acid (10 g.; Victor Chemical Works, Chicago, Ill.) was added in one portion. Stirring was continued for 2 hr., after which 6.32 g. of thioacetic acid in 10 ml. of benzene was added during 1 hr. The mixture was then allowed to warm to room temperature while stirring was continued overnight. It was then cooled, and 25 ml. of ice water was added. A benzene extract of the product was washed with water and dried over anhydrous sodium sulfate. Removal of solvent and distillation resulted in 0.4 g. of forerun [b.p. 117–130° (0.2 mm.); n_D^{25}, 1.5802] and 11.1 g. (61%) of phenylmethanedithiol diacetate, b.p. 130–133° (0.2 mm.), m.p. 37–38°, n_D^{25} (supercooled), 1.5810.

Similarly prepared material recrystallized from petroleum ether (resulting diacetate m.p. 38–39°, n_D^{25} 1.5798), *n*-pentane, and cyclohexane had m.p. 38.5–39°; reported,[3] b.p. 122° (0.5 mm.), n_D^{25} 1.580, m.p. 37–38°.

Anal. Calcd. for $C_{11}H_{12}O_2S_2$: C, 54.97; H, 5.03; S, 26.68. Found: C, 55.08; H, 4.97; S, 26.90.

The infrared spectrum (cm.$^{-1}$) of phenylmethanedithiol diacetate, recorded with a liquid film between sodium chloride plates in a Model 137 Perkin-Elmer Infracord spectrophotometer, was as follows (s, strong; m, medium; w, weak; sh, shoulder): 3289 w; 2994 m; 2882 m; 1792 sh, w; 1706 s; 1595 sh, m; 1580 m; 1517 sh, m; 1495 s; 1456 s; 1422 s; 1359 s; 1290 w; 1220 w; 1179 sh, m; 1143–1093 s; 1033 m; 1003 m; 964–955 s; 917 sh, m; 837 m; 791 m; 722–712 s, broad; 692 s.

Aniline (7.75 g.) in benzene was added (1 hr.) to the diacetate (10 g.) in benzene at 10°. The mixture was allowed to warm with stirring (8 hr.) and was then heated at 40° (8 hr.) and let stand for 3 days. Filtration, removal of benzene, and addition of *n*-pentane resulted in 9.36 g. (83%) of acetanilide, m.p. and mixture m.p. 112–114°. Phenylmethanedithiol could not be isolated by distilling the filtrate or, in other experiments, by cleavage of phenylmethanedithiol diacetate with less aniline, with glycine, or with acidic methanol. When *p*-nitroaniline (11 g.) was heated with the diacetate (10 g.) in refluxing benzene for 24 hr., it was recovered in 83% yield.

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Formation of a Fluorocarbon Acid Chloride by the Electrochemical Fluorination Process[1]

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Received April 25, 1958

Electrochemical fluorination[2] is at present the chief synthetic process for the synthesis of monobasic perfluoro acids. In this method an organic acid chloride or fluoride in liquid hydrofluoric acid is subjected to a low direct current voltage, resulting in replacement of all alkyl hydrogens by fluorine. Although an acid fluoride gives somewhat better yields, an acid chloride can be employed since even without an impressed voltage the latter reacts with HF, usually very readily, to give the acid fluoride. Although there are numerous side reactions during the process, depending on the complexity of the starting material, the resulting perfluoro acids are always obtained as acid fluorides and there is no record in the literature of the appearance, in appreciable quantities, of acid chlorides among the cell products. This note describes the identification of bis(trifluoromethyl)-carbamyl chloride, $(CF_3)_2NCOCl$, as an electrochemical product from dimethylcarbamyl chloride, $(CH_3)_2NCOCl$.

It has been reported[3] that electrochemical fluorination of the latter compound gave chiefly $(CF_3)_2NCOF$; however, an unidentified product, b.p. 38.5°, mol. wt. 213–214, was often obtained. Dr. Max Rogers of Michigan State University, in a recent study[4] of the nuclear magnetic resonance spectrum of this material, found all the fluorine atoms to be equivalent and present in the form of CF_3 groups, and thereby suggested that the compound was the acid chloride, $(CF_3)_2NCOCl$. This structure has now been confirmed by elemental analysis and represents the first reported instance of a fluorocarbon acid chloride as a major component of the electrochemical products form an organic acid chloride.

