transformation products formed by the gland are being separated and identified.

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RECEIVED JULY 29, 1949

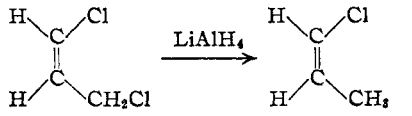
THE CONFIGURATION OF THE 1,3-DICHLOROPROPENES

Sir:

Considerable interest has been shown[1] in the structure of the two isomeric 1,3-dichloropropenes and there has not been complete agreement as to which isomer should be assigned the *cis* configuration and to which the *trans* configuration. This difference of opinion has been caused, in part, by the lack of an unequivocal proof of structure. The configuration of each of the two isomers of 1,3-dichloropropene has now been determined by chemically transforming each isomer into a compound the configuration of which has been established.

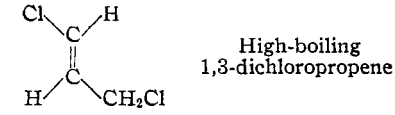
The low boiling isomer of 1,3-dichloropene (b. p. 57.5° (150 mm.), $n^{25}D$ 1.4652, d^{25}_4 1.2048) was refluxed for four hours with sufficient lithium aluminum hydride in isopropyl ether[2] to replace one chlorine atom with a hydrogen atom. By this treatment there was obtained a 50% conversion with a 46% yield of *cis*-1-chloropropene-1 having the following constants: b. p. 32.5° (749 mm.), $n^{20}D$ 1.4054 (lit.[3] b. p. 32.0–32.2° (747 mm.), $n^{20}D$ 1.4053). Similar treatment of the high boiling isomer of 1,3-dichloropropene (b. p. 112.2° (760 mm.), $n^{25}D$ 1.4712, d^{25}_4 1.2139) gave a 56% conversion with a 50% yield of *trans*-1-chloropropene-1, b. p. 37.2° (750 mm.), $n^{20}D$ 1.4048 (lit.[3] b. p. 36.7° (747 mm.), $n^{20}D$ 1.4054). In neither reaction was there any indication of the formation of a mixture of *cis*- and *trans*-1-chloropropene-1.

From these experimental data it follows that the low boiling isomer of 1,3-dichloropropene has the following configuration



Low-boiling 1,3-dichloropropene — *cis*-1-Chloropropene-1

while the high boiling isomer has the remaining configuration



High-boiling 1,3-dichloropropene

This assignment of configuration is in agreement with that proposed by Andrews and Kepner[1b] and not that proposed by Hatch and co-workers.[1a,c]

This method of ascertaining configuration is also being applied to other allylic chlorides which yield compounds of known structure upon replacement of the allylic chlorine atom by a hydrogen atom.

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RECEIVED JULY 16, 1949

PREPARATION OF ADRENAL CORTICAL HORMONES

Sir:

We have made certain observations in the partial synthesis of adrenal cortical hormones which show that it is possible to introduce the 17α-hydroxy group in 11,20-diketo steroids. In addition we have studied the preparation of the dihydroxyacetone side-chain as exemplified by Reichstein's Compounds S and P. Since the reactions appear to be generally applicable, it is possible to prepare adrenal cortical hormones of both the 11-keto series such as Kendall's Compound E and its 11-desoxy analog, Reichstein's Compound S, both of current interest in their medical application.

When the dienol acetate derived from 3α-hydroxypregnane-11,20-dione (m. p. 200–201°; $[\alpha]^{33}D$ +105° (chloroform); $C_{27}H_{38}O_6$, calcd.: C, 70.71; H, 8.35; found: C, 70.80; H, 8.21) is treated with perbenzoic acid according to the procedure of Kritchevsky and Gallagher[1] the reaction product after saponification yielded 3α,17α-dihydroxypregnane-11,20-dione, m. p. 198–201°; $[\alpha]^{32}D$ +66° (acetone). The monoacetate of this compound, m. p. 202–204°, $[\alpha]^{34}D$ +81° (acetone), upon oxidation with chromic anhydride yielded 3α-acetoxyetiocholane-11,17-dione identical in all respects with the known compound. The enol of the 11-keto group therefore either does not react or reacts to such a negligible extent that isolation of the desired product in good yield is easily possible. This establishes the formation of a 17α-hydroxy derivative from a 20-keto steroid with an 11-keto group.

The preparation of the dihydroxy acetone side-chain characteristic of the most active adrenal hormones is illustrated by the reactions leading to the formation of Reichstein's Compounds P and S. Bromination of 3α-acetoxy-17α-hydroxyallopregnan-20-one with one mole of bromine yielded the 21-bromo derivative, m. p. 184–187°; $C_{23}H_{35}O_4Br$, calcd. Br, 17.76; found: Br, 17.47. Hydrolysis

(1) (a) Hatch and Roberts, THIS JOURNAL, **68**, 1196 (1946); (b) Andrews and Kepner, *ibid.*, **69** 2230 (1947); (c) Hatch, Gordon and Russ, *ibid.*, **70**, 1093 (1948); (d) Smith and King, *ibid.*, **70**, 3528 (1948); (e) "Data Sheet" on the 1,3-dichloropropenes published by Shell Chemical Corporation, 8/4/47.

(2) Nystrom and Brown, *ibid.*, **70**, 3738 (1948).

(3) Kharasch, Englemann and Mayo, *J. Org. Chem.*, **2**, 288 (1938).

(1) Kritchevsky and Gallagher, *J. Biol. Chem.*, **179**, 507 (1949).