644. *Homolytic Aromatic Substitution. Part I. The Action of Aryl Radicals on Nitrobenzene.*

By D. H. Hey, A. Nechvatal, and T. S. Robinson.

In an attempt to obtain more accurate quantitative information on substitution reactions effected by free radicals and atoms, an experimental investigation has been carried out on the extent of substitution at the *o*-, *m*-, and *p*-positions in nitrobenzene by phenyl, *p*-bromophenyl, and *p*-tolyl radicals. Four different reactions were studied, namely, those of the sodium aryldiazoate, the acylarylnitrosamine, the 1-aryl-3 : 3-dimethyltriazen, and the acyl peroxide, and the percentage of substitution at the *m*-position was found to be of the order of 12% for *p*-bromophenyl and 9% for *p*-tolyl, which figures were independent of the particular reaction used. The products were analysed both by a bromometric method on the mixture of bases obtained on reduction and by means of infra-red spectroscopy. The two methods showed excellent agreement and the results substantiate the theoretical views originally proposed by one of us in 1934.

Investigations on the arylation of aromatic compounds by the action of certain diazo-compounds and the peroxides of aromatic acids revealed a series of reactions in which the normal directive influence of substituent atoms or groups was not operative (Grieve and Hey, *J.*, 1934, 1797; Hey, *ibid.*, p. 1966). In order to explain the course of these reactions it was suggested that the substituting agent was an electrically neutral free aryl radical of short life, the reactions of which would not be subject to the electrical charges which are responsible for the position taken up by the entering group in, for example, nitration or sulphonation. Such reactions have been referred to as "amphoteric aromatic substitution" because the entering group behaved as if it were either electrophilic (cationoid) or nucleophilic (anionoid) in type, as "invariable *ortho-para* substitution" because in all the reactions studied the main and often the sole products isolated were the *o*- and *p*-isomerides, irrespective of the nature of the substituent atom or group present, and also as "radical substitution" (Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900). Many further examples of this type of aromatic substitution have now come to light, and it appears more logical to classify such reactions as "homolytic substitution" reactions in order to distinguish them from the better-known reactions involving electrophilic or nucleophilic reagents which may be termed "heterolytic substitution" reactions.

Among aromatic substitution reactions which are considered to involve free atoms or radicals and which may therefore be classified as homolytic substitution reactions are those of (*a*) the diazoic acids or the diazoates (the Gomberg reaction) (Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2339; Gomberg and Pernert, *ibid.*, 1926, **48**, 1372; Grieve and Hey, *J.*, 1938, 108; Heilbron, Hey, and Wilkinson, *J.*, 1938, 113, 699; Elks, Haworth, and Hey, *J.*, 1940, 1284, etc.), (*b*) the acylarylnitrosamines or the acyl derivatives of the diazoic acids (Bamberger, *Ber.*, 1897, **30**, 366; Grieve and Hey, *J.*, 1934, 1797; France, Heilbron, and Hey, *J.*, 1938, 1364; 1939, 1283, 1288; Haworth and Hey, *J.*, 1940, 361; Hey and Lawton, *J.*, 1940, 374, etc.), (*c*) the 1-aryl-3 : 3-dimethyltriazens (I.G. Farb. Akt., B.P. 513,846; Elks and Hey, *J.*, 1943, 441), (*d*) the arylazotriarylmethanes (Wieland, Popper, and Seefried, *Ber.*, 1922, **55**, 1816; Hey, *J.*, 1934, 1966; Wieland *et al.*, *Annalen*, 1934, **514**, 145), and (*e*) the acyl peroxides (Gelissen and Hermanns, *Ber.*, 1925, **58**, 285 *et seq.*; Hey, *J.*, 1934, 1966; Wieland, Ploetz, and Indest, *Annalen*, 1937, **532**, 166; Hey and Walker, *J.*, 1948, 2213, etc.). All these reactions are considered to give rise to a free aryl radical, Ar•, which reacts with an aromatic compound C_6H_5R to give a mixture of unsymmetrical diaryls $Ar{\cdot}C_6H_4{\cdot}R$, in which the *o*- and *p*-isomerides predominate. In addition to the above arylation processes, further examples of homolytic substitution have been provided by reactions involving methylation and hydroxylation. In the former process the methyl radical may be derived from acetyl peroxide (Fieser and Oxford, *J. Amer. Chem. Soc.*, 1942, **64**, 2060), lead tetra-acetate (Fieser, Clapp, and Daudt, *ibid.*, p. 2052; Fieser and Chang, *ibid.*, p. 2043), phenyl iodosoacetate (Sandin and McCormack, *ibid.*, 1945, **67**, 2051), or from the electrolysis of acetates (Fieser, Clapp, and Daudt, *loc. cit.*), while in the latter the hydroxyl radical may originate from a ferrous salt and hydrogen peroxide (Loebl, Stein, and Weiss, *J.*, 1949, 2074), from the action of ionising radiations on aqueous solutions (*idem*, *J.*, 1950, 2704), or from the irradiation of aqueous solutions of ion-pair complexes (Bates, Evans, and Uri, *Nature*, 1950, **166**, 869). Evidence has also recently been brought forward (Klapproth and Westheimer, *J. Amer. Chem. Soc.*, 1950, **72**, 4461) which indicates that aromatic mercuration may follow one of two courses according to whether mercuric perchlorate in perchloric acid or mercuric acetate in non-polar solvents is used. In the latter case it seems highly probable that a homolytic substitution process is largely involved, whereas under the former conditions the normal orientation effects of an electrophilic substitution process are observed.

