411. *The Nitration of Phthalonaphthylimides and the Facile Preparation of* 8-*Nitro*-1-*naphthylamine.*

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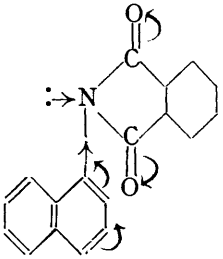
AN electron-attracting substituent, such as the nitro- or the sulpho-group, when in the α-position of the naphthalene nucleus deactivates its ring so far as kationoid reagents are concerned and thereby promotes substitution in positions 5 and 8, with a marked preference for the latter. Based on this effect, a previous observation (Hodgson and Walker, unpublished work) had indicated that phthalo-α-naphthylimide, despite the possession of a lone electron pair by the nitrogen, also is nitrated mainly in the 8′-position: this reaction has now been investigated in detail.

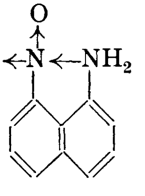
The 8′-, 5′-, and 4′-nitro-derivatives of phthalo-α-naphthylimide are formed approximately in the proportion 60 : 28 : 5 and from this it would appear that the two electron-attracting carbonyl groups (I) restrain the lone pair of electrons on the nitrogen atom to such an extent that they are almost unavailable for electromeric changes, since otherwise 4′-nitration should predominate. Substitution in the phthalic acid nucleus appears to produce only minor variations (see table) in the amount of the 8′-nitro-compound formed.

From the mixture of nitro-α-naphthylamines produced by acid hydrolysis of the phthalimides, the 8-nitro-compound is extracted with 10% sulphuric acid and then the 5- is separated from the 4-nitro-compound by means of hot dilute hydrochloric acid, in which the latter is insoluble.

The nitrations of diaceto-, dibenzo-, and di-*m*-nitrobenzenesulphon-α-naphthalides were undertaken because it was expected that they would be similar to that of the phthalo-naphthylimide. The diaceto-compound appeared to hydrolyse during the nitration and all attempts to hydrolyse the nitrated dibenzo- and di-*m*-nitrobenzenesulphon-α-naphthalides failed.

From the nitration product of phthalo-β-naphthylimide, after hydrolysis, only 5- and 8-nitro-2-naphthylamines were isolated. This method of preparation of these compounds appears to be much more convenient than that of Friedländer and Szymanski (*Ber.*, 1892, **25**, 2077).


(I.)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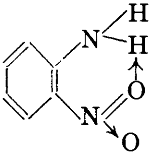
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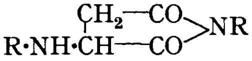

$$\begin{array}{l}\mathrm{CH_2{-}CO}\\ \mathrm{R{\cdot}NH{\cdot}CH{-}CO}\end{array}\!>\mathrm{NR}$$

(IV.)

The volatility in superheated steam (0·75 g. per litre of distillate), the ready solubility in non-dissociating solvents, and the low melting point (97°) of 8-nitro-1-naphthylamine (cf. the m. p.'s of the 1 : 2-, 1 : 7-, and 1 : 6-isomerides, 144°, 123°, and 167° respectively) may be regarded as evidence of chelation of type (II) giving a stable five-membered ring. Chelation involving the amino-hydrogen atoms, such as occurs in *o*-nitroaniline (III), is much less probable, since a seven-membered ring would then be involved, and such rings have not yet been detected (see Sidgwick, "Electronic Theory of Valency," 1927, p. 251).

The *m*-nitrobenzenesulphonyl derivatives of 5- and 8-nitro-1-naphthylamine exhibit an interesting difference, in that the 8-nitro-compound is soluble, and the 5-nitro-compound insoluble, in aqueous sodium carbonate solution, thereby indicating the very powerful electron-attracting effect of the proximate *peri*-nitro-group (*vide* previous paragraph).

All attempts to prepare malein-α-naphthylimide gave substances of indefinite m. p. (*ca.* 150—200°) and since the m. p. of this imide would not be expected to exceed that of the corresponding *amic acid* (150°) (by analogy with maleinanil, m. p. 91°, and maleic acid monoanilide, m. p. 198°), it is probable that addition of the reactants occurred to give compounds of type (IV). These mixtures were quantitatively hydrolysed, α-naphthylamine being regenerated, by boiling them under reflux with alcoholic potassium hydroxide for 8 hours.

EXPERIMENTAL.

