the electron pair of the nitrogen atom, coordination with the oxygen atom occurs preferentially.

Further work on the reduction of the *N*-substituted heterocyclics with aromatic character is in progress.

EXPERIMENTAL

Reduction of II *with lithium aluminum hydride.* A suspension of 10 g. (0.04 mole) of II[2] in 330 ml. of ether was added over 50 min. to a solution of 4 g. of lithium aluminum hydride in 250 ml. of ether. The milky white suspension was refluxed for 1 hr. before standing overnight. A grayish deposit covered with a fine white solid separated during the standing period. A total of 100 ml. of tetrahydrofuran was added and the mixture was refluxed for an additional 2 hr. Decomposition was carried out with 4 ml. of water, 4 ml. of 15% sodium hydroxide, and 12 ml. of water, in that order. The mixture was filtered and the filter cake washed with ether. The combined solvent extracts were washed with a saturated solution of sodium carbonate and the solvent phase dried over magnesium sulfate. Acidification and concentration of the sodium carbonate wash solution failed to yield any organic product. Concentration of the dried solvent phase produced 4 g. (93% yield) of benzyl alcohol, identified by its physical constants and the identity of its phenylurethan with an authentic specimen.

The filter cake was extracted in a Soxhlet extractor with benzene. Concentration of the benzene extract failed to yield any product. Extraction of the filter cake with dioxane gave 1 g. of solid having a m.p. above 210°. Flame ignition of a sample indicated a non-organic content. Extraction of the filter cake with ethyl acetate yielded 0.4 g. of a similar solid. The solid was dissolved in water and acidified to yield 1 g. (17% yield) of I, m.p. 149°. I gave the picrate of 1*H*-benzotriazole, m.p. 171–172° (reported[5] m.p. 173–174°).

The filter cake was suspended in water and acidified until a clear solution was obtained. The aqueous solution was extracted with 3 × 100 ml. portions of ethyl acetate, followed by concentration of the organic extracts to dryness. A total of 22 g. (46.8%) of 1*H*-benzotriazole, m.p. and mixed m.p. 95–97° (reported[5] m.p. 97–99°), was isolated.

Reduction of I *with sodium borohydride.* A solution of 10 g. (0.067 mole) of I in 200 g. of ethanol was added over 15 min. to a solution of 4.4 g. (0.116 mole) of sodium borohydride in 125 g. of ethanol. The clear reaction mixture was maintained at 35–40° during the addition and for an additional 1.5 hr. Decomposition was carried out with 25 ml. of water and the *p*H was adjusted to 7 with dilute hydrochloric acid. The mixture was filtered and the filtrate was concentrated to yield a white solid which was recrystallized from water. A total of 4.9 g. (61.5%) of benzotriazole was obtained.

Reduction of II *with sodium borohydride.* A solution of 10 g. (0.039 mole) of II in 175 g. of ethanol was added over a period of 10 min. to a solution of 2 g. of sodium borohydride in 75 g. of ethanol. The clear reaction mixture was maintained at 35–40° during the addition and for an additional 2 hr. Decomposition was carried out with 20 ml. of water and the *p*H was adjusted to 5 with dilute hydrochloric acid. After filtration the filter cake was washed with 25 ml. ethanol and the wash liquors were combined with the filtrate. The filtrate was concentrated and the residual oil and solid were taken up in ether and extracted with dilute hydrochloric acid. The dried ether layer was distilled to yield 2.9 g. (54.7%) of methyl benzoate, identified by physical constants and infrared spectrum. The aqueous acid extract was neutralized and on cooling gave 3.6 g. (78%) of benzotriazole.

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Phenylmethanedithiol Diacetate[1]

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Behringer and Grunwald recently described a series of diesters of *gem*-dithiols which had the general structure $RCH(SCOR')_2$.[2] Their study of preparations and properties was confined to symmetrical esters in which R and R′ were identical, presumably because they were interested chiefly in the catalyzed conversion of thio acids, alone, to such esters.

Prior to their report, we had prepared phenylmethanedithiol diacetate in yields of about 60% by reaction of thioacetic acid, benzaldehyde, and polyphosphoric acid.

$$C_6H_5CHO + 2\ CH_3COSH \xrightarrow{\text{Polyphosphoric acid}} C_6H_5CH(SCOCH_3)_2$$

Although Behringer and Grunwald mentioned a synthesis of 1,1-propanedithiol dipropionate from thiopropionic acid, propionaldehyde, and phosphorus pentoxide, description also seemed desirable of our work, since it illustrates the use of polyphosphoric acid, probably a milder condensing agent, and extends the method to the preparation of an unsymmetrical ester.

Phenylmethanedithiol diacetate melts at about 37–38°[3] rather than at 147–148°.[4] It has an infrared spectrum resembling those of alkyl thiolacetates,[5] and it acylates aniline under mild conditions[6] but not *p*-nitroaniline which (like 2,4-dinitrophenylhydrazine)[2] evidently is too weakly basic.

Application of the method to cyclohexanone gave unpromising results; the distilled product had a wide range of boiling point and refractive index and differed in analysis by several per cent from the values calculated for 1,1-cyclohexanedithiol diacetate.

EXPERIMENTAL[7]

Thioacetic acid (6.32 g.) was added in one portion with stirring to 8.0 g. of benzaldehyde cooled in an ice bath. After 2 hr. of stirring, the mixture began to solidify and was allowed to warm to a mushy consistency, after which stirring was continued for 2 hr. The mixture was then completely immersed again in the ice bath and polyphosphoric

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[1] Research supported by the Office of Ordnance Research, U. S. Army.

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[6] Cf. R. Schwyzer, *Helv. Chim. Acta*, **36**, 414 (1953).

[7] Melting points are corrected and boiling points uncorrected. Analyses by Micro-Tech Laboratories, Skokie, Ill.

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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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-

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[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.

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[4] Personal communication from Dr. Rogers.