[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Action of Alkalies on Mixtures of Aromatic Aldehydes

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It has been shown[1] that a crossed Cannizzaro reaction may take place between two aliphatic aldehydes or an aromatic and an aliphatic aldehyde. This paper reports some experiments which demonstrate that a crossed Cannizzaro reaction may also take place between two aromatic aldehydes.

The first experiments undertaken were directed toward carrying out such a reaction between benzaldehyde (which undergoes the Cannizzaro reaction readily) and *p*-dimethylaminobenzaldehyde (which does not react under the conditions of our experiments). That the reaction might take place seemed logical in view of Staudinger's discovery[2] that both benzaldehyde and *p*-chlorobenzaldehyde form mixed benzoins with *p*-dimethylaminobenzaldehyde although *p*-dimethylaminobenzaldehyde alone does not undergo the benzoin condensation. It was found, however, that the *p*-dimethylaminobenzaldehyde could be recovered unchanged, the benzaldehyde reacting in the normal manner. Likewise, when a mixture of benzaldehyde and *m*-nitrobenzaldehyde was stirred with 14% potassium hydroxide, only the *m*-nitrobenzaldehyde seemed to react. Benzaldehyde undergoes the Cannizzaro reaction readily with concentrated alkali but will not react in a solution of this concentration.

When a mixture of *p*-chlorobenzaldehyde and anisaldehyde was allowed to react with alkali, a definite disproportionation took place. This discovery led to a study of several mixtures containing halogen substituted benzaldehydes, the results of which are summarized in Table I. In every case a crossed Cannizzaro reaction took place. In two cases (numbers 7 and 14) the individual acids were separated from their mixtures, but in most cases the mixtures were simply analyzed for halogen and the composition of the mixture calculated. Experiments 1, 2 and 8 were carried out under different conditions than the rest.

The analysis of the alcohol mixtures containing benzyl alcohol did not give consistent results. This evidently is due to the volatility of benzyl alcohol, which makes it difficult to free the alcohol mixture from ether and water without losing benzyl alcohol, and so altering the composition of the mixture. On this account, the analyses for the alcohol mixtures obtained from meta- and para-bromobenzaldehyde with benzaldehyde are not reported, and the results in these cases must be considered as tentative.

While the data are insufficient to allow any theoretical deductions, they indicate plainly that crossed Cannizzaro reactions can take place with mixtures of aromatic aldehydes. It is interesting to note that in every case the halogen substituted aldehyde is preferentially oxidized at the expense of the other aldehyde.

Experimental

Benzaldehyde and *p*-Dimethylaminobenzaldehyde.—A mixture of five grams of each of the aldehydes was shaken vigorously with 20 g. of a 50% solution of potassium hydroxide for two hours and allowed to stand for twenty-four hours. The mixture was diluted with 300 cc. of water, and extracted with three 40-cc. portions of ether. The ether extract was shaken with a saturated solution of sodium bisulfite (which precipitated part of the dimethylaminobenzaldehyde as the bisulfite addition product) and was then distilled. The fraction boiling between 200–206° was taken as benzyl alcohol. The yield was 2.2 g. (88% of the theoretical). The residue from the distillation solidified on cooling. After recrystallization, this solid melted at 73°. *p*-Dimethylaminobenzaldehyde melts at 74°. The recovery of the substituted aldehyde from the bisulfite compound and from the distillation was almost quantitative.

The aqueous residue from the ether extraction was acidified, and the precipitated benzoic acid was filtered off. It melted at 121° and weighed 2.1 g. (84% yield). The filtrate was neutralized carefully, but no *p*-dimethylaminobenzoic acid could be obtained.

Benzaldehyde and *m*-Nitrobenzaldehyde.—A mixture of 18.1 g. of *m*-nitrobenzaldehyde and 13.7 g. benzaldehyde was allowed to drip into 280 g. of a 14% solution of potassium hydroxide with vigorous stirring. After standing for twenty-four hours, the solution was diluted and extracted with ether as before. Treatment with sodium bisulfite resulted in the recovery of 11.9 g. of unchanged aldehydes, practically all of which was benzaldehyde. The aqueous residue from the ether extractions was acidified, and the copious precipitate of acid steam distilled. No benzoic acid was present in the distillate, as was shown by extracting it with ether and evaporating the extract.

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(1) Nord, *Biochem. Z.*, **106**, 275 (1920); *Beitrage Physiol.*, **2**, 301 (1924); Nakai, *Biochem. Z.*, **152**, 258 (1924); Endoh, *Rec. trav. chim.*, **44**, 866 (1925); Orloff, *Bull. soc. chim.*, [4] **35**, 360 (1924); Nenitzescu and Gavat, *Bull. soc. chim. Romania*, **16A**, 42 (1934) (*British Chemical Abstracts*, 74 (1936)); Davidson and Bogert, THIS JOURNAL, **57**, 905 (1935).

