of inter- and intra-molecular bonding occurring. As this bonding will not, in general, be the same in every system the agreement obtained in Fig. 1 is considered reasonable.*

Frequency–Frequency Relations

It was illustrated in the methyl series that since both ν_d^2 and ν_r^2 depended linearly on electronegativity they would be linearly related to each other. Similar relations must hold between ν_r^2 and ν_d^2 in other MH_3X series.

Since the H—X stretching frequency depends (13) on the electronegativity of X, it would be expected that external relationships exist between it and the internal frequencies of the MH_3-group in the MH_3X series and this has been shown to hold true for the eight internal methyl group frequencies in the CH_3X series (1). Similar relationships would also be expected for the silyl, germanyl, and ammine series. Again, of course, since all the internal frequencies in the MH_3-groups are related to electronegativity, relations must exist between the internal frequencies of one MH_3-group with those of any other and this is illustrated in Fig. 2 for the symmetrical deformation and rocking frequencies.

It can be appreciated that the frequency–frequency relations suggested here are of use to the spectroscopist enabling him to predict the internal vibrational frequencies of any MH_3-group in MH_3X if the internal frequencies of the YH_3-group in YH_3X are known, or even more simply, if the HX stretching frequency is known.

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Received September 14, 1959.
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DECARBOXYLATION OF DIMETHYLTRIFLUOROACETOXYARSINE

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This paper includes the preparation of the new compound dimethyltrifluoroacetoxyarsine and the characterization of fluorodimethylarsine. These compounds are best obtained as follows:

$$(CH_3)_2AsCl + AgOOCCF_3 \rightarrow (CH_3)_2AsOOCCF_3 + AgCl,$$

$$(CH_3)_2AsI + AgF \rightarrow (CH_3)_2AsF + AgI.$$

Further, some coupling might be expected between the rocking modes when more than one ammine group is attached to the same metal atom, although this would, in general, be slight for the rather large central metal atoms experienced here.

Dimethyltrifluoroacetoxyarsine is a colorless mobile liquid stable in nitrogen at its boiling point of 136 to 137°. It is moderately stable in the absence of air at 150° but decomposes at 205° to give, among other products, the known compound dimethyltrifluoromethylarsine (1) and carbon dioxide.

$$(CH_3)_2AsOOCCF_3 \rightarrow (CH_3)_2AsCF_3 + CO_2$$

Organometallic haloacetates have been prepared by this method previously (2, 3) and the trifluoroacetates are unusually stable in comparison with other haloacetates (3, 4), probably because of the stability of the C—F bond. The actual mode of decomposition of the haloacetates has been incompletely studied and such decarboxylation reactions may be useful in synthesizing other perfluoroalkyl derivatives of the metals and metalloids. This is now being investigated.

Fluorodimethylarsine is a very reactive liquid isolated by Bunsen (5) but not characterized. The fluorodimethylarsine attacks glass very readily and is unstable to oxygen and moisture. It boils in a nitrogen atmosphere at 75°, a value in good agreement with the estimated 72° (6). The yield of the fluorodimethylarsine from silver fluoride and chlorodimethylarsine is very low. The reaction of iododimethylarsine with the appropriate silver salt gives good yields of dimethylchloro-, dimethylbromo-, and dimethylcyanoarsine. The bromide is not obtainable from the chloride by this method. Similar reactions are known in the bis(trifluoromethyl)arsine series (6) and previous workers have obtained cyanodimethylarsine from chlorodimethylarsine and silver cyanide in benzene solution (7).

A reinvestigation of the reaction between chlorodimethylarsine and dimethylamine has led to the characterization of dimethylaminodimethylarsine, first isolated by Cullen and Emeléus (8).

$$(CH_3)_2AsCl + 2HN(CH_3)_2 \rightarrow (CH_3)_2As—N(CH_3)_2 + (CH_3)_2NH_2Cl$$

The amino compound boils at 112° and is unstable to oxygen and moisture. The compounds $(CH_3)_2P—N(CH_3)_2$ and $(CF_3)_2M—N(CH_3)_2$ (M = As or P) are obtained by similar reactions (8, 9, 10).

