the former alone yields the product in a reaction stage whose rate can be measured; and therefore a comparison of rates and product compositions in competing reactions, such as those of an alkyl halide in aqueous alcohol, affords a criterion of mechanism. Such a criterion was applied by Farinacci and Hammett to the reactions of benzhydryl chloride but Olson and Halford have made proposals to change the quantitative basis of such comparisons. We consider whether Farinacci and Hammett's rejection of the bimolecular mechanism stands in the light of this work, which we have more fully examined with respect to the reactions of *t*-butyl chloride; and we conclude that it does stand. Thus the hydrolyses of *t*-butyl chloride and benzhydryl chloride are mutually confirmatory examples in which the application of the criterion mentioned favors the unimolecular mechanism, some details concerning which are discussed.

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A New Method for the Preparation of 3,5-Cholestadiene

BY KENZO HATTORI

The various methods for the preparation of the so-called cholesterilene have been discussed recently by H. E. Stavely and W. Bergmann.[1] These authors also prepared 3,5-cholestadiene (I) by the Wolf–Kishner reduction of the semicarbazone of the 7-ketocholesterilene (II). Since this procedure involves prolonged heating at 180–200°, the possibility of a rearrangement of the double bonds is not excluded. In order to eliminate such possibility, 3,5-cholestadiene was prepared by the treatment of pseudocholestene dibromide (III) with silver nitrate in pyridine solution at room temperature.[2] The diene obtained by this reaction seems to be identical with the 3,5-cholestadiene described by Stavely and Bergmann.

Nine-tenths of a gram of pseudocholestene dibromide was dissolved in 20 cc. of pyridine containing 18% of silver nitrate. The reaction mixture was kept in the dark at room temperature for one month. The solution was then diluted with water, acidified with sulfuric acid and extracted with ether. The residue obtained on evaporation of the ether extract was recrystallized from a mixture of alcohol and ether. The diene crystallizes in needles, m. p. 79–80°, $[\alpha]^{15}\mathrm{D}$ $-68.7°$.

Anal. Calcd. for $C_{27}H_{44}$: C, 87.96; H, 12.04%. Found: C, 88.3; H, 11.7%.

The diene gave a positive reaction with Rosenheim's reagent and with antimony trichloride. Mixed with a sample of cholesterilene, prepared from cholesterol,[3] m. p. 79°, $[\alpha]^{15}\mathrm{D}$ $-76.0°$, it gave no depression of the melting point.

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[1] W. Bergmann, *J. Org. Chem.*, **1**, 567 (1937).

[2] E. Dane, *Z. physiol. Chem.*, **245**, 80 (1937); **248**, I (1937).

[3] Mauthner, *Monatsh.*, **17**, 34 (1896).

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Identification of Methylisopropylcarbinol in Sharples Diethylcarbinol

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In connection with another research,[1] an attempt was made to obtain pure 3-pentanol by a series of careful fractional distillations of a sample of commercial diethylcarbinol supplied by the Sharples Solvents Corporation. It was noted that even after many fractionations the material of almost constant refractive index boiled over a range of 4°. Since the refractive index of methylisopropylcarbinol is very near that of 3-pentanol ($n^{20}\mathrm{D}$ 1.4095 and 1.4100, respectively), the lower boiling portion of the sample was carefully refractionated by parts in an efficient column. In this way a fraction was obtained, b. p. 111.5° (732 mm.), $n^{20}\mathrm{D}$ 1.4096, which gave the α-naphthylurethan of methylisopropylcarbinol,[2] m. p. and mixed m. p. 108–110°.

The identification of this alcohol, which had not been found in the hydrolysis products of the chloropentanes by previous investigators,[3] is of considerable theoretical interest. It demonstrates that the hydrolysis of 3-chloro-2-methylbutane to the alcohol does not involve complete rearrangement. The conversion of the alcohol to the chloride even under the mildest conditions gives the rearranged product, 2-chloro-2-methylbutane.[4] Both these conversions are being studied further to determine the relative amounts of rearranged and non-rearranged products from each.

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[1] Whitmore and Karnatz, THIS JOURNAL, **60**, 2536 (1938).

[2] Whitmore and Johnston, *ibid.*, **55**, 5022 (1933).

[3] Ayres, *Ind. Eng. Chem.*, **21**, 899 (1929); Clark, *ibid.*, **22**, 439 (1930).

[4] Whitmore and Johnston, THIS JOURNAL, **60**, 2265 (1938).