Experimental

Isolation of Di-*n*-propyl Carbinol.—*n*-Butyraldehyde (7.93 moles) and di-*t*-butyl peroxide (0.79 mole) were heated at 2 atmospheres pressure and 115° for sixteen and one-half hours in an all-glass system. The evolved propane and carbon monoxide were bled off at a rate which would maintain pressure. The product was washed with concentrated sodium bisulfite solution. The remaining organic phase was separated and steam distilled to remove hexane and unreacted di-*t*-butyl peroxide. The remaining product was dried and fractionated. The fraction distilling at 153–155.5° had an index n^{20}_D 1.4193 and contained 71.6% carbon and 13.7% hydrogen. The corresponding literature values for 4-heptanol are b. p. 153.4–154.4°,[4] n^{20}_D 1.4199,[4] carbon 72.3% and hydrogen 13.8%. The 3,5-dinitrobenzoate was prepared; m. p., 64.5° (lit. m. p., 64°).[5] This alcohol was isolated in a yield of 8–10% based on the consumed aldehyde. Over 70% of the aldehyde was converted to propane and carbon monoxide.

Isolation of Di-*n*-hexyl Carbinol.—*n*-Heptaldehyde (1.75 moles) and di-*t*-butyl peroxide (0.34 mole) were heated at 130° for five and one-half hours in a glass system provided with a reflux condenser. Carbon monoxide (0.61 mole) was evolved and hexane (0.59 mole) was recovered by distillation. Finally nearly all of the material which could be steam distilled was separated and the remainder, after drying, was run through a falling film molecular still at 71°. The distillate amounting to 24 cc. was cooled in ice and the crystals filtered off. The solid waxy material was evaporated under 0.1 mm. pressure onto an ice-cooled thimble. This material melted at 40.5–41° and analyzed 77.7% carbon and 13.8% hydrogen. Di-*n*-hexylcarbinol has a reported melting point of 41–42°[6] and contains 78.0% carbon and 14.0% hydrogen.

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[4] Dillon and Lucas, THIS JOURNAL, **50**, 1712 (1928).

[5] Adkins, Connor and Cramer, *ibid.*, **52**, 5192 (1930).

[6] Kipping, *J. Chem. Soc.*, **57**, 536 (1890).

SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIFORNIA
RECEIVED JULY 20, 1948

The Reaction between Morpholine and Chloral[1]

BY G. B. L. SMITH[2], MEYER SILVER[3] AND ERNEST I. BECKER

The products of the reaction of an aqueous solution of morpholine and chloral at 25° are chloroform and morpholine formate.[4] It was believed that in anhydrous solution N-containing analogs of DDT could be obtained. It was hoped that the alcohol-like product, similar to that for morpholine and formaldehyde,[5] would condense with a second molecule or morpholine to give an analog of DDT. However, in the present work it was found that when a slight excess of morpholine was added to a solution of chloral in isopropyl or *n*-butyl ether, N-formylmorpholine was formed in 90–92% yield. The product was identified by its physical constants, by analysis, and by preparation of derivatives of the morpholine and formic acid obtained from its hydrolysis. Chloroform was recovered in 84% yield as the only other product of the reaction.

Similar reactions with chloral or chloral hydrate have been reported in which ethylenediamine gives the diformyl derivative[6] and with N-methyl-α-homopiperonylamine and piperidine to give the monoformyl derivatives.[7]

Experimental

Materials.—Anhydrous chloral was prepared by shaking crude chloral with concentrated sulfuric acid and distilling the chloral from the mixture, b. p. 96–97° (767 mm.). Morpholine was dried over fused potassium hydroxide, filtered and distilled, b. p. 125–128° (767 mm.). Isopropyl ether was washed with ferrous sulfate to remove peroxides, dried, and distilled, b. p. 67–69° (759 mm.). *n*-Butyl ether was distilled, b. p. 140–142° (760 mm.).

Procedure.—In a 500-ml., 3-neck, round-bottom flask, equipped with a reflux condenser, dropping funnel and mechanical stirrer, was placed a solution of 74 g. (49.2 ml., 0.50 mole) of chloral in 150 ml. of *n*-butyl ether. To the stirred solution was added rapidly 48 g. (48 ml., 0.55 mole) of morpholine. A white precipitate formed, and the solution rapidly reached the boiling point of the *n*-butyl ether.

