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Studies in the Methylcyclopentane Series. II. Preparation and Reactions of Methylcyclopentenes[1]

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During the course of an investigation on methylcyclopentane and its derivatives, methods for the preparation of the isomeric methylcyclopentenes were studied. Both the dehydration of methylcyclopentanols and the dehydrochlorination of methylcyclopentyl chlorides were investigated. The results obtained indicated that the physical constants reported in the literature[3] for 4-methylcyclopentene are in error and led to a more detailed study of this olefin.

The preparation of 1-methylcyclopentene by dehydration of 1-methylcyclopentanol has been described by several investigators.[4]

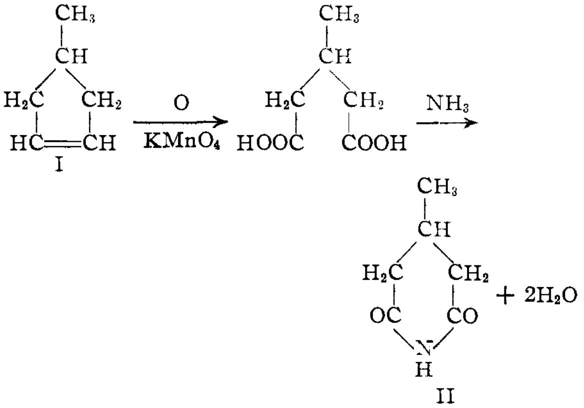
Starting with methylcyclopentane, we prepared the mixed monochlorides as described in the first paper in this series.[5] The monochlorides were converted by dehydrochlorination into a mixture of isomeric methylcyclopentenes. Only the tertiary olefin reacted with hydrogen chloride and the separation of the resulting tertiary chloride from the secondary methylcyclopentenes was accomplished readily by distillation. The tertiary chloride on dehydrochlorination gave only 1-methylcyclopentene.

Dehydration experiments with all three of the isomeric methylcyclopentanols were carried out. 1-Methylcyclopentanol on warming with a trace of iodine gave an 89% yield of 1-methylcyclopentene. 2-Methylcyclopentanol, when dehydrated over activated alumina, gave 1-methylcyclopentene and 3-methylcyclopentene in approximately a 3:1 mole ratio.

The dehydration of 3-methylcyclopentanol with oxalic acid,[3a] sulfuric acid[3b] and phosphoric oxide[6] has been reported by different investigators. Mousseron[3b] obtained methylcyclopentenes boiling at 65 and 75° by dehydrating 3-methylcyclopentanol with sulfuric acid. The lower boiling olefin was considered to be 3-methylcyclopentene and the higher boiling product was thought to be 4-methylcyclopentene on the basis of oxidation studies. However, we have found that the 75° fraction reacts with hydrogen chloride to give 1-chloro-1-methylcyclopentane, identified by hydrolysis to 1-methylcyclopentanol. This indicated that the olefin boiling at 75° is 1-methylcyclopentene formed by isomerization, and not 4-methylcyclopentene as claimed by Mousseron. Dehydration of 3-methylcyclopentanol with activated alumina and the dehydrochlorination of 3-methylcyclopentyl chloride with quinoline gave exclusively methylcyclopentene boiling at 65°.

Since the dehydration of 3-methylcyclopentanol and the dehydrochlorination of 3-methylcyclopentyl chloride should give both 3- and 4-methylcyclopentene, it was suggested that the material boiling at 65° was a mixture of these two olefins. It is apparent from the work of Crane, Boord and Henne[7] that 3-methylcyclopentene boils at 65°. This synthesis was repeated and the physical properties of the product were found to be substantially as reported and very nearly the same as those of the 65° fraction obtained by dehydration of 3-methylcyclopentanol or by dehydrochlorination of methylcyclopentyl chlorides.

Oxidation of the 65° olefin fraction with potassium permanganate gave an acid product from which β-methylglutarimide was obtained. It is obvious that β-methylglutarimide (II) could be formed only from 4-methylcyclopentene (I).