As might be expected, the yield of $(CF_3)_2NCOCl$ relative to that of $(CF_3)_2NCOF$, increased with increasing concentration of the starting material in the electrolyte. At a minimum concentration, the yield of $(CF_3)_2NCOCl$ became very small, as the following table shows.

Dependence of $(CF_3)_2NCOCl$ Yield on Concentration

Mole % $(CH_3)_2NCOCl$ in electrolyte (approx.)	Ratio $(CF_3)_2NCOF$:$(CF_3)_2NCOCl$
0.2	30:1
0.6	8:1
0.9	5:1

Reproducibility of the figures above is not very good and the acid fluoride : acid chloride ratio may also be influenced by other variables such as cell temperature, condenser temperatures, or current density. In contrast to aliphatic acid chlorides, which react rapidly and completely with liquid HF, $(CH_3)_2NCOCl$ evolves HCl slowly and incompletely during the process, and it is evidently this reluctance to undergo halogen exchange with HF that permits the formation of $(CF_3)_2NCOCl$. Since $(CF_3)_2NCOCl$ is isolated from solution in liquid HF, it must share this peculiarity.

Pyrolysis of $(CF_3)_2NCOF$ gives good yields of perfluoro-2-azapropene, $CF_3N{=}CF_2$.[3] This reaction did not succeed with $(CF_3)_2NCOCl$ and except for a small amount of COF_2, no fractions with con-

(1) This work was supported by the Chemistry Branch of the Office of Naval Research. Reproduction of all or any part of this paper for purposes of the United States Government is permitted.

(2) J. H. Simons, *et al.*; *J. Electrochem. Soc.* **95**, 47 (1949); A. F. Clifford, H. K. El-Shamy, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.*, 2372 (1954); F. W. Hoffmann, T. C. Simmons, et. al., *J. Am. Chem. Soc.*, **79**, 3424 (1957).

(3) J. A. Young, T. C. Simmons, and F. W. Hoffmann, *J. Am. Chem. Soc.*, **78**, 5637 (1956).

(4) Personal communication from Dr. Rogers.

stant boiling point or constant molecular weight were obtained. With methanol, $(CF_3)_2NCOCl$ gave an ester identical with that obtained from $(CF_3)_2NCOF$.

EXPERIMENTAL

Conditions for the electrochemical fluorinations were similar to those described elsewhere.[2] If additions of starting material were made in accordance with the number of Faradays passed or with the amount of hydrogen liberated, it was observed that the amount of $(CF_3)_2NCOCl$ increased; on the other hand, when the concentration of starting material was kept to the minimum required for conductance purposes, the product was almost exclusively $(CF_3)_2NCOF$.

$(CF_3)_2NCOCl$ was obtained as a colorless liquid, b.p. 38.5°. The infrared spectrum showed a well defined doublet at 5.32, 5.48 microns, and other peaks at 6.96, 7.40, 7.72, 8.10, 8.72, 9.92, 11.70, 13.05, and 13.85 microns. The NMR spectrum showed a single peak, δ-value (relative to CF_3COOH) 20.6 cps.

Anal. Calcd. for C_3ClF_6NO: C, 16.7; Cl, 16.5; F, 52.8; mol. wt. 215. Found: C, 17.9; Cl, 16.4; F, 52.7; mol. wt. 214.

Pyrolysis. Thirty grams (0.14 mole) $(CF_3)_2NCOCl$ was heated in a stainless steel vessel for 6 hr. at 380–400°. Fractionation under a Dry Ice head gave 5 g. overhead, mol. wt. 65–65 (COF_2 mol. wt. 66, b.p. −90°); no other fractions of constant mol. wt. were obtained, and no distillation flats at −42° (COClF), or −30° to −33° ($CF_3N{=}CF_2$).

