329. *Orientation in the Substitution Reactions of Alkylnaphthalenes. Part II. Nitration of 1-Methylnaphthalene.*

By Henry W. Thompson.

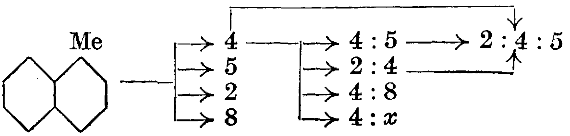
Previous workers (Lesser, *Annalen*, 1913, **402**, 1; Veselý, Štursa, Olysíček, and Rein, *J. Czech. Chem. Comm.*, 1929, **1**, 493) have detected much 4·nitro- and a trace of 8·nitro·1·methylnaphthalene in the product of nitration of 1·methylnaphthalene. Careful examination now reveals that there is produced about 70% of the 4·nitro·compound, some of the 5- and less of the 2-nitro·isomeride.

Vesely *et al.* (*ibid.*, 1930, **2**, 145) have shown that nitration of 4-nitro-1·methylnaphthalene produces much 4 : 5· together with some of the 2 : 4·dinitro·compound. It is now shown that there is produced about 45% of the first, some of the second, a small amount of 4 : 8·dinitro·1·methylnaphthalene, and a trace of a *dinitromethylnaphthalene*, m. p. 176°, of undetermined constitution.

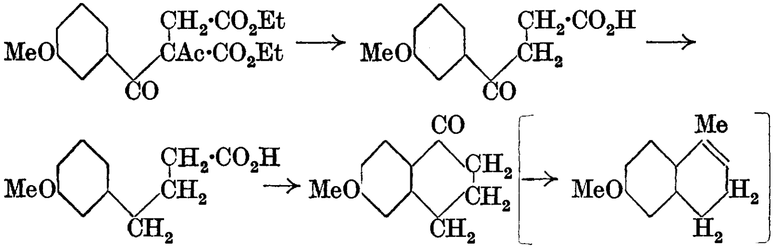
The trinitro·compound obtained from 4-nitro-1-methylnaphthalene by following Lesser's directions (*loc. cit.*) has m. p. 170° and not, as he states, 180—181°. It is shown to be 2 : 4 : 5·*trinitro*·1·*methylnaphthalene* by its identity with the product of nitration of either 2 : 4- or 4 : 5·dinitro-1·methylnaphthalene.

The following scheme summarises the facts of nitration of 1-methylnaphthalene.

Positions of Nitro-Groups.



The following synthetic work was undertaken to facilitate the determination of the structures of any heteronuclear nitro-1-methylnaphthalenes which might arise. *Ethyl* α-m-*methoxybenzoyl*-α-*acetylsuccinate* was hydrolysed to give β-m-*methoxybenzoylpropionic acid*, which was reduced to γ-m-*methoxyphenylbutyric acid*, from which, by the action of sulphuric acid, 5-keto-2-methoxy-5 : 6 : 7 : 8-tetrahydronaphthalene was obtained. It had been intended to introduce a methyl group into this compound and then prepare 6-amino- and 5-nitro-1-methylnaphthalene and their derivatives, but this work was rendered unnecessary by the syntheses performed by Veselý *et al.* (*loc. cit.*).



EXPERIMENTAL.

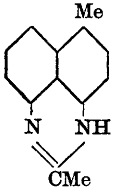
Mononitration of 1-*Methylnaphthalene.*—Nitration experiments with pure HNO_3 in Ac_2O, AcOH, or $MeNO_2$ at 0°, or with HNO_3 (*d* 1·42) at room temp., all gave the same result. The following method was most convenient. HNO_3 (65 c.c. ; *d* 1·42) was added slowly to 1-methylnaphthalene (20 g.) with shaking and cooling (the reaction may become uncontrollable if a larger amount of hydrocarbon is treated at one time); H_2O (100 c.c.) having been added, C_6H_6 extracted a substance which, after being washed with dil. NaOH aq. and cooled, was separated into a solid, consisting mainly of 4-nitro-1-methylnaphthalene, and an oil (380 g. and 200 g. respectively from 500 g. 1-methylnaphthalene). This oil was repeatedly distilled, a small quantity of crystals (33 g. in all, of 4-nitro-1-methylnaphthalene) being frozen out between each distillation, and gave an oil (80 g.) which was reduced by Fe powder (West, J., 1925, **127**, 494) to a liquid mixture of aminomethylnaphthalenes (Found: C, 83·5; H, 6·4; N, 9·1. Calc. for $C_{11}H_{11}N$: C, 84·1; H, 7·0; N, 8·9%). The crude acetyl compound (30 g.), m. p. 120—135°, obtained from this mixture was dissolved in boiling CCl_4 (300 c.c.); the cooled solution deposited a first fraction of crystals (2 g.), m. p. 186—190°, which when recryst. from CCl_4 and from EtOH gave 5-acetamido-1-methylnaphthalene in needles, m. p. 192° (Found: C, 78·4; H, 6·5; N, 7·0. Calc. for $C_{13}H_{13}ON$: C, 78·4; H, 6·5; N, 7·0%). Hydrolysis of this with KOH yielded 5-amino-1-methylnaphthalene in needles, m. p. 77°, which gave 5-benzamido-1-methylnaphthalene in needles (from EtOH), m. p. 172°. For these three compounds, Veselý *et al.* record m. p.'s of 194—195°, 77·5°, and 173·5° respectively. Further fractions deposited from the CCl_4 were fractionally crystallised from CCl_4 and from EtOH without any other pure compound being obtained, but one of the fractions (1·5 g.), m. p. 125—130°, was converted *via* an oily amine into a benzoyl compound which, repeatedly recryst. from EtOH, gave 2-benzamido-1-methylnaphthalene in white sheeny flakes, m. p. 219—221° (Veselý *et al.* give 222°) (Found : C, 83·0; H, 5·7; N, 5·5. Calc. for $C_{18}H_{15}ON$: C, 82·8; H, 5·7; N, 5·4%). It was not possible to hydrolyse this compound even by boiling for several hours with H_2SO_4 in AcOH.