The condenser was set for downward distillation and distilled at atmospheric pressure to remove the chloroform. The remainder was distilled at reduced pressure to remove the *n*-butyl ether and finally to give 53 g. (0.46 mole, 92%) of formylmorpholine, b. p. 239.5–240.5° (760 mm.) (cor.), b. p. 120–122° (19–20 mm.), m. p. 20–21°, n^{25}_D 1.4840, d^{26}_4 1.145.[8]

Anal. Calcd. for $C_5H_9NO_2$: C, 52.17; H, 7.83; N, 12.17; morpholine, 75.5. Found: C, 52.27; H, 7.30; N, 12.12; morpholine 75.3.

A portion of the morpholide was hydrolyzed with 10% sulfuric acid and distilled. Neutralization and concentration of the filtrate gave sodium formate, m. p. 254.5° (cor.) (reported m. p. 253°).[9] The sulfuric acid solution was made alkaline and distilled to give morpholine which was identified by its picrate, m. p. 149–150°, m. m. p. with authentic morpholine picrate 149–150°, and by its thiuram disulfide prepared according to Shupe,[10] m. p. 150–151° (reported m. p. 150–151°).

The forerun obtained in the original reaction was distilled through a 12-in. Hempel column packed with glass beads to give 50 g. (0.418 mole, 83.8%) chloroform b. p. 59–61°, n^{25}_D 1.4483.

When isopropyl ether was substituted for *n*-butyl ether the same yield of N-formylmorpholine was obtained, but the chloroform could not be separated readily from this ether.

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[1] This work was begun under the guidance of Professor G. B. L. Smith and completed under the supervision of Professor Ernest I. Becker.

[2] Present address: Naval Ordnance Testing Station, Inyokern, California.

[3] Present address: Nopco Chemical Company, Harrison, New Jersey. This paper was taken from the Master's Thesis of Meyer Silver, June, 1947, Department of Chemistry, Polytechnic Institute of Brooklyn.

[4] Ling Yang and Pin-Fong Hu, *J. Chinese Chem. Soc.*, **10**, 190 (1943).

[5] M. Zief and J. P. Mason, *J. Org. Chem.*, **8**, 1 (1943).

[6] A. W. Hofmann, *Ber.*, **5**, 247 (1872).

[7] E. Merck, German Patent 334,555 (M. 66126), Kl. 120.

[8] P. Médard, who prepared the compound from morpholine and formic acid, reported the following constants: b. p. 234° (760 mm.), m. p. 17.5° (*Bull. soc. chim.*, [5] **3**, 1343 (1936)).

[9] Lange's "Handbook," 6th Ed., 1946.

[10] I. S. Shupe, *J. Assoc. Offic. Agr. Chemists*, **23**, 824 (1940).

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RECEIVED AUGUST 3, 1948

Hydrocarbon By-products from the Methyl Chloride–Silicon Reaction

BY ROBERT O. SAUER, W. J. SCHEIBER AND E. M. HADSELL

During a fairly large-scale study of the synthesis of methylchlorosilanes by the direct reac-

