Summary

1. New condensations of unsaturated ketones with phenols were investigated and the condensation system monohydroxybenzenes–mesityl oxide was studied. The condensation products are apparently chromanols or dichromanyl ethers, respectively.

2. These condensation products are valuable intermediates for the preparation of phenyl-substituted aldehydes and acids (by oxidation) and by the distillation of the acids or their sodium salts so obtainable, the corresponding *iso*propyl and *iso*butyl phenols can be synthesized; hence the condensation process just described furnishes an additional means for the introduction of alkyl groups into the benzene ring.

Further investigations of the condensation possibilities of unsaturated ketones, unsaturated aldehydes, unsaturated acids and unsaturated alcohols with phenols (both mono- and polyhydroxylic, mono- and polycyclic), aromatic hydroxy-aldehydes and aromatic hydroxy-acids are being carried on and positive results already have been obtained.

NEW YORK CITY

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

THE REACTIONS OF ALLYL ALCOHOL OVER ALUMINUM AND ZINC OXIDE CATALYSTS

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F. H. Constable[1] suggested that propionaldehyde was formed from allyl alcohol over *copper* through the intramolecular rearrangement of allyl alcohol, as in Equation 1.

$$CH_2{=}CHCH_2OH = CH_3CH_2CHO \qquad (1)$$

He demonstrated that it was not formed according to Equations 2 and 3

$$CH_2{=}CHCH_2OH = CH_2{=}CHCHO + H_2 \qquad (2)$$

$$CH_2{=}CHCHO + H_2 = CH_3CH_2CHO \qquad (3)$$

Evidence was presented in a previous paper[2] from this Laboratory that part if not all of the propionaldehyde formed over a *zinc oxide* catalyst from allyl alcohol resulted from the reduction of acrolein by allyl alcohol as in Equation 4

$$CH_2{=}CHCHO + CH_2{=}CHCH_2OH = CH_3CH_2CHO + CH_2{=}CHCHO \qquad (4)$$

It now seems certain that over alumina propionaldehyde is formed from allyl alcohol through intramolecular rearrangement. When allyl alcohol was passed over alumina at 330° gas was formed rapidly for a few minutes but the action died off within ten minutes after less than

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[1] Constable, *Proc. Roy. Soc. London*, **113A**, 254 (1926).

[2] Weston and Adkins, THIS JOURNAL, **50**, 1930 (1928).

200 cc. of gas had been produced. The catalyst was then dark colored but produced propionaldehyde at a fair rate. No acrolein was formed at any time and the amount of hydrogen produced was no more than a total of 10 cc. Moreover, there is no evidence that alumina will dehydrogenate any alcohol at 330°. Almost the only conceivable mechanism for the formation of propionaldehyde is that suggested by Constable (Equation 1).

The amounts of propionaldehyde formed in the interval from 40 to 110 minutes when 50 cc. of allyl alcohol per hour was passed over 0.6 cc. of various alumina catalysts at 330° is Catalyst (A), 1.48 g., (B), 0.43 g. and (C) 2.14 g. If the catalyst was previously dried for ten hours at 125° or for four hours at 420°, the amounts of propionaldehyde formed were as follows: Catalyst (A), 5.11 g., (B), 1.17 g. and (C), 3.62 g. If the alcohol was passed at a rate of 20 cc. per hour the amount of *propionaldehyde was reduced to 1.12 g. for Catalyst (B) and to 2.97 g. for* Catalyst (C). The relative reactivities of these catalysts are about the same as those shown for ethylene production from ethyl alcohol at 330°.

For the reasons given in the introduction to our previous paper we were interested in determining the effect of modifications of the catalyst upon its activity and upon the ratio of the reaction products. The method of experimentation has already been described on pages 1931, 1932 and the first paragraph on page 1934 of our previous paper. An abstract of the experimental results obtained in using 13 different zinc oxide catalysts is given in the table.

