

over solidified on cooling and scratching. Recrystallization from benzene gave crystals melting at 145°. Michaelis,⁶ who prepared it by the oxidation of tri-*p*-tolylphosphine, reported the same melting point.

Triphenylphosphine oxide, m.p. 153–154°, was obtained from triphenylphosphine⁷ by the method of Michaelis and Soden.⁸ Tri-*p*-tolylphosphine sulfide, m.p. 185–186°, was prepared by the action of sulfur on tri-*p*-tolylphosphine⁵ as described by Michaelis.⁶ *p,p'*-Dimethoxybenzophenone, m.p. 143–144°, was prepared by the method of Bergmann and Harvey.⁹ *p,p'*-Dimethylbenzophenone, m.p. 93–94°, was obtained by the Friedel-Crafts reaction of *p*-toluoyl chloride with toluene. The sample of *p*-nitrosodimethylaniline used was recrystallized from petroleum ether (b.p. 30–50°) and melted at 94–95°.

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Preparation of Difunctional Cyanoalkylsilanes by the Grignard Reaction

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Recent reports that the reaction of methylmagnesium bromide with β -cyanoethyltrichlorosilane in diethyl ether results in a low yield of a mixture of products¹ and that a tertiary amine is required as a cosolvent for improved results² has prompted us to report on a brief investigation along similar lines. By carrying out the Grignard reaction at -50° in tetrahydrofuran solution, greatly improved selectivity of the Grignard reagent

is realized, workup of the products is simplified, and difunctional β -cyanoethylchlorosilanes are readily isolated in good yield. The results of the reaction of methyl- and ethylmagnesium chlorides with β -cyanoethyltrichlorosilane are summarized in Table I.

The effect of reaction temperature on product distribution was examined for the reaction of methylmagnesium chloride with β -cyanoethyltrichlorosilane. The results are summarized in Table II.

TABLE II
EFFECT OF TEMPERATURE ON SELECTIVITY IN THE REACTION OF β -CYANOETHYLTRICHLOROSILANE WITH METHYLMAGNESIUM CHLORIDE^a

Reaction Temperature	Mole-% Conversion to	
	β -NC(CH ₂) ₂ -Si(CH ₃) ₂ Cl ₂	β -NC(CH ₂) ₂ -Si(CH ₃) ₂ Cl
-50°	73	7
-30°	61.6	10.6
+5°	52.4	16.1

^a Grignard reagent and β -cyanoethyltrichlorosilane were allowed to react in equimolar quantities.

It is noteworthy that as the reaction temperature is raised from -50° to $+5^\circ$ the conversion to β -cyanoethylchlorodimethylsilane falls about 20% while an equivalent amount of Grignard reagent is consumed by the formation of by-product β -cyanoethylchlorodimethylsilane. It is likely that at 20–35° reaction of the Grignard reagents will be rather nonselective. In addition, at these temperatures attack of the cyano group by the Grignard reagent probably becomes important. From these results it is concluded that for optimum conversion to difunctional cyanoalkylsilanes the reaction with Grignard reagents should be carried out at -30° or lower.

EXPERIMENTAL

All experiments were carried out following essentially the same procedure. Workup of the reaction products was simplified by removal of the salts by filtration while the reaction mixture was still cold.

β -Cyanoethylchlorodimethylsilane (I). To 3.3 moles of β -cyanoethyltrichlorosilane (II) in 1.4 l. of tetrahydrofuran previously cooled to -50° with a Dry Ice-acetone bath there was added over a 2-hr. period the Grignard reagent prepared from 80 g. (3.3 moles) of magnesium turnings treated with excess methyl chloride in 1 l. of tetrahydrofuran. The reaction mixture was stirred for an additional hour as it was allowed to warm to $+10^\circ$ and then rapidly filtered. The filtrate was stripped of solvent under vacuum and refiltered. Flash distillation gave 457 g. of crude product which was fractionally distilled at atmospheric pressure through a 20-inch column packed with Helipak Hastelloy B (0.1 inch \times 0.05 inch \times 0.1 inch) rated at 20 plates. The forerun b.p. 200–214°/750 mm. (60 g., hydrolyzable chlorine, 34.7%) was a mixture of 34 g. (7% conversion) of β -cyanoethylchlorodimethylsilane (calcd. hydrol. chlorine, 24.0%) and 26 g. of I. The presence of minor amounts of II and β -cyanoethyltrimethylsilane cannot be rigidly

TABLE I

REACTION PRODUCTS OF β -CYANOETHYLTRICHLOROSILANE WITH GRIGNARD REAGENTS AT -50° ^a

RMgCl	Mole-% Conversion to	
	β -NC(CH ₂) ₂ -SiRCl ₂	β -NC(CH ₂) ₂ -SiR ₂ Cl
Methyl	73	7
Ethyl	69	9

^a Grignard reagents and β -cyanoethyltrichlorosilane were allowed to react in equimolar amounts. See Experimental section.

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(2) M. Prober, U. S. Patent 2,913,472 (1959).

excluded. The main fraction (379 g. + 26 g. from forerun = 405 g. or 73 mole-% conversion) was I, b.p. 215°/750 mm., n_D^{25} 1.4550 (hydrol. chlorine, 42.3%; calcd., 42.2%).

