

NOTES.

The Absorption Spectra of Some Substituted Nitrosobenzenes. Evidence for the Mesomeric Effect.
By HERBERT H. HODGSON.

By the method previously described (Hodgson, J., 1937, 520), the absorption spectra of nitrosobenzene and the following *o*-substituted derivatives have been measured in 4×20^{-4} M-alcoholic solution :

	<i>o</i> -Ethoxy-	Nitrosobenzene.	<i>o</i> -Iodo-	<i>o</i> -Bromo.	<i>o</i> -Chloro-
Peak of band (A).....	3800	3160	2930	2900	2880
Extinction coefficient (ϵ)	1875	1750	2187	3125	3281

Relative to nitrosobenzene the shifts of the absorption bands of the *o*-halogeno-derivatives are in the order of the negative inductive ($-I$) effects of the halogens, *viz.*, $I < Br < Cl$. The relatively small displacement differences would appear to indicate in each case the existence of positive mesomeric ($+M$) effects (Baddeley, Bennett, Glasstone, and Jones, J., 1935, 1827) of the order $Cl > Br > I$, which, while opposed to the negative inductive ($-I$) effects, do not exceed them, since the resultant effect in each case is shown by a displacement of the absorption band in the direction of the shorter wave-lengths, thereby denoting a progressive tightening of the electronic structures.

In the case of *o*-ethoxynitrosobenzene there is a difference of 640 A on the positive side of the nitrosobenzene, which indicates that the feeble negative inductive ($-I$) effect of the ethoxy-group has been completely exceeded by a powerful positive effect which must be ascribed to the positive mesomeric polarisation produced by the ethoxy-group. Supporting evidence is also to be obtained from the absorption spectra of *p*-nitrobenzaldehyde-*o*- and -*p*-methoxyphenylhydrazones (Hodgson and Handley, J., 1928, 1882) and of *p*-methoxybenzaldehyde-*p*-nitrophenylhydrazone (Hodgson and Cooper, J., 1929, 231).

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Improved Methods for the Nitrosation of m-Halogenophenols and their Conversion into Benzoquinonemonoximes. By HERBERT H. HODGSON and DONALD E. NICHOLSON.

IN the nitrosation of *m*-halogenophenols (excluding *m*-fluorophenol) by the methods previously used (Hodgson and Moore, J., 1923, 123, 2499; 1925, 127, 2260; Hodgson and Kershaw, J., 1929, 1553; 1930, 967, 1969) the best yield of the nitroso-compound obtained was about 40% and a small amount of the 3-halogeno-6-nitrophenol and much diazonium salt were also produced. It has now been found that yields of 3-halogeno-4-nitrosophenol as high as 80% are obtained from *m*-chloro- and *m*-iodo-phenol by the following procedure.

Nitrosation of a m-Halogenophenol.—The phenol (2 g.), dissolved in 50% acetic acid (25 c.c.), is treated gradually below 20° with a solution of sodium nitrite (4 g.) in water (10 c.c.). When the mixture, which now contains about 30% acetic acid, is kept with occasional shaking, precipitation should commence within 30 minutes. Should the reaction be delayed, as in the case of *m*-bromophenol, the liquor is diluted with water until a faint turbidity is produced and is then filtered; precipitation should gradually ensue. The resulting greenish-yellow *m*-halogeno-*p*-nitrosophenols are obtained free from tar in the cases of the *m*-chloro- and the *m*-iodo-compound, and in yields of *ca.* 2 g.; they are sufficiently pure for immediate use. The velocity of precipitation is greatest for the iodo- and least for the bromo-compound. After removal of the nitrosophenol by filtration, the filtrate affords a volatile 3-halogeno-6-nitrophenol when steam-distilled.

The nitrosation of *m*-bromophenol under these conditions is less effective than that in dilute sulphuric acid.

Conversion of 3-Halogenophenols into 3-Halogenobenzoquinone-4-oximes.—By the following method (compare Hodgson and Walker, J., 1933, 1620. See also Schoutissen, *Rec. Trav. chim.*, 1921, 40, 753, who used a variation of this procedure) *m*-chloro-, *m*-bromo-, and *m*-iodo-phenol are almost quantitatively converted into the *m*-halogeno-*p*-benzoquinonemonoximes. The *m*-halogenophenol (2 g.), dissolved in glacial acetic acid (20 c.c.), is added below 20° to a solution of sodium nitrite (2 g.) in concentrated sulphuric acid (10 c.c.) which has previously been heated to 70°. The mixture is kept at 0° for *ca.* 10 minutes and then poured on ice; the *m*-halogeno-*p*-benzoquinoneoxime is precipitated as a slightly reddish solid, which is pure after one crystallisation (charcoal) from aqueous alcohol. Yield, *ca.* 2.0 g.

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A New Colour Reaction for Diarylamines. By E. MARSHALL MEADE.

THE amine is dissolved in a little anisole, and a solution of methylmagnesium iodide in anisole added; methane is evolved as in the ordinary Zerewitinov test for active hydrogen. When benzoyl chloride is now added, a strong red coloration is produced if a diarylamine was originally present. This test is particularly useful for following the course of *N*-substitution of diarylamines, *e.g.*, it will easily detect 1% of unchanged diphenylamine in a sample of *N*-methyl-diphenylamine.

The following substances gave the test: diphenylamine, 4'-methoxy-4-methyldiphenylamine, 4:4'-dimethoxydiphenylamine, phenyl- α -naphthylamine, *o*- and *p*-methoxyphenyl- β -naphthylamines. The following substances failed to give the test: *N*-methyldiphenylamine, *N*-methyl-, -acetyl-, and -benzoyl-4:4'-dimethoxydiphenylamines, aniline, methylaniline, dimethylaniline, benzylaniline, and *p*-anisidine.—THE COLLEGE OF TECHNOLOGY, ROTHERHAM, YORKS. [Received, September 28th, 1939.]
