Anal. Calcd. for $C_{12}H_{20}$: C, 87.8; H, 12.2. Found: C, 87.2; H, 12.1.

Acknowledgment.—This investigation was carried out under the sponsorship of the Standard Oil Company (Indiana), and the results are published with their permission.

Summary

1. Methods have been developed for the preparation of methylcyclopentenes from methylcyclopentane.

2. A method has been described for the separation of 1-methylcyclopentene from mixtures of isomeric methylcyclopentenes.

3. The dehydration of the isomeric methylcyclopentanols and the dehydrochlorination of the methylcyclopentyl chlorides have been investigated.

4. It has been shown that the cyclic olefin boiling at 75° obtained by dehydration of 3-methylcyclopentanol is 1-methylcyclopentene and not 4-methylcyclopentene as reported by previous investigators.

5. Several new reactions of the methylcyclopentenes have been studied and some new compounds in the methylcyclopentane series have been synthesized.

COLUMBUS, OHIO RECEIVED MARCH 4, 1948

[CONTRIBUTION FROM MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

Synthesis of Alkoxymethyltrimethylsilanes

BY JOHN L. SPEIER

Whitmore and Sommer[1] have studied the reactivity of chloromethyltrimethylsilane relative to the reactivity of *n*-hexyl chloride in a series of nine reactions involving replacement of the chlorine, sometimes in alkaline solution, and apparently without isolation of the products of the reactions. The subsequent work of Krieble and Elliott[2] showed that alkaline reagents caused hydrolytic cleavage of chloromethylsiloxanes. Speier and Daubert[3] similarly showed that rapid hydrolytic cleavage of dichloromethyltrimethylsilane occurred in alcoholic sodium ethoxide. In view of these data it seemed well to examine the products of the reaction of chloromethyltrimethylsilane and sodium alkoxides and to determine whether or not cleavage of the chloromethyl group occurred in this reaction as well.

The results of this investigation showed that sodium methoxide in boiling methanol solution caused no detectable amount of cleavage, but resulted in a good yield of methoxymethyltrimethylsilane. Sodium ethoxide in boiling ethanol solution caused a moderate amount of cleavage (about 11%) and afforded a 70% yield of ethoxymethyltrimethylsilane. Sodium *n*-butoxide in boiling *n*-butanol caused considerable cleavage resulting in about 31% of butoxytrimethylsilane, and only 19% butoxymethyltrimethylsilane.

Experimental Part

Preparation of Ethers. *Preparation of Methoxymethyltrimethylsilane.*—Sodium (26 g., 1.13 moles) was dissolved in dry methanol (400 ml.). To the solution chloromethyltrimethylsilane (122.5 g., 1 mole) was added and the solution was refluxed for twenty-four hours before being distilled through a three-foot Stedman column. The distillation curve revealed only three plateaus. The first, b. p. 60° (165 ml.) proved to be an azeotropic mixture of methoxymethyltrimethylsilane and methanol containing 64% of the ether by volume. A sample from this plateau washed with water yielded the ether, b. p. 83°, $n^{25}\text{D}$ 1.3878. The second plateau was poorly defined (85 ml.) b. p. 61°, and contained the ether, methanol and chloromethyltrimethylsilane. The third plateau at 64° contained methanol and no silicon compound. The residue contained no silicon. The first and second fractions were combined, washed with water and redistilled. There was thus obtained methoxymethyltrimethylsilane (114 ml., 75%), b. p. 83° at 740 mm., $n^{25}\text{D}$ 1.3878, d^{25}_4 0.7576. *Anal.* Calcd.[4] for Me_3SiCH_2OMe: mol. refr., 36.68. Found: mol. refr., 36.80. Calcd. for $C_5H_{14}OSi$: C, 50.80; H, 11.94; mol. wt., 118.2. Found: C, 50.57, 50.45; H, 11.83, 11.81; mol. wt. (Victor Meyer), 116.5, 116.2.

There was recovered unreacted chloromethyltrimethylsilane (20 g., 16% of original b. p. 97° at 740 mm., $n^{25}\text{D}$ 1.4145). No indication was found that cleavage of the chloromethyl compound had occurred.