Esterification. Reaction with methanol and distillation of the washed and dried product gave a 61% yield of $(CF_3)_2NCOOCH_3$, b.p. 73–77°, n_D^{25} 1.2990, mol. wt. 211. Known values[3] are b.p. 76°, n_D^{25} 1.2997, mol. wt. 211. Infrared spectra of the two products were identical.

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Aliphatic Reserpine Analogs[1]

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Received May 2, 1958

Miller and Weinberg[3] reported recently that 3-(*N*-*N*-diethylamino)propyl 3,4,5-trimethoxybenzoate has significant reserpine-like activity (equivalent to one third of the potency of reserpine); they added that the corresponding diethylaminoethyl ester did not exhibit the same properties. In view of these statements, one would anticipate that the incorporation of four instead of three carbon atoms between the tertiary nitrogen and the ether oxygen of the ester linkage would yield a moiety (IV) resembling reserpine (I) more closely in its properties. In order to evaluate this conception we have prepared 4-(*N*,*N*-diethylamino)-butyl 3,4,5-trimethoxybenzoate (IV). Since the duration of pharmacological effectiveness may be occasionally extended by replacing an ester linkage with the corresponding amide coupling, we have also prepared the *N*-[4-(*N'*,*N'*-diethylamino)butyl]-3,4,5-trimethoxybenzamide (VII). The pharmacological evaluation of these compounds is in progress.

EXPERIMENTAL[4]

4-(N,N-Diethylamino)butyl acetate (II) was obtained (66% yield) from a condensation of 4-bromobutyl acetate and diethylamine; it distilled at 110–113°/22 mm., $n_D^{26.5}$ 1.4306, in accordance with the literature.[5]

4-(N,N-Diethylamino)butanol (III). Lithium aluminum hydride reduction of II yielded 76% III; it distilled at 110–112°/22 mm., $n_D^{27.5}$ 1.4459, in accordance with the literature.[6,7]

4-(N,N-Diethylamino)butyl 3,4,5-trimethoxybenzoate hydrochloride (IV). The acid chloride of 3,4,5-trimethoxybenzoic acid (10.6 g., 0.050 mole) was prepared as described by

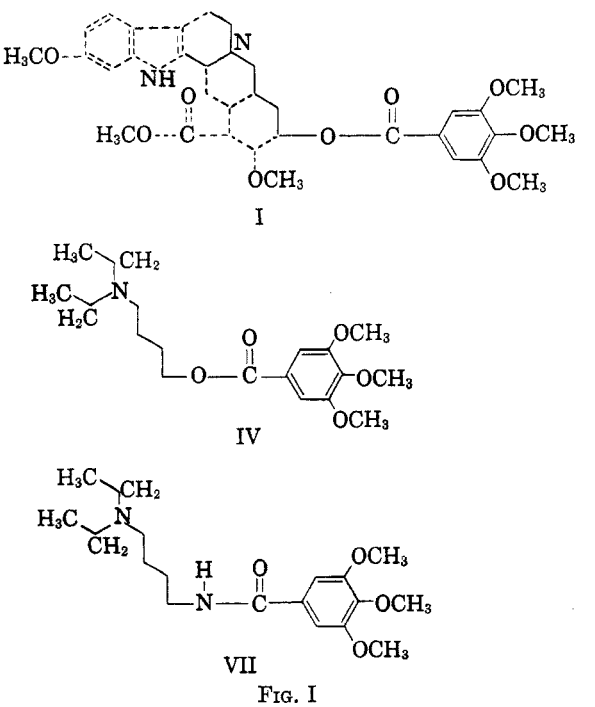

FIG. I

Lasslo and Jordan.[8] The acid chloride was dissolved in 300 ml. of dry benzene, and a solution of 7.3 g. (0.050 mole) of III in 100 ml. of dry benzene was added dropwise with continuous stirring; the temperature of the reaction mixture was maintained at 29–34°. The reaction mixture was agitated for 2 additional hr. at room temperature and, subsequently, refluxed for 2 hr. (steam bath). The hydrochloride of the ester crystallized out upon cooling; it was filtered off and

(1) This investigation is supported by a grant from the Geschickter Fund for Medical Research.

(2) Lecturer, Department of Pharmacy, Andhra University, Waltair, India (on study leave).

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