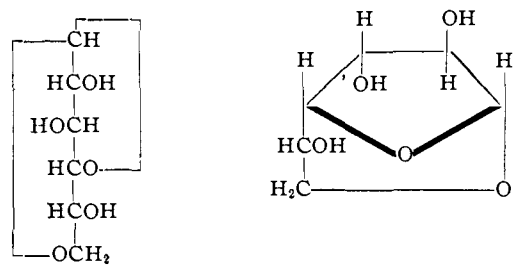
[CONTRIBUTION FROM THE STARCH AND DEXTROSE DIVISION, NORTHERN REGIONAL RESEARCH LABORATORY[1]]

A New Anhydride of D-Glucose: D-Glucosan <1,4>β<1,6>

BY R. J. DIMLER, H. A. DAVIS AND G. E. HILBERT

The vacuum pyrolysis of starch yields, in addition to D-glucosan <1,5>β<1,6> (levoglucosan),[2] a complex mixture of other compounds. A new anhydride of D-glucose has now been isolated from this mixture and shown to be D-glucosan <1,4>β<1,6> (I).



(I) D-Glucosan <1,4>β<1,6>

The isolation of D-glucosan <1,4>β<1,6> from the starch pyrolysate was facilitated particularly by the ease of distillation of the glucosan triacetate and by the resistance of the glucosan to oxidation with periodic acid. D-Glucosan <1,4>β<1,6> remained in the mother liquor after crystallization of most of the levoglucosan from the pyrolysis distillate.[2] Further fractionation was effected by distillation of the acetylated mother liquor. Although the acetates of D-glucosan <1,4>β<1,6> and of levoglucosan co-distilled, part of the triacetyllevoglucosan was removed from the distillate by crystallization from isopropanol. The D-glucosan <1,4>β<1,6> was freed of the last portion of accompanying levoglucosan by oxidation of the deacetylated material with periodic acid. Acetylation of the residue, followed by distillation, then yielded the crystalline triacetate of the new glucosan.

On the basis of its properties, including stability in 0.2 *N* hydrochloric acid at 25°, D-glucosan <1,4>β<1,6> apparently differs from the cellu-glucosan of Hess,[3] the α-glucosan of Pictet,[4] and the Brigl anhydride.[5] The physical constants and greater solubility of the glucosan and its derivatives clearly differentiate it from levoglucosan.

The D-glucosan <1,4>β<1,6> structure (I) has been assigned on the basis of the following evidence:

1. The compound is non-reducing and yields D-glucose on acid hydrolysis. These facts, in conjunction with the elementary analysis, indicate that the compound is an anhydride of D-glucose with the hydroxyl group on carbon atom number 1 participating in an anhydro-linkage.

2. The acetate has the correct molecular weight and analysis for a monomeric glucosan triacetate.

3. The ring structure was established as <1,4> <1,6> by a study of the trimethyl ether of the glucosan. Acid hydrolysis of this derivative gave the known sirupy 2,3,5-trimethyl-D-glucose,[6] which was characterized as the crystalline phenylhydrazide of 2,3,5-trimethyl-D-gluconic acid.

4. Confirmatory evidence for the ring closure on carbon atom number 4 was provided by the preparation of 2,3,5,6-tetramethyl-D-glucose from the trimethyl glucosan. The transformation was effected by methanolysis of the trimethylglucosan followed by methylation of the resulting methyl trimethylglucoside to a methyl tetramethylglucoside which was hydrolyzed to 2,3,5,6-tetramethyl-D-glucose. The tetramethyl glucose was identified by conversion to the known phenylhydrazide of 2,3,5,6-tetramethyl-D-gluconic acid.[7]

5. The presence of the <1,6> ring was further substantiated by preparation of the tri-*p*-toluenesulfonate of the glucosan. The toluenesulfonyl groups were stable toward sodium iodide in acetone for two hours at 100°, as would be expected if the primary hydroxyl on carbon atom 6 were engaged in ring closure.

