CCCVI.—*A New Orientation Rule and the Anomaly of the Nitroso-group.*

By DALZIEL LLEWELLYN HAMMICK and WALTER S. ILLINGWORTH.

THE facts as to the orienting influence of single atoms and groups present in the benzene nucleus on further substitution can be expressed, without any theoretical implications whatever, by the following rule :

If in the benzene derivative ⬡XY, Y is in a higher group of the periodic table than X, or if, being in the same group, Y is of lower atomic weight than X, then a second atom or group of atoms that

enters the nucleus will do so in the meta-position to the group XY. In all other cases, including that in which the group XY is a single atom, a second entering atom or group goes to the ortho- and para-positions.

The effect of ionic charges on XY is given by the statement that a positive charge directs meta-, and a negative charge directs ortho- and para-.

The common meta-directing groups, $CO_2H$, CHO, CO, $NO_2$, CN, $CCl_3$, etc., are obviously covered by the first part of the rule. The meta-directing sulphonic acid group is a common example of an atom attached to the nucleus and also joined to atoms in the same group of the periodic table but of lower atomic weight. The latter part of the rule covers the ordinary cases of ortho–para-directing groups such as $CH_3$, $NH_2$, OH, $OCH_3$, etc. The correct orienting effect of the recently investigated thiocyanate and seleno-cyanate groups SCN and SeCN, which direct ortho–para, is also given (Challenger and Collins, J., 1924, **125**, 1377; Challenger and Peters, J., 1928, 1364). Application of the rule to the case where X and Y are the same, as in $-N{=}N-$ and $-C{=}C-$, again gives the correct orienting effect; the atom next to the nucleus is not in a lower group of the periodic table than the atom to which it is joined, so the effect cannot be meta-directing and hence must be ortho–para. It will be noticed that the rule thus assigns the correct ortho–para influence in the difficult case of the $-C-C-$ group in cinnamic acid.

Strict application of the rule to mixed groupings, such as $CH_2Cl$, $CHCl_2$, etc., gives the correct answer; thus nuclear substitution in benzal chloride yields ortho- and para-derivatives, as required by the CH part of the directing group, as well as meta-, due to the $CCl_2$.

The one apparent exception to the above rule that the authors have been able to discover is the well-known case of the nitroso-group, NO. On any empirical rule hitherto formulated, this group should be meta-directing. Ingold has shown, however (J., 1925, **127**, 513), and our own experiments confirm his results, that nitration and bromination of nitrosobenzene in carbon disulphide and in carbon tetrachloride give para-derivatives.

In discussing the orienting effect of the nitroso-group, it does not appear to have been generally recognised that nitrosobenzene is associated in the liquid state. Before we can be sure that the nitroso-group actually does direct ortho–para, we need information as to the molecular complexity of nitrosobenzene in carbon disulphide or carbon tetrachloride. In addition, a solvent must, if possible, be found in which nitrosobenzene is entirely unimolecular, in order that the true orienting effect of the undissociated nitroso-

group may be investigated. Such a solvent has been found in acetic acid.

*The Molecular Weight of Nitrosobenzene in Carbon Disulphide and in Acetic Acid.*—The apparent molecular weight of nitrosobenzene in carbon disulphide at the boiling point has been determined by the Landsberger–Walker method. By using carefully purified carbon disulphide (b. p. 45·9°/760 mm.) and pure naphthalene, the following data were obtained :

| | | | |
|---|---|---|---|
| Vol. of $CS_2$ (c.c.) | 12·09 | 17·65 | 25·28 |
| G. of $C_{10}H_8$ per c.c. | 0·0712 | 0·0487 | 0·0340 |
| Elevation of b. p. | 0·955° | 0·655° | 0·465° |

Elevations of boiling point plotted against concentration of nitrosobenzene in g. per c.c. of solution give a straight line passing through the origin. The slope of this line is 13·33° per unit change in concentration and hence the elevation of boiling point for 1 g.-mol. per 100 c.c. of solution is 17·59°.

Repetition of the determinations with pure nitrosobenzene as solute, the above boiling-point constant being used, yielded the following results :

| | | | |
|---|---|---|---|
| Vol. of $CS_2$ (c.c.) | 8·47 | 16·32 | 25·72 |
| G. of $C_6H_5 \cdot NO$ per c.c. | 0·1336 | 0·0693 | 0·0440 |
| Elevation | 1·995° | 1·045° | 0·645° |
| $M$. apparent | 117·6 | 116·7 | 114·9 |

Mean, 116·4 ($M$ for $C_6H_5 \cdot NO = 107$).

Taking the mean value of 116 for the apparent molecular weight of nitrosobenzene in carbon disulphide over the concentration range traversed, we can calculate the average degree of association as 16% (compare Bamberger and Rising, *Ber.*, 1901, **34**, 3877, who found 118 as the apparent molecular weight of nitrosobenzene in boiling acetone).

