# 80. *The Nitration of 6- and 7-Methoxyaceto-2-naphthalide.*

By D. H. Hey and S. E. Lawton

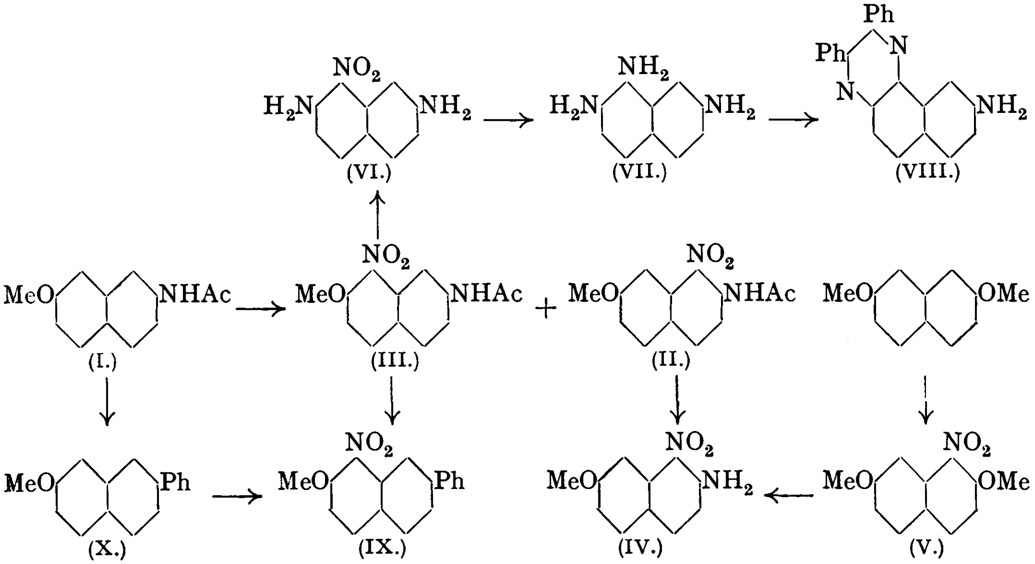
Nitration of 7-methoxyaceto-2-naphthalide gives a mixture of 1- and 8-*nitro*-7-*methoxyaceto*-2-*naphthalide.* Hydrolysis of the former gives a base identical with the 1-nitro-7-methoxy-2-naphthylamine prepared by Fischer and Kern (*J. pr. Chem.*, 1916, **94**, 34) : the constitution of the latter is established by conversion into 8-nitro-2 : 7-naphthylenediamine, reduction to the triamine, and condensation of this with benzil to give a *quinoxaline* derivative. Similarly, nitration of 6-methoxyaceto-2-naphthalide gives a mixture of 1- and 5-*nitro*-6-*methoxyaceto*-2-*naphthalide* and the constitution of the former is established by hydrolysis to give 1-*nitro*-6-*methoxy*-2-*naphthylamine,* identical with the base obtained from 1-nitro-2 : 6-dimethoxynaphthalene on amination. Both 1-nitro-6-methoxy- and 1-nitro-7-methoxy-aceto-2-naphthalide give with nitrous fumes nitroso-derivatives, which do not evolve nitrogen in benzene solution, but 5-nitro-6-methoxy- and 8-nitro-7-methoxy-aceto-2-naphthalide give normal nitroso-derivatives, which react with benzene to give 5-*nitro*-6-*methoxy*- and 8-*nitro*-7-*methoxy*-2-*phenylnaphthalene* respectively. The latter are identical with the compounds obtained from 6- and 7-methoxy-2-phenylnaphthalene by direct nitration.