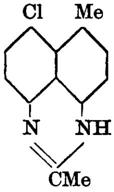
4-*Amino*-1-*naphthaldehyde* (compare Geigy and Co., D.R.-P. 86874; *Ber.*, 1896, **29**, R 530).—Powdered S (6 g.) was dissolved in boiling 12% NaOH aq. (90 c.c.), the nitro-compound (14 g.) in EtOH (40 c.c.) added, and the mixture refluxed for 1½ hrs. to give a dark oily suspension. Steam distillation removed a small amount of 4-amino-1-methylnaphthalene. The mixture was cooled, a brown powder collected and boiled with H_2O (1½ l.), and the extract filtered hot from a dark residue. (This dark product may be a polymeride of the Schiff's base type. The amount produced varies in different expts., but increases with time of reaction.) On cooling, light brown, hair-needles (1—5 g.) separated, m. p. 161°. To avoid polymerisation, this product was purified as follows. About 0·2 g. was shaken with Et_2O and filtered from the insol. polymeride. The solution was evaporated to dryness in a desiccator, the residue dissolved in EtOH at *ca.* 30°, H_2O added until a faint milkiness appeared, and the mixture cooled to 0°, to give yellow hair needles, m. p. 163° (Found : C, 76·7; H, 5·4; N, 7·4. $C_{11}H_9ON$ requires C, 77·2; H, 5·3; N, 8·2%).

Nitration of 4-*Nitro*-1-*methylnaphthalene.*—4-Nitro-1-methylnaphthalene (45 g.) was treated slowly with HNO_3 (90 c.c.; *d* 1·5) with shaking and cooling. Alternatively, a solution of the nitro-compound in HNO_3 (100 c.c.; *d* 1·42) was warmed on the steam-bath for a few mins. In either case, H_2O (1·5 l.) was added, the ppt. ground with Na_2CO_3 aq., and washed with H_2O to give a yellow powder (55 g.), m. p. 70—100° [Found, by $TiCl_3$: N, 11·5. Calc. for $C_{11}H_8(NO_2)_2$: N, 12·1%], which was digested with boiling CCl_4 (200 c.c.). The undissolved portion, cryst. from EtOH, gave 4 : 5-dinitro-1-methylnaphthalene in white needles (22 g.), m. p. 143° (Found : C, 56·8; H, 3·3; N, 12·0. Calc. for $C_{11}H_8O_4N_2$: C, 56·9; H, 3·45; N, 12·1%. Estimation of this compound in the usual manner with $TiCl_3$ gave low results). The CCl_4-sol. dinitro-compound was fractionally crystallised from CCl_4 and from EtOH, fractions with similar colour reactions (see p. 2314) and m. p.'s being segregated. A fraction (1·2 g.), m. p. 116°, which gave only a very slight colour reaction, was melted with a small amount of piperonal and a drop of piperidine to convert any 2 : 4-dinitro-1-methylnaphthalene associated with it into the insol. piperonylidene derivative, and the melt gave 4 : 8-dinitro-1-methylnaphthalene in buff needles (from EtOH), m. p. 122—123° (Found : C, 57·0; H, 3·5; N, 11·8%). Veselý *et al.* (*loc. cit.*) record m. p. 120—121°. A further fraction (5 g.), m. p. 117°, and evidently not a single substance, was obtained (Found : C, 56·1; H, 3·5; N, 11·9%); this was deemed to consist mainly of 2 : 4-dinitro-1-methylnaphthalene and not to contain any 4 : 5- or 4 : 8-dinitro-1-methylnaphthalene, from consideration of (i) its colour reaction (see p. 2314), (ii) the m. p.'s of mixtures with the known (2 : 4; 4 : 5; 4 : 8)-dinitro-1-methylnaphthalenes, (iii) the m. p.'s of mixtures of the derived diacetamido-compound (m. p. 270—280°) with the two known diacetamido-compounds. This fraction was treated with piperonal, in the manner described above, and a small quantity of 4 : x-*dinitro*-1-*methylnaphthalene* thus obtained in lustrous brown plates (from AcOH), m. p. 176° (Found : C, 57·15; H, 3·6; N, 11·8%).