6. The β-configuration for the <1,6> ring was assumed, since it gave the only structure for which a molecular model could be constructed.

The new glucosan thus has been shown to differ structurally from levoglucosan only in containing a furanose (1,4) ring instead of a pyranose (1,5) ring. The stability of D-glucosan <1,4>β<1,6> in 0.2 *N* hydrochloric acid at 25° is noteworthy in view of the ease of hydrolysis of furanosides. The combination of a 1,6-ring with the furanose ring has stabilized the furanose structure so that D-glucosan <1,4>β<1,6> is similar qualitatively to alkyl glucopyranosides and levoglucosan in its behavior toward acid hydrolysis. Hudson has called attention to the even more remarkable stability of the double lactol ring system in the case of sedoheptulosan, which he has shown to contain an ethylene oxide and septanose ring.[8]

D-Glucosan <1,4>β<1,6>, containing a *trans*-glycol structure, showed essentially complete resistance to periodate oxidation under the conditions used for estimation of vicinal hydroxyl groups.[9] Lead tetraacetate in acetic acid also

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Wolff, Olds and Hilbert, in preparation.

(3) Hess, Weltzien and Messmer, *Ann.*, **435**, 1 (1923).

(4) Pictet and Caston, *Helv. chim. acta*, **3**, 645 (1920).

(5) Brigl, *Z. physiol. Chem.*, **116**, 20 (1921); **122**, 245 (1922).

(6) Smith, *J. Chem. Soc.*, 571 (1944).

(7) Levene and Dillon, *J. Biol. Chem.*, **92**, 769 (1930).

(8) Hudson, THIS JOURNAL, **60**, 1241 (1938).

(9) Jackson (Adams, Editor in Chief), "Organic Reactions," Vol. II, John Wiley and Sons, New York, N. Y., 1944, pp. 341-375.

failed to oxidize the glucosan during six days at 25°. It seems probable that the unique resistance of the glycol group to oxidation is a combined effect of the *trans*-glycol configuration and the rigidity conferred upon the spatial arrangement of the hydroxyl groups by the double lactol ring structure. *trans*-Glycols have been shown to be less readily oxidized than *cis*-glycols by periodate. None of the reported compounds, however, with the possible exception of D-glucosaccharo-1,4-lactone, failed to react in a relatively short time. The *trans*-glycol grouping in the 1,4-lactone of glucosaccharic acid was, according to Smith,[10] unaffected by periodate in a period of one hour at room temperature; no quantitative data were given for this or longer periods of reaction. Other compounds containing *trans*-glycol groupings which have been studied by various workers include cyclohexanediol,[11] 1,4-monoanhydro-D,L-xylitol,[12] α-methyl arabofuranoside,[13] 5,6-monoacetone-β-ethyl galactofuranoside,[14] and starch.[15] All of these compounds were completely oxidized at the glycol group in less than twenty-four hours at room temperature, and in most cases were nearly through reacting in one or two hours.

The unexpected failure of the *trans*-glycol group in D-glucosan <1,4>β<1,6> to be cleaved by periodate oxidation may be characteristic of such a group in other compounds with similar ring systems. Conclusions concerning the absence of vicinal hydroxyl groups in compounds of this type, therefore, cannot be based merely on the failure of periodate oxidation to effect cleavage.

Experimental

Starting Material.—Most of the levoglucosan in the starch pyrolysate was removed by crystallization from acetone.[2] The concentrated mother liquor was acetylated in pyridine (5 parts) with acetic anhydride (3 parts), initially at about 5°, then at room temperature for fifteen hours. Concentration of the acetylation mixture at 15 mm. pressure and a bath temperature of 80° gave a thick sirup which was distilled at 0.1 mm. pressure. The material distilling at a vapor temperature of about 110–150° was collected as the "glucosan acetate" fraction. Some levoglucosan triacetate, usually amounting to about one-third of the distilled acetate, was separated by dissolving the "glucosan acetate" fraction in 5 parts of hot isopropanol and allowing the solution to stand at 25° until crystallization was complete. The filtrate from the levoglucosan triacetate separation was concentrated, and deacetylated with an excess of either methanolic barium hydroxide or barium methylate. The deacetylation mixture was filtered and concentrated to a sirup, which was dissolved in water and freed of barium with sulfuric acid. After being concentrated under vacuum to remove some of the acetic acid, the solution was diluted with water to give a concentration of about 5% solids and adjusted, if necessary, to *p*H 4.5 to 6.0 with sodium carbonate.

