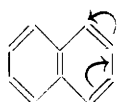


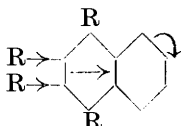
280. *Orientation in the Substitution Reactions of Alkyl-naphthalenes. Part I. Side-chain Nitration of 1 : 4-Dimethylnaphthalene.*

By ROBERT ROBINSON and HENRY W. THOMPSON.

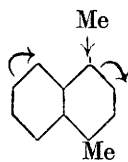
THE remarkable aptitude of naphthalene and its derivatives for substitution in the α -positions is doubtless to be attributed to the polarisation illustrated in (I).



(I.)



(II.)



(III.)

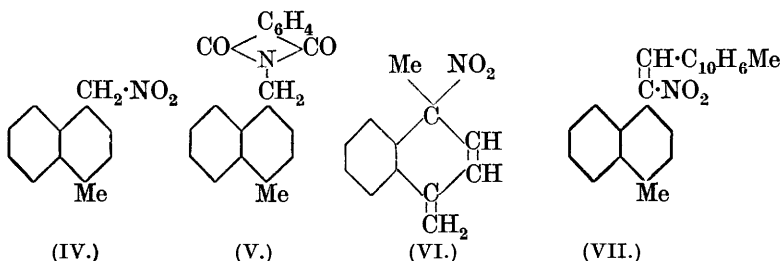
It was thought possible that the accumulation of alkyl groups in one of the benzenoid nuclei might bring about the condition exhibited in (II) as the result of a general electronic displacement. Again, with less highly alkylated hydrocarbons, the question arises as to whether the facilitation of β -substitution in the nucleus bearing the alkyl group in the α -position will be able to compensate effectively for the proneness to α -substitution in the other nucleus (III).

In the course of such enquiries we have examined the behaviour of 1 : 4-dimethylnaphthalene towards nitrating agents. Under normal

conditions the reaction appeared uncontrollable, but a clean product was obtained in acetic anhydride solution. Later the same product was obtained by nitration in nitromethane solution and also in aqueous suspension. This substance was neither an α - nor a β -nitrodimethylnaphthalene but was a methylnaphthyl nitromethane (IV). On reduction it furnished the related amine, the phthalimido-derivative (V) of which was identical with the substance prepared from methylnaphthylmethyl bromide and potassium phthalimide.

The only doubtful point is therefore the possible occurrence of migration in the reduction of a nitro-compound of the formula (VI); the properties of the nitro-derivative do not support this suggestion.

On oxidation with alkaline ferricyanide the substance yielded naphthalene-1:4-dicarboxylic acid together with a by-product which we regard as (VII).



Further work on the circumstances connected with this somewhat abnormal reaction is in progress and we reserve our comments.

E X P E R I M E N T A L.

1-Methyl-4-naphthalaldehydesemicarbazone.— α -Methylnaphthalene, condensed with HCN and HCl in presence of AlCl_3 , gave only poor yields of the aldehyde, which was isolated as its *semicarbazone*; white powder, m. p. 237° , from AcOH (Found: C, 68.4; H, 5.8; N, 18.0. $\text{C}_{13}\text{H}_{13}\text{ON}_3$ requires C, 68.7; H, 5.7; N, 18.5%).

4-Bromo-1-methylnaphthalene.—This was prepared by bromination of α -methylnaphthalene in cold CCl_4 with exclusion of light (compare Mayer and Sieglitz, *Ber.*, 1922, **55**, 1839). Previous workers have stated that this substance is liquid at -18° , but our distilled product was a nearly colourless oil, m. p. 2° (yield, 55%). Crystallisations from EtOH, using solid CO_2 , furnished faintly yellow material, m. p. $5.5\text{--}6.0^\circ$ (corr.), b. p. $157\text{--}158^\circ/10$ mm. (Found: C, 59.9; H, 4.1; Br, 35.4. Calc. for $\text{C}_{11}\text{H}_9\text{Br}$: C, 59.7; H, 4.1; Br, 36.2%); picrate, reddish-yellow needles, m. p. $126\text{--}127^\circ$. The same bromo-compound was produced by the Sandmeyer or the Gattermann reaction with diazotised 4-amino-1-methylnaphthalene, but the yields were unsatisfactory.