4 : 5-*Diamino*-1-*methylnaphthalene*.—Attempts to reduce the corresponding dinitro-compound by means of $(NH_4)_2S$, Fe powder, or $SnCl_2$ were all unsuccessful, but the following method (cf. Meyer and Müller, *Ber.*, 1897, **30**, 775) was effective. H_2O (20 c.c.) was added to a mixture of the nitro-compound (2·1 g.) and PI_3 (25 g.). Slight warming initiated a violent reaction, which was completed by heating on the steam-bath for 1 hr. Excess of NH_3 aq. was added in the cold and the red ppt. afforded pale pink needles, m. p. 64°, from light petroleum (Found: C, 75·7; H, 7·0; N, 16·05. $C_{11}H_{12}N_2$ requires C, 76·7; H, 7·0; N, 16·3%); *dihydrochloride*, white needles, m. p. 260° (decomp.) (Found: N, 12·1; Cl, 28·5. $C_{11}H_{12}N_2,2HCl$ requires N, 11·4; Cl, 29·0%), from dil. alc. HCl. On treatment with Ac_2O, the diamine gave 2 : 6-*dimethylperimidine* (I) (compare Sachs, *Annalen*, 1909, **365**, 53), green needles, m. p. 210—220°, from EtOH (Found: C, 78·2; H, 6·3; N, 13·7. $C_{13}H_{12}N_2$ requires C, 79·6; H, 6·1; N, 14·3%).

(I.)





(II.)

7-*Chloro*-2 : 6-*dimethylperimidine* (II).—Consecutive reduction, halogenation, and acetylation occur when 4 : 5-dinitro-1-methylnaphthalene is treated in AcOH with $TiCl_3$ (compare de Kiewiet and Stephens, J., 1931, 82, for similar reductions with $SnCl_2$). A hot solution of the dinitro-compound (10 g.) in glac. AcOH (500 c.c.) was added to a boiling 15% solution of $TiCl_3$ (533 c.c.) and conc. HCl (266 c.c.), CO_2 being passed over the surface of the liquid. The mixture was boiled for 1 hr., cooled, and conc. NaOH aq. (500 g.) added. After a day, the flocculent ppt. of $Ti(OH)_4$ and adherent org. base was collected, dried in the steam-oven, and extracted with Et_2O (Soxhlet); the extract crystallised from EtOH (sparingly sol.) in green needles (2 g.), m. p. 228° (Found: C, 67·9; H, 4·9; N, 11·5; Cl, 15·8. $C_{13}H_{11}N_2Cl$ requires C, 67·7; H, 4·75; N, 12·15; Cl, 15·4%).

4 : 8-*Diacetamido*-1-*methylnaphthalene*.—The corresponding dinitro-compound (0·5 g.) was suspended in EtOH and shaken with a trace of PtO_2 and H_2 at atm. press. until the calc. quantity had been absorbed (½ hr.). The product was filtered, concentrated, and the residue converted into the *diacetyl* compound; white prisms, m. p. 320—323°, from EtOH (Found: C, 70·2; H, 6·45; N, 10·9. $C_{15}H_{16}O_2N_2$ requires C, 70·3; H, 6·25; N, 11·0%).

2 : 4 : 5-*Trinitro*-1-*methylnaphthalene*.—(*a*) Following the procedure of Lesser (*Annalen*, 1913, **402**, 14) for the dinitration of 4-nitro-1-methylnaphthalene, pale yellow prisms (from C_6H_6), m. p. 170°, were obtained in about 50% yield [Found: C, 47·8; H, 2·7; N, 14·4. $C_{11}H_7(NO_2)_3$ requires C, 47·65; H, 2·5; N, 15·2%. As before, titration with $TiCl_3$ gives anomalously low results]. (*b*) 2 : 4-Dinitro-1-methylnaphthalene (1 g.) (from 2 : 4-dinitro-1-naphthol; Veselý and Pastak, *Bull. Soc. chim.*, 1925, **37**, 1444) was boiled with HNO_3 (3 c.c.; *d* 1·5) for 2 mins., poured into water, and the ppt. crystallised from EtOH; yellow crystals, practically quantitative yield; m. p. 170°, no de-

pression with the above trinitro-1-methylnaphthalene. (*c*) 4 : 5-Dinitro-1-methylnaphthalene treated as described in (*b*) gave exactly similar results.