TABLE I

FORMATION OF PROPIONALDEHYDE AND ACROLEIN ON VARIOUS ZINC OXIDE CATALYSTS FOR THE PERIOD FROM 40 TO 110 MINUTES

	From zinc oxalate			From zinc hydroxide					From zinc oxalate plus 1% (molar) promoter				
Catalyst	1A	2A	3A	4B	5B	6B,	7B	8B	9C, H_3BO_3	10D CrO_3	11E NaOH	12F H_2SO_4	13G H_2WO_4
Aldehydes, g.	1.58 (1.13)	1.48	1.56	1.25	1.71	1.66	2.64	2.02	1.73 (1.26)	2.48 (2.08)	2.75 (1.91)	1.14 (0.93)	3.10
Acrolein (molar), %	11.5, (14.0)	11.0	10.3	7.5	5.3	5.3	4.2	7.4	9.3 (10.1)	6.3 (8.5)	8.0 (9.4)	10.4, (11.2)	6.5
Acrolein, g.	0.16 (0.15)	0.16	0.15	0.09	0.09	0.09	0.11	0.15	0.16 (0.12)	0.16 (0.17)	0.22 (0.17)	0.12 (0.16)	0.20

The figures in parentheses are for a rate of flow of 20 cc. of allyl alcohol per hour. All other figures are for a rate of flow of 50 cc. per hour of the alcohol. All experiments were duplicated at least once, 0.6 cc. of catalyst, as determined from the actual dimensions of the pellets, being used at 330°.

An accurate comparison of catalysts as to their effect upon a given reaction depends upon obtaining a standard catalyst which is easily and precisely reproducible. For reasons which will be more fully developed in another paper by Dr. Paul E. Millington, the zinc oxide obtained through the thermal decomposition of zinc oxalate was chosen as a standard.

The first three experiments serve to illustrate the reproducibility of the catalysts from zinc oxalate. Three entirely different preparations were used, two of them from zinc carbonate and oxalic acid (1A and 3A), and one from zinc sulfate and oxalic acid (2A). The total activity, as measured by the total amounts of aldehydes formed, ranged from 1.48 to 1.58 g., while the percentage of acrolein ranged from 10.3 to 11.5%. The variation in the percentage of acrolein in duplicate experiments was generally less than 0.7% and rarely more than 1.0%. The amounts of aldehydes produced could not be checked so closely because the volume of the catalyst, and the activity of separate portions, varied slightly.

Catalysts prepared from zinc hydroxide could not be duplicated. (This fact is treated more fully in a paper by Dr. Paul E. Millington.) Even though two preparations were treated as nearly alike as possible, they would give different results, both in the amount of reaction and in the ratio of the two reactions. In Expts. 4 and 5 the catalysts were prepared in the same manner, yet the total activity was 1.25 and 1.71 g., and the percentage of acrolein was 7.5 and 5.3%, respectively. The method of washing the catalyst did not change its properties, because in Expt. 5 the catalyst was washed by repeatedly dropping the hot oxide into boiling water and in Expt. 6 all of the washing was done with cold water, yet they are alike both in activity (1.71–1.66 g.) and in percentage of acrolein (5.3–5.3%). However, the amount of washing seems to be important. The catalysts in Expts. 4, 5 and 6 were washed until they were free from sulfates. The catalyst used in Expt. 7 was washed only twice, and it contained considerable sulfate. This catalyst gave irregular results, the activity being very high (2.64 compared to 1.70 g.), and the percentage of acrolein being quite low (4.2%). These results are probably due to the large amount of sodium sulfate which it contained. Experiment 8 shows the results obtained with a catalyst which should be exactly like 3B, but which was prepared by Dr. Millington. This gave a different percentage of acrolein (7.4% instead of 5.3%) and had an entirely different activity (2.02 g. compared to 1.66 g.). Regardless of the variation in different catalysts from zinc hydroxide, the results were entirely different from those of the oxides from zinc oxalate. The catalysts from the hydroxides gave from 4.2 to 7.5% of acrolein, while those from the oxalates gave from 10.3–11.5% of acrolein.

