183. *Reactions of Nitrosophenols. Part I. Diazomethane as an Agent for detecting Nitrosophenolic Structure.*

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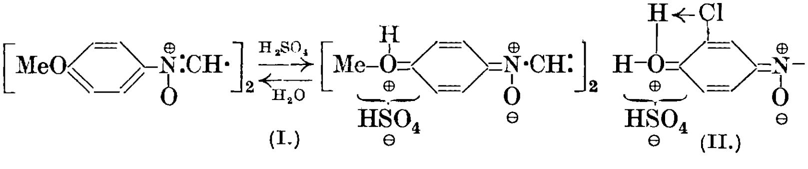
PICRIC acid has previously been used successfully as a means of discriminating between the nitroso- and the quinoneoxime forms of nitrosophenols, the former exhibiting basic (J., 1931, 1495), and the latter acidic (*ibid.*, p. 2227), characteristics. The suitability of diazomethane for the same purpose has now been investigated.

The interaction of diazomethane with nitrosobenzene (von Pechmann, *Ber.*, 1897, **30**, 2461) and with *p*-nitrosophenol (von Pechmann and Seel, *Ber.*, 1898, **31**, 296) has been re-examined. In addition to the formation of glyoxime *NN′*-di-4-hydroxyphenyl ether reported by von Pechmann and Seel, considerable methylation of the hydroxyl groups has been observed; in fact, from diazomethane and 2-chloro-4-nitrosophenol in ether, only a trace of hydroxy-compound was isolated, the main products being *glyoxime* NN′-*di*-3-*chloro*-4-*methoxyphenyl ether* and 2-chlorobenzoquinone-4-oxime methyl ether in approximately equal amounts. In methyl-alcoholic solution, however, these two nitrosophenols reacted mainly in the quinoneoxime forms, and from 2-chloro-4-nitrosophenol, in which isomerisation to the nitroso-form is retarded by chelation between hydroxyl and chlorine, a large yield of 2-chlorobenzoquinone-4-oxime methyl ether was obtained together with a small amount of glyoxime *NN′*-di-3-chloro-4-hydroxyphenyl ether, but no methoxy-derivative was isolated.

No glyoxime diphenyl ether could be isolated when 3-chlorobenzoquinone-4-oxime was treated with diazomethane, the product consisting almost entirely of 3-chlorobenzoquinone-4-oxime methyl ether. It seems, therefore, that any nitrosophenol which gives a glyoxime diphenyl ether on treatment with diazomethane must exist, at any rate in part, in the nitroso-form.

Since isomerisation takes place readily in reacting nitrosophenols, the fact that a large percentage yield of glyoxime *NN′*-di-4-hydroxy- and -4-methoxyphenyl ether is obtained from *p*-nitrosophenol indicates that this compound exists mainly in the nitroso-form, in accordance with its low melting point (compare J., 1925, **127**, 2260; 1929, 1555).

The glyoxime *NN′*-di-hydroxy- and -methoxy-phenyl ethers give brilliant colours with concentrated sulphuric acid, whereas glyoxime *NN′*-diphenyl ether itself gives a yellow colour. The methoxy-compounds are precipitated unchanged from such solutions by water, and the scheme (I) is suggested to explain the property:

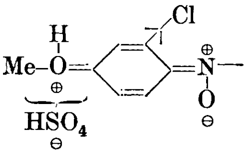


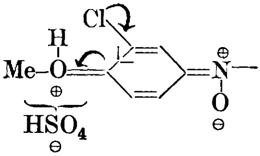
(I.) (II.)

The following colours, in the order of increasing blueness, are given by the respective substituted glyoxime *NN′*-diphenyl ethers: 3-chloro-4-hydroxy- (orange-scarlet), 4-hydroxy- (magenta), 2-chloro-4-methoxy- (red-violet), 4-methoxy- (blue-violet), 3-chloro-

4-methoxy- (blue). The marked difference in the colours given by the first and the last member of the series may be due to chelation (II) in the former ether. Chlorine in the ortho-position to the nitrogen (III) definitely exerts a hypsochromic effect, *i.e.*, its negative general (*–I–D*) effect (Allan, Oxford, Robinson, and Smith, J., 1926, 401; Ingold and Shaw, *ibid.*, p. 2918; Ingold and Vass, J., 1928, 417), whereas chlorine in the ortho-position to the oxonium oxygen (IV) produces the opposite (bathochromic) effect, thereby indicating that the electropositively charged oxygen is compelling the chlorine atom to exert its positive alternating effect (+ *T*).