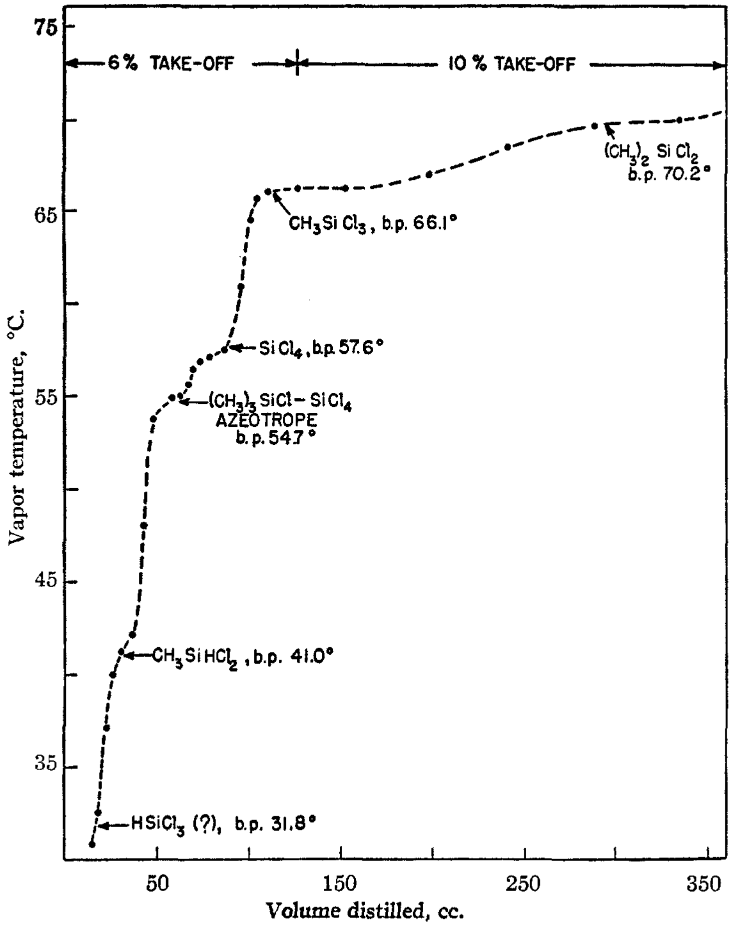

Fig. 1.—Analytical distillation of crude methylchlorosilanes.

tion of methyl chloride with silicon[1] it became apparent that several compounds other than the desired products were present. Certain of these substances, because of their boiling points and the formation of azeotropes, complicated the purification of the methylchlorosilanes. It is our purpose to describe the isolation, identification and distillation behavior of these substances more or less independently of a detailed description of the operation of the reactors.

With trimethylchlorosilane, b.p. 57.7°, one often finds silicon tetrachloride, b.p. 57.6°, and the C_6 paraffin hydrocarbons. The appearance of these compounds in the crude product reflects inadequate temperature control of the exothermic reaction of silicon with methyl chloride. The methyl groups thus thermally destroyed appear as hydrocarbons, or sometimes as chlorohydrocarbons (*e.g.*, ethylidene chloride). The disproportionately high ratio of chlorine to the methyl groups remaining increases the yield of silicon tetrachloride. A further manifestation of the decomposition of methyl groups under these conditions is the appearance in the crude product of compounds containing hydrogen bonded to silicon, that is, trichlorosilane, b.p. 32°, and methyldichlorosilane, b.p. 41°. A typical distillation curve for such a crude product from our 4"-diameter vertical, static bed reactors is shown in Fig. 1.

Although hydrocarbons have also appeared with dimethyldichlorosilane the most serious distillation difficulty was encountered in the purification of trimethylchlorosilane (Figs. 2, 3). First of all, silicon tetrachloride forms an azeotrope[2] with this compound, b.p. 54.7°. Secondly, we now have found that both the 2- and 3-methylpentanes form azeotropes with trimethylchlorosilane. Further, we suspect the occasional presence of ethylidene chloride, b.p. 57.4°; this forms minimum-boiling, binary azeotropes with both trimethylchlorosilane and silicon tetrachloride, and possibly forms a ternary with these compounds.

In considering the proper batch distillation procedure for the crude products (before we knew of the presence of hydrocarbons) we had planned to take off the dimethyldichlorosilane, b.p. 70.2°, at a rather low reflux ratio, after the difficult separation between this compound and methyltrichlorosilane, b.p. 66.1°, had been effected. We

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(1) Rochow, This Journal, 67, 963 (1945).

(2) Sauer and Hadsell, This Journal, 70, 4258 (1948).

