[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

MERCURATION IN ALKALINE SOLUTION. PRELIMINARY PAPER

BY A. L. FOX WITH FRANK C. WHITMORE

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Mercuration is ordinarily carried out by means of mercuric acetate in a solution acidified with acetic acid. When 2,3-hydroxynaphthoic acid was mercurated in this way, the mixture was tested with sodium hydroxide to detect any unreacted inorganic mercury. It was found that rapid addition of sodium hydroxide gave a precipitate of mercuric oxide but that slow addition did not do so. After some study it was found that the addition of the base was increasing the speed of mercuration. It was finally found that 2,3-hydroxynaphthoic acid could be mercurated in strongly alkaline solution. This method of mercuration was applied successfully to salicylic acid and to phenol. It *failed* when applied to *m*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, α-naphthol, *o*-nitrophenol, aniline, anthranilic acid, sulfanilic acid, benzenesulfonic acid, 1-naphthoic acid and phthalic acid. It should be noted that traces of mercuration products may have been formed but none could be isolated using the same technique which gave good yields with 2,3-hydroxynaphthoic acid, salicylic acid and phenol.

The mercuration product obtained by this method from phenol corresponded to an anhydro-hydroxymercuriphenol.

Experimental Part

Mercuration of 2,3-Hydroxynaphthoic Acid in Alkaline Solution.—A solution of 30 g. (0.16 mole) of the acid in 500 cc. of water and 150 cc. (0.9 mole) of 6 *N* sodium hydroxide was heated to boiling and stirred during the gradual addition of 52 g. (0.16 mole) of mercuric acetate dissolved in 300 cc. of water and 10 cc. (0.15 mole) of acetic acid. As the mercuric acetate solution was added a momentary precipitate of mercuric oxide formed. The mixture was boiled for a few minutes, treated with decolorizing carbon, filtered and treated with a slight excess of sodium chloride and slightly less than enough dilute hydrochloric acid to make the mixture acid. The precipitate was dried. It formed a yellow powder which was probably **anhydro-4-hydroxymercuri-3-hydroxy-2-naphthoic acid.**

Anal. Calcd. for $C_{11}H_6O_3Hg$: Hg, 51.9. Found: 51.8, 51.4.

The mercuration was repeated with cold dilute solutions with similar results.

Mercuration of Salicylic Acid.—This mercuration was carried out in an exactly similar way. From 15 g. of salicylic acid was obtained 27 g. of hydroxymercurisalicylic acid.

Anal. Calcd. for $C_7H_6O_4Hg$: Hg, 56.6. Found: 57.0, 56.8.

Mercuration of Phenol.—This process was similar to the other two, 100 g. of phenol yielding 215 g. of anhydro-hydroxymercuriphenol.

Anal. Calcd. for C_6H_4OHg: Hg, 68.6. Found: 68.9.

A similar mercuration of phenol using mercuric chloride instead of the acetate gave the same product.

Unsuccessful Attempts at Mercuration in Alkaline Solution. **α-Naphthol** was oxidized immediately by this procedure. Similar results were obtained with aniline.

o-**Nitrophenol.**—On adding mercuric acetate solution to a boiling alkaline solution of *o*-nitrophenol a permanent precipitate of mercuric oxide formed. The experiment was discontinued. Similar results were obtained with anthranilic acid, sulfanilic acid, benzenesulfonic acid, 1-naphthoic acid and phthalic acid.

Summary

It has been found that certain organic compounds can be mercurated in alkaline solution while other compounds of very similar structure cannot.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD, UNIVERSITY OF ST. ANDREWS]

THE MOLECULAR STRUCTURE OF INULIN. ISOLATION OF A NEW ANHYDROFRUCTOSE

BY JAMES COLQUHOUN IRVINE AND JOHN WHITEFORD STEVENSON

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The first researches designed to investigate the molecular structure of inulin with the precision rendered possible by the methylation method were carried out by Irvine and Steele.[1] These authors showed that the polysaccharide although converted by hydrolysis into the normal levorotatory form of fructose is actually based on the unstable dextrorotatory variety of the hexose known as γ-fructose. The research was subsequently extended[2] to include a more detailed examination of dimethyl- and trimethylinulin, together with the dimethyl- and trimethylfructoses obtained, respectively, from these derivatives by hydrolysis.

The collective evidence, although complicated by a number of minor irregularities such as the tendency of trimethylinulin to undergo depolymerization from a levorotatory powder to a dextrorotatory sirup, pointed to the idea that the molecule of inulin is symmetrical in the sense that all of the fructose residues belong to the γ-type and that in each fructose residue three hydroxyl groups occupy the same positions. This view was based on the fact that on hydrolysis trimethylinulin gave a homogeneous trimethyl-γ-fructose, and all subsequent speculations on the structure of inulin have been founded on this observation. In the course of the past five years we have, however, accumulated much incidental evidence that the inulin problem is not so simple as at one time appeared, and we have accordingly continued our investigations; in the meantime Haworth has published what is, in effect, a repetition of our earlier work,

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[1] Irvine and Steele, *J. Chem. Soc.*, **117**, 1474 (1920).

[2] Irvine, Steele and Shannon, *ibid.*, **121**, 1060 (1922).