

12. *The Exchange Reactions of 4-Nitro-1-naphthyl Methyl Ether and 4-Nitro-1-naphthyl Ethyl Ether with Sodium Ethoxide and Methoxide respectively, and the Reduction of Certain 1-Nitronaphthalene Derivatives.*

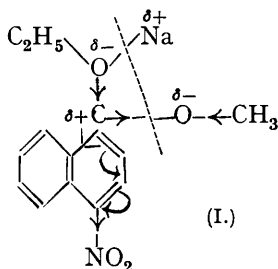
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Nitronaphthalene derivatives are more completely reduced than the corresponding benzene compounds. Methyl-alcoholic potassium hydroxide readily replaced chlorine by the hydroxyl group in the *o*- and *p*-chloronitronaphthalenes in contrast with tardy replacement of chlorine in the *o*- and *p*-chloronitrobenzenes. 4-Nitro-1-naphthyl methyl ether reacted with sodium ethoxide in excess of ethyl alcohol to give 4-nitro-1-naphthyl ethyl ether, and 4-nitro-1-naphthyl ethyl ether reacted with sodium methoxide in excess of methyl alcohol to give 4-nitro-1-naphthyl methyl ether. These exchange reactions are discussed.

UNDER neutral conditions the nitronaphthalenes are reduced more completely than nitrobenzene (cf. Cumming and Steele, J., 1923, **123**, 246), and this greater facility of reduction is now established for 4-chloro-1-nitronaphthalene and 4-nitro-1-naphthyl methyl ether, which are reduced as far as the azo-stage. These facts indicate that the nitro-group in the nitronaphthalenes and their derivatives is more

positive than in the corresponding benzene compounds, and this can be ascribed to the additional negative ($-I$) inductive effect of the second benzene nucleus (Hodgson and Elliot, J., 1935, 1850; *J. Soc. Dyers and Col.*, 1938, 54, 264).

Treatment of 4-nitro-1-naphthyl methyl ether with a deficiency of sodium ethoxide in ethyl alcohol for 10 minutes resulted in replacement of methoxyl by ethoxyl, the nitro-group remaining unattacked. This exchange did not take place with *p*-nitroanisole, which reacted at the nitro-group to give a mixture of *p*-azoxy- and *p*-azo-anisoles (cf. Rotarski, *Ber.*, 1903, 36, 3158). Conversely, when sodium methoxide reacted with 4-nitro-1-naphthyl ethyl ether in methyl-alcoholic solution, a corresponding exchange of ethoxyl for methoxyl occurred. Such an easy reversal of behaviour might be tentatively explained as follows: The 1-carbon atom in 4-nitro-1-naphthyl methyl ether is very strongly kationoid owing to



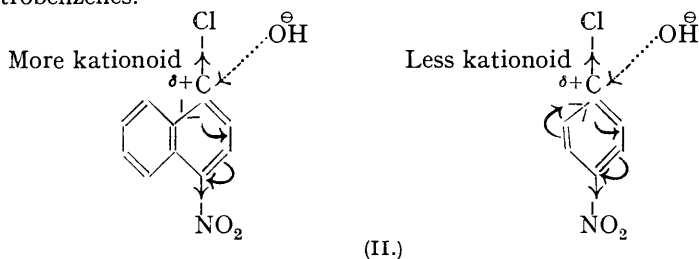
a combination of the ($-I$) effects of the nitro-group and the second nucleus, and the attached methoxy-group has also a negative ($-I$) inductive effect (cf. Ingold, *Ann. Reports*, 1928, 25, 122; Hodgson and Clay, J., 1929, 2776). The net result is a very strained polarised covalent link, which in consequence is subject to attack by the strongly anionoid reagent sodium ethoxide (I) with resulting displacement of methoxyl by ethoxyl. In 4-nitro-1-naphthyl ethyl ether, exactly the same set of electronic conditions obtains as in the methyl ether, *viz.*, a strained polarised covalent linkage between the ethoxy-group and the attached 1-carbon atom, with consequent attack by the powerful anionoid reagent (sodium methoxide) whereby replacement of ethoxyl by methoxyl

takes place. Further, the action of the sodium is apparently catalytic, *i.e.*, it is the carrier of the alkoxy-group, since a very good yield of exchange product is obtained with less than the stoichiometric amount of sodium.

The above replacements, however, failed to occur with the more readily oxidisable sodium *n*- and *iso*-propoxides, and reaction was probably at the nitro-group, since insoluble coloured mixtures resulted in both cases.

