COMMUNICATIONS TO THE EDITOR

DI-TERTIARY BUTYL ETHER

Sir:

A review of the literature reveals that for a period of more than fifty years, futile attempts have been made to prepare di-tertiary butyl ether. We wish to report that we have been successful in its synthesis, and feel that certain classical predictions as to its stability and properties should now be revised, in view of the fact that this relatively simple, but heretofore elusive, substance is now available.

Reboul[1] found that the Williamson method gave only isobutylene and *t*-butyl alcohol. The methods employed by Henry[2] to synthesize this compound have led only to a series of repeated failures. From a study of the model of this molecule, it has been pointed out[3] that it would appear to be impossible to place two tertiary butyl groups on an oxygen atom having a bond angle as small as 110°. We are of the opinion that such models are inadequate when applied to such borderline cases as this ether, and do not doubt that the method we employed can be utilized to synthesize other di-tertiary aliphatic ethers in substantially the same manner as we have produced this unique substance.

We have found that the reaction between freshly prepared[4] carefully dried silver carbonate and *t*-butyl chloride in a diethyl ether medium produces the desired di-tertiary butyl ether in addition to some *t*-butyl alcohol, isobutylene, carbon dioxide and silver chloride. The reacting mixture was shaken intermittently for twenty-four hours, after which the ether layer was decanted and the residue washed with more ether. The combined ether solutions were then distilled through an efficient fractionating column and the di-tertiary butyl ether was then collected. After washing three times with water, and drying over solid potassium hydroxide, it was distilled several times over sodium to assure thorough dryness. From one mole of silver carbonate and two moles of *t*-butyl chloride a yield of 35% was obtained. However, no attempt was made to adjust conditions to obtain a maximum yield. We have been unable to establish that the ether is formed via decomposition of the carbonate.

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.93; mol. wt., 130.2. Found: C, 73.74, 73.66; H, 13.63, 13.54; mol. wt., 128.9, 131.4. B. p. 106.5–107.0°, d^{20}_4 0.7658, n^{20}_D 1.3949, MR_D calcd. 40.79, found 40.72.

Upon shaking di-tertiary butyl ether with concd. hydrochloric acid, an appreciable amount of heat developed immediately with the result that cleavage of the molecule occurred, resulting in the formation of *t*-butyl chloride, which was identified by its boiling point and refractive index. One mole of ether gave 1.9 moles of *t*-butyl chloride.

Di-*t*-butyl ether is a colorless, water-white, mobile liquid with an apparently high vapor pressure, and a distinct penetrating camphoraceous odor. It is stable toward alkali and no decomposition was observed upon repeated distillations.

The reaction between *t*-butyl chloride, and other alkyl halides, with silver carbonate and other metallic carbonates is now being investigated.

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[1] Reboul, *Compt. rend.*, **108**, 162 (1889).

[2] Henry, *Rec. trav. chim.*, **23**, 324 (1904).

[3] Hare and Mack, THIS JOURNAL, **54**, 4272 (1932).

[4] Spencer and Le Pla, *Z. anorg. allgem. Chem.*, **65**, 10 (1909).

STEROLS. CXXIII. SAPOGENINS. XLIV. THE BIOLOGICAL TRANSFORMATION OF 4-DEHYDROTIGOGENONE TO DIOSGENIN

Sir:

Schoenheimer, Rittenberg and Graff [*J. Biol. Chem.*, **111**, 183 (1935)] observed an increase in the excretion of cholesterol by a dog fed cholestenone. Fieser [THIS JOURNAL, **63**, 1485 (1941)] suggests the possibility that the cholesterol was produced through some indirect effect of the administered cholestenone and was not a direct conversion product from the cholestenone.

We have now tested the possibility of the biotransformation of a Δ^4-3-keto-steroid to a Δ^5-3-hydroxy-steroid with 4-dehydrotigogenone [(Marker, *et al.*, *ibid.*, **62**, 2525 (1940)], the analog of cholestenone in the sapogenin series. A 20-kg. male dog which was maintained on a dog biscuit ration was fed 3 g. of 4-dehydrotigogenone in 30 g. of lard daily for three days. In addition there was a daily subcutaneous injection of 1 g. of 4-