XL.—*The Structure of Organic Molecular Compounds.*

By George Macdonald Bennett and Gervase Hewitson Willis.

The formulation of organic additive compounds by means of the electronic theory of valency follows at once in many cases from Sidgwick's interpretation (J., 1923, **123**, 725) of Werner's theory. A number of other complexes, particularly those formed by the union of two different organic substances, cannot be simply represented in this manner and have been generally regarded as having their constituent molecules united by means of molecular rather than atomic forces. The union is, in fact, attributed to the action of the fields of residual valency of either molecules or groups of atoms (Pfeiffer, " Organische Molekülverbindungen," 2nd ed., 1927, p. 23; Kremann, *Ahrens Vorträge*, 1924, **27**, 58, 78). Forces such as these may indeed account for the cohesion of a liquid and for the stable association of molecules in a crystal, but where molecular compounds exist in the liquid phase their components must be held together more firmly than by residual valency. We shall assume that the union is by means of covalent linkages, a point of view which has also been adopted by Lowry (*Chem. and Ind.*, 1924, **43**, 218).

A variety of evidence is available to show that many organic molecular compounds persist in solution. Behrend (*Z. physikal. Chem.*, 1894, **15**, 183) and Brown (J., 1925, **127**, 345) have shown that the compounds of picric acid and trinitrotoluene with hydrocarbons are only partly dissociated in solution. The relationships between the composition of mixtures and their physical properties such as freezing point (Kremann and Grasser, *Monatsh.*, 1916, **37**, 761) or viscosity (Bramley, J., 1916, **109**, 10, 434, 469) point to the occurrence of complexes in the liquid. The compounds $CHCl_3,Et_2O$ and $Me_2CO,PhOH$, the presence of which in the mixed liquids was deduced from the vapour-pressure curve (Dolezalek and Schulze, *Z. physikal. Chem.*, 1913, **83**, 45; Weissenberger, Schuster, and others, *Monatsh.*, 1925, **46**, 47, 295), have been proved to exist by means of freezing-point curves (Smits and Berckmans, *Proc. K. Akad. Wetensch. Amsterdam,* 1919, **21**, 401; Schmidlin and Lang, *Ber.*, 1910, **43**, 2806).

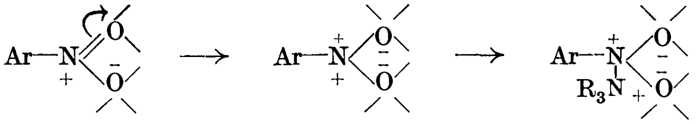
Considerable importance also attaches to the occurrence of visible colour. This has been a valuable indication of the presence of compounds in solution (Werner, *Ber.*, 1909, **42**, 4324; Pfeiffer, *Annalen*, 1924, **440**, 265). Moreover, when two organic substances together yield a solid having a colour much deeper than that of the components, this (apart from any consideration of the liquid phase) is evidence of the formation of a true molecular compound. If the union of these molecules depended merely on the more complete saturation of their stray fields of residual valency, a decrease rather than an increase of colour should result.

The molecular ratio in which organic substances combine is in most cases a simple one (1 : 1 or 2 : 1, usually the former). The occurrence of any simple stoicheiometric ratio is strong evidence against the residual valency theory of union. Yet the formation of the equimolecular compound between, for example, trinitrobenzene and quinoline (Sudborough and Beard, J., 1910, **97**, 773) has been regarded as evidence in favour of this indefinite type of attachment on the ground that direct union of a molecule of quinoline with one nitro-group must lead to a similar reaction with all three such groups and the formation of a complex with the molecular ratio 1 : 3. But this is not necessarily to be expected according to the electronic theory. The formation of a dative bond to one of the nitro-groups will introduce a new electrical dipole at the point of attachment. Further combination at a second adjacent group (to yield a 1 : 2 compound) would now be opposed by a certain extra force, since the creation of the new bond must involve the introduction of another similar dipole near the first. Thus the second and third nitro-groups may remain unattached (although they will contribute by their general polar effects to the stability of the complex formed through the first nitro-group). The case may be compared with that of the monomethiodides of diazines and 1 : 4-dithian (see Bennett and Hock, J., 1927, 2496). These considerations are of general application and account for a tendency towards simplicity of molecular ratios in complexes. Less simple ratios are, nevertheless, observed in some cases, and these are theoretically possible up to the limit set by the numbers of active groups present in the molecules which unite.

