397. *Amphoteric Aromatic Substitution. Part I. Reactions of Sodium Benzenediazoate and Nitrosoacetanilide.*

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It is now well established (a) that an aromatic nucleus can display both anionoid and kationoid reactivity, and (b) that the influence of any group R on the reactivity of the nucleus in $R{\cdot}C_6H_5$ towards substituting agents is, in general, most pronounced at the ortho- and para-positions. In substitution by a kationoid reagent (*e.g.*, HNO_3) this is true whether R is a *so-called* ortho-para-directive * group or a *so-called* meta-directive group, in the former case the effect at the ortho- and para-positions being one of increased reactivity, and in the latter case one of decreased reactivity. In substitution by an anionoid reagent the effect is reversed, a *so-called* meta-directive group, such as NO_2, now causing an enhanced reactivity at the ortho- and para-positions (Lapworth, J., 1901, **79**, 1265; 1922, **121**, 416; *Mem. Manchester Phil. Soc.*, 1920, **64**, No. 3; 1925, **69**, xviii; *Nature*, 1925, **115**, 625; Kermack and Robinson, J., 1922, **121**, 427; Allan, Oxford, Robinson, and Smith, J., 1926, 401; Bradley and Robinson, J., 1932, 1254; Robinson, " Outline of an Electrochemical Theory of the Course of Organic Reactions," Institute of Chemistry, London, 1932; Ingold, *Rec. trav. chim.*, 1929, **48**, 797; *Ann. Reports*, 1928, 137; 1929, 132; 1930, 130; 1931, 115; etc.). Certain reactions, however, give rise to ortho-para-substitution *irrespective of the nature of the so-called directing group* R, but no attention appears to have been paid to this type of substitution in any of the recent surveys of the problem of aromatic substitution.

Kühling (*Ber.*, 1895, **28**, 41, 523; 1896, **29**, 165) studied the reaction between dry sodium aryldiazoates and an aromatic compound in the presence of acetyl chloride or acetic acid. From the sodium salt of diazotised *p*-nitroaniline and benzene he obtained 4-nitrodiphenyl, and with toluene 4-nitro-2'-methyldiphenyl was formed (cf. Kliegl and Huber, *Ber.*, 1920, **53**, 1646). Using nitrobenzene in place of benzene, he obtained 4 : 4'- and 4 : 2'-dinitro-

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* The terms ortho-para-directive and meta-directive signify, as usual, direction to substitution by kationoid reagents.

diphenyls. Bamberger (*Ber.*, 1895, **28**, 403) also utilised the above reaction with slight modifications, and later (*ibid.*, 1897, **30**, 366) he showed that nitrosoacetanilide would react with aromatic compounds to give biaryl compounds with the liberation of nitrogen, thus :

$$\mathrm{Ph{\cdot}N(NO){\cdot}CO{\cdot}CH_3 + C_6H_6 \longrightarrow Ph{\cdot}Ph + CH_3{\cdot}CO_2H + N_2}$$

He does not appear, however, to have carried out the reaction with an aromatic compound containing a meta-directing group, but a close correspondence with the reactions of the diazoates would be expected, especially in view of the fact that both v. Pechmann and Frobenius (*Ber.*, 1894, **27**, 651) and Hantzsch and Wechsler (*Annalen*, 1902, **325**, 226) have shown that nitrosoacetanilide is probably tautomeric with benzene *iso*(*anti*)-diazoacetate, $\mathrm{Ph{\cdot}N(NO){\cdot}CO{\cdot}CH_3 \rightleftharpoons Ph{\cdot}N{:}N{\cdot}O{\cdot}CO{\cdot}CH_3}$. This correspondence is now confirmed, since, when nitrosoacetanilide was allowed to react in turn with (a) toluene, (b) chlorobenzene, (c) nitrobenzene, and (d) benzaldehyde, 4-methyldiphenyl, 4-chlorodiphenyl, 4-nitrodiphenyl, and diphenyl-4-aldehyde respectively were isolated. Further examples of the utilisation of this reaction are also now given and in every instance substitution occurs at the ortho- and/or para-positions with respect to the group already present.

Gomberg and his co-workers (*J. Amer. Chem. Soc.*, 1924, **46**, 2339; 1926, **48**, 1372) also have developed a method for the preparation of biaryl compounds, which affords further examples of this type of invariable ortho-para-aromatic substitution. Further examples of the application of their reaction for synthetic purposes have already been reported (J., 1932, 1888, 2245, 2636) and additional examples are included in the present communication.

In the reactions studied by Gomberg, two methods of procedure are possible. Either a solution of a diazonium salt is run into a mixture of aqueous alkali and an aromatic compound, in which case an excess of alkali is present throughout the reaction; or aqueous alkali is run into a mixture of the diazonium salt and the aromatic compound, in which case the bulk of the reaction probably takes place in a neutral medium. Gomberg and his workers found that such bases as aniline and the toluidines react better in the alkaline medium, whereas for nitro- and chloro-anilines the neutral reaction is the better (cf. Jolles and Camiglieri, *Gazzetta*, 1932, **62**, 720). It therefore became of interest to carry out reactions by both methods on toluene, *m*-xylene, chlorobenzene, etc., and to compare them with similar reactions on nitrobenzene, ethyl benzoate, etc., since the former reactants normally demand a kationoid and the latter an anionoid reagent in order to give substitution at the ortho- and para-positions. A series of experiments was carried out with benzenediazonium chloride, both in alkaline and in neutral solution, successively with benzene, toluene, *m*-xylene, chlorobenzene, nitrobenzene, and ethyl benzoate. In each case the yield of biaryl compound was practically the same whether the reaction was carried out in alkaline or in neutral solution. It was thus apparent that the properties of the substituting agent were not appreciably affected by a change in the reaction medium from alkaline to neutral.