Having chosen one catalyst as a standard, catalysts were prepared in which various acidic and basic compounds were incorporated, and then the ratio of the reactions was determined as usual. These promoters were chosen because of their known activity in modifying the ratio of dehydration to dehydrogenation of alcohols and having in mind the hypothesis of Professor Hugh Stott Taylor (Colloid Symposium Monographs, **4**, 19 (1926), Chemical Catalog Co., Inc., New York City) with respect to the effect of acid and alkaline promoters or poisons. In all but one case the promoted catalysts had a greater activity than the standard catalyst, and also the ratios of the reactions were different. In view of the fact that the rate of alcohol flow and the activity of the catalyst affect the ratio of the reactions, it may seem at first that the selective activation is only apparent and not real. An examination of the data in the table and a consideration of the following reasoning, however, indicates that real selective activation of the catalyst for one or the other of these two reactions was accomplished.

It has been shown that a decrease in the rate of flow of allyl alcohol increased the percentage of acrolein in the products, as did also an increase in the volume of the catalyst for a constant rate of flow of alcohol. Increasing the activity of a catalyst then should have the same effect as increasing the volume of the catalyst, that is, increasing the activity of the catalyst should increase the percentage of acrolein in the reaction products. The data in the table show that decreasing the rate of alcohol from 50 to 20 cc. per hour (equivalent to increasing the activity of the catalyst) increased the percentage of acrolein from 11.5 to 14.0. If the effect of these promoters on the catalyst were just the effect produced by an increase in activity, the percentage of acrolein should have increased, but *in all cases the percentage of acrolein decreased.* The addition of boric acid to the catalyst lowered the percentage of acrolein from 10.3 to 9.3, and then a decrease in the rate of flow of alcohol to 20 cc. per hour increased the percentage of acrolein back to 10.1. In a similar manner the chromic acid lowered the percentage of acrolein to 6.3, but a decrease in the alcohol rate increased the percentage of acrolein to 8.5, and so on for the other promoted catalysts. This shows that the increase in activity of the catalyst due to the promoter was accompanied by an effect opposite to that decreasing the rate of flow of alcohol, instead of the same effect, showing that the real selective activation of the catalyst for one or the other of these two reactions of allyl alcohol had been accomplished.

The nature and extent of modification of the ratio of the simultaneous reactions may be summarized as follows. If the 3A catalyst is used as a standard, boric acid lowered the percentage of acrolein by 1%. Chromic acid lowered it 4%, sodium hydroxide lowered it 2.3% and tungstic acid lowered it 3.8%. Sulfuric acid caused only a slight change in the ratio of the two reactions. The total aldehyde produced was increased by all those substances which lowered the percentage of acrolein. Sulfuric acid lowered the activity decidedly. The boron in the catalyst increased the amount of propionaldehyde produced from 1.40 to 1.57 g. and chromium increased it from 1.40 to 2.33 g., but neither of them changed the amount of acrolein produced (0.16 g.). Sodium hydroxide increased the propionaldehyde from 1.40 to 2.53 g. and also increased the acrolein from 0.16 to 0.22 g. Sulfuric acid decreased the propionaldehyde from 1.40 to 1.02 g., and also decreased the acrolein from 0.16 to 0.12 g. Tungstic acid increased the propionaldehyde from 1.40 to 2.90 g., and also increased the acrolein from 0.16 to 0.20 g., being like sodium hydroxide in its action, except that the changes were in different amounts. These results indicate that foreign oxides (assuming the added materials decomposed to give oxides) do effect a selective activation, but the result is specific for the particular oxide, and does not depend on its acidic or basic character.

The alumina catalysts formed by the incorporation of 0.01 mole of boric acid, chromic oxide (F), sodium hydroxide (G) or sulfuric acid (H) with aluminum ethoxide showed a marked lowering in activity for propionaldehyde formation, the figures for similar experimental conditions being as follows: standard Catalyst (D) 1.20 g., (E) 0.56, (F) 0.87, (G) 0.62 and (H) 0.63 g.