An important group of organic molecular compounds results from the union of nitro-compounds on the one hand with various amines, aromatic hydrocarbons or their derivatives on the other. The most stable and numerous of these are formed from bases : moreover the union of the nitro-compound with the base is clearly analogous to the combination of acid and base. Kremann has, in fact, called amines and hydrocarbons heteropolar with respect to nitro-compounds. This implies that the amine is the donor molecule, the nitro-compound the acceptor, and the union would appear to be through the basic nitrogen atom and the nitro-group.

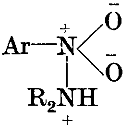
That the nitro-group itself is involved follows, as Werner showed (*loc. cit.*), from the formation of similar compounds by tetranitromethane. Pfeiffer contends (*Annalen*, 1916, **412**, 253) that the amine is attached through the aromatic nucleus, but his arguments are not convincing. The direct participation of the basic group in the union is, moreover, indicated by the coloration developed by polynitro-compounds with alcoholic ammonia (compare, for example, Kenner and Parkin, J., 1920, **117**, 852) and by the coloured compound of piperidine with trinitroanisole (Giua, Marcellino, and Curti, *Gazzetta*, 1920, **50**, 300), for no point of attachment but the basic group is conceivable in the case of ammonia or a saturated amine. Certain physical properties of the nitrobenzyldialkylamines, to be described presently, also support our view of the union through both the nitro-group and the amino-nitrogen.

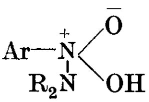
The union may be represented as occurring after a preliminary activation of the nitro-compound (I), the resulting form (II) uniting



(I.) (II.) (III.)

with a tertiary amine by accepting from it its lone pair of electrons to give the complex (III), in which each nitrogen atom carries a single positive charge and each oxygen atom a negative one. Thus the structure is to some extent stabilised by the fact that each charge has near to it an opposite charge on an adjacent atom. The corresponding complex (IV) produced from a secondary or primary amine may pass into the second form (V) by the movement of one proton.


(IV.)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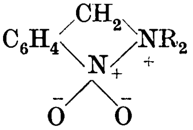

(VI.)

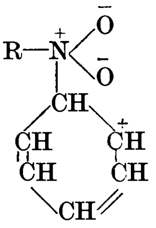
Formula (V) is identical with that recently suggested by Brewin and Turner for coloured intermediates in reactions between secondary amines and nitro-compounds (J., 1928, 336).

From this point of view it appeared to follow that the *o*-nitrobenzyldialkylamines would show intramolecular co-ordination as in (VI), and any corresponding self-co-ordination in the *m*- and *p*-isomerides would necessarily be *inter*-molecular. The *o*-isomeride should therefore have a somewhat lower boiling point than the others and differences in solubility might also arise (compare Sidgwick and Callow, J., 1924, **125**, 527). The three isomeric nitrobenzyldiethylamines do in fact show a marked difference of volatility, boiling at 175—177° (*o*-), 206—208° (*m*-) and 219—221° (*p*-) under 42 mm. pressure (Noelting and Kregczy, *Bull. Soc. chim.*, 1916, **19**, 336). We have redetermined and confirmed this difference and have also found a similar difference for the three isomeric nitrobenzyldimethylamines. The solubility curves of naphthalene in the three nitrobenzyldiethylamines and of these three (liquid) nitroamines in trimethylene glycol over a limited range are shown in Figs. 1 and 2. In each case the *m*- and *p*-isomerides have almost identical solubilities and the *o*-isomeride differs to a small but definite extent.

