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-Cyanoethylethyldichlorosilane (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-cyanoethylchlorodiethylsilane (calcd. hydrol. chlorine, 20.2%) and 5 g. of III.

SILICONES DIVISION
UNION CARBIDE CORPORATION
TONAWANDA, N. Y.

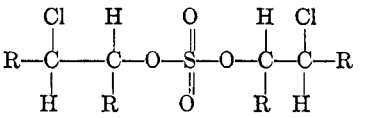
Reactions of *t*-Butyl Hypochlorite

D. E. WINKLER AND G. W. HEARNE

Received March 23, 1960

t-Butyl hypochlorite is a highly reactive and versatile intermediate. Walling[1] 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 Bell[7] 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 $C_{12}H_{20}O_4SCl_2$: 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 $C_{10}H_{19}OCl$: 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 $C_6H_{12}O_4SCl_2$: 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 1*N* 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 $C_{18}H_{30}PCl_3$: 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.

SHELL DEVELOPMENT CO.
EMERYVILLE, CALIF.

(1) C. Walling, B. B. Jacknow, and W. Thaler, 136th Meeting Am. Chem. Soc., Atlantic City, N. J., Sept. 13–18, 1959.

(2) W. E. Hanby and H. N. Rydon, *J. Chem. Soc.*, 114 (1946).

(3) C. G. Harford (to Arthur D. Little, Inc.) U. S. Patent 2,107,789.

(4) C. T. Irwin and G. T. Hennion, *J. Am. Chem. Soc.*, 63, 858 (1941).

(5) C. G. Harford (to Arthur D. Little, Inc.) U. S. Patent 2,207,983.

(6) C. G. Harford (to Arthur D. Little, Inc.,) U. S. Patent 2,054,814.

(7) H. M. Teeter and E. W. Bell, *Org. Syntheses*, 32, 20 (1952).