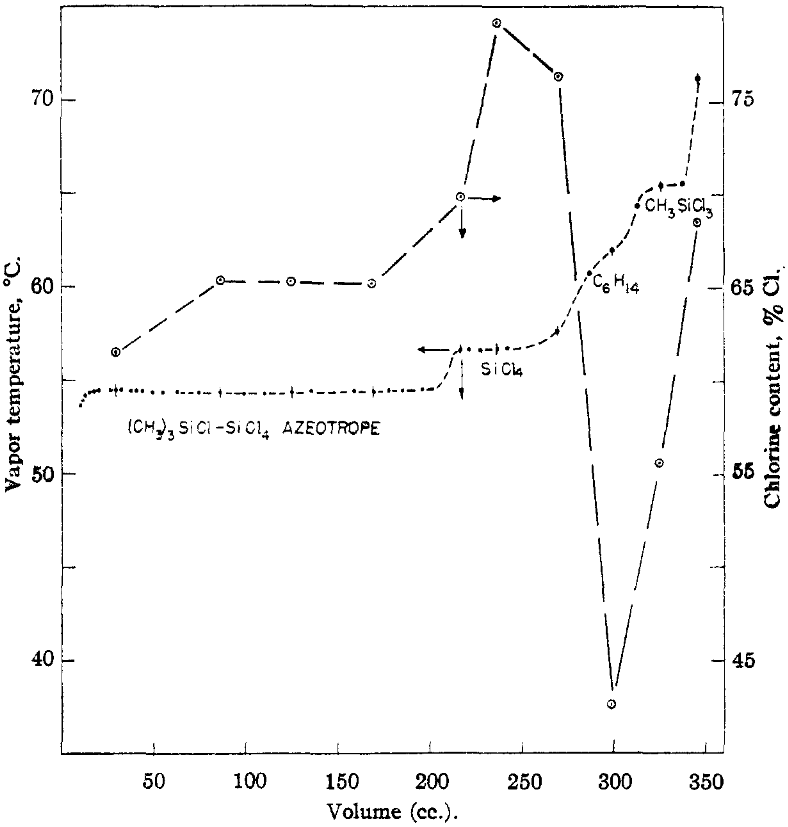

Fig. 2.—Analytical distillation of "trimethylchlorosilane fraction" from process still (excess $SiCl_4$).

found, however, that such a procedure at a reflux ratio of 3:1 gave a product of low density and low hydrolyzable chlorine content. This proved to be due to the presence of some C_7 paraffins distilling at about 81° and at about 90° (Fig. 4). No azeotropism was involved, however.

In order to isolate the inert but complicating substances, which were generally present in rather small concentrations, we hydrolyzed large batches of the chlorosilane concerned and distilled the hydrocarbons from the relatively high boiling siloxanes.

Experimental

Hydrocarbons Associated with Trimethylchlorosilane.—Four consecutive fractions of impure trimethylchlorosilane were hydrolyzed: 32.2 kg., 24.4% Cl; 26.3 kg., 27.8% Cl; 32.7 kg., 29.3% Cl; 18.3 kg., 31.3% Cl. (The calculated hydrolyzable chlorine content for $(CH_3)_3SiCl$ is 32.64% Cl). Distillation of the resulting product (71.3 kg.) gave, in addition to hexamethyldisiloxane, 15.4 kg. (nine fractions) of a mixture of hydrocarbons (b.p. 56–64°) of which roughly 40–50% was 2-methylpentane and 45–50% was 3-methylpentane. The identification of these compounds was established by careful redistillation in a 2.2 m., 9.5 mm. diameter Stedman column.[3] A portion of the first fraction was twice distilled, yielding, finally, ten 25-ml. fractions of 2-methylpentane, each of which gave the constants given in Table I. A portion of the seventh fraction from the large-scale distillation gave twenty-four 25-ml. fractions of 3-methylpentane with physical properties within the ranges given in Table I. Only a very small amount of unsaturated material could be detected in the foreruns.

TABLE I

PHYSICAL CONSTANTS OF THE METHYLPENTANES

	2-Methylpentane		3-Methylpentane	
	Found	Accepted[4]	Found	Accepted[4]
n^{20}_D	1.3714	1.3715	1.3764–6	1.3766
d^{20}_4 (vac.)	0.6529	0.6532	0.6640–1	0.66435
Normal b. p., °C.[5]	60.4	60.30	63.2–63.5	63.23

Several binary mixtures with trimethylchlorosilane were tested for the existence of minimum boiling azeotropes. The more volatile of the two liquids was placed in a boiling point apparatus[5] and the second component added portionwise, observing meanwhile the effect on the boiling point. 2-Methylpentane was found to produce a maximum depression of boiling point (1.3°) at approximately 35 volume per cent of the hydrocarbon. 3-Methylpentane also forms a minimum boiling azeotrope at about 30 volume per cent of hydrocarbon, but with a much smaller depression (0.4°). The effect of these two hydrocarbons during the purification of the desired chlorosilane is illustrated in Fig. 3.