A further point of interest which now arises is whether such substitution at the ortho- and para-positions with regard to (say) a methyl group proceeds with greater or less readiness than that at the ortho- and para-positions with respect to a nitro-group. Sodium benzenediazoate was therefore allowed to react with an equimolecular mixture of toluene and nitrobenzene, both in excess, and the yield of mixed isomeric nitrodiphenyls was about four times as great as the yield of isomeric methyldiphenyls. The same result was obtained whether the reaction was carried out in an alkaline or a neutral medium. Secondly, sodium benzenediazoate was allowed to react with *o*-nitrotoluene and the only isolable product was 4-nitro-3-methyldiphenyl. The same product was obtained from the action of nitrosoacetanilide on *o*-nitrotoluene. No 3-nitro-4-methyldiphenyl could be detected in the product in either case. From these results it may be concluded that, in the substitution reactions under consideration, reaction at the ortho- and para-positions with respect to the nitro-group proceeds more rapidly than that at the ortho- and para-positions with respect to the methyl group.

The above results clearly substantiate the fact that by means of these reactions it is possible to introduce a phenyl group into an aromatic nucleus $C_6H_5{\cdot}R$, the group *invariably* entering at the para- and/or ortho-positions with respect to R. In order to fulfil these conditions it would appear that the substituting agent must be amphoteric in type, being capable of functioning alternatively as if it were a kationoid or an anionoid reagent as occasion demands. It is therefore significant to observe that the entering group in all these reactions is a phenyl or substituted phenyl group, which is well known to be capable of acting both as an electron source and as an electron sink (cf. Ingold, *Ann. Reports*, 1928, **25**, 121; Ingold and Patel, *J. Indian Chem. Soc.*, 1930, **7**, 95; etc.). It is highly probable that the reactions of the diazoates and of the nitrosoacylarylamines proceed by a similar mechanism and the results obtained are explained most readily by postulating a mechanism involving the formation and transient existence of free phenyl radicals, the free phenyl radical being capable of acting as a potential donor or acceptor of electrons, in virtue of which reaction will always ensue at the ortho- and/or para-positions to all directing groups.

The suggestion of the decomposition of aliphatic diazo-compounds into free radicals is, of course, not new, but the authors are not aware of any previous implication that the reactions of the aromatic diazonium compounds and cognate substances proceed in this manner. In the decomposition reactions of the diazonium compounds, the view is held by Hantzsch and others that the reaction measured by observing the rate of evolution of nitrogen is the decomposition of an addition compound formed between the diazonium salt and the compound with which it reacts (reaction *b*). Reactions (*a*) and (*c*) are regarded as rapid.

$$(a)\ \mathrm{PhN_2Cl + RH \longrightarrow PhN_2Cl,RH}$$
$$(b)\ \mathrm{PhN_2Cl,RH \longrightarrow PhN_2R + HCl}$$
$$(c)\ \mathrm{PhN_2R \longrightarrow PhR + N_2}$$

According to this mechanism the rate-determining stage would obviously be dependent on the nature of R. In 1926, however, Pray (*J. Physical Chem.*, 1926, **30**, 1417, 1477) studied the rate of decomposition of benzenediazonium salts in water and in a series of aliphatic alcohols and acids. He found that for a series of aliphatic alcohols the observed reaction velocities, as measured by the rate of evolution of nitrogen, were all of the same order and in the case of the lower members of the series were practically identical, *i.e.*, the measured reaction was independent of the nature of R. Similar results were obtained with a series of aliphatic acids, though these constants were somewhat smaller than those observed in the alcohol series. In view of these results Pray claimed that Hantzsch's mechanism was no longer tenable and concluded that no theory could be put forward which would explain satisfactorily all the then known facts. It appears, however, that a mechanism involving the formation of a free aryl radical would satisfy all the requirements of the results of both Pray and Hantzsch. The reaction velocity measured by the rate of evolution of nitrogen would then be the rate of formation of free aryl radicals, which would be a true unimolecular reaction, independent or practically independent of the second component, which merely acts as a medium for the decomposition. Other observations also lend support to this view. For example, although benzenediazonium chloride and methyl alcohol give mainly anisole, while with ethyl alcohol a considerable portion of the product consists of benzene (a manifestation of the amphoteric character of the phenyl radical), yet the rate of evolution of nitrogen is the same in both cases. Further, the diazonium salts, alkali diazoates and nitrosoacylarylamines are all capable of spontaneous decomposition, the presence of a second reacting component being unnecessary. They thus resemble thermal decompositions, differing from them only in that the temperature required to effect the process is somewhat lower, and it is now well known that many thermal decompositions result initially in the formation of free radicals, which subsequently undergo reaction either with themselves, with unchanged reactant, or with any extraneous molecules which may be present.