Phthalo-α-naphthylimide.—α-Naphthylamine (286 g.; 2 mols.) was added in small portions to a boiling solution of phthalic anhydride (297 g.; 2 mols.) in tetrahydronaphthalene (500 c.c.), the water formed being allowed to distil away during the reflux period of 2 hours. The phthalo-α-naphthylimide obtained (490 g.; 90% yield), after being washed with cold benzene, crystallised from glacial acetic acid in small white prisms, m. p. 185° (Piutti, *Gazzetta*, 1885, **15**, 480, gives m. p. 180—181°) (Found : N, 5·2. Calc. : N, 5·1%).

3-*Nitrophthalo-α-naphthylimide.*—3-Nitrophthalic acid (13·2 g.) was converted into the anhydride by boiling with tetrahydronaphthalene (50 c.c.), α-naphthylamine (9 g.), dissolved in tetrahydronaphthalene (15 c.c.), was added, and the mixture boiled for 5 minutes only. The bright red product (15·8 g.) (if the boiling is continued for 3 hours, the product is a black tar) was crystallised from glacial acetic acid (charcoal), giving 3-*nitrophthalo-α-naphthylimide* in pale yellow plates, m. p. 225° (Found : N, 9·0. $C_{18}H_{10}O_4N_2$ requires N, 8·8%).

4-*Nitrophthalo-α-naphthylimide*, prepared similarly, crystallised from glacial acetic acid (charcoal) in lemon-yellow plates, m. p. 212° (Found : N, 9·0%). It was much less readily decomposed by boiling in tetrahydronaphthalene solution than was the 3-nitro-isomeride.

3-*Chlorophthalo-α-naphthylimide* formed colourless micro-needles, m. p. 191·5° (Found : Cl, 11·5. $C_{18}H_{10}O_2NCl$ requires Cl, 11·6%), 3 : 4-*dichlorophthalo-α-naphthylimide* (boiling continued for 30 minutes) colourless micro-needles, m. p. 170° (Found : Cl, 20·8. $C_{18}H_9O_2NCl_2$ requires Cl, 20·8%), 3 : 6-*dichlorophthalo-α-naphthylimide* colourless plates, m. p. 217° (Found :

Cl, 20·6%), and *tetrachlorophthalo-α-naphthylimide* colourless micro-crystals, m. p. 244° (Found : Cl, 34·5. $C_{18}H_7O_2NCl_4$ requires Cl, 34·6%), all being crystallised from glacial acetic acid.

Succino-α-naphthylimide, formed when succinic acid (60 g.; 0·5 mol.) and α-naphthylamine (71·5 g.) were refluxed for 2 hours in tetrahydronaphthalene (120 c.c.), separated from glacial acetic acid in crystals, m. p. 153° (Pellizzari and Matteucci, *Annalen*, 1888, **248**, 158, give m. p. 153°). Phthalo-β-naphthylimide, prepared in the same way as the α-isomeride, crystallised from glacial acetic acid in colourless needles, m. p. 218° (Piutti, *loc. cit.*, gives m. p. 216°).

Diaceto-α-naphthalide crystallised from a cooling solution of α-naphthylamine (143 g.) and acetic anhydride (240 c.c.) which had been refluxed for 1 hour (cf. Bamberger, *Ber.*, 1899, **32**, 1803; Sudborough, J., 1901, **79**, 539).

Dibenzo-α-naphthalide.—A solution of α-naphthylamine (14·3 g.) in benzoyl chloride (50 c.c.; 60% excess) was boiled under reflux for 3 hours and kept overnight, and the separated *dibenzo-α-naphthalide* (17·5 g.) was removed, washed with alcohol, and recrystallised from glacial acetic acid, forming large, pale yellow plates, m. p. 198° (Found : N, 4·2. $C_{24}H_{17}O_2N$ requires N, 4·0%). It was quantitatively hydrolysed to α-naphthylamine by boiling for 8 hours with alcoholic potash, and was converted into benzo-α-naphthalide by heating with concentrated aqueous ammonia at 150° for 3 hours.