An alternative hypothesis for the arylation process applicable to the reactions of alkali diazoates and acylarylnitrosamines has been put forward by Hodgson (*J.*, 1948, 348; *J. Soc. Dyers Col.*, 1948, **64**, 99; 1949, **65**, 347; cf. Hey and Waters, *J.*, 1948, 882; *J. Soc. Dyers Col.*, 1948, **64**, 359), who considers that in these reactions nitrogen must be evolved from a diazonium ion, thus giving rise to an aryl cation and not a neutral free radical. The aryl cation is considered to react at the *o*- and *p*-positions to the nitro-group in nitrobenzene, which by solvent effects is converted into a quinonoid form showing anionoid reactivity at these positions, thus revealing why the *m*-position should not be attacked. Such a mechanism is not supported by the present investigation.

The absence of accurate quantitative data with regard both to orientation and to the activation or deactivation of the nucleus by the presence of substituent atoms or groups has hitherto made any comprehensive theoretical interpretation of the substitution reactions of free radicals and atoms highly speculative. The present communication is the first of a series designed to provide an adequate quantitative background to the general problem.

If the substituent atom or group R in $C_6H_5{\cdot}R$ exerts no influence at all on the position taken up by an entering atom or group, the distribution of isomerides would be represented by 40% *o*-, 40% *m*-, and 20% *p*-. It will therefore be convenient to represent any disturbance of this ratio by the presence of the substituent R by classifying R as *op*-directing if the proportion of the *m*-isomeride is less than 40%, and as *m*-directing if it exceeds 40%. In electrophilic and nucleophilic substitution reactions the ease of reaction at any position in an aromatic nucleus is largely controlled by the net electric charge at that point. If the substituting agent is electrically neutral, it might be inferred that all the available nuclear positions are equally favoured, but the completion of the reaction requires the provision of an odd electron which has to be paired with the odd electron provided by the free radical, and the ease with which such an electron can be made available may be significantly different at the various positions.

The first example reported of the isolation of all three isomerides in a homolytic arylation process referred to reactions with ethyl benzoate (R = CO_2Et) (Hey, *J.*, 1934, 1966), and, later, the careful fractionation of the products of the reaction between 4-nitrosoacetamidodiphenyl and (*a*) chlorobenzene, (*b*) bromobenzene, and (*c*) toluene (France, Heilbron, and Hey, *J.*, 1938, 1364; 1939, 1283) gave all three isomeric *p*-terphenyls in the proportions shown below:

	Yield of isomerides *p*-$Ph{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}R$, %		
R in $C_6H_5{\cdot}R$	*ortho-*	*meta-*	*para-*
Cl	32	20	48
Br	33	15	52
Me	50	6	44

Such figures, which represent percentages based on the total terphenyl isolated, can be accepted as no more than rough approximations, but they give an unmistakable indication that in these reactions the group R is predominantly *op*-directive in character. For the substitution reactions of nitrobenzene (R = NO_2) more accurate figures have recently been provided by Loebl, Stein, and Weiss (*locc. cit.*), who have investigated the action of hydroxyl radicals, using saturated aqueous solutions of nitrobenzene and (*a*) the ferrous sulphate–hydrogen peroxide reaction (Fenton's reagent) and (*b*) ionising radiations. Analysis of the mixture of isomeric nitrophenols gave the following figures, which for the ionising radiation experiments were claimed to have an accuracy of ±5% for the *o*- and ±10% for the *m*- and *p*-values :

		Yield of isomeric nitrophenols, %		
Source of hydroxyl radical	pH	*ortho-*	*meta-*	*para-*
Fenton's reagent	—	25—30	20—25	50—55
$H_2O \rightsquigarrow H\cdot + OH\cdot$	2	34·5	31	34·5
,,	6	35·5	29	35·5
,,	12	27·5	27	45·5

The above figures again show that in these reactions the nitro-group, like methyl and the halogens, belongs to the *op*-directing type, as in fact had been indicated in the earlier qualitative work on the arylation processes.

