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Synthesis of Pentafluoroethyl Trifluoroacetate by Low-Temperature Direct Fluorination

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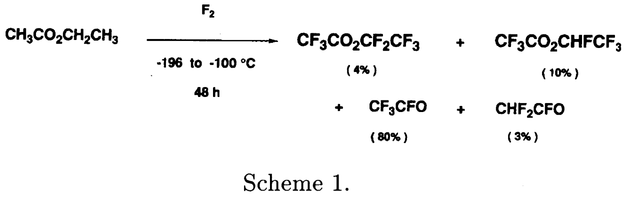
Synopsis. Ethyl acetate was perfluorinated by direct fluorination in the presence of cesium fluoride, affording pentafluoroethyl trifluoroacetate in excellent yield. In the reaction pathway, the dimerization of trifluoroacetyl fluoride with cesium fluoride gives pentafluoroethyl trifluoroacetate.

Oxygen-containing fluorocarbon molecules have received some attention regarding possible applications as lubricating oils, hydraulic fluids, and so on. Although some have been prepared by fluorination using fluorinating reagents, such as cobalt trifluoride, the majority have been prepared by the electrochemical techniques pioneered by Simon.[1—3] The inability to control direct fluorination reactions to produce high yields of the desired fluorinated reactant without any concomitant fragmentation of the desired product has thus prevented direct fluorination from becoming a widely accepted method of fluorination, since elemental fluorine acts as a strong oxidizing reagent.[4] However, direct fluorination is particularly useful for preparing perfluoro esters which are either impossible or difficult to obtain by cobalt trifluoride[5] or electrochemical methods.[4] In fact, the low-yield synthesis (5%) of pentafluoroethyl trifluoroacetate ($CF_3CO_2CF_2CF_3$) by direct fluorination was the only previously known method.[6] We now report on the excellent yield preparation of $CF_3CO_2CF_2CF_3$ from ethyl acetate derivatives by low-temperature direct fluorination in the presence of cesium fluoride (CsF).

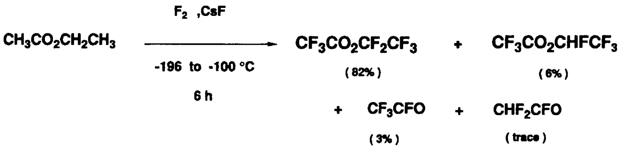
Results and Discussion

Adcock and Lagow[6] reported that the reaction of ethyl acetate and elemental fluorine afforded a complex mixture containing $CF_3CO_2CF_2CF_3$ and 2,3,3,3-tetrafluoroethyl trifluoroacetate ($CF_3CO_2CHFCF_3$) in 5 and 20% yields at −78 °C. We first examined the temperature effect of the direct fluorination of ethyl acetate, as shown in Scheme 1. Upon lowering of the temperature, the reactor was placed in a cold bath (−196 °C) and allowed to slowly warm up to −100 °C for 48 h, a mixture of $CF_3CO_2CF_2CF_3$ (4%), $CF_3CO_2CHFCF_3$ (10%), difluoroacetyl fluoride (CHF_2CFO) (3%), and trifluoroacetyl fluoride (CF_3CFO) (80%) as major products was obtained. A major factor affecting the low yield of $CF_3CO_2CF_2CF_3$ is presumed to be the decomposition of $CF_3CO_2CF_2CF_3$ into two moles of CF_3CFO catalyzed by hydrogen fluoride, which is produced in the reaction. In the next step, the reaction was carried out in the presence of dried alkali metal fluoride in order to trap the generated hydrogen fluoride. Although sodium fluoride (15 mmol) or potassium fluoride (15 mmol) was added to the reactor, $CF_3CO_2CF_2CF_3$ was obtained in 3—12% yield, giving CF_3CFO in high yield. However, the direct fluorination of ethyl acetate in the presence of CsF (15 mmol) for 48 h afforded $CF_3CO_2CF_2CF_3$ in 74% yield with a small amount of CF_3CFO. Furthermore, the effect of the amount of CsF was investigated by the reaction of ethyl acetate (1 mmol) with elemental fluorine (12 mmol); the results, as shown in Table 1, indicated that $CF_3CO_2CF_2CF_3$ was obtained in the highest yield when 20 mmol of CsF was employed (Entry 5). If a large amount of CsF (40 mmol) was added to the reactor, the yield of $CF_3CO_2CF_2CF_3$ decreased to 65%. In addition, 6 h for the reaction time was sufficient to afford $CF_3CO_2CF_2CF_3$ in high yield, similar to Entry 5 (Scheme 2, Entry 7). Diluted fluorine ($F_2/N_2=4/1$) instead of pure fluorine, however, reduced the reaction rate (Entry 8).

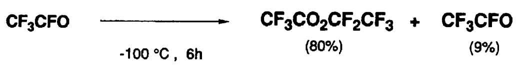


Scheme 1.

In the formation of $CF_3CO_2CF_2CF_3$, one may suggest that CF_3CFO dimerizes to form $CF_3CO_2CF_2CF_3$ in the presence of CsF. In fact, the reaction of CF_3CFO (1 mmol) in the presence of CsF (15 mmol) at −100 °C for 6 h gave $CF_3CO_2CF_2CF_3$ (80%) with the recovery of CF_3CFO (9%) (Scheme 3). The dimerization of CF_3CFO gradually occurred at around −115 °C. CF_3CFO was recovered quantitatively at −140 °C, and $CF_3CO_2CF_2CF_3$ was obtained in 20% yield at −155—−110 °C.