The similarity in type of the complexes formed by polynitro-compounds with bases and with hydrocarbons justifies the assumption that the function of the latter is analogous to that of bases. The hydrocarbon, like the base, is a donor molecule. This property appears to be characteristic of the ethylene group, as may be seen from the platinum complexes

$$[PtCl_2,NH_3,C_2H_4] \text{ and } [PtCl_3,C_2H_4]K,H_2O$$

(Jörgensen, *Z. anorg. Chem.*, 1900, **24**, 153), in which the molecule of ethylene functions as the equivalent of a molecule of ammonia in the co-ordination sphere. A single ethylene bond can thus provide one covalency, but the considerations advanced above provide an adequate explanation of the fact that the three actual or potential double bonds in the benzene nucleus also, in general, provide only one covalency. This is the case in the complex [$Ni(CN)_2,NH_3,C_6H_6$] and others of the same type (Hofmann and Küspert, *Z. anorg. Chem.*, 1897, **15**, 203) and it also seems to be the rule with the compounds of trinitrobenzene. With substances containing several separate aromatic nuclei (not fused together), each tends to attach one molecule of trinitrobenzene to itself (Sudborough, J., 1916, **109**, 1341).



(VII.)

The union of benzene with a nitro-compound may be represented as in (VII), one ethylene bond having reacted in the polarised form $\overset{|\,-}{—CH}—\overset{+}{CH}—$. The negative charges on the oxygen atoms may help to stabilise the positive charge on the nuclear carbon atom, the structure being of the betaine type. This positively charged tervalent carbon atom is partly responsible for the deep colour developed, the case being similar to that of the triarylmethyl ion and the metal ketyls.

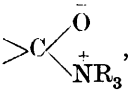
The well-known fact that nitro-compounds containing several nitro-groups, such as trinitrobenzene and trinitrotoluene, yield the most stable additive compounds with hydrocarbons and bases is to be attributed to the influence of other such groups in assisting the one active group to function. Any group which attracts electrons (any " electron sink ") should be able to contribute to the stability of such complexes, so that carbomethoxy- or sulphonyl chloride groups might be substituted for one or two of the nitro-groups of the complex. Complexes of this kind derived from mononitro-compounds have been hitherto unknown, but we find that, in agreement with the considerations advanced above, methyl 5-nitro*iso*phthalate forms an orange crystalline *compound* with α-naphthylamine. Several mononitro- and dinitro-sulphonyl chlorides have, moreover, been described in the literature as crystallising with (usually one molecular proportion of) benzene, toluene, or xylene and must be regarded as instances of the complex formation now under discussion—namely, nitrobenzene-3 : 5-disulphonyl chloride (Heinzelmann, *Annalen*, 1877, **188**, 164), 4-nitronaphthalene-2 : 6- and -2 : 7-disulphonyl chlorides (Beilstein, "Organische Chemie," 4th edn, vol. XI, pp. 216, 218), 4 : 5-dinitronaphthalene-2 : 7-disulphonyl chloride (*op. cit.*, p. 218), and 4 : 5-dinitronaphthalene-2-sulphonyl chloride (*op. cit.*, p. 189). We have subjected the first of these to a closer investigation and have obtained pale yellow *compounds* of it with toluene and mesitylene and bright yellow *compounds* with naphthalene and anisole. It also combines with bases of the quinoline series.

The molecular compounds of picric acid with bases or hydrocarbons fall into two classes. The picrates of relatively strong bases have a characteristic bright yellow colour and are formulated by Pfeiffer as $(NO_2)_3C_6H_2{\cdot}OH \ldots NC_nH_m$ (*op. cit.*, p. 343). As this colour is also shown by quaternary ammonium and trialkylsulphonium picrates, it must be attributed to the picrate ion, and the complexes should be written $[BH]^+ [C_6H_2(NO_2)_3{\cdot}O]^-$. Complexes of the second class are formed by picric acid with weak bases or hydrocarbons and usually have a deeper colour. In these the union is presumably through one nitro-group of the picric acid in the way already discussed, but in the case of bases an electrovalent union is conceivable with the picrate ion in an isomeric form,

$$O{:}C_6H_2(NO_2)_2{:}NO_2^-.$$

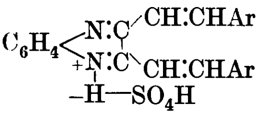
Some such alternative modes of attachment must be involved in the "complex isomerism" of the yellow and red forms of *o*-bromoaniline picrate (Hertel, *Annalen*, 1927, **451**, 179) and in the contrast between the bright yellow picrate of 2 : 4-dichloroaniline and the deep red *compound* of *s*-trichloroaniline and picric acid which we have isolated. This is evidently a closely connected, if not an identical phenomenon with that of the existence of the red and yellow thallium picrates and salts of the nitrophenols.

