# **67.** *γ-Substitution in the Resorcinol Nucleus. Part III.*

## 2 : 6-*Dihydroxy*-3-*ethylbenzaldehyde.*

By H. A. Shah and R. C. Shah.

Application of Shah and Laiwalla's modified Gattermann reaction (J., 1938, 1828) to methyl 2 : 4-dihydroxy-5-ethylbenzoate afforded *methyl* 2 : 4-*dihydroxy*-3-*formyl*-5-*ethylbenzoate*, which on hydrolysis and decarboxylation gave 2 : 6-*dihydroxy*-3-*ethylbenzaldehyde*.

IN continuation of the work described in Part I (Shah and Laiwalla, J., 1938, 1828) we have applied the Gattermann reaction to methyl 2 : 4-dihydroxy-5-ethylbenzoate (Sethna and Shah, J., 1938, 1067) and obtained *methyl* 2 : 4-*dihydroxy*-3-*formyl*-5-*ethylbenzoate*. The constitution of the aldehydo-ester follows by analogy with the aldehydo-ester obtained from methyl β-resorcylate (Shah and Laiwalla, *loc. cit.*) and from its reaction as an *o*-hydroxy-aldehyde with ethyl malonate and ethyl acetoacetate in presence of piperidine (Knoevenagel, *Ber.*, 1904, **37**, 4461). The Knoevenagel condensation products are formulated as *methyl* 5-*hydroxy*-3-*carbethoxy*-8-*ethylcoumarin*-6-*carboxylate* and *methyl* 5-*hydroxy*-3-*acetyl*-8-*ethylcoumarin*-6-*carboxylate* on account of their insolubility in aqueous alkali and their positive ferric chloride reaction.

The aldehydo-ester on Clemmensen reduction afforded *methyl* 2 : 6-*dihydroxy*-5-*ethyl*-m-*toluate*, which gave on hydrolysis 2 : 6-*dihydroxy*-5-*ethyl*-m-*toluic acid*.

Hydrolysis of the aldehydo-ester by the prolonged action of cold dilute alkali solution produced 2 : 4-*dihydroxy*-3-*formyl*-5-*ethylbenzoic acid*, which on decarboxylation afforded 2 : 6-*dihydroxy*-3-*ethylbenzaldehyde*, a γ-resorcylaldehyde derivative which dissolved in dilute alkali solution with a deep yellow colour (cf. Shah and Laiwalla, *loc. cit.*).

## EXPERIMENTAL.

*Methyl* 2 : 4-*Dihydroxy*-3-*formyl*-5-*ethylbenzoate*.—To a mechanically stirred solution of anhydrous methyl 2 : 4-dihydroxy-5-ethylbenzoate (10 g.; 1 mol.) in dry ether cooled by a freezing mixture, zinc cyanide (12 g.; 2 mols.) was added, followed by anhydrous aluminium chloride (13·4 g.; 2 mols.) in dry ether, and dry hydrogen chloride was passed in for 4½ hours. The mixture was kept at 0° for 24 hours, the ether decanted, and the aldimine hydrochloride washed with ether (3 × 30 c.c.) and heated with water (100 c.c.) on a steam-bath for 20 minutes. On cooling, a brownish-red solid separated. *Methyl* 2 : 4-*dihydroxy*-3-*formyl*-5-*ethylbenzoate* crystallised from alcohol (charcoal) in colourless needles (6·5 g.), m. p. 84—86° (Found : C, 58·8; H, 5·4. $C_{11}H_{12}O_5$ requires C, 58·9; H, 5·4%), insoluble in water, very sparingly soluble in cold and easily soluble in hot alcohol and readily in benzene. It was easily volatile in steam, and gave a bright yellow colour in alkaline solution and a deep red colour with alcoholic ferric chloride.

