Notes

The Chemistry of Carbonyl Chloride Fluoride. II.[1] The Reaction between Vicinal Diols and Carbonyl Chloride Fluoride

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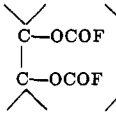
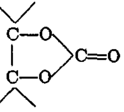
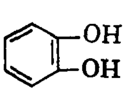
The preparation of carbonyl chloride fluoride[1,2] and its reaction with cyclic ethers[1] was described earlier. This paper deals with the preparation of ethylene bisfluoroformate and *o*-phenylene bisfluoroformate from the corresponding vicinal diols and carbonyl chloride fluoride and the successful decarboxylation of ethylene bisfluoroformate to ethylene difluoride, which generally is difficult to prepare.[3]

By treating ethylene glycol, the simplest aliphatic vicinal diol, with carbonyl chloride fluoride, ethylene bisfluoroformate was obtained as the main product in very high yields when proper reaction conditions were used. For example, the use of a small amount of tertiary amine as a catalyst, an inert solvent (*e.g.*, benzene), and a moderate reaction temperature were required to suppress the formation of the undesired ethylene glycol carbonate. Table I shows the results of these reactions and of the reactions with pyrocatechol.

Table I

Reaction between Vicinal Diols and Carbonyl Chloride Fluoride

Starting material	Temp., °C.	Catalyst	Conversion of the diol, %	Yield,[a] %	
					
$CH_2—OH$ | $CH_2—OH$	60	$N(But)_3$	100	73	27
	20	$N(But)_3$	99	99	1
	90	$N(But)_3$	100	8	92
	40	$N(But)_3$	100	29	71
	30	$N(But)_3$	100	45	55
	20	$N(Et)_3$	100	48	52

[a] The yields were determined by gas chromatographic ratios of the crude reaction products before distillation. The yields after distillation were slightly lower owing to mechanical losses.

The purity of the carbonyl chloride fluoride is not critical if this reagent is applied in excess. For example impurities of 10 to 15% of carbonyl chloride and carbonyl fluoride in the carbonyl chloride fluoride did not influence the reaction. Therefore, it must be assumed, that COFCl enters the reaction preferably. Ethylene bisfluoroformate can also be prepared from ethylene glycol and carbonyl fluoride[4]; however, the yield is given as only 79% compared with 98.9% obtained in our case. In addition, the formation of hydrogen fluoride as reaction product is less desirable than that of hydrogen chloride.

With pyrocatechol, the simplest aromatic vicinal diol, it was found much more difficult to suppress the formation of the cyclic carbonate. This was expected based on the different steric conditions of the aliphatic and aromatic vicinal diols. Table I shows the results of these reactions.

Decarboxylation of ethylene bisfluoroformate was investigated in the liquid phase using catalysts such as tertiary amines and boron trifluoride etherate,[5] and in the vapor phase with sodium pyrophosphate–boron trifluoride complex.[6] Tertiary amines, such as pyridine, gave only traces of ethylene difluoride. The use of boron trifluoride diethyletherate resulted in 28.6% yield of ethylene difluoride and 21.9% yield of FCH_2CH_2OCOF. In addition, 49% of ethylene was obtained, which was identified as the dibromoethane derivative. The decarboxylation of ethylene bisfluoroformate was repeated in the presence of boron trifluoride tetrahydrofuran etherate. In this case, no ethylene was obtained. These results indicate that the ethylene had formed from the $BF_3–(C_2H_5)_2O$ and not from the ethylene bisfluoroformate. Attempts to decarboxylate ethylene bisfluoroformate in the vapor phase on the surface of $Na_4P_2O_7–4BF_3$ complex were unsuccessful. At 300° no reaction occurred and above 320° the complex melted. *o*-Phenylene bisfluoroformate could not be converted to 1,2-difluorobenzene by any of these methods. Its preparation by a multistep method will be described in a following paper.

Experimental

Materials.—Carbonyl chloride fluoride was prepared from arsenic trifluoride and phosgene.[1] The boron trifluoride etherates were prepared by passing gaseous boron trifluoride (Matheson) through the corresponding ether cooled to 0° until saturated, followed by a vacuum distillation. The sodium pyrophosphate–boron trifluoride complex was prepared from $Na_4P_2O_7$ and BF_3 in a platinum crucible. All the other chemicals were obtained commercially.

Preparation of Ethylene Bisfluoroformate.—Ethylene glycol (0.4 mole), tri-*n*-butylamine (2 ml.) as catalyst, and benzene (80 g.) as solvent were placed into a 350-ml. stainless steel lecture bottle. Carbonyl chloride fluoride (1.5 mole of 88% purity; impurities, phosgene and COF_2) was added, keeping the reaction mixture cool. The lecture bottle was shaken at room temperature or 60° for 12 hr. The volatile products (unreacted carbonyl halides and HCl) were bled off at room temperature and the conversion and yields (Table I) were determined by v.p.c. The residue was treated with anhydrous $CaCl_2$, filtered, and vacuum distilled.

