NOTES

Reduction with Alcohols of Cinnamaldehyde to Beta-Phenylpropionaldehyde.—It was shown in a previous paper[1] that acrolein was reduced over alumina by propanol at 330° according to the equation

$$CH_2{=}CHCHO + CH_3CH_2CH_2OH = CH_3CH_2CHO + CH_3CH_2CHO \quad (1)$$

Since it seemed possible that this was a general reaction for 2,3-unsaturated aldehydes, and since it offered a means of reducing the carbon to carbon double bond without reducing the carbon to oxygen bond, attempts were made to reduce cinnamaldehyde to β-phenylpropionaldehyde according to the equation

$$C_6H_5CH{=}CHCHO + C_3H_7OH = C_6H_5CH_2CH_2CHO + C_2H_5CHO \quad (2)$$

The reduction was performed by passing 100 g. of cinnamaldehyde dissolved in 100 cc. of propanol over 5 g. of alumina catalyst (from hydrated alumina) at 330° and at the rate of 75 cc. per hour. The liquid product was distilled at atmospheric pressure to remove the low-boiling fraction (propionaldehyde, propyl ether, propyl alcohol and water) and under a pressure of 40 mm. of mercury to separate the β-phenylpropionaldehyde. Twenty grams of β-phenylpropionaldehyde was obtained, b. p. 130–133° at 40 mm.; 55 g. of cinnamaldehyde was recovered, b. p. 155–158° at 40 mm.; and 15 g. of a dark brown, viscous liquid boiling above 250° remained. The β-phenylpropionaldehyde was identified by the preparation of the oxime which was recrystallized until it had a melting point of 97° (corr.). The melting point is given in the literature as 93–94.5°.

From the amounts of the products obtained, it is estimated that 35% of the cinnamaldehyde and 50% of the propyl alcohol introduced had reacted in some way. About 60% of the cinnamaldehyde which reacted was converted into β-phenylpropionaldehyde, the rest having undergone polymerization, decomposition, etc. About 50% of the alcohol which reacted was used in the formation of propionaldehyde and β-phenylpropionaldehyde, almost all of the remainder forming propyl ether, except a very small amount which was converted into propylene and water.

Similar reactions occurred and approximately the same yields of β-phenylpropionaldehyde were obtained using 50 g. of cinnamaldehyde in 100 cc. of methanol, ethanol or propanol.

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Acetoxymercuric Chloride, $CH_3COOHgCl$.—The replacement of hydrogen in organic compounds by mercury, mercuration, is practically always

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[1] Weston and Adkins, This Journal, **50**, 1930 (1928).

effected by the use of mercuric acetate.[1] Other mercuric salts, like the nitrate and sulfate, may be used less conveniently. Salts like mercuric chloride which are not hydrolyzed do not give the mercuration reaction. For instance, pure phenol can be refluxed for days with mercuric chloride without giving any organic mercury compound.[2] With mercuric acetate, phenol gives a mixture of mono- and di-mercurated products instantly.

Since the chloromercuri compounds are often easier to purify than the acetoxymercuri compounds, a common practice is to mercurate a substance with mercuric acetate and immediately add sodium chloride to produce the chloromercuri compound.

A double salt of mercuric chloride and mercuric acetate, $HgCl_2 \cdot Hg(OCOCH_3)_2$ is recorded in the literature.[3] It was thought that this might really be a mixed salt, $ClHgOCOCH_3$, and might be used as a mercurating agent to give the chloromercuri compounds directly. The results showed that the salt is actually a *mixed* instead of a double salt but that it cannot be used for mercuration.

The salt was prepared from equimolar quantities of mercuric chloride and mercuric acetate in water solution. Evaporation under a variety of conditions gave large clear rhombic crystals entirely different from either of the original substances.

Anal. Subs. 0.1745, 0.1729: Hg, 0.1185, 0.1173. Calcd. for $C_2H_3O_2ClHg$: Hg, 67.97. Found: Hg, 67.91, 67.84.