*Di-*m*-nitrobenzenesulphon-α-naphthalide.*—(a) α-Naphthylamine (14·3 g.), *m*-nitrobenzenesulphonyl chloride (55·2 g.; 25% excess), and water (200 c.c.) were heated together at 90°, powdered sodium carbonate being added gradually until permanent alkalinity was obtained (after 1 hour's stirring). Cold water (*ca.* 1 l.) was then added and the solid product was filtered off and stirred with 2% aqueous sodium hydroxide (300 c.c.) at 50° until no further dissolution occurred. The residual *di-*m*-nitrobenzenesulphon-α-naphthalide* (9·7 g.) was washed with cold water and crystallised from glacial acetic acid (charcoal), forming colourless needles, m. p. 252° (Found : S, 12·4. $C_{22}H_{15}O_8N_3S_2$ requires S, 12·5%). The alkaline solution above, when acidified, deposited *m*-nitrobenzenesulphon-α-naphthalide (22·0 g.), which crystallised from glacial acetic acid or alcohol in colourless plates, m. p. 165° (Consden and Kenyon, J., 1935, 1593, give m. p. 162—164°) (Found : S, 9·7. Calc. : S, 9·8%). (b) A saturated solution of *m*-nitrobenzenesulphon-α-naphthalide in 5% aqueous sodium hydroxide at 50°, on cooling to 15°, deposited large orange needles of the tetrahydrated sodium salt (cf. Hodgson and Smith, J., 1935, 1854), which were removed, dried, and dissolved in benzene, and the solution refluxed for 15 minutes with *m*-nitrobenzenesulphonyl chloride (25 g.). After cooling, the solid product was worked up as above.

Malein-α-naphthylamic Acid.—When cold chloroform solutions of α-naphthylamine (14·3 g.) and maleic anhydride (9·8 g.) were shaken together, the mixture became warm and bright yellow needles of the *amic acid* rapidly separated. The product was very soluble in alcohol, from which it crystallised slowly in yellow micro-needles, m. p. 150° (Found : N, 5·6. $C_{14}H_{11}O_3N$ requires N, 5·8%). Dilute hydrochloric acid precipitated the amic acid unchanged from its colourless solution in aqueous sodium carbonate.

Nitration of Phthalo-α-naphthylimide.—The compound (300 g.) was added portionwise to nitric acid (300 c.c. of *d* 1·4 + 300 c.c. of *d* 1·5), maintained below 15°. After 1 hour's agitation, the thick suspension was stirred gradually into water (2 l.) and the bright yellow mixture of phthalonitro-α-naphthylimides was filtered off, pressed, and washed with cold water.

Hydrolysis of the mixture. (a) *Complete hydrolysis* (*general method*). The above mixture was heated for 1 hour at 120—130° with aqueous ammonia (600 c.c.; *d* 0·88) in an autoclave fitted with a mechanical stirrer. The tarry product was washed with water, dried, dissolved in nitrobenzene (1500 c.c.), and treated with dry hydrogen chloride until precipitation of the mixed nitronaphthylamine hydrochlorides was complete; the solid was filtered off, pressed, and washed with benzene to remove nitrobenzene. Yield, 222 g.

(b) *Partial hydrolysis* (*special method*). The details are as for (a), except that the maximum temperature during the hydrolysis was 105°. The product was dissolved as far as possible in nitrobenzene (1500 c.c.); on passage of hydrogen chloride through the filtered solution, the salts of 4- and 5-nitro-1-naphthylamines only were precipitated (they were separated as described below). The 8-nitro-isomeride was obtained by hydrolysis of the material insoluble in nitrobenzene and was purified as described under (a).

Separation of the mixed 4-, 5-, *and* 8-*nitro-*1-*naphthylamines.* The bases obtained from the mixed hydrochlorides (40 g.) were warmed to 95° with 10% sulphuric acid (2 l.) during 1 hour, and the cooled (15°) filtered solution made alkaline with ammonia. The 8-nitro-1-naphthylamine (20 g.) thus precipitated was purified by dissolution (15 g.) in 10% sulphuric acid (1 l.) at 95° and reprecipitation (14 g.) by ammonia. It then crystallised from ligroin (b. p. 80—100°) in large red plates, m. p. 96—97° (Meldola and Streatfeild, J., 1893, **63**, 1055, give m. p. 96—97°). The residue remaining after the initial extraction with 10% sulphuric acid was warmed to 95° with concentrated hydrochloric acid (340 c.c.) and water (4 l.); 5-nitro-1-naphthylamine (9·4 g.), precipitated from the cooled filtered solution by ammonia, crystallised from ligroin in deep red needles, m. p. 118—119° (Beilstein and Kuhlberg, *Annalen*, 1873, **169**, 87, give m. p. 118—119°). The insoluble residue of 4-nitro-1-naphthylamine (1·8 g.) crystallised from 90% formic acid in orange needles, m. p. 195° (*lit.* 195°).