By careful fractional crystallisation from EtOH and conversion of the residues into picrate and further crystallisation, it was found that α -methylnaphthalene yields about 70% of the 4-bromo-isomeride.

1 : 4-Dimethylnaphthalene.—None of the known methods is suitable for the preparation of the hydrocarbon; further, they all appear to give mixtures, as is indicated by a comparison of the recorded properties (liquid at -18° ; picrate, m. p. given variously from 137° to 141°) with those of the product obtained as follows.

To the Grignard reagent prepared from 4-bromo-1-methylnaphthalene (221 g.), Mg (30 g.), and Et_2O (750 c.c.), purified Me_2SO_4 (130 c.c.) in Et_2O (200 c.c.) was added slowly, and the mixture refluxed for 24 hrs. The oily product was isolated by known methods, refluxed with conc. KOH aq. for 2 hrs., and distilled. In order to remove unchanged bromo-compound, the yellow oil obtained (120 g.), f. p. -12° , was heated to 220° with Na (15 g.), violently shaken for a short time, cooled, and filtered with the aid of some Et_2O ; it then distilled from Na as a colourless oil (105 g.), f. p. -8° . Two crystallisations from EtOH (with which it is miscible in all proportions at room temp.) using solid CO_2 , gave a product (yield, 55 g. or 35%), m. p. $4.5-5.0^{\circ}$, which was employed for the nitrations.

By further crystallisations from EtOH, a product, m. p. $5.5-6.5^{\circ}$ (corr.), b. p. $118^{\circ}/10$ mm., with a faint naphthalenoid odour was obtained (Found: C, 92.1; H, 7.7. Calc. for $\text{C}_{12}\text{H}_{12}$: C, 92.3; H, 7.7%). With conc. H_2SO_4 it gives a mauve suspension in the cold, and a green solution on warming; this may be due to impurity, but it is noteworthy that the ω -bromo-, -nitro-, and -hydroxy-derivatives give similar colour reactions. Picrate, m. p. $143-144^{\circ}$.

Nitration. No previous investigations are recorded. The hydrocarbon reacted very energetically with HNO_3 (d 1.42), alone or in AcOH. From the dark oil produced, much amorphous brown material was removed by washing with dil. alkali. The oil then deposited a small amount of a mixture of dinitro-compounds, m. p. 150° (Found: C, 57.8; H, 4.1. $\text{C}_{12}\text{H}_{10}\text{O}_4\text{N}_2$ requires C, 58.5; H, 4.1%). The residual oil was probably mainly mononitrodimethylnaphthalene (Found by TiCl_3 reduction: N, 5.7. $\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}$ requires N, 7.0%), but no pure substance was obtained from it.

ω -Nitro-1 : 4-dimethylnaphthalene (IV).—(A) A solution of 1 : 4-dimethylnaphthalene (20 g.) in Ac_2O (100 c.c.) was stirred mechanically, cooled with solid CO_2 , and HNO_3 (9 c.c.; d 1.52) added from a capillary during 1 hr. The faintly green solution was kept at -5° for 6 days, then cooled in solid CO_2 , and the white crystals washed with Ac_2O ; m. p. 106° (10 g.). The filtrate was worked up and furnished more white crystals, m. p. 105° (1—2 g.; total yield, 45%). The substance crystallised from EtOH in hair-like needles, m. p. 107° (Found: C, 71.5; H, 5.5; N, 6.6. $\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}$ requires C, 71.6; H, 5.5; N, 7.0%).