In order to gain further information on the mechanism underlying these reactions determinations were made of the velocity of reaction of nitrosoacetanilide with benzene and a series of its derivatives, as measured by the rate of evolution of nitrogen. These reactions take place in homogeneous solution and proceed at a conveniently measurable speed at or about room temperature (see experimental part). If the free-radical mechanism is valid, then unimolecular velocity constants should be obtained, which would vary but little from case to case, since the reaction with the second component (solvent) would be a secondary one, involving one of the products—the free phenyl radical—of the primary unimolecular rate-determining reaction. Good unimolecular velocity constants were in fact obtainable for the greater part of the reactions, and the constants were all of the same order. The highest values were given with anisole, mesitylene, and nitrobenzene and were about one and a half times as great as that of the lowest, given by toluene (see Figs. 1 and 2). The rate of evolution of nitrogen in carbon tetrachloride solution was also of the same order, being practically identical with the rate in chlorobenzene solution. In the decomposition of nitrosoacetanilide in glacial acetic acid solution, a smaller constant was obtained. These results resemble closely those of Pray (*loc. cit.*) and together they give support to the view that the reactions involved proceed by a mechanism of which the primary measurable reaction is the formation of a free aryl radical together with molecular nitrogen.

Fig. 1.

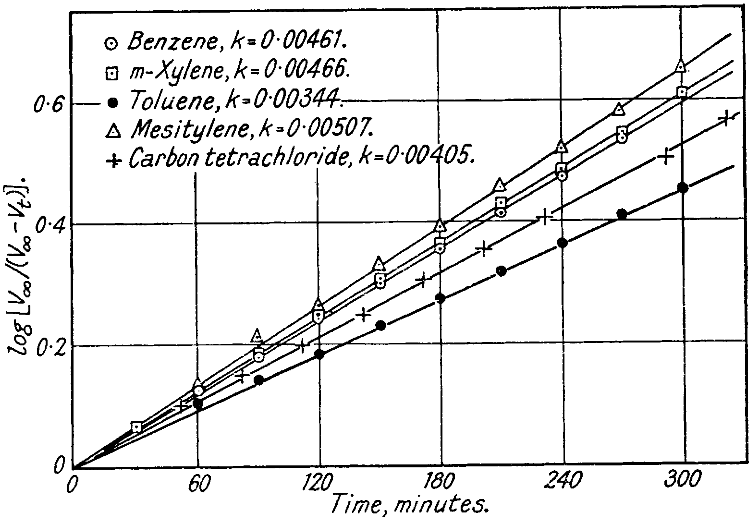
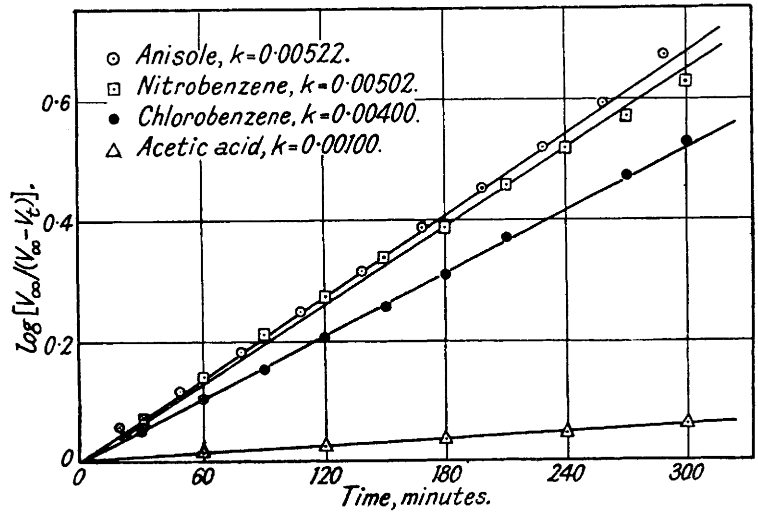


Fig. 2.



It might be contended, however, that, if the free-radical mechanism were valid, some polymerisation would occur with the formation of diphenyl, which should be found in appreciable quantity in the reaction product, whenever sodium benzenediazoate or nitrosoacetanilide were used, irrespective of the nature and presence of any second component. Actually diphenyl was never found in the product (apart from one instance) unless, of course, benzene was also present. On the other hand, there is reason to believe that free phenyl radicals, under conditions such as are encountered in these reactions, would *not* normally polymerise to give any appreciable quantity of diphenyl. Wieland and his co-workers, in their study of chemical reactions involving free radicals, have investigated the decomposition reactions of phenyl- and substituted phenyl-azotriphenylmethanes in so-called inert solvents (Wieland, Popper, and Seefried, *Ber.*, 1922, **55**, 1816; see also *Ann. Reports*, 1930, **27**, 127), and they conclude that the azo-compounds decompose with the formation of free triphenylmethyl and phenyl (or substituted phenyl) radicals together with nitrogen molecules. They further state that the phenyl radicals so formed do not polymerise to form the bimeric hydrocarbon, since a careful and extended search for diphenyl always proved fruitless. On the other hand, the formation of free phenyl radicals in the gaseous phase at relatively high temperatures, as, for example, in the thermal decomposition of tetraphenyl-lead (Dull and Simons, *J. Amer. Chem. Soc.*, 1933, **55**, 3898, 4328), does lead to diphenyl formation. Again, when a number of decomposition reactions of the type under consideration are carried out in the presence of benzene, the product contains not only diphenyl but also, in lesser quantity, ter-, quater-, and even quinque-phenyl as well. This seems to indicate reaction between a free radical and a hydrocarbon molecule (as in A), rather than reaction between two phenyl radicals (as in B), which could result in the formation of the binuclear hydrocarbon only :