The Arylation of Nitrobenzene.—The present communication describes the quantitative results which have been obtained on the arylation of nitrobenzene. Use has been made of four different reactions as the source of the aryl radical, namely, (*a*) the diazoate, (*b*) the acylarylnitrosamine, (*c*) the 1-aryl-3 : 3-dimethyltriazen, and (*d*) the acyl peroxide, and the resulting mixture of nitrodiphenyls was reduced and submitted to a bromometric titration by means of a mixture of potassium bromide and potassium bromate in aqueous acid. Arylation at the *m*-position with regard to the nitro-group will give rise on reduction to a 3-aminodiphenyl which will require three molecules of bromine, whereas arylation at the *o*- and *p*-positions will give 2- and 4-aminodiphenyls, which will require only two molecules of bromine. Thus the bromometric titration can give the ratio $m : (o + p)$. Preliminary experiments on the analytical method showed that 4-aminodiphenyl itself could not be brominated quantitatively by this method (R. E. Parker, unpublished results), presumably owing to the occurrence of oxidation involving the 4′-position. It was found, however, that when the hydrogen atom at the 4-position was replaced by a bromine atom or a methyl group no such difficulty arose and accordingly the aryl radicals chosen for use in this method were *p*-bromophenyl and *p*-tolyl. The 2-, 3-, and 4-amino-4′-methyldiphenyls and the 2-, 3- and 4-amino-4′-bromodiphenyls were all shown to behave normally on bromometric titration. The detailed experimental procedure developed for these determinations is described below, and its reliability for the purpose in hand was rigorously tested by means of determinations on synthetic mixtures of known composition.

The results obtained in this way show that when the entering radical is *p*-bromophenyl the percentage substitution at the *m*-position with respect to the nitro-group is of the order of 12%, whereas for the *p*-tolyl radical the corresponding figure is 9%, as indicated in Table I (p. 2902).

These results again show that the nitro-group is predominantly *op*-directing in character in these reactions but that some reaction takes place at all three positions in the nucleus, an observation which had not previously been established experimentally, either quantitatively or qualitatively, in an arylation process. It is also revealed that the ratio of *m*- to *op*-substitution is substantially independent of the source from which the aryl radical is derived, which observation gives strong confirmation of the view that there is one mechanism common to all four reactions. The anomalous figures shown for the reactions carried out with 1-*p*-bromophenyl-3 : 3-dimethyltriazen have been shown to be due to the fact that in the decomposition of the triazen with dry hydrogen chloride some of the *p*-bromobenzenediazochloride rearranges to *p*-chlorobenzenediazobromide, the extent of the conversion depending on the time of the reaction. Such interchange reactions have been reported previously by Hantszch and Smythe (*Ber.*, 1900, **33**, 505). A further example of such rearrangement was encountered during the attempted preparation of 2-nitrodiphenyl by the interaction of 1-*o*-nitrophenyl-3 : 3-dimethyltriazen and boiling benzene in the presence of dry hydrogen chloride. The sole diaryl isolated as the product of this reaction was 2-chlorodiphenyl, which indicates an apparently complete conversion of *o*-nitrobenzenediazochloride into *o*-chlorobenzenediazonitrite before the diazo-compound decomposes (cf. Meldola and Eyre, *J.*, 1902, **81**, 988).

FIG. 1.

Nitrodiphenyls in Nujol mull.

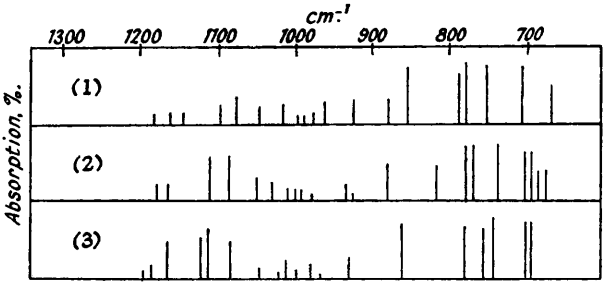
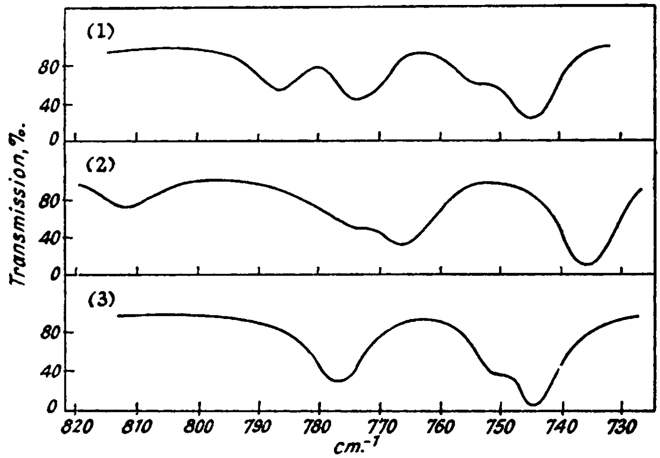


FIG. 2.



(1) 2-*Nitrodiphenyl.* (2) 3-*Nitrodiphenyl.* (3) 4-*Nitrodiphenyl.*

In order further to confirm the existence of substitution at the *m*-position with regard to the nitro-group, a reaction was carried out between benzoyl peroxide and nitrobenzene, and the resulting mixture of nitrodiphenyls was subjected to careful fractional crystallisation. In addition to 2- and 4-nitrodiphenyl, 3-nitrodiphenyl was isolated and identified by a mixed melting point.

