

higher oxide under the conditions mentioned by him. I made a number of determinations using very pure antimonious oxide and found no evidence of the conversion into the higher oxide.

Further, several experiments were made using different proportions of the acids, alcohol and water but always with the same result.

PERCY EDGERTON.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

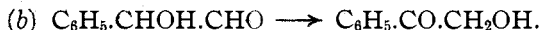
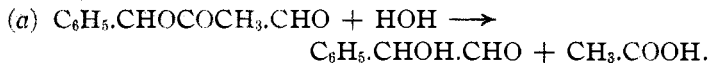
THE EXISTENCE OF MANDELIC ALDEHYDE IN AQUEOUS SOLUTION.

BY WILLIAM LLOYD EVANS AND CHARLES RAYMOND PARKINSON.

Received September 17, 1913.

In a recent report¹ from this laboratory, on the "Preparation and the Oxidation of Styrolene Alcohol," it was stated that the authors of the present paper were engaged in an attempt to synthesize mandelic aldehyde. We were anxious to know whether this compound was capable of existence, under the conditions employed in the studies with styrolene alcohol, *viz.*, at ordinary temperature and pressure, and in the presence of water.

The only other previously recorded attempt to isolate this substance was that of Nef.² He prepared mandelic aldehyde acetate by the interaction of α -bromphenylacetaldehyde and silver acetate in absolute ether. He then attempted to hydrolyze the product thus obtained at 100°, and found that the reaction products were benzoyl carbinol and acetic acid:



In a similar study, Nef³ found that acetol and acetic acid were formed by the hydrolysis, at 100°, of lactic aldehyde acetate, which had in turn been prepared by the action of α -iodopropionic aldehyde and silver acetate in absolute ether.

Subsequently, Wohl and Lange⁴ prepared lactic aldehyde at ordinary temperature. They prepared diethoxyacetic acid by the interaction of dichloroacetic acid and sodium ethylate. This product was condensed with piperidine, and on treatment of the piperidide thus formed with methyl magnesium iodide, by Grignard's general method, they obtained the acetal of pyruvic aldehyde. By reduction, the acetal of lactic aldehyde was obtained, which, in turn, was hydrolyzed with 0.1 *N* sulfuric acid. By this latter reaction the free aldehyde was prepared. It is therefore clear, that lactic aldehyde is incapable of existence in water at 100°,

¹ THIS JOURNAL, 35, 54.

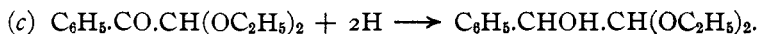
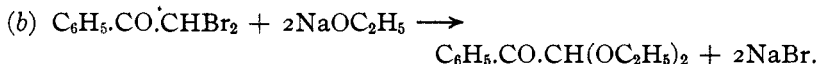
² *Ann.*, 335, 268.

³ *Ibid.*, 335, 266.

Ber., 41, 3612.

while at ordinary temperature it is a sufficiently stable substance to be studied experimentally. The facts in reference to mandelic aldehyde are these: (a) Nef¹ has conclusively proven that it is incapable of existence at 100° in the presence of water; (b) from the experiments briefly described below, it is firmly established, that this compound cannot exist in the presence of water and dilute sulfuric acid at either room temperature or at the freezing point of this solvent; (c) nor can it exist in the presence of water and dilute ethyl alcohol under the same conditions.

Mandelic aldehyde acetal was prepared by the reduction of benzoyl-formaldehyde acetal, which, in turn, had been prepared by the interaction of sodium ethylate and dibromoacetophenone; *i. e.*,



During the progress of this work an excellent paper by Dr. Cyril Kranz,² of Pragué, appeared on the preparation of lactic aldehyde. He employed for his purposes the same general reactions as are here outlined. The substance prepared by him was identical with that obtained by Wohl and Lange.¹

Experimental Part.

Preparation of Dibromoacetophenone.—Dibromoacetophenone was first prepared by Hunnius³ and subsequently by Fittig and Wurster,⁴ by the bromination of acetophenone dissolved in carbon disulfide. For these experiments, it was made by the bromination of acetophenone dissolved in chloroform. A solution of 133.3 grams (2 mols) of bromine, dissolved in 200 cc. of chloroform, was added, slowly in direct sunlight, to a solution of 50 grams of acetophenone dissolved in an equal volume of the same solvent. The time required was four hours. The first red color of the successively added portions of the bromine solution was immediately discharged, the final color of the reaction mixture being yellow.⁵ The hydrobromic acid remaining in solution was removed by passing a current of air through the reaction mixture and subsequently washing with water. After distilling the chloroform, again washing with water, dissolving the residue in ether, and drying with calcium chloride, a yield of 118 grams (theory = 115.8 grams) of the crude product was obtained. The oil thus obtained was distilled *in vacuo*, the boiling point being 175–176° at

¹ *Loc. cit.*

² *Chemische Listy*, 5, 323–7; *C. A.*, 6, 739.