Preparation of Catalysts

A. Alumina from hydrated alumina. Hydrated alumina was prepared by adding a very slight excess of ammonium hydroxide to a dilute solution of aluminum nitrate. The precipitate was allowed to settle and was washed by decantatation three times. Finally it was filtered and dried in an oven at 125° for ten hours. *B*. Crystalline aluminum hydroxide. The product obtained from the Aluminum Company of America, New Kensington, Pa., was washed with water until free from alkali. *C* was alumina from aluminum *iso*propoxide. This was prepared in a manner similar to *D*. *D*. Alumina from aluminum ethoxide. Aluminum ethoxide was prepared by the reaction of amalgamated aluminum with dried ethyl alcohol. It had a boiling point of 194.5–200° (uncorr.) (7 mm.). The ethoxide was broken into small lumps and exposed to moist air for two weeks. The powdered material was made into pills as usual. *E*. Alumina plus boric acid. All of these promoted aluminas were prepared in the same general manner. One hundredth of a mole of the promotor was added to one mole of the fused aluminum ethoxide and the mass was stirred until it solidified. It was then hydrolyzed as in *D*. *F*. Alumina plus chromic oxide. Difficulty was encountered in getting all of the chromic acid in solution. This catalyst had a gray-green color, probably from the reduction of the chromium trioxide. *G*. Alumina plus sodium hydroxide. The aluminum ethoxide was moistened with the correct quantity of an ethyl alcohol solution of sodium hydroxide and then the mass was fused and stirred as in *E* and hydrolyzed. Sulfuric acid was added in a similar fashion to aluminum ethoxide to give catalyst *H*.

1A was zinc oxide from zinc oxalate which was obtained by the reaction of zinc carbonate with oxalic acid. One mole of oxalic acid dissolved in 400 cc. of hot water was added slowly to one-half mole of zinc carbonate held in suspension by vigorous stirring in one liter of boiling water. One hour was allowed for the reaction to become complete. The precipitated oxalate was dried, powdered, heated to 130° and dropped into boiling water. These operations were performed three times. Finally the dried oxalate was converted to the oxide by heating it at 400° for one hour. 2A was zinc oxide from zinc oxalate which was obtained by the reaction of zinc sulfate with oxalic acid. One-half mole of zinc sulfate dissolved in 400 cc. of water was added dropwise to three-quarters of a mole of oxalic acid dissolved in 1000 cc. of water which was stirred vigorously. The precipitated oxalate was washed with cold water until one gram of it dissolved in dilute hydrochloric acid gave no precipitate with barium chloride in one hour. It was dried and heated at 400° for one hour. 3A was a second batch of 1A. 4B was zinc oxide from zinc hydroxide. One-half mole of zinc sulfate dissolved in 400 cc. of water was added dropwise to one and one-half moles of sodium hydroxide dissolved in one liter of cold water which was stirred vigorously. The precipitated hydroxide was washed with cold water, then twice by heating it to 130° and dropping it into boiling water. The final product showed a slight test for sulfate. It was converted into zinc oxide by heating it at 400° for one hour. 5B. A second batch of zinc hydroxide prepared according to 4B was divided into two parts, one of which was treated exactly like 4B. This was 5B. 6B. The second portion of the hydroxide in 5B was washed with cold water only, instead of dropping it into hot water. This was 6B. 7B. A third batch of zinc hydroxide was washed only twice with cold water so that it contained considerable sulfate. 8B was zinc oxide prepared by Dr. Paul E. Millington as described under 6B. 9C was zinc oxide (1 mole) plus boric acid (0.01 mole). This catalyst was prepared by covering one mole of zinc oxalate from 1A with a dilute aqueous solution containing 0.01 mole of boric acid and evaporating the whole mass to dryness. This "promoted" oxalate was then heated to convert it into the oxide, just as in the case of 1A. The other promoted oxides were made in a similar manner using appropriate solutes as indicated. Catalysts 9C, 10D, 11E, 12F and 13G were prepared by Dr. Paul E. Millington. 10D was zinc oxide (1 mole) plus chromic acid (0.01 mole). The green color of the catalyst indicated that some of the chromium trioxide was reduced to chromic oxide. 11E was zinc oxide (1 mole) plus sodium hydroxide (0.01 mole); 12F, zinc oxide (1 mole) plus sulfuric acid (0.01 mole); 13G, zinc oxide (1 mole) plus tungstic acid (0.01 mole).