Analysis of the Isomeric Nitrodiphenyl Mixtures by Infra-red Absorption Spectroscopy.—The reliability of the bromometric technique for the analysis of the mixtures of isomeric nitrodiphenyls outlined above was substantiated by the application of infra-red absorption spectroscopy which, in addition, gave the individual proportions of all three isomers present with the unsubstituted phenyl radical as the substituting agent. A preliminary study of the infra-red absorption spectra taken in a Nujol mull of 2-, 3-, and 4-nitrodiphenyl in the crystalline state showed that the strongest characteristic bands for each isomer are in the region 660—900 cm.$^{-1}$ (Fig. 1). A suitable solvent covering this region is nitromethane (Nielsen and Smith, *Ind. Eng. Chem.*, 1943, **15**, 609) and the spectrum of the available nitromethane (B.D.H.) showed that a clear region extended only from about 700 to 800 cm.$^{-1}$. Spectra in the region 710—810 cm.$^{-1}$ of solutions of each of the three isomers in nitromethane are presented in Fig. 2, the solution concentrations being 1 g. of solute in 25 ml. of solution.

FIG. 3.

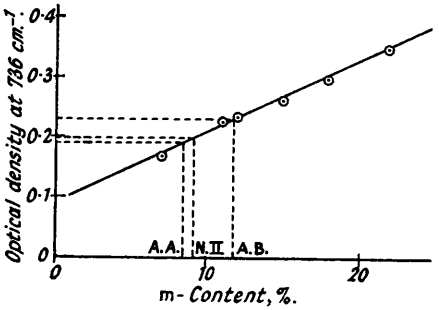
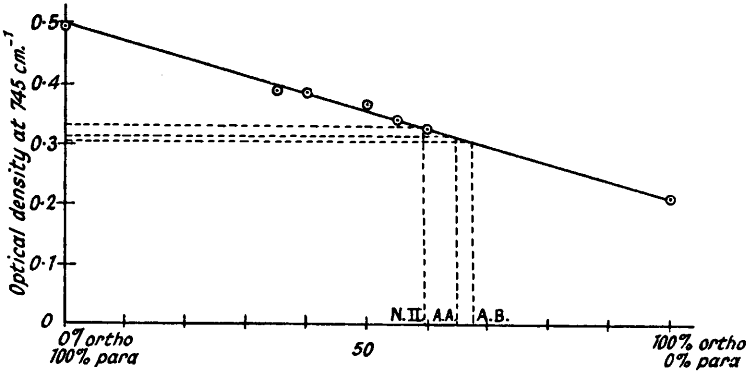


FIG. 4.



There is considerable overlapping in the characteristic absorption bands of the three isomers, and a quantitative analysis of solutions of an unknown mixture based on measurements of the absorption of solutions of the pure isomers could not be expected to give sufficient accuracy. Accordingly, a family of solutions of the three isomers was prepared, each containing a known fraction of the 2-, 3-, and 4-nitrodiphenyl such that the total nitrodiphenyl content was always 1 g. in 25 ml. of solution. In attempting to match these synthetic isomeric mixtures with one of the unknown mixtures it became clear that the *m*-content of the latter was about 10% and that the absorption at 736 cm.$^{-1}$ was a direct measure of the amount of this isomer present. The graph (Fig. 3) shows the variation of optical density at 736 cm.$^{-1}$ with *m*-content of various members of this family of solutions of synthetic mixtures. The optical densities at 736 cm.$^{-1}$, due to the pure *o*- and *p*-compounds are 0·036 and 0·063, respectively, and it has been shown that for the particular points on this graph the variation in optical density, due to change in *o*- and *p*-content, is less than 0·005, *i.e.*, less than one-thirtieth of the optical density due to the *m*-isomer. All the measurements were made in the same cell of thickness about 130 μ.

After the *m*-content had been estimated in this way, the *o*- and the *p*-proportion were obtained by measurement of optical density at 745 cm.$^{-1}$, which is sensitive to the *o* : *p*-ratio. As the absorption with the original solutions gave rather high optical densities, these measurements were carried out in solutions at one-third of the initial concentrations, *i.e.*, with 1 g. in 75 ml. of solution. In Fig. 4 a graph is shown giving the observed optical densities of the pure *o*- and *p*-isomers and of mixtures of the two. The latter were actually estimated from measurements on the original family of synthetic mixtures, after dilution to one-third of the original concentration and allowance for the extra dilution due to the small amount of *m*-isomer present. From this graph the *o* : *p*-ratio of the unknown mixtures was estimated.

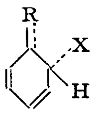
The results obtained by means of the above procedure are given below :

	Percentage composition of the mixture of isomeric nitrodiphenyls :		
Source of phenyl radical	*ortho-*	*meta-*	*para-*
Sodium benzenediazoate (N.II)	54 ± 4	9 ± 2	37 ± 4
Benzoyl peroxide * (A.A.)	59·5 ± 4	8·5 ± 2	32 ± 4
Benzoyl peroxide * (A.B.)	59·5 ± 4	11·5 ± 2	29 ± 4

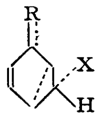
* Mixtures supplied by D. R. Augood.

