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The Reduction of α -Bromocyclohexanone with Aluminum Isopropoxide

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The reduction of some α -bromo ketones by aluminum isopropoxide was the subject of a recent communication to the Editor by Stevens,¹ who obtained from α -bromopropiophenone a 35% yield of bromohydrin and about an equal yield of product not containing bromine. Presumably hydrogen bromide was split out. Tertiary α -bromo ketones and cyclic secondary α -bromo ketones were reported to yield not bromohydrins but products almost entirely free of bromine. What type of product he obtained was not indicated. In the course of other work the author has had occasion to reduce with aluminum isopropoxide the cyclic secondary α -bromo ketone, α -bromocyclohexanone. Since Stevens is continuing his investigation of the reaction of α -bromo ketones with aluminum isopropoxide, the results obtained with this cyclic ketone should be reported.

The reaction product from the reduction of α -bromocyclohexanone was found to be a mixture

(1) Stevens, *THIS JOURNAL*, **60**, 3089 (1938).

of bromohydrin and cyclohexanol, in yields of 30 and 33%, respectively, with no unsaturated compound being isolated. It is possible that the cyclohexanol arises from dismutation of bromocyclohexanone to cyclohexanone and dibromocyclohexanone with subsequent reduction of the cyclohexanone to cyclohexanol.

Experimental

75.8 g. (0.428 mole) of α -bromocyclohexanone, b. p. 69–71° (1.5 mm.), prepared by the method of Kötzt,² dissolved in 200 ml. of anhydrous isopropanol (Shell) was added to aluminum isopropoxide solution prepared from 7.5 g. of aluminum and 75 ml. of anhydrous isopropanol, according to the directions of Young, Hartung and Crossley.³ The mixture was refluxed for three and one-half hours. Then it was concentrated to a thick residue by distillation first of acetone, then of solvent through a 20-cm. column of glass helices for two hours at atmospheric pressure and finally with the aid of an aspirator. One hundred ml. of water and 130 ml. of 6 *N* sulfuric acid were added to the residue and all lumps were broken up. A little ether was added and the oil phase was separated, washed with bicarbonate solution and dried over sodium sulfate. Distillation and then refractionation at reduced pressure through a 40-cm. Weston⁴ column yielded 22.6 g. (30%) of 2-bromocyclohexanol, b. p. (10 mm.) 85.5–86.5°, n_D^{25} 1.5164, and 14.3 g. (33%) of cyclohexanol, b. p. (10 mm.) 61.0–61.2°, n_D^{25} 1.4649, m. p. of 3,5-dinitrobenzoate and mixed m. p. with authentic specimen, 112°.

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(2) Kötzt, *Ann.*, **358**, 195 (1907).

(3) Young, Hartung and Crossley, *THIS JOURNAL*, **58**, 100 (1936).

(4) Weston, *Ind. Eng. Chem., Anal. Ed.*, **5**, 179 (1933).

COMMUNICATIONS TO THE EDITOR

COLOR REACTIONS IN VITAMIN K CONCENTRATES

Sir:

During studies of the inactivation of vitamin K by its reaction with bases, we have detected and separated an alcohol-soluble reddish pigment. Recently, Dam, *et al.* [*Helv. Chim. Acta*, **22**, 310 (1939)] described a color reaction of vitamin K concentrates with sodium ethylate in which a transient purple color changing to a reddish-brown color developed. We have determined that our pigment is the end stage of this color reaction and that the quantity of pigment formed

is closely correlated with antihemorrhagic activity. The transient, deep purple color is considerably masked when carotenoid pigments are present; however, it is possible to employ the final, less intense but relatively stable, reddish-brown color as a quantitative measure of the vitamin.

The color reaction is carried out easily by dissolving a few milligrams of concentrate in 1 or 2 cc. of methanol and then adding 1 cc. of sodium methylate (2 to 3 g. of sodium dissolved in 50 cc. of methanol). When warmed for a few minutes, the mixture slowly develops a distinct purple