Derivatives of 8-*Nitro*-1-*naphthylamine.*—The *picrate* formed yellow prisms, m. p. 139—141°, from alcohol (Found: N, 17·0. $C_{10}H_8O_2N_2,C_6H_3O_7N_3$ requires N, 16·8%), and the *benzoyl* derivative colourless needles, m. p. 181°, from glacial acetic acid (Found: N, 9·6. $C_{17}H_{12}O_3N_2$ requires N, 9·6%).

m-*Nitrobenzenesulphon* - 8 - *nitro* - α - *naphthalide.* Equimolecular quantities of 8-nitro-1-naphthylamine and *m*-nitrobenzenesulphonyl chloride reacted readily in aqueous sodium carbonate solution at 95° to give an orange-red solution of the sodium derivative of the desired product, which separated as a hydrate from the filtered liquid, on cooling, in orange needles, m. p. 190—200° (with loss of water); the anhydrous *sodium* salt had m. p. 265° (Found: Na, 5·6. $C_{16}H_{10}O_6N_3SNa$ requires Na, 5·8%). Neutralisation of the alkaline solution above precipitated the m-*nitrobenzenesulphon*-8-*nitro*-α-*naphthalide*, which was sparingly soluble in alcohol and separated therefrom in colourless needles, m. p. 200° (Found: S, 8·4. $C_{16}H_{11}O_6N_3S$ requires S, 8·6%).

Di-m-*nitrobenzenesulphon*-8-*nitro*-α-*naphthalide.* The last-named compound was dissolved in aqueous sodium carbonate at 70—80° and shaken with excess of *m*-nitrobenzenesulphonyl chloride, and the insoluble product was filtered off, extracted with hot sodium carbonate solution, and crystallised from glacial acetic acid, forming colourless plates, m. p. 198—199° (Found: S, 11·3. $C_{22}H_{14}O_{10}N_2S_2$ requires S, 11·5%).

Malein-8-*nitro*-α-*naphthylamic acid* separated slowly when warm chloroform solutions containing equimolecular quantities of maleic anhydride and 8-nitro-1-naphthylamine were mixed; it crystallised from alcohol in pale yellow prisms, m. p. 198° (decomp.) (Found: N, 9·5. $C_{14}H_{10}O_5N_2$ requires N, 9·8%), and was readily soluble in aqueous sodium carbonate, from which it was precipitated unchanged by hydrochloric acid.

Relative percentage amounts of 4-, 5-, and 8-nitro-1-naphthylamines (based on the amount of imide nitrated) obtained in a large number of moderately large-scale experiments by the method described for phthalo-α-naphthylimide.

Imide.	% Amounts of nitro-α-naphthylamines. 4-Nitro-.	5-Nitro-.	8-Nitro-.
Phthalo-α-naphthylimide	5	28	60
3-Nitrophthalo-α-naphthylimide	5	11	58
4-Nitrophthalo-α-naphthylimide	7	12	63
4-Chlorophthalo-α-naphthylimide	5	11	61
3 : 4-Dichlorophthalo-α-naphthylimide	8	18	50
3 : 6-Dichlorophthalo-α naphthylimide	10	15	68
Tetrachlorophthalo-α-naphthylimide	23	—	53
Succino-α-naphthylimide	22	20	34

Nitration of Phthalo-β-*naphthylimide.*—The imide (60 g.) was nitrated (nitric acid, 180 c.c., *d* 1·45) in the same way as the α-isomeride. Hydrolysis of the product with aqueous ammonia furnished a mixture of bases (37 g.) which was entirely free from tar (contrast the α-compounds). The mixture was crystallised first from alcohol (cf. Friedländer and Szymanski, *Ber.*, 1892, **25**, 2077) and then from benzene. The 5-nitro-2-naphthylamine (9·9 g., m. p. 110—120°) thus obtained was recrystallised from ligroin (b. p. 100—120°), forming long crimson needles, m. p. 145—146° (Friedländer and Szymanski, *loc. cit.*, give m. p. 143·5°) (Found: N, 15·0. Calc.: N, 14·9%). The *picrate* crystallised from alcohol in yellow hair-like needles, m. p. 208° (decomp.) (Found: N, 17·2. $C_{10}H_8O_2N_2,C_6H_3O_7N_3$ requires N, 16·8%). Concentration of the mother-liquors above afforded 8-nitro-2-naphthylamine (11 g.), which was purified through its acetyl derivative.

Nitration of Diaceto-α-*naphthalide.*—The naphthalide (23 g.; 0·1 mol.) was added gradually to nitric acid (75 c.c., *d* 1·4) at 0—15°, the reaction being complete in a few minutes. After 30 minutes, the mixture was poured into water (400 c.c.) and the mixed nitro-compounds were worked up and separated by the procedure of Hodgson and Walker (J., 1933, 1206), yielding

5·3 g. of 2-nitro- and 9·0 g. of 4-nitro-1-naphthylamine. Analysis of the mixed nitro-compounds prior to hydrolysis showed that one acetyl group had been removed during the nitration.

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