With silicon tetrachloride the boiling point depression observed with 2-methylpentane was too small to justify a definite statement on the existence of a binary azeotrope at atmospheric pressure. 3-Methylpentane added to silicon tetrachloride gave only an elevation of the boiling

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(3) Bragg, *Ind. Eng. Chem., Anal. Ed.*, **11**, 283 (1939).

(4) M. P. Doss, "Physical Constants of the Principal Hydrocarbons," 4th ed., The Texas Co., New York, N. Y., 1943.

(5) Quiggle, Tongberg and Fenske, *Ind. Eng. Chem., Anal. Ed.*, **6** 466 (1934).

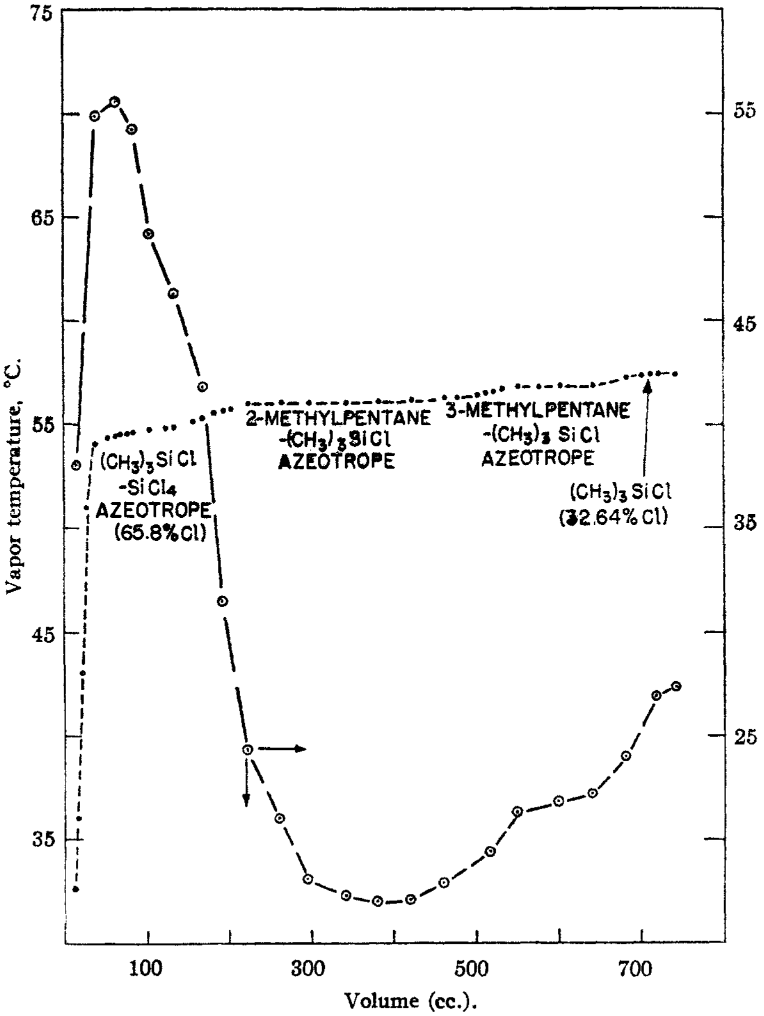

Fig. 3.—Analytical distillation of "trimethylchlorosilane fraction" from process still (excess $(CH_3)_3SiCl$).

point. The effect of these on the separation of silicon tetrachloride is illustrated in Fig. 2.

