CCCXI.—*Substitution in Vicinal Trisubstituted Benzene Derivatives. Part III.*

By LEON RUBENSTEIN.

THE mixture of 5- and 6-nitro-3-methoxy-2-ethoxybenzaldehydes produced by nitrating 3-methoxy-2-ethoxybenzaldehyde (Davies and Rubenstein, J., 1923, **123**, 2839) has now been separated into its constituents by the method employed by Perkin, Robinson, and Stoyle to separate the isomerides formed in the nitration of *o*-veratraldehyde (J., 1924, **125**, 2355); it contains 60% of the 5-nitro- and 40% of the 6-nitro-compound.

The same method was applied in an attempt to separate the mixture of 5- and 6-nitro-2 : 3-diethoxybenzaldehydes obtained in the nitration of 2 : 3-diethoxybenzaldehyde (Davies and Rubenstein, *loc. cit.*); these were condensed with *p*-toluidine and with *m*-nitroaniline, but in neither case could a complete separation of the Schiff bases be effected by fractional crystallisation.

Evidence was obtained, however, that both in the nitration of 3-methoxy-2-ethoxybenzaldehyde and of 2 : 3-diethoxybenzaldehyde the 4-nitro-aldehyde is formed in small quantity.

EXPERIMENTAL.

Nitration of 3-*Methoxy*-2-*ethoxybenzaldehyde and Separation of the Products.*—The following modified method of nitration (compare *loc. cit.*) renders the subsequent separation easier: 3-Methoxy-2-ethoxybenzaldehyde (12 g.) cooled to 0° is added drop by drop with vigorous stirring to nitric acid (30 c.c.; *d* 1·42), the temperature being maintained at 0°. The crystals of 5-nitro-3-methoxy-2-ethoxybenzaldehyde (7·4 g.) that separate after several hours are removed. The filtrate, on dilution with water, deposits a yellowish-white mixture of 5- and 6-nitro-3-methoxy-2-ethoxybenzaldehydes, which is collected and dried. This mixture (7·4 g.) is heated with *p*-toluidine (3·6 g.) on the steam-bath during 30 minutes, and alcohol is added until a boiling solution is obtained. 5-Nitro-3-methoxy-2-ethoxybenzylidene-*p*-toluidine separates on cooling, and the 6-nitro-isomeride from the filtrate after concentration. These substances can be almost completely separated by careful fractional crystallisation from alcohol.

5-*Nitro*-3-*methoxy*-2-*ethoxybenzylidene*-p-*toluidine* crystallises in pale yellow, slender needles, m. p. 148° (Found : N, 9·1. $C_{17}H_{18}O_4N_2$ requires N, 8·9%). It is readily hydrolysed by hot dilute hydrochloric acid, giving 5-nitro-3-methoxy-2-ethoxybenzaldehyde, m. p. 137°. 6-*Nitro*-3-*methoxy*-2-*ethoxybenzylidene*-p-*toluidine* crystallises in golden prisms, m. p. 88° (Found : N, 9·0%).

6-*Nitro*-3-*methoxy*-2-*ethoxybenzaldehyde*, readily obtained by hydrolysing the pure *p*-toluidine derivative with hot dilute hydrochloric acid, crystallises from aqueous alcohol in colourless, slender prisms, m. p. 57° (Found : N, 6·4. $C_{10}H_{11}O_6N$ requires N, 6·2%); the p-*nitrophenylhydrazone* consists of stout, brown needles, m. p. 188—189°. Treatment with acetone and alkali gives an indigotin derivative.

6-*Nitro*-3-*methoxy*-2-*ethoxybenzoic Acid.*—A mixture of the aldehyde (1 g.), water (10 c.c.), and potassium bicarbonate (0·6 g.) is boiled during the addition of hot 10% potassium permanganate solution (10 c.c.). The filtered, cooled solution is separated from a little unchanged aldehyde and acidified with hydrochloric acid. The 6-*nitro*-3-*methoxy*-2-*ethoxybenzoic acid* thus precipitated melts at 119—120° after crystallisation from hot water, in which it is fairly soluble (yield 50%) (Equiv., 240. $C_{10}H_{11}O_6N$ requires equiv., 241).

Nitration of 2 : 3-*Diethoxybenzaldehyde.*—This was carried out similarly to the nitration of 3-methoxy-2-ethoxybenzaldehyde. The material obtained (5·7 g.) was treated with *p*-toluidine (2·5 g.), and the product with alcohol, as described above; 5-*nitro*-2 : 3-*diethoxybenzylidene*-p-*toluidine* (2·4 g.) crystallised in long, slender, cream needles, m. p. 105—106° (Found : N, 8·6. $C_{18}H_{20}O_4N_2$ requires N, 8·5%); further fractionation yielded a small quantity of a substance, m. p. 100° (Found : N, 8·7%).

5-*Nitro*-2 : 3-*diethoxybenzaldehyde*, which is readily obtained by hydrolysing the pure *p*-toluidine derivative, m. p. 105—106°, with hot dilute hydrochloric acid and recrystallising the product from aqueous alcohol, consists of white needles, m. p. 71°. It does not yield an indigotin derivative with acetone and alkali and gives no depression of m. p. when mixed with a sample of 5-nitro-2 : 3-diethoxybenzaldehyde obtained by nitrating 2-hydroxy-3-ethoxybenzaldehyde and methylating the product.

6-*Nitro*-2 : 3-*diethoxybenzaldehyde*, similarly obtained from the compound, m. p. 100°, crystallises from dilute alcohol in almost colourless needles, m. p. 75—76° (Found : N, 6·0. $C_{11}H_{13}O_5N$ requires N, 5·8%). It turns green on exposure to the air, as do its solutions in all solvents. With acetone and alkali an indigotin derivative is obtained. The p-*nitrophenylhydrazone* consists of bright yellow, stout needles, m. p. 268—270°.

The author is indebted to the Research Fund Committee of the Chemical Society which has defrayed some of the expenses of this investigation.

THE DYSON PERRINS LABORATORY,
OXFORD.

[*Received, August* 14*th*, 1925.]