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SHORT COMMUNICATION

The Reaction of Molybdenum Hexafluoride with Carboxylic Acids

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The conversion of organic functional groups to fluorinated derivatives in which oxygen has been replaced by fluorine represents an attractive route to organic fluorochemicals. Sulfur tetrafluoride is well known for affecting such transformations [1], although MoF_6 [2], and more recently, the SF_4 derivative, diethylaminosulfur trifluoride [3] have also been reported to display reactions of this type with certain functional groups.

In the presence of BF_3 , molybdenum hexafluoride has been shown to react with acid chlorides in methylene chloride solution to form trifluoromethyl compounds [2]. Although MoF_6 reacted with benzoyl chlorides to form the corresponding benzotrifluorides, benzoic acid itself could not be converted to benzotrifluoride at temperatures up to 200°C. The reaction of acetic acid with MoF_6 , WF_6 , or UF_6 has been reported to yield acetyl fluoride [4]. We have found that at about 130°, MoF_6 can convert aliphatic carboxylic acids to trifluoromethyl compounds in good yields (Table 1). Particularly surprising is the lack of halogen exchange in substituted acetic acids such as bromoacetic acid which forms CH_2BrCF_3 in 89% yield, indicating that MoF_6 is a rather weak halogen exchange reagent.

The molybdenum containing product from these reactions is $MoOF_4$ (isolated from the reaction of MoF_6 with chloroacetic acid) which does not react further under these conditions (exp 3). The stoichiometry must therefore be as shown in Equation 1.

eqn 1 $2MOF_6$ + $CH_2CICOOH \rightarrow 2MOOF_4$ + HF + CH_2CICF_3

MOF ₆
with
derivatives
and
acids
carboxylic
of
Reactions

TABLE 1

CH ₃ CF ₃			Substrate	тета
	133	17	2.96	63
CH ₂ C1CF ₃	140	16	2.12	88
nonea	131	17.5	1.04	1
CH2BrCF3	158	64	2.14	68
CF3CH2CF3	135	136	4.4	79
CHCl2CF3, CO2,	140	16	2.58	1
CHClF2, CHF3, CO				
CHCl $_2$ CF $_3$, CO, CHF $_3$	130	06	2.00	ı
CF 3 COF	130	19	2.02	54
CH3CF3	130	16.5	2.20	46
CH ₃ CF ₃ , CH ₃ F	134	19	0.89	I
	CHC12CF3, CO2, CHC1F2, CHF3, CO CHC12CF3, CO, CHF3 CH3CF3, CO, CHF3 CH3CF3 CH3CF3, CH3F	CHC12CF3, CO2, 140 CHC1F2, CHF3, CO CHC12CF3, CO, CHF3 130 CH2CF3, CO, CHF3 130 CH3CF3 130 CH3CF3 130 CH3CF3, CH3F 134	CHC12CF3, CO_2 ,14016CHC12CF3, CO_2 ,14016CHC12CF3, $CO,$ CHF3130CHC12CF3, $CO,$ CHF3130CH3CF313019CH3CF3, CH_3F 13419CH3CF3, CH_3F 13419	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

(a)Although the work-up procedure involved loss of weight from the contents of the reaction vessel, no volatile products were found which were not absorbed by KF (see Expl.).

Methane derivatives were formed from the reaction of MoF_6 with dichloroacetic, difluoroacetic, and glycolic acids. These can arise from decarboxylation of the acid or decarbonylation of the initially formed acid fluoride. That decarbonylation can occur readily under these conditions is seen from the reaction of CHCl₂COCl with MoF₆ which afforded CO, CHF₃, and CHCl₂CF₃ (exp 7). Although CHCl₂CF₃ accounted for about 58% of the product mixture from dichloroacetic acid, only cleavage products were seen from the reaction with difluoroacetic or glycolic acid. On the basis of these results we anticipated carbon-carbon bond cleavage would also be a major reaction pathway with CF₃COOH, but CF₃COF was the sole product, even after prolonged heating (114 h) at 170°.

Tungsten hexafluoride does not lead to trifluoromethyl derivatives by reaction with either acetic or chloroacetic acid under conditions similar to those with MoF_6 , but low yields of volatile products were observed, including CO_2 . These data suggest strongly that the metal fluoride plays an important role in the decarboxylations and decarbonylations and that these are not simple thermal reactions.

As expected, the reaction of methyl acetate with MoF_6 gave both CH_3F and CH_3CF_3 , but ethyl acetate gave only CH_3CF_3 ; CH_3CH_2F was absent. One possible explanation is shown by the sequence of reactions given below. MoF_6 reacts destructively

 $CH_{3}COOCH_{2}CH_{2} \longrightarrow CH_{3}CF_{2}OCH_{2}CH_{3} \longrightarrow CH_{3}COF + H_{2}C = CH_{2} + HF$ $CH_{3}CF_{3} \qquad polymer$

with active olefinic compounds under these conditions and would explain the absence of volatile products arising from ethylene. In this sense MoF_6 has greater limitations as an oxygen-fluorine exchange reagent than does SF_4 [1].

No added catalysts were necessary for the reactions reported in Table 1, and the same procedure can be used in some instances to effect an oxygen-fluorine exchange with other functional groups, extending the similarity between MoF_6 and SF_4 . Thus, MoF_6 reacted with acetone in the absence of solvent or BF_3 to give 2,2-difluoropropane (40%), with ethylene oxide to give 1,1-difluoroethane (42%), and with trifluoroethanol to give 1,1,1,2-tetrafluoroethane (85%).

EXPERIMENTAL

 MoF_6 (used as received from Ozark-Mahoning) and organic substrate were condensed into a cooled (-196°) and evacuated 300 ml stainless steel cylinder. After warming to room temperature, the cylinder was placed in an oil bath at the temperature indicated in the Table. Quantities of reactants were such that maximum pressures at reaction temperatures were <1/10 the nominal burst pressure of the cylinder. Hydrogen fluoride and unreacted MoF₆ were removed from volatile products by allowing the mixture to pass through a KF scrubber (1" X 8" cylindrical tube filled with anhydrous KF and held at 100°) into a cooled, evacuated receiver. This was done at least three times. The products were identified by comparison of their ir spectra with spectra recorded in the literature and by nmr (when possible). GC purities were >95% for products of exps 1,2,4,5,8 and 9 (Table 1).

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