Failure to find α-methylglutaric acid, which might arise from the 3-methylcyclopentene present in the olefin mixture, is attributed to the fact that acids of this type are unstable toward strong oxidizing agents in alkaline medium.[8] It is concluded, therefore, that the physical properties which have been assigned in the past to 4-methylcyclopentene are erroneous. Instead of boiling at 75°, this cyclic olefin has substantially the same boiling point (65°), refractive index, and density as 3-methylcyclopentene.

Addition of chlorine and bromine to a mixture of 3- and 4-methylcyclopentene resulted in good

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[3] (a) Zelinsky, *Ber.*, **35**, 2491 (1902); *ibid.*, **66**, 479 (1933); (b) Mousseron, *Bull. Soc. Chim.*, [5] **13**, 218 (1946).

[4] (a) Zelinsky, *Ber.*, **35**, 2683 (1902); (b) Chavanne, *Bull. Soc. Chim. Belg.*, **37**, 141 (1928).

[5] Lutz, Bearse, Leonard and Croxton, THIS JOURNAL, **70**, 4135 (1948).

[6] Vogel, *J. Chem. Soc.*, 1331 (1938).

[7] Crane, Boord and Henne, THIS JOURNAL, **67**, 1237 (1945).

[8] Price, *ibid.*, **61**, 1848 (1939).

yields of the saturated dihalides. Reaction of *t*-methylcyclopentene with chlorine led to a mixture of products including trichlorides, dichlorides and 1-chloro-1-methylpentane.

The technique of treating olefinic compounds with hydrogen peroxide in formic acid to form glycols has been described by Swern.[9] Application of this method to the *s*-methylcyclopentenes gave a 70% yield of the corresponding glycols. When *t*-methylcyclopentene was converted to *t*-methylcyclopentene glycol monoformate and the latter hydrolyzed with aqueous sodium hydroxide, there was obtained a 58% yield of 1-methyl-*trans*-1,2-cyclopentanediol[10] and some 2-methylcyclopentanone. Hydrolysis of the monoformate with sulfuric acid gave a 58% yield of 2-methylcyclopentanone. Similarly, *t*-methylcyclopentene oxide[10] was converted to 2-methylcyclopentanone when warmed with sulfuric acid. The conversion of 1-methyl-*cis*- and -*trans*-1,2-cyclopentanediol to 2-methylcyclopentanone has been observed previously.[11]

The oxidation of *t*-methylcyclopentene with potassium permanganate gave γ-acetylbutyric acid as reported by Chavanne.[4b] Oxidation of the olefin with 35% nitric acid gave oxalic acid. Reaction with perbenzoic acid gave *t*-methylcyclopentene oxide in 75% yield.[10]

With sulfuric acid stronger than about 35%, or with phosphoric acid, dimerization of methylcyclopentenes occurred.[12]

The methylcyclopentenes showed little tendency to polymerize at low temperatures in the presence of catalysts such as aluminum chloride and boron trifluoride.

Tertiary and secondary methylcyclopentanethiols were prepared by heating the corresponding methylcyclopentenes with hydrogen sulfide in the presence of cobalt polysulfide[13] as a catalyst.

A 75% yield of *t*-methylcyclopentyl isothiocyanate was obtained by adding a mineral acid to a mixture of *t*-methylcyclopentene and aqueous ammonium thiocyanate. The *s*-methylcyclopentenes showed no tendency to react with thiocyanic acid.

Etherification of *t*-methylcyclopentene with methanol in the presence of sulfuric acid gave 60 to 75% yields of 1-methoxy-1-methylcyclopentane.

Experimental[14]

Preparation of 1-Methylcyclopentene.—To 260 g. (2.0 moles) of freshly distilled quinoline heated at 160 to 190° in a modified Claisen flask was added 119 g. (1.0 mole) of mixed methylcyclopentyl monochlorides[5] over an eight-hour period. After drying, the mixture of methylcyclopentenes (72 g., 87.5% yield) boiled at 67–75°, n^{20}_{D} 1.4271.