β -Cyanoethylethylchlorosilane (III). Similar treatment of 254 g. (1.35 moles) of II with ethylmagnesium chloride prepared from 36.4 g. (1.5 moles) of magnesium turnings and 97 g. (1.5 moles) of ethyl chloride in a total of 1 l. of tetrahydrofuran at -50° gave after filtration and removal of the solvent, 205 g. of crude product. Fractional distillation gave 168 g. total (conversion, 69 mole-%) of III as the main product (hydrol. chlorine, 37.9%; calcd., 38.9%) b.p. 234-235°/751 mm. and a forerun b.p. 200-234°/751 mm. (hydrol. chlorine, 34.8%) consisting of a mixture of 21.5 g. (conversion, 9 mole-%) of β -cyanoethylethylchlorodiethylsilane (calcd. hydrol. chlorine, 20.2%) and 5 g. of III.

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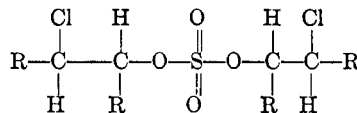
Reactions of *t*-Butyl Hypochlorite

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t-Butyl hypochlorite is a highly reactive and versatile intermediate. Walling¹ has recently shown that in the presence of light or free radical initiators it leads to the free radical chlorination of hydrocarbons. Good yields of allylic chlorides are claimed from many olefins with little or no competing addition to the double bond. An older and more familiar reaction of *t*-butyl hypochlorite is its reaction with olefins in the presence of water and a small amount of acid (acetic) to produce chlorohydrins.^{2,3} If water is excluded and the *t*-butyl hypochlorite and olefin are treated with a primary or secondary alcohol in the presence of a small amount of *p*-toluenesulfonic acid, a chlorohydrin ether results.^{4,5} If acetic acid is substituted for alcohol, then a chlorohydrin ester is the chief product.^{4,6}

We have found that if *t*-butyl hypochlorite is added to a solution of an olefin in *t*-butyl alcohol containing more than a catalytic amount of sulfuric acid, then a sulfate of the following general formula results:



where R may be hydrogen or an alkyl group. By-products of the above reaction are believed to be a chloro-*t*-butyl ether and a chloroacid sulfate of the starting olefin.

Phosphoric acid may be used in place of sulfuric acid to give phosphate esters.

EXPERIMENTAL

t-Butyl hypochlorite. A modification of the method described by Teeter and Bell⁷ was used. Chlorine (171 g., 2.4 moles) was bubbled into a solution of 96 g. (2.4 moles) of sodium hydroxide and 133 g. (1.8 moles) *t*-butyl alcohol in 1550 g. of water at a temperature of 15-20°. The top oil layer was separated and washed with 200 ml. of 10% sodium carbonate, twice with water, and once with a saturated sodium chloride solution. The product was recovered in 88% yield based on alcohol. It was 99% pure by analysis for active chlorine.

Bis(2-chlorocyclohexyl) sulfate. To a solution of 18.5 g. (0.25 mole) of *t*-butyl alcohol in 150 ml. of benzene there was added 13.3 ml. (0.25 mole) of concd. sulfuric acid while stirring and maintaining the temperature at 25°. Cyclohexene, 41 g. (0.5 mole) was then added, followed by 54.5 g. (0.5 mole) of *t*-butyl hypochlorite which was added dropwise at 25°. Reaction was immediate. The product was washed with water and after removing the solvent under vacuum the solid was crystallized from cyclohexane. The purified product weighed 32 g. (39% yield) and melted at 94°.

Anal. Calcd. for C₁₂H₂₀O₄SCl₂: C, 43.5; H, 6.1; S, 29.0; Cl, 21.4. Found: C, 43.4; H, 6.1; S, 29.2; Cl, 21.3.

The chief by-product was probably 1-chloro-2-*t*-butoxy cyclohexane. A cut from a Claisen distillation, b.p. 86-97°/20 mm., weighed 38 g. (40% yield).

Anal. Calcd. for C₁₀H₁₈OCl: Cl, 18.6. Found: Cl, 19.6.

Bis(1-chloro-2-propyl)sulfate. To a solution of 74 g. (1.0 mole) of *t*-butyl alcohol in 200 g. of benzene there was added 49 g. (0.5 mole) of concd. sulfuric acid while stirring and cooling. To this solution maintained at 0-5° there was added simultaneously 108.5 g. (1 mole) of *t*-butyl hypochlorite and slightly more than 1 mole of gaseous propylene. The product was neutralized with aqueous sodium hydroxide and washed with water. Claisen distillation gave 56 g. of material (22% yield) boiling 106-114°/1 mm.

Anal. Calcd. for C₆H₁₂O₄SCl₂: C, 28.7; H, 4.82; S, 28.3; Cl, 12.7. Found: C, 29.0; H, 4.8; S, 28.1; Cl, 12.5.

Tris(2-chlorocyclohexyl)phosphate. To a solution of 26 g. of 85% phosphoric acid (0.23 mole) in 74 g. (1.0 mole) of *t*-butyl alcohol and 200 g. of benzene there was added 82 g. (1.0 mole) of cyclohexene followed by the dropwise addition of 108.5 g. (1.0 mole) of *t*-butyl hypochlorite at 20-25°. After 2 hr. at this temperature the reactants were heated for 1 hr. at 40° for completion. The product was neutralized with 1N sodium hydroxide and thoroughly washed with water. The solvent and medium boiling products were removed from a Claisen still to a kettle temperature of 100° at 1 mm. The residue was taken as product and corresponded to a 34% yield.

Anal. Calcd. for C₁₈H₃₀PCl₃: C, 48.2; H, 6.75; P, 6.92; Cl, 23.8. Found: C, 49.6; H, 7.0; P, 6.0; Cl, 23.1.

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