The large group of complexes formed by the union of benzoquinone or its substituted derivatives with aromatic hydrocarbons, amines, and phenols has developed from the study of the smaller group known as the quinhydrones. The function of the amines and hydrocarbons being necessarily to donate, it follows that the quinone is the acceptor-component in these molecular compounds. This is in agreement with the fact (Pfeiffer, *op. cit.*, pp. 290 *et seq.*) that introduction of halogen into the nucleus of the quinone enhances its power of forming such compounds and the depth of colour of the products. The polar effect of the halogen would facilitate the acceptance of electrons but would oppose their donation (the chloroanilines are weaker bases than aniline). That quinone does not readily act as a donor is, moreover, shown by the fact that it does not combine with picric acid. In compounds of quinones with bases, neither the halogen atoms nor hydrogen attached to nitrogen is essential to the existence of a complex, for we have isolated coloured compounds of benzoquinone itself with the tertiary amines *pp'*-tetramethyldiaminodiphenylmethane and *pp'*-tetramethyldiaminodiphenylcarbinol. The molecular ratio in these complexes (2 of base : 1 of quinone) indicates that only one of the two dimethylamino-groups in the molecule of the base is functioning, the case being analogous to that of the polynitro-compounds discussed above.

This property of quinones was attributed by Kurt Meyer (*Ber.*, 1909, **42**, 1149; 1910, **43**, 157) to the carbonyl group and particularly to the oxygen atom of that group. The same view is adopted by Pfeiffer. It is, however, impossible to suppose that this oxygen atom should accept electrons : the carbonyl group can in fact only do so if it becomes activated to the form $>\overset{+}{C}-\overset{-}{O}$ in which free positive affinity is developed on the carbon atom. Union with a tertiary base should therefore yield the complex  $>C\begin{matrix}\diagup\overset{-}{O}\\ \diagdown\overset{+}{N}R_3\end{matrix}$, and a complex with an aromatic hydrocarbon may be similarly represented by a formula analogous to that (VII) of the nitro-compound complex. A consideration of the formulæ for quinhydrones to which this conception points is reserved for a future communication.

The halochromic properties of the quinones displayed in presence of concentrated sulphuric acid are influenced by substituents in exactly the opposite sense. The intensity and depth of colour produced are decreased by those substituents which increase the stability and the depth of colour of the quinone complexes referred to above (Pfeiffer, *op. cit.*, p. 286), and conversely with groups of opposite general polar character. This contrast is to be expected, for the halochromic effects are to be attributed to the molecular compounds of the quinone and sulphuric acid formed by donation from the ketonic oxygen atom to the hydrogen of the acid which becomes doubly co-ordinated : $>C=\underset{+}{O}-\underset{-}{H}-SO_4H$. The function of the quinone is thus the reverse of that which it performs when uniting with an aromatic molecule and the polar influences are consequently also in opposite directions.

The variations in depth of colour of the complexes and also of the halochromic effects, not only in the instance just referred to but also among substituted aromatic ketones and quinoline bases (Pfeiffer, *op. cit.*, pp. 66—85, 191), are throughout in the directions to be expected from the nature of the substituent groups if Pfeiffer's conception of the origin of the colour is accepted. The colour is in fact connected with the positive unsaturation developed on the carbon atom doubly bound in these substances to oxygen or nitrogen, as a result of the co-ordination of the oxygen or nitrogen atom with the acid present. As an illustration we may refer to the halochromic effects, which we now record, of a series of styrylquinoxalines



