CXIII.—*The Position of the Nitroso-group among Substituents capable of activating suitably placed Halogens, etc., in Aromatic Nuclei.*

By RAYMOND JAMES WOOD LE FÈVRE.

DURING a preliminary survey of suitable reagents for the detection and estimation of labile halogen in compounds which could not exist in an alkaline medium, experiments with a solution of silver nitrate in slightly diluted acetic acid (various halogenonitrobenzenes being used as reference substances) showed that this reagent was somewhat unreactive : under the standard conditions adopted, 1-chloro- and 1-bromo-4-nitro- and -2 : 4-dinitrobenzenes were not hydrolysed by the boiling solution even after many hours, but picryl chloride and bromide each showed appreciable formation of silver halide after 1 hour.

In view of these facts Hammick and Illingworth's observation (J., 1930, 2363) that *p*-bromonitrosobenzene produces silver bromide in a cold solution of silver nitrate in glacial acetic acid (a much more dilute silver nitrate solution than that used here—see exptl. part) can only mean that their conclusion that " the activating effect of the nitroso-group on the *ortho*- and *para*-halogen is the same as that of the nitro- and other *meta*-directing groups " must not be considered as having a quantitative implication.

Indeed, the above results suggest immediately that one 4-nitroso-group is *more than equal*, as regards conferment of lability on a 1-halogen atom, to two nitro-groups in the 2- and 4-positions respectively (Brewin and Turner, J., 1928, 334, evidently consider it equal).

In order to get more accurate information on this point equivalent quantities of *p*-bromonitrosobenzene, picryl chloride, picryl bromide, 1-chloro- and 1-bromo-2 : 4-dinitrobenzene, each dissolved in the same volume of the standard silver nitrate solution, were kept at the ordinary temperature. In the first case alone was any weighable quantity of silver halide formed, and this only after 24 hours. The second and the third compound gave a faint milkiness after 36 hours, but even after 1 month the weight of halide formed was negligible. The two last solutions have remained clear for several months.

The effect of one nitroso-group on a halogen atom *para*- to it therefore appears to outweigh even that of three nitro-groups in the 2 : 4 : 6-positions.

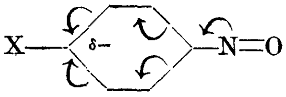
The following qualitative experiments suggest that the above results are not due merely to the reagent : (1) *p*-Nitrosodimethylaniline was readily and completely hydrolysed by boiling *N*-sodium hydroxide solution, whereas 2 : 4-dinitrodimethylaniline was, under identical conditions, barely attacked; 2 : 4 : 6-trinitrodimethylaniline (Romburgh, *Rec. trav. chim.*, 1883, **2**, 105), however, underwent rapid hydrolysis. (2) The same relative order stands for nitroso- and nitro-phenylpiperazines, since under the conditions under which 4 : 4′-dinitrosodiphenylpiperazine is hydrolysed to piperazine (Pratt and Young, *J. Amer. Chem. Soc.*, 1918, **40**, 1428) the 2 : 4 : 2′ : 4′-tetranitrodiphenyl derivative remained unaffected.

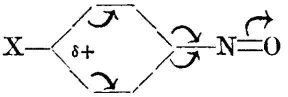
The Supposed Anomaly of the Nitroso-group.—Hammick and Illingworth (*loc. cit.*) considered the nitroso-group to behave anomalously because, although its activation of the 4-bromine atom in 4-bromonitrosobenzene was a result to be expected of a *m*-directing group, yet, as Ingold (J., 1925, **127**, 513) and the authors themselves showed, it definitely promoted *op*-replacement of chlorine, bromine, and nitroxyl.

Such apparent contradictions disappear if the mechanisms underlying both types of reaction are considered.

Robinson (*Chem. and Ind.*, 1925, **44**, 456) envisaged nitrosobenzene as containing *either* a crotenoid or a crotonoid system (I and II).

(I.)





(II.)

This is a satisfactory formulation, since in any given reaction that electronic structure can arise which best suits the reagent presented. Thus the replacement of halogen or nitroxyl is controlled by a valency distribution of type (I), whereas hydrolytic reactions, in which X becomes detached (*e.g.*, hydrolysis of *p*-nitrosodimethylaniline is specifically cited), are initiated according to formula (II).

A further point in Hammick and Illingworth's paper (*loc. cit.*) is of interest. From (1) their failure to induce bromination of nitrosobenzene in acetic acid solution, and (2) the lability of halogen in the *o*- or *p*-position to the nitroso-group, it is concluded that "when unimolecular nitrosobenzene alone is present, as in acetic acid solution, *para*-substitution is inhibited, and . . . if it were not for the fragility of the nitrosobenzene molecule, more drastic conditions would result in the production of *meta*-substituted derivatives. . . ."

