gen–chlorine chains[2] indicates a very rapid absorption of chlorine atom by the double bond. Moreover, it was concluded[2] that in mixtures of pentane, ethylene and chlorine the pentane was substituted, not ethylene or ethylene dichloride, and that the intermediate which permitted excess of ethylene to favor substitution must contain ethylene itself. Therefore the competitive reactions in the present case may similarly be represented (Eq. 5a, 5b)

$$Cl_2 \longrightarrow 2Cl \text{ (Thermally)} \tag{3}$$

$$C_5H_{10} + Cl \longrightarrow C_5H_{10}Cl \tag{4}$$

$$Cl_2 + C_5H_{10}Cl \longrightarrow C_5H_{10}Cl_3 \longrightarrow C_5H_{10}Cl_2 + Cl \tag{5a}$$

$$C_5H_{10} + C_5H_{10}Cl \longrightarrow C_5H_9 + C_5H_{10} + HCl \tag{5b}$$

$$C_5H_9 + Cl_2 \longrightarrow C_5H_9Cl + Cl \tag{6}$$

with appropriate chain breaking steps. This mechanism also conforms to the ones consistent with the kinetics of the photochlorinations of both pentane and ethylene.

The competitive steps must have nearly the same activation energy. It would appear highly fortuitous that insensitiveness to temperature would be found, except as the activation energies were very low, as well as equal; therefore the limitation of the effect to rapidly reacting ethylenes may well be expected.

Summary

Chlorine and 2-pentene react in carbon tetrachloride solution to yield 1-chloro-2-pentene as well as the normal addition product. Substitution is favored by increasing the pentene concentration, addition by increasing the relative concentration of chlorine. The same effect is observed in 1-phenyl-2-propene to a smaller extent, but not at all in the slowly reacting 2-chloropropene. A tentative explanation is suggested, based upon competitive reactions involving a common intermediate.

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Reduction of Aldehydes with Aluminum Isopropoxide[1,2]

BY WILLIAM G. YOUNG, WALTER H. HARTUNG AND FRANK S. CROSSLEY

Knowledge of the chemistry of crotyl compounds is much less developed than that of the allyl compounds. Crotyl derivatives are ordinarily obtained from crotyl bromide prepared from methylvinylcarbinol since Bouis reported[3] that alcohols of the type $RCHOHCH{=}CH_2$ with phosphorus tribromide give bromides of the type $RCH{=}CHCH_2Br$. However, *trans*-crotonaldehyde[4] now commercially available, is a better source for crotyl compounds. Repeated attempts to reduce it to the corresponding unsaturated alcohol by means of zinc and iron,[5] or zinc–copper couple[6] invariably gave low yields of product contaminated with butyl alcohol, and the saturated and unsaturated alcohols and could not be separated.[7] Selective hydrogenation by means of platinum oxide catalyst[8] was successful several times in tenth molar quantities or less, but could not be extended to larger amounts.

Although Meerwein and Schmidt[9] report the preparation of crotyl alcohol in 60% yields, we have been unable to approach this figure with either aluminum ethoxide or chloromagnesium ethoxide. Our yields were usually little better than by the zinc–copper couple method.

Since polymerization of one of the reaction products, acetaldehyde, was the cause of most of the difficulty, it appeared likely that an alkoxide which oxidizes to a ketone, should prove more effective. Of these, the isopropoxide is the simplest, yielding volatile acetone.

With aluminum isopropoxide, crotyl alcohol has been prepared in satisfactory yields in two different solvents. The quantities that may be prepared at one time are apparently limited only by the size of apparatus.[10]

Experimental Part

Aluminum Alkoxides.—These were prepared from aluminum amalgam and the appropriate alcohol, according to the directions of Child and Adkins.[11] Frequently, the aluminum dissolves with difficulty, but fortunately this

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(1) This work was aided by a grant from the Board of Research of the University of California.

(2) Presented at the San Francisco meeting of the American Chemical Society, August 19–23, 1935.

(3) Bouis, *Bull. soc. chim.*, [4] **41**, 1160 (1927).

(4) Young, THIS JOURNAL, **54**, 2498 (1932).

(5) Lieben and Zeisel, *Monatsh.*, **1**, 823, 840 (1880).

(6) Charon, *Ann. phys. chim.*, [7] **17**, 217 (1899).

(7) Claisen and Tietze, *Ber.*, **59B**, 2344 (1926).

(8) Tuley and Adams, THIS JOURNAL, **47**, 306 (1925).

(9) Meerwein and Schmidt, *Ann.*, **444**, 221 (1925).

(10) Professor Homer Adkins, working independently in his laboratories at the University of Wisconsin, has obtained similar results. Private communication.

(11) Child and Adkins, THIS JOURNAL, **45**, 3013 (1923).

reaction may be catalyzed by introducing a portion of the crude reaction product from a preceding batch.

