[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Preparation of Aldehydes and Ketones by Dehydrogenation of Alcohols over Copper–Chromium Oxide

BY HOMER ADKINS, C. E. KOMMES, E. F. STRUSS AND WALDEMAR DASLER

Apparently the best method described in the literature for the dehydrogenation of an alcohol to an aldehyde or ketone is that of Bouveault, who used a copper catalyst.[1] The experiences in this Laboratory with Bouveault's method may be described by a quotation from a paper of Conant, Webb and Mendum.[2] "The copper catalyst prepared according to Bouveault's directions was found satisfactory for the preparation of both trimethyl acetaldehyde, and dimethyl acetaldehyde and was used in a number of runs. The catalyst is subject to poisoning rather easily, however, and in subsequent work many attempts to prepare an active catalyst failed for no apparent reason."

Oxide catalysts in general are much more easily prepared, and are more stable and resistant to poisoning than are metallic catalysts so that for some time it has seemed that a catalyst more satisfactory than copper could be found. Zinc oxide has long been known to be active for dehydrogenation but it requires a rather high temperature and induces a considerable amount of dehydration. Moreover, the catalyst does not retain its activity for many hours. The activity shown by zinc–chromium oxide for dehydrogenation under 100 to 200 atmospheres pressure[3] led to a study of this catalyst and of copper–chromium oxide for the preparation of aldehydes and ketones from the corresponding alcohols at atmospheric pressure.

The apparatus originally used was essentially the same as previously described in another connection,[4] modified in that the catalyst was held in an aluminum U-tube.[5] This equipment was very satisfactory but it is rather cumbersome and expensive for general use. The essential part of the glass apparatus recently used in this Laboratory and recommended for the preparation of aldehydes or ketones is illustrated in Fig. 1. The inner tube of the apparatus for dehydrogenation is 2.5 by 25 cm., while the outer tube is 4 by 35 cm. There are ground-glass joints at A and B for the attachment of a water and an air condenser. A buret or dropping funnel is connected at C. The outer tube of the dehydrogenator is wrapped with asbestos paper, then with 8 meters of No. 22 nichrome wire (26 ohms) and finally with five layers of asbestos paper. The ends of the nichrome wire are attached to binding posts mounted on a short narrow strip of transite. The asbestos paper and transite are held in place by wrapping the whole with electrician's tape.

The catalyst, copper–chromium oxide,[6] was put in tablets weighing approximately

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(1) Bouveault, *Bull. soc. chim.*, [4] **3**, 119 (1908).
(2) Conant, Webb and Mendum, THIS JOURNAL, **51**, 1250 (1929).
(3) Adkins, Folkers and Kinsey, *ibid.*, **53**, 2714 (1931).
(4) Weston and Adkins, *ibid.*, **50**, 1930 (1928).
(5) Adkins and Peterson, *ibid.*, **53**, 1513 (1931).
(6) Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).

0.15 g. each by the use of a pharmaceutical pill machine. About 70 ml. of these pellets was placed in the inner tube. A stable substance of suitable boiling point such as diphenylamine, benzophenone or heptadecane[7] was placed in the outer tube. The condensers were attached and the current turned on the heater. With such a heater as that described above the apparatus may be heated to 300° with 3.5 amperes (110 volts) in twenty minutes and maintained there with a current of 3.2 to 3.5 amperes depending upon the alcohol being dehydrogenated. (The temperatures given in this paper are those observed on a thermometer suspended in the vapors near the bottom of the air condenser.) The alcohol is then allowed to flow from the buret at a suitable rate (1 to 2 cc. per minute) and drop on glass wool which has been placed between the tip of the buret and the catalyst. The alcohol is vaporized before it reaches the catalyst.

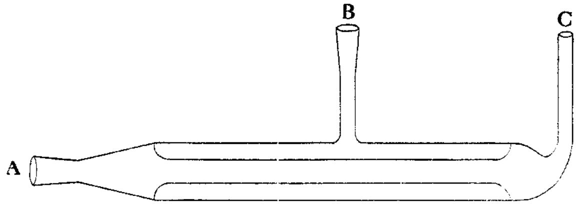

Fig. 1.—Reaction tube for catalytic dehydrogenation of alcohols.

In a representative dehydrogenation 470 cc. (437 g.) of cyclohexylcarbinol was passed over the catalyst during a period of four hours. The product weighed 425 g. A portion of this product (138 g.) was fractionated and from it was obtained 6.4 g. of alkenes and water boiling below 163°, 46.7 g. of aldehyde 163–167°, 70 g. of cyclohexylcarbinol 180–184°, and 10 g. of higher boiling product (ester, etc.). The yield of aldehyde was thus 34% of the theoretical based upon the amount of alcohol passed over the catalyst or 61% if allowance is made for the recovered alcohol.

