[CONTRIBUTION FROM ST. LOUIS RESEARCH DEPARTMENT, ORGANIC CHEMICALS DIVISION,
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Condensation of Alcohols

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A study has been made of the condensation of ethanol and 1-butanol to higher alcohols under more mildly basic conditions than normally employed in the Guerbet reaction. A catalyst system employing magnesium oxide, potassium carbonate, and copper chromite is effective in promoting condensation to higher alcohols with a negligible amount of carboxylic acid by-product.

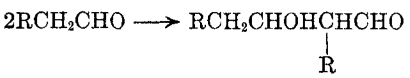
The classical Guerbet reaction[2] consists in heating an alcoholic solution of a sodium alkoxide under pressure to effect condensation to higher alcohols. This reaction has proved to be a useful synthetic procedure for the preparation of certain alcoholic materials. When considered for industrial use, however, it suffers an economic disadvantage in that a portion of the starting alcohol (and possibly some of the product) is consumed by oxidation to the corresponding carboxylic acid.

The beneficial effect of copper bronze in minimizing this oxidation is described by Weizmann and coworkers,[3,4] but even under these conditions the loss of alcohol by oxidation is appreciable. In fact, it has been established in these laboratories that for each mole of higher alcohol produced by the Guerbet reaction, whether catalyzed by active metals or not, a corresponding amount of alcohol is converted to carboxylic acid by oxidation.

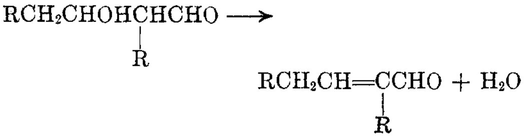
Other publications[5–7] disclose the efficacy of removing the water of condensation as rapidly as formed, thereby appreciably reducing the amount of alcohol consumed by oxidation. This is indeed an elegant improvement over the original Guerbet procedure. A mixture of potassium hydroxide and boric anhydride is the subject of two publications[8,9] which claim good yields of higher alcohols with little or no oxidation to carboxylic acids.

In the Guerbet reaction, the dimolecular weight alcohols are believed to be formed by dehydrogenation to a carbonyl intermediate followed by aldolization, crotonization, and hydrogenation.[7,10,11] Generally, these steps may be represented by the following equations:

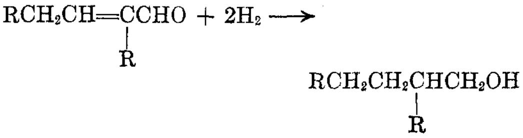
$$RCH_2CH_2OH \longrightarrow RCH_2CHO + H_2 \qquad (1)$$



$$2RCH_2CHO \longrightarrow RCH_2CHOH\underset{\substack{|\\ R}}{C}HCHO \qquad (2)$$

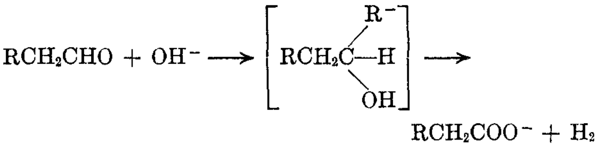


$$RCH_2CHOH\underset{\substack{|\\ R}}{C}HCHO \longrightarrow RCH_2CH{=}\underset{\substack{|\\ R}}{C}CHO + H_2O \qquad (3)$$



$$RCH_2CH{=}\underset{\substack{|\\ R}}{C}CHO + 2H_2 \longrightarrow RCH_2CH_2\underset{\substack{|\\ R}}{C}HCH_2OH \qquad (4)$$

The formation of carboxylic acids probably occurs by attack of hydroxide ion upon the carbonyl intermediate:



$$RCH_2CHO + OH^- \longrightarrow \left[RCH_2\overset{R^-}{\underset{OH}{C}}{-}H \right] \longrightarrow RCH_2COO^- + H_2$$

Although there is a paucity of literature[12,13] describing the condensation of alcohols under more mildly basic conditions, it seemed reasonable that a weaker base in conjunction with a catalyst to assist dehydrogenation, should minimize the consumption of alcohols by oxidation during condensation. Assuming the reaction sequence outlined above, Step 1 would be facilitated by an active dehydrogenation catalyst to produce the carbonyl intermediate. By choosing a weaker base than hydroxide for aldolization, the attack at the carbonyl function to produce a carboxylic acid would be minimized or eliminated and the conversion to higher alcohol should proceed without appreciable oxidation.

