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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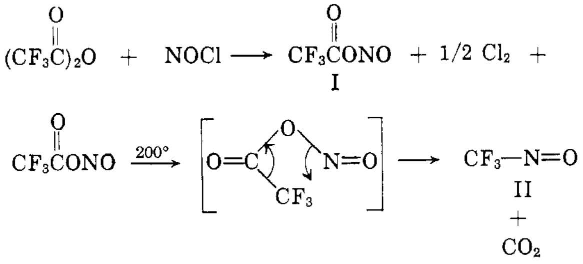
When trifluoroacetic anhydride is treated with nitrosyl chloride at room temperature, distillation of the products at atmospheric pressure leads to low yields of trifluoronitrosomethane. However, under vacuum distillation a yellow liquid is obtained which is quite reactive toward common solvents and 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.



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

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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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

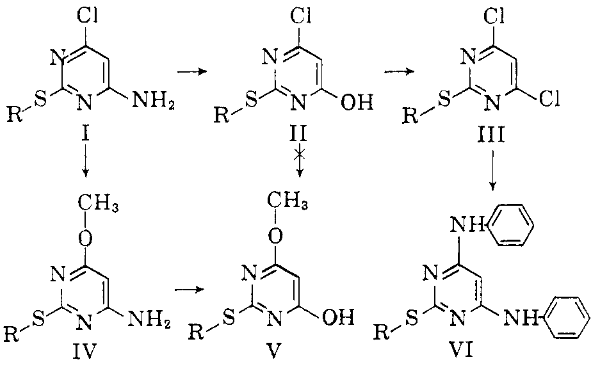

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TABLE I

Compound	R	Yield, %	M.P., °C.	Carbon, %		Hydrogen, %		Nitrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
I	n-C_3H_7	23	97	41.28	40.94	4.95	5.17	20.64	20.38
I	i-C_3H_7	16	98	41.28	41.42	4.95	5.11	20.64	20.75
II	CH_3	85	215–216	34.00	34.32	2.85	3.01	15.86	15.38
II	$C_6H_5CH_2$	99	207–208	52.27	52.43	3.95	4.01	11.09	11.34
III	CH_3	96	41–42	30.77	31.15	2.05	2.42	14.36	15.02
V	CH_3	90	191	41.85	41.54	4.68	4.82	16.27	16.01
VI	CH_3	75	132	66.21	66.42	5.23	5.41	18.17	17.94

obtained by the previously reported procedures. The reaction of dichloro compound (III) (1 mole) with aniline (2 moles) gave the 4,6-dianilino compound (VI).

Lythgoe *et al.*[3] pointed out that the reaction of 2-methylthio-4-chloro-6-aminopyrimidine (I, R $= CH_3$) with nitrous acid did not give the 5-nitrosopyrimidine, but they did not confirm that I ($R = CH_3$) gave the 6-pyrimidinol (II, $R = CH_3$). We found that both 2-methylthio-4-methoxy-6-aminopyrimidine (IV, $R = CH_3$),[4,5] and 2-alkylthio-4-chloro-6-aminopyrimidine (I),[4,6] when treated with sodium nitrite, gave a good yields of the corresponding 6-pyrimidinols (II, V). The preparation of II ($R = CH_3$) from III ($R = CH_3$) has been reported by Koppel *et al.*[1]

The methoxylation of compound I ($R = CH_3$) with sodium methoxide at 120° gave IV ($R = CH_3$), but compounds II did not give V by the same method at 120–160°. The 6-pyrimidinols II and V showed strong infrared absorption at 1660 cm.$^{-1}$.

Table I lists the data obtained with the above compounds.

EXPERIMENTAL

2-Alkylthio-4-chloro-6-aminopyrimidine (I). The compound I ($R = CH_3$) was made by previously described procedures.[4] Compounds I ($R = C_6H_5CH_2$, n-C_3H_7, i-C_3H_7) were synthesized in the presence of dimethylaniline.[6]

2-Methylthio-4-methoxy-6-aminopyrimidine (IV, $R = CH_3$).[5] A 5.0-g. sample of 2-methylthio-4-chloro-6-aminopyrimidine was dissolved in 50 ml. of methyl alcohol to which 1.2 g. of metallic sodium had previously been added. The mixture heated in a sealed vessel at 120° for 3 hr. The alcohol was removed by evaporation under reduced pressure and the residue was stirred with water and mixture was acidified with hydrochloric acid and filtered. The white residue was recrystallized from aqueous alcohol; yield 4.4 g.

2-Alkylthio-4-chloro(or methoxy)-6-pyrimidinols (II, V). To the 6-aminopyrimidines (I, V) (1 mole) dissolved in a minimal amount of glacial acetic acid was gradually added an excess of sodium nitrite (2 moles) at room temperature. During the addition the temperature was maintained at room temperature. The reaction mixtures were allowed to stand at room temperature for 40 hr. with occasional stirring and then filtered to give light-yellow solids. The crude products were recrystallized from aqueous alcohol. Yields and analyses are given in Table I.

2-Methylthio-4,6-dichloropyrimidine (III). Dimethylaniline (3.5 g.) was added to a suspension of 2-methylthio-4-chloro-6-pyrimidinol (5.0 g.) in phosphoryl chloride (50 ml.) and heated at boiling point for 2 hr. After removal of the excess of phosphoryl chloride under reduced pressure, the reaction mixture was poured on ice (100 g.) and filtered. The precipitate was extracted with three 100-ml. portion of ether, each of which was then used to extract the aqueous filtrate. The combined ether extract was washed with three 50-ml. portion of water and dried over anhydrous sodium sulfate. Upon evaporation of ether, crude crystals (5.0 g.) were obtained, m.p. 38–39°. After one recrystallization from aqueous alcohol, the m.p. was 41–42°.

2-Methylthio-4,6-dianilinopyrimidine (VI).—A mixture of 2-methylthio-4,6-dichloropyrimidine (1 g.), aniline (0.9 g.), glacial acetic acid (25 ml.), and concentrated hydrochloric acid (2 ml.) was heated at refluxing temperature for about 4 hr. The resulting solution was treated with charcoal for decolorization and filtered hot. The desired product precipitated partially on cooling, but for complete precipitation the solution was neutralized with 10*N* sodium hydroxide. The precipitate was filtered, thoroughly washed with water, and crystallized from 60% alcohol. Yield and analyses are given in Table I.

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Azo and Hydrazo Compounds. I. An Attempt to Prepare the *N*-Oxide of 3,6-Diphenyl-1,2,4,5-tetrazine

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As part of an over-all study of new preparations and reactions of azo compounds, the synthesis of

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