Into 69 g. (0.84 mole) of the mixed methylcyclopentenes cooled to 0°, anhydrous hydrogen chloride was introduced until 17.5 g. (0.48 mole) had been absorbed. Distillation yielded 29 g. (0.35 mole) of olefins boiling at 65° and 53 g. (0.45 mole) of tertiary methylcyclopentyl chloride, b. p. 67° (125 mm.), n^{20}_{D} 1.4474.

One hundred and ninety-one grams (1.6 moles) of tertiary methylcyclopentyl chloride dehydrochlorinated with quinoline gave 123 g. (93% yield) of 1-methylcyclopentene, b. p. 75°, n^{20}_{D} 1.4325.

Preparation of 1-Methylcyclopentene from 1-Methylcyclopentanol.—Dehydration of 24 g. (0.24 mole) of tertiary methylcyclopentanol containing 0.1 g. of iodine gave 17.5 g. (89% yield) of 1-methylcyclopentene, b. p. 75°, n^{20}_{D} 1.4325.

Preparation of 1-Methylcyclopentene and 3-Methylcyclopentene from 2-Methylcyclopentanol.—Using a 2.5-cm. glass tube packed with 8–14-mesh activated alumina and heated to 280–290° over a 30-cm. length, 45 g. (0.45 mole) of 2-methylcyclopentanol[5] was dehydrated in three hours. The olefin distillate was fractionated through a small Stedman column. For every cc. of 3-methylcyclopentene, b. p. 65° (747 mm.), n^{20}_{D} 1.4214,[7] there was obtained 3 cc. of 1-methylcyclopentene, b. p. 75° (747 mm.), n^{20}_{D} 1.4322. The latter was identified by conversion to the tertiary chloride, b. p. 67° (125 mm.).

Dehydrochlorination of 1-Chloro-2-methylcyclopentane.—Fifty-five grams (0.46 mole) of 1-chloro-2-methylcyclopentane[5] was added over a four-hour period to 181 g. (1.4 moles) of quinoline heated to 185–195°. Fractionation of the olefin distillate (35 g.) gave only a small amount of material distilling at 65° (749 mm.); the remainder was 1-methylcyclopentene, b. p. 75° (749 mm.).

Dehydration of 3-Methylcyclopentanol with Sulfuric Acid.—Fifty grams (0.5 mole) of 3-methylcyclopentanol was added slowly to five grams of sulfuric acid heated at 160°. The olefin distillate was dried and fractionated. The major fraction boiled at 65° (749 mm.), n^{20}_{D} 1.4215, and the minor fraction distilled at 75° (751 mm.), n^{20}_{D} 1.4314.

The olefin boiling at 75° was converted to tertiary methylcyclopentyl chloride by treating with anhydrous hydrogen chloride. Hydrolysis of the chloride gave tertiary methylcyclopentanol which yielded a 3,5-dinitrobenzoate melting at 115.5°.

Dehydration of 3-Methylcyclopentanol over Alumina.—Dehydration of 50 g. (0.50 mole) of 3-methylcyclopentanol gave 38 g. of olefin boiling exclusively at 65° (747 mm.), n^{20}_{D} 1.4215.

Dehydrochlorination of Mixed Chlorides with Super-Filtrol.—Three grams of Superfiltrol (Filtrol Corporation) and 117.6 g. (0.99 mole) of methylcyclopentyl chlorides[5] were placed in a flask attached to a distilling column. On refluxing for three hours, 72 g. of distillate was collected at approximately 65–75° (750 mm.). Fractionation gave 32.5 g. (40%) of methylcyclopentenes, b. p. 65–75° (750 mm.), and 34.7 g. (29%) of 1-chloro-1-methylcyclopentane, b. p. 67° (125 mm.).

