282. *The Nitration of Aceto-α-naphthalide, and the Preparation of 2- and 4-Nitro-1-naphthylamines.*

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VARIATION of the amounts of nitric acid and acetic anhydride in Hodgson and Kilner's method (J., 1924, **125**, 807), modified by omission of sulphuric acid, only slightly affected the optimum total yield of mixed 2- and 4-nitroaceto-α-naphthalides (83·5%), whilst differences of nitration procedure, *e.g.*, use of nitric acid alone (87% yield), or copper nitrate with acetic anhydride (86%), or diacetylorthonitric acid (82%), did not appreciably alter the ratio of 2- to 4-nitro-1-naphthylamine ultimately obtained. The simplest procedure, use of nitric acid alone, appears to afford the best yield with highest quality of product, and the method of isolation now described renders 2- and 4-nitro-1-naphthylamines readily available for the first time.

Among previous methods, that of Morgan and Micklethwait (J., 1905, **87**, 928) is stated to give more satisfactory results than that of Lellmann and Remy (*Ber.*, 1886, **19**, 797; 1887, **20**, 892), but it is tedious for separating large quantities. Superheated steam has now been found to remove the slowly volatile 2-nitro-1-naphthylamine from its mixture with the 4-nitro-isomeride, but a still more simple and rapid procedure depends on the ease with which the latter forms a stable salt when hydrogen chloride is passed through a solution of the mixed isomerides in a dry solvent such as benzene or nitrobenzene; the hydrochloride of 4-nitro-1-naphthylamine is completely precipitated, and that of the 2-nitro-compound is only slightly precipitated after prolonged passage of the gas. The latter product rapidly evolves hydrogen chloride on exposure to the atmosphere, reverting to the amine. When, however, concentrated sulphuric acid is shaken with a nitrobenzene or glacial acetic acid solution of 2-nitro-1-naphthylamine, the more stable sulphate is precipitated, from which the base is readily obtained by trituration with water.

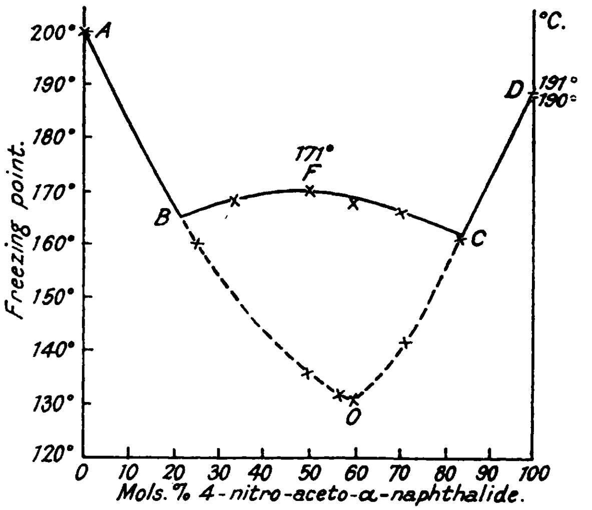
In order to ascertain whether Lellmann and Remy's double compound of 2- and 4-nitroaceto-α-naphthalides (*loc. cit.*, m. p. 171°) has a real existence, the accompanying freezing-point diagram was plotted from determinations on 5—10 g. of material; it indicates the formation, not only of an equimolecular compound at the maximum *F*, but also of a metastable eutectic at *O*. The curve *BFC* was obtained from mixtures of the double compound with the 2- and the 4-nitroaceto-α-naphthalide separately. The freezing-point diagram for mixtures of 2-nitro-1-naphthol and -1-naphthylamine does not indicate a double compound, although the products readily crystallise together in equimolecular proportion.

EXPERIMENTAL.

Nitration of Aceto-α-naphthalide.—(a) *In glacial acetic acid containing acetic anhydride.* The optimum conditions were obtained when α-naphthylamine (60 g.) was heated (20 mins.) on the water-bath with acetic anhydride (55 c.c.) and glacial acetic acid (400 c.c.), the solution cooled, and nitric acid (10 c.c.; *d* 1·42) added in one portion at 22°, a further 19 c.c. being run in gradually during 15 mins. at 15—20°; by this device, crystallisation of the aceto-α-naphthalide was prevented, and stirring difficulties avoided. When all the nitric acid had been used, the solution was quite clear, but continued agitation produced crystallisation which was completed during 20 hours. The mother-liquor, after removal of the crystals, was diluted with water, thereby precipitating the remainder of the 4-nitroaceto-α-naphthalide.

(b) *In nitric acid only.* Aceto-α-naphthalide (60 g.) was added gradually to nitric acid (400 c.c.; *d* 1·42) at 5—10°; at the outset, the nitrated naphthalide passed into solution, but at about the half-way stage the mixed products began to separate. After a further 30 mins.' shaking, the mixture was stirred into water (1 litre) and a bright yellow precipitate was obtained, only mononitration having occurred.