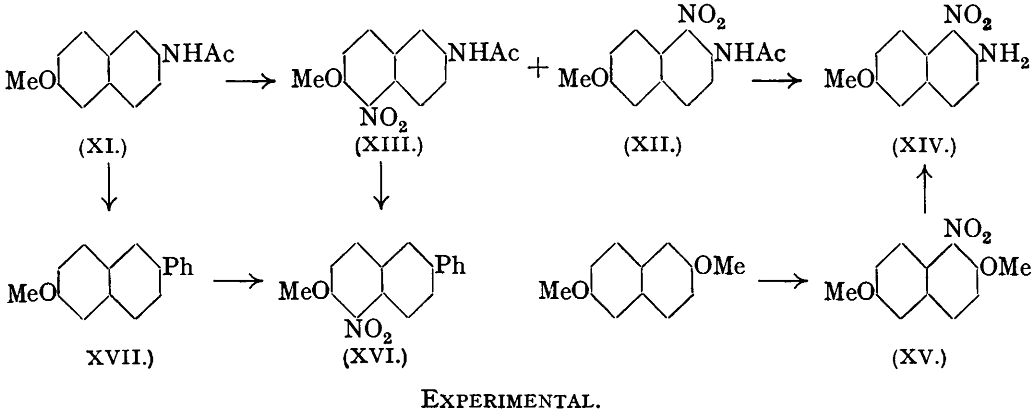
Nitration of 7-methoxyaceto-2-naphthalide (I) gave a mixture of 1- (m. p. 160°) (II) and 8-*nitro*-7-*methoxyaceto*-2-*naphthalide* (m. p. 229—230°) (III). The constitution of the former was established by the identity of the 1-nitro-7-methoxy-2-naphthylamine (IV) obtained on hydrolysis with the compound of that constitution prepared by Fischer and Kern (*J. pr. Chem.*, 1916, **94**, 34) from 1-nitro-2 : 7-dimethoxynaphthalene (V) by treatment with alcoholic ammonia at 180—190°. That this reaction actually gave 1-nitro-7-methoxy-2-naphthylamine (IV) was proved by Fischer and Kern by reduction of the nitro-group and condensation of the resulting 7-methoxy-1 : 2-naphthylenediamine with benzil or phenanthraquinone. A sample of 1-nitro-7-methoxy-2-naphthylamine (IV) thus prepared gave a *diacetyl* derivative, m. p. 165—166°, on acetylation with acetic anhydride, but under milder experimental conditions a monoacetyl derivative, m. p. 160°, was obtained, identical with the compound of the same melting point formed in the nitration of 7-methoxyaceto-2-naphthalide. The identity of the two bases was also confirmed by a mixed melting point of their picrates. The melting point recorded by Fischer and Kern (*loc. cit.*) for 1-nitro-7-methoxyaceto-2-naphthalide was 149—150°, but since they prepared it by acetylation of the base with acetic anhydride, their product probably contained some of the diacetyl derivative, which would account for its low melting point.

The constitution of the 8-nitro-7-methoxyaceto-2-naphthalide (III) was established by its conversion into 8-nitro-2 : 7-naphthylenediamine (VI) by the action of alcoholic ammonia at 180—190°, which on reduction yielded the triamine (VII) ; this condensed with benzil to form a *quinoxaline* derivative (VIII), indicating that two of the amino-groups in the triamine are situated at adjacent positions in the naphthalene nucleus and, if the possibility of nitration at a β-position in 7-methoxyaceto-2-naphthalide is disregarded, a course which is fully warranted by the known facts of orientation in the naphthalene series, nitration must have been effected at the 8-position.

8-Nitro-7-methoxyaceto-2-naphthalide (III) formed a nitroso-derivative in the normal manner on treatment with nitrous fumes, and reaction of the nitroso-compound with benzene gave 8-*nitro*-7-*methoxy*-2-*phenylnaphthalene* (IX), identical with the single product obtained from 7-methoxy-2-phenylnaphthalene (X) by direct nitration. 1-Nitro-7-methoxyaceto-2-naphthalide (II) also formed a *nitroso*-compound in similar manner, but this latter did not react normally with benzene ; no nitrogen was evolved and the original 1-nitro-7-methoxyaceto-2-naphthalide was regenerated. Such behaviour has been encountered previously with certain substituted acylarylamines (Haworth and Hey, this vol., p. 361). The conversion of 7-methoxyaceto-2-naphthalide (I) into 7-methoxy-2-phenylnaphthalene (X) has been described elsewhere (Hey and Lawton, this vol., p. 383).

Like the corresponding 7-methoxy-derivative, 6-methoxyaceto-2-naphthalide (XI) gave two compounds on nitration, namely, 1- (m. p. 157°) (XII) and *5-nitro-6-methoxyaceto-2-naphthalide* (m. p. 208—209°) (XIII). The constitution of the former was established by hydrolysis to give *1-nitro-6-methoxy-2-naphthylamine* (XIV), which was identical with the base formed by the action of alcoholic ammonia at 180—190° on 1-nitro-2 : 6-dimethoxynaphthalene (XV). Further evidence in support of this constitution was provided by the fact that the 1-nitro-6-methoxyaceto-2-naphthalide formed a nitroso-derivative in the normal manner, which in benzene solution reverted to the acetyl derivative, thus simulating the behaviour of 1-nitro-7-methoxyaceto-2-naphthalide. On the other hand, nitrosation of 5-nitro-6-methoxyaceto-2-naphthalide (XIII) proceeded normally and subsequent reaction of the nitroso-compound with benzene gave *5-nitro-6-methoxy-2-phenylnaphthalene* (XVI), identical with the single product obtained from 6-methoxy-2-phenylnaphthalene (XVII) by direct nitration. Conclusive proof of the entry of the nitro-group into the 5-position in these reactions is lacking, but circumstantial evidence, including analogy to the nitration of the corresponding 7-methoxy-derivatives, gives strong support to the correctness of the views now expressed (cf. Chakravarti and Pasupati, J., 1937, 1859). The conversion of 6-methoxyaceto-2-naphthalide (XI) into 6-methoxy-2-phenylnaphthalene (XVII) has been described elsewhere (Hey and Lawton, *loc. cit.*).