Preparation of Ethoxymethyltrimethylsilane.—The procedure just described was repeated using absolute ethanol in place of the methanol. In this case, however, the solution was neutralized with dry hydrogen chloride and filtered before distillation. Distillation of the material revealed the presence of about 20 ml. of trimethylethoxysilane–ethanol azeotrope,[5] b. p. 65.5°, containing some unreacted chloromethyltrimethylsilane; 25 ml. of a chloromethyltrimethylsilane–ethanol azeotrope containing some ethoxymethyltrimethylsilane, b. p. 72°, and 205 ml. of the ether–ethanol azeotrope, b. p. 74°, containing an appreciable amount of unreacted chloride. Ethanol followed these fractions at 78° and contained no silicon compounds. No silicon was found in the residue.

The fractions were analyzed in the following manner: The first fraction was shaken with dilute hydrochloric acid. Heat was evolved and 10 ml. of liquid was recovered, b. p. 100°, $n^{25}\text{D}$ 1.3890. Qualitative analysis showed the presence of silicon and chlorine in this liquid. The liquid was shaken with cold concentrated sulfuric acid. Approximately 1.5 ml. of chloromethyltrimethylsilane separated, b. p. 97°, $n^{25}\text{D}$ 1.4142. When this had been removed the sulfuric acid solution was diluted with water. Hexamethyldisiloxane separated, b. p. 99°, $n^{25}\text{D}$ 1.3785. The second fraction was 56% by volume, water-insoluble, and also contained silicon and chlorine, b. p. 97°, $n^{25}\text{D}$ 1.4050. This fraction was washed out with water and shaken with cold concentrated sulfuric acid. The acid-insoluble por-

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(1) Whitmore and Sommer, THIS JOURNAL, **68**, 481 (1946).

(2) Krieble and Elliott, *ibid.*, **68**, 2291 (1946).

(3) Speier and Daubert, *ibid.*, **70**, 1400 (1948).

(4) Warrick, *ibid.*, **68**, 2455 (1946).

(5) Sauer, *ibid.*, **66**, 1707 (1944).

tion was separated, b. p. 97°, n^{25}_D 1.4134, and identified as chloromethyltrimethylsilane. The acid-soluble portion was recovered b. p. 102°, n^{25}_D 1.3904, and was apparently the ethyl ether. The third fraction was washed several times with water and dried over calcium chloride to yield a product (101 ml.) which was distilled b. p. 99–102°, n^{25}_D 1.3972–1.3915, d^{25}_4 0.798–0.761. An appreciable amount of chloride was present in this material. The last fraction obtained (30 ml.) was free of the chloride by qualitative tests and possessed the properties: b. p. 102° at 739 mm., n^{25}_D 1.3915, d^{25}_4 0.761. Calcd. for $Me_3SiCH_2OC_2H_5$: mol. refr.,[4] 41.31; mol. wt., 132. Found: mol. refr., 41.32; mol. wt. (Victor Meyer), 136. The other slightly lower boiling fractions were refluxed for several hours over sodium and redistilled, b. p. 103° at 751 mm., n^{25}_D 1.3911, d^{25}_4 0.755. *Anal.* Calcd. for $C_6H_{16}OSi$: Si, 21.2. Found: Si, 20.8, 20.9, 21.6; mol. refr., 41.61; mol. wt., 131. From distillation curves, density data on various fractions obtained, etc., the following approximate composition was arrived at in mole percentages: trimethylethoxysilane, 11%; unreacted chloromethyltrimethylsilane, 18%; ethoxymethyltrimethylsilane, 70%. The presence of no other silicon compounds was indicated.

The ethyl ether exploded with extreme violence when vaporized in a stream of oxygen, when analysis for carbon and hydrogen was attempted. The product did not give a positive test for peroxide, nor did its physical constants vary over a period of several weeks. It also exploded when mixed with sodium peroxide for fusion to determine the silicon content, but the silicon content could be determined by a wet combustion technique,[6] care being taken to avoid loss by volatilization during the early stages of the analysis.