In support the authors found a mean value of 107 (calc., 107) for the molecular weight of nitrosobenzene in glacial acetic acid. No comment is made on the discrepancy between this value and the molecular weights determined by Bamberger and Renauld (*Ber.*, 1897, **30**, 2278) and Bamberger and Rising (*Ber.*, 1901, **34**, 3878), who, using the same cryoscopic solvent, obtained the average value of 112—a figure which, if correct, would seriously invalidate the argument of Hammick and Illingworth.

Further, although the two extreme values, 101·2 and 106, recorded for the molecular weight of nitrosobenzene in benzene (Bamberger and Rising, *loc. cit.*) demonstrate that the dissolved nitrosobenzene is unpolymerised, it has now been shown (see exptl.) it can be satisfactorily mono*para*brominated by bromine in this solvent.

The following contrasted observations do, however, appear to present an anomaly : (1) It has been shown above that the halogen of *p*-bromonitrosobenzene is *at least as reactive*, under suitable conditions, as that of picryl bromide; (2) brief warming of *p*-bromonitrosobenzene with aniline in glacial acetic acid gives *p*-bromoazobenzene in high yield with no perceptible hydrolysis at the bromine atom; (3) *exact* repetition of the conditions, of (2), picryl bromide being used instead of bromonitrosobenzene, leads to the quantitative isolation of 2 : 4 : 6-trinitrodiphenylamine in a pure state.

EXPERIMENTAL.

Preparation of the Reagent.—A solution of 17 g. of silver nitrate in 100 c.c. of water was made up to 1 l. with glacial acetic acid. Some silver nitrate separated as white needles; the solution was therefore filtered into the storage flasks. 20 C.c. portions of this solution at 16° gave on evaporation 0·2666, 0·2665, and 0·2666 g. of silver nitrate. 1000 C.c. therefore contain 13·3 g. of silver nitrate and the solution is approximately 0·08N.

1 C.c. of N/200-hydrochloric acid immediately produced an opalescence in 10 c.c. of the reagent.

Solubility of Silver Nitrate in Glacial Acetic Acid.—When a boiling saturated solution of silver nitrate in glacial acetic acid was cooled, the salt crystallised in well-formed needles. Three 20 c.c. lots of the filtrate, evaporated to dryness at 100°, left 0·0241, 0·0226, and 0·0227 g. respectively of silver nitrate. 1000 C.c. of the saturated solution at 16° therefore contain approximately 1·13 g. of silver nitrate.

Standard Conditions employed.—(*a*) The halogenonitro-compound (0·01 g.-mol.) was dissolved in 200 c.c. of the standard silver nitrate solution. After being gently boiled for a definite time, the solution was cooled and the silver halide collected.

No silver halide was obtained from *p*-chloronitrobenzene (35 hours), 1-chloro-2 : 4-dinitrobenzene (22 hours), 1-bromo-2 : 4-dinitrobenzene (15 hours), 1-bromo-2-nitrobenzene (12 hours), and 1-bromo-4-nitrobenzene (14 hours).

Picryl chloride gave 0·1541 g. of silver chloride (corresponding to about 10% hydrolysis) after 2½ hours' boiling, and picryl bromide was observed qualitatively to behave similarly.

(*b*) In a second series of experiments the solutions were kept at the ordinary temperature. The results are described in the theoretical part of the paper.

Alkaline Hydrolysis of Substituted Phenylpiperidines.—The following qualitative observations are described, practical difficulties having made the intended quantitative comparison impossible. Picrylpiperidine readily yielded piperidine on brief boiling with 2*N*-sodium hydroxide solution, but longer heating in the case of 2- and 4-nitro-, 4-bromo-2-nitro-, 2-nitro-4-carboxy-, and 2 : 4-dinitro-phenylpiperidines failed to produce piperidine in detectable quantity or depress the m. p. of the recovered initial material.

Experiments on the nitrosation of *N*-phenylpiperidine proved unsuccessful.

Preparation of 4-*Bromonitrosobenzene.*—A solution of freshly prepared dry nitrosobenzene (5 g.) in 200 c.c. of benzene was cooled to 6°, 3·5 g. of bromine in 40 c.c. of similarly cooled benzene were added quickly, and the mixture was shaken and kept at 6—8° for 10 minutes. Scarcely any heat was evolved. The benzene solution was decanted from a reddish-black sludge and evaporated to dryness in a current of dry air. The brown oily residue, after being pressed on a porous tile, yielded about 2 g. of a cream-coloured crystalline powder. This, alone or mixed with 4-bromonitrosobenzene, melted at 86—88° to a green liquid. The identity of the product was confirmed by the method adopted by Ingold (J., 1925, **127**, 513).

Interaction of Aniline and Picryl Bromide.—The bright red solution produced when solutions of picryl bromide (1 mol.) and of aniline (2½ mols.) in warm acetic acid were mixed was kept at 90° for 1 minute and poured into water. The bright yellow precipitate, crystallised from much alcohol, gave 2 : 4 : 6-trinitrodiphenylamine, m. p. and mixed m. p. 177—178°. The aqueous filtrate gave a copious precipitate with silver nitrate–nitric acid solution.

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THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, February 5th,* 1931.]