A simplified procedure for making isopropoxide is as follows: 100 g. of aluminum wire or turnings, 1200 ml. of isopropyl alcohol (the absolute isopropyl alcohol from Carbide and Carbon Chemicals Corp. is satisfactory) and 5 g. of mercuric chloride are placed in a 2-liter, round-bottomed flask, provided with an efficient reflux condenser. The flask is gently warmed on a steam-bath, and in ten to twenty minutes a grayish precipitate appears. Soon the reaction becomes so vigorous that heating must be interrupted and the flask cooled externally. After this vigorous reaction subsides, heating is resumed and gentle refluxing maintained for six to seven hours. The product may be purified by distillation, b. p. 145–150 (5 mm.), yield 645–680 g. (85–90%); or it may be used directly as described later.

Effect of Solvent, Concentration, Reaction Time, etc., on the Yield of Crotyl Alcohol.—A series of thirty experiments[12] was made in which crotonaldehyde was reduced with aluminum isopropoxide in several solvents at different temperatures and concentrations for intervals of six to fourteen hours, during which time the acetone was slowly removed or left in the reaction mixture. In each solvent, the yield of both crotyl alcohol and polymerization products increased in proportion to the time, the maximum yield of alcohol being obtained after approximately ten hours. With a high boiling solvent, *m*-xylene, the maximum yield of alcohol was 36% while the polymerization yield was 73% of the weight of crotonaldehyde used. The best yield in benzene was 40–45% while in isopropyl alcohol it amounted to 58–60% with the polymerization falling to 40–45% in these solvents. Isopropyl alcohol was also a better solvent than benzene for the reduction of butyraldehyde, the yields being 19 and 36%, respectively. Isopropyl alcohol offers the added advantage that the isopropoxide need not first be isolated. Failure to remove the acetone during the reaction results in greatly reduced yields of alcohol. Although this difficulty may be offset by increasing the ratio of solvent to aldehyde, the lower rate of reaction makes the procedure inadvisable. In order to minimize the amount of polymerization, it is necessary to use an excess of alkoxide rather than aldehyde.

The Reduction of Crotonaldehyde in Isopropyl Alcohol.—The best method of preparing crotyl alcohol is the following. The apparatus consists of a 2-liter flask, equipped with an 80-cm. Vigreux column, the upper end of which is connected to a downward-directed, water-cooled condenser; this permits removal of the acetone as it forms. Aluminum isopropoxide is prepared, as described above, in the 2-liter flask from 47 g. (2 moles) of aluminum, 500 ml. of isopropyl alcohol and 2.5 g. of mercuric chloride. After this phase of the reaction is complete, there is added to the contents of the flask 210 g. (3.0 moles) of crotonic aldehyde b. p. 102–103°, purity 99.5%, and 1000 ml. of isopropyl alcohol. The flask is now attached to the column-condenser outfit. The mixture is slowly distilled for eight to nine hours, the vapors being kept at 60–70°; this is satisfactorily accomplished by means of a heating bath at about 110°. The remaining solvent is removed at reduced pressures. After being cooled to 40°, the reaction mixture is hydrolyzed with 900 ml. of 6 *N* sulfuric acid. The oil phase is removed and distilled at 60–70° by slowly lowering the pressure from 275 to 65 mm., and finally at 100° and 20 mm. This procedure assures the removal of the last traces of crotyl alcohol without distillation of the higher boiling polymerization products.

The aqueous phase, after hydrolysis, is distilled until the distillate no longer gives a test for unsaturation with bromine in carbon tetrachloride. The distillate is saturated with potassium carbonate, and the organic layer which separates is removed and added to the distillate from the oil phase. The yield is increased about 10% by this procedure.

The combined products are dried over 10 g. of potassium carbonate and fractionated through an 80-cm. Vigreux column at 760 mm., the product collected between 117–122° amounts to 130 g., 60% of theoretical, and the product averages 93% unsaturated alcohol. If the crude alcohol is dried several days the purity, determined by titration with a solution of bromine in carbon tetrachloride, is 97%.

Satisfactory yields of crotyl alcohol, 40–45%, may also be obtained from the above directions when benzene is used as a solvent. In this case the benzene is not removed before hydrolyzing the reaction mixture but is used as an extraction solvent to recover the crotyl alcohol.

Purification of Crotyl Alcohol.—Fractional crystallization of the 97% crotyl alcohol with the aid of solid carbon dioxide and alcohol gave practically no purification. The same product was then distilled through a 110-cm. bead column, having a Hopkins condenser at the top. A small fraction distilling between 119.2–121° was removed and the remainder came over at 121.2° and gave bromination values of 99.1–99.7%.

The reduction of cinnamaldehyde and citronellal with aluminum isopropoxide gave citronellol, b. p. 222–224°, in 32% yield and cinnamyl alcohol, b. p. 133–142° (6–8 mm.) in 68% yield.

Isopropoxide vs. Ethoxide

In view of our disappointing results with the aluminum ethoxide and chloromagnesium ethoxide of Meerwein and Schmidt, a comparison was made of the merits of the primary *vs.* the secondary alkoxides. Parallel experiments were made with butyraldehyde, crotonaldehyde and benzaldehyde. The results were always consistent, and in every instance the isopropoxide revealed itself as far superior.