(A) $\mathrm{Ph} + \mathrm{C_6H_6} \longrightarrow \mathrm{Ph{\cdot}Ph} + \mathrm{H}$; $\mathrm{Ph} + \mathrm{Ph{\cdot}Ph} \longrightarrow \mathrm{Ph{\cdot}C_6H_4{\cdot}Ph} + \mathrm{H}$;
$\mathrm{Ph} + \mathrm{Ph{\cdot}C_6H_4{\cdot}Ph} \longrightarrow \mathrm{Ph{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}Ph} + \mathrm{H}$; etc.
(B) $\mathrm{Ph} + \mathrm{Ph} \longrightarrow \mathrm{Ph{\cdot}Ph}$

The one example in which diphenyl formation was observed in the absence of benzene was the decomposition of nitrosoacetanilide in methyl-alcoholic solution. In this case it appears likely that the methyl alcohol functions as a reducing agent, thereby supplying sufficient benzene to account for the diphenyl formation :

$$2\mathrm{Ph} + \mathrm{CH_3{\cdot}OH} \longrightarrow 2\mathrm{C_6H_6} + \mathrm{HCHO};\quad \mathrm{Ph} + \mathrm{C_6H_6} \longrightarrow \mathrm{Ph{\cdot}Ph} + \mathrm{H}$$

The isolation of formaldehyde in the reaction product adds confirmation to the validity of this mechanism, which recalls the reduction of benzenediazonium hydroxide by ferrous hydroxide, investigated by Jolles and Busoni (*Gazzetta*, 1932, **62**, 1150), who also report the formation of diphenyl.

In addition to the quantitative measurements described above, qualitative investigations have also been carried out on the reactions of nitrosoacetanilide with various compounds of diverse types. In most solvents decomposition takes place readily, but it is not always possible to isolate definite reaction products, since the decomposition is frequently accompanied by tar formation. When the reaction is carried out on a small scale, as, for example, in the quantitative experiments with benzene, at least 90% of the nitrogen is evolved and it is possible to isolate diphenyl in good yield. On a larger scale, however, the formation of tarry by-products cannot be avoided. In the reaction with toluene and mesitylene, some acetaldehyde is formed. In acetic acid solution or in aqueous suspension nitrosoacetanilide gives some phenol and *p*-hydroxyazobenzene, while in carbon tetrachloride solution some *p*-hydroxyazobenzene and benzenediazonium chloride are formed. In ether, malonic ester, and ethyl acetate solutions, decomposition proceeded with considerable evolution of nitrogen, but the products could not be identified, although in the case of malonic ester the red product probably contained the phenylhydrazone of mesoxalic ester.

Attention has also been given to the reactions of nitrosoacetobenzylamide in order to gain information on the manner in which the benzyl group would differ from the phenyl group, as shown in the reactions of nitrosoacetanilide. It is known that nitrosoacetobenzylamide reacts with alcohols in the presence of potassium carbonate to give benzyl alkyl ethers (Paal and Lowitsch, *Ber.*, 1897, **30**, 869; Paal and Apitzsch, *ibid.*, 1899, **32**, 78): $CH_2Ph{\cdot}N(NO){\cdot}CO{\cdot}CH_3 + Alk{\cdot}OH \longrightarrow CH_2Ph{\cdot}OAlk + N_2 + CH_3{\cdot}CO_2H$. The decomposition of nitrosoacetobenzylamide in an aromatic solvent, which does not appear to have been previously studied, proceeds readily with evolution of nitrogen in warm benzene, toluene, and chlorobenzene solution, but only after the addition of potassium carbonate. In each case the product of the decomposition is mainly benzyl acetate, together with some stilbene, thus indicating that the solvent served merely as an inert medium for the greater part of the reaction. If any action had taken place with the aromatic solvent, the product should contain, in addition, some diphenylmethane or a substituted diphenylmethane. In the reaction in benzene solution, diphenylmethane was actually identified by its oxidation to benzophenone, while in the other cases the products of similar oxidations, although ketonic in character, could not be identified as single substances, but were probably mixtures of isomeric substituted benzophenones. Owing to the small yield in which these derivatives were formed, it was not possible to obtain sufficient material to make a separation of the mixtures. In its decomposition to give benzyl acetate and stilbene, nitrosoacetobenzylamide behaves in a similar manner to nitrosobenzobenzylamide (v. Pechmann, *Ber.*, 1898, **31**, 2640), and the necessity for the addition of potassium carbonate indicates a close relationship to nitrosomethylurethane and to the aliphatic diazo-compounds. It would therefore seem likely that nitrosoacetobenzylamide would give phenyldiazomethane in the presence of potassium carbonate as the first stage in its decomposition:

$$CH_2Ph{\cdot}N(NO){\cdot}CO{\cdot}CH_3 + K_2CO_3 \longrightarrow Ph{\cdot}CHN_2 + CH_3{\cdot}CO_2K + KHCO_3$$

The reactions of nitrosoacetobenzylamide thus simulate closely those of diazomethane, and the formation of benzyl acetate and stilbene is the natural outcome when the decomposition takes place in an inert solvent. In addition, however, to the main trend of the reaction, a side reaction appears to take place with the solvent, but only to a small extent, as follows:

$$CH_2Ph{\cdot}N(NO){\cdot}CO{\cdot}CH_3 + C_6H_6 \longrightarrow Ph{\cdot}CH_2Ph + N_2 + CH_3{\cdot}CO_2H$$

It is not possible to say whether the diphenylmethane is formed by the interaction of benzene with a benzyl radical (as in *a*) or with a phenylmethylene radical (as in *b*):

$$(a)\ PhCH_2 + C_6H_6 \longrightarrow Ph{\cdot}CH_2Ph + H$$
$$(b)\ PhCH + C_6H_6 \longrightarrow Ph{\cdot}CH_2Ph$$

In the search for further evidence to support the view that the examples of amphoteric aromatic substitution here discussed proceed by a free-radical mechanism, attention is now being directed to other reactions, which might serve as sources of free aryl radicals under conditions similar to those employed in the present cases. Convenient reactions for these purposes have been found in the decomposition of arylazotriphenylmethanes and of aroyl peroxides.