³ *Ber.*, 10, 2010.

⁴ *Ann.*, 195, 161; compare Wittorf, *Chem. Zentr.*, 2, 29 (1900); also Siegfried, *Ibid.*, 1, 606 (1899).

⁵ Compare THIS JOURNAL, 30, 406.

23 mm. pressure. The distillate was a clear, colorless liquid, which turned to a light yellow color on standing. Dibromoacetophenone has an exceedingly sharp, penetrating odor and it also produces severe lachrymation.¹ The following is the result of the quantitative estimation of bromine:

Calculated for $C_8H_6OBr_2$, 57.55%; found, 57.37%, 57.45%.

Preparation of Benzoylformaldehyde Acetal.—A solution of 103 grams of freshly distilled dibromoacetophenone, in 200 cc. of absolute alcohol, was slowly added to a well-cooled (0°) solution of sodium ethylate, prepared by adding 19.4 grams (2.2 atoms) of sodium chips to 348 grams of absolute alcohol. Sodium bromide, colored slightly yellow, began to separate immediately. After allowing the reaction mixture to stand over night, filtering the sodium bromide, concentrating the alcoholic filtrate *in vacuo*, and filtering the further separated portion of sodium bromide, the resulting alcoholic solution was poured into 500 cc. of water. A dark red oil separated out. The supernatant water was decanted and extracted six times with 50 cc. portions of ether. The red oil was now dissolved in the combined ether extracts, and the resulting solution was dried with calcium chloride. After distilling the ether, there remained 48.2 grams of oil (theory = 77 grams, therefore 62.6%). A clear, colorless liquid, boiling at 110° at 15 mm., was obtained by distillation of the reaction product *in vacuo*. The operation was accompanied by considerable decomposition and the formation of large amounts of tar. Kranz² made a similar observation in the distillation of pyruvic aldehyde acetal. Benzoylformaldehyde acetal, prepared as indicated here, has a pleasant odor when free of the unchanged dibromoacetophenone. The following results were obtained by analysis:

Calculated for $C_{12}H_{16}O_3$: C, 67.75%; H, 7.52%. Found: C 67.52%; H, 7.76%.

Preparation of Mandelic Aldehyde Acetal.—Twenty-five grams (theory = 5.5 grams) of sodium in chips were added to a well-cooled solution (0°) of 25 grams of benzoylformaldehyde acetal in 400 cc. of absolute alcohol. During the reaction the alcoholic solution turned dark brown. After the action had ceased, the reaction mixture was treated with carbon dioxide for 14 hours. The alcoholic filtrate from the sodium salt was distilled *in vacuo* and the remaining oil was dried over sulfuric acid in a vacuum desiccator. The product weighed 18 grams (theory = 25.2 grams, therefore 71.4%). On distillation, a clear, colorless oil was obtained which boiled at $105-110^\circ$ at 22 mm. Considerable decomposition took place. Mandelic aldehyde acetal, thus prepared, turned slightly yellow in color on standing and it possessed a pleasant odor. The acetal was prepared several times in the original alcoholic solution, in which the benzoyl-

¹ Compare Hunnius, *loc. cit.*

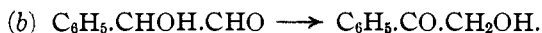
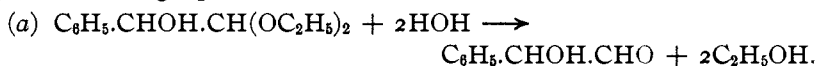
² *Loc. cit.*

formaldehyde acetal had been prepared as described above. A slightly larger yield was obtained in these cases, owing to the elimination of one fractional distillation *in vacuo*.

Hydrolysis of Mandelic Aldehyde Acetal.—Five grams of freshly distilled mandelic aldehyde acetal were suspended in 100 cc. of 0.05 *N* sulfuric acid in a sealed tube, which was kept at 0°, and was shaken at frequent intervals. After standing three days, crystals began to be formed. At the end of four weeks the crystallin substance was filtered, and the aqueous solution was extracted four times with 50 cc. portions of ether. The crystals were dissolved in the combined ether extracts. The resulting solution was dried and evaporated, by drawing air over the ether. A yield of 2.8 grams (theory = 2.66 grams) was obtained. The white crystallin material, thus obtained, was found to reduce both Fehling's solution in the cold and ammoniacal silver nitrate solution. The reaction product was found to be identical in every respect with benzoyl carbinol described by Zincke and others.¹