Preparation of 3-Methylcyclopentene.—The procedure of Crane[7] was used. The product boiled at 64.5–64.8° (747 mm.), n^{20}_{D} 1.4213, d^{20}_{4} 0.7616.

Characterization of Olefins (B. p. 65°)

(A) **Oxidation with Potassium Permanganate.**—The olefin, n^{20}_{D} 1.4207, used in this experiment was obtained by dehydrochlorinating methylcyclopentyl monochlorides[5] followed by removal of the tertiary olefin as the tertiary chloride. To a suspension of 80 g. of potassium permanganate in 500 cc. of water cooled to 0°, 20 g. of olefin was added. The solution was agitated for three days at 5°. After filtering, the solution was acidified with sulfuric acid, and saturated with ammonium sulfate. Exhaustive extraction with ethyl ether gave 13 g. of viscous product which distilled mostly at 165–167° (2–3 mm.).

(B) **Conversion of Oxidation Product to β-Methylglutarimide.**—Excess anhydrous ammonia was introduced into 12.2 g. of the oxidation product at 110–150°. The mixture was heated to 280° and 9 g. of a viscous distillate was collected. The crude product melted at 110–130°.

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[9] Swern, THIS JOURNAL, **68**, 1504 (1946).

[10] Maan, *Rec. trav. chim.*, **48**, 342 (1927).

[11] Tiffeneau, *Compt. rend.*, **209**, 449 (1939).

[12] Bearse and Leonard, U. S. Patent 2,419,668, April 29, 1947.

[13] Farlow, U. S. Patent 2,402,613.

[14] All melting points are uncorrected.

Four recrystallizations from ethyl ether–acetone gave m. p. 143–144°. Sicar[15] reports m. p. 142–143° for β-methylglutarimide. β-Methylglutaric acid was prepared according to the procedure described in "Organic Syntheses"[16] and converted to the imide. The purified imide melted at 143.5–144.5° and when admixed with the imide of the acids obtained by oxidation of the cyclic olefin mixture, there was no depression in melting point.

Preparation of Dichlorides from 3- and 4-Methylcyclopentenes.—A mixture of 77 g. (0.94 mole) of *s*-methylcyclopentenes, b. p. 64–65° (747 mm.) dissolved in 155 g. (1.0 mole) of dry carbon tetrachloride was chlorinated during two and one-half hours at 0 to 10°. Fractionation of the mixture gave 103.5 g. (71% yield) of dichlorides, b. p. 57–63° (15 mm.), n^{20}_D 1.4723, d^{20}_4 1.154.

Anal. Calcd. for $C_6H_{10}Cl_2$: Cl, 46.3. Found: Cl, 46.5.

Chlorination of 1-methylcyclopentene under similar conditions gave a complex mixture of chlorides from which a substantial quantity of 1-chloro-1-methylcyclopentane was isolated.

Bromination of *s*-Methylcyclopentenes.—A solution of 42 g. (0.51 mole) of methylcyclopentenes, b. p. 64–65° (744 mm.), in 80 g. (0.52 mole) of carbon tetrachloride was cooled to 0° and 81 g. (0.51 mole) of bromine in 80 g. (0.52 mole) of carbon tetrachloride was added during ninety minutes. Fractionation gave 100 g. (82% yield) of the dibromides boiling at 70–72° (4 mm.), n^{20}_D 1.5315, and d^{20}_4 1.717.

Anal. Calcd. for $C_6H_{10}Br_2$: Br, 66.1. Found: Br, 66.7.