Hydrolysis of the Mixed 2- *and* 4-*Nitroaceto-α-naphthalides.*—The mixture (80 g.) was refluxed with a solution of ethyl alcohol (250 c.c.) and sulphuric acid (250 c.c.; 50%), complete hydrolysis occurring in 8 hours; the free amines were precipitated by addition of water.



Freezing-point diagram for mixtures of 2- *and* 4-*nitroaceto-α-naphthalides.*

Separation of the Isomerides.—(a) *By superheated steam at* 160°. Pure 2-nitro-1-naphthylamine distilled at the rate of 1 g. per litre of condensed water.

(b) *By salt formation.* The solution in nitrobenzene (7 g. per 100 c.c.) was treated with dry hydrogen chloride until a thick paste was formed and fuming began. 4-Nitro-1-naphthylamine hydrochloride separated quantitatively, and was filtered off, washed successively with nitrobenzene, the washings being added to the filtrate, and benzene (to remove nitrobenzene), dried, and converted into the base by trituration with water. The filtrate was then treated with concentrated sulphuric acid (1 c.c. acid per 70 c.c. nitrobenzene), and the 2-nitro-1-naphthylamine sulphate which separated was filtered off, washed successively with nitrobenzene and benzene, dried, and basified by water. The quantitative results were as follows:

Mode of nitration.		Yield of nitro-α-naphthylamine, %.		Total yield, %.	*o*/*p* Ratio.
		2-Nitro-.	4-Nitro-.		
In glacial acetic acid	Ex crystals	21·1	38·3	69·5	0·44
	Ex solution	Nil	10·1		
,, nitric acid (*d* 1·42)		20·2	55·0	75·2	0·37
With $Cu(NO_3)_2$ and Ac_2O		22·0	50·0	72·0	0·44
,, diacetylorthonitric acid		21·0	52·5	73·5	0·40

The hydrochloride of the 4-nitro-isomeride can be obtained by using benzene or similar solvents, and also by shaking these solutions with concentrated hydrochloric acid, showing that the water present does not hydrolyse the salt; in the latter case, subsequent manipulation is more tedious and glacial acetic acid is then the best solvent to employ; after treatment of the mixed nitroamines (50 g.) in the acid (500 c.c.) with concentrated hydrochloric acid (33 c.c.) and removal of the precipitate (m. p. of crude 4-nitro-1-naphthylamine, 190°), the 2-nitro-1-naphthylamine can be obtained from the filtrate by addition of water; separation *via* the sulphate, however, is more efficient.

2-Nitro-1-naphthylamine crystallised from 90% formic acid in orange-yellow prisms, m. p. 143—144° (Found: N, 14·9. Calc.: N, 14·9%). 4-Nitro-1-naphthylamine, crystallised as above, was obtained in bright yellow needles, m. p. 193—194° (Morgan and Micklethwait, *loc. cit.*, give m. p. 191—192°) (Found: N, 14·88%).

Preparation of 2- and 4-Nitroaceto-α-naphthalides.—Whereas the 4-nitro-isomeride was readily obtained by the action of acetic anhydride on the amine in glacial acetic acid solution, the 2-nitro-compound was best prepared by partial hydrolysis of Lellmann and Remy's double compound (*Ber.*, 1886, **19**, 797), their procedure being modified as follows: The double compound, dissolved in ethyl alcohol (20 g. per 250 c.c.), was treated hot with concentrated aqueous sodium hydroxide solution equivalent to all the double compound taken (instead of half this quantity; L. and R., *loc. cit.*) and then kept for 36 hours. Since the nitroaceto-α-naphthalides are much more soluble in aqueous ethyl-alcoholic sodium hydroxide than in ethyl alcohol alone, sufficient alkali was present after the hydrolysis of the 4-nitro-product to prevent the co-precipitation of the 2-nitroaceto-α-naphthalide. Under the above conditions complete hydrolysis of the 4-nitroaceto-α-naphthalide occurred, whilst the 2-nitro-isomeride remained unchanged.

An alternative procedure was to dilute the mixture after hydrolysis as above, and dissolve the dried precipitate of 4-nitro-1-naphthylamine and 2-nitroaceto-α-naphthalide in hot glacial acetic acid (1 g. per 10 c.c.), subsequently adding 1 c.c. of concentrated hydrochloric acid per 10 c.c. of acetic acid; the 4-nitro-1-naphthylamine thereby precipitated was filtered off, and the filtrate, after dilution with water, treated with sufficient sodium nitrite to diazotise the small amount of residual amine present. The precipitate of crude 2-nitroaceto-α-naphthalide (m. p. 190—195°) had m. p. 199—200° after one crystallisation from glacial acetic acid, and the respective products were obtained in total yield equivalent to 93% of the double compound taken. Both the 4-nitroaceto-α-naphthalide and the double compound gave a pronounced orange colour with concentrated sulphuric acid, whereas the 2-nitro-isomeride gave a pale yellow.

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