The Silicon Tetrachloride–Ethylidene Chloride Azeotrope.—Occasionally hydrolysis of trimethylchlorosilane fractions low in hydrolyzable chlorine yielded traces of low boiling (b.p. 54–57.5°) material which gave a strongly positive Beilstein test for halogen but did not react with hot aqueous silver nitrate nor decolorize bromine. This substance had the odor of chloroform but gave a negative result in the characteristic isonitrile test. Refractive indices (n^{20}_D) ranged from 1.394 to 1.415. Later, large scale distillation of crude chlorosilane mixtures indicated a fairly constant-boiling fraction at 52–53° (760 mm.) with a specific gravity (27/27) of 1.263 and which contained 53.4% of hydrolyzable chlorine. This was believed to be essentially a minimum boiling binary of silicon tetrachloride and ethylidene chloride (b. p. 57.4°) or possibly a ternary of these with trimethylchlorosilane. By distilling a mixture of silicon tetrachloride and ethylidene chloride the existence of such a binary azeotrope was confirmed. It has the following properties: b. p. 52.7° (753 mm.), 53.0% hydrolyzable chlorine, d^{27}_{27} 1.352. A cooling effect was noted on mixing the two components.

A binary azeotrope apparently exists also between ethylidene chloride and trimethylchlorosilane which mixture has a boiling point approximately 1° lower than that of the two components. Its composition is at present ill-defined.

It might be remarked, parenthetically, that with silicon tetrachloride, chloroform was found to form an azeotrope, b. p. 55.6° (742 mm.), containing 59.0% of hydrolyzable chlorine. Although ethylene chloride was observed to depress the boiling point of silicon tetrachloride the effect is so slight that it is difficult to decide whether or not it is real. No minimum boiling azeotrope is formed by trimethylchlorosilane with either chloroform or carbon tetrachloride.

Hydrocarbons Associated with Dimethyldichlorosilane.—In order to isolate the contaminating but inert materials from dimethyldichlorosilane 117 kg. of this substance which was somewhat low in hydrolyzable chlorine (54.6 *vs.* 54.95%, calcd.) was hydrolyzed, and the neutral hydrolyzate stripped by distillation yielding 262 g. of liquid, b. p. 80–150°. After drying, this distillate was charged to a 2.2 m., 9.5 mm. diameter Stedman column for fractional distillation. The normal boiling points,[5] refractive indices and densities were measured on each of the fifteen 10-g. fractions removed at 50:1 reflux ratio. These data are presented graphically in Fig. 4. About 20% (four fractions) of the charge (240 g.) had the following properties: b. p. 90.1°, n^{20}_D 1.3885, d^{20}_4 0.6879, specific refraction 0.3434, and is presumably a mixture of 2-methyl- and 3-methylhexanes for which accepted constants[4] are as follows: 2-methylhexane, b. p. 90.10°, n^{20}_D 1.3849, d^{20}_4 0.6787; 3-methylhexane, b. p. 91.96°, n^{20}_D 1.3887, d^{20}_4

