

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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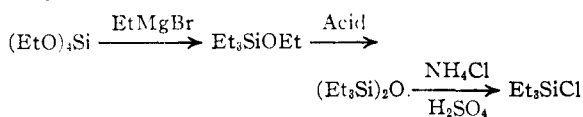
## NOTES

### Preparation of Triethylchlorosilane from Ethyl Orthosilicate<sup>1</sup>

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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 hexaethylidisiloxane by acid hydrolysis. Addition of ammonium chloride to a concentrated sulfuric acid solution of the disiloxane gave pure triethylchlorosilane.<sup>2</sup>



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

**Hexaethylidisiloxane 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.<sup>3</sup> 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

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

(2) Cf. Flood, *ibid.*, **66**, 1735 (1933).

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

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 hexaethylidisiloxane,<sup>4</sup> b. p. 233° (734 mm.), *n*<sub>D</sub><sup>20</sup> 1.4340, a yield of 66%.

**Triethylchlorosilane from Hexaethylidisiloxane.**—To 275 cc. of cold concentrated sulfuric acid there was added 265 g. (1.08 moles) of hexaethylidisiloxane. 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*<sub>D</sub><sup>20</sup> 1.4314, *d*<sub>4</sub><sup>20</sup> 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<sub>6</sub>H<sub>15</sub>SiCl: Cl, 23.5. Found: Cl, 23.5, 23.6.

Isolation of the hexaethylidisiloxane 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.

(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<sup>1</sup> 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.