

## 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  $4 \times 20^{-4}$ 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 ( $\epsilon$ ) .....	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 Å 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- $\alpha$ -naphthylamine, *o*- and *p*-methoxyphenyl- $\beta$ -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.]

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