Discussion.—It is evident that the normal directive influence of atoms or groups already present in the aromatic nucleus no longer operates when the entering substituent is a free radical. The available experimental evidence confirms the fact that in such reactions all substituent atoms or groups are invariably *op*-directing in type, as was originally proposed in 1934. Waters (*Trans. Faraday Soc.*, 1941, **37**, 772) has suggested that one of the essential differences between homolytic and heterolytic substitution is due to the fact that an attacking ion or polar reagent perturbs the aromatic molecule when still at a distance, converting it by a tautomeric change into a transition state which is quite different from the mesomeric stable state, whereas a free-radical reagent, being non-polar, would attack the unperturbed molecule. Waters (*J.*, 1948, 727) has attempted to explain some of the anomalies of the theory of electrophilic substitution by estimating the energy difference between the normal state and each of the possible transition states of the molecule and the entering substituent. In homolytic substitution the initial attack by a free radical (X•) on the aromatic nucleus $C_6H_5{\cdot}R$ may be regarded as an addition reaction to give transition states which may be represented as (I), (II), and (III), which then achieve stability by the loss of a hydrogen atom which is probably never free. The predominance of substitution at the *o*- and *p*-positions is in agreement with the greater stability of (I) and (III) (cf. Loebl, Stein, and Weiss, *J.*, 1949, 2075).

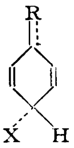
(I)



(II)



(III)



A quantum-mechanical interpretation of aromatic substitution by means of free radicals has been provided by Wheland (*J. Amer. Chem. Soc.*, 1942, **64**, 900), who used a molecular-orbital method which also embraces within its treatment substitution reactions by electrophilic and nucleophilic reagents. In the case of radical substitution, one electron is required which with the odd electron provided by the radical can form a new covalent bond in the activated complex formed between the nucleus and the substituting agent. The energy (ΔW) required to perturb the stable structure of the aromatic compound so as to produce an odd electron at the various positions in the nucleus was calculated, and these energies are regarded as the controlling factors governing the reactivity of the various positions in the nucleus. The greater the value of ΔW for any particular position in the nucleus, the less energetically favoured is that particular transition state, and therefore that position will be relatively less reactive towards the approaching radical.

These calculations show that all substituents activate mainly the *o*- and *p*-positions, but that some *m*-substitution should be expected in all reactions, although only as a minor constituent. Calculations which lead to a similar conclusion with regard to free-radical substitution have been made by Coulson (*J. Chim. physique*, 1949, **45**, 243; *Research*, 1951, **4**, 307 ; and personal communications), making use of the concept of free valence.

Addendum.—After this paper was written DeTar and Scheifele (*J. Amer. Chem. Soc.*, 1951, **73**, 1442) published the results of their investigation on the orienting influence of the nitro-group in the formation of nitrodiphenyls by the reaction of nitrobenzene with nitrosoacetanilide, with benzoyl peroxide, and with benzenediazonium chloride and alkali. The mixture of nitrodiphenyls was determined by an ultra-violet spectroscopic method and it was shown that the nitro-group was largely *op*-directing but gave rise to the formation of a small proportion of the *m*-isomer. These results are in substantial agreement with those reported above.

EXPERIMENTAL.

(All m.p.s are uncorrected. Microanalyses are by Drs. Weiler and Strauss, Oxford.)

Preparation of Reference Compounds.—*4-Bromo-4′-nitrodiphenyl.* 4-Nitrodiphenyl was treated with bromine in acetic acid at 100° as described by Le Fèvre and Turner (*J.*, 1926, 2041). 4-Bromo-4′-nitrodiphenyl crystallised from acetic acid in colourless needles, m. p. 172·5°. Le Fèvre and Turner record m. p. 170—172°.

4-Bromo-3′-nitrodiphenyl. 3-Nitrodiphenyl, prepared from *m*-nitrobenzoyl peroxide and benzene (Hey and Walker, *J.*, 1948, 2217), was brominated as described by Blakey and Scarborough (*J.*, 1927, 3000). 4-Bromo-3′-nitrodiphenyl was obtained in light brown plates, m. p. 94° after crystallisation from ethanol. Blakey and Scarborough record m. p. 95°.

