

# Dialkylaminomethyl Sulfides: An Improved Synthesis

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Dialkylaminomethyl sulfides are obtained in excellent yields from the reaction of secondary amines with formaldehyde and either aliphatic or aromatic thiols. The reaction occurs smoothly at room temperature in the absence of added catalyst.

DURING another study, several dialkylaminomethyl alkyl (aryl) sulfides were required. A survey of the literature revealed two significant references on their preparation (1,2). According to these reports, the dialkylaminomethyl sulfides are formed in erratic yields. For example, from the reactions of morpholine and formaldehyde with thiophenol and *m*-thiocresol, the corresponding morpholino-methyl aryl sulfides were obtained in yields of 33 and 79%, respectively (1). Grillot prepared the dialkylaminomethyl aryl sulfides by combining the reactants at 20°C. and then holding at 80°C. for 2 to 3 hours. McLeod and Robinson used somewhat milder conditions to prepare the dialkylaminomethyl alkyl sulfides in yields of 50 to 60% (2). Their reactions were at room temperature employing a saturated potassium carbonate solution. The inconsistent yields prompted an investigation of this seemingly simple reaction.

Dialkylaminomethyl sulfides can be formed in high yields by appropriate modifications of the reported procedures.

The method of McLeod implies that the reaction will occur under moderate conditions; however, the use of  $K_2CO_3$  seemed superfluous. If a basic medium is required, the amine should furnish the necessary basicity even after reaction with formaldehyde.

Working on this premise, a series of aminosulfides was prepared. The reaction was carried out by adding the secondary amine to a formaldehyde solution maintained at 25 to 30°C., then the thiol was added while maintaining the same temperature. Excellent yields (85 to 95%) of dialkylaminomethyl sulfides were obtained from both aliphatic and aromatic mercaptans. The reaction can be represented by the equation:



$R$  = alkyl or alkylene



$R'$  = alkyl or aryl

Table I. Dialkylaminomethyl Alkyl (Aryl) Sulfides  $R_2NCH_2SR'$

Reactants		Products					
Mercaptan	Amine	B.P., °C. (Mm.)	Yield, %	Calcd., %		Found, %	
				S	N	S	N
<i>sec</i> -Butyl	Diethyl	48-49(0.6)	87	18.3	8.1	18.2	7.9
<i>iso</i> -Propyl	Diethyl	42(1.2)	90.5 <sup>a</sup>	19.9	8.7	20.0	9.2
<i>m</i> -Thiocresol	Diethyl	97(0.5)	91.5 <sup>b</sup>	15.3	6.7	15.8	6.8
<i>p</i> -Chlorothiophenol	Diethyl	104-105(0.6)	84.1 <sup>c</sup>	14.0	6.1	14.3	6.2
Thiophenol	Morpholine <sup>f</sup>	125-126(1.0)	91.5 <sup>d</sup>	15.3	6.7	15.5	6.6
<i>sec</i> -Butyl	Morpholine	68(0.4)	91.5	17.0	7.4	17.3	7.9
<i>tert</i> -Butyl	Morpholine	73(0.9)	90.5	17.0	7.4	17.0	7.6
Thiophenol	Piperidine <sup>e</sup>	113-114(0.5)	95.0 <sup>e</sup>	15.5	6.8	15.7	6.8

<sup>a</sup>50.8% yield reported in (2). <sup>b</sup>55% yield, (1). <sup>c</sup>43% yield, (1). <sup>d</sup>33% yield, (1). <sup>e</sup>67% yield, (1). <sup>f</sup>Product,  $N_D^{25}$  1.5815; value given in (1)  $N_D^{25}$  1.5809. <sup>g</sup>Product  $N_D^{25}$  1.5787; value given in (1)  $N_D^{25}$  1.5789.

Table II. Proton Chemical Shifts<sup>a</sup> for Dialkylaminomethyl Sulfides

Compound	Proton	$\delta$ , P.P.M.	Multiplicity	No. Protons
$C_6H_5SCH_2N$ 	ArH	7.3	Multiplet	5
	SCH <sub>2</sub> N	4.26	Singlet	2
	CH <sub>2</sub> O	3.5	Multiplet	4
	CH <sub>2</sub> N	2.5	Multiplet	4
$p\text{-ClC}_6\text{H}_4\text{SCH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$	ArH	7.2	Multiplet	4
	SCH <sub>2</sub> N	4.44	Singlet	2
	NCH <sub>2</sub>	2.57	Quartet	4
	CH <sub>3</sub>	0.96	Triplet	6
$(\text{CH}_3)_3\text{CSCH}_2\text{N}$ 	SCH <sub>2</sub> N	3.66	Singlet	6
	CH <sub>2</sub> O	3.6	Multiplet	6
	CH <sub>2</sub> N	2.5	Multiplet	4
	CH <sub>3</sub>	1.31	Singlet	9

<sup>a</sup>P.p.m. downfield from tetramethylsilane. Measured in carbon tetrachloride.

