48. *The Nitration of Some α-Naphthalides.*

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THIS investigation was undertaken to ascertain whether variation of the acyl substituent would alter the ortho-para ratio, 0·37—0·44, already found for the mononitration of aceto-α-naphthalide (J., 1933, 1205). The ortho-para ratios, *i.e.*, the ultimate relative amounts of 2-nitro- and 4-nitro-1-naphthylamine, were found to be 0·4—0·6, 1·1—1·3, and 1·1—1·3 for formo-, benzo-, and *o*-carboxybenzo-α-naphthalide, respectively: considerable dinitration always occurred with *p*-toluenesulphon-α-naphthalide. Increase of 2-nitration thus accompanies the weakening of the basic character of the amino-group by acid substituents, but the carboxyl group in *o*-carboxybenzo-α-naphthalide appears to be without influence on the nitration.

2- and 4-Nitroformo-α-naphthalide are more readily hydrolysed by alkali than are the corresponding acetyl compounds, and the 4-nitro- is more easily hydrolysed than the 2-nitro-isomeride. These properties are attributed to the condition of the amino-nitrogen atom, which in the former case is rendered more kationoid (electro-positive) by the formyl than by the acetyl group, and, in the latter case, owing to the degree of ionisation of the imino-hydrogen atom, is rendered less anionoid by the 4- than by the 2-nitro-group, and therefore more prone to attack by the anionoid alkaline reagent. As would be expected, formo- and aceto-α-naphthalide are much more readily mononitrated than are the two benzoyl derivatives, which require much stronger nitric acid.

EXPERIMENTAL.

(a) *Nitration of Formo-α-naphthalide.*—The naphthalide (40 g.) was added gradually to well-stirred nitric acid (250 c.c.; *d* 1·42) at 5—10°; crystals appeared when about half had been added. Agitation was continued for ½ hour, the paste then poured into water, and the precipitated mixture of 2- and 4-nitroformo-α-naphthalide filtered off, washed, and dried (yield, 44 g.).

Hydrolysis and separation of the isomerides. The above mixture (44 g.) was refluxed for 4 hours with ethyl alcohol (200 c.c.), concentrated sulphuric acid (70 c.c.), and water (140 c.c.). The mixture of 2- and 4-nitro-1-naphthylamine precipitated on dilution with water (1000 c.c.) was removed, washed, and dried (yield, 37 g.). The separation was effected as in the case of the acetyl compounds (*loc. cit.*).

Separation of 2- *and* 4-*nitroformo-α-naphthalide by caustic alkali.* The mixture (40 g.) was extracted thrice with 5% aqueous sodium hydroxide (200 c.c.), rapid working being necessary on account of the ease of hydrolysis of the 2-nitro-compound, which dissolved. The insoluble 4-*nitroformo-α-naphthalide* crystallised from 90% formic acid in greenish-yellow micro-prisms, m. p. 182° (Found: N, 13·1. $C_{11}H_8O_3N_2$ requires N, 13·0%). The alkaline solution ultimately deposited 8 g. of nearly pure 2-nitro-1-naphthylamine.

(b) *Nitration of Benzo-α-naphthalide.*—Nitration was effected as in (a), with nitric acid (*d* 1·42) and synthetic nitric acid (*d* 1·49) in equal volumes. An 88% yield of mixed benzo-2- and -4-nitro-α-naphthalide was obtained; these were separated by aqueous sodium hydroxide as described above. The insoluble benzo-4-nitro-α-naphthalide (yield, 44%) crystallised from glacial acetic acid in yellow prisms, m. p. 224° (Found: N, 9·8. Calc.: N, 9·6%). The soluble 2-nitro-isomeride, precipitated on acidification of the alkaline solution, crystallised from glacial acetic acid in yellow prisms, m. p. 175° (Found: N, 9·7%).

Attempts to hydrolyse the nitrated benzoyl compounds with 50% sulphuric acid at 100° or with boiling concentrated hydrochloric acid were unsuccessful, and with hot alkali 2- and 4-nitro-1-naphthol were produced. Heating with concentrated aqueous ammonia in a sealed tube at 150°, however, proved successful.

(c) *Nitration of* o-*Carboxybenzo-α-naphthalide.*—The naphthalide was precipitated when a solution of α-naphthylamine (20 g.) in xylene (50 c.c.) at 100° was gradually added to a boiling solution of phthalic anhydride (20 g.) in xylene (300 c.c.). The m. p., 185°, was not raised by several crystallisations (in colourless needles) from glacial acetic acid (Tingle and Rolker, *J. Amer. Chem. Soc.*, 1908, **30**, 1891, give m. p. 189°) (Found: C, 74·0; H, 4·3; N, 5·0. Calc.: C, 74·2; H, 4·5; N, 4·8%). The yield was 95%.

The mononitration and the subsequent hydrolysis of the mixed nitro-compounds were carried out as in (b).

