29. *Application of the Conditions of the Tiemann–Reimer Reaction to Benzaldehyde.*

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Addition of chloroform to the carbonyl group of benzaldehyde was the only reaction observed (apart from the Cannizzaro reaction) in an attempt to repeat Chaudhuri's synthesis of *o*- and *m*-dichloromethylbenzaldehyde by the interaction of benzaldehyde, chloroform, and aqueous potassium hydroxide. Under Chaudhuri's conditions this addition led to the formation of mandelic acid; but, by reducing the amount of alkali and adding alcohol, the initial addition product, phenyltrichloromethylcarbinol, also was isolated.

Chaudhuri (*J. Amer. Chem. Soc.*, 1942, **64**, 315) has reported the direct introduction of dichloromethyl groups into the *o*- and *m*-positions of benzaldehyde through the action of chloroform and aqueous caustic potash.

We have had occasion to attempt the preparation of the corresponding phthalaldehydes through the medium of this reaction, and our findings have been so much at variance with those of Chaudhuri that it seems desirable that they be placed on record.

Under the conditions described (*loc. cit.*), no neutral product other than benzyl alcohol was isolated, and the alkali-soluble part of the product consisted of benzoic acid and substantial quantities of mandelic acid. In no experiment could the dichloromethylbenzaldehydes described by Chaudhuri, or any products derived from these, be obtained. Our experience indicated that the only interaction of chloroform and benzaldehyde occurring under the conditions specified was the normal addition of the chloroform to the carbonyl group of the benzaldehyde (cf. Jozitsch, *Chem. Zentr.*, 1897, I, 1013), and this was supported by the fact that, when the proportion of alkali was diminished from 5 mols. to 1 mol., alcohol added till the mixture was homogeneous, and the reaction period reduced from 6 hours to ½ hour, phenyltrichloromethylcarbinol was isolated in appreciable amount in the neutral fraction, along with mandelic acid in the acid fraction.

Although sufficient data are not available on which to base a decision, it seems possible that Chaudhuri has handled crude phenyltrichloromethylcarbinol, and that he has incorrectly characterised this as a mixture of *o*- and *m*-dichloromethylbenzaldehydes. Particularly is this the case in view of the fact that his found and calculated percentages of halogen in the products described by him are both grossly in error for the formulations given (Found by Chaudhuri : Cl, 43·9, 43·9. Calc. for $C_8H_6OCl_2$: Cl, 37·5%. Chaudhuri, however, records Calc. for $C_8H_6OCl_2$: Cl, 44·7%). Moreover, we find it difficult to reconcile the survival of the dichloromethylbenzaldehydes through 6 hours' boiling with 60% potassium hydroxide solution with their subsequent facile hydrolysis in 45 mins. under conditions of unspecified severity. Equally difficult to understand is the statement that the Cannizzaro reaction of benzaldehyde does not occur in the presence of chloroform : this is completely counter to our experience.

Reaction between carbon tetrachloride and benzaldehyde, and between benzotrichloride and benzaldehyde under similar conditions has also been explored, but again no products of the Tiemann–Reimer type have been obtained.

EXPERIMENTAL.

The Reaction between Benzaldehyde, Chloroform, and Potassium Hydroxide in Aqueous Solution.—A solution of potassium hydroxide (60 g., 1·1 mols.) in water (100 c.c.) was added to a mixture of pure benzaldehyde (20 c.c., 0·20 mol.) and chloroform (16 c.c., 0·20 mol.), and the whole refluxed for 6 hours, exactly as specified by Chaudhuri (*loc. cit.*). No vigorous reaction was observed on mixing the reagents. Neutral materials were extracted from the alkaline solution with ether. The residue remaining after the drying of the extract and the removal of the ether gave on distillation the following fractions : (*a*) b. p. 63—78°/14 mm., consisting predominantly of benzaldehyde (4·5 g., 0·043 mol.) ; (*b*) b. p. 95°/14 mm., consisting of benzyl alcohol (4·5 g., 0·042 mol.). The residue was negligible. The alkaline solution was acidified with concentrated hydrochloric acid, and the crude material which was precipitated gave benzoic acid (9·1 g., 0·075 mol.), m. p. and mixed m. p. 121° on recrystallisation from water. No phthalic acid could be isolated or detected. The water-soluble acidic product was extracted with ether, and distillation of the ether left a solid residue, which on recrystallisation from benzene gave mandelic acid (3·0 g., 0·20 mol.), m. p. and mixed m. p. 118°.

Repetition of this experiment with molecular proportions of chloroform varying from 1 to 1·5 and reaction times varying from 15 mins. to 1 hour did not give any different results.

The Reaction between Benzaldehyde, Chloroform, and Sodium Hydroxide in Aqueous-alcoholic Solution.—A mixture of benzaldehyde (212 g., 2·00 mols.), chloroform (262 g., 2·20 mols.), and sufficient ethyl alcohol (250 c.c.) to render the resulting reaction medium homogeneous was treated with a solution of sodium hydroxide (80 g., 2·00 mols.) in water (200 c.c.). (The use of potassium hydroxide was not found to offer any advantage.) The mixture was heated on a water-bath for ½ hour ; its reaction was then acidic. The alcohol and the chloroform were distilled off, along with some benzaldehyde, which was recovered by extracting the distillate with chloroform. The remaining aqueous solution was extracted with ether, and the extract freed from acidic material by washing with dilute sodium hydroxide solution, the washings being added to the main aqueous solution. The ethereal extract, together with the chloroform extract of benzaldehyde, was dried over calcium chloride, and the ether and the chloroform distilled off. On fractionation the residue gave benzaldehyde and benzyl alcohol (129 g. ; b. p. up to 110°/4 mm.), phenyltrichloromethylcarbinol (22 g., 5% ; b. p. 115—117°/4 mm.), and a little higher-boiling material (3 g.), which gave only benzoic acid (m. p. and mixed m. p. 121°) on oxidation with alkaline permanganate, and was therefore not felt to warrant further investigation. The phenyltrichloromethylcarbinol was redistilled, and the fraction boiling at 117°/4 mm. collected. The aqueous solution was treated as described in the first experiment, and from it were obtained benzoic acid (12 g.) and mandelic acid (7 g., 2½%). The redistilled phenyltrichloromethylcarbinol was oxidised by alkaline permanganate to benzoic acid, m. p. and mixed m. p. 121° after recrystallisation from dilute ethyl alcohol. The crude oxidation product gave a negative fluorescein reaction. A sample of the phenyltrichloromethylcarbinol was refluxed for 2 hours with 20% alcoholic potassium hydroxide, the reaction mixture acidified with dilute nitric acid, silver nitrate added, and the precipitated silver chloride removed (Found : Cl, 45·9. Calc. for $C_8H_7OCl_3$: Cl, 47·1%) Extraction of the filtrate with ether led to the isolation of an oily material, which crystallised overnight in contact with benzene. The crystals were identified as mandelic acid (mixed m. p.).

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