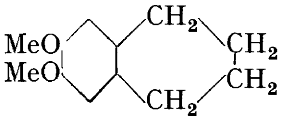
270. *Formation of an Intermediate Product in the Nitration and Simultaneous Demethylation of* 6 : 7-*Dimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene.*

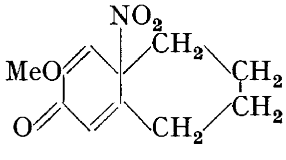
By H. J. Lewis and Robert Robinson.

The nitration of 6 : 7-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (I) was investigated because it was hoped, in connexion with synthetic work, to find a method for the fission of the aromatic ring in veratroles substituted in positions 4 and 5.

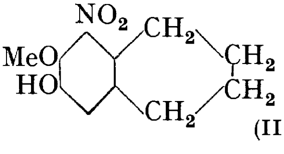
The outcome was unexpected, and it was found that nitration was accompanied by demethylation and occurred with the formation of a colourless *substance*, $C_{11}H_{13}O_4N$, containing but a single methoxyl group. This is not soluble in cold dilute aqueous alkaline solutions, but on heating with water, or better, alcohol, it is rapidly transformed into a yellow isomeride possessing all the properties of a nitrophenol. The nitrohydroxymethoxytetrahydronaphthalene (III or IV) furnishes a methyl ether which is undoubtedly 5-*nitro*-6 : 7-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (V). This does not absorb bromine in chloroform solution and hence is not a butenylnitroveratrole. The corresponding amine can be diazotised and then coupled to form an azo-compound.

(I.)

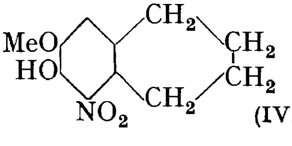




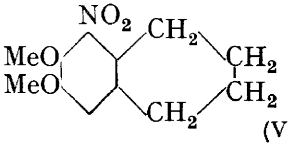
(II.)



(III.)



(IV.)

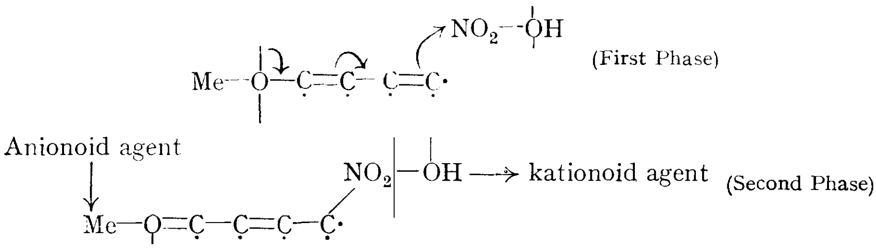


(V.)

There seems little doubt but that the colourless product of the original nitration must have the constitution (II), and this accords with its relative instability. The alternative, with the group $-C(OMe)(NO_2)-$, is improbable in view of the strong tendency for 4-nitration of veratroles, and also because this type of reaction has not previously been observed in the veratrole series. A good illustration of the reactivity of position 4 is the displacement of bromine by nitroxyl in the nitration of bromohomoveratrole (Heap, Jones, and Robinson, J., 1927, 2021). As we are unable to distinguish at this stage between the constitutions (III or IV) for the nitrophenol, it is premature to discuss the mechanism of the migration of the nitro-group.

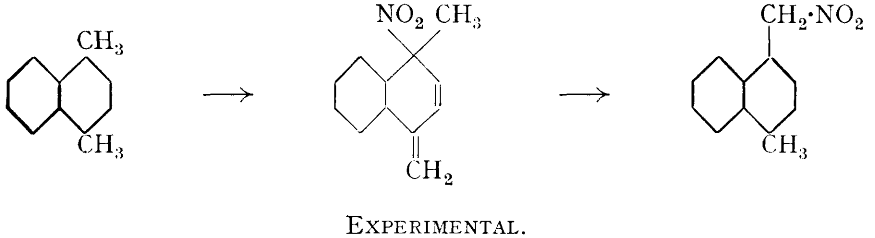
The formation of (II) is of considerable interest, because it cannot be brought into line with any theory of the mechanism of aromatic substitution which postulates expulsion of a proton of the aromatic nucleus *prior* to the attack of the nuclear carbon by the reagent. Similar reactions in which one of the halogens or diazo-groups occupies a blocked hydro-aromatic position have long been known and their occurrence was cited by Lapworth and Robinson (*Nature*, 1932, **129**, 278; **130**, 273) as affording strong evidence of the secondary nature of proton-removal in aromatic substitutions. The first phase is considered to be the donation of electrons by anionoid carbon of the nucleus to the kationoid reagent, and this is followed by detachment of a proton in the usual cases.

In the present instance the expulsion of a methyl kation takes the place of that of a proton, and there can be no suggestion that this event precedes the formation of the $C-NO_2$ link.