Scheme 2.



Scheme 3.

Table 1. The Direct Fluorination of Ethyl Acetate[a)]

Entry	Additive	Time	Products (Yield/%)[b)]			
	mmol	h	$CF_3CO_2CF_2CF_3$	$CF_3CO_2CHFCF_3$	CF_3CFO	CHF_2CFO
1	None	48	4	10	80	3
2	NaF(15)	48	3	9	80	3
3	KF(15)	48	12	11	70	Trace
4	CsF(15)	48	74	12	5	Trace
5	CsF(20)	48	82	6	4	Trace
6	CsF(40)	48	65	8	15	Trace
7	CsF(20)	6	82(79)[c)]	6	3	Trace
8[d)]	CsF(20)	6	45	4	36	Trace

a) Reaction conditions; Ethyl acetate (1 mmol), F_2 (12 mmol) at -196—-100 °C. b) Yields of $CF_3CO_2CF_2CF_3$ and FCO_2CHFCF_3 were below 1%. Yields were determined by ^{19}F NMR. Trace means yield below 1%. Yield of CF_3CFO (2 mmol) was based on ethyl acetate (1 mmol). CF_4 was detected in all reactions. c) Isolated yield. d) Diluted F_2 ($F_2/N_2=4/1$) was employed.

Table 2. The Direct Fluorination of Partially Fluorinated Ethyl Acetates[a)]

Substrate	Products (Yield/%)[b)]		
	$CF_3CO_2CF_2CF_3$	$CF_3CO_2CHFCF_3$	CF_3CFO
$CH_2FCO_2CH_2CH_3$	82(80)[c)]	6	3
$CH_3CO_2CH_2CHF_2$	84	5	4
$CHF_2CO_2CH_2CH_3$	82	5	5
$CF_3CO_2CH_2CH_3$	85	4	4
$CF_3CO_2CH_2CF_3$	93(85)[c)]	Trace	2

a) Reaction conditions; Substrate (1 mmol), CsF (20 mmol), F_2 (12 mmol) at -196—-100 °C (6 h). b) Yields were determined by ^{19}F NMR. Trace means yield below 1%. c) Isolated yields.

As shown in Table 2, the reactions of partially fluorinated ethyl acetates with elemental fluorine proceeded smoothly and $CF_3CO_2CF_2CF_3$ was obtained in high yield. The yield of $CF_3CO_2CF_2CF_3$ increased from 82 to 93% upon increasing the number of fluorine atom in ethyl acetate. Presumably, ethyl acetate having more fluorine atoms would not be decomposed by elemental fluorine.

The direct fluorination process described here did not show any radical recombination problems, despite the fact that fluorination proceeded as a radical mechanism. This might be because the fluorination of the bulk of the materials occurs in a condensed phase at low temperature.

Experimental

Appararus. All of the volatile liquilds and gaseous materials were handled in a glass-and-stainless-steel vacuum system equipped with glass-Teflon or stainless steel valves, similar to those previously described.[7,8)] Pressures were measured with an MKS Baratoron absolute-pressure gauge (Type 122A). Differential pressures were measured with a differential-pressure gauge (Type 127A). All of the reactions were carried out in 100 ml stainless-steel cylinders (Hoke 4HS100) fitted with a ball valve (Nupro SS-4JB). The amounts of volatile products were determined by PVT measurements. The temperature were measured using a digital indicating copper–constantan thermocouple for an Advantest digital multithermometer (Model TR2114). The infrared spectra were recorded on a JASCO FT/IR-7000 spectrometer. The ^1H and ^{19}F NMR spectra (chemical shifts in parts per million from internal references, such as tetramethylsilane and $CFCl_3$, respectively) were measured on a JEOL JNM-EX 270 (270 MHz) spectrometer with ca. 10 mol% solutions in $CDCl_3$. Purification of volatile products was achieved by trap-to-trap distillation (low-temperature separation based on the differences in the volatility of the compounds).

Preparation of $CF_3CO_2CF_2CF_3$ (Entry 7 in Table 1). General Procedure: CsF (20 mmol) was placed into a reactor made of stainless steel. Ethyl acetate (1 mmol) was introduced into the reactor at -196 °C. Elemental fluorine (2 mmol) was added 6 times each to the reactor at -196 °C using a vacuum-line system. The reactor was then allowed to warm up slowly to -100 °C for 6 h. Hydrogen fluoride was removed from the crude mixture by dried sodium fluoride (15 mmol) at -70 °C. The volatile products of the reaction were transferred from the collection trap and separated by vacuum-line trap-to-trap fractionation into five fractions: -60, -80, -90, -110, and -196 °C. Further trap-to-trap purification of the products collected in the -80 through -110 °C traps yielded $CF_3CO_2CF_2CF_3$ (79%), bp 19—20 °C (lit,[6)] 21.4 °C). The ^{19}F NMR and IR spectra were very compatible with those published by Lagow et al.[6)]

Authentic Method: CF_3CFO (1 mmol) was introduced into a stainless-steel reactor containing CsF (15 mmol) at −196 °C using a vacuum-line system. The reactor was then placed in a cold bath (−120 °C) and allowed to remain at −100 °C for 6 h. After this time, any volatile materials were pumped away. The reaction mixture was fractionated through a trap at a temperature low enough to trap any CF_3CFO (80%).

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