Preparation of *s*-Methylcyclopentene Glycols.—Twenty-seven grams of 30% hydrogen peroxide was added at 25° to a well-stirred mixture of 185 cc. of formic acid (90% grade) and 17 g. (0.21 mole) of *s*-methylcyclopentenes. In about five minutes, the temperature rose to 40°. Stirring was continued for three hours. The formic acid was removed under reduced pressure and the residue was saponified with aqueous sodium hydroxide after acidifying with hydrochloric acid and saturating with sodium chloride. The solution was extracted with ether. Distillation yielded 17 g. (70% yield) of a glycol, b. p. 121–123° (11 mm.), n^{20}_D 1.4732, d^{20}_4 1.065. This material has physical properties close to those of the 1-methyl-2,3-cyclopentanediols reported by Godchot.[17]

Reaction of *t*-Methylcyclopentene with Performic Acid.—Eighty grams of 30% hydrogen peroxide cooled to 0° was added to a well-stirred mixture of 185 cc. of formic acid (90% grade) and 17 g. (0.21 mole) of *t*-methylcyclopentene at 0°. In about ten minutes, the temperature rose to 40° where it was maintained for six hours. Purification gave 17 g. of material boiling at 70–100° (1 mm.), and 7 g. boiling at 100–150° (1 mm.). When redistilled, the 17-g. fraction boiled at 71–78° (1 mm.), n^{20}_D 1.4595.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.3; H, 8.4; sapn. equiv., 144. Found: C, 57.6; H, 8.9; sapn. equiv., 153. (7-g. fraction) Found: C, 53.9; H, 8.4; sapn. equiv., 153.

Hydrolysis of *t*-Methylcyclopentene Glycol Monoformate

(A) With Sodium Hydroxide.—To 90 cc. of water were added 5.7 g. (0.04 mole) of *t*-methylcyclopentene glycol monoformate, b. p. 88–93° (7 mm.), and 14.5 cc. of 2.5 *N* sodium hydroxide at 25°. The solution was saturated with sodium chloride and extracted with ethyl ether. Distillation gave 2.7 g. (58% yield) of 1-methyl-*trans*-1,2-cyclopentanediol boiling at 120–121° (20 mm.). It crystallized to form a wax-like solid melting at 64–65°. Maan[10] reported m. p. 64–65°.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.1; H, 10.7. Found: C, 62.1; H, 10.6.

(B) With Sulfuric Acid.—A mixture of 93 cc. of water, 7 cc. of concentrated sulfuric acid and 5.7 g. (0.04 mole) of *t*-methylcyclopentene glycol monoformate, b. p. 70–80° (1 mm.), was heated for ninety minutes at 100°. On purifying as in the preceding experiment, there was obtained 2.3 g. (58% yield) of 2-methylcyclopentanone distilling at 137.5–138° (754 mm.), n^{20}_D 1.4350. The 2,4-dinitrophenylhydrazone melted at 153–154°.

When 1-methyl-*trans*-1,2-cyclopentanediol was warmed with sulfuric acid, 2-methylcyclopentanone was formed readily.

Preparation of *t*-Methylcyclopentanethiol.—A mixture of 27.5 g. (0.33 mole) of *t*-methylcyclopentene, 83 g. (2.4 moles) of hydrogen sulfide, and 5 g. of cobalt polysulfide catalyst[13] was heated for two and one-half hours at 200° in a 230-cc. stainless steel autoclave. There was obtained 32.5 g. (84% yield) of *t*-methylcyclopentyl mercaptan, distilling mostly at 133–135° (747 mm.), n^{20}_D 1.4763, d^{20}_4 0.937. The 2,4-dinitrophenyl thioether derivative melted at 74°.

Anal. Calcd. for $C_{12}H_{14}O_4N_2S$: S, 11.3; N, 9.9. Found: S, 11.9; N, 9.8.

Preparation of *s*-Methylcyclopentanethiols.—Under similar conditions *s*-methylcyclopentenes gave a 53% yield of *s*-methylcyclopentanethiols, distilling at 130–145° (745 mm.), n^{20}_D 1.4780, d^{20}_4 0.934.

Anal. Calcd. for $C_6H_{12}S$: S, 27.6. Found: S, 27.7.