Hence the suggestion of E. Hückel (*Z. Physik*, 1931, **72**, 310; also E. and W. Hückel, *Nature*, 1932, **129**, 937), representing an inversion of current views on electronic mechanisms, that the aromatic carbon atoms of *low* electron density are those at which substitutions of the ordinary type (nitration, sulphonation, etc.) are most prone to occur, is one that cannot be accepted.

In view of the observation now recorded, it seems highly probable that the nitration of 1 : 4-dimethylnaphthalene, leading to formation of a methylnaphthylnitromethane (Robinson and Thompson, J., 1932, 2015), proceeds according to the following mechanism :



EXPERIMENTAL.

6 : 7-*Dimethoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (I).—This substance was prepared, but not characterised or analysed, by Haworth and Mavin (J., 1932, 1485). 6 : 7-Dimethoxy-1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (16 g.), prepared by their method, was reduced by means of a large excess of amalgamated zinc and boiling hydrochloric acid during 48 hours; the acid was replenished at intervals of 6 hours. The product was isolated in the known manner, b. p. 125°/1 mm. (yield, 10·5 g.), and crystallised in large prisms, m. p. 53—54° (Found : C, 74·8; H, 8·4. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%).

9-*Nitro*-6-*keto*-7-*methoxy*-1 : 2 : 3 : 4 : 6 : 9-*hexahydronaphthalene* (II).—Dimethoxytetrahydronaphthalene (3 g.) was dissolved in acetic acid (25 c.c.), cooled to below 10°, and vigorously stirred. A mixture of nitric acid (2·5 c.c., *d* 1·42) and acetic acid (10 c.c.) was slowly added during 30 mins.; a portion of the product then crystallised. The mixture was added to crushed ice, and the cream-coloured solid collected, m. p. 92°, and m. p. 95° (decomp.) after crystallisation from ethyl acetate. The best method of purification was, however, addition of light petroleum to a solution in cold chloroform, and the *substance* then separated in six-sided, thin, elongated plates, m. p. 92—93° (decomp.) (Found : C, 59·2, 59·3; H, 5·8, 6·0; N, 6·4, 6·4; MeO, 14·0, 14·2, 14·8. $C_{11}H_{13}O_4N$ requires C, 59·2; H, 5·8; N, 6·3; 1MeO, 13·9%). The observed m. p. depends on the rate of heating, and is doubtless a decomposition point; fusion was accompanied by rapid evolution of gas and discoloration. The solution in sulphuric acid is yellow, and becomes brown with a violet tinge on keeping. The substance is insoluble in cold aqueous alkalis, and on heating with aqueous sodium carbonate it partly dissolves to a dirty brown solution. The transformation into the nitro-phenol occurs on heating a solution in any neutral hydroxylic solvent.

5 (or 8)-*Nitro-6-hydroxy-7-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene* (III or IV).—The foregoing substance is heated with alcohol, and almost at once the solution becomes orange-brown. On addition of water, the *nitrophenol* separates in yellow plates, which recrystallise from aqueous alcohol in thin, elongated plates, m. p. 133° (Found : C, 59·2; H, 5·6; N, 6·7; MeO, 14·0, 14·2. $C_{11}H_{13}O_4N$ requires C, 59·2; H, 5·8; N, 6·3; 1MeO, 13·9%). This substance has the properties of its type; it forms a sparingly soluble, brick-red sodium salt, and is not appreciably volatile in steam. The crystals do not melt under boiling water (indication of chelation), and methylation by means of methyl sulphate and aqueous sodium hydroxide is slow. On the addition of *p*-nitrobenzenediazonium acetate to a solution in methyl-alcoholic aqueous sodium carbonate, a reddish-violet brown coloration is obtained; deep yellow on acidification. This seems to indicate definite diazo-coupling potentiality.

The evidence, so far as it goes, favours the *m*-nitrophenol configuration, but further work is required in order to establish the constitution of the substance. Its solution in sulphuric acid is orange-brown and becomes dark green on keeping.

5-*Nitro-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene* (V).—The foregoing nitrophenol was dissolved in hot aqueous sodium hydroxide and a little methyl alcohol, and vigorously shaken with excess of methyl sulphate. The reagents were added alternately until the disappearance of the orange-red colour indicated the completion of the reaction. On the addition of water the oil solidified; it crystallised from aqueous methyl alcohol and then from ethyl alcohol in very pale yellow needles, m. p. 88—89° (Found : C, 60·6; H, 6·4; N, 6·0; MeO, 25·7. $C_{12}H_{15}O_4N$ requires C, 60·7; H, 6·3; N, 5·9; 2MeO, 26·1%). The solution in sulphuric acid is pale yellow, and becomes deep blackish-green on keeping. On reduction by means of zinc and hydrochloric acid, an amine is produced which may be diazotised and coupled with β-naphthol to a bluish-red azo-derivative.

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