

Summary

2,3-Dichloroquinoxaline, 2,3-dimethylquinoxaline and 2,3-diphenylquinoxaline have been shown to be substitution products, respectively, of an ammono oxalyl chloride, an ammono diacetyl and an ammono benzil, and experimental evidence confirming this view has been presented.

Two new methods for the synthesis of 2,3-dialkylquinoxalines have been developed.

The alkylation of an ammono diketone by converting it into a salt of the ammono dienol modification and treating this with an alkyl halide has been carried out for the first time.

Evidence of a benzylic acid rearrangement of an ammono benzil has been found.

The following new compounds have been prepared: *o*-phenylene ethylene oxamidine, 2,3-di-*n*-propylquinoxaline, the dipotassium salt of 2,3-dimethylquinoxaline dienol, 1,2-dihydro-2,2-diphenyl-3-aminoquinoxaline (structure not definitely proven).

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

SOME RELATIONSHIPS OF THE RATIO OF REACTANTS TO THE EXTENT OF CONVERSION OF BENZALDEHYDE AND FURFURALDEHYDE TO THEIR ACETALS

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Most of the measurements which have been made in this Laboratory upon the relationship of the structure of aldehydes and alcohols to the extent of the acetal reaction have been made upon mixtures resulting from the reaction of approximately eleven moles of alcohol with one mole of aldehyde.¹ This ratio of reactants was originally selected in order to preserve the homogeneity of the reaction mixtures, and has been used in other cases in order to obtain a direct comparison of the extent of conversion of various pairs of reactants. More recently it has seemed desirable to ascertain to what extent, if at all, the calculated equilibrium constants for this reaction are dependent upon the ratio of reactants. Such a study has now been made for certain of the acetals of benzaldehyde and furfuraldehyde.

The Reaction of Benzaldehyde with Alcohols.—Test-tubes (1 × 15 cm.) so marked as to make it easy to measure into them approximately the desired volume of alcohol and benzaldehyde, were drawn out preparatory to

¹ Adkins, Adams, Hartung, Street and Broderick, *THIS JOURNAL*, **47**, 1358 (1925); **49**, 2517 (1927); **50**, 162 (1928); **50**, 178 (1928).

sealing, placed in an oven at 115° overnight, cooled in a desiccator and weighed. Approximately the desired quantity of ethanol and 0.00045 g. of hydrogen chloride in ethanol were added and the tube again weighed. Approximately the desired amount of benzaldehyde was added and the tube sealed off and weighed. The tube was then placed in a thermostat and held at 25° for approximately four days. The tubes were opened and samples varying from 0.9 to 5.0 ml., depending upon the concentration of the benzaldehyde, were removed by means of a pipet for analysis.

The Determination of Benzaldehyde.—The sulfite method² is not satisfactory in the analyses for benzaldehyde because of the indefiniteness of the end-point. The hydrogen peroxide method was found to be much more satisfactory if the method of Adams³ was modified as in the following procedure. Thirty ml. of 3% hydrogen peroxide, prepared by diluting "superoxol," was added to 20 ml. of 0.34 *N* sodium hydroxide previously heated in a 250-ml. Erlenmeyer flask to 40°. The sample to be analyzed, and which contained approximately 0.35 g. of benzaldehyde, was added and followed by 5 ml. of ethanol. The reaction mixture was kept with occasional shaking in a thermostat at 40° for thirty-five minutes, after which 10 ml. more of the hydrogen peroxide solution was added and the flask again placed in the thermostat. After a total of fifty minutes in the thermostat the reaction mixture was titrated with standard acid. Blanks containing all the reagents noted above except the sample from the acetal reaction mixture were subjected to the same treatment as in the analyses and a correction made for the acidity so developed. The effect of varying the size of the sample, the quality of the hydrogen peroxide, and the temperature and time for oxidation were investigated and the above procedure was found to be quite accurate and the most satisfactory. The reliability of the method is indicated by the fact that in five successive analyses a sample of benzaldehyde showed a purity of 98.6, 99.2, 97.6, 97.4 and 99.0%.

The Reaction of Furfural with Alcohols.—The desired amounts of furfural and ethanol containing hydrogen chloride were weighed into a flask so that they were in the desired ratio and the total volume was 25 ml. The reaction mixture contained 0.0001 g. of hydrogen chloride. The reaction of furfural and ethanol is complete within a few hours but in these experiments the mixtures were allowed to stand for at least twenty-four hours before an analysis was made.

The Determination of Furfural.—The sulfite method was used for the analysis and the procedure was essentially the same as that previously described.⁴ The equation on which this analysis is based is



² Seyewetz and Bardin, *J. Soc. Chem. Ind.*, **25**, 202 (1906).

³ Adams and Adkins, *THIS JOURNAL*, **47**, 362 (1925).

⁴ Adkins and Broderick, *ibid.*, **50**, 184 (1928).

