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(7) A white crystalline contaminant is sometimes present in the crude product and could readily be removed by filtering through a short silica gel column.

An Efficient and Convenient Synthesis of Fluoroformates and Carbamoyl Fluorides

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Methods for the preparation of enol carbonates, $R_2C{=}C\text{-}ROCO_2R$ (**1**), and enol carbamates, $R_2C{=}CROCONR_2$ (**2**), have been reported[1,2] and some of the advantages of these synthetic intermediates have been outlined[2] in recent publications from this laboratory. In our search for other broadly useful and complementary routes to **1** and **2**, we have now developed[3] a simple, regiospecific preparation from enol silyl ethers and fluoroformates, ROCOF (**3**), or tertiary carbamoyl fluorides, R_2NCOF (**4**).

The success of this new procedure requires that **3** and **4** be readily available and here the literature is discouraging. Both **3** and **4** have been made in high yield by acylation of alcohols or amines with COF_2 or COFCl,[4] but the method is economically impractical because of the price of commercial COF_2 ($700 per lb) and the preparative inaccessibility of both COF_2 and COFCl in a standard laboratory.[5] Chloroformates also have been converted to **3** but the yields are only moderate and the halogen exchange process requires special apparatus (e.g., UV light with KF[6]) or reagents (e.g., freshly prepared thallous fluoride[7]).[8] More complex fluoroformate syntheses also have been described.[9]

We have now found that the conversion of chloroformates (**5**) and carbamoyl chlorides (**6**) to **3** and **4**, respectively, is easily achieved in excellent yield just by treatment with KF activated by the phase transfer agent, 18-crown-6.[10] The results for several syntheses are summarized in Table I. For liquids **5** and **6** (often commercially available), it is merely sufficient to stir the neat starting material with KF and a little 18-crown-6 (ca. 5 mol %) at room temperature until none of the carbonyl chloride remains (IR assay).[11] The pure product is then simply isolated by distillation of the reaction mixture. When the reactant is a solid, an inert solvent such as dichloromethane is used to facilitate the process.

That the halogen exchange, **5** → **3**, can be performed as described above may be somewhat surprising since the analogous transformation of **5** to a cyanoformate with 18-crown-6 activated KCN reported by Childs and Weber is extremely sluggish in the absence of a little water[12]—a contaminant which would destroy the product in the present reaction. In the only other close precedent for the present work, Liotta and Harris[13] showed that acetyl fluoride could be generated from acetyl chloride with crown ether activated KF. However, that process may be complicated by the equilibrium intermediacy of an anion-hungry *N*-acetylacetonitrilium cation and also is not a practical route to pure acetyl fluoride. Even careful fractional distillation yields a product contaminated by ca. 20% acetonitrile. By our procedure (see Table I), both butyryl fluoride[14] and benzoyl fluoride[8] were obtained pure in 90% yield from the corresponding chlorides.

From Table I, a large variation in required reaction time vs. substrate structure is evident. At a given temperature and catalyst concentration, the smaller molecules generally exchange halogen faster in accord with expectation: shorter alkyl residues on the carbonyl chloride increase its polarity as a solvent thus increasing the solution concentration of the other reactant, the polar KF crown ether complex. The concentration of complex also can be raised by using more crown ether, a simple way to speed up those reactions which are slower than desired.

Raising the temperature is another way to accelerate the exchange. However, this mechanism must be used with caution here. Alkyl chloroformates are known to decompose to alkyl chlorides or alkenes and CO_2 when heated[15] (usually at 120–150 °C or higher) and this process seems to be strongly catalyzed by both KF and 18-crown-6 at elevated temperatures. For example, *i*-BuOCOF (**7**) was isolated in 91% yield when the chloroformate was allowed to react at room temperature. At 100 °C the yield of **7** was only 35% and much isobutyl chloride also was found. The result cannot be accommodated by invoking product decomposition, since **7** was reasonably stable under these conditions. However, when *i*-

Table I. Fluoroformates, Carbamoyl Fluorides, and Acyl Fluorides Prepared from Their Respective Chlorides[a]