Methyl-alcoholic potassium hydroxide displaced chlorine readily at 55° from 1-chloro-2-nitro-, 1-chloro-4-nitro-, and 2-chloro-1-nitro-naphthalene to give the potassium salts of 2-nitro- and 4-nitro-1-naphthol and 1-nitro-2-naphthol, respectively, in *ca.* 90% yield. These reactions are in striking contrast with the tardy reactivity of either aqueous or alcoholic potassium hydroxide with 1- and 4-chloronitrobenzenes, which for complete conversion into the 1- and 4-nitrophenols require heating under pressure. When, however, sodium or potassium methoxide or ethoxide was heated with the above chloronitronaphthalenes or chloronitrobenzenes, the halogen was replaced with ease by the methoxy- or ethoxy-group. These results indicate that the dipolarised alkoxides are much more powerful anionoid reagents than the ionic alkali hydroxides.

The following tentative explanation is offered to explain the great difference between the reactivities of *o*- and *p*-chloronitronaphthalenes and *o*- and *p*-chloronitrobenzenes towards alcoholic alkali hydroxides. The hydroxyl ion (with completed octet of electrons) is very stable compared with the polarised alkoxides and will only react at a powerful kationoid centre. Now the carbon atom to which chlorine is attached in the chloronitronaphthalenes differs from that in the chloronitrobenzenes by the negative ($-I$) effect due to the second nucleus, which makes it more kationoid, and owing to the less mobile (Erlenmeyer) structure of naphthalene, relief of strain (to produce less positivity) is well-nigh impossible, whereas in the chloronitrobenzenes this accommodation is possible from the third double bond (II). Both these influences combine to make the 1-carbon atom in the chloronitronaphthalenes much more kationoid than that in the chloronitrobenzenes.



EXPERIMENTAL.

Neutral Reduction of 4-Chloro-1-nitronaphthalene.—The chloronitro-compound (10 g.) in ethyl-alcoholic solution was treated with zinc dust (30 g.) according to the directions of Cumming and Steele (*loc. cit.*).

(The use of less zinc dust produced tar and not the azoxy-compound.) The somewhat tarry product was crystallised once from glacial acetic acid, by which the tar was removed, and then three times from benzene, 4 : 4'-dichloro-1 : 1'-azonaphthalene being obtained in *ca.* 10% yield in bright orange needles, m. p. 262—263° (Found : N, 8.1. $C_{20}H_{12}N_2Cl_2$ requires N, 8.0%).

The Action of Sodium Methoxide and Sodium Ethoxide on 4-Chloro-1-nitronaphthalene.—Hot solutions of 4-chloro-1-nitronaphthalene (2.5 g.) in methyl alcohol (30 c.c.) and in ethyl alcohol (30 c.c.) were separately treated under reflux with sodium (1.1 g.), added in small pieces and with continuous stirring at a temperature near the b. p. of each mixture. The liquids were heated for 10 minutes, filtered, and allowed to cool gradually. From the first solution 4-nitro-1-naphthyl methyl ether separated in pale yellow needles, m. p. 85° (lit., 85—86°) (Found : N, 7.1. Calc. : N, 6.9%), and from the second solution 4-nitro-1-naphthyl ethyl ether crystallised in yellow needles, m. p. 116—117° (see Heermann, later) (Found : N, 6.6. Calc. : N, 6.45%).

The Action of Methyl-alcoholic Potassium Hydroxide on 1-Chloro-2-nitronaphthalene.—The chloronitro-compound (10 g.) was heated at 55° with 25% methyl-alcoholic potassium hydroxide (100 c.c.). After 4 hours the dark red potassium salt of 2-nitro-1-naphthol was collected, washed with methyl alcohol (yield, 9.5 g.), and acidified. The 2-nitro-1-naphthol crystallised from 50% aqueous alcohol in yellow needles, m. p. 128°. Similarly, 1-nitro-2-naphthol was obtained from 2-chloro-1-nitronaphthalene in yellow needles, m. p. 103°. The process proved very convenient and satisfactory for the preparation of these nitronaphthols in the pure state.