EXPERIMENTAL.

Reactions with Sodium Benzenediazoate.—These reactions were carried out by the two methods described by Gomberg and his co-workers (*loc. cit.*).

(i) *With benzene.* Aniline (93 g.) in concentrated hydrochloric acid (200 c.c., *d* 1·16) was diazotised in the normal manner, and the clear diazonium solution was divided into two equal parts. One half was used for method *a* and the other for method *b*.

Method a. The diazonium solution was run into a vigorously stirred mixture of benzene (300 c.c.) and aqueous sodium hydroxide (48 g. in 150 c.c.) at 0—5°. After 8 hours, during which the temperature was allowed to rise to 20—25°, the benzene layer was separated and distilled, diphenyl (14·5 g.) being obtained, b. p. 245—255° (yield, 19% calculated on the weight of aniline used).

Method b. Aqueous sodium hydroxide (48 g. in 150 c.c.) was run into a vigorously stirred mixture of the diazonium solution and benzene (300 c.c.) at 0—5°. The subsequent treatment, similar to that in method *a*, gave diphenyl (15 g., b. p. 245—255°).

The following reactions were carried out by methods *a* and *b* as described above, unless otherwise stated.

(ii) *With toluene.* The crude fractions, obtained by distilling the toluene extracts under reduced pressure, were redistilled at atmospheric pressure. Method *a* gave 8 g. of methyldiphenyls (b. p. 255—275°; yield, 10%) and method *b* gave 7 g. of methyldiphenyls (b. p. 255—275°; yield, 9%).

(iii) *With* m-*xylene.* Method *a* gave 8 g. of 2 : 4-dimethyldiphenyl (b. p. 264—267°; yield, 9%), and method *b* gave 7 g. (b. p. 264—267°; yield, 8%).

(iv) *With chlorobenzene.* Method *a* gave 14·5 g. of chlorodiphenyls (b. p. 265—285°; yield, 15%), and method *b* gave 12 g. (b. p. 265—285°; yield, 13%).

(v) *With nitrobenzene.* Method *a* gave, by distillation under reduced pressure, 8 g. of nitrodiphenyls (b. p. 180—210°/20 mm.; yield, 8%), and method *b* gave 6 g. (b. p. 180—210°/20 mm.; yield, 6%). In their reaction between sodium benzenediazoate and nitrobenzene Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1924, **46**, 2343) record the formation of 4-nitrodiphenyl only, but fractionation of the above products by further distillation gave both 4-nitrodiphenyl (m. p. 114°) and 2-nitrodiphenyl. The latter was identified by reduction and acetylation to 2-acetamidodiphenyl (m. p. and mixed m. p. 118—119°). The reaction is thus similar to that between sodium *p*-toluenediazoate and nitrobenzene, which gives both 4-nitro-4'-methyldiphenyl and 2-nitro-4'-methyldiphenyl (Grieve and Hey, J., 1932, 1893).

(vi) *With ethyl benzoate.* Method *a* gave 15·5 g. of ethyl diphenylcarboxylates (b. p. 180—210°/15 mm.; yield, 14%), and method *b* gave 13·5 g. (b. p. 180—210°/15 mm.; yield, 12%). Redistillation of the products gave ethyl diphenyl-4-carboxylate, b. p. 325—330° (cf. Döbner, *Annalen*, 1874, **172**, 114), which solidified when cold, and a lower fraction (b. p. 314—316°) probably containing ethyl diphenyl-2-carboxylate (cf. Graebe and Rateanu, *Annalen*, 1894, **279**, 260).

(vii) *With* o-*nitrotoluene* [with C. HORREX]. This reaction was carried out according to method *b*, 93 g. of aniline being used. The *o*-nitrotoluene layer was separated, washed with concentrated hydrochloric acid and water, dried over calcium chloride, and distilled. The excess of *o*-nitrotoluene was collected at atmospheric pressure (up to 245°), and the residue under reduced pressure. A red viscous liquid was obtained (18·5 g., b. p. 175—195°/2 mm.), which would not solidify at −10°. A portion (13 g.) was reduced by means of stannous chloride (70 g.) in alcoholic hydrochloric acid solution, and the resulting liquid base, isolated in the normal manner, gave on acetylation 4-acetamido-3-methyldiphenyl, which separated from aqueous alcohol in small needles, m. p. and mixed m. p. 166° (Grieve and Hey, J., 1932, 2247). Evaporation of the mother-liquor yielded further quantities of this compound, and no indication of the presence of a second acetamidomethyldiphenyl was obtained. A second portion of the reaction product (5·5 g.) was oxidised by heating for 6 hours in acetic acid (100 c.c.) with the gradual addition of a hot solution of chromic anhydride (25 g.) in 90% acetic acid, and was then poured into water. The pale yellow solid which separated was recrystallised from aqueous alcohol, 4-nitro-3-methylbenzoic acid being obtained, m. p. and mixed m. p. 214°. No other nitrotoluic acid could be detected in the mother-liquor.