Summary

Allyl alcohol is converted to propionaldehyde over alumina at 330°. This conversion apparently involves an intramolecular rearrangement. This is in contrast to the conversion of allyl alcohol to propionaldehyde over zinc oxide, which depends at least in part upon the reduction of acrolein by a molecule of alcohol.

The activity of alumina for the conversion of allyl alcohol to propionaldehyde was reduced by the addition of 1% boric acid, chromic oxide, sodium hydroxide or sulfuric acid. All except the last of these materials promoted the activity of zinc oxide toward allyl alcohol.

A study has been made of the effect of modifications of zinc oxide catalysts upon the relative amounts of acrolein or propionaldehyde produced from allyl alcohol at 330°.

The source of the zinc oxide determines its selective action toward the two reactions of allyl alcohol. For example, zinc oxide from zinc oxalate gave a higher percentage of acrolein than did zinc oxide from zinc hydroxide. The oxide from zinc oxalate could be reproduced easily, but that from zinc hydroxide could not.

The introduction of acidic or basic substances, such as boric acid, chromic acid, tungstic acid, sulfuric acid and sodium hydroxide, into

the zinc oxide caused a selective activation toward one or the other of the two reactions, but the effect seems to be specific for the particular substance and does not depend on its acidic or basic character.

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THE MECHANISM OF THE AZIDE REARRANGEMENT

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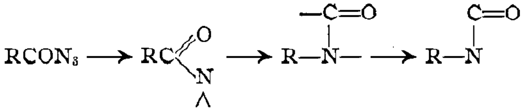
The Beckmann rearrangement and other rearrangements involving the migration of a radical from carbon to nitrogen, including the azide rearrangement to isocyanate, involve a problem of mechanism which is still not solved, though the plausible univalent nitrogen explanation of Stieglitz[1] can be employed as a formulation of the rearrangement in many cases. In the case of the azides the rearrangement involves the univalent nitrogen, thus



Experimental support for the postulate by the examination of the products of decomposition of a di-azide compound has been adduced by Schroeter,[2] and the results are indeed a support of the hypothesis in that they are most simply and directly explained or, rather, represented theoretically, in such a way. There are, however, many possible theories of such mechanisms and the desirable test is one in which the phases postulated in the reaction are shown to exist. In the case of the univalent nitrogen hypothesis the question arises, indeed, as to the possibility of determining the truth of the hypothesis by ordinary chemical means at all. Thus the alkaline reduction of the azides leads to diacyl hydrazines, a reaction well formulated by the univalent nitrogen hypothesis, but not impossible to formulate otherwise. The acid reduction of azides to acid amides is of the same kind. Experiments by the author on the decomposition of azides in a neutral solvent in the presence of triphenylmethyl in the hope of isolating addition compounds of the formula $RCONM_2$ would, if successful, give more valuable support to the hypothesis because of the greater limitation of variables. Benzoyl azide decomposes in benzene solution to give nitrogen and phenyl isocyanate and if the univalent nitrogen phase formed an amide $RCONM_2$ by simple addition in the same solution with a body MM known to be stable in the same solution and not to react with phenyl isocyanate, the number of alternative formulations of the mechanism

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[1] Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); This Journal, **25**, 289 (1903); etc.

[2] Schroeter, *Ber.*, **42**, 2336, 3356 (1909).