In the case of certain aldehydes the amount of aldehyde may be calculated on the basis of a titration with a solution of an acid which has been standardized by one of the methods commonly used in acidimetry. However, this is not a justifiable procedure for all aldehydes at various concentrations and it is far more accurate to standardize the acid against the aldehyde, under the conditions in which the acid is to be used in analysis. In this case samples containing from 0.10 to 0.25 g. of furfural with and without the addition of alcohol and furfural acetal were added to 40 ml. of a 10% sodium sulfite solution and the solution titrated with acid having a normality of 0.215 *N* as standardized against a solution of sodium hydroxide. In seven determinations 1 ml. of the acid was equivalent to 0.0231 \pm 1 g. of furfural. The normality of the acid against furfural was thus 0.241. This relationship between the normality of an acid against alkali and against furfural is not fixed but varies somewhat with the operator, because the end-point in the furfural titration is rather indefinite and is determined by a color comparison. This makes it necessary for each operator to standardize his acid solution against furfural.

Preparation of Furfural Acetal.—This acetal has been prepared by the reaction of the aldehyde with orthoformic ester as described by Claisen.⁵ The preparation of the acetal by the less costly method involving the reaction of furfural with alcohol has apparently hitherto not been successful because of the sensitivity of the aldehyde toward hydrogen chloride, and because of its low equilibrium point in the acetal reaction. A practical method for carrying out this preparation has been developed after a rather extended study. A reaction mixture containing 96 g. (1 mole) of furfural, 276 g. (6 moles) of dry ethanol and 0.0012 g. of anhydrous hydrogen chloride was allowed to stand for one day. Ten ml. of water containing 1 g. of sodium carbonate was then added and the mixture subjected to fractionation through a Widmer column 30 cm. in length. The fractionation was carried out slowly so that the distillate was not more than 2 ml. per minute. After removal of the alcohol the liquid was filtered, transferred to a 250-ml. flask and fractionated through the Widmer column under a pressure of 16 to 19 mm. A yield of 24% of the theoretical amount, *i. e.*, 41 g. of acetal of b. p. 77–79° (16 mm.) and 184–185° (740 mm.) was obtained on the average. Claisen reported the boiling point of the acetal as 189–191°, while Scheibler, Sotschek and Friese⁶ reported 180–184°. If the amount of alcohol in proportion to the furfural was much less than that recommended above or if the concentration of catalyst was much greater the yields of acetal were materially reduced. The acetal may also be obtained from the reaction mixture by pouring it into a liter of water containing 1 g. of sodium carbonate. The water-insoluble layer was

⁵ Claisen, *Ber.*, **40**, 3907 (1907).

⁶ Scheibler, Sotschek and Friese, *ibid.*, **57B**, 1444 (1924).

then placed over anhydrous sodium sulfate, while another liter of water was added to the aqueous layer in order to throw out more of the acetal. The combined water-insoluble layers after drying were then fractionated. The yield of acetal so obtained was usually about 2 g. less than by the first process in which the alcohol was removed by distillation.

Ratio of Reactants and Extent of Acetal Reaction.—There are recorded in Table I the percentage conversions of benzaldehyde and furfuraldehyde to their acetals in their reaction with various alcohols at various concentrations. The average deviation from the mean in these determinations is indicated in column two of the table after the sign for plus or minus. The number of reaction mixtures which were analyzed is indicated by the figures in parentheses in column two of the table. The value for the equilibrium constant given in column three of the table was calculated on the basis of the concentrations at equilibrium expressed as mole fractions.

TABLE I
RATIO OF REACTANTS AND EXTENT OF ACETAL REACTION

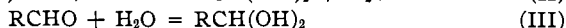
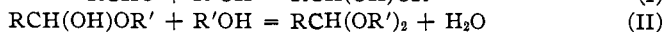
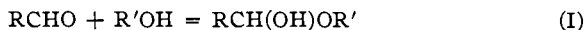
Moles of alcohol per mole of aldehyde	Conversion of aldehyde to acetal, %	K
Ethanol and Benzaldehyde		
2.08	25.1 ± 1.1 (8)	0.091
3.90	34.1 ± 0.8 (6)	.079
5.87	41.9 ± 2.0 (6)	.089
7.80	48.6 ± 1.8 (7)	.082
9.96	53.0 ± 1.1 (8)	.081
<i>n</i> -Butanol and Benzaldehyde		
2.02	24.8 ± 1.5 (7)	.091
4.17	36.0 ± 1.9 (6)	.082
6.13	44.0 ± 2.2 (6)	.084
8.01	48.9 ± 1.3 (7)	.080
9.90	52.7 ± 0.7 (6)	.080
Propanol-2 and Benzaldehyde		
1.85	6.7 ± 1.1 (5)	.0045
5.86	11.1 ± 0.8 (3)	.0030
10.41	18.7 ± 0.5 (2)	.0047
Ethanol and Furfuraldehyde		
2.02	17.1 ± 0.5 (2)	.036
6.06	32.6 ± 0.5 (2)	.036
6.21	32.9 ± 0.3 (2)	.035
9.80	39.8 ± 0.7 (2)	.034
11.08	43.7 ± 0.6 (2)	.039
Methanol and Furfuraldehyde		
4.40	39.5 ± 0.5 (2)	.098

In addition to these determinations upon the synthesis of acetals a reaction mixture was made containing 0.3 mole of furfural acetal, 0.181 mole

of water, 3.335 moles of ethanol and 0.0001 g. of hydrogen chloride. After equilibrium had been established the concentrations of the reactants were 0.193 mole of acetal, 3.549 moles of ethanol, 0.074 mole of water and 0.107 mole of furfuraldehyde. The equilibrium constant is thus 0.041. The analysis of another equilibrium mixture resulting from the hydrolysis of furfuraldehyde acetal indicated the value of K to be 0.039.