(B) HNO_3 (1.7 c.c.; d 1.5) in MeNO_2 (6 c.c.) was gradually added to a solution of 1 : 4-dimethylnaphthalene (5 g.) in MeNO_2 (20 c.c.) at -10° with stirring. After remaining at 0° for a day and then at room temp. for 3 hrs., the product was isolated; white needles (2.0 g.), m. p. 105° , from EtOH.

(C) The hydrocarbon (9 g.), mixed with H_2O (9 c.c.), was nitrated with HNO_3 (40 c.c.; d 1.42) and H_2O (30 c.c.) with cooling in running H_2O . Agitation was continued for $1\frac{1}{4}$ hrs., and the oil then separated and dissolved in the minimum of EtOH; 4 g. of white needles, m. p. 105° , crystallised on keeping, and the substance was identified with that described under (A) above.

ω -Nitro-1 : 4-dimethylnaphthalene darkens slowly when exposed to light and decomposes before volatilisation when heated under 1 mm. It dissolves in cold conc. H_2SO_4 to a deep blue solution, the colour of which is discharged on

dilution. It does not respond to Konowalow's reaction for primary nitro-compounds. It dissolves in boiling dilute NaOH aq.; in contact with conc. alkali a yellow ppt. is produced, and this dissolves on dilution with H₂O.

The addition of dil. HCl to the alkaline solution produces a white ppt. which, treated with FeCl₃, affords a dark brown compound soluble in Et₂O. Apparently this is the *aci*-form, and it is converted into the original form by crystn. from org. solvents. When a trace of the nitro-compound is heated with PhOH and H₂SO₄, the mixture poured into H₂O, and excess of alkali added, a mauve colour is produced (Gabriel's reaction for primary nitro-compounds; *Ber.*, 1885, 18, 1254; compare Wislicenus and Wren, *Ber.*, 1905, 38, 503).

Oxidation.—(A) K₃Fe(CN)₆ (102 g.), KOH (46 g.), H₂O (390 c.c.), and the nitro-compound (3 g.) were refluxed together for 5 hrs. and the mixture was then cooled and filtered. The residue of iron oxide contained yellow specks, which were extracted in hot Me₂CO and crystallised from Me₂CO, from C₆H₆, and from AcOH (sparingly sol. in all); canary-yellow needles (1.5 g.), m. p. 203° (Found: C, 81.7; H, 5.7; N, 4.0. C₂₄H₁₈O₂N requires C, 81.6; H, 5.4; N, 4.0%). This substance is doubtless a *methyl-naphthylidene-ω-nitro-dimethylnaphthalene* (VII). It does not react with Br, but this is by no means unusual in the case of heavily substituted stilbene derivatives.

An excess of HCl aq. was added to the filtrate from the iron oxide: the ppt. crystallised from AcOH as a white powder (0.8 g.), m. p. 320°, which was identified as naphthalene-1:4-dicarboxylic acid (Found: equiv. by titration, 105. Calc. for C₁₂H₈O₄: equiv., 108). Its properties agree with those recorded in the literature, except that Mayer and Sieglitz (*loc. cit.*, p. 1841) give m. p. 288°. The alcoholic solution fluoresced blue, and when the acid was heated with soda-lime, naphthalene was produced.

(B) Oxidation with KMnO₄ in alkaline solution gave similar results.

ω-Amino-1:4-dimethylnaphthalene.—The nitro-compound (3.8 g.), suspended in abs. EtOH (50 c.c.) containing a trace of platinum oxide, was shaken with H₂ until 1,650 c.c. had been absorbed (5 hrs.). After filtration the solvent was removed; as the residual oil rapidly absorbed CO₂ from the air, it was converted into the *hydrochloride*, white needles, m. p. 285° (Found: C, 68.0; H, 7.0; N, 16.3. C₁₂H₁₃N.HCl requires C, 69.3; H, 6.7; N, 17.1%). The *acetamido*-derivative occurred as white flakes, m. p. 142° (Found: C, 78.6; H, 7.0. C₁₄H₁₆ON requires C, 78.8; H, 7.0%).

