

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

Notes on the Chemistry of the Aloins. Formation of Formaldehyde and Furfural¹

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In 1932, Cahn and Simonson² reported the detection of methanol among the products formed when aloin is hydrolyzed by an aqueous solution of borax. Some time later, Rosenthaler³ repeated their work and found that a compound was formed which would give Denigè's reaction for methanol, but that when the solution was made alkaline and distilled, the test was no longer given. In attempting to obtain an explanation for these results, we have re-investigated this problem. No methanol was detected, but, under a wide variety of conditions, formaldehyde was found, although in exceedingly small amounts.

Since the work of Leger,⁴ it has been known that both barbaloin and its isomer, isobarbaloin, yield *d*-arabinose among other products when decomposed under a variety of conditions. As the isolation of small quantities of *d*-arabinose from much larger amounts of inorganic salts and other organic materials is a process of sufficient difficulty that negative results are inconclusive, we have studied the conditions for *d*-arabinose formation by means of the standard pentose tests.

Experimental

Borax Hydrolysis of Commercial Aloin. A. Detection of Formaldehyde.—A mixture of 60 g. of aloin, 60 g. of borax and 600 cc. of water was boiled under reflux for a half hour. After cooling to room temperature, the solution was made acid to litmus with hydrochloric acid. After standing for some time, it was filtered. The process was repeated, giving a total of filtrate and washings from both runs of 1500 cc. This was distilled, with one-half of the volume being collected in the distillate. The distillation was repeated several times until the final distillate was 75 cc. This was treated with 75 cc. of a saturated aqueous solution of methone. On standing, there was deposited 15 mg. of formaldimethone, m. p. 190° (cor.).

Anal. Calcd. for C₁₇H₂₄O₄: C, 69.86; H, 8.22. Found: C, 69.91, 69.74; H, 8.25, 8.19.

There was no depression in melting point when mixed with an equal quantity of formaldimethone prepared from commercial formalin.

B. Test for Furfural.—Aloin was hydrolyzed with aqueous borax solution as above, the solution made just acid, filtered and the filtrate made up to 12% hydrochloric acid. On distillation repeated as before, the final distillate gave

only a faint, transient pink color to aniline acetate paper. No furfural *p*-nitrophenylhydrazone was obtained. At most traces of furfural could have been formed.

Sodium Perborate Decomposition of Aloin. A. Isolation and Identification of Furfural.—A solution of 5 g. of commercial aloin in 375 cc. of water was heated almost to boiling and 20 g. of sodium perborate was added in three portions. After each addition, the solution was heated to boiling until the reaction subsided. After cooling, the solution was treated with 125 cc. of concd. hydrochloric acid. This process was repeated until 8 liters of the solution had been prepared. The solution was distilled as described for the borax hydrolysis solution. On concentrating the more volatile material to 30 cc., about 2 cc. of furfural settled out. This was separated and dried over anhydrous magnesium sulfate; b. p. 160° (uncor., Emich micro-method⁵). Analysis indicated that the material was not entirely free of water.

Anal. Calcd. for C₅H₄O₂: C, 62.50; H, 4.16. Found: C, 62.11; H, 4.81.

For further identification, the *p*-nitrophenylhydrazone was prepared, m. p. 151–152°. There was no depression on mixing with a sample of furfural *p*-nitrophenylhydrazone.

Anal. Calcd. for C₁₁H₈O₃N₂: C, 57.14; H, 3.89. Found: C, 56.97; H, 3.92.

B. Detection of Formaldehyde.—On treating the residues from the intermediate distillations with methone in aqueous solution, there was obtained a total of about 60 mg. of formaldimethone, m. p. 187° after crystallization from ethyl alcohol. There was no depression in melting point on mixing with an equal quantity of formaldimethone prepared from commercial formaldehyde solution.

Borax Hydrolysis of Aloin without Acidification.—The borax hydrolysis was repeated as described except that the hydrolysate was distilled without preliminary acidification. Neither formaldehyde nor furfural was detected in the distillate.

Sodium Perborate Decomposition without Acidification.—On repeating the sodium perborate decomposition but omitting the addition of hydrochloric acid, formaldehyde was detected as before, but no furfural was formed, indicating that the latter must come from the action of the acid on a pentose.

Decomposition of Barbaloin and of Iso-barbaloin.—All of the experiments described above were repeated with barbaloin and with iso-barbaloin prepared as described by Leger.⁴ The results were the same as with commercial aloin.

Hydrolysis of Barbaloin with Hydrochloric Acid.—A solution of 20 g. of barbaloin in 338 cc. of 12% hydrochloric acid was boiled under reflux for 131 hours, with occasional interruptions to filter the black precipitate which formed slowly. The resulting solution was fractionated and the

(1) Original manuscript received February 14, 1938.

