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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The conversion of organic functional groups to fluorinated derivatives in which oxygen has been replaced by fluorine represents an attractive route to organic fluorochemicals.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<sub>6</sub> [2], and more recently, the SF<sub>4</sub> derivative, diethylaminosulfur trifluoride [3] have also been reported to display reactions of this type with certain functional groups.

In the presence of BF<sub>3</sub>, molybdenum hexafluoride has been shown to react with acid chlorides in methylene chloride solution to form trifluoromethyl compounds [2]. Although MoF<sub>6</sub> reacted with benzoyl chlorides to form the corresponding benzo-trifluorides, benzoic acid itself could not be converted to benzotrifluoride at temperatures up to 200°C. The reaction of acetic acid with MoF<sub>6</sub>, WF<sub>6</sub>, or UF<sub>6</sub> has been reported to yield acetyl fluoride [4]. We have found that at about 130°, MoF<sub>6</sub> 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<sub>2</sub>BrCF<sub>3</sub> in 89% yield, indicating that MoF<sub>6</sub> is a rather weak halogen exchange reagent.

The molybdenum containing product from these reactions is MoOF<sub>4</sub> (isolated from the reaction of MoF<sub>6</sub> with chloroacetic acid) which does not react further under these conditions (exp 3). The stoichiometry must therefore be as shown in Equation 1.

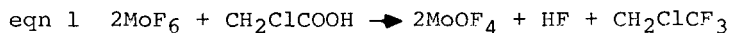


TABLE 1  
Reactions of carboxylic acids and derivatives with MoF<sub>6</sub>

Substrate	Volatile Organic Products	Temp (°C)	Time (h)	Moles MoF <sub>6</sub> /Moles Substrate	Yield
(1) CH <sub>3</sub> COOH	CH <sub>3</sub> CF <sub>3</sub>	133	17	2.96	63
(2) CH <sub>2</sub> ClCOOH	CH <sub>2</sub> ClCF <sub>3</sub>	140	16	2.12	88
(3) CH <sub>2</sub> ClCOOH	none <sup>a</sup>	131	17.5	1.04	-
(4) CH <sub>2</sub> BrCOOH	CH <sub>2</sub> BrCF <sub>3</sub>	158	64	2.14	89
(5) CH <sub>2</sub> (COOH) <sub>2</sub>	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	135	136	4.4	79
(6) CHCl <sub>2</sub> COOH	CHCl <sub>2</sub> CF <sub>3</sub> , CO <sub>2</sub> , CHClF <sub>2</sub> , CHF <sub>3</sub> , CO	140	16	2.58	-
(7) CHCl <sub>2</sub> COCl	CHCl <sub>2</sub> CF <sub>3</sub> , CO, CHF <sub>3</sub>	130	90	2.00	-
(8) CF <sub>3</sub> COOH	CF <sub>3</sub> COF	130	19	2.02	54
(9) CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub> CF <sub>3</sub>	130	16.5	2.20	46
(10) CH <sub>3</sub> COOCH <sub>3</sub>	CH <sub>3</sub> CF <sub>3</sub> , CH <sub>3</sub> F	134	19	0.89	-

(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.).



## EXPERIMENTAL

MoF<sub>6</sub> (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 MoF<sub>6</sub> 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 expts 1,2,4,5,8 and 9 (Table 1).

## REFERENCES

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