RCOF product, R =	registry no.	yield,[b] %	KF, equiv	18-C-6, mol %	temp, °C	time, h	bp, °C/torr found	bp, °C/torr lit.[c]
$MeCH_2O$–	461-64-3	89	1.6	6	0	68	55–57/atm	57/atm[4a]
Me_2CHO–	461-71-2	95	1.6	6	13	47	66–70/atm	81–82/atm[7]
Me_2CHCH_2O–	53813-78-8	91	1.3	4	r.t.	45	92–93/atm	27/0.1[9a]
$MeCH_2CH_2CH_2O$–	2253-35-2	84	1.8	8	r.t.	73	99–100/atm	97–99/atm[4b]
c-$C_6H_{11}O$—	351-79-1	89	1.5	9	70	4	52–53/21	64–65/25[7]
cholesteryl-3-O[d]	65928-85-0	89	3.9	15	r.t.	53	mp 112–113[e]	
PhO–	351-80-4	80	1.6	6	15–19	144	60–64/120	153/atm[4a]
Me_2N–	431-14-1	95	1.3	4	r.t.	27	65–70/80	54–56/51[5b]
N-piperidino–	657-99-8	88	1.9	5	r.t.	31	75–77/10[f]	61/11[9b]
N-morpholino–	68928-13-2	97	2.9	6	r.t.	68	60–65/2[g]	
$MeCH_2CH_2$–	461-53-0	90	1.4	4	r.t.	27	66–67/atm	69/atm[14]
phenyl–	455-32-3	90	2.1	7	r.t.	234	56–57/20	159–161/atm[8]

[a] Made by the general procedure in the Experimental Section with variations indicated in the table. [b] Of distilled or recrystallized product. [c] Superscripts refer to reference numbers in the text. [d] Prepared from the solid chloroformate in CH_2Cl_2; see text. [e] New compound; converted to and compared with known cholesteryl vinyl carbonate.[2c] [f] Converted to and compared with known *N*-vinyloxycarbonylpiperidine.[2b] [g] New compound; converted to and compared with the known enol carbamate of methyl vinyl ketone.[3]

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BuOCOCl (8) was heated with 5 mol % 18-crown-6 at 100 °C for 44 h, it could be recovered in only 47% yield and again *i*-BuCl was obtained. Moreover, after 60 h at 100 °C with KF and no crown ether, only 7% of the original 8 was recovered. The fluoroformate 7 also was identified in ca. 8% yield, an indication that halogen exchange occurs though inefficiently, even in the absence of crown ether. In our reaction system, the fate of some other chloroformates is even more temperature dependent than that of 8. For example, *n*-BuOCOF was obtained in 84% yield when the chloroformate was reacted at room temperature but in only 1% yield at a reaction temperature of 125 °C; also the 89% yield of EtOCOF isolated at 0 °C decreased to 6% at 85 °C and the 95% yield of *i*-PrOCOF measured at 13 °C deteriorated to 8% at 95 °C. The carbamoyl chloride (6) reactions also were exceptionally temperature dependent, though these substrates are not subject to the decomposition pathways followed by the chloroformates. For example, the 95% yield of Me_2NCOF found in the room temperature reaction decreased to 54% at 110 °C and 5% at 145 °C; also the morpholinylcarbamoyl chloride exchange which was 97% efficient at room temperature gave a thick brown intractable tar and 0% carbamoyl fluoride at 130 °C. These latter decompositions are probably initiated by the precedented fragmentation:[16] $R_2NCOCl \rightleftarrows R_2N{=}C{=}O^+ + Cl^-$.

It should be noted, in conclusion, that the convenient fluoroformate synthesis described here has a preparative value beyond that discussed in the introduction. The ready availability of 3 now makes these species highly attractive intermediates in a known but previously impractical conversion of alcohols to alkyl fluorides.[7,17]

Experimental Section

Melting points were taken in a Thomas-Hoover apparatus equipped with a calibrated thermometer. Infrared spectra were obtained on a Perkin-Elmer 267 spectrophotometer and NMR spectra on a Varian A60-A spectrometer.