Properties of ethylene bisfluoroformate show it to be a colorless liquid of strong fluoroformate odor, which decomposes above 120° (lit.[4] 100–120°). It is soluble in CS_2 and benzene, but not in CCl_4, b.p. 33–34° at 1.5 mm. (lit.[4] 36° at 1.7 mm.), refractive index

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[1] Paper I: K. O. Christe and A. E. Pavlath, *J. Org. Chem.*, **30**, 1639 (1965).

[2] K. O. Christe and A. E. Pavlath, *ibid.*, **29**, 3007 (1964).

[3] W. Bockemüller, *Ann.*, **506**, 20 (1933); *Ber.*, **64**, 516, 522 (1931); A. L. Henne and T. Midgley, *J. Am. Chem. Soc.*, **58**, 884 (1936).

[4] P. E. Aldrich and W. A. Sheppard, *J. Org. Chem.*, **29**, 11 (1964).

[5] S. Nakanishi, T. C. Myers, and E. V. Jensen, *J. Am. Chem. Soc.*, **77**, 3099 and 5033 (1955).

[6] P. Baumgarten and H. Hennig, *Ber.*, **72**, 1743 (1939).

n^{25}_D 1.3673, d^{26} 1.435 g./cc. N.m.r. (F^{19}) showed a singlet at 18.5 p.p.m. above $CFCl_3$ characteristic for a fluoroformate group, and proton resonance at 4.3 p.p.m. consistent with a OCH_2CH_2O group. The infrared spectrum shows the following absorptions: 1830 ($\nu_{C=O}$ in fluoroformate group) and 1240 cm.$^{-1}$ (ν_{COC}), and the characteristic CH_2 and CF absorptions.

Anal. Calcd. for $C_4H_4F_2O_4$: C, 31.17; H, 2.60; F, 24.68. Found: C, 31.81; H, 2.88; F, 23.2.

Preparation of *o*-Phenylene Bisfluoroformate.—All reactions between pyrocatechol and COFCl were carried out in the same way. Pyrocatechol (0.3 mole), toluene (150 g.) as a solvent, and tertiary amine (0.5 to 20 ml.) as a catalyst were placed into a 500-ml. stainless steel lecture bottle. Carbonyl chloride fluoride (1.0 to 1.5 mole of 89% purity) was added, keeping the reaction mixture cool. The lecture bottle was shaken at different temperatures for 12 hr. The conversion of the pyrocatechol and the yield of *o*-phenyl bisfluoroformate mainly depended on the reaction temperature and time, but not on the amount of catalyst or excess of COFCl. The reaction product was analyzed and isolated as described for the ethylene bisfluoroformate.

o-Phenylene bisfluoroformate is a colorless liquid of strong fluoroformate odor. It has a b.p. 77° at 7 mm. and decomposes at higher temperature. The F^{19} n.m.r. spectrum shows a singlet at 17.6 p.p.m. above $CFCl_3$, which is characteristic for the fluoroformate group. The infrared spectrum also confirmed the structure.

Anal. Calcd. for $C_8H_4F_2O_4$: C, 47.54; H, 1.99; F, 18.80. Found: C, 47.93; H, 2.31; F, 18.7.

Decarboxylation.—All decarboxylation reactions in the liquid phase were carried out in the same way. The catalyst (15 ml. of pyridine or BF_3 etherate) wasp laced into a 50-ml., two-necked flask, equipped with a magnetic stirrer, dropping funnel, inlet for nitrogen, and a water-cooled condenser, which was connected to two cold traps (−78 and −196°) and a mercury blow off. The flask was purged with dry N_2 (50 ml./min.) for 0.5 hr. Then, the flask was heated to 120° and the bisfluoroformate was added dropwise, using stirring and a slow N_2 purge. The products, collected in the traps, and the residue in the flask were analyzed and identified by v.p.c. and infrared. The unsaturated products, such as ethylene, were brominated and identified as the bromo compound by analysis, refractive index, and their infrared spectra. The vapor phase decarboxylation was carried out by passing the bisfluoroformate vapors with dry nitrogen as carrier gas at a contact time of 10 sec. through an electrically heated quartz tube, which was connected to three cold traps (two at −78° and one at −196°) and a mercury blow off. The heated zone (300°) of the quartz tube (length, 30 cm.; o.d., 1 cm.) was filled with $Na_4P_2O_7$–$4BF_3$ as a catalyst. The gas inlet was heated by an infrared lamp to prevent condensation of the starting material.