Isolation of Triacetyl-D-glucosan <1,4>β<1,6>.—For the destruction of the levoglucosan still in the mixture, a 30% solution of periodic acid was added, the quantity being 25% in excess of the amount shown to be required by analysis[9] of an aliquot. The temperature of the solution was held at about 15° during and for about four hours after addition of the periodic acid. The solution was then allowed to stand at room temperature for fifteen hours. After neutralization with a hot solution of barium hydroxide, the oxidation mixture was cooled and filtered to remove the barium salt precipitate. To the filtrate was added an amount of 30% solution of phenylhydrazine in ethanol, equivalent to 3 moles of phenylhydrazine for each mole of periodic acid used in the oxidation. After standing twenty-four hours at 25°, the mixture was decanted through a filter to remove the precipitated oil containing the reaction product of phenylhydrazine with the dialdehyde[16] formed by periodate oxidation of levoglucosan.[17] The filtrate, after five extractions with benzene, was concentrated to a sirup at 15 mm. pressure. This residue was extracted with absolute ethanol, and the extract concentrated to a sirup.

Acetylation of the sirup was effected in 7 parts pyridine with 5 parts of acetic anhydride, initially at about 5°, then at room temperature for fifteen hours. The mixture was concentrated to a sirup at 15 mm. pressure in a bath at 80°. After extraction of the residue with chloroform and concentration of the extract, the resulting sirup was distilled at 0.1–0.3 mm. pressure without fractionation, the temperature of the vapors being about 145–160°. A solution of the distillate in 5 parts hot isopropanol was cooled to 25° and seeded with triacetyl-D-glucosan <1,4>β<1,6>. After twenty-four hours at 25° the crystalline product was separated. The crude triacetate, usually amounting to about 5 g. from 100 g. of original mother-liquor sirup, was recrystallized from 5–10 parts of isopropanol.

Purified triacetyl-D-glucosan <1,4>β<1,6> was obtained as colorless plates; m.p. 82.5–83.5°, $[\alpha]^{25}D$ −15.3° (*c*, 2; $CHCl_3$).

Anal. Calcd. for $C_{12}H_{16}O_8$: C, 50.0; H, 5.60; acetyl, 44.8; mol. wt., 288. Found: C, 50.2; H, 5.66; acetyl, 45.2; mol. wt., 289 (Rast, camphor).

D-Glucosan <1,4>β<1,6>.—The triacetate was deacetylated catalytically with sodium methoxide or barium methylate. After recrystallization from *n*-butanol or absolute ethanol the D-glucosan <1,4>β<1,6> was isolated as colorless needles which were usually slightly hygroscopic; m.p. 110.5–111.5°; $[\alpha]^{25}D$ + 43.3° (*c*, 2; H_2O).

Anal. Calcd. for $C_6H_{10}O_5$: C, 44.4; H, 6.22. Found: C, 44.6; H, 6.33.

Hydrolysis to D-Glucose.—A 2% solution of D-glucosan <1,4>β<1,6> in 0.2 *N* hydrochloric acid was allowed to stand twenty-four hours at 25°. No hydrolysis occurred, the Fehling test remaining negative and the specific rotation constant at +43.3°.

After being heated five hours at 100°, the solution had a specific rotation of +53.9° (calcd. for glucose, 52.6°) calculated on the basis of the hexose equivalent of the weight of glucosan used. The presence of D-glucose was confirmed by preparation of the phenylosazone, in 50% yield, and conversion of this to the osatriazole[18]; as well as by application of the benzimidazole procedure[19] for carbohydrate characterization. In all cases the melting points of the derivatives coincided with those of the corresponding glucose derivatives and were unchanged by admixture of the products with known samples.