The ratio of aldehyde produced to the amount of alcohol passed over the catalyst is a function of the rate of passage. For example, the yield of hexahydrobenzaldehyde from cyclohexylcarbinol was increased from 34% (or 61%) to 55% (or 75%) when the rate of passage of the alcohol was decreased from 2 to 1 cc. per minute. Thus the percentage conversion of alcohol to aldehyde was considerably increased but the amount of aldehyde produced in unit time was decreased.

The method also has been applied to the dehydrogenation of *n*-butyl, isobutyl, *n*-pentyl, and *n*-heptyl alcohols and *tert*-butyl and diethylcarbinylcarbinols. There have been prepared from each of these primary alcohols the corresponding aldehydes in quantities of from 60 to 150 g. The yields of aldehydes based upon the amount of alcohol passed over the catalyst were 28 to 35%, while if allowance be made for the alcohols recovered by fractionation the yields of aldehydes were more than twice as large, in some cases being above 90%.

There are at least four rather important types of reaction which occur when alcohols are passed over catalysts of the type of copper–chromium oxide, *i. e.*, I, dehydrogenation, II, dehydration, III, condensation (aldolization followed by dehydration), and IV, ester formation, *i. e.*

$$n\text{-}C_4H_9OH \longrightarrow n\text{-}C_3H_7CHO + H_2 \qquad \text{(I)}$$

$$n\text{-}C_4H_9OH \longrightarrow C_4H_8 + H_2O \qquad \text{(II)}$$

$$2\ n\text{-}C_3H_7CHO \longrightarrow CH_3CH_2CH_2CH{=}C(C_2H_5)CHO + H_2O \qquad \text{(III)}$$

$$2\ n\text{-}C_3H_7CHO \longrightarrow n\text{-}C_3H_7COOC_4H_9\text{-}n \qquad \text{(IV)}$$

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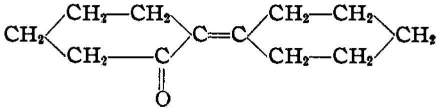
(7) Wojcik and Adkins, THIS JOURNAL, **55**, 1293 (1933).

Reaction II does not occur to any great extent with primary alcohols over copper–chromium oxide at temperatures as low as 300°. For example, the amount of the unsaturated hydrocarbon(s), C_7H_7, fractionated from the product of the dehydrogenation of cyclohexylcarbinol was less than 5%. Reactions III and IV are the chief reactions[3] when the dehydrogenation is carried out under pressures of 100–300 atmospheres at 300–400°. Even at atmospheric pressure considerable amounts of ester (20%) (reaction IV) may be formed, especially at higher temperatures or if the copper–chromium oxide catalyst has been partially reduced. However, the amount of ester normally produced at 300° from the alcohols so far investigated was less than 10% of the alcohol passed over the catalyst.

Condensation (reaction III) apparently does not occur to any great extent at atmospheric pressure in the case of the primary alcohols. However, with cyclohexanol this is an important side reaction. Over zinc–chromium oxide at 360° the yield of 2-cyclohexylidene-cyclohexanone-1, b. p. 274–276°



was 20% accompanied by 56% cyclohexanone and 6% cyclohexene, b. p. 81–83°. Copper–chromium oxide catalyst was unsatisfactory with this alcohol because the rate of reaction was too slow at 300° while at 360° the yield of cyclohexanone was only 26% accompanied by 51% cyclohexene.

The yields of products reported above are with one exception based upon their isolation by fractionation of the dried reaction product. The yield of cyclohexanone was determined by analysis (with *p*-nitrophenylhydrazine) of the mixture of cyclohexanone and cyclohexanol fractionated from the reaction mixture. The activity of the catalyst during the dehydrogenations was followed by collecting from time to time the hydrogen evolved and also by titrating the aldehyde in the product of reaction. Calculations of the yield of aldehyde based upon these values were usually 5 to 10% higher than those actually obtained by fractionation of the aldehyde.

The copper–chromium oxide catalyst did not deteriorate appreciably in activity during ten hours of use. When necessary it may be reactivated by treating it in place in the dehydrogenator at 250° with steam for an hour, followed by air for a similar length of time. After such a treatment the activity of the catalyst is greater than it was originally.

Summary

A process has been described which is quite satisfactory for the dehydrogenation of alcohols to the corresponding aldehydes or ketones.

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