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Thiolcarbamates from the Reaction of Dialkylamines with Carbon Monoxide and Sulfur

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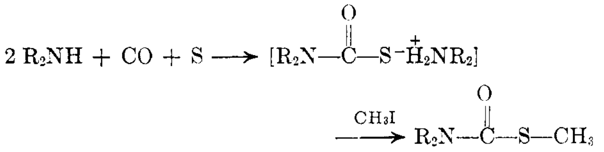
A new synthesis for mono-, di-, and trisubstituted ureas involving the reaction of carbon monoxide and sulfur with amines has been reported recently.[1] It was of interest, therefore, to investigate the hitherto unreported reaction of dialkylamines with carbon monoxide and sulfur. It was found that di-*n*-butylamine and diisopropylamine reacted to yield their respective dialkylammonium dialkylthiolcarbamates in substantial yields.



$$2\,R_2NH + CO + S \longrightarrow [R_2N{-}\overset{O}{\overset{\|}{C}}{-}S^{-}\overset{+}{H_2}NR_2] \xrightarrow{CH_3I} R_2N{-}\overset{O}{\overset{\|}{C}}{-}S{-}CH_3$$

R = isopropyl or *n*-butyl

EXPERIMENTAL[2,3]

Reaction of diisopropylamine with carbon monoxide and sulfur followed by reaction with methyl iodide. A mixture of diisopropylamine (101 g., 1 mole), sulfur (32 g., 1 mole), and tetrahydrofuran (200 ml.) was charged to a 1.4-l. bottom-stirred autoclave which was purged with nitrogen and then sealed. Carbon monoxide was injected into the autoclave until a pressure of 300 p.s.i. was reached. The stirred mixture was heated to 120° during 35 min. The temperature of the mixture was then maintained at 120° and the pressure at 400 p.s.i. by occasional injection of carbon monoxide during 1 hr. The autoclave was cooled to 0° and the gases were vented. Methyl iodide (142 g., 1 mole) was added dropwise to the stirred mixture at 0–10°. The thick slurry was stirred at room temperature for 3 hr. The mixture was filtered, and the crystals were washed with ether. Ether was added to the filtrate until no more crystals separated. The mixture was filtered and the filtrate was evaporated to an oil which was distilled to yield *S*-methyl diisopropylthiolcarbamate (53 g., 0.30 mole, 60% yield), b.p. 92–96.5°/14 mm., n_D^{25} 1.4831.

The infrared spectrum had a peak at 6.05 μ (C=O) and was identical with that of a sample prepared in the same manner having b.p. 96–96.5°/14 mm., n_D^{25} 1.4822.

Anal. Calcd. for $C_8H_{17}NOS$: C, 54.81; H, 9.78; N, 7.99; S, 18.22. Found: C, 54.99; H, 9.42; N, 7.92; S, 18.57.

In another experiment the mixture of crystals and liquid obtained from the reaction of diisopropylamine with carbon monoxide and sulfur was cooled to −10°. The slurry was filtered; the crystals were washed with ether (200 ml.) and pressed dry with a filter dam for 1 hr. The filtrate was cooled to −80° for 1 hr. The solid which separated was combined with the first crop to yield diisopropylammonium diisopropylthiolcarbamate (79.6 g., 0.30 mole, 60% yield). The infrared spectrum was identical with that of an authentic sample prepared from the reaction of carbonyl sulfide with diisopropylamine.

Reaction of di-n-butylamine with carbon monoxide and sulfur followed by methyl iodide. A mixture of di-*n*-butylamine (129 g., 1 mole), sulfur (32 g., 1 mole), and tetrahydrofuran (200 ml.) was treated in a similar manner to the case of diisopropylamine. The reaction mixture was heated to 90° during 30 min. at a carbon monoxide pressure of 200 p.s.i. The autoclave was maintained at a temperature of 90–94° and 200 p.s.i. for 10 min., then cooled to room temperature. Methyl iodide (142 g., 1 mole) was added under the usual conditions. There was obtained *S*-methyl di-*n*-butylthiolcarbamate (62.5 g., 0.31 mole, 62% yield), b.p. 79–80°/0.2 mm., n_D^{25} 1.4781 (lit.[4] b.p. 144.5–146°/20 mm.; n_D^{30} 1.4761).

The infrared spectrum had a peak at 6.1 μ (C=O) and was identical with that of a sample prepared in the same manner.

Anal. Calcd. for $C_{10}H_{21}NOS$: C, 59.07; H, 10.41; N, 6.89 S, 15.77. Found: C, 59.05; H, 10.57; N, 6.71; S, 15.77.

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[1] (a) F. Applegath, M. Barnes, and R. Franz, U. S. Pat. **2,857,430** (1958); *Chem. Abstr.*, **53**, 5296h (1959). (b) *Cf.*, F. Applegath and R. Franz. U. S. Pat. **2,874,149** (1959); *Chem. Abstr.*, **53**, 12187f (1959). (c) *Cf.*, F. Applegath and R. Franz, U. S. Pat. **2,857,392** (1958); *Chem. Abstr.*, **53**, 5286e (1959).

[2] All boiling points are uncorrected.

[3] Elemental analyses were performed by the Galbraith Laboratories, P. O. Box 4187, Knoxville, Tenn.

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The Structure of the Crystalline Peroxide Formed in the Oxidation of Acetaldehyde

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Wieland[1] first proposed an addition product of peracetic acid and acetaldehyde to be an intermediate in the liquid-phase autoxidation of acetaldehyde to acetic acid, and Lösch[2] later isolated, analyzed, and determined the physical properties of such an intermediate. Since then there has been controversy over its structure. The following structures for this peroxide intermediate have been proposed. Wieland,[1] Lubarsky and Kagen,[3] Lösch,[2] Golding,[4]

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[1] H. Wieland, *Ber.*, **54**, 2357 (1921).

[2] H. Lösch, P.B. 52007, pp. 23, 101. Office of Technical Service, U. S. Department of Commerce, Washington, D. C.

[3] G. D. Lubarsky and M. J. Kagen, *J. Phys. Chem.*, **39**, 847 (1935).

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