The percentage conversion of benzaldehyde to the acetals in its reaction with ethanol and propanol-2, and for the reaction of furfuraldehyde with ethanol and methanol, have been determined previously for reaction mixtures which contained 1 mole of aldehyde to 11 moles of the alcohol.⁷ The values for the equilibrium constants calculated from Adams' data on the basis of the concentrations at equilibrium expressed as mole fractions are as follows: benzaldehyde with ethanol, 0.024, with propanol-2, 0.0030; furfuraldehyde with methanol, 0.113, with ethanol, 0.029. It may be seen from a comparison of these values with those given in Table I that there is a fair agreement between the values of K now reported and those calculated from Adams' data except for the reaction of benzaldehyde and ethanol. It is believed that this discrepancy is due to his procedure for the oxidation of benzaldehyde, which has been proved in this investigation to give inaccurate results.

The values for the equilibrium constant recorded in Table I indicate that there is very little if any change in the constant when the moles of alcohol per mole of aldehyde is increased from 2 to 10. It is possible that there is a small decrease in the value of the constant with increasing concentrations of alcohol. Such a change in the calculated equilibrium constant is not surprising if it is considered that the acetal reaction is not the only reaction which may modify the concentration of the components of the system under study.



It was previously shown⁸ that the formation of acetals probably proceeds through Reactions I and II. Some of the water formed according to Equation II would add to the aldehyde as in Equation III. Thus as the extent of the acetal reaction increased with increase in the ratio of alcohol to aldehyde, there would also occur an increase in Reaction III which would decrease the actual concentration of aldehyde (or hemiacetal) and thus the increase in the conversion of aldehyde to acetal would not be as great as would be calculated. On the basis of this argument such an effect would become even more marked with those aldehydes which show much higher percentage conversion. It is hoped that the effect of the ratio of reactants

⁷ Adkins and Adams, *THIS JOURNAL*, **47**, 1370 (1925).

⁸ Adkins and Broderick, *ibid.*, **50**, 499 (1928).

upon the equilibrium constant may be extended to the study of aldehydes which show much higher percentage conversion than do those referred to in this paper.

Summary

For the first time a method for the preparation of furfural acetal from the aldehyde and ethanol has been described.

The effect of the ratio of reactants upon the extent of the reaction of benzaldehyde with ethanol, butanol and propanol-2 and of furfural with ethanol has been determined when the ratio of aldehyde to alcohol is varied from 1 to 2 to 1 to 10. The equilibrium constant for the first two of these reactions was found to be identical for the two alcohols but to decrease slightly with increase in ratio of alcohol to aldehyde.⁹ The equilibrium constant for the reaction of benzaldehyde with propanol-2 and of furfuraldehyde with ethanol appeared to be independent of the concentration of reactants. The equilibrium constant for the reaction of furfuraldehyde and methanol has been redetermined.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

RESIN STUDIES. I. THE PREPARATION AND AUTOXIDATION OF PRECIPITATED LEAD ROSINATE

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I. Preparation of Precipitated Lead Rosinate

Introduction.—In attempting to study quantitatively the absorption of oxygen by lead rosinate it was obviously important to begin with a material of known and reproducible composition, preferably a normal salt, which had not been exposed to oxidation. Lead rosinate was made by several of the methods proposed in the literature for the preparation of rosinate and abietates¹ and was found objectionable for two reasons. (1) The rosinate responded positively to the starch-iodide test for peroxides immediately after the preparation was completed. (2) The composition (usually complex) of the precipitates obtained according to the

⁹ The equilibrium constants for the reactions of butanol and ethanol with benzaldehyde are the same only when they are calculated upon the basis of concentrations expressed as mole fractions. They are not identical if the calculation is made upon the basis of concentrations expressed as moles per liter as was done in previous papers in this series.

¹ Pardeller, *Seifensieder-Ztg.*, 1256 (1909); Ellingson, *THIS JOURNAL*, 36, 325 (1914); Bontoux, *Rev. chim. ind.*, 28, 157 (1919); Steele, *THIS JOURNAL*, 44, 1332 (1922); Dupont, Desalbres and Bernette, *Bull. soc. chim.*, 39, 488 (1926); Uzac, *ibid.*, 37, 1194 (1925); Uzac, *Chimie et industrie*, 14, 186 (1925).