

**67.**  *$\gamma$ -Substitution in the Resorcinol Nucleus. Part III.*

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

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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  $\beta$ -resorcyate (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  $\gamma$ -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<sub>11</sub>H<sub>12</sub>O<sub>5</sub> 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<sub>17</sub>H<sub>16</sub>O<sub>8</sub>N<sub>4</sub> requires N, 13.9%), and the semicarbazone in tiny colourless needles, m. p. 279—280° (decomp.) (Found : N, 14.7. C<sub>12</sub>H<sub>15</sub>O<sub>5</sub>N<sub>3</sub> 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<sub>16</sub>H<sub>16</sub>O<sub>7</sub> 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<sub>15</sub>H<sub>14</sub>O<sub>6</sub> 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<sub>11</sub>H<sub>14</sub>O<sub>4</sub> 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<sub>10</sub>H<sub>12</sub>O<sub>4</sub> 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.

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[Received, January 9th, 1939.]

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