Preparation of 1-Methoxy-1-methylcyclopentane.—To 64 g. (2 moles) of methyl alcohol were added 5 cc. of concentrated sulfuric acid and 16 g. (0.20 mole) of *t*-methylcyclopentene. After six days at room temperature there was obtained 16 g. (75% yield) of 1-methoxy-1-methylcyclopentane distilling at 67–68° (125 mm.), n^{20}_D 1.4263, d^{20}_4 0.859.

Anal. Calcd. for $C_7H_{14}O$: C, 73.6; H, 12.4. Found: C, 74.0; H, 12.2.

Preparation of *t*-Methylcyclopentyl Isothiocyanate.—To a solution of 26 g. (0.34 mole) of ammonium thiocyanate in 100 cc. of water was added 27 g. (0.33 mole) of *t*-methylcyclopentene. The mixture was refluxed while 34 cc. of concentrated hydrochloric acid was added during one hour. After refluxing an additional three hours, there was isolated 35 g. (75% yield) of *t*-methylcyclopentyl isothiocyanate distilling at 99–101° (30 mm.).[5]

Attempts to add thiocyanic acid to *s*-methylcyclopentenes were unsuccessful.

Oxidation of *t*-Methylcyclopentene with Nitric Acid.—Gradual addition of 10 g. (0.12 mole) of *t*-methylcyclopentene to 193 cc. (1.25 mole) of 35% nitric acid at 70–105° gave 2.3 g. (43% yield) of succinic acid, m. p. 187–188°.

When the oxidation was carried out with 50% nitric acid, oxalic acid dihydrate, m. p. 99–100°, was obtained in 63% yield. There was no glutaric acid formed as has been reported.[18]

Preparation of *t*-Methylcyclopentene Oxide.—Oxidation of *t*-methylcyclopentene according to the procedure of Maan[10] gave a 75% yield of *t*-methylcyclopentene oxide, b. p. 109° (740 mm.), n^{20}_D 1.4297, d^{20}_4 0.926.

When 0.5 cc. of *t*-methylcyclopentene oxide was warmed with 5 cc. of dilute sulfuric acid and subsequently treated with a solution of 2,4-dinitrophenylhydrazine, there was obtained the 2,4-dinitrophenylhydrazone of 2-methylcyclopentanone.

Dimerization of Methylcyclopentenes.—To 42 g. (0.51 mole) of *s*-methylcyclopentenes, b. p. 65° (747 mm.), was added 50 cc. of 65% sulfuric acid. After two hours at 70 to 105° there was obtained 30 g. (71% yield) of material, b. p. 122–124° (50 mm.), n^{20}_D 1.4940, d^{20}_4 0.906.

Anal. Calcd. for $C_{12}H_{20}$: C, 87.8; H, 12.2. Found: C, 87.5; H, 12.0.

By adding *t*-methylcyclopentene to concentrated sulfuric acid at 5°, a good yield of dimer was obtained, b. p. 126–128° (50 mm.), n^{20}_D 1.4962, d^{20}_4 0.915.

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(15) Sicar, *J. Chem. Soc.*, 603 (1927).

(16) "Organic Syntheses," **23**, 50 (1943).

(17) Godchot, *Compt. rend.*, **200**, 1599 (1935).

(18) Shuikin, *Bull. Acad. Sci., U. S. S. R., Chem.*, 440 (1944) (U. O. P. Translation 512).

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.

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[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°, $n^{25}\mathrm{D}$ 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., $n^{25}\mathrm{D}$ 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., $n^{25}\mathrm{D}$ 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°, $n^{25}\mathrm{D}$ 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°, $n^{25}\mathrm{D}$ 1.4142. When this had been removed the sulfuric acid solution was diluted with water. Hexamethyldisiloxane separated, b. p. 99°, $n^{25}\mathrm{D}$ 1.3785. The second fraction was 56% by volume, water-insoluble, and also contained silicon and chlorine, b. p. 97°, $n^{25}\mathrm{D}$ 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).