XI.—*The Preparation of 4-Nitrophthalimide and Derivatives.*

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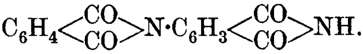
THE preparation of 4-nitrophthalimide has hitherto depended on the action of ammonia on 4-nitrophthalic acid or its anhydride (Seidel and Bittner, *Monatsh.*, 1902, **23**, 415; Bogert and Boroschek, *J. Amer. Chem. Soc.*, 1901, **23**, 740). Since the preparation of the acid is troublesome, an attempt was made to prepare 4-nitrophthalimide by the direct nitration of phthalimide. The use of nitric and acetic acids was unsuccessful under all the conditions tried. Nitric acid in presence of sulphuric acid containing 10% of sulphur trioxide gave a 78% yield of 4-nitrophthalimide, m. p. 198° (Bogert and Boroschek give m. p. 197°; Seidel and Bittner, 202°; Chapman and Stephen, J., 1925, **127**, 1791, give 197—198°). In the mother-liquor from the nitration, no 3-nitrophthalimide was found. Replacing the fuming acid by ordinary concentrated sulphuric acid diminished the yield to 40%.

Nitration of *N*-phenylphthalimide under the conditions described above showed that the nitro-group enters the phenyl nucleus only, the final product being a mixture of *p*-nitroaniline and phthalic acid.

Phthalic anhydride nitrated by means of sulphuric and nitric acids gives a mixture of 3- and 4-nitrophthalic acids (Lawrance, *J. Amer. Chem. Soc.*, 1920, **42**, 1872). When the nitration is carried out in the presence of fuming sulphuric acid as for phthalimide, 4-nitrophthalic acid and unattacked phthalic acid are obtained, no 3-nitrophthalic acid being produced. As Bentley and Weizmann (J., 1907, **91**, 101) obtained only 4-sulphophthalic acid by the action of fuming sulphuric acid on phthalic anhydride, nitration is probably subsequent to sulphonation.

An improved method of reducing 4-nitrophthalimide to the corresponding base is described. The diazotised base couples with phenol and α- and β-naphthol in alkaline solution, giving orange, maroon, and light brown dyes respectively, and with aniline and α- and β-naphthylamine in acid solution, giving deep red, red, and yellow dyes respectively.

4-Aminophthalimide condenses readily with phthalic anhydride to give 4-*phthalimidophthalimide*,  $C_6H_4{<}\substack{CO\\CO}{>}N{\cdot}C_6H_3{<}\substack{CO\\CO}{>}NH$.

EXPERIMENTAL.

4-*Nitrophthalimide*.—Phthalimide (20 g.) was added gradually to a cold mixture of 24 c.c. (3 mols.) of nitric acid (*d* 1·44) and 200 c.c. of fuming sulphuric acid containing 10% of sulphur trioxide, the temperature rising to about 80°. After being maintained at this temperature for not more than 30 minutes, the wine-red solution was cooled and poured on 400 g. of ice, the temperature not being allowed to rise above 20° (otherwise the imide is hydrolysed to 4-nitrophthalic acid). The precipitate of 4-nitrophthalimide was washed and crystallised from alcohol, forming buff-coloured plates, m. p. and mixed m. p. 198° (Found : N, 7·2. Calc. for $C_8H_4O_4N_2$: N, 7·3%). Yield, 78%.

From the ice-cold acid mother-liquor of the imide, ether extracted 4-nitrophthalic acid, which was obtained as a yellow crystalline mass, m. p. 166° (efferv.; 114° after resolidifying).

4-*Aminophthalimide*.—This was prepared by a modification of the method of Bogert and Renshaw (*J. Amer. Chem. Soc.*, 1908, **30**, 1135). 4-Nitrophthalimide (20 g.; 1 mol.) was stirred into a solution of stannous chloride (84 g.; 1·1 mols.) in 450 c.c. of hydrochloric acid (*d* 1·14) and 150 c.c. of water. The temperature rose to 50°, the 4-nitrophthalimide dissolved, and 4-aminophthalimide hydrochloride gradually separated as a crystalline paste. The precipitate was collected at 0° and washed with hot water until free from acid, the hydrochloride thus being completely hydrolysed and the base obtained as golden-yellow needles (15·3 g.), m. p. 294° (corr.), of sufficient purity for the later experiments. The base may be recrystallised from hot glacial acetic acid (Found : N, 17·7. Calc. for $C_8H_6O_2N_2$: N, 17·3%. Found for the hydrochloride : HCl, 18·2. Calc. for $C_8H_6O_2N_2,HCl$: HCl, 18·4%).

4-Aminophthalimide hydrochloride is appreciably soluble in hydrochloric acid. The yield of base could be slightly increased by neutralising the mother-liquor from the hydrochloride with ammonia and extracting the precipitate with alcohol.

The *acetyl* derivative, prepared by warming the base with acetic anhydride, crystallised from glacial acetic acid in minute, pale straw-coloured needles, m. p. 331° (corr.; decomp.) (Found: N, 7·0. $C_{10}H_8O_3N_2$ requires N, 6·9%). The *benzoyl* derivative was obtained by dissolving the base (5 g.) in 150 c.c. of boiling pyridine, adding benzoyl chloride (4·5 g.) to the cold solution, and boiling the mixture for $\frac{1}{2}$ hour and pouring it into water : the precipitate was boiled with water to remove benzoic acid and crystallised from acetic acid, forming small cream-coloured needles, m. p. 322° (corr.), moderately easily soluble in hot ethyl alcohol but insoluble in most other solvents (Found : N, 5·3. $C_{15}H_{10}O_3N_2$ requires N, 5·3%).

4-*Phthalimidophthalimide*.—4-Aminophthalimide (2 g.; 1 mol.) was intimately mixed with phthalic anhydride (1·90 g.; 1·1 mols.) and heated at 180° for an hour. The solid mass was powdered when cold, boiled with 100 c.c. of water to remove phthalic anhydride, and crystallised from acetic acid, giving a yellow crystalline powder, m. p. 319° (corr.; decomp.) (Found : N, 5·0. $C_{16}H_8O_4N_2$ requires N, 4·8%).

4-*Chlorophthalimide*.—The finely divided suspension of hydrochloride obtained from 4-aminophthalimide (10 g.; 1 mol.), 100 c.c. of hydrochloric acid, and 100 c.c. of water was diazotised at 0—3° (5 g. of sodium nitrite in 15 c.c. of water). The violet diazonium solution was added rapidly to a solution of cuprous chloride (prepared from 42 g. of copper sulphate) in 66 g. of hydrochloric acid (*d* 1·14) at 0°, a double compound separating. After 3 hours' stirring, the mixture was warmed on the water-bath. 4-Chlorophthalimide, which separated as a thick paste, crystallised from acetic acid as colourless needles (6 g.), m. p. 210° alone or mixed with an authentic specimen prepared from 4-chlorophthalic acid (Reé, *Annalen*, 1886, **233**, 238).

4-*Hydroxyphthalimide*.—The base (2 g.) was diazotised, and the solution after 15 minutes was warmed on the water-bath until the evolution of nitrogen ceased. The solution when cold deposited

4-hydroxyphthalimide, which crystallised from hot water as colourless prismatic needles, m. p. 290° (corr.). Bentley and Weizmann (*loc. cit.*) give m. p. 290° and Reé (*loc. cit.*) gives 288—289°.

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