recently prepared (J., 1928, 1960). The coloured complex involved is of the annexed type. The unsubstituted substance (Ar = Ph) gives a deep reddish-purple colour in sulphuric acid which disappears on dilution. The colour with the nitrostyryl bases ($Ar = C_6H_4\cdot NO_2$) is less deep, that with methoxystyryl derivatives ($Ar = C_6H_4\cdot OMe$) deeper than with the parent substance. This bathochromic effect of the methoxy-group and the opposed hypsochromic effect of the nitro-group are the result of their respective polar effects, which favour or hinder, respectively, the essential co-ordination of the nitrogen atom with the acid. Moreover, the observations recorded show clearly that these two groups each have an increased effect when in the *o*- or *p*-position in the phenyl group as compared with that exercised in the *m*-position. This "alternating effect" is as usual satisfactorily explained by the superposition of the inductive and tautomeric electronic effects in the *o*- and *p*-positions but not in the *m*-position.

Finally, reference must be made to the class of organic complexes in which the separate molecules are united through a halogen atom. These are usually addition compounds of ether or an amine with various halogen compounds, particularly chloroform and iodoform. Examples of this type are the relatively stable ether–chloroform complex $CHCl_3,Et_2O$ (Smits and Berckmans, *loc. cit.*; compare also Wyatt, *Trans. Faraday Soc.*, 1929, **25**, 48), the quinoline–iodoform compound $CHI_3,3C_9H_7N$, which has long been known (Rhoussopoulos, *Ber.*, 1883, **16**, 202), and chloroform or chloral addition compounds of bases such as toluquinaldine, berberine, quinine, phenylacridine, and colchicine. These compounds must be held together by a dative bond from the nitrogen (or oxygen) atom to a halogen atom. The latter becomes 2-covalent as happens in a variety of other cases, the tendency to do this increasing from chlorine to iodine (Sidgwick, "The Electronic Theory of Valency," pp. 291—293). The numerous addition compounds of organic ammonium, sulphonium, arsonium, and stibonium iodides with one molecular proportion of iodoform (Steinkopf and others, *Ber.*, 1921, **54**, 2969; *J. pr. Chem.*, 1925, **109**, 230) may be included in this class of complex and regarded as analogous to potassium tri-iodide, KI_3, having the structure $[R_nM]^+(I\text{-}\overset{\diagdown\diagup}{\underset{|}{I}}\text{-}CHI_2)^-$. The simple complexes of amines with halogen compounds are of considerable theoretical importance, as there can be little doubt that the first step in the union of an amine or sulphide with an alkyl halide is the formation of compounds of this kind, which are subsequently transformed into the ammonium or sulphonium halide. This mechanism of reaction accounts for the fact that alkyl iodides react in such cases faster than the chlorides.

EXPERIMENTAL.

Preparation and Examination of the Nitrobenzyldiethyl- and dimethyl-amines.—The *o*-, *m*-, and *p*-nitrobenzyldiethylamines were prepared by the action of an excess of diethylamine on the respective nitrobenzyl chlorides (yield, 70—85%). The products were yellow oils (the *o*-isomeride having a more intense colour than the others), which were redistilled twice under comparable conditions in the same apparatus. The *o*-nitrobenzyldiethylamine had b. p. 144°/13 mm. (picrate, m. p. 117°). The *p*-isomeride had b. p. 160°/13 mm. (picrate, m. p. 131°). The *m*-isomeride had b. p. 158°/13 mm. and gave a picrate of m. p. 151° (Found : N, 16·2. Calc. : N, 16·0%). Noelting and Kregczy give this m. p. as 161°.