The apparent molecular weight of nitrosobenzene in pure acetic acid, m. p. 16·3°, was next determined cryoscopically. With pure naphthalene as solute, a cryoscopic constant was found from the following data :

Weight of acetic acid, 30·390 g.

| | | | |
|---|---|---|---|
| $C_{10}H_8$, g. | 0·1239 | 0·2505 | 0·4159 |
| Depression of f. p. | 0·127° | 0·255° | 0·396° |

These lowerings of freezing point plotted against concentration give a straight line passing through the origin, and yield the value of 40·0 for the gram-molecular lowering per 100 g. of solvent.

With nitrosobenzene as solute, the following results were obtained :

Weight of acetic acid, 45·2578 g.

| | | | | |
|---|---|---|---|---|
| $C_6H_5 \cdot NO$, g. | 0·0739 | 0·2653 | 0·4815 | 0·6003 |
| Depression of f. p. | 0·0615° | 0·2180° | 0·3980° | 0·4950° |
| $M$, apparent | 106·2 | 107·5 | 106·9 | 107·2 |

Mean, 107 (Calc. : 107).

From this it appears that nitrosobenzene in dilute solution in acetic acid is entirely unimolecular.

*Bromination of Nitrosobenzene in Carbon Disulphide and in Acetic Acid.*—Ingold's experiments on the bromination of nitrosobenzene in carbon disulphide (J., 1925, **127**, 513) were repeated ; his results were entirely confirmed, *p*-bromonitrosobenzene being obtained rapidly at low temperatures ($- 5°$). With acetic acid as solvent, however, negative results were obtained. Thus 5 g. of nitrosobenzene in 50 g. of acetic acid at $0°$ were treated with 7·5 g. of bromine (1 mol.) in 25 g. of acetic acid. After standing for 4 hours, the mixture still contained much bromine, which was removed by pouring into water and treatment with sulphur dioxide. Subsequent steam distillation resulted in the recovery of 3 g. of unchanged nitrosobenzene. The presence of anhydrous sodium acetate in the acetic acid did not produce any acceleration of reaction, and chlorine appeared to be no more reactive than bromine. After prolonged standing at room temperature (24 hours), bromine and nitrosobenzene in acetic acid containing excess of anhydrous acetate deposited a solid, m. p. $123°$, which is probably a *tribromoazoxybenzene* (Found : C, 31·5 ; H, 1·55 ; N, 6·64 ; Br, 56·8. $C_{12}H_7ON_2Br_3$ requires C, 33·0 ; H, 1·6 ; N, 6·45 ; Br, 55·2%. Compare Ingold, *loc. cit.*, who obtained small quantities of 4 : 4'-dibromoazoxybenzene).

It thus appears that the rapid production of para-substituted nitrosobenzenes occurs only when experiment shows that the nitroso-compound is present to some extent in the bimolecular form. When unimolecular nitrosobenzene alone is present, as in acetic acid solution, para-substitution is inhibited, and it is not unreasonable to suppose that, if it were not for the fragility of the nitrosobenzene molecule, more drastic conditions would result in the production of meta-substituted derivatives, in accordance with our empirical rule.

There is, however, the possibility that nitrosobenzene in acetic acid may interact with the solvent. The production of co-ordinated compounds between nitrosobenzene and acetic acid by means of the two unshared electrons on the nitrogen atom would give a positive charge to that atom and thus, in the usual way, inhibit ortho–para-substitution. Two kinds of intermolecular complex are possible, *viz.*,



(I.)            (II.)
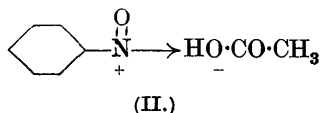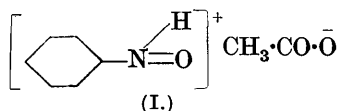
(I) would be a polar substance analogous to the anilinium salts, with a positive charge located on the nitrogen atom; (II) would be a non-polar co-ordination compound, again with a positive charge on the nitrogen.

That the salt (I) is not produced to any appreciable extent is shown by the fact that the electrical resistance of pure acetic acid is entirely unaffected by the addition of nitrosobenzene. In order to ascertain whether a complex of type (II) has any appreciable existence, we have determined solid–liquid equilibria in the system acetic acid–nitrosobenzene.