## EXPERIMENTAL.

*Nitration of 7-Methoxyaceto-2-naphthalide.*—Nitric acid (*d* 1·42, 2 c.c.) was added dropwise to a fine suspension of 7-methoxyaceto-2-naphthalide (4 g.) (Windaus, *Ber.*, 1924, **57**, 1731) in glacial acetic acid (20 c.c.) cooled in ice. After 1½ hours' stirring, the yellow solid (3·1 g.) was filtered off, washed, dried, and dissolved in boiling alcohol (120 c.c.), from which, on cooling, 8-*nitro*-7-*methoxyaceto*-2-*naphthalide* (1·2 g.) separated; on further crystallisation this formed yellow prisms, m. p. 229—230° (Found: C, 60·3; H, 4·6. $C_{13}H_{12}O_4N_2$ requires C, 60·0; H, 4·6%). The original alcoholic mother-liquor on evaporation to about 50 c.c. and cooling deposited a second crop of crystals, which after several recrystallisations from alcohol gave 1-*nitro*-7-*methoxyaceto*-2-*naphthalide* (1·1 g.) in orange-yellow needles, m. p. 160° (Found: C, 60·1; H, 4·9%).

1-Nitro-7-methoxyaceto-2-naphthalide was boiled under reflux for ½ hour with alcoholic potassium hydroxide. Addition of water precipitated the free base, which crystallised from aqueous alcohol in reddish-yellow needles, m. p. 115—116°, both alone and on admixture with a specimen of 1-nitro-7-methoxy-2-naphthylamine prepared from 2 : 7-dimethoxynaphthalene by nitration and subsequent amination as described by Fischer and Kern (*loc. cit.*). The picrates prepared from the two specimens separated from methyl alcohol in red needles, m. p. and mixed m. p. 125°.

1-Nitro-7-methoxy-2-naphthylamine (0·5 g.), prepared by the method of Fischer and Kern (*loc. cit.*), was boiled under reflux for 1 hour with a mixture of glacial acetic acid (5 c.c.) and acetic anhydride (2 c.c.). The solid obtained when the product was poured into water was filtered off, washed, and dried; on crystallisation from alcohol it gave 1-nitro-7-methoxyaceto-2-naphthalide in orange-yellow needles, m. p. 160°, both alone and on admixture with the product of the same m. p. obtained above by the nitration of 7-methoxyaceto-2-naphthalide. Acetylation of the base (0·5 g.) by boiling under reflux for 1 hour with acetic anhydride (7 c.c.) alone gave, on dilution with water, a yellow precipitate, which was washed, dried, and crystallised from alcohol. *Diacetyl*-1-*nitro*-7-*methoxy*-2-*naphthylamine* was obtained in greenish-yellow needles, m. p. 166° (Found: C, 59·7; H, 4·7. $C_{15}H_{14}O_5N_2$ requires C, 59·6; H, 4·6%). The same product was obtained on boiling 1-nitro-7-methoxyaceto-2-naphthalide with acetic anhydride. A mixture of the diacetyl and the monoacetyl derivative melted at 132—140°.