Potassium fluoride (Mallinckdrodt) was dried at 150 °C for 24 h, then finely pulverized and redried overnight at the same temperature in the reaction vessel. All chloroformates, acid chlorides, and carbamoyl chlorides were obtained commercially except cyclohexyl chloroformate[18] and the carbamoyl chlorides[19] of piperidine and morpholine which were made by standard acylations of the precursor alcohol or amines with phosgene. Before use, the liquid chloroformates and carbamoyl chlorides were distilled under N_2 and the acid chlorides were refluxed with PCl_5 and distilled under N_2. Glassware was dried at 150 °C, assembled hot in a stream of dry N_2, and set up to maintain a slight positive N_2 pressure during the main reaction sequences.

Isobutyl Fluoroformate. (Except for the variations indicated in Table I, liquid chloroformates, carbamoyl chlorides, and acid chlorides were allowed to react by the procedure given here.) Isobutyl chloroformate (26.3 g, 0.193 mol) was syringed into a three-neck flask containing dried KF (14.7 g, 0.253 mol) and 18-crown-6[10] (1.80 g, 0.0068 mol) and fitted with a Teflon stirring bar, a condenser topped by an N_2 gas inlet, a septum cap, and a ground glass stopper. The mixture then was stirred efficiently at room temperature until IR analysis of an aliquot indicated that no chloroformate remained (C=O stretch at 5.62 μm in CCl_4; fluoroformate C=O stretch at 5.46 μm). After a few more hours (total reaction time 45 h), the product fluoroformate was isolated directly from the reaction apparatus by simple distillation (stirred to minimize bumping, oil bath): yield 21.0 g (91%); bp 92–93 °C (atmospheric pressure) (lit.[9] bp 27 °C at 0.2 torr).

When the halide exchange was performed at 13 °C for 78 h with 1.3 equiv of KF and 7.5 mol % 18-crown-6, the fluoroformate yield was 87%. Only a 35% yield of fluoroformate was obtained at a reaction temperature of 100 °C (1.3 equiv of KF, 7.6 mol %, 18-crown-6, 24 h). A substantial forerun of isobutyl chloride was also obtained. When isobutyl chloroformate was heated with 18-crown-6 (5 mol %) at 100 °C for 44 h, only 47% of the chloroformate could be recovered. In contrast, isobutyl fluoroformate was recovered in 87% yield after similar treatment. After 10 g of isobutyl chloroformate was heated with KF (1.7 equiv) at 100 °C for 60 h, only 1.4 g of liquid remained. This analyzed as an ca. 1:1 mixture of chloroformate to fluoroformate. Isobutyl fluoroformate was recovered in 83% yield after analogous treatment.

Cholesteryl Fluoroformate. (This procedure was followed when the chloride precursor was a solid.) The chloroformate of cholesterol (Aldrich) (6.79 g, 0.0151 mol) was dissolved in the minimum amount of CH_2Cl_2 (5 mL). KF (3.5 g, 0.059 mol) and 18-crown-6 (0.60 g, 0.0023 mol) were added and the mixture was stirred at room temperature until reaction completion (53 h). After adding more CH_2Cl_2, the mixture was filtered and the filtrate was evaporated at reduced pressure. The yellow solid product residue was recrystallized from dry acetonitrile: yield 5.82 g (89%); mp 112–113 °C.

Anal. Calcd for $C_{28}H_{45}O_2F$: C, 77.7; H, 10.5. Found: C, 77.7; H, 10.4.

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Registry No.—Ethyl chloroformate, 541-41-3; isopropyl chloroformate, 108-23-6; isobutyl chloroformate, 543-27-1; butyl chloroformate, 592-34-7; cyclohexyl chloroformate, 13248-54-9; cholesteryl chloroformate, 7144-08-3; phenyl chloroformate, 1885-14-9; dimethylcarbamic chloride, 79-44-7; 1-piperidinecarbonyl chloride, 13939-69-0; 4-morpholinecarbonyl chloride, 15159-40-7; butanoyl chloride, 141-75-3; benzoyl chloride, 98-88-4.

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α-Trimethylsiloxy Ketones from Bis(trimethylsiloxy) Enol Ethers

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The Schräpler–Rühlman modification[2] has become the standard method for carrying out acyloin condensations. In

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