4-Bromo-2′-nitrodiphenyl. 2-Nitrodiphenyl (9 g.) was stirred with bromine (3·2 ml.), anhydrous ferric chloride (0·5 g.), and water (25 ml.) for 5 hours at room temperature (cf. Le Fèvre and Turner, *loc. cit.*). After being kept overnight at room temperature the mixture was stirred with excess of aqueous sodium carbonate and the resulting oil was extracted with ether, the ethereal extract washed (aqueous sodium carbonate) and dried (K_2CO_3), and the ether evaporated. The resulting oil was dissolved in ethanol and cooled to −80°. The crude 4-bromo-2′-nitrodiphenyl which separated crystallised from ethanol in pale yellow plates, m. p. 64° (1 g.). Schultz, Schmidt, and Strasser (*Annalen*, 1881, **107**, 351) record m. p. 65°. Attempts to increase the yield of 4-bromo-2′-nitrodiphenyl by brominating 2-nitrodiphenyl at higher temperatures, both in the absence and in the presence of acetic acid and ferric chloride failed, the main product consisting of an oil from which only about 10% of 4-bromo-2′-nitrodiphenyl could be isolated. The more vigorous brominations at 100° in the presence of ferric chloride resulted in the production of a *dibromo-2-nitrodiphenyl* (*ca.* 20%), which crystallised from ethanol in light brown prisms, m. p. 131—131·5° (Found: C, 40·1; H, 1·8. $C_{12}H_7O_2NBr_2$ requires C, 40·3; H, 2·0%).

2-, 3-, and *4-Amino-4′-bromodiphenyl hydrochlorides.* The three isomeric amino-4′-bromodiphenyl hydrochlorides were prepared from the 4′-bromonitrodiphenyls by reduction in ethanolic solution with stannous chloride and concentrated hydrochloric acid. The bases were extracted with ether from the reaction products which had been made strongly alkaline, and the ethereal solutions were dried (K_2CO_3). Passage of a stream of dry hydrogen chloride through the ethereal solutions precipitated the base hydrochlorides, which were separated by filtration, washed well with dry ether, and kept in a vacuum for 12 hours before use.

4-Methyl-4′-nitrodiphenyl. 4-Methyldiphenyl (Gomberg and Pernert, *J. Amer. Chem. Soc.*, 1926, **48**, 1373) was nitrated by the method of Grieve and Hey (*J.*, 1932, 1888). 4-Methyl-4′-nitrodiphenyl separated from ethanol, and had m. p. 140°. Grieve and Hey record m. p. 140°.

4-Methyl-3′-nitrodiphenyl. (*a*) A suspension of 4-acetamido-4′-methyldiphenyl (2·5 g.) in a mixture of acetic acid (25 ml.) and concentrated sulphuric acid (4 ml.) was well-stirred at 30° during the addition of a mixture of fuming nitric acid (2 ml.) and concentrated sulphuric acid (1·5 ml.). The resulting brown solution was kept at 30° for 2 hours and then poured on ice. The yellow precipitate was filtered off and washed with water. The crude *4-acetamido-4′-methyl-3-nitrodiphenyl* crystallised from ethanol in yellow needles, m. p. 162·5—163° (2·1 g.). Crystallisation from light petroleum (b. p. 40—60°)–benzene gave pale yellow needles, m. p. 165·5—166° (Found: C, 66·9; H, 4·8; N, 10·2. $C_{15}H_{14}O_3N_2$ requires C, 66·65; H, 5·2; N, 10·4%). 4-Acetamido-4′-methyl-3-nitrodiphenyl (2·0 g.) was boiled under reflux with 70% sulphuric acid (50 ml.) for 1 hour. A small portion of the resulting colourless suspension was made alkaline with aqueous sodium hydroxide, and the *4-amino-4′-methyl-3-nitrodiphenyl* thus obtained was collected, and crystallisation from ethanol and then from light petroleum (b. p. 60—80°)–benzene gave bright red prisms, m. p. 186·5—187° (Found: C, 68·4; H, 5·3; N, 12·1. $C_{13}H_{12}O_2N_2$ requires C, 68·45; H, 5·3; N, 12·3%). The main bulk of the colourless suspension of 4-amino-4′-methyl-3-nitrodiphenyl sulphate was mixed with 50% sulphuric acid (10 ml.) and cooled to 0°, and the stirred suspension diazotised with excess of aqueous sodium nitrite. The diazonium solution was added to cold aqueous hypophosphorous acid which had been prepared by adding concentrated sulphuric acid (20 ml.) to an ice-cold, well-stirred suspension of calcium hypophosphite (60 g.) in water (60 ml.) and filtering off the calcium sulphate. The mixture of diazonium solution and hypophosphorous acid was kept at 0° for 2 days and then extracted with ether. Evaporation left *4-methyl-3′-nitrodiphenyl*, m. p. 65—74° (0·91 g.), which crystallised from ethanol and then from light petroleum (b. p. 40—60°) in pale yellow plates, m. p. 77·5° (Found: C, 73·35; H, 5·2; N, 6·4. $C_{13}H_{11}O_2N$ requires C, 73·25; H, 5·2; N, 6·6%).