Tri-*p*-toluenesulfonyl-D-glucosan <1,4>β<1,6>.—To 0.166 g. (0.001 mole) of D-glucosan <1,4>β<1,6> dissolved in 3 ml. of dry pyridine was added 0.75 g. (0.004 mole) of *p*-toluenesulfonyl chloride. After the mixture had remained at room temperature for seven days, a small amount of water was added to decompose the excess toluene-

(10) Smith, *J. Chem. Soc.*, 633 (1944).
(11) Price and Knell, THIS JOURNAL, **64**, 552 (1942).
(12) Carson and Maclay, *ibid.*, **67**, 1808 (1945).
(13) Jackson and Hudson, *ibid.*, **59**, 994 (1937).
(14) Pacsu and Trister, *ibid.*, **62**, 2301 (1940).
(15) Jackson and Hudson, *ibid.*, **59**, 2049 (1937).
(16) Jackson and Hudson, THIS JOURNAL, **62**, 958 (1940).
(17) The dialdehyde, if left in the mixture, interferes with the isolation of the glucosan acetate from the distilled acetylated mixture. The dialdehyde can be eliminated by bromine oxidation, but the considerable quantities of inorganic salts introduced by this method are objectionable in subsequent operations.
(18) Hann and Hudson, THIS JOURNAL, **66**, 735 (1944).
(19) Moore and Link, *J. Biol. Chem.*, **133**, 293 (1940).

sulfonyl chloride. The mixture was then diluted with water to about 30 ml. and extracted twice with benzene. The benzene solution was washed successively with dilute hydrochloric acid, saturated sodium bicarbonate solution, and water, and then dried over anhydrous sodium sulfate. Evaporation of the benzene left a sirup, wt. 0.580 g. (93% of calcd.), which crystallized on treatment with ethanol. The crude product was recrystallized from 15 ml. of ethanol, giving tri-*p*-toluenesulfonyl-D-glucosan <1,4> β <1,6> as colorless needles; m. p. 127–128°.

Anal. Calcd. for $C_{27}H_{28}O_{11}S_3$: C, 51.9; H, 4.52; S, 15.40. Found: C, 52.0; H, 4.47; S, 15.30.

No replacement of toluenesulfonyl groups with iodine occurred when the tri-toluenesulfonyl derivative was heated with a 15% solution of sodium iodide in acetone in a sealed tube for two hours at 100°, the derivative being recovered unchanged.

Tri-*p*-nitrobenzoyl-D-glucosan <1,4> β <1,6>.—One millimole (0.162 g.) of D-glucosan <1,4> β <1,6> dissolved in 2 ml. of pyridine was added to a cold solution of 3.4 millimoles (0.60 g.) of *p*-nitrobenzoyl chloride in 2 ml. of pyridine. After the mixture had remained in an ice-bath two hours with frequent shaking, it was allowed to stand forty hours at room temperature. Excess reagent was destroyed by allowing the mixture to stand two hours after adding 0.2 ml. of water. The product was precipitated with 20 ml. of water, filtered and washed with hot water. After repeated recrystallization of the crude product (0.59 g.) from an acetone–ethanol mixture, tri-*p*-nitrobenzoyl-D-glucosan <1,4> β <1,6> was obtained as small prisms of very faint yellow color; m. p. 231–232°, $[\alpha]^{25}D$ + 25.3° (*c*, 1.1; acetone).

Anal. Calcd. for $C_{27}H_{19}O_{14}N_3$: C, 53.2; H, 3.14; N, 6.89. Found: C, 53.5; H, 3.07; N, 6.85.