When butyraldehyde was reduced with aluminum ethoxide in ethanol at 25° and in refluxing benzene, 0.0 and 6.0% of the product was butanol and 94 and 84% was high boiling material. On the other hand, aluminum isopropoxide in the same solvents gave 30 and 28% butanol and 59 and 66% higher boiling products, respectively. The higher boiling products included ethyl, isopropyl, and butyl butyrates and aldol condensation products. The ethoxide favored the condensation products.

Crotonaldehyde gives analogous results except that dipropenyl glycol was also isolated along with the aldol condensation products.[13]

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[12] These experiments were carried out with the technical assistance of Jack Waterhouse and Nathan Loshokoff.

[13] See Chalmers, "Organic Syntheses," John Wiley and Sons, Inc., New York City, Vol. XV, 1935, p. 80, for an example where the ethoxide gives a high yield of product.

In order to circumvent the possibility of aldol condensation products, analogous experiments were made with one mole of benzaldehyde in benzene. Yields of benzyl alcohol were 28 and 55%, respectively, for the ethoxide and isopropoxide. In each case some benzoic acid or benzyl benzoate was obtained.

Chloromagnesium Alkoxides

Chloromagnesium ethoxide, according to Meerwein and Schmidt, gave 60% yields of crotyl alcohol. The details are not given for the reduction of crotonic aldehyde, but their description with cinnamaldehyde was followed. It is to be noted that these investigators used 2 g. of metallic magnesium (0.083 mole) to reduce 100 g. of cinnamaldehyde (0.76 mole). In a typical experiment, following the same procedure, but with methylacrolein (crotonaldehyde) replacing the phenylacrolein (cinnamaldehyde) of Meerwein and Schmidt, the following results were obtained: 300 ml. of crotonaldehyde was reduced with the chloromagnesium ethoxide from 6 g. of magnesium. Distillation after hydrolysis gave 33 g. of crude crotyl alcohol (13%), 25 g. of esters of crotonic acid, 23 g. of a product containing dipropenyl glycol and 200 g. of resinous material.

The magnesium dissolves incompletely and with difficulty in isopropyl alcohol containing hydrogen chloride. Consequently, no parallel experiments were made with chloromagnesium isopropoxide.

It is quite apparent from these results that the mechanism of the reaction is not a simple adaptation of the Cannizzaro reaction, as Meerwein and Schmidt propose, although crossed Cannizzaro reactions are known to be promoted by aluminum ethoxide.[14]

Summary

Aluminum isopropoxide has been found effective for the reduction of aldehydes to the corresponding alcohols; other products are esters, aldol derivatives and resinous material.

The reaction mechanism is shown to be more complicated than previously reported.

[14] (a) Nord, *Biochem. Z.*, **106**, 275 (1920); (b) Davidson and Bogert, THIS JOURNAL, **57**, 905 (1935).

LOS ANGELES, CALIFORNIA
PHILADELPHIA, PENNA. RECEIVED AUGUST 12, 1935

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Dibromide Method of Analysis of Butene Mixtures[1]

BY WILLIAM G. YOUNG AND SAUL WINSTEIN

The general procedure of identifying butene mixtures by converting them into the corresponding dibromobutanes has been criticized sharply by workers using high precision fractionating columns.[2] The differences in composition of butene mixtures observed in various laboratories during the catalytic decomposition of 1-butanol have been attributed mainly to faults in the dibromide method of analysis rather than to the effect of catalyst, temperature, efficiency of fractionation, etc.

In view of the fact that many laboratories interested in butene analysis do not possess special costly fractionating columns, it seems desirable to present further evidence that the dibromide method of analysis does give a reliable estimate of the composition of butene mixtures when conducted with the proper care; further, that the amount of decomposition and isomeric change accompanying the distillation of dibromobutanes at atmospheric pressure has been greatly over-emphasized; and finally that the results obtained by the dibromide method of analysis by different workers on the decomposition of 1-butanol with phosphoric acid catalysts fall almost without exception within the limits of variation reported by investigators using the butene distillation method of analysis.

Discussion.—The objections which have been raised against the dibromide method of analysis were originally considered and met by Dillon, Young and Lucas[3] in the development of the reaction-rate dibromide method.

Their method of analysis was originally shown to give a reliable estimate of the composition of dibromobutane mixtures made by mixing the pure dibromobutanes in known proportions. We have now demonstrated that the process of converting butene mixtures into dibromobutane mixtures and preparing the sample for analysis does not cause an appreciable change in composition of the mixture. Known mixtures of dibromobutanes have been converted into butenes by treatment with zinc and alcohol and back into dibromobutanes without changing their composition. In this process the butenes being generated were converted into dibromides which were

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[1] The research included in this paper was accomplished with the aid of a grant from the Board of Research of the University of California.

[2] (a) Komarewsky, Johnstone and Yoder, THIS JOURNAL, **56**, 2705 (1934); (b) Pines, *ibid.*, **55**, 3892 (1933).

[3] Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930).