*Proof of the Constitution of* 8-*Nitro*-7-*methoxyaceto*-2-*naphthalide*.—8-Nitro-7-methoxyaceto-2-naphthalide (5 g., m. p. 229—230°) was heated in an autoclave with alcoholic ammonia (100 c.c.) for 1 hour at 160° and then for 3 hours at 200°. The solid residue obtained on evaporation of the reaction mixture to dryness was recrystallised from aqueous alcohol to give 8-nitro-2 : 7-naphthylenediamine (3·5 g.) in brown needles, m. p. 203—204°. Granulated tin (7 g.) was added to a solution of the diamine (2·5 g.) in a mixture of alcohol (150 c.c.) and hydrochloric acid (*d* 1·2, 30 c.c.) heated on the steam-bath. After 2 hours the solution was cooled, and the white crystalline mass filtered off, washed with hydrochloric acid, and dissolved in hot water. After addition of concentrated hydrochloric acid and cooling, 1 : 2 : 7-triaminonaphthalene hydrochloride (1·6 g.), which sintered at about 200°, was deposited. A solution of benzil (1 g.) in 80% aqueous alcohol (30 c.c.) was added to a solution of the triamine hydrochloride (1·4 g.) in 80% aqueous alcohol (10 c.c.) and boiled under reflux for ½ hour. The white crystalline product was filtered from the cooled mixture and treated with warm dilute aqueous sodium hydroxide, which liberated the free base (1·5 g.). After filtration, washing, and drying, it was crystallised from benzene–light petroleum (b. p. 60—80°), 3′-*amino*-2 : 3-*diphenyl*-5 : 6-*benzquinoxaline* being obtained in orange needles, m. p. 215°, which turned yellow on heating. Crystallisation from benzene alone gave bright yellow needles, m. p. 215° (Found: C, 82·7; H, 4·8; N, 11·9. $C_{24}H_{17}N_3$ requires C, 83·0; H, 4·9; N, 12·1%).

8-*Nitro*-7-*methoxy*-2-*phenylnaphthalene*.—Nitrous fumes were passed for 3 hours into an ice-cold solution of 8-nitro-7-methoxyaceto-2-naphthalide (2·5 g.) in a mixture of glacial acetic acid (600 c.c.) and acetic anhydride (100 c.c.). When the product was poured into ice-water, the nitroso-compound (2 g.) separated as a yellow solid, which was filtered off, washed, and dried [m. p. 85° (decomp.)]. The dry nitroso-compound was added to benzene (150 c.c.) and after 36 hours the benzene was removed by distillation. The residue, purified by sublimation in a vacuum, gave 8-*nitro*-7-*methoxy*-2-*phenylnaphthalene* (0·6 g.), which separated from alcohol in long yellow needles, m. p. 128° (Found: C, 72·9; H, 4·4. $C_{17}H_{13}O_3N$ requires C, 73·1; H, 4·7%).

*Nitration of* 7-*Methoxy*-2-*phenylnaphthalene*.—Nitric acid (*d* 1·42, 0·5 c.c.) was added gradually to 7-methoxy-2-phenylnaphthalene (1 g.) (Hey and Lawton, *loc. cit.*), which had been dissolved in hot glacial acetic acid (10 c.c.) and cooled in ice. After 15 minutes' stirring, the temperature was raised to 8° and the clear solution was kept in the refrigerator for several hours. 8-Nitro-7-methoxy-2-phenylnaphthalene (0·7 g.) slowly separated; it crystallised from alcohol in yellow needles, m. p. 128° alone and mixed with the compound described above.

*Nitrosation of* 1-*Nitro*-7-*methoxyaceto*-2-*naphthalide*.—Nitrous fumes were passed for 2½ hours into a cold solution of 1-nitro-7-methoxyaceto-2-naphthalide (2 g.) in a mixture of glacial acetic acid (120 c.c.) and acetic anhydride (50 c.c.), which was then poured into water. 1-*Nitro*-7-*methoxy*-N-*nitrosoaceto*-2-*naphthalide* (1·4 g.) separated as a yellow solid, which was filtered off, washed with water and dried, m. p. 71° (decomp.) (Found : N, 14·3. $C_{13}H_{11}O_5N_3$ requires N, 14·5%). The dry nitroso-compound was added to benzene (100 c.c.) and after 36 hours the benzene was removed by distillation. The residue on crystallisation from alcohol gave 1-nitro-7-methoxyaceto-2-naphthalide in orange-yellow needles, m. p. and mixed m. p. 160°.

*Nitration of* 6-*Methoxyaceto*-2-*naphthalide*.—A solution of 6-methoxyaceto-2-naphthalide (4 g.) (Windaus, *loc. cit.*) in hot glacial acetic acid (20 c.c.) was cooled in ice and stirred during the gradual addition of nitric acid (*d* 1·42, 2 c.c.). After 2 hours the separated yellow solid (2·8 g.) was filtered off, washed, dried, and dissolved in boiling methyl alcohol (80 c.c.). On cooling, 5-*nitro*-6-*methoxyaceto*-2-*naphthalide* (0·5 g.) separated, which crystallised from methyl alcohol in pale yellow needles, m. p. 208—209° (Found : C, 59·9; H, 4·9. $C_{13}H_{12}O_4N_2$ requires C, 60·0; H, 4·6%). On evaporation of the original methyl-alcoholic mother-liquor to 25—30 c.c. a second crop was deposited, which on repeated crystallisation from alcohol gave 1-*nitro*-6-*methoxyaceto*-2-*naphthalide* (0·9 g.) in brownish-yellow needles, m. p. 157° (Found : N, 11·1. $C_{13}H_{12}O_4N_2$ requires N, 10·8%). The latter was boiled under reflux for ½ hour with alcoholic potassium hydroxide; addition of water then precipitated 1-*nitro*-6-*methoxy*-2-*naphthylamine*, which separated from aqueous alcohol in red needles, m. p. 149—150° (Found : N, 13·3. $C_{11}H_{10}O_3N_2$ requires N, 12·9%).