Trimethyl-D-glucosan <1,4> β <1,6>.—Methylation of 1.6 g. of D-glucosan <1,4> β <1,6> was carried out with methyl iodide and silver oxide. The operation was repeated three times, methanol being added only the first time to dissolve the glucosan. A mixture of the partially crystalline product with 50 ml. of low-boiling petroleum ether (b. p. 35–59°) was heated to boiling, and the solution decanted from the insoluble sirup. Crystallization occurred when the solution was cooled, seeded, and kept in the refrigerator for an hour. The crude crystals, mixed with a little sirup, weighed 0.7 g. and had a m. p. of 48–50°. Recrystallization from 30 ml. of petroleum ether gave 0.3 g. (15%) of trimethyl-D-glucosan <1,4> β <1,6> as colorless needles; m. p. 51–52°, $[\alpha]^{25}D$ + 18.9° (*c*, 2.4; acetone).

Anal. Calcd. for $C_9H_{16}O_5$: C, 52.9; H, 7.90; OCH_3, 45.6. Found: C, 53.1; H, 8.10; OCH_3, 45.5.

A further yield of about 35% was obtained by combining the sirup and mother liquor from the first preparation and subjecting the mixture to another methylation.

2,3,5-Trimethyl-D-glucose from Trimethyl-D-glucosan <1,4> β <1,6>.—A 2-g. (0.01-mole) sample of trimethyl-D-glucosan was hydrolyzed with 25 ml. 0.5 *N* hydrochloric acid at 100° for five hours. The hydrolysis mixture was concentrated *in vacuo* to a sirup after removal of chloride ions with silver carbonate. The sirup was treated with ether, and the solution separated from a brown gummy residue by filtration through carbon. Evaporation gave 1.85 g. of trimethyl glucose as a slightly hygroscopic, thin, colorless sirup, $[\alpha]^{25}D$ − 4.5° (*c*, 3.2; H_2O). Smith[6] reports $[\alpha]^{15}D$ + 17° (*c*, 1.8; H_2O) for 2,3,5-trimethyl-D-glucose.

Anal. Calcd. for $C_9H_{18}O_6$: OCH_3, 41.9. Found: OCH_3, 42.5.

For characterization, the trimethyl glucose was converted to the phenylhydrazide of the corresponding acid. This was effected by oxidizing the trimethyl glucose (0.25 g.) with bromine, purifying the lactone by sublimation, and treating the lactone with phenylhydrazine. Recrystallization of the crude phenylhydrazide (0.12 g., m. p. 154–156°) from ethanol gave the pure phenylhydrazide of 2,3,5-trimethyl-D-gluconic acid, m. p. 156–157°, $[\alpha]^{25}D$ + 38° (*c*, 0.7; MeOH). The melting point was not depressed by admixture of the derivative with a sample of the 2,3,5-trimethyl-D-gluconic acid phenylhydrazide, m. p. 155–156°, prepared by Smith.[6]

Anal. Calcd. for $C_{15}H_{24}O_6N_2$: N, 8.53; OCH_3, 28.3. Found: N, 8.65; OCH_3, 28.3.

2,3,5,6-Tetramethyl-D-glucose from Trimethyl-D-glucosan <1,4> β <1,6>.—The mixed methyl glucosides of 2,3,5-trimethyl-D-glucose were prepared by heating a solution of 1 g. of trimethyl-D-glucosan in 25 ml. of 0.4% hydrogen chloride in methanol in a sealed tube for twenty-four hours at 100°. Methylation of the glucosides by two treatments with silver oxide–methyl iodide gave a hygroscopic sirup which was hydrolyzed with 0.5 *N* hydrochloric acid at 100° for five hours. The tetramethyl glucose was isolated as a colorless sirup, wt. 0.4 g., $[\alpha]^{25}D$ − 10° (*c*, 1.4; H_2O). Values for 2,3,5,6-tetramethyl-D-glucose given in the literature range from $[\alpha]^{25}D$ − 7° to − 14°.

Anal. Calcd. for $C_{10}H_{20}O_6$: OCH_3, 52.5. Found: OCH_3, 49.4.