(viii) *With a mixture of toluene and nitrobenzene.* This reaction was carried out by both method *a* and method *b*. 93 G. of aniline were used in each case, together with aqueous sodium hydroxide (100 g. in 300 c.c.), 317 c.c. of toluene, and 307 c.c. of nitrobenzene. From method *a* a liquid fraction was obtained (31 g., b. p. 150—210°/18 mm.), which was separated on redistillation into two fractions, (i) b. p. 260—300°/760 mm., 5 g., consisting of a mixture of methyldiphenyls, and (ii) b. p. above 300°/760 mm., 24 g., consisting mainly of 4-nitrodiphenyl (m. p. and mixed m. p. 114°) together with some 2-nitrodiphenyl. Similarly, method *b* gave a product (16 g., b. p. 160—230°/30 mm.) which on redistillation gave two fractions, (i) b. p. 260—300°/760 mm., 3 g., consisting of methyldiphenyls, and (ii) b. p. above 300°/760 mm., 12 g., consisting of nitrodiphenyls.

Reactions with Nitrosoacetanilide.—Qualitative. Nitrosoacetanilide was prepared by passing nitrous fumes into a solution of acetanilide (20 g.) in glacial acetic acid (100 c.c.) at 5—10° until a dark green colour developed (cf. Fischer, *Ber.*, 1876, **9**, 463; Bamberger, *ibid.*, 1894, **27**, 915). The yellow solid which separated when the solution was poured into water was filtered off, washed well with water, and dried, first by suction and finally on a porous tile. The material so obtained was crystalline (m. p. 50—51°, decomp.) and could be kept in a desiccator for a few days without serious decomposition. On rapid heating, it exploded. Recrystallisation could be effected from ether or light petroleum, the product separating in fine yellow needles (m. p. 51—52°), but although of better appearance than the non-recrystallised product, it invariably turned brown and decomposed more rapidly on keeping.

The following qualitative experiments were carried out with nitrosoacetanilide;

(i) *With benzene* (cf. Bamberger, *Ber.*, 1897, **30**, 366). Nitrosoacetanilide (2 g.) was dissolved in benzene (100 c.c.) and kept at room temperature. The yellow solution became darker and nitrogen was steadily evolved. After 2 days, 248 c.c. of nitrogen (measured at N.T.P.) had been evolved, which, assuming that the nitrosoacetanilide is 100% pure, represents over 90% of the nitrogen content. Actually the percentage of nitrogen evolved must be greater than this, since it is very improbable that the nitrosoacetanilide is entirely free from water and possibly some acetanilide. On the other hand, if any appreciable time is expended in attempting to remove the final traces of water, the advantage thus gained is outweighed by the incipient decomposition which sets in. Further, in the above computation no allowance has been made for the solubility of nitrogen in the benzene. After the removal of the excess of benzene and acetic acid, diphenyl was obtained (1·5 g.; yield, 80%).

On repeating this experiment on a larger scale (25 g. of nitrosoacetanilide in 1000 c.c. of benzene), the yield of diphenyl was reduced to 40% in spite of vigorous stirring and careful temperature control. There was a considerable tarry residue. No evidence could be obtained of the formation of either acetaldehyde or phenyl acetate during this experiment.

(ii) *With toluene* (cf. Bamberger, *loc. cit.*). A solution of nitrosoacetanilide (6 g.) in toluene (150 c.c.) was kept at room temperature. Nitrogen was freely evolved. After completion of the reaction distillation gave acetaldehyde, toluene, acetic acid, and finally methyldiphenyls (3 g., b. p. 260—275°) and a higher-boiling black residue.

(iii) *With* m-*xylene.* A solution of nitrosoacetanilide (2 g.) in *m*-xylene (100 c.c.) evolved nitrogen at room temperature. Distillation of the product gave acetaldehyde, acetic acid, *m*-xylene, and 2 : 4-dimethyldiphenyl (1 g., b. p. 260—265°).

(iv) *With mesitylene* (cf. Hey, J., 1932, 2638). Nitrosoacetanilide (2 g.) in mesitylene (100 c.c.) readily evolved nitrogen, and distillation yielded acetaldehyde, acetic acid, mesitylene, and 2 : 4 : 6-trimethyldiphenyl (1 g., b. p. 265—275°).

(v) *With chlorobenzene.* The product from nitrosoacetanilide (2 g.) in chlorobenzene (100 c.c.) gave on distillation acetic acid, chlorobenzene, and a yellow oil (b. p. 240—280°), which was heated on the water-bath with a solution of bromine in acetic acid. When cold, a solid separated, which on recrystallisation from alcohol gave 4-chloro-4′-bromodiphenyl, m. p. and mixed m. p. 154—155° (Shaw and Turner, J., 1932, 285).

(vi) *With nitrobenzene.* Nitrosoacetanilide (15 g.) was added gradually to nitrobenzene (200 c.c.). The solution became warm and nitrogen was steadily evolved. After 2 days the excess of nitrobenzene was removed, and the residue distilled under reduced pressure. Two fractions were obtained, (i) b. p. 175—190°/20 mm., and (ii) b. p. 190—210°/20 mm. The former was identified as 2-nitrodiphenyl by reduction and acetylation to give 2-acetamidodiphenyl, while the latter solidified and on recrystallisation from alcohol gave 4-nitrodiphenyl.