(*b*) The interaction of diazotised *m*-nitroaniline and toluene in the presence of sodium acetate provides confirmation for earlier observations (France, Heilbron, and Hey, *J.*, 1938, 1283) of the predominant *o*-directing property of the methyl group in reactions of this type, and for this reason the reaction did not constitute a satisfactory route to 4-methyl-3′-nitrodiphenyl. *m*-Nitroaniline (70 g.), suspended in concentrated hydrochloric acid (160 ml.), was diazotised at 0° by slow addition of a solution of sodium nitrite (40 g.) in water (60 ml.). A solution of sodium acetate (88 g. of the hydrated salt) in water (200 ml.) was added to a well-stirred, cooled mixture of the diazonium solution and toluene (1 l.), and the reaction mixture was left at room temperature for 12 hours and then heated to 60—70° for a further 12 hours before the dark brown toluene layer was separated, washed (aqueous sodium hydroxide), and dried ($CaCl_2$). The residual aqueous emulsion was continuously extracted with benzene for 16 hours and this extract was added to the dry toluene solution. Removal of the solvents left a dark tar, which on distillation gave (i) a yellow oil (9·6 g.), b. p. 40—120°/0·07 mm., (ii) a yellow oil (31·9 g.), b. p. 120—129°/0·07 mm., and (iii) a brown oil (15·4 g.), b. p. 129—164°/0·07 mm. Fractions (ii) and (iii) deposited 2-*methyl*-3′-*nitrodiphenyl* (20·3 g.), which crystallised from ethanol and then from light petroleum (b. p. 40—60°) in yellow needles, m. p. 72·5—73° (Found: C, 72·8; H, 5·05; N, 6·2. $C_{13}H_{11}O_2N$ requires C, 73·25; H, 5·2; N, 6·6%).

From the oils which remained after the separation of the main product, several crops of mixed crystals, m. p. 30—50°, and *m*-dinitrobenzene, m. p. 89—90°, separated. The crops of mixed crystals were bulked (4·35 g.), dissolved in light petroleum (b. p. 40—60°) (100 ml.), and allowed to percolate through a column (90 × 3 cm.) packed with alumina (200 g.; B.D.H. " For chromatographic analysis " grade) which had previously been heated to about 400°. The column was eluted with ten successive portions of benzene–light petroleum (b. p. 60—80°) mixtures ranging from 10% benzene–90% light petroleum to 50% benzene–50% light petroleum. The residues from fractions 3 and 4, after crystallisation from light petroleum (b. p. 40—60°), gave 2-methyl-3′-nitrodiphenyl in white needles, m. p. 72° both alone and when mixed with the main product of this reaction (m. p. 72·5°). The residues from fractions 5, 6, and 7 consisted of mixed crystals, m. p. 54—58°, and the residues from fractions 8, 9, and 10, after crystallisation from light petroleum (b. p. 40—60°), gave 4-methyl-3′-nitrodiphenyl, m. p. 75—77°, which gave a strong depression in m. p. on admixture with 2-methyl-3′-nitrodiphenyl (m. p. 72·5°) and showed no depression of m. p. on admixture with 4-methyl-3′-nitrodiphenyl which had been prepared from 4-acetamido-4′-methyldiphenyl as described in (*a*) above.

Structure of 2-*methyl*-3′-*nitrodiphenyl*. 2-Methyl-3′-nitrodiphenyl (5 g.) was reduced in the usual manner in ethanol solution with stannous chloride and hydrochloric acid. A portion (3·2 g.) of the resulting base (5·1 g.) was dissolved in 5N-sulphuric acid (20 ml.) and cooled to 0°, and the suspension of base sulphate diazotised with a solution of sodium nitrite (1·4 g.) in water (2 ml.). The diazonium solution was added to a cold solution of sodium hypophosphite (27 g.) in 5N-sulphuric acid (100 ml.), and the mixture was kept at 0° for two days. Extraction of the reaction mixture gave 2-methyldiphenyl which distilled as a colourless oil, b. p. 123°/13 mm. (1·1 g.), n_D^{20} 1·5933. Sherwood, Short, and Stansfield (*J.*, 1932, 1834) record b. p. 130—136°/27 mm. Oxidation of this hydrocarbon with boiling aqueous potassium permanganate afforded diphenyl-2-carboxylic acid, m. p. 112—113°, which showed no depression of m. p. on admixture with an authentic specimen, m. p. 113°. A second portion (2·0 g.) of the base was distilled at 94—100°/0·05 mm., and crystallisation from light petroleum (b. p. 40—60°) gave 3-*amino*-2′-*methyldiphenyl* in colourless prisms, m. p. 37·5—38° (Found: C, 85·4; H, 7·1; N, 7·6. $C_{13}H_{13}N$ requires C, 85·2; H, 7·1; N, 7·6%). Passage of keten through a dry benzene solution of the base gave plates of 3-*acetamido*-2′-*methyldiphenyl*, m. p. 94° (Found: C, 80·3; H, 6·8; N, 6·0. $C_{15}H_{15}ON$ requires C, 80·0; H, 6·7; N, 6·2%). Quantitative bromination of 3-amino-2′-methyldiphenyl hydrochloride (by the method described below) required three molecular proportions of bromine, thus confirming the *m*-position of the amino-group in the diphenyl molecule (Found: for 0·1 g. of base hydrochloride of 99·0% purity: 26·98 ml. of 0·1N-Br–BrO_3. Calc. for 3 mol. proportions: 27·34 ml.).