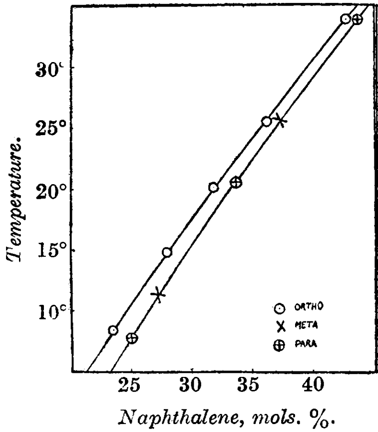
The three nitrobenzyldimethylamines were prepared from the respective nitrobenzyl chlorides in each case by two methods : (*a*) as described by Goss, Ingold, and Wilson (J., 1926, 2458), hexamethylenetetramine being used (yield, 50—60%), and (*b*) by means of dimethylamine hydrochloride and alkali in alcoholic solution as for the diethyl bases (yield, 60%). The substances obtained by the two methods were identical. They were yellow oils (the *o*-isomeride having a more intense colour than the others), and were redistilled twice under comparable conditions in the same apparatus. o-*Nitrobenzyldimethylamine* (Found : N, 16·1. $C_9H_{12}O_2N_2$ requires N, 15·6%) yielded a *hydrochloride*, colourless crystals, m. p. 215°, readily soluble in water (Found : Cl, 16·4. $C_9H_{12}O_2N_2$,HCl requires Cl, 16·4%), and a *picrate*, readily soluble in boiling ethyl alcohol, from which it crystallised in small yellow plates, m. p. 143° (Found : N, 17·4. $C_{15}H_{15}O_9N_5$ requires N, 17·1%). The *m*-isomeride yielded a *picrate*, bright yellow, microscopic crystals, m. p. 217°, sparingly soluble in boiling ethyl alcohol (Found: N, 17·5%). The *p*-isomeride gave a *picrate* crystallising in bright yellow prisms, m. p. 149°, sparingly soluble in hot ethyl alcohol (Found : N, 17·4%).

These six substances were also examined by the method of Smith and Menzies (*J. Amer. Chem. Soc.*, 1910, **32**, 1412) in order to obtain a more accurate comparison of their vapour pressures or boiling points. Unfortunately, however, the compounds showed signs of slow decomposition at the temperatures used, so these observations are less precise than was desired. They serve, however, to confirm the definite difference in boiling point. The figures are in the following table :

	B. p. observed in distillation.	B. p. by Smith and Menzies' method.
Nitrobenzyldimethylamines :		
o	133°/16 mm.	116—117°/11 mm.
m	144°/16 mm.	130—132°/10 mm.
p	146°/16 mm.	131—133°/10 mm.
Nitrobenzyldiethylamines :		
o	144°/13 mm.	124—127°/10 mm.
m	158°/13 mm.	139—142°/10 mm.
p	160°/13 mm.	146—148°/10 mm.

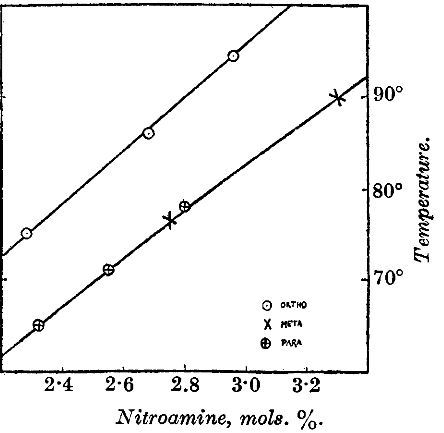
Measurements of Solubility with the Nitrobenzyldiethylamines.—The method used for the determination of the solubility of naphthalene was that of Ward (*J. Physical Chem.*, 1926, **30**, 1316). The naphthalene was carefully purified, and melted at 80·05—80·07°. The thermometer was graduated in 0·1° and had been recently standardised. The results are given in Table I and plotted in Fig. 1.

FIG. 1.



Solubilities of naphthalene in isomeric nitrobenzyldiethylamines.

FIG. 2.



Solubilities of isomeric (liquid) nitrobenzyldiethylamines in trimethylene glycol.

The determinations of solubility of the amines in trimethylene glycol were of necessity less precise. The critical solution temperatures of the mixtures could not be determined with greater accuracy than 0·5—1°. The range of observations was limited by the small solubility of the amine in the glycol and by the fact that signs of decomposition appeared when the mixtures were heated for long above 100°. The glycol was repeatedly fractionated, and distilled constantly at 214° (uncorr.). The observations are given in Table II and plotted in Fig. 2.

Table I.

