various infrared and elemental analyses. We are also indebted to Drs. F. C. Meyer, M. C. Freerks, and F. B. Zienty for valuable suggestions and advice.

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Preparation of Perfluoronitrosoalkanes. Reaction of Trifluoroacetic Anhydride with Nitrosyl Chloride

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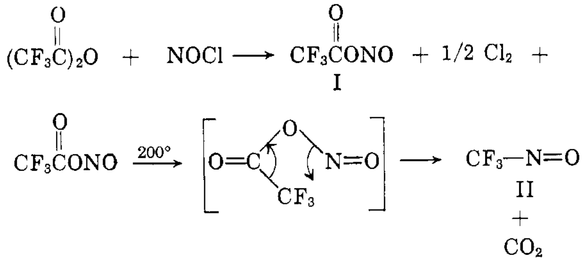
When trifluoroacetic anhydride is treated with nitrosyl chloride at room temperature, distillation of the products at atmospheric pressure leads to low yields of trifluoronitrosomethane. However, under vacuum distillation a yellow liquid is obtained which is quite reactive toward common solvents and various metals. Analysis of this compound shows it to be trifluoroacetyl nitrite (I). Pyrolysis of I at 200° produces trifluoronitrosomethane (II) in greater than 85% yields.



$$(CF_3\overset{O}{\overset{\|}{C}})_2O + NOCl \longrightarrow \underset{I}{CF_3\overset{O}{\overset{\|}{C}}ONO} + 1/2\,Cl_2 +$$

$$CF_3\overset{O}{\overset{\|}{C}}ONO \xrightarrow{200^\circ} [\ldots] \longrightarrow \underset{II}{CF_3{-}N{=}O} + CO_2$$

Care must be exercised in heating the acyl nitrites for they have a tendency to detonate at high temperatures.

The scope of this reaction may prove to be quite extensive as it has been successfully applied to the pentafluoropropionic and heptafluorobutyric anhydrides.

EXPERIMENTAL

Reaction of trifluoroacetic anhydride with nitrosyl chloride. In an evacuated 7-l. flask equipped with one two-way stopcock and one three-way stopcock, 45 g. of trifluoroacetic anhydride, and 22 g. of nitrosyl chloride were introduced in the vapor state. The gases were condensed by cooling the flask with Dry Ice and then allowed to warm up to room temperature.

A 300-watt incandescent lamp was positioned a few inches from the flask and irradiation was continued for two days with intermittent shaking.

Yield: 10.1 g. of trifluoroacetyl nitrite, n_D^{25} 1.3722, b.p. 46°/80 mm.

Anal. Calcd. for $C_2F_3O_3N$: C, 16.80; N, 9.79; F, 39.72. Found: C, 17.00; N, 9.85; F, 39.72.

Trifluoronitrosomethane was characterized by its infrared spectrum and the physical properties found to be identical with that produced by the method of Haszeldine.[1]

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(1) R. N. Haszeldine, *J. Chem. Soc.*, 2075 (1953).

A New Preparation of 2-Methylthio-4,6-dichloropyrimidine and Synthesis of 2-Alkylthio-4-chloro(or methoxy)-6-pyrimidinols

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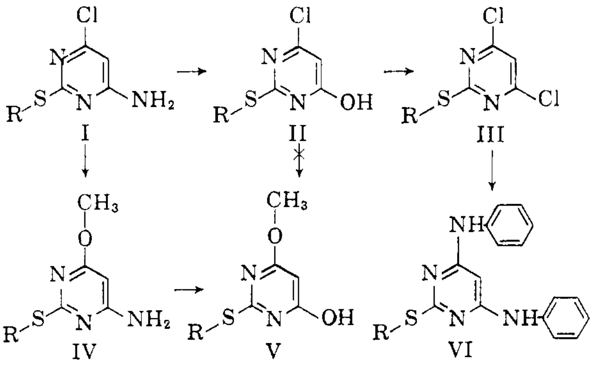
2-Methylthio-4,6-dichloropyrimidine (III, R = CH_3)[1,2] is a very important intermediate for the preparation of a number of pyrimidine derivatives. The present communication describes a convenient synthesis of this compound by chlorination of 2-methylthio-4-chloro-6-pyrimidinol (II, R = CH_3)[1] with phosphoryl chloride in the presence of the dimethylaniline.

Unlike previously described syntheses of 2-methylthio-4,6-dichloropyrimidine, this method does not involve the 2-methylthio-4,6-pyrimidinediol as intermediate.[2] The yield of dichloropyrimidine (III, R = CH_3) from 6-pyrimidinol (II, R = CH_3) (96%) compares favorably with those



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(1) H. C. Koppel, R. H. Springer, R. K. Roland, and C. C. Cheng, *J. Org. Chem.*, **26**, 794 (1961); H. C. Koppel, R. H. Springer, and C. C. Cheng, *J. Org. Chem.*, **26**, 1884 (1961).

(2) H. L. Wheeler and G. S. Jamieson, *Am. Chem. J.*, **32**, 342 (1904).