(2) Cahn and Simonson, *J. Chem. Soc.*, 2537 (1932).

(3) Rosenthaler, *Pharm. Acta Helv.*, 9, 9 (1934).

(4) Leger, *Ann. chim.*, [9] 6, 318 (1916).

(5) Emich-Schneider, "Microchemical Laboratory Manual," John Wiley and Sons, Inc., New York, N. Y., 1932, p. 32.

fractions tested for formaldehyde and furfural as described above. Neither was detected.

Discussion

The experiments described show that when either of the isomeric aloins is decomposed by treatment with borax followed by hydrochloric acid, formaldehyde is formed. The same result is obtained when sodium perborate is used, but in this case the acid treatment is unnecessary, indicating that the oxidizing action of the perborate can bring about the same change as the acid. Hydrochloric acid, without the preliminary borax treatment, cannot bring about the formation of formaldehyde.

These results show, also, that hydrolysis with borax produces little if any pentose, whereas with sodium perborate, presumably due, again, to the oxidizing action, pentose is formed in appreciable amounts as indicated by the formation of furfural after acidification and distillation. This is in agreement with the results of Goldner.⁶

Summary

Some of the conditions for the formation of formaldehyde and of a pentose (detected by furfural formation) from the aloins have been determined.

(6) Goldner, *J. Am. Pharm. Assoc.*, **21**, 658 (1932).

ST. LOUIS, MISSOURI

RECEIVED APRIL 13, 1942

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dielectric Investigation of Polypeptides. I. The Dielectric Increments of Amino Acid Polypeptides

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Structural discontinuities in the glycine polypeptides have been suggested by the condensation experiments of Pacsu¹ and others² with the peptide esters. The abnormality in the dissociation constants³ and the unexpected increase in the rate of alcoholysis⁴ of hexaglycine offered support to the view that the slightly low value for the dielectric increment of hexaglycine reported by Wyman⁵ as compared to the linear relation between increment and the number of glycine residues found by him might be indicative of a structural change for this peptide. With this in mind, it was thought significant to examine further the question of this linear relation indicated by the excellent measurements of Wyman, and, at the same time, to determine the dielectric increments of other peptide combinations of glycine, alanine, and leucine with the object of observing the influence of substituent groups upon the incremental values of the glycine peptides.

* Research Assistant on Special Funds from the Rockefeller Foundation.

(1) Pacsu, *Nature*, **144**, 551 (1939).

(2) (a) Fischer, *Ber.*, **37**, 2501 (1901); (b) **39**, 453 (1906); (c) Curtis, *ibid.*, **16**, 734 (1883); (d) **37**, 1283 (1904); (e) *J. prakt. Chem.*, **37**, 173 (1888).

(3) Glasstone and Hammel, *THIS JOURNAL*, **63**, 243 (1941).

(4) Glasstone and Hammel, *ibid.*, **63**, 2003 (1941).

(5) (a) Wyman and McMeekin, *ibid.*, **55**, 908 (1933); (b) Wyman, *ibid.*, **56**, 536 (1934); (c) Wyman, *Chem. Rev.*, **19**, 213 (1936).

Experimental

Materials.—The glycine polypeptides were prepared⁶ according to the well-known Fischer methods as reviewed by Glasstone and Hammel³ in their determination of dissociation constants of these peptides. Dr. E. J. Wilson⁷ prepared the di- and tripeptides of glycine, alanine, and leucine following a modification of Fischer's general procedure. The purity of all the glycine polypeptides used in this investigation was checked by formol titrations carried out potentiometrically with the glass electrode. In all dielectric constant measurements exceptional care was taken to reduce the salt conductance of the water solutions. Each peptide was purified by dissolving it in a minimum of warm distilled water and then precipitating it with ethyl alcohol. This purification was repeated until the water solution of the desired peptide concentration could be readily balanced in the dielectric constant apparatus. The dioxane used in the calibration of the condenser cell was purified by fractional distillation over sodium hydroxide pellets, followed by six fractional crystallizations. The dioxane, so purified, had a melting point of 11.78° and a dielectric constant of 2.2131 ± 0.0008 at 25°. However, inasmuch as only mixtures of water and dioxane with high water content are critical in determining the cell constant, no attempt was made to maintain the hygroscopic dioxane in this high state of purity.

Method.—The dielectric constant measurements were made with a General Radio Company Twin-T impedance

(6) We are indebted to Mr. A. F. Chadwick for the tetraglycine, and to Mr. E. F. Hammel for the penta- and hexaglycine.

(7) Wilson and Pacsu, *J. Org. Chem.*, **7**, 126 (1942).