Solubilities of Naphthalene in Isomeric Nitrobenzyldiethylamines.

p-Isomeride :						
Naphthalene, mols. % ...	24·97	33·58	43·56	52·29		
Temperature	7·7°	20·5°	33·9°	43·5°		
m-Isomeride :						
Naphthalene, mols. % ...	27·32	37·19	46·85			
Temperature	11·3°	25·7°	37·5°			
o-Isomeride :						
Naphthalene, mols. % ...	23·54	27·97	31·86	36·23	42·76	50·13
Temperature	8·4°	14·9°	20·1°	25·5°	33·9°	42·3°

Table II.

Solubilities of Isomeric Nitrobenzyldiethylamines in Trimethylene Glycol.

p-Isomeride :	Nitroamine, mols. %	2·32	2·55	2·80
	Temperature	65°	71°	78°
m-Isomeride :	Nitroamine, mols. %	2·75	3·30	
	Temperature	76·5°	90°	
o-Isomeride :	Nitroamine, mols. %	2·28	2·68	2·96
	Temperature	75°	86°	94·5°

*Addition Compound of Methyl 5-Nitro*iso*phthalate.*—The colourless ester is dissolved in a warm solution of α-naphthylamine in light petroleum, saturated in the cold; the molecular *compound*, $C_6H_3(NO_2)(CO_2Me)_2,C_{10}H_7{\cdot}NH_2$, separates, on cooling, in orange crystals, m. p. 82° (Found : N, 7·6. $C_{20}H_{18}O_6N_2$ requires N, 7·3%).

Addition Compounds of 5-Nitrobenzene-1 : 3-disulphonyl Chloride.—The required nitrodisulphonic acid was obtained by heating benzene with oleum (60% SO_3; 2 mols.) at 210—230° for 4 hours, cooling, adding an excess (50—100 c.c.) of fuming nitric acid, and boiling under reflux for 8 hours. The crystalline acid deposited from the cold solution (yield, 50%) was converted, by warming with an excess of phosphorus pentachloride, into the disulphonyl chloride.

The nitrobenzenedisulphonyl chloride is obtained in almost colourless crystals, m. p. 97—98°, from carbon tetrachloride (Found : Cl, 21·85. Calc. : Cl, 22·2%). The large yellow crystals from toluene are a compound with one molecule of the latter (Found : Cl, 17·7. Calc. : Cl, 17·3%). These crystals effloresce rapidly on keeping. From mesitylene, lemon-yellow prisms, m. p. 68—70°, of a *compound* with one molecular proportion of the hydrocarbon are obtained (Found : Cl, 16·4. $C_{15}H_{15}O_6NCl_2S_2$ requires Cl, 16·1%). They effloresce on keeping. From anisole there are deposited bright yellow prisms of the *compound* (mol. ratio 1 : 1) which melts indefinitely at 55—60° (Found : Cl, 16·3. $C_{13}H_{11}O_7NCl_2S_2$ requires Cl, 16·6%). The crystals become opaque on keeping. The *compound* with naphthalene (mol. ratio 1 : 1) is obtained in tufts of bright yellow needles, m. p. 102—103°, by crystallising the components together from carbon tetrachloride (Found : Cl, 15·7. $C_{16}H_{11}O_6NCl_2S_2$ requires Cl, 15·8%).

The acid chloride dissolves with considerable evolution of heat in pure dry quinoline to form dark-coloured viscous solutions. A similar behaviour is shown with other tertiary bases, but no analytically pure compound has yet been separated.

Addition Compounds of Benzoquinone with Two Bases.—Absolute ethyl alcohol, saturated with benzoquinone and *pp'*-tetramethyldiaminodiphenylcarbinol at laboratory temperature and filtered, deposited, on keeping, a *compound*, $C_6H_4O_2,2C_{17}H_{22}ON_2$, in large, intensely dark green prisms, m. p. 169—170° (Found : N, 8·7. $C_{40}H_{48}O_4N_4$ requires N, 8·6%).

Xylene, saturated with benzoquinone and *pp'*-tetramethyldiaminodiphenylmethane, yielded in similar manner, after 1 week, a *compound*, $C_6H_4O_2,2C_{17}H_{22}N_2$, in pale purple prisms, m. p. 71° (Found : N, 9·0. $C_{40}H_{48}O_2N_4$ requires N, 9·1%).