That this reaction takes place even in the absence of sulfuric acid is proven by the following experiment: One and twelve-hundredths grams (1.12) of mandelic aldehyde acetal were suspended in 25 cc. of water under the same conditions as the preceding experiment. At the end of 5 days, the reaction mixture was found to contain 0.58 gram (theory = 0.72 gram, therefore 80%) of benzoyl carbinol. A small amount of oil (0.18 gram) was also obtained. This gave no reaction with phenylhydrazine and was undoubtedly unchanged mandelic aldehyde acetal. At the same time this experiment was also performed at room temperature, with the same general result.

A specimen of mandelic aldehyde acetal was allowed to remain standing in the open air for twelve weeks. During this time crystals began to be formed and finally the whole specimen had solidified. After removing the adhering oil, the white crystallin material was found to be identical with that obtained by the hydrolysis of mandelic aldehyde acetal in the presence of dilute sulfuric acid. On the other hand, a specimen of the oil, when kept out of contact with the moisture of the air, was found to remain unchanged. It is to be concluded, therefore, that the reactions taking place in the above hydrolysis may be represented by the following equations:



Finally, from the experiments of Nef, Wohl and Lange, Kranz² and those described in this paragraph, the following conclusions may be drawn:

¹ *Ann.*, 216, 306; *Amer. Chem. J.*, 35, 119.

² *Loc. cit.*

(a) lactic aldehyde and mandelic aldehyde in the presence of water, at 100°, rearrange to acetol and benzoyl carbinol, respectively; (b) lactic aldehyde does not undergo this rearrangement at ordinary temperature; (c) mandelic aldehyde, the aromatic analogue of lactic aldehyde, not only undergoes this rearrangement to benzoyl carbinol at ordinary temperature in the presence of water and dilute sulfuric acid, but this transformation also takes place at 0°; (d) mandelic aldehyde undergoes rearrangement to benzoyl carbinol even in the presence of water and dilute ethyl alcohol, both at ordinary temperature and at 0°; (e) mandelic aldehyde undergoes rearrangement to benzoyl carbinol with the water vapor of the atmosphere. In conclusion we wish to thank Mr. J. E. Day, of this laboratory, for the analysis of the benzoylformaldehyde acetal prepared by us.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

CATALYSIS ON THE BASIS OF WORK WITH IMIDO ESTERS: A CONTRIBUTION TO THE PROBLEM OF SAPONIFICATION AND ESTERIFICATION.

BY JULIUS STIEGLITZ.

Received May 16, 1913.

The well-known explanation of the accelerating (catalytic) effect of acids on the saponification of esters by water assumes that the complex oxonium ion¹, formed by the ester with the hydrogen ion of the catalyzer, is the chief² reacting component of the ester which is saponified by the

¹ Stieglitz, *Report of the Congress of Arts and Science*, St. Louis, 4, 278 (1904); *Am. Chem. J.*, 39, 29, 166, 402 (1908), and later articles. See also Bredig and Walton, *Z. Elektrochem.*, 9, footnote, p. 118 (1903), and *Ibid.*, 10, 586 (1904); Acree and co-workers, *Am. Chem. J.*, 37, 410; 38, 258 (1907), etc.; and Goldschmidt, *Z. physik. Chem.*, 60, 728 (1907) and later articles. Closer examination of Lapworth's theory shows that it was not in conflict with the laws of equilibrium (cf. Lapworth, *Proc. Chem. Soc.*, 24, 101, 152 (1908)), as was unfortunately concluded in the discussion of his theory by the present author (*Loc. cit.*, p. 424), but the criticism of the assumptions of the theory for the other reasons given appears justified and Lapworth himself later withdrew his theory. (See Fitzgerald and Lapworth, *J. Chem. Soc.*, 93, 2165 (1908).)

² Questions concerning the rôle of non-ionized ionogens in reactions of this type have been brought to the fore in recent years, especially by Goldschmidt and Acree. Goldschmidt first suggested the possible activity of non-ionized acids in catalysis (*Z. physik. Chem.*, 29, 118 (1899)). The present author first demonstrated with imido esters that the non-ionized molecules of an ionogen are active as well as its anions (Schlesinger's Dissertation, University of Chicago, 1905; *Am. Chem. J.*, 39, 167 (1908)), where the general importance of the results both for organic and inorganic compounds was emphasized; finding, however, that the molecules react with velocities very much smaller than those of the ions, he considered the molecules capable only of very slow parallel reactions (see applications of this idea, *THIS JOURNAL*, 32, 229 (1910) and