(2) Staudinger, *Ber.*, **46**, 3535 (1913).

TABLE I

Substituted benzaldehydes	Expt.	Ratios							
		Halo acid to other acid				Halo alcohol to other alcohol			
p-Chloro- and *p*-methoxy-	1, 2, 3, 4	2.3:1	2.3:1	1.6:1	1.6:1	1:2.7	1:2.5	1:2.0	....
p-Chloro- and benz-	5, 6, 7, 8	1.45:1	1.3:1	1.7:1	2.5:1	1:1.3	1:1.3	....	1:2.8
p-Chloro- and (*m*,*p*-methylenedioxy)-	9			1.8:1					1:1.95
p-Bromo- and *p*-methoxy-	10, 11			2.3:1	2.8:1			1:1.8	1:2.1
p-Bromo- and benz-	12, 13, 14		1.4:1	1.3:1	1.2:1				
m-Bromo- and *p*-methoxy-	15, 16			1.9:1	1.7:1			1:1.8	1:2.0
m-Bromo- and benz-	17, 18, 19		2.4:1	2.1:1	2.2:1				

Procedure for Experiments Recorded in Table I (Except Numbers 1, 2 and 8).—A mixture of the two aldehydes (0.05 mole of each) was allowed to drop slowly into a solution of 27.5 g. of potassium hydroxide in 25 cc. of water with vigorous stirring. When the addition was complete, the temperature was raised slowly to 100° and held at that point for two hours. The solution was diluted to 400 cc. and extracted with four portions of ether. The ether extracts were combined, treated with bisulfite (which in no case gave more than 0.1 g. of precipitate), washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was analyzed for halogen by decomposition in the Parr bomb and titration by the Volhard method. The aqueous residue from the ether extractions was acidified with hydrochloric acid, and extracted with four portions of ether. The ether solutions were dried and evaporated and the residue analyzed as described for the alcohols.

Procedure for Experiments 1, 2 and 8 of Table I.—A mixture of five grams of each aldehyde, 10 g. of potassium hydroxide, and 10 cc. of water was shaken vigorously for two hours and allowed to stand a day. The remainder of the procedure was the same as that described above.

In Experiments 7 and 14 the acids were separated by steam distillation. This does not give a sharp separation of *p*-chlorobenzoic acid and benzoic acid, so the ratio given in Experiment 7 is only approximate. The separation of *p*-bromobenzoic acid and benzoic acid is very good, however, the recovered acids melting at 249 and 120° (reported, 251–253 and 122°).

Summary

It has been shown that 50% potassium hydroxide solution, acting on a mixture of benzaldehyde and *p*-dimethylaminobenzaldehyde induces the Cannizzaro reaction for the benzaldehyde only. The other aldehyde is not affected. A mixture of *m*-nitrobenzaldehyde and benzaldehyde, under the action of 14% potassium hydroxide, gives nitrobenzoic acid and nitrobenzyl alcohol, without attacking the benzaldehyde.

Seven reactions have been studied in which a crossed Cannizzaro reaction takes place between aromatic aldehydes. One member of the aldehyde pair in each of these was halogen substituted, and in every case, the halogen substituted molecule showed a tendency to be oxidized to the acid at the expense of the other aldehyde.

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Dipole Moment and Structure of Organic Compounds. XVI.[1] The Electric Moments of Some Chlorinated Diphenyls

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It has been suggested[2] that the electric moments of mono- and dichloronaphthalenes indicate a polarization of the naphthalene system by the polar C–Cl link, this polarization causing the observed moments to deviate considerably from those calculated when this effect is neglected, and a similar behavior has been found with the chlorodiphenyls. In the case of the dichlorodiphenyls with substituents in *both* rings, in either the ortho or meta position, a further complication is introduced, for there the moment will depend primarily on the configuration of the two rings about the diphenyl link. In view of the forces which govern the probability of the various configurations, special attention has been drawn to the case of *o*,*o*′-dichlorodiphenyl. The moment of this compound is larger than that of the *m*,*m*′-isomeride, and this is even more surprising in view of the fact that in the *o*,*o*′-compound the *cis*-configuration and a wide range of positions in the neighborhood of the *cis*-position which would contribute to a large moment are precluded for steric reasons. To account for the facts we suggested that *London forces* play an important role in determining the inner configuration of the molecule.

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[1] Hampson and Weissberger, Paper XV, *J. Chem. Soc.*, 393 (1935).

[2] Weissberger, Sängewald and Hampson, *Trans. Faraday Soc.*, **30**, 884 (1934).