*The System Acetic Acid–Nitrosobenzene.*—Weighed quantities of pure acetic acid and nitrosobenzene were sealed in small glass bulb tubes, which were rapidly rotated in a thermostat. The equilibrium temperatures were found by slowly varying the temperature of the thermostat until the last small trace of solid just failed to dissolve. One point on the melting-point curve for acetic acid (7 mols.% $C_6H_5 \cdot NO$) was obtained in a Beckmann apparatus. The results are given below, together with the nominal heats of solution $Q$ calculated from the formula (Sidgwick and Ewbank, J., 1921, **119**, 979)

$$\log_e S/S_1 = Q(T_1 - T)/2T^2$$

$S$ being in terms of mol.% of nitrosobenzene and $T$ being the equilibrium temperature.

| $S$ | 0·0 | 7·0 | 11·06 | 20·49 | 29·16 | 39·57 | 55·31 | 58·82 | 69·42 | 100·0 |
|---|---|---|---|---|---|---|---|---|---|---|
| $T$ | 16·3° | 16·0° | 27·5° | 41·0° | 47·0° | 52·0° | 57·7° | 58·5° | 62·0° | 68·5° |
| $Q$, Cals. $\times 10^{-3}$ | | | 8·2 | 11·5 | 12·5 | 12·4 | 12·2 | 10·9 | 12·6 | |

The above solid–liquid equilibrium curve shows no indication of compound formation. The small variation of the nominal heats of solution with composition indicates that the system is of the normal type where neither combination between the components nor dissociation of either of them occurs (compare Sidgwick and Ewbank, *loc. cit.*). Hence it is legitimate to conclude that a solution of nitrosobenzene in acetic acid is unlikely to contain any appreciable quantity of complex molecules of type (II). It is, of course, obvious that to inhibit ortho–para-substitution by complex formation of either type (I) or (II), practically all the simple nitrosobenzene molecules must be removed, since ortho–para-substitution is always faster than meta-.

We have thus reached the position that where we have bimolecular nitrosobenzene we get para-substitution, and where the nitroso-compound is entirely unimolecular we find no ortho–para-substitution. We therefore conclude that the nitroso-group is essentially meta-directing.

*Reactivity of the Bromine Atom in* o-, m-, *and* p-*Bromonitroso-benzenes.*—Pure specimens of *o*- and *p*-bromonitrosobenzenes were dissolved in pure acetic acid and treated with an acetic acid solution of silver nitrate in an atmosphere of nitrogen. In each case silver bromide was slowly produced. A blank test of the acetic acid by itself gave no precipitate, and none was obtained under similar conditions with *m*-bromonitrosobenzene. Attempts to bring the

FIG. 1.
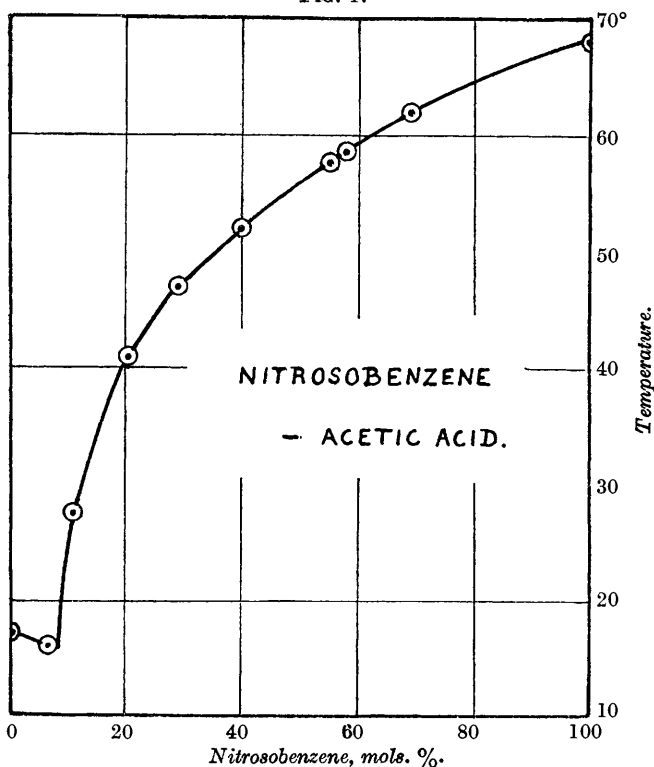


reaction with the *o*- and *p*-derivatives to completion failed owing to the fragility of the nitroso-molecule, decomposition products only being obtained on heating or prolonged standing. Neverthe-less, the experiments indicate that the activating effect of the nitroso-group on the ortho- and para-halogen is the same as that of the nitro- and other meta-directing groups, thus confirming our view that the nitroso-group is also meta-orienting. Further con-firmation may be expected from a determination of the sense of the electrical polarity of the nitroso-group; this determination is being undertaken.

On our view the bimolecular form must contain an *o,p*-directing group; the structure of this form of nitrosobenzene is now being investigated.

### *Summary.*

A new orientation rule for substitution in the benzene nucleus is given. The one apparent exception is nitrosobenzene, which is shown to give para-substituted products only when experiment demonstrates that it is present in the bimolecular form.

Experiments are recorded indicating that the reactivity of the halogen in the bromo-substituted nitrosobenzenes is in accordance with the view that the nitroso-group is meta-directing when present in the unimolecular form.

[*Note, added October 2nd*, 1930.] A further example of the correctness of our rule is contained in the paper (this vol., p. 2171) by Ainly and Challenger, who find that phenylboric acid, $C_6H_5 \cdot B(OH)_2$, gives on nitration over 70% of meta-derivative.

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