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.

DEPARTMENT OF CHEMISTRY
LOUISIANA STATE UNIVERSITY
BATON ROUGE, LOUISIANA
J. L. E. ERICKSON
WILLIAM H. ASHTON

RECEIVED MAY 20, 1941

---

[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).

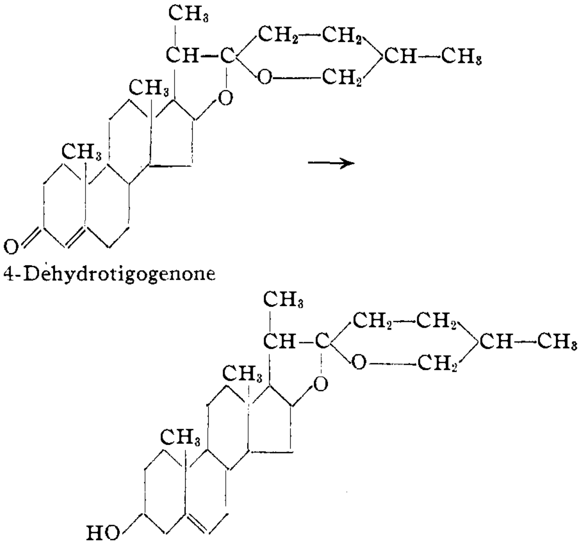
STEROLS. CXXIII. SAPOGENINS. XLIV. THE BIOLOGICAL TRANSFORMATION OF 4-DEHYDROTIGOGENONE TO DIOSGENIN

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-

dehydrotigogenone in 20 cc. of peanut oil. The 4-dehydrotigogenone was carefully purified and gave no precipitate with digitonin. The feces were collected for six days and treated essentially by the method of Schoenheimer, Rittenberg and Graff. From the fraction precipitated with digitonin 0.2 g. of diosgenin, m. p. 207–209°, was obtained. This was also identified as its acetate, m. p. 199–200°. The fraction (7.2 g.) of nonsaponifiable material not precipitated with digitonin gave 3.2 g. of unchanged 4-dehydrotigogenone.


4-Dehydrotigogenone

Diosgenin

Since diosgenin could only have been produced from the administered 4-dehydrotigogenone, this experiment definitely establishes the bio-reduction of a Δ^4-3-keto-steroid to a Δ^5-3-hydroxy-steroid.

The experiments of Callow [*Biochem. J.*, **33,** 559 (1939)] cited by Fieser are subject to the same objection raised by Fieser in connection with Schoenheimer's work since the administered testosterone propionate was not "labelled." In addition it should be pointed out that negative results in urine work can hardly be regarded as significant.

It does not seem to be generally known that cholestenone has been converted to cholesterol by purely chemical methods. This has been reported by several authors [Wagner-Jauregg and Werner, *Z. physiol. Chem.*, **208,** 72 (1932); Lettré, *ibid.*, **221,** 73 (1933)].

RUSSELL E. MARKER
THE SCHOOL OF CHEMISTRY AND PHYSICS R. B. WAGNER
THE PENNSYLVANIA STATE COLLEGE D. L. TURNER
STATE COLLEGE, PENNA. EMERSON L. WITTBECKER

RECEIVED MAY 16, 1941

IMPROVED COMPUTATIONS ON CONJUGATION AND HYPERCONJUGATION

Sir:

Using molecular orbital theory, we recently computed conjugation and hyperconjugation energies and corresponding bond distance changes in good agreement with observation, but could explain observed hyperconjugation shifts in ultraviolet spectra only qualitatively.[1] New computations, using a better approximation, give satisfactory quantitative agreements with spectra as well as energies and distances, for both conjugation and hyperconjugation.

The secular equation for a molecule containing two conjugated bonds is (*cf.* (6) of ref. 1)

$$\begin{vmatrix} x & \gamma^* - S^*E & 0 & 0 \\ \gamma^* - S^*E & x & \gamma - SE & 0 \\ 0 & \gamma - SE & x & \gamma^* - S^*E \\ 0 & 0 & \gamma^* - S^*E & x \end{vmatrix} = 0 \tag{1}$$

where $x \equiv \alpha - E$. Asterisks denote integrals for multiple bonds. In solving this equation it has been customary to neglect all SE's, but this procedure is invalid, since γ and SE are approximately equal (sec. 7). Nevertheless it has seemingly given useful results.

To understand how, we write

$$\gamma - SE = (\gamma - S\alpha) + S(\alpha - E) \equiv \beta + Sx \tag{2}$$

and (1) becomes

$$\begin{vmatrix} x & \beta^* + S^*x & 0 & 0 \\ \beta^* + S^*x & x & \beta + Sx & 0 \\ 0 & \beta + Sx & x & \beta^* + S^*x \\ 0 & 0 & \beta^* + S^*x & x \end{vmatrix} = 0 \tag{3}$$

In general, x is of the order of the β's, and since S for unsaturation electrons is about 0.25, the Sx's are of smaller magnitude than the β's. However, for the quasi-unsaturation electrons of hyperconjugation, S is about 0.6 and the Sx's are more important.

Equation (1) neglecting SE is formally identical with (3) neglecting Sx. Thus while previous workers seemingly solved (1) with the poor approximation $SE = 0$, we see that in effect they solved (3) with the better approximation $Sx = 0$, if we merely reinterpret their empirical resonance parameter as β instead of γ. This was done in our paper.

Our present procedure solves (3) exactly.[2] The numerical labor is increased, but no real difficul-

---

[1] THIS JOURNAL, **63**, 41 (1941).

[2] Eqs. (1), (3) themselves involve an approximation in that relatively small matrix elements of non-neighboring atoms are replaced by zero. Our ability to fit spectroscopic as well as thermal data supports the assumption that these may still be neglected.