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[1] Died, October 6, 1954.

[2] M. Guerbet, *Compt. rend.*, **128**, 511, 1002 (1899) and subsequent papers.

[3] C. Weizmann, E. Bergmann, and M. Sulzbacher, *J. Org. Chem.*, **15**, 54 (1950).

[4] C. Weizmann, E. Bergmann, and L. Haskelberg, *Chemistry & Industry*, 587 (1937).

[5] C. A. Carter, U. S. Patent **2,457,866**, Jan. 4, 1949.

[6] E. F. Pratt and D. G. Kubler, *J. Am. Chem. Soc.*, **76**, 52 (1954).

[7] J. Bolle and L. Bourgeois, *Compt. rend.*, **233**, 1466 (1951).

[8] M. Sulzbacher, Brit. Patent **655,864**, Aug. 1, 1951.

[9] M. Sulzbacher, *J. Appl. Chem.*, **5**, 637 (1955).

[10] H. Machemer, *Angew. Chem.*, **64**, 213 (1952).

[11] Pratt and Kubler (ref. 6) suggest that Step 4 is partially accomplished by a disproportionation reaction involving the starting alcohol. In either event, the net result is the same.

[12] N. D. Scott, U. S. Patent **2,004,350**, June 11, 1935, describes the use of potassium carbonate and copper chromite but the relative amounts of ester, alcohol, and carboxylic acid formed are not clearly disclosed.

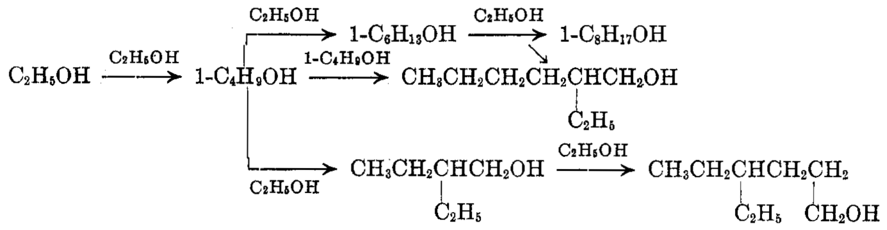
[13] Subsequent to the completion of this work, R. E. Miller and G. E. Bennett, U. S. Patent **2,762,847**, Sept. 11, 1956, described the use of an alkaline reacting phosphate for the condensation of alcohols.

In the present study, several basic reagents and dehydrogenation catalysts were investigated in the condensation of ethanol and 1-butanol to higher alcohols. Combinations of these were shown to be effective in promoting the condensation to higher alcohols with negligible conversion to carboxylic acids. Basic reagents employed include magnesium oxide, calcium oxide, potassium carbonate and sodium carbonate. Raney nickel, copper chromite, manganese chromite, copper-magnesium chromite, and zinc chromite were used as dehydrogenation catalysts. The most effective catalyst system was found to be equal parts by weight of potassium carbonate, magnesium oxide, and copper chromite.

Applying this system to the condensation of ethanol, at 230° a conversion of 20% to higher alcohols was realized in 8 hr. Under these conditions it was established that the molar ratio of higher alcohol to carboxylic acid produced was approximately 20 to 1. An attempt to increase the conversion in this reaction by using a time cycle of 16 hr. failed. The possibility of catalyst deactivation being responsible for the static condition at 20% conversion was considered. However, when fresh catalyst was charged at the end of 8 hr., additional reaction time did not produce an increase in conversion. If, at the end of the first 8-hr. period, the reaction mixture was dehydrated by distillation, then made up to original volume with dry ethanol (the same catalyst being used) followed by an additional 8-hr. reaction time, the conversion was approximately doubled. In an experiment using a synthetic mixture of ethanol and water corresponding to a 20% conversion to higher alcohols, no condensation of the ethanol took place.