The product was characterized as 2,3,5,6-tetramethyl-D-glucose by oxidation and preparation of the phenylhydrazide of the acid. The melting point of the phenylhydrazide was 134.5–135° and was unchanged when the derivative was mixed with a known sample (m. p. 135.5–136°) made from the barium salt of 2,3,5,6-tetramethyl-D-gluconic acid prepared by Levene and Dillon.[7]

Resistance of D-Glucosan <1,4> β <1,6> to Periodate Oxidation.—Two samples, each of 0.14 g. (0.9 millimole) of D-glucosan <1,4> β <1,6>, were treated with 5-ml. portions of aqueous solution containing, in one case, 1.2 millimoles of periodic acid, and in the other, the same quantity of sodium periodate. After twenty hours at 25°, the solutions were diluted to 25 ml., and 10-ml. aliquots were analyzed for excess periodate.[9] The diluted solutions were then allowed to stand nine days longer at 25°, and again analyzed for excess periodate. The amount of periodate consumed per mole of glucosan was, for periodic acid, 0.03 mole in twenty hours and 0.12 mole in ten days and, for sodium periodate, 0.01 mole in twenty hours and 0.08 mole in ten days. If the glycol group had been oxidized completely, 1 mole of periodate would have been consumed per mole of glucosan.

Resistance of D-Glucosan <1,4> β <1,6> to Lead Tetraacetate Oxidation.—A sample of D-glucosan <1,4> β <1,6> was treated with lead tetraacetate in acetic acid essentially as described by Hocket, *et al.*[20] Analysis of aliquots of the oxidation mixture showed that no reaction occurred during a period of six days.

Acknowledgment.—The authors are grateful for the sample of 2,3,5-trimethyl-D-gluconic acid phenylhydrazide prepared by Dr. F. Smith[6] and provided through the courtesy of Dr. M. Stacey of the University of Birmingham; also for the sample of barium 2,3,5,6-tetramethyl-D-gluconate prepared by Levene and Dillon[7] and supplied by the Rockefeller Institute for Medical Research through Mr. E. B. Smith. The starch pyrolyses were carried out by Dr. I. A. Wolff and the microanalyses by Mr. C. H. VanEtten of this Laboratory.

Summary

1. A new hexosan, dextro-rotatory and stable at room temperature in 0.2 *N* hydrochloric acid, has been isolated from the mixture of products resulting from the vacuum pyrolysis of starch.

2. This anhydrohexose has been shown to be D-glucosan <1,4> β <1,6>.

(20) Hockett, Dienes and Ramsden, THIS JOURNAL, **65**, 1474 (1943).

3. The properties of its triacetate, tri-*p*-toluenesulfonate, tri-*p*-nitrobenzoate, and trimethyl ether are described.

4. The glucosan contains a *trans*-glycol group which is not oxidized by periodic acid or lead tetraacetate under conditions used for the detection of adjacent hydroxyl groups.

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NOTES

Preparation of Triethylchlorosilane from Ethyl Orthosilicate[1]

BY P. A. DI GIORGIO, W. A. STRONG, L. H. SOMMER AND F. C. WHITMORE

For studies on organosilicon compounds, large quantities of pure triethylchlorosilane and other trialkylchlorosilanes were needed. The preparation from silicon tetrachloride and ethylmagnesium bromide required a time-consuming fractional distillation to separate the desired compound (b. p. 144°) from diethyldichlorosilane (b. p. 128°). Moreover, the yield of triethylchlorosilane by this method is only 30–35%. The present method gives a 60% yield of pure product, diethyldichlorosilane not being formed.

Reaction of ethyl orthosilicate with three equivalents of ethylmagnesium bromide gave triethylethoxysilane which was converted to hexaethyldisiloxane by acid hydrolysis. Addition of ammonium chloride to a concentrated sulfuric acid solution of the disiloxane gave pure triethylchlorosilane.[2]

$$(EtO)_4Si \xrightarrow{EtMgBr} Et_3SiOEt \xrightarrow{Acid} (Et_3Si)_2O \xrightarrow[H_2SO_4]{NH_4Cl} Et_3SiCl$$

It is not necessary to isolate the disiloxane. The unpurified product from the reaction of ethyl orthosilicate and ethylmagnesium bromide can be dissolved directly in concentrated sulfuric acid and treated with ammonium chloride to give triethylchlorosilane. Diethyldichlorosilane and ethyltrichlorosilane are not formed in this step.

