[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Hydrogenation of Acetophenone to Cyclohexylmethylcarbinol in the Presence of Solvent

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Acetophenone can be selectively hydrogenated in isopentane solution to a 70% yield of cyclohexylmethylcarbinol[1] but the conditions must be controlled carefully.

Experimental

A 3350 cc. bomb was charged with 200 cc. of acetophenone, 400 cc. of isopentane, 40 g. of nickel catalyst,[2] and 100 kg./sq. cm. of hydrogen. The bomb was rotated for six hours at 100°. The product was distilled through a Podbielniak column with a reflux ratio of 10/1. The isopentane was first evaporated. The residue consisted of 20% (by vol.) of ethylbenzene (b. p. 135–137°; $n^{20}D$ 1.4925), 7% of intermediate fraction (b. p. 137–189°; $n^{20}D$ 1.4874), 70% of cyclohexylmethylcarbinol (b. p. 189–190°; $n^{20}D$ 1.4688), and 3% of bottoms ($n^{20}D$ 1.4940).

The ethylbenzene fraction contained about 1% of ethylcyclohexane on the basis of its refractive index and solubility in cold 15% fuming sulfuric acid.

The redistilled cyclohexylmethylcarbinol showed the following constants: b. p. 189.4–189.8° at 761 mm.; $n^{20}D$ 1.4677; d^{20}_4 0.925. *Anal.* Calcd. for $C_8H_{16}O$: C, 74.9; H, 12.6; mol. wt., 128. Found: C, 74.8; H, 12.5; mol. wt., 126.

When an isopentane solution of acetophenone was heated for six hours at 75°, the product was a mixture of 8% of ethylbenzene and 92% of an approximately 50/50 mixture of phenylmethylcarbinol and cyclohexylmethylcarbinol, and when the hydrogenation temperature was 50° the product was mainly unchanged acetophenone.

In the absence of solvent, and using reduced copper as catalyst[3] at 225°, 95% of the product was ethylbenzene. Using cyclohexane as solvent at 100°, the product was a mixture of ethylbenzene, the two alcohols, and acetophenone.

Summary

Acetophenone has been selectively hydrogenated in isopentane solution to cyclohexylmethylcarbinol.

(1) Cyclohexylmethylcarbinol has previously been made through the Grignard reaction (Bouveault, *Bull. soc. chim.*, [3] **29**, 1049 (1903); Sabatier and Mailhe, *Compt. rend.*, **139**, 343 (1904).

(2) The catalyst was a kieselguhr supported nickel (about 70% of nickel) which had been reduced at 430°.

(3) Prepared by reduction in hydrogen at 225° and ordinary pressure of Kahlbaum–Schering granular copper oxide (nickel content, 0.1%).

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Pseudo-eleostearic Acid[1]

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Moore[2] has shown that prolonged saponification of linseed oil induces a partial isomerization of its spectroscopically inactive liquid linolenic acid to an absorptive crystalline substance, m. p. 77°, bearing a striking resemblance to the eleostearic acids in the position and intensity of its absorption band and in its failure to form an ether-insoluble hexabromide.

In the course of a spectroscopic study of isomerism in the fatty acids[3] we found it expedient to determine the constitution of this compound, the oxidation products of which, consisting of sebacic, oxalic and butyric acids, establish its structure as 10,12,14-octadecatrienoic acid-1. The shift to a conjugated configuration induced by alcoholic alkalies is thus analogous to the rearrangement of linoleic acid under similar treatment.[4] Like the eleostearic acids (9,11,13-octadecatrienoic acids),[5] the new isomer adds only two molecules of bromine easily, the introduction of the third requiring considerable time or exposure to ultraviolet light. However, its maleic anhydride addition product is not homogeneous and could not be separated into its clearly defined individual components. This points to the geometric configuration of the parent substance as the *trans-trans-trans* or *trans-cis-trans* isomer, either of which may form more than one condensation product.[6]

Since the completion of this investigation, we

(1) This work was supported by grants from the Hormel Foundation, the National Live Stock and Meat Board, and the Graduate School of the University of Minnesota.

(2) Moore, *Biochem. J.*, **31**, 142 (1937).

(3) Kass, Miller, and Burr *Proc. Am. Soc. Biol. Chem.*, **32**, 66 (1938).

(4) Kass, Miller and Burr, THIS JOURNAL, **61**, 482 (1939).

(5) Böeseken, *et al.*, *Rec. trav. chim.*, **46**, 619 (1927).

(6) Morrell and Davis, *Trans. Faraday Soc.*, **32**, 209 (1936).