

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.

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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

Table I. Hydrocarbons Identified in Products of the Reaction $\text{CH}_3\text{Cl} + \text{Si} \xrightarrow{\text{Cu}}$

Compound	Boiling Point, ° C. ^a	Found in Waterford Methylchlorosilanes	Found by Other Investigators (Ref.) ^b
Methane	-161	X	(3, 6, 7)
Ethene	-104		(7)
Ethane	-88.6		(7)
2-Methylpropane	-11.7	X	
2-Methylpropene	-6.9	X	
2-Methylbutane	27.9	X	
2-Methyl-1-butene	31.2	X	
2-Methyl-2-butene	38.6	X	
2,2-Dimethylbutane	49.7	X	
2,3-Dimethylbutane	58.0	X	
2-Methylpentane	60.3	X	(5)
3-Methylpentane	63.3	X	(5)
2,3-Dimethyl-2-butene	73.2	X	
Benzene	80.1	X	(1)
2,2,3-Trimethylbutane	80.9	X	
Dimethylpentanes	80-90	X	
Heptenes of the types RR'C=CH ₂ and RR'C=CHR''	80-95	X	
2-Methylhexane	90.1	X	(1, 5)
3-Methylhexane	91.8	X	(1, 5)
Methylcyclohexane	100.9		(1)
Toluene	110.6	X	(1)
Ethylbenzene	136.2		(1)
Methylethylbenzene(s)	161-165		(1)
Diethylbenzene(s)	181-184		(1)

^a (4). ^b Zuckerman's review (8) pointed out some of these references.

with a few drops of carbon disulfide. Some gas chromatography fractions were examined directly in a 10-cm. gas cell.

Hydrocarbons were identified by comparison of the infrared patterns with the reference spectra in the catalog of infrared spectral data published by American Petroleum Institute Research Project 44 (2).

Because of the complexity of certain C₇ fractions, two hydrocarbons are described only by type and molecular weight. Mass spectroscopy showed the presence of C₇H₁₆ alkanes and C₇H₁₄ alkenes, while infrared spectroscopy revealed the nature of the branching and the types of double bonds.

RESULTS

Table I shows twenty-four hydrocarbons that have been identified, thus far, in methylchlorosilanes produced by the Rochow direct process. Thirteen of these hydrocarbons already have been reported in the literature. The remaining 11—six alkanes and five alkenes—are reported here, the author believes, for the first time. The accepted value (4) of the boiling point of each hydrocarbon is included to help predict where the hydrocarbon will appear in a gas chromatogram.

An outstanding feature of the alkanes and alkenes from the direct process is the prevalence of branched structures. One is tempted to start writing free-radical reactions and to explain the finding of 2-methylpropane rather than *n*-butane by the greater stability of a secondary propyl free radical compared with a primary propyl free radical. There are at least two reasons why such explanations of the hydrocarbon structures might be invalid:

Some of the hydrocarbon by-products may come from impurities in the methyl chloride used. Like previous investigators, we worked with products from the industrial-scale direct process, where it is difficult to associate a distillation fraction with a particular batch of methyl chloride.

The list of hydrocarbons found in the methylchlorosilanes is a composite of results of separate analyses of various

plant streams. All parts of the distillation range were not studied with equal thoroughness; consequently, the absence of a hydrocarbon from the list does not necessarily mean that the hydrocarbon is not present in methylchlorosilanes.

Despite these limitations, this list of hydrocarbon by-products may be useful to others who are working on fractionation and analysis of methylchlorosilanes from the direct process. As analytical techniques get better, more hydrocarbons will likely be added to the list.

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