Phthalimido-derivative (V).—An intimate mixture of the amino-hydrochloride, fused AcONa, and phthalic anhydride was heated for a few mins. over a free flame. The product crystallised from AcOH aq. in small white needles, m. p. 148° alone or mixed with authentic *ω*-phthalimido-1:4-dimethylnaphthalene (below).

ω-Hydroxy-1:4-dimethylnaphthalene.—This was prepared by the method of Ziegler and Tiemann (*Ber.*, 1922, 55, 3406) by the action of gaseous formaldehyde on the Grignard reagent prepared from 4-bromo-1-methylnaphthalene. The crude alcohol was converted into the acid phthalate by heating on the steam-bath for a few hrs. with a little toluene and an excess of phthalic anhydride. The product was isolated by solution in Na₂CO₃ aq., an excess of KOH added to the extract, and the oily suspension steam-distilled. Fine white needles separated from the distillate; m. p. 77° after crystallisation from C₆H₆ (yield, 26%). A trace of this substance developed with conc. H₂SO₄, slowly in the cold, but rapidly on warming, a deep bluish-green coloration.

ω -Bromo-1 : 4-dimethylnaphthalene.—A solution of the hydroxy-compound in C_6H_6 to which anhyd. Na_2SO_4 was added was saturated in the cold with HBr, kept at room temp. for 4 hrs., and filtered, the C_6H_6 distilled, and the residue crystallised from light petroleum; white silky needles, m. p. 80° (yield, nearly quantitative) (Found : C, 61.5; H, 4.8; Br, 33.6. $C_{12}H_{11}Br$ requires C, 61.3; H, 4.7; Br, 34.0%). A pale blue colour developed with warm conc. H_2SO_4 .

ω -Phthalimido-1 : 4-dimethylnaphthalene (V).—An intimate mixture of the bromo-compound (3 g.) and potassium phthalimide (3 g.) was heated at 180 – 200° for $3\frac{1}{2}$ hrs., the product boiled with H_2O , and the white insol. powder crystallised in turn from AcOH and EtOH– Me_2CO ; small hard needles, m. p. 148° (Found : C, 79.7; H, 5.1; N, 4.6. $C_{20}H_{15}O_2N$ requires C, 79.7; H, 5.0; N, 4.7%). The crude material was heated with an excess of very dil. NaOH aq., the solution filtered, washed with Et_2O to remove a trace of ω -hydroxy-1 : 4-dimethylnaphthalene, and the white powder which was pptd. by the addition of HCl aq. crystallised from EtOH; white needles, m. p. 179° (decomp.) (Found : C, 74.9; H, 5.4; N, 4.3; equiv. by titration, 323. $C_{20}H_{17}O_3N$ requires C, 75.2; H, 5.3; N, 4.4%; *M*, 319). This *phthalamic acid* is quantitatively converted into the phthalimido-derivative by boiling conc. HCl.

Dinitro-1 : 4-dimethylnaphthalene.—A solution of the hydrocarbon (20 g.) in Ac_2O (65 c.c.) was cooled in solid CO_2 , stirred mechanically, and HNO_3 (8 c.c.; *d* 1.52) added through a capillary. The mixture was kept at -5° for 2 days, again cooled in solid CO_2 , more HNO_3 (3 c.c.) added, and the mixture kept at -5° for 3 days. Cooling in solid CO_2 yielded yellow crystals (6.5 g., m. p. 125°), which were recrystallised from EtOH; pale yellow needles, m. p. 128° (Found : C, 58.5; H, 4.0; N, 11.0. $C_{12}H_{10}O_4N_2$ requires C, 58.5; H, 4.1; N, 11.4%). This compound gives in cold H_2SO_4 a yellow solution which becomes green on heating or long standing.

The Ac_2O mother-liquors contained a *substance* crystallising from EtOH in yellow needles (2 g.), m. p. 174° (decomp.) (Found : C, 58.5; H, 4.3%). This substance, the nature of which is not yet known, develops a deep blue coloration with cold conc. H_2SO_4 .

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