Preparation of Butoxymethyltrimethylsilane.—The same procedure described for the preparation of the ethyl ether was followed using dry *n*-butanol in place of the ethanol. Distillation of the products revealed a small amount of material (5 cc.) b. p. 70°, containing no silicon which might be methoxybutane. The next fraction was unreacted chloromethyltrimethylsilane (13 ml., 9% of starting material), b. p. 92–102°. The third fraction (100 ml.) was identified as butoxytrimethylsilane-*n*-butanol azeotrope,[4] b. p. 111°, n^{25}_D 1.394–1.398, corresponding to about a 31% yield of this product. (To confirm the identity of this fraction, a portion of it was heated to reflux for eight hours with a 100% excess of acetyl chloride to convert the butoxy silane to the corresponding chlorosilane and *n*-butyl acetate and the alcohol to the same ester, an easily separable mixture. The products were distilled and yielded only two fractions. The first was a mixture of acetyl chloride and trimethylchlorosilane, b. p. 49°, which yielded hexamethyldisiloxane on washing with water, b. p. 100°, n^{25}_D 1.3750. The second fraction was *n*-butyl acetate, b. p. 125°, d^{25}_4 0.881.) After most of the *n*-butanol, b. p. 116°, had been distilled from the reaction mixture, solids in the flask caused severe bumping. The distillation was interrupted and the material was washed with water, dried and the distillation was continued. The butyl ether was obtained (36 ml., 19%), b. p. 150° at 738 mm., d^{25}_4 0.774, n^{25}_D 1.4038. Calcd. for $C_8H_{20}OSi$: Si, 17.5; mol. refr.,[4] 50.67. Found: Si, 17.6, 17.1; mol. refr., 50.64.

The molecular weight of the compound could not be determined by the Victor Meyer method because the samples repeatedly exploded when vaporized in air. No qualitative test for peroxides was obtained from samples of the liquid, nor did its physical constants change on standing. A thick semi-solid non-volatile residue remained after the distillation. This residue contained silicon and was flammable, but was not identified.

The infrared absorption spectra of all three ethers prepared were very much alike, and revealed the strong maximum at 1100 cm.$^{-1}$ characteristic of alkyl ethers.

Summary

The synthesis of three new ethers, methoxymethyl-, ethoxymethyl- and butoxymethyltrimethylsilanes is reported, and the tendency of chloromethyltrimethylsilane to undergo hydrolytic cleavage under the influence of alcoholic sodium alkoxides was studied.

PITTSBURGH 13, PA. RECEIVED JULY 6, 1948

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[6] Speier, Daubert and McGregor, THIS JOURNAL, **70**, 1118 (1948).

[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE]

Studies on the Willgerodt Reaction. VI. A Mechanism for the Primary Thiol Oxidation[1]

BY FREEMAN H. MCMILLAN[2] AND JOHN A. KING[2]

An earlier communication[3] from this Laboratory suggested a mechanism for the Willgerodt reaction which has seemed to account satisfactorily for all the known facts. At that time, as well as subsequently,[4] experimental data have been presented and pertinent contributory literature has been cited in support of the reactions postulated to occur intermediate to the starting material (A) and a primary thiol (B). Although a suggestion was also made concerning the conversion of the primary thiol (B) to an amide or thioamide (C), no supporting evidence was offered for this conversion. There have now been carried out experiments which enable us to draw definite conclusions regarding the mechanism of the transformation of B to C. These experiments and the interpretation of their results form the subject of the present paper.

$$\underset{A}{RCOCH_3} \longrightarrow \underset{B}{RCH_2CH_2SH} \longrightarrow \underset{C}{RCH_2CSNR_2'}$$

Before proceeding directly with a discussion of these experiments, it is thought worthwhile to briefly consider a few other relevant points. It seems highly probable to us that the intrinsic mechanism of the reaction, as applied to aldehydes, ketones, alcohols, olefins, acetylenes and imines, is the same, whether it is carried out with aqueous ammonium polysulfide as originally done by Willgerodt or whether it is carried out with sulfur and an amine as was first used by Kindler; Stanek[5] has recently carried out the following reactions, by heating the material with three moles

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[1] For the preceding paper of this series see McMillan and King, THIS JOURNAL, **69**, 1207 (1947).

[2] Present address: Warner Institute for Therapeutic Research, 113 West 18th Street, New York 11, N. Y.

[3] King and McMillan, THIS JOURNAL, **68**, 632 (1946).

[4] King and McMillan, *ibid.*, **68**, 1369 (1946).

[5] Stanek, *Collection Czechoslov. Chem. Commun.*, **12**, 671 (1947).