Dimethylaniline, phenol and *p*-cresol were selected as substances easy to mercurate.[1] From dimethylaniline a white crystalline product was obtained which gave no precipitate with sodium hydroxide but gave mercuric sulfide with hydrogen sulfide. It did not melt. It was therefore not a mercurated dimethylaniline but a molecular compound similar to that obtained from dimethylaniline and mercuric chloride. When the mixed salt was heated for two weeks with a large excess of *p*-cresol in aqueous alcohol, inorganic mercury still remained. No mercurated cresol could be isolated. A similar negative result was obtained with phenol.

These results show not only that the acetoxymercuric chloride cannot be used in place of mercuric acetate as a mercurating agent but that it is very stable in solution. If it gave any appreciable amount of mercuric acetate in solution, the latter would mercurate the substances tested.

This mercuric salt should be subjected to a physical chemical study.

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[1] Pesci, *Z. anorg. Chem.*, **15**, 217 (1897); Dimroth, *Ber.*, **35**, 2044 (1902).

[2] Private communication from Louis Ehrenfeld.

[3] Donk, *Rec. trav. chim.*, **26**, 216 (1907).

Synthesis of *Iso*-amylcyclopentane.—*Iso*-amylcyclopentane was prepared by methods similar to those used by Chavanne and Becker in the synthesis of ethylcyclopentane.[1] *Iso*-amylcyclopentanol was prepared from cyclopentanone and *iso*-amyl bromide by a Grignard reaction; this alcohol was dehydrated with *p*-toluenesulfonic acid and the resulting cyclopentene was hydrogenated with platinum black as a catalyst.

The following physical constants were determined: *iso*-amylcyclopentanol—colorless, oily liquid, pleasant odor, b. p. 101° at 17 mm., $d_4^{26} = 0.8848$, $n_D^{26} = 1.4549$; *iso*-amylcyclopentene—colorless, mobile liquid, petroleum-like odor, b. p. 168–170° at 760 mm., $d_4^{25} = 0.8010$, $n_D^{25} = 1.4467$; *iso*-amylcyclopentane—colorless, mobile liquid, petroleum-like odor, b. p. 168–170° at 760 mm., $d_4^{25} = 0.7837$, $n_D^{25} = 1.4321$.

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NEW BOOKS

Volumetric Analysis. By I. M. Kolthoff, Professor of Analytical Chemistry at the University of Minnesota, with the collaboration of Dr. Ing. H. Menzel, Dresden. Translated by N. Howell Furman, Ph.D., Associate Professor of Analytical Chemistry, Princeton University. **Vol. II. Practical Volumetric Analysis.** John Wiley and Sons, Inc., 440 Fourth Avenue, New York, 1929. xiv + 552 pp. 18 figs. 15 × 23.5 cm. Price $5.00.

This book represents, beyond all question, a scholarly, interesting and valuable contribution to the literature of analytical chemistry and one which deserved translation. The original intention had been to write merely a treatise on the underlying theories of titration methods with the idea that H. Beckurt's revision of F. Mohr's well-known book would still serve as a text-book of practical methods, but since the publication of the Beckurt book there has been such a marked development in this branch of analytical chemistry that it seemed wise to write a new, critical and comprehensive work. The text of Beckurt, however, has been used freely in the preparation of this new book. To give some idea of the thoroughness with which Dr. Kolthoff has combed the journal literature, it may be mentioned that there are about one thousand footnotes and in one case more than fifty references are given in a single footnote. There is hardly a paper written during the last fifteen years on volumetric procedure that does not receive consideration or mention.

The book is not intended as a text for beginners. The discussion presupposes a considerable knowledge of chemical principles and only rarely are the directions given in sufficient detail for the beginner to follow.

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[1] Chavanne and Becker, *Bull. soc. chim. Belg.*, **36**, 591 (1927).