These experiments point to equilibrium being reached in this reaction at approximately 20% conversion. In line with this thought, removal of one of the products allows the reaction to proceed in the desired direction once again.

The possible reaction products (through alcohols containing eight carbon atoms) from the condensation of ethanol are outlined below:



The major product of this condensation was shown to be 1-butanol. 1-Hexanol and 2-ethyl-1-butanol, obtained in appreciably smaller amounts, were isolated by fractional distillation, while the octyl and higher alcohols were not separated. Only traces of esters and other nonalcoholic products were observed in this condensation.

The self-condensation of 1-butanol was shown to take place under conditions similar to those effective for ethanol. Once again at approximately 20% conversion, equilibrium was reached. The product of this reaction consisted almost entirely of 2-ethyl-1-hexanol with only traces of higher condensation products. This is consistent with observations of other workers[3,4,10] who have pointed out the necessity for an alcohol to have two β-hydrogens in order to participate in a Guerbet dimerization reaction.

Other catalyst combinations were found to be less effective than the three component system involving potassium carbonate, magnesium oxide, and copper chromite. Substitution of sodium carbonate for potassium carbonate resulted in a much lower conversion. Raney nickel could be substituted for copper chromite with essentially the same conversion to higher alcohols, but an appreciable amount of the starting alcohol was converted to gaseous by-products when this was done. Manganese chromite and copper–magnesium chromite, when substituted for copper chromite, gave a somewhat lower conversion. Zinc chromite was ineffective under the conditions employed. When magnesium oxide was omitted from the catalyst system, only about 10% conversion was obtained. Calcium oxide functioned poorly in the place of magnesium oxide.

EXPERIMENTAL

The autoclave used in these experiments was constructed of steel and had a capacity of 1.3 l. It was fitted with an an impeller agitator, thermometer well, pressure gauge, and vapor and liquid sampling outlets. Heating was accomplished by a series of electrical strip heaters.

Condensation of ethanol by potassium carbonate, magnesium oxide, and copper chromite. The autoclave was charged with 368 g. (8.0 moles) of dry ethanol, 18.5 g. of anhydrous potassium carbonate, 18.5 g. of magnesium oxide (light powder) and 18.5 g. of copper chromite catalyst (obtained from the Girdler Corp., Louisville, Ky.). The mixture was then heated rapidly with stirring to 225–230° and held at this temperature for 8 hr. during which time a pressure of 900–1000 p.s.i.g. was developed. At the end of the heating period the autoclave was cooled and the contents were transferred to a distilling flask where unreacted ethanol was separated by direct distillation from the catalyst. The recovered ethanol amounted to 248.5 g. The residue containing higher alcohols was steam-distilled to separate the alcohols from the catalyst. After drying, the alcoholic product was subjected to fractional distillation. There was obtained 37.3 g. of 1-butanol, b.p. 116–118° (13% conversion, 47% yield on the ethanol actually used), 10.3 g. of hexyl alcohols, b.p. 150–169° (3.7% conversion, 11% yield on the ethanol used), and a residue amounting to 11.8 g. (4.5% conversion, 14% yield calculated as octyl alcohols). Redistillation of the fraction b.p. 150–169° yielded approximately equal parts of 2-ethyl-1-butanol, b.p. 149–151°, and 1-hexanol, b.p. 156–158°, identified as their 3,5-dinitrobenzoates.

Acidification of the steam distillation residue with sulfuric acid followed by further steam distillation effected isolation of the carboxylic acids produced during higher alcohol formation. Titration showed a total of 0.035 equivalents to be present, which represents a ratio of higher alcohol to carboxylic acid of approximately 20:1.

When the reaction time was extended to 16 hr., no appreciable increase in conversion was realized. This was also the case when, at the end of 8 hr., additional quantities of potassium carbonate, magnesium oxide, and copper chromite were added and the reaction continued an additional 8 hr. In another experiment, at the end of 8 hr. the reaction mixture was subjected to distillation and ethanol-water distilled until no more water came over. The mixture was made up to the original volume with dry ethanol and subjected to an additional 8 hr. reaction time. Recovery of ethanol and isolation of the higher alcohol in the previously described manner resulted in a 35% conversion and a 76% yield of higher alcohols.