(vii) *With ethyl benzoate.* A solution of nitrosoacetanilide (15 g.) in ethyl benzoate (200 c.c.) gradually evolved nitrogen. Distillation of the product gave a mixture of ethyl diphenylcarboxylates (b. p. 310—330°).

(viii) *With benzaldehyde.* Nitrosoacetanilide (20 g.) was added gradually to benzaldehyde (135 c.c.) cooled in ice. The clear solution was kept for several days at room temperature. On distillation, acetic acid and benzaldehyde were collected, leaving a residue which contained much benzoic acid. It was therefore dissolved in benzene and washed with aqueous sodium carbonate. After removal of the benzene two fractions were collected, (i) b. p. 150—220°, consisting mainly of benzaldehyde, and (ii) b. p. 220—300°, which solidified when cold (5·7 g.). Crystallisation from light petroleum and then from aqueous alcohol yielded benzanilide (m. p. and mixed m. p. 158—160°). After the removal of further portions of benzanilide the mother-liquors were evaporated and the residue was treated with 2 : 4-dinitrophenylhydrazine in the presence of alcohol and concentrated sulphuric acid (cf. Brady, J., 1931, 756); a dark red precipitate was immediately formed, which on recrystallisation from alcohol–toluene gave *p*-phenylbenzaldehyde-2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 236—238° (cf. Hey, J., 1931, 2477).

(ix) *With* o-*nitrotoluene* [with C. HORREX]. Nitrosoacetanilide (10 g.) was added gradually to *o*-nitrotoluene (60 c.c.), and the solution left for 2 days. The excess of *o*-nitrotoluene and acetic acid were removed by distillation at atmospheric pressure, and the residue collected at 175—195°/2 mm. (2 g.). Reduction and acetylation, as described under the corresponding reaction with sodium benzenediazoate, gave 4-acetamido-3-methyldiphenyl, m. p. and mixed m. p. 165—166°.

(x) *With acetic acid.* A solution of nitrosoacetanilide (16 g.) in glacial acetic acid (150 c.c.) was kept for several days. After the evolution of nitrogen had ceased, water was added, which precipitated *p*-hydroxyazobenzene (m. p. and mixed m. p. 150—152°); phenol was extracted from the filtrate and identified by formation of tribromophenol.

(xi) *With water.* A suspension of nitrosoacetanilide (15 g.) in water (300 c.c.) was kept, with frequent shaking, for several days. The solid in suspension was then filtered off and shown to be *p*-hydroxyazobenzene. Addition of bromine water to the filtrate deposited tribromophenol.

(xii) *With carbon tetrachloride.* A solution of nitrosoacetanilide (15 g.) in carbon tetrachloride (200 c.c.), on standing for several days, became very dark and gradually deposited a solid, which was filtered off. This solid (4 g.) commenced to decompose after one day, with liberation of hydrogen chloride. It was shaken with cold water and filtered. The insoluble residue consisted of *p*-hydroxyazobenzene; the filtrate gave (*a*) a red precipitate with alkaline β-naphthol, (*b*) nitrogen and phenol on warming, and (*c*) a precipitate of silver chloride with silver nitrate solution and nitric acid. The filtrate therefore probably contained benzenediazonium chloride.

(xiii) *With methyl alcohol.* A solution of nitrosoacetanilide (25 g.) in methyl alcohol (200 c.c.) was left for some days, and then distilled. After removal of the excess of methyl alcohol, distillation was continued under reduced pressure to give a main fraction, b. p. 150—180°/30 mm., which solidified. Recrystallisation from alcohol gave diphenyl (m. p. and mixed m. p. 70°). Addition of aqueous 2 : 4-dinitrophenylhydrazine hydrochloride to the recovered methyl alcohol gave a copious precipitate of formaldehyde-2 : 4-dinitrophenylhydrazone (m. p. and mixed m. p. 157—159°).

(xiv) *With ethyl acetate, ethyl malonate, and ether.* Solutions of nitrosoacetanilide in these solvents readily evolved nitrogen. In the case of ethyl acetate and ether, acetaldehyde was detected in the product, while in the case of malonic ester a red product was obtained having the characteristics of the phenylhydrazone of mesoxalic acid.

Quantitative. The measurements of the rate of evolution of nitrogen from solutions of nitrosoacetanilide were carried out at 20°, the reaction vessel being submerged in a thermostat and the volume of gas liberated being measured at ½ hour intervals over a period of 6 or 7 hours by collection in an ordinary nitrometer. In each experiment 2 g. of nitrosoacetanilide were used in 100 c.c. of solvent, the latter being previously saturated with dry nitrogen at the required temperature. The complete apparatus consisted of three separate reaction vessels, each connected to a nitrometer, so that measurements could be made simultaneously in duplicate or triplicate. Independent experiments were carried out to find (*a*) the effect of stirring during the reaction (compare *inter alia*, Lamplough, *Proc. Camb. Phil. Soc.*, 1908, **14**, 580), (*b*) the effect of light, and (*c*) the effect of increasing the glass surface exposed to the solution. In all three cases, however, the effects were small and within the limits of accuracy obtainable from the apparatus. About 20—30 c.c. of nitrogen were allowed to escape before periodical readings were commenced, and the final volume was recorded after the lapse of at least 24 hours. The volumes of gas evolved were corrected, and the results obtained by plotting $\log [V_\infty/(V_\infty - V_t)]$ against t, where V_∞ is the final observed volume, and V_t the volume at time t, are shown in Figs. 1 and 2, together with the unimolecular velocity constants k. In every case (except in acetic acid solution) at least 70% of the reaction is complete within 5½ hours. The total volumes of nitrogen liberated from the different solutions differ from case to case. An exact comparison of the figures is not possible owing to the difficulty of preparing uniformly pure nitrosoacetanilide each time, but it was apparent that with benzene and its homologues, chlorobenzene and acetic acid, the total volume of nitrogen evolved from 2 g. of nitrosoacetanilide was 200—248 c.c., while with anisole and carbon tetrachloride the total volumes were smaller (120—140 c.c.). Nitrobenzene occupied an intermediate position, giving 180—190 c.c. of nitrogen. In the case of acetic acid, only about 15% of the reaction is completed within 5½ hours, and the velocity constant recorded was calculated, not from the curve shown in Fig. 2, but from a curve representing the course of the reaction over a period of 35 hours.