Exchange Reactions in 4-Nitronaphthyl Methyl and Ethyl Ethers.—(a) A solution of 4-nitro-1-naphthyl methyl ether (13.5 g.) in ethyl alcohol (200 c.c.) was treated with sodium (8 g.), added gradually in small pieces and with vigorous stirring; the temperature rose to 65° and was maintained there for 10 minutes after addition was complete. The solution darkened considerably and, on cooling, deposited thick yellow needles (11 g.) of 4-nitro-1-naphthyl ethyl ether, which crystallised from ethyl alcohol in well-formed, light yellow needles, m. p. 116—117° (Heermann, *J. pr. Chem.*, 1891, **44**, 238, gives m. p. 116—117°) (Found : N, 6.6. Calc. : N, 6.45%).

(b) Solutions of 4-nitro-1-naphthyl ethyl ether (5 g.), obtained as in (a) and also by the action of sodium ethoxide on 1-chloro-4-nitronaphthalene, in methyl alcohol (75 c.c.) were treated under reflux as in (a) with sodium (3 g.); the quantities are approximately the equivalents of those in (a). When the solutions cooled, they deposited 4-nitro-1-naphthyl methyl ether, which crystallised from dilute ethyl alcohol in long, pale yellow needles, m. p. 85° (Found : N, 7.0. Calc. : N, 6.9%), identical with the initial material used in (a).

(c) Reactions (a) and (b) were repeated with sodium in *n*-propyl and *isopropyl* alcoholic solutions, but only coloured amorphous uncrystallisable substances resulted. In attempts to carry out the reactions at room temperature and without subsequent heating the initial materials were recovered unchanged.

Some Reductions of 4-Nitro-1-naphthyl Methyl and Ethyl Ethers.—(a) By the usual reduction method with zinc dust and alkali hydroxide, only small amounts of 4-amino-1-naphthyl methyl ether (identified by the acetyl derivative) and 4-amino-1-naphthyl ethyl ether (isolated by steam-distillation) were obtained, the rest of the product being insoluble tar.

(b) 4-Nitro-1-naphthyl methyl ether (2.5 g.), reduced according to the directions of Cumming and Steele (*loc. cit.*), afforded a tarry product, from which, after one crystallisation from glacial acetic acid and several from ethyl alcohol, 4 : 4'-dimethoxy-1 : 1'-azonaphthalene (0.5 g.) was obtained in short orange-yellow needles, m. p. 105—107° (Found : N, 8.4. $C_{22}H_{18}O_2N_2$ requires N, 8.2%). It was necessary to use a large excess of zinc dust before any definite product whatever could be isolated from the reduction mixture.

(c) The most favourable conditions for the reduction of 4-nitro-1-naphthyl ethyl ether to the amine were as follows : A solution of crystallised stannous chloride (5 g.) in hydrochloric acid (25 c.c., *d* 1.16) was added gradually to a boiling solution of 4-nitro-1-naphthyl ethyl ether (2 g.) in glacial acetic acid (75 c.c.), the boiling under reflux being continued for 20 minutes after the addition was complete. On cooling, 4-amino-1-naphthyl ethyl ether hydrochloride separated (1.6 g.; yield, *ca.* 80%); this crystallised from ethyl alcohol in fine colourless needles, m. p. 275° (Heermann, *J. pr. Chem.*, 1892, **45**, 545, gives m. p. 275°) (reddened at *ca.* 260° and melted to a deep red liquid) (Found : Cl, 15.6. Calc. : Cl, 15.9%). The amine was liberated from the hydrochloride by treatment with dilute aqueous ammonia, isolated by steam distillation, and crystallised from light petroleum; it formed colourless needles, m. p. 96° (Heermann, *loc. cit.*, gives m. p. 96°) (Found : N, 7.6. Calc. : N, 7.5%), which rapidly became discoloured on exposure to air.

The yields obtained by reduction with stannous chloride in alcohol were *ca.* 50%.

In the case of 4-nitro-1-naphthyl methyl ether a dilution of 90 c.c. of glacial acetic acid was required for control of the somewhat violent reaction, and 4-amino-1-naphthyl methyl ether hydrochloride did not crystallise when the reaction mixture had cooled. The solution was made nearly alkaline with sodium carbonate and finally alkaline with aqueous ammonia, and then steam-distilled. 4-Amino-1-naphthyl methyl ether passed over as an oil which did not crystallise on cooling (cf. Woroshzow, *Chem. Zentr.*, 1911, I, 650; Hodgson and Smith, *J.*, 1935, 671); it was identified by its acetyl derivative, which crystallised from alcohol in colourless needles, m. p. 187° (Hodgson and Smith, *loc. cit.*, give m. p. 187°).

The authors thank Imperial Chemical Industries (Dyestuff) Ltd. for various gifts.