Keeping the reaction temperature low and the conditions simple apparently minimizes side reactions, which could account for the reported inconsistent yields. The results are summarized in Table I, along with the yields obtained with one of the other methods. Refractive indices confirmed that the earlier materials and those from this study were comparable. Nuclear magnetic resonance, in addition to elemental analyses, was used to substantiate the purity. The proton chemical shifts for several representative members are given in Table II. Decomposition of the dialkylaminomethyl aryl sulfides is appreciable above 150° C.; consequently, some of the previously reported low yields may be a result of loss during distillation (3).

#### EXPERIMENTAL

**General Procedure for Preparation of Dialkylaminomethyl Alkyl (and Aryl) Sulfides.** A secondary amine (0.5 mole) was added in 30 to 40 minutes to 41 grams (0.5 mole) of a 36% formaldehyde solution (<1% methanol) main-

tained at 25 to 30° C. with a water bath. The thiol (0.5 mole) was then added in 15 to 20 minutes. Again, cooling was required to control the temperature at 25° to 30° C. The mixture was stirred for an additional 2 to 3 hours at room temperature, and then 50 ml. of ether was added and the aqueous layer removed. The organic layer was washed twice with 50-ml. portions of water and dried over anhydrous magnesium sulfate. After filtration, the ether was distilled and the product purified by fractional distillation.

#### LITERATURE CITED

- (1) Grillot, G.F., Felton, H.R., Garrett, B.R., Greenberg, H., Green R., Clementi, R., Moskowitz, M., *J. Am. Chem. Soc.* **76**, 3969 (1954).
- (2) McLeod, C.M., Robinson, G.M., *J. Chem. Soc.* **119**, 1470 (1921).
- (3) Vineyard, B.D., Monsanto Co., St. Louis, Mo., unpublished data, 1966.

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## Hydrocarbon By-Products from the Rochow Direct Process for Methylchlorosilanes

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**In the reaction of methyl chloride with silicon by the Rochow direct process, hydrocarbons are troublesome by-products. They complicate distillation of methylchlorosilanes, and in gas chromatograms, their peaks can be mistaken for peaks of minor organosilicon components. Hydrocarbons were separated by distillation of hydrolyzed methylchlorosilanes and by gas chromatography; they were identified by infrared spectroscopy. Twenty-four hydrocarbons—11 reported here for the first time—have been found thus far in products of the industrial-scale direct process. A table is given listing the hydrocarbon by-products together with their boiling points.**

EVER SINCE the early days of the silicone industry, it has been known that hydrocarbons are present in the methylchlorosilanes produced in the reaction of methyl chloride with silicon by the Rochow direct process (3). Certain of these hydrocarbons, because of their boiling points and the formation of azeotropes (5), complicated laboratory and plant distillations of methylchlorosilanes. Recently, there has been a new interest in these hydrocarbon by-products because of the wide use of gas chromatography in the silicone industry. Hydrocarbons are troublesome because, in a chromatogram, their peaks can be mistaken for peaks of minor organosilicon components. To prevent such mistakes, it helps to know which hydrocarbons have been identified, thus far, in the methylchlorosilanes from the direct process.

The work reported here confirms the presence of some of the hydrocarbons found by previous investigators. In addition, 11 more hydrocarbons, not reported previously, were separated from direct-process products and identified by infrared spectroscopy.

#### EXPERIMENTAL

**Separation of Hydrocarbons from Methylchlorosilanes.** Before the use of gas chromatography, hydrocarbons were separated from methylchlorosilanes by converting the methylchlorosilanes to polysiloxanes, and then distilling lower-boiling hydrocarbons from the polysiloxanes. In a typical experiment, 2000 grams of methylchlorosilanes from the

plant were hydrolyzed by the slow addition of 1000 grams of water at a temperature below 25° C. After hydrolysis, the lower aqueous hydrochloric acid layer was drawn off and discarded. The upper siloxane layer was washed and dried over anhydrous sodium sulfate. This siloxane portion then was distilled, and the low boiling distillation cuts were collected for infrared analysis. The distillation was stopped at the boiling point of the lowest-boiling siloxane. The infrared bands of hydrocarbons are so much weaker than those of siloxanes that there was little chance of infrared identification of a hydrocarbon present as a minor component in a siloxane.

Recently, gas chromatography has been used to fractionate further the distillation cuts from hydrolyzed methylchlorosilanes. Several instruments were used: Autoprep A-700, F & M 500, and F & M 720. The carrier gas was helium. The most useful column proved to be a 10-foot column packed with 60- to 80-mesh Chromosorb P coated with General Electric Co. SE-30 silicone gum. Fractions from the gas chromatograph were condensed in U-shaped glass capillaries cooled with dry ice. In other experiments, chromatographic fractions were passed directly into an infrared gas cell.

**Infrared Analysis.** Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrometer, equipped with a sodium chloride prism, or a Perkin-Elmer Model 521 grating spectrometer. Distillation cuts were examined in 0.03- and 0.1-mm. sealed liquid cells. Gas chromatography fractions, trapped in capillaries, were washed into a 0.1-mm. cell