

THE ACTION OF HEXAMETHYLENETETRAMINE ON THE METHYL ESTERS OF PHENOLCARBOXYLIC ACIDS

Part I. The Synthesis of 2:4-Dihydroxy-5-formyl-benzoic Acid

BY R. D. DESAI AND (MISS) K. S. RADHA

(From the Department of Chemistry, St. Xavier's College, Bombay)

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A CONVENIENT method for the introduction of a formyl group (CHO) into salicylic acid was discovered by Duff and Bills¹, but when they tried to generalise it using monohydric phenols, the reaction was found to be abnormal and eccentric. However, Späth and Pailer² introduced the formyl group into 7-hydroxy-coumarin, whilst Rangaswamy and Sheshadri³ prepared aldehydo-hydroxy-coumarins, -chromones, and -flavones by the same method. Our attempts to extend this method to the dihydric phenols failed but when the methyl ester of β -resorcylic acid was taken, an excellent yield of an aldehydo-acid was obtained. It gave readily the semicarbazone, the 4-nitrophenylhydrazone and 2:4-dinitrophenylhydrazone. On decarboxylation, it was converted into β -resorcylaldehyde, whilst its m.p. was considerably depressed by an admixture with an authentic specimen of the isomeric 2:4-dihydroxy-3-formyl benzoic acid which was kindly supplied by Dr. R. C. Shah of the Royal Institute of Science, Bombay. The acid had, therefore, the only possible constitution of 2:4-dihydroxy-5-formylbenzoic acid. Other interesting properties of this acid, as well as the extension of this reaction to the methyl esters of other hydroxy acids are being actively pursued.

Experimental

Preparation of 2:4-dihydroxy-5-formylbenzoic acid.—A mixture of anhydrous methyl β -resorcyate (10 g.), hexamethylene tetramine (30 g.) and glacial acetic acid (50 c.c.) was refluxed on sand-bath for 10 hours, and further 3–4 hours after the addition of dilute (1:1) hydrochloric acid (100 c.c.). The solid that separated out on cooling the mixture was filtered off, washed and purified through a 5 per cent. sodium bicarbonate solution. The pale-yellow acid crystallised from benzene in yellowish, lustrous needles, m.p. 185–86°. The acid was soluble in alkali with a yellow colour while its alcoholic solution gave an intense red colouration with alcoholic ferric chloride. It was fairly soluble in warm alcohol, acetic acid, acetone, etc., but insoluble in petrol. (Yield : 45 per cent.) The reaction failed if the methyl

ester was replaced by the acid and a yellow solid having a high m.p. and containing an appreciable amount of nitrogen was formed. (Found: C, 52.6; H, 3.6, $C_9H_6O_5$ requires C, 52.8, H, 3.3 per cent.)

When the acid was mixed with an equal amount of Shah and Laiwalla's 2 : 4-dihydroxy-3-formylbenzoic acid, the m.p. was depressed to 159–62°. On heating its solution in glacial acetic acid containing traces of hydrochloric acid, in a sealed tube at 180°, it was decomposed into β -resorcylaldehyde, identified by a mixed m.p. with an authentic specimen. The *semicarbazone*, prepared by the usual method, was an amorphous powder which did not melt upto 290°. (Found: N = 17.4; $C_9H_9O_5N_3$ requires N, 17.6 per cent.)

The *4-nitrophenylhydrazone* was an orange powder unmelted upto 280°. (Found : N, 13.2, $C_{14}H_{11}O_6N_3$ requires N, 13.24 per cent.)

The *2 : 4-dinitrophenylhydrazone* was also an orange-red microcrystalline solid melting above 280°. (Found : N, 15.2; $C_{14}H_{10}O_8N_4$ requires N, 15.5 per cent.)

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Summary

An excellent yield of 2 : 4-dihydroxy-5-formyl-benzoic acid is obtained by the action of hexamethylene-tetramine on methyl β -resorcylate.

REFERENCES

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4. Shah and Laiwalla .. *J.*, 1938, 1828.