(III.)





(IV.)

EXPERIMENTAL.

An ethereal solution of diazomethane was added to the nitrosophenol, dissolved or suspended in ether or methyl alcohol.

p-*Nitrosophenol.*—A vigorous reaction occurred in ether. The brownish-red precipitate formed was removed and treated with warm aqueous sodium hydroxide; the greater part dissolved, and the deep red solution on acidification yielded glyoxime *NN'*-di-4-hydroxyphenyl ether, decomp. 250° (Found : N, 10·5. Calc. : N, 10·3%). The alkali-insoluble residue of *glyoxime* NN'-*di*-4-*methoxyphenyl ether* was very sparingly soluble in methyl alcohol and crystallised in brilliant yellow, rectangular plates, m. p. 204° (decomp.) (Found : N, 9·5. $C_{16}H_{16}O_4N_2$ requires N, 9·3%). The ethereal filtrate gave benzoquinone-4-oxime methyl ether when steam-distilled.

p-*Nitrosoanisole.*—An almost theoretical yield of the above methoxyphenyl ether was obtained, m. p. and mixed m. p. 204° (decomp.) (Found : N, 9·4%).

2-*Chloro*-4-*nitrosophenol.*—The reaction was vigorous in ether, and only a very small amount of the reddish-orange precipitate was soluble in aqueous sodium hydroxide; the residue of *glyoxime* NN'-*di*-3-*chloro*-4-*methoxyphenyl ether* was very sparingly soluble in the ordinary solvents, from which it crystallised in deep yellow, rectangular plates, m. p. 223° (decomp.) (Found : N, 7·6; Cl, 19·0. $C_{16}H_{14}O_4N_2Cl_2$ requires N, 7·6; Cl, 19·2%).

Ethereal diazomethane and methyl-alcoholic 2-chloro-4-nitrosophenol gave scarcely any precipitate; after addition of benzene, the mixture was shaken with aqueous sodium hydroxide. The ether–

alcohol–benzene layer gave a large yield of 2-chlorobenzoquinone-4-oxime methyl ether on steam-distillation, and the aqueous alkaline solution afforded a small amount of *glyoxime* NN′-*di*-3-*chloro*-4-*hydroxyphenyl ether*, which crystallised from methyl alcohol in red-brown micro-needles, m. p. 175° (decomp.) (Found : N, 8·4; Cl, 20·7. $C_{14}H_{10}O_4N_2Cl_2$ requires N, 8·2; Cl, 20·8%).

2-*Chloro*-4-*nitrosoanisole.*—An almost theoretical yield of glyoxime *NN′*-di-3-chloro-4-methoxyphenyl ether was obtained.

3-*Chloro*-4-*nitrosoanisole.*—*Glyoxime* NN′-*di*-2-*chloro*-4-*methoxyphenyl ether*, obtained in almost theoretical yield, crystallised from the ordinary solvents, in which it was sparingly soluble, in long, bright yellow needles, m. p. 182° (decomp.) (Found : N, 7·8; Cl, 19·0. $C_{16}H_{14}O_4N_2Cl_2$ requires N, 7·6; Cl, 19·2%).

3-*Chloro*-4-*nitrosophenol.*—The reaction in ether gave no trace of precipitate. After extraction with aqueous sodium hydroxide, the ethereal solution afforded only a poor yield of 3-chlorobenzoquinone-4-oxime methyl ether on steam-distillation. The alkaline extract when acidified, gave a mixture, m. p. about 100°, which could not be separated into its constituents. A similar mixture, containing a little unmethylated 3-chlorobenzoquinone-4-oxime, was obtained when the reaction was carried out in methyl alcohol.

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