Reactions with Nitrosoacetobenzylamide.—Acetobenzylamide was prepared by the method of Nicholas and Erickson (*J. Amer. Chem. Soc.*, 1926, **48**, 2174) or by the direct acetylation of benzylamine, prepared by the method of Ing and Manske (J., 1926, 2348). It boiled at 300—302° and was converted into nitrosoacetobenzylamide by passing nitrous fumes into its solution in cold acetic acid until a dark green colour was developed. The solution was then poured on ice; the nitroso-compound separated as a yellow solid, which melted to a yellow oil as the temperature rose, and was extracted with ether. The ethereal extract was washed with sodium bicarbonate solution and dried over sodium sulphate, after which the solvent was removed at room temperature under diminished pressure, leaving the nitrosoacetobenzylamide as a thick yellow oil. If any heat is applied to assist the removal of the solvent, a violent explosion may result.

The following reactions were carried out with nitrosoacetobenzylamide. In each case the nitrosoacetobenzylamide (20 g.) was dissolved in the aromatic solvent (150 c.c.), potassium carbonate (5 g.) was added, and the whole heated under reflux on the steam-bath for 2 hours; nitrogen was then freely evolved. The liquid was poured off from the potassium salts and distilled.

(i) *With benzene.* After removal of the excess of benzene, two fractions were collected, (i) b. p. 210—230° (9 g.) and (ii) b. p. 230—270° (3·5 g.). Fraction (i) on redistillation gave benzyl acetate (b. p. 216—220°); fraction (ii), which completely solidified, was recrystallised from absolute alcohol and gave stilbene in white plates, m. p. and mixed m. p. 124° (Found : C, 93·2; H, 6·9. Calc. for $C_{14}H_{12}$: C, 93·3; H, 6·7%). A repetition of the experiment, with doubled quantities, gave three fractions on distillation, (i) b. p. 210—230° (17·8 g.), (ii) b. p. 230—290° (3 g.), and (iii) b. p. 290—340° (2 g.). Fraction (i) gave benzyl acetate (16·7 g.). Fractions (ii) and (iii) were triturated with light petroleum and filtered. The crystalline residue consisted of stilbene (0·8 g.), and further quantities were obtained from the filtrates on distillation. Finally, a fraction (2 g.), b. p. 240—280°, from which no more stilbene could be separated, was boiled for 2 hours in acetic acid solution with the gradual addition of a solution of chromic anhydride (2 g.) in 90% acetic acid. The product was poured into water, extracted with ether, washed with aqueous sodium hydroxide, and dried. Acidification of the alkaline washings precipitated benzoic acid. Evaporation of the ether left an oil, which on treatment with 2 : 4-dinitrophenylhydrazine and sulphuric acid in the presence of alcohol (cf. Brady, *loc. cit.*) gave an immediate red precipitate. Crystallisation from benzene–alcohol gave benzophenone-2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 233—235° (Found : N, 15·8. Calc. for $C_{19}H_{14}O_4N_4$: N, 15·5%). When pure benzyl acetate was oxidised in this manner, benzoic acid only was formed and no ketonic or aldehydic product.

(ii) *With toluene.* After removal of the excess of toluene, two fractions were collected, (i) b. p. 200—230° (11·5 g.), and (ii) b. p. 230—300° (2·5 g.). The former consisted mainly of benzyl acetate, and the latter of stilbene (m. p. and mixed m. p. 124°). After the removal of these two compounds an intermediate fraction (2 g., b. p. 240—270°) was obtained, which on oxidation with chromyl chloride, according to the method of Perkin and Law (J., 1908, **93**, 1637), gave an oil which readily reacted with 2 : 4-dinitrophenylhydrazine. The red product, even after repeated crystallisation, melted indefinitely at 165—173°.

(iii) *With chlorobenzene.* As above, two fractions were collected, (i) b. p. 200—230° (9 g.), consisting mainly of benzyl acetate, and (ii) b. p. 230—300° (2·5 g.), consisting mainly of stilbene. Oxidation of a small intermediate fraction by means of chromic anhydride in acetic acid solution gave an oil, which with 2 : 4-dinitrophenylhydrazine gave a derivative, m. p. 185—200°. Repeated crystallisation from absolute alcohol raised the melting point to 212—218°, but the greater portion still melted below 200°.

The 2 : 4-*dinitrophenylhydrazones* of 4-methylbenzophenone and of 4-chlorobenzophenone, prepared by Brady's method, melt at 199—200° and 184—185° respectively (Found : N, 14·7, and 13·7. $C_{20}H_{16}O_4N_4$ requires N, 14·9%. $C_{19}H_{13}O_4N_4Cl$ requires N, 14·1%).

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[*Received, July* 18*th*, 1934.]