EXPERIMENTAL

Apparatus and Technique

Conventional vacuum techniques were used for the manipulation of volatile reactants and products out of contact with moisture and oxygen. Reactions were carried out in sealed Pyrex tubes (50-ml capacity) in the absence of air and light. Infrared spectra were measured on a Perkin–Elmer Model 21 double-beam instrument with rock-salt optics.

Dimethyltrifluoroacetoxyarsine

Chlorodimethylarsine (10.5 g) and silver trifluoroacetate (22 g) were heated to 60° for 15 hours. Trap-to-trap distillation of the volatile products followed by distillation of the least volatile fraction in a nitrogen atmosphere at 760 mm gave dimethyltrifluoroacetoxyarsine, b.p. 136–137° (4.5 g, 32% yield). Anal. calc. for $C_4H_6AsF_3O_2$: As, 34.3%. Found: As, 33.7%.

Decarboxylation of Dimethyltrifluoroacetoxyarsine

The arsine (1.919 g) was heated to 150° for 17 hours and little decomposition was detected. When the same sample was heated to 205° a black solid was slowly deposited, and after 17 hours at this temperature trap-to-trap distillation of the volatile products gave a fraction condensing at −196° (0.194 g), a fraction condensing at −98° (0.354 g), and a fraction condensing at −64°. Spectroscopic examination showed the most volatile fraction to be mainly carbon dioxide together with traces of silicon tetrafluoride and fluoroform, and the least volatile fraction to contain no unchanged dimethyltrifluoroacetoxyarsine. The middle fraction was dimethyltrifluoromethylarsine (23% yield). Anal. found: mol. wt., 173. Calc.: mol. wt., 174. The infrared spectrum was identical with that of the pure compound (11, 12).

Preparation of Fluorodimethylarsine

Iododimethylarsine (12.5 g) and silver fluoride (12 g) were left at 20° for 48 hours. Distillation of the volatile products in a nitrogen atmosphere at 760 mm gave a 1-g (15% yield) fraction, b.p. 75°, identified as fluorodimethylarsine. Anal. calc. for C_2H_6AsF: As, 60.6%. Found: As, 61.2%.

Reaction of Iododimethylarsine with Silver Chloride

The arsine (8.5 g) and silver chloride (28 g) were heated to 60° for 14 hours. The volatile products were distilled in a nitrogen atmosphere to give 4.5 g (90% yield) of chlorodimethylarsine, b.p. 107° (published b.p. 106.5–107° (13)).

Reaction of Iododimethylarsine with Silver Bromide

The arsine (9.0 g) and silver bromide (38 g) were heated to 60° for 14 hours. The contents of the tube gave in the usual manner 6.0 g (81% yield) of bromodimethylarsine, b.p. 129° (published b.p. 128–129° (13)).

Reaction of Iododimethylarsine with Silver Cyanide

The arsine (12 g) and silver cyanide (13 g) were left at 20° for 48 hours. The solid cyanodimethylarsine (5 g, 76% yield) was sublimed *in vacuo* from the reaction tube. On distillation in a nitrogen atmosphere, the cyanodimethylarsine boiled at 162° (770 mm) (published b.p. 158–160° (730 mm) (7)).

Reaction of Chlorodimethylarsine with Dimethylamine

The arsine (4.8 g) and anhydrous dimethylamine (5.6 g) were left at 20° for 7 days. After removal of the excess dimethylamine by trap-to-trap distillation the least volatile fraction was distilled at 760 mm in a nitrogen atmosphere at 112°, with a middle cut of 2.1 g. This 2.1-g fraction on redistillation again boiled at 112° and was dimethylaminodimethylarsine. Anal. calc. for $C_4H_{12}AsN$: As, 50.3%. Found: As, 50.8%. The infrared spectrum showed the following absorption bands: liquid film: 2980(s), 2890(s), 2860(s), 2820(s), 2780(s), 2480(w), 1453(s), 1423(s), 1259(m), 1237(m), 1177(vs), 1140(m), 1095(w), 1054(s), 946(vs), 880(s), 813(s), 805(m), 775(w), 735(m) cm^{-1}.

ACKNOWLEDGMENT

The authors wish to acknowledge financial assistance from the National Research Council of Canada.

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Received November 17, 1959.

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