Electrolytic Reductive Coupling. V.[1]
Reactions with 2- and 4-Vinylpyridine

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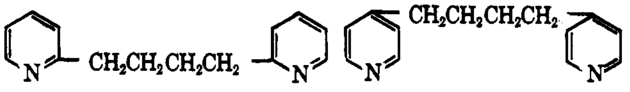
Both 2- and 4-vinylpyridine have been used extensively as acceptors in the Michael reaction.[2] Polarographic examination in this laboratory showed that these olefins in mildly alkaline solution are reduced at −1.6 and −1.5 v., respectively (beginning of wave *vs.* the saturated calomel electrode). Since these values are more positive than those reported for pyridine derivatives not bearing an unsaturated side chain,[3] it is apparent that the vinyl group reduces before the ring. Therefore, these vinylpyridines could serve as either donors or acceptors and thereby meet our criteria[1] for versatile participation in electrolytic reductive coupling.

A concentrated solution of 2-vinylpyridine in 67% aqueous tetraethylammonium *p*-toluenesulfonate was electrolyzed at a mercury cathode. The expected hydro dimer I, b.p. 110° (0.15 mm.), m.p. 43–45° (m.p. of diperchlorate, 191–191.5°; of dipicrate, 226–227°; of dimethiodide, 260–261°), was obtained in 69% yield.[4] The structure was established by elemental, molecular weight, infrared, and n.m.r. analyses.



I II

Bianchetti[5] has reported the preparation of a homologous series of α,ω-bis(2-pyridyl)alkanes by reaction of α-picolyllithium with $Br(CH_2)_nBr$. When $n = 2$ his putative product I boiled at 104–105° (0.8 mm.) and yielded a diperchlorate, m.p. 260–265°; a dipicrate, m.p. 234–240°; and a dimethiodide, m.p. 169–171°. In our hands Bianchetti's procedure was found to yield not I but the known 1,2-bis(2-pyridyl)ethane, m.p. 49–50°; dipicrate, m.p. 241–243°; and dimethiodide, m.p. 170–171°. The base was further identified by elemental analyses, mass spectral molecular weight, and comparison with an authentic sample. The abnormalities[6] in the reaction of ethylene bromide with organolithium compounds may well be due to the interchange reaction described by Wittig,[7] which, in this case,[8] would lead to the following sequence.

$$\alpha\text{-}C_5H_4NCH_2Li + BrCH_2CH_2Br \longrightarrow \alpha\text{-}C_5H_4NCH_2Br + LiBr + C_2H_4$$

$$\alpha\text{-}C_5H_4NCH_2Br + \alpha\text{-}C_5H_4NCH_2Li \longrightarrow 1,2\text{-bis(2-pyridyl)ethane} + LiBr$$

An electrolysis of a concentrated solution of 4-vinylpyridine in 85% methyltriethylammonium *p*-toluenesulfonate containing dimethylformamide[9] was conducted. The reaction was interrupted when precipitation of the product began to cause coating of the cathode. II was isolated in 82% yield[4]; previous multistep routes to II[10] have given poor yields.

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[1] Paper IV: M. M. Baizer, *J. Org. Chem.*, **29**, 1670 (1964).

[2] E. D. Bergmann, D. Ginsburg, and R. Rappo, *Org. Reactions*, **10**, 179 (1959).

[3] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 2, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, p. 812.

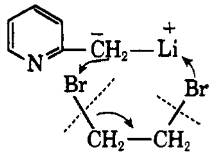
(4) Based on current input.

(5) G. Bianchetti, *Farmaco (Pavia), Ed. Sci.*, **11**, 346 (1956); *Chem. Abstr.*, **53**, 9209*g* (1959).

(6) *E.g.*, V. Ramanathan and R. Levine, *J. Org. Chem.*, **27**, 1667 (1962).

(7) G. Wittig and G. Harborth, *Ber.*, **77B**, 306 (1944).

(8) One can also postulate that the α-bromomethylpyridine arises *via* a six-membered cyclic intermediate transition state.



(9) The vinylpyridine was sufficiently soluble in the quaternary salt solution that use of an auxiliary solvent would not have been necessary.

(10) M. W. Goldberg and L. M. Jampolsky, U. S. Patent 2,624,735 (1953); *Chem. Abstr.*, **47**, P12426*i* (1953); L. M. Jampolsky, *et al.*, *J. Am. Chem. Soc.*, **74**, 5222 (1952); G. Magnus and R. Levine, *ibid.*, **78**, 4127 (1956); *J. Org. Chem.*, **22**, 270 (1957).