Picrate of s-*Trichloroaniline.*—This substance was obtained from its components in ethyl alcohol or benzene–light petroleum solution and crystallised in long, deep red needles, m. p. 80—83° (Found: picric acid, 53·4. Mol. ratio 1 : 1 requires picric acid, 53·8%).

Preparation of 3-*Styryl*-2-*methylquinoxaline.*—Although attempts to isolate this substance had previously been unsuccessful (Bennett and Willis, J., 1928, 1968), we subsequently obtained it in good yield as follows : 2 : 3-Dimethylquinoxaline is heated, with seven times its weight of a mixture of equal volumes of benzaldehyde and benzyl alcohol or nitrobenzene, at 180° for ½ hour. The chief product is 3-*styryl*-2-*methylquinoxaline*, which is isolated by removing other substances in a current of steam. It crystallises in clusters of pale yellow bipyramids, m. p. 137° (Found : N, 11·7. $C_{17}H_{14}N_2$ requires N, 11·3%). It dissolves in concentrated sulphuric acid with an intense reddish-purple colour, which fades to an orange-yellow on dilution with water.

Comparative Colorations of Styrylquinoxalines with Sulphuric Acid.—The method used by Stobbe and Haertel (*Annalen*, 1909, **370**, 99) in observing the halochromic effects of ketones was adopted, except that a greater dilution of the substance was necessary owing to the greater intensity of the colours developed with these styrylquinoxalines. Actually, 0·5 c.c. of concentrated sulphuric acid was added to a solution of 0·00002 mol. of the quinoxaline derivative in methyl acetate (5 c.c.). The colour produced is recorded in column 3 of Table III, and the figures in column 4 are the comparative volumes of water required to discharge this colour to a permanent pale yellow or orange tint.

TABLE III.

Base.	Colour in H_2SO_4.	Colour with H_2SO_4 in methyl acetate.	"Basicity."
Styrylmethyl-quinoxaline	Reddish-purple	—	—
Distyryl-	Reddish-purple	Orange-red	1·0
Di(*p*-nitrostyryl)-	Orange-red	Brownish-orange	—
Di(*m*-nitrostyryl)-	Scarlet	Orange	—
Di(*o*-nitrostyryl)-	Orange-red	Lemon-yellow	—
m-Nitrostyrylmethyl-	Orange-red	Yellow	—
2 : 4-Dinitrostyrylmethyl-	Yellow-orange	—	—
2 : 4 : 6-Trinitrostyrylmethyl-	Yellow	—	—
Di(*o*-iodostyryl)-	Reddish-purple	Orange	0·5
Di(*o*-chlorostyryl)-	Reddish-purple	Reddish-orange	0·9
Di(*m*-chlorostyryl)-	Reddish-purple	Orange	0·5
Di(*p*-chlorostyryl)-	Reddish-violet	Orange-red	1·1
o-Methoxystyrylmethyl-	Magenta	Rose-red	2·5
m-Methoxystyrylmethyl-	Orange-red	Orange-red	1·4
p-Methoxystyrylmethyl-	Violet	Intense violet	4·3
Di(*p*-methoxystyryl)-	Prussian-blue	—	—
Di(3 : 4-dimethoxystyryl)-	Pale blue	—	—
Methylenedioxystyrylmethyl-	Prussian-blue	Purple-blue	4·7
Di(methylenedioxystyryl)-	Blue-green	Purple-blue	4·9
Di(β-furylvinyl)-	Mulberry	Mulberry	3·6
2 : 3-Distyryl-6-methyl-	Reddish-purple	—	—
Di(*m*-nitrostyryl)-6-methyl-	Scarlet	—	—
Di(2 : 4-dinitrostyryl)-6-methyl-	Orange	—	—
2-(*p*-Methoxystyryl)-3 : 6-dimethyl-	Violet	—	—
Di(methylenedioxystyryl)-6-methyl-	Prussian-blue	—	—
o-Nitrostyryl-	Orange-red	—	—
m-Nitrostyryl-	Scarlet	—	—
p-Nitrostyryl-	Orange-red	—	—
2 : 4-Dinitrostyryl-	Orange-yellow	—	—

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