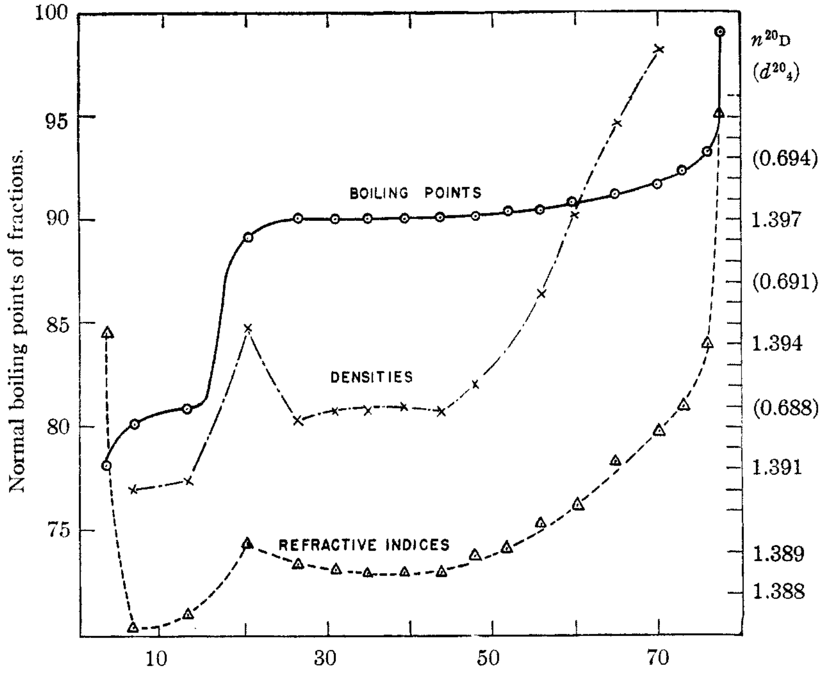

Fig. 4.—Distillation of C_7 hydrocarbons from dimethyldichlorosilane hydrolyzates.

0.6870. No azeotrope is formed between this material and dimethyldichlorosilane.

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RECEIVED MAY 17, 1948

Azeotropes of Trimethylchlorosilane and Silicon Tetrachloride

BY ROBERT O. SAUER AND E. M. HADSELL

In the course of identifying some of the less abundant products[1] of the reaction of methyl chloride with silicon[2] a constant-boiling material (b.p. 54.7°) was obtained which proved to be a mixture of silicon tetrachloride (b.p. 57.6°) and trimethylchlorosilane (b.p. 57.7°). We thought it might be of some interest to describe our characterization of this material and to summarize (Tables I and II) the properties of several other azeotropes of these two substances. These latter azeotropes were characterized in our attempts to discover azeotroping agents for resolving the $(CH_3)_3SiCl-SiCl_4$ binary. Both acetonitrile and acrylonitrile were found to be suitable for this purpose.[3]

Experimental

The first isolation of the $(CH_3)_3SiCl-SiCl_4$ binary was accomplished in a 90 cm., 19 mm. diameter vacuum-jacketed Stedman column.[4] The material then obtained possessed the following properties: b. p. 54.6 ± 0.1° (755 mm.), 65.57 ± 0.05% Cl, mol. wt. (vapor density extrapolated to zero pressure) 140–145, mol. wt. (f. p. depression in cyclohexane) 245–250, vapor pressure at 0° 86 ± 0.5 mm. A portion of the mixture upon treatment[5] with ethylene oxide (Method A) yielded a mixture of trimethyl-2-chloroethoxysilane and tetrakis-2-chloroethyl silicate containing 45 mole per cent. of the former (46 mole per cent. would be required for a $(CH_3)_3SiCl-SiCl_4$ mixture with 65.6% Cl).

TABLE I

AZEOTROPES WITH TRIMETHYLCHOLOROSILANE (A-COMPONENT)

B-Component	B. p. (B), °C.	B. p. (azeo), °C.	Wt. % A
Silicon tetrachloride	57.6	54.7	35.2
2-Methylpentane[1]	60.3	56.4	*ca.* 70
3-Methylpentane[1]	63.2	57.3	*ca.* 75
Acetonitrile	82	56.0	92.6
Acrylonitrile	79	57.0	93
Ethylidene chloride[1]	57.4	*ca.* 56	?

TABLE II

AZEOTROPES WITH SILICON TETRACHLORIDE (A-COMPONENT)

B-Component	B. p. (B), °C.	B. p. (azeo), °C.	Wt. % A
Trimethylchlorosilane	57.7	54.7	64.8
Ethylidene chloride[1]	57.4	53	63.5
Acetonitrile	82	49.0	90.6
Acrylonitrile	79	51.2	89
Propionitrile	97	55.6	92
Nitromethane	101	53.8	94
Chloroform[1]	61.3	56	*ca.* 70

Sauer and Reed[3] have reported the resolution of this azeotrope with inert components such as acetonitrile and acrylonitrile which behave as azeotropizing agents. With

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[1] Sauer, Scheiber and Hadsell, THIS JOURNAL, **70**, 4254 (1948).

[2] Rochow, *ibid.*, **67**, 963 (1945).

[3] Sauer and Reed, U. S. Patent 2,388,575 (Nov. 6, 1945).

[4] Bragg, *Ind. Eng. Chem., Anal. Ed.*, **11**, 283 (1939).

[5] Patnode and Sauer, THIS JOURNAL, **67**, 1548 (1945).