Colour Reactions (compare Rudolph, *Z. anal. Chem.*, 1921, **60**, 239).—Characteristic colours are developed when, to a solution of 2 : 4-dinitro- or 2 : 4 : 5-trinitro-1-methylnaphthalene (about 0·001 g.) in EtOH or $COMe_2$ (10 c.c.), 2*N*-NaOH or -NH_4OH (1 c.c.) is added. None of the other nitromethylnaphthalenes described in this paper gives such colours.

	2*N*-NaOH.		2*N*-NH_4OH.	
Compound.	Alcohol.	Acetone.	Alcohol.	Acetone.
2 : 4-Dinitro-	Mauve	Deep blue	No colour	Pink
2 : 4 : 5-Trinitro-	Red	Deep mauve	Pink	Red

Ethyl α-m-*Methoxybenzoyl*-α-*acetylsuccinate.*—Ethyl acetylsuccinate (214 g.) in Et_2O (2 l.) was treated with granulated Na (23 g.) for 1 hr., and the solution then decanted from the excess. *m*-Methoxybenzoyl chloride (153 g.) was added. A slight evolution of heat occurred, and NaCl was pptd. After 1 hr., the mixture, which was no longer alkaline, was washed with dil. alkali and concentrated to a viscous pale yellow oil (290 g.), which decomposed on vac. distn., and was therefore used in the next stage without further purification.

β-m-*Methoxybenzoylpropionic Acid.*—The above ester (470 g.) was stirred with KOH aq. (170 g. in 5½ l.). After 12 hrs., more KOH (85 g.) was added, and an equal quantity again at the end of 20 hrs. After 24 hrs., the solution was decanted from a small amount of undissolved oil, kept for 2 days, concentrated to 750 c.c., and a large excess of HCl aq. added. From the ppt., a *semicarbazone* was obtained, which crystallised from EtOH in white needles (58 g.), m. p. 177° (Found: C, 54·3; H, 5·7; N, 15·5. $C_{12}H_{15}O_4N_3$ requires C, 54·3; H, 5·7; N, 15·8%), which were boiled for 2—3 mins. with 2*N*-HCl (250 c.c.) to give the *keto-acid* (46 g.; m. p. 110°); white needles, m. p. 111°, from dil. EtOH (Found: C, 63·7; H, 5·8. $C_{11}H_{12}O_4$ requires C, 63·5; H, 5·8%).

γ-m-*Methoxyphenylbutyric Acid.*—The best yield of this material sufficiently pure for the next stage was obtained as follows. Amalgamated Zn (75 g.), keto-acid (14 g.), conc. HCl aq. (75 c.c.), and AcOH (30 c.c.) were refluxed for 24 hrs. H_2O was added, and the oil which was extracted by Et_2O was fractionally distilled. Under 20 mm., distillation occurred almost continuously from 150° to 340°, with no apparent decomp., and a considerable glassy residue remained. A fraction (2 g.), b. p. 200—205°/20 mm., was collected and used in the next stage (Found: C, 68·0; H, 8·1. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%).

5-*Keto*-2-*methoxy*-5 : 6 : 7 : 8-*tetrahydronaphthalene.*—A solution of the foregoing acid (4·4 g.) in conc. H_2SO_4 (50 c.c.) was kept at 70° for 10 mins. and then poured on ice. Ether extracted a yellow semi-solid mass (1 g.), from which a *semicarbazone* was obtained in white needles (0·8 g.), from EtOH, m. p. 235° (Found: C, 61·8; H, 6·8; N, 17·7. $C_{12}H_{15}O_2N_3$ requires C, 61·8; H, 6·4; N, 18·0%). This (0·6 g.) was warmed on the steam-bath with 2*N*-HCl (5 c.c.), and 5-*keto*-2-*methoxy*-5 : 6 : 7 : 8-*tetrahydronaphthalene* crystallised from dil. EtOH in white needles, m. p. 82° (Found: C, 74·7; H, 6·7. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%). (Schroeter, *Ber.*, 1930, **63**, 1319, records m. p. 80° for the compound obtained by the oxidation of *ar*-β-methoxytetralin, and to which this constitution was ascribed.) This compound has only a faint odour when cold, but gives a peppermint odour when warmed (compare 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene; Kipping and Hill, J., 1899, **75**, 149).

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