Condensation of 1-butanol by potassium carbonate, magnesium oxide and copper chromite. The autoclave was charged with 370 g. (5.0 moles) of 1-butanol, 18.5 g. of anhydrous potassium carbonate, 18.5 g. of magnesium oxide (light powder), and 18.5 g. of copper chromite. It was heated rapidly with stirring to 245–250° and maintained at this temperature for 8 hr. during which time the pressure registered 700–800 p.s.i.g. At the end of the heating period the autoclave was cooled and its contents were subjected to steam distillation to recover butanol and higher alcohols. Redistillation of the organic phase resulted in a recovery of 278 g. 1-butanol and 58.6 g. of 2-ethyl-1-hexanol, b.p. 180–182° (18% conversion, 70% yield on the 1-butanol actually used). A very small amount of higher boiling alcoholic residue remained from this distillation.

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Reactions of Acetylenic Compounds under Hydroformylation Conditions[2]

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The reaction of 1-pentyne with carbon monoxide and hydrogen in the presence of a cobalt catalyst at elevated temperatures and pressures produces low yields of the same C_6 alcohols as are obtained from the hydroformylation of 1-pentene. Under these conditions, diphenylacetylene is hydrogenated to 1,2-diphenylethane.

The reaction of acetylene with stoichiometric quantities of cobalt hydrocarbonyl at room temperature and atmospheric pressure results in the formation of propionaldehyde.

All simple olefins undergo the hydroformylation (oxo) reaction. This involves the addition of carbon monoxide and hydrogen to an olefin in the presence of a cobalt carbonyl catalyst at elevated temperatures and pressures to produce aldehydes containing one carbon atom more than the starting olefin.[5-8] For example, propylene yields a mixture of butyraldehyde and isobutyraldehyde.

Although the hydroformylation of olefins has received considerable attention and is of industrial importance, little work has been done on acetylenes. It has been reported that a mixture of high boiling, unidentified products was produced by the reaction of acetylene with carbon monoxide and hydrogen in the presence of metallic cobalt catalysts at 120° to 150° and 200 to 300 atm. pressure[9]. This reaction took place at a slower rate than does the hydroformylation of olefins.

In the present work we have investigated the reactions of 1-pentyne and of diphenylacetylene under hydroformylation conditions. We have studied the effect of small amounts of alkynes on several reactions of nonacetylenic compounds that take place under hydroformylation conditions. We have also reacted acetylene with stoichiometric amounts of cobalt hydrocarbonyl at room temperature and atmospheric pressure.

Reaction of 1-pentyne under hydroformylation conditions. The 1-pentyne began to absorb gas at about 130°. The temperature was then raised to about 185° in order to convert any aldehydes into the corresponding alcohols[10] which are less reactive and easier to isolate. A 6% yield of 1-hexanol and a 5.5% yield of 2-methyl-1-pentanol were obtained. The remainder of the product was higher-boiling material. Infrared and mass spectroscopic analyses showed the presence of C_{12} esters in a fraction distilling at

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(1) Contribution No. 1001.

(2) This paper is based, in part, on the Ph.D. thesis of Harold Greenfield, University of Pittsburgh, 1955.

(3) Branch of Coal-to-Oil Research, Bureau of Mines, Bruceton, Pa.

(4) Department of Chemistry, University of Pittsburgh.

(5) O. Roelen, U. S. Patent **2,327,066** (1943).

(6) H. Adkins and G. Krsek, *J. Am. Chem. Soc.*, **70**, 383 (1948).

(7) H. Adkins and G. Krsek, *J. Am. Chem. Soc.*, **71**, 3051 (1949).

(8) I. Wender and M. Orchin, *U. S. Bur. Mines Rept. Invest. No. 4270* (1948).

(9) G. Natta and P. Pino, paper presented at the 12th International Congress of Pure and Applied Chemistry, New York, N. Y., September 1951.

(10) I. Wender, R. Levine, and M. Orchin, *J. Am. Soc.*, **72**, 4375 (1950).