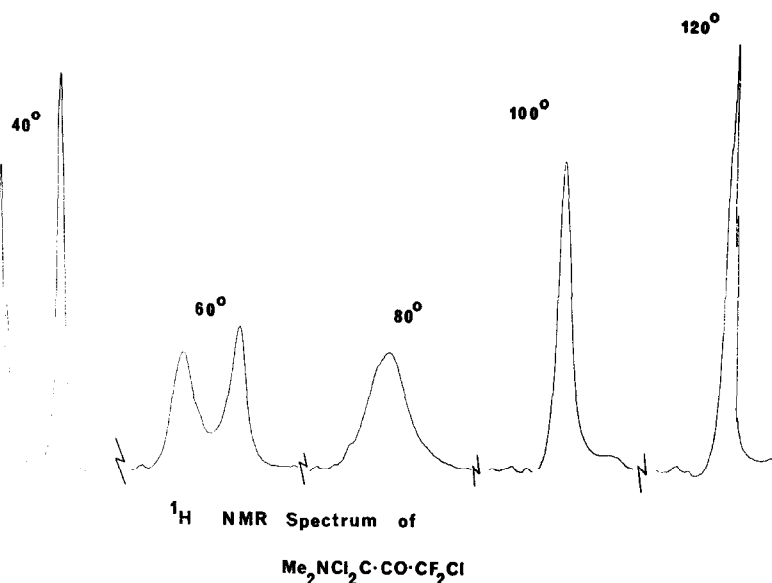


Fig. 1. Illustrating the temperature variation of the ^1H NMR spectrum of $(\text{CH}_3)_2\text{NCl}_2\text{CCOCF}_2\text{Cl}$.

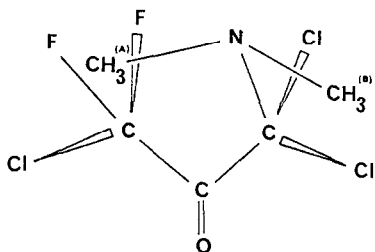


Fig. 2. Illustration of the different environments of the two methyl groups in $(\text{CH}_3)_2\text{NCl}_2\text{CCO-CF}_2\text{Cl}$.

result of suitable vicinal angles for "through-bond" coupling, then it is likely that it is the $\text{CH}_3^{(B)}$ protons that are coupled to CF_2Cl .

Presumably at increased temperatures rotation about the C-N bond takes place to equate the methyl environments. Thus at 120° , we see the averaged ^{19}F coupling, be it "through space" or "through bond", at only one half of that of the unique methyl group at 40° .

The well-documented restricted rotation in amides⁹ causes a similar non-equivalence of the methyl groups in the compound illustrated in Figure 3. There is a coupling of 1.2 Hz for the methyl group adjacent to fluorine in contrast to the zero coupling of the other methyl group. It is suggested this may be due to "through-space" coupling¹⁰.

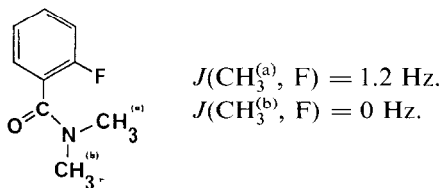


Fig. 3. Illustration of the non-equivalence of the dimethylamido methyl groups due to C-N restricted rotation.

Experimental

Reactions between 1,1,3-trichloro-1,3,3-trifluoroacetone (3 moles) and the boron compound (1 mole) (equation 2), were carried out in sealed tubes (70°/7 days). After opening the tubes, boron trifluoride was allowed to boil off in virtually quantitative yield to produce the crude ketone which was distilled. These ketones are characterised below in Table I.

TABLE I
NEW POLYHALOGENOKETONES

Ketone	B.p. (°C/mmHg)	Yield ^e	¹⁹ F NMR (ppm upfield from CFC1 ₃)	¹ H NMR ^f (τ)
Cl ₂ BrCCOCF ₂ Cl ^a	147	47	57.2	—
Cl ₃ CCOCF ₂ Cl ^b	122	45	58.1	—
(CH ₃ S)Cl ₂ CCOCF ₂ Cl ^c	91/15	30	57.8	7.6
[(CH ₃) ₂ N]Cl ₂ CCOCF ₂ Cl ^d	50/9	31	58.1 ^g	7.80 (triplet) 7.97 (singlet)

^a Found: C, 13.2; Br, 28.4; Cl, 38.3 %. Required: C, 13.0; Br, 28.9; Cl, 38.5 %. n_D^{20} 1.4552. Strong infrared absorptions at 1775 (7), 1210 (5), 1170 (7), 1070 (7), 940 (10), 850 (4), 790 (3), 730 (5), 710 (4), 665 (6).

^b Found: C, 15.7; Cl, 61.2 %. Required: C, 15.5; Cl, 61.2 %. n_D^{20} 1.4261. Strong infrared absorptions at 1780 (8), 1215 (5), 1170 (8), 1110 (2), 1070 (9), 940 (10), 855 (5), 805 (3), 740 (6), 660 (8).

^c Found: C, 19.4; H, 1.1 %. Required: C, 19.7; H, 1.2 %. Strong infrared absorptions at 3000 (1), 2930 (2), 1755 (9), 1435 (5), 1420 (5), 1325 (1), 1215 (7), 1170 (9), 1065 (9), 980 (6), 935 (10), 855 (6), 805 (3), 785 (3), 735 (7), 715 (5), 660 (8).

^d Characterised by parent ion and cracking pattern of mass spectrum. Strong infrared absorptions at 2950 (3), 2920 (2), 1695 (10), 1500 (3), 1450 (3), 1410 (5), 1260 (3), 1215 (5), 1140 (8), 1100 (9), 1065 (6), 1035 (5), 1005 (5), 970 (8), 890 (7), 865 (2), 800 (2), 740 (4), 710 (2), 670 (6).

^e Crude yields were virtually quantitative, but the figures quoted here are those for pure fractionated products (~3 g) prepared for spectroscopy.

^f At 40°.

^g The predictable quartet on this absorption could not be resolved, but a broadened peak is observed.

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