*Proof of the Constitution of* 1-*Nitro*-6-*methoxyaceto*-2-*naphthalide*.—To a stirred mixture of 2 : 6-dimethoxynaphthalene (10 g.) (Willstätter and Parnas, *Ber.*, 1907, **40**, 1410) and glacial acetic acid (200 c.c.), nitric acid (*d* 1·42, 16 c.c.) was slowly added. 1-Nitro-2 : 6-dimethoxynaphthalene separated slowly and after 3 hours it was filtered off and washed with water (cf. Chakravarti and Pasupati, *loc. cit.*). Crystallisation from glacial acetic acid gave yellow needles (9 g.), m. p. 186° (Found : C, 61·6; H, 4·4. Calc. for $C_{12}H_{11}O_4N$ : C, 61·8; H, 4·7%). The nitro-compound (0·5 g.) was heated in an autoclave with alcoholic ammonia (100 c.c.) for 1 hour at 160° and then for 3 hours at 200°. The residue obtained on evaporation to dryness was sublimed at $10^{-3}$ mm. Crystallisation of the sublimate from aqueous alcohol gave 1-nitro-6-methoxy-2-naphthylamine (2·3 g.) in red needles, m. p. 149—150° alone and mixed with the base described above.

*Nitrosation of* 1-*Nitro*-6-*methoxyaceto*-2-*naphthalide*.—Nitrous fumes were passed for 2 hours into a cold solution of 1-nitro-6-methoxyaceto-2-naphthalide (1 g.) in a mixture of glacial acetic acid (40 c.c.) and acetic anhydride (20 c.c.). The nitroso-compound (0·6 g.) was precipitated with water, filtered off, washed, dried [m. p. 89° (decomp.)], and added to benzene (100 c.c.). After 36 hours evaporation of the benzene left 1-nitro-6-methoxyaceto-2-naphthalide, m. p. and mixed m. p. 157° after crystallisation from alcohol.

5-*Nitro*-6-*methoxy*-2-*phenylnaphthalene*.—Nitrous fumes were passed for 2 hours into an ice-cold solution of 5-nitro-6-methoxyaceto-2-naphthalide (1 g.) in a mixture of glacial acetic acid (40 c.c.) and acetic anhydride (30 c.c.), which was then poured into ice-water. The nitroso-compound (0·7 g.) was filtered off, washed, dried [m. p. 91° (decomp.)], and added to benzene (100 c.c.); after 36 hours, removal of the benzene left a residue, which was purified by sublimation in a vacuum. Crystallisation of the sublimate from alcohol gave 5-*nitro*-6-*methoxy*-2-*phenylnaphthalene* (0·2 g.) in pale yellow plates, m. p. 178° (Found: C, 72·6; H, 4·4. $C_{17}H_{13}O_3N$ requires C, 73·1; H, 4·7%).

*Nitration of* 6-*Methoxy*-2-*phenylnaphthalene*.—A solution of 6-methoxy-2-phenylnaphthalene (1 g.) (Hey and Lawton, *loc. cit.*) in hot glacial acetic acid (10 c.c.) was cooled in ice and stirred during the addition of nitric acid (*d* 1·42, 0·5 c.c.). After 15 minutes the temperature was raised to 8° and the clear solution was left in the refrigerator. 5-Nitro-6-methoxy-2-phenylnaphthalene (0·8 g.) slowly separated; after being washed and dried, it crystallised from alcohol in pale yellow plates, m. p. 178° alone and mixed with the compound described above.

The authors thank Imperial Chemical Industries Ltd. (Dyestuffs Group) for grants and gifts of chemicals and Messrs. Tootal Broadhurst Lee Co. Ltd. for the award of a scholarship to one of them (S. E. L.).

THE UNIVERSITY, MANCHESTER. [*Received, January 8th,* 1940.]