The 2 : 4-*dinitrophenylhydrazone* crystallised from glacial acetic acid in yellow needles, m. p. 253—254° (decomp.) (Found : N, 13·4. $C_{17}H_{16}O_8N_4$ requires N, 13·9%), and the *semicarbazone* in tiny colourless needles, m. p. 279—280° (decomp.) (Found : N, 14·7. $C_{12}H_{15}O_5N_3$ requires N, 14·6%).

*Methyl* 5-*Hydroxy*-3-*carbethoxy*-8-*ethylcoumarin*-6-*carboxylate*.—Piperidine (4 drops) was added to a mixture of the aldehydo-ester (0·5 g.) and ethyl malonate (0·5 g.) cooled by a freezing mixture. Next day, on treatment with dilute hydrochloric acid, a pale yellow solid was obtained, which crystallised from alcohol in colourless needles (0·42 g.), m. p. 138° (Found : C, 60·2; H, 5·2. $C_{16}H_{16}O_7$ requires C, 60·0; H, 5·0%), insoluble in dilute alkali solution. It gave a deep red colour with alcoholic ferric chloride.

*Methyl* 5-*Hydroxy*-3-*acetyl*-8-*ethylcoumarin*-6-*carboxylate*.—Ethyl acetoacetate was substituted for ethyl malonate in the preceding preparation. The red solid obtained crystallised from dilute alcohol in small yellow needles, m. p. 138—140° (Found : C, 62·7; H, 5·1. $C_{15}H_{14}O_6$ requires C, 62·1; H, 4·8%).

*Methyl* 2 : 6-*Dihydroxy*-5-*ethyl*-m-*toluate*.—The aldehydo-ester (2 g.), dissolved in hot alcohol, was gradually added to a mixture of zinc amalgam (prepared from 25 g. of zinc dust; Robinson and Shah, J., 1934, 1497) and dilute hydrochloric acid (1 : 1; 50 c.c.) at 100°. From the filtered liquid and the unchanged amalgam, ether extracted a solid, which crystallised from xylene in thin colourless plates (1·5 g.), m. p. 164—166° (Found : C, 63·4; H, 6·3. $C_{11}H_{14}O_4$ requires C, 62·9; H, 6·7%).

This *ester* (0·5 g.) was kept in contact with 20% sodium hydroxide solution (10 c.c.) for 50 hours, and the clear solution then acidified with hydrochloric acid. The precipitated 2 : 6-*dihydroxy*-5-*ethyl*-m-*toluic acid*, after purification by means of sodium hydrogen carbonate, crystallised from dilute methanol in colourless needles (0·25 g.), m.p. 244—246° (efferv.) (Found: C, 61·5; H, 5·8. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1%).

2 : 4-*Dihydroxy*-3-*formyl*-5-*ethylbenzoic Acid*.—The aldehydo-ester (10 g.) was dissolved in 15% sodium hydroxide solution (150 c.c.) and kept at room temperature for 72 hours. The *acid*, precipitated on acidification and purified as above, crystallised from methanol in long

stout needles (7·5 g.), m. p. 192—195° (efferv.) (Found : C, 57·3 ; H, 4·9. $C_{10}H_{10}O_5$ requires C, 57·2 ; H, 4·8%).

2 : 6-*Dihydroxy*-3-*ethylbenzaldehyde*.—The foregoing acid (1 g.) and water (30 c.c.) were heated together in a sealed tube at 95—100° for 9 hours, and the red crystalline solid extracted with boiling water. The solution, on cooling, deposited tiny yellow needles (0·2 g.), m. p. 117—118° (Found : C, 64·2 ; H, 5·9. $C_9H_{10}O_3$ requires C, 65·1 ; H, 6·0%). The *aldehyde* was sparingly soluble in cold water and dissolved in alkali solution with a deep yellow colour. It gave a dark brown coloration with aqueous or alcoholic ferric chloride.

All the analyses recorded are micro-analyses by Dr. Schoeller.

ROYAL INSTITUTE OF SCIENCE, BOMBAY. [*Received, January 9th*, 1939.]