(d) p-*Toluenesulphon-α-naphthalide.*—A mixture of α-naphthylamine (28·6 g.), *p*-toluenesulphonyl chloride (58 g.; 50% excess), and water (300 c.c.) was heated at 90° while powdered sodium carbonate was added until there was permanent alkalinity after 30 minutes' stirring. The naphthalide was removed from the cooled mixture and shaken at 50° with 10% aqueous sodium hydroxide (150 c.c.) until no more dissolved; the warm liquid, on cooling, separated into 2 layers, but was rendered homogeneous by addition of water prior to filtration. The alkali-insoluble *di*-p-*toluenesulphon-α-naphthalide* (yield, 2—3%) crystallised from glacial acetic acid in colourless prisms, m. p. 224° (Found : S, 14·3. $C_{24}H_{21}O_4NS_2$ requires S, 14·2%), which were quantitatively hydrolysed to α-naphthylamine by 95% sulphuric acid. The filtrate above, after acidification with dilute hydrochloric acid, gave *p*-toluenesulphon-α-naphthalide (yield, 94·5%), which crystallised from glacial acetic acid in colourless prisms, m. p. 157°.

Nitration. (α) *With dilute nitric acid.* *p*-Toluenesulphon-α-naphthalide (29·7 g.) was stirred into 30% nitric acid (300 c.c.) at 50° and after 1 hour the mixture was diluted with water. The precipitated *p*-toluenesulphon-2 : 4-dinitro-α-naphthalide (yield, poor) was washed with water and crystallised from ethyl alcohol, forming pale yellow needles, m. p. 166° (Found : N, 11·0. Calc. : N, 10·8%). The substance was easily hydrolysed by concentrated sulphuric acid to give 2 : 4-dinitro-α-naphthylamine, which crystallised from glacial acetic acid in bright yellow prisms, m. p. 244° (Ullmann and Bruck, *Ber.*, 1908, **41**, 3935, give m. p. 241°).

(β) *In glacial acetic acid.* A solution of the naphthalide (15 g.) in the hot acid (100 c.c.) was cooled to 20° (with agitation) to produce fine crystals and then nitrated at 20° with 65% nitric acid (a trace of nitrous acid being necessary). The naphthalide dissolved, but yellow crystals soon appeared; these were removed and the filtrate was diluted with water to precipitate the remainder of the product :

Excess of nitric acid, %	0	25	50	100
Yield of crystals, %	24	35	45	65
M. p. of crystals	175—183°	140—150°	130—140°	135—140°

When the theoretical quantity of nitric acid was taken, all of it was consumed, and the precipitate finally obtained gave, on crystallisation from glacial acetic acid, some 2 : 4-dinitro-1-naphthylamine. Since *p*-toluenesulphon-4-nitro-α-naphthalide is only slightly soluble in glacial acetic acid, it appears that considerable dinitration occurs even when only sufficient nitric acid for mononitration is used. The product obtained with 100% excess of nitric acid was mainly *p*-toluenesulphon-2 : 4-dinitro-α-naphthalide. Nitration with 20% nitric acid at 5° did not improve the yield of mononitrated product.

(γ) *In ethylene dichloride.* Mono- and di-nitration occurred as in (β).

(δ) *In nitrobenzene.* The naphthalide (15 g.) was dissolved in the hot solvent (40 c.c.) and nitrated at 20° with nitric acid (*d* 1·42; 50% excess) containing a trace of nitrous acid. An equal volume of water was then added to the mixture, the excess of acid neutralised with aqueous sodium hydroxide, and the 4-nitro-α-naphthalide filtered off; yield, 40%. The nitrobenzene solution contained most of the dinitrated product. The hydrolysis of *p*-toluenesulphon-4-nitro-α-naphthalide was accomplished by dissolution in 93% sulphuric acid below 30°, otherwise considerable charring occurred.

Some Di-p-*toluenesulphonamides.*—The following compounds were prepared from the respective bases by the above method; each crystallised readily from glacial acetic acid in colourless prisms : *di*-p-*toluenesulphonanilide*, m. p. 184° (Found : S, 16·1. $C_{20}H_{19}O_4NS_2$ requires S, 15·9%); *di*-p-*toluenesulphon*-o-*toluidide*, m. p. 169° (Found : S, 15·6. $C_{21}H_{21}O_4NS_2$ requires S, 15·4%); *di*-p-*toluenesulphon*-p-*toluidide*, m. p. 158° (Found : S, 15·6%).

The authors are indebted to Dr. A. E. Everest for kindly pointing out that they have overlooked D.R.-P. 221383 and related patents, in which the action of neutral sulphites on 1 : 5- and 1 : 8-dinitronaphthalene and its use for the separation of the 1 : 5-dinitro-compound from its isomeride are described (see J., 1933, 1346).

The authors thank Imperial Chemical Industries Ltd. (Dyestuffs Group) for various gifts.

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