We have applied this method to the corresponding *n*-propyl and *n*-butyl compounds.

Experimental

Hexaethyldisiloxane from Ethyl Orthosilicate.—In a 12-liter three-necked flask, fitted with a mercury-sealed stirrer, reflux condenser and dropping funnel, there was prepared 22 equivalents of ethylmagnesium bromide in 10 liters of ether.[3] The flask was cooled with tap water and 1450 g. (7.0 moles) of ethyl orthosilicate was added during one hour. After stirring at room temperature for another hour, the ether was distilled and the product heated on the steam-bath for twelve hours. The ether was then returned to the flask followed by hydrolysis of its contents with ice water and acid. After separation of the ether layer, the ether was distilled from the product; a small amount of ethanol was also removed by distillation. The product was then dissolved, with cooling, in 1.5 liters of concentrated sulfuric acid. This was then added to 6 liters of cold water and the organic layer separated, dried with calcium chloride, and fractionated. There was obtained 573 g. (2.5 moles) of hexaethyldisiloxane,[4] b. p. 233° (734 mm.), $n^{20}D$ 1.4340, a yield of 66%.

Triethylchlorosilane from Hexaethyldisiloxane.—To 275 cc. of cold concentrated sulfuric acid there was added 265 g. (1.08 moles) of hexaethyldisiloxane. To this there was added, with stirring, 175 g. (3.1 moles) of ammonium chloride over a period of two hours. Stirring was continued for an additional hour, and the upper layer was then separated and fractionated in a column of 15 theoretical plates. All but 8 g. of this material proved to be triethylchlorosilane, 286 g. (1.9 moles), b. p. 144° (735 mm.), $n^{20}D$ 1.4314, d^{20} 0.8967, a yield of 86%. Triethylchlorosilane was analyzed for chlorine content as follows: Weighed samples, about 0.5 g., were added to a mixture of 30 cc. of methanol and excess standard alkali, followed by titration with acid.

Anal. Calcd. for $C_6H_{15}SiCl$: Cl, 23.5. Found: Cl, 23.5, 23.6.

Isolation of the hexaethyldisiloxane is unnecessary; in other preparations, the undistilled reaction product from ethyl orthosilicate and ethylmagnesium bromide was dissolved in concentrated sulfuric acid and ammonium chloride was added. The yield of pure triethylchlorosilane by this shorter method was 60–70%.

The success of this shorter method depends on: (1) no tetraethylsilane (b. p. 154°) is formed from ethyl orthosilicate even with four or more equivalents of ethylmagnesium bromide under the conditions used. (2) Diethyldichlorosilane is not formed on treatment of the corresponding diethoxy compound with sulfuric acid and ammonium chloride.

(1) Paper VI on Organosilicon Compounds; for V see Sommer, Goldberg, Dorfman and Whitmore, THIS JOURNAL, **68**, 1083 (1946).

(2) *Cf.* Flood, *ibid.*, **55**, 1735 (1933).

(3) We now use copper lined reactors for all large Grignard reactions.

(4) Ladenburg, *Ann.*, **164**, 325 (1872), first prepared this compound.

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The Purification of Thionyl Chloride

BY D. L. COTTLE

This substance is ordinarily purified by treatment with quinoline and linseed oil, a procedure that gives poor yields and difficult-to-handle residues. Pratt[1] modified the method by using a lower aliphatic ketone in place of quinoline and sulfur in place of the linseed oil. The latter procedure has been modified herein as follows: Nine hundred milliliters of crude technical thionyl

(1) H. R. C. Pratt, British Patent 538,028, July 17, 1941.