4-*Methyl*-2′-*nitrodiphenyl*. Diazotised *p*-toluidine was allowed to react with excess of nitrobenzene in the presence of aqueous potassium hydroxide as described by Grieve and Hey (*J.*, 1932, 1888). The resulting mixture of 4-methylnitrodiphenyls was allowed to crystallise, and the precipitated 4-methyl-4′-nitrodiphenyl was separated. The residual oil was twice fractionated through a 12-cm. Dufton column, and the middle cuts from the second fractionation (b. p. 179°/10 mm., n_D^{20} 1·6116) were bulked and induced to crystallise by strong cooling (solid carbon dioxide). 4-Methyl-2′-nitrodiphenyl crystallised from light petroleum (b. p. 40—60°) in pale yellow needles, m. p. 37—37·5°. The identity of the product as 4-methyl-2′-nitrodiphenyl was confirmed by reduction and acetylation to give the known 2-acetamido-4′-methyldiphenyl. The 4-methylnitrodiphenyl was reduced (stannous chloride) and acetylated by passing keten through the dry benzene solution of the base for 30 minutes. The resulting colourless solution was washed (aqueous sodium carbonate) and dried (K_2CO_3), and the benzene evaporated. The residual 2-acetamido-4′-methyldiphenyl crystallised from ether in colourless needles, m. p. 104° undepressed on admixture with an authentic specimen (m. p. 102—103°). Grieve and Hey (*loc. cit.*) record m. p. 103°.

2-, 3- and 4-*Amino*-4′-*methyldiphenyl hydrochlorides*. The three isomeric amino-4′-methyldiphenyl hydrochlorides were prepared as described above for the amino-4′-bromodiphenyl hydrochlorides.

Volumetric Determination of the Reference Compounds.—Each of the two series of three isomeric base hydrochlorides were estimated (*a*) as total base hydrochlorides by titration with alkali and (*b*) by nuclear bromination with a standard bromide–bromate mixture.

General procedure. (*a*) A known weight of the base hydrochloride (approx. 0·1 g.) was dissolved in a mixture of " AnalaR " acetone (25 ml.) and 0·1N-aqueous sodium hydroxide (20·00 ml.). In some estimations it was necessary to warm the mixture in order to facilitate dissolution. The excess of alkali was then back-titrated, when cold, with standard 0·1N-aqueous hydrochloric acid, methyl-red being used as indicator.

(*b*) Redistilled carbon tetrachloride (10 ml.) was added to a known weight of base hydrochloride (approx. 0·1 g.), followed by water (30 ml.) and excess of standard bromide–bromate solution (20·00 ml.; 0·2N. with respect to bromine). Finally, sulphuric acid (5 ml.; 10N.) was added and the flask was quickly closed by a ground-in glass stopper and the mixture vigorously shaken for 30 minutes, all particles of base hydrochloride then having dissolved. The flask was then cooled to avoid loss of solution and bromine vapour by spurting on removal of the stopper due to pressure of carbon tetrachloride vapour inside the flask. Potassium iodide (15 ml.; 10% aqueous) was added, the mixture well shaken, and the iodine liberated by the excess of bromine titrated with standard thiosulphate (0·2N.). "AnalaR" potassium bromate which had been dried at 100° for 1 hour was used for preparation of the standard bromide–bromate solution ($KBrO_3$, 11·1340 g., and KBr, 140 g., in 2 l. of solution).

Results.—

Amino-4′-bromodiphenyl hydrochloride series

	Purity, %, by:	
	acid–base titration	nuclear bromination
4-Amino-	99·7 ± 0·2	98·9 ± 0·4
3-Amino-	99·8 ,,	96·0 ,,
2-Amino-	98·3 ,,	98·4 ,,

Amino-4′-methyldiphenyl hydrochloride series

	Purity, %, by:	
	acid–base titration	nuclear bromination
4-Amino-	98·8 ± 0·2	99·6 ± 0·4
3-Amino-	99·3 ,,	99·5 ,,
2-Amino-	98·5 ,,	98·7 ,,

Volumetric Determination of Mixtures of 2-, 3-, *and* 4-*Nitrodiphenyl*.—Reactions were carried out between nitrobenzene and (*a*) the sodium aryldiazoates (the Gomberg reaction), (*b*) the aryl diazoacetates (the labile tautomer of the acylarylnitrosamine), (*c*) the aroyl peroxides, and (*d*) the 1-aryl-3 : 3-dimethyltriazens in which the aryl group was successively *p*-bromophenyl and *p*-tolyl. The nitrobenzene used in these reactions was purified by shaking it with solid sodium hydroxide for 12 hours, followed by steam-distillation and drying (NaOH). The nitrobenzene was finally fractionated through a 70 × 3-cm. Fenske column and collected at 90—92°/14 mm. After completion of the reaction the dark nitrobenzene solution was heated with two successive portions of aqueous sodium hydroxide (20%), and after separation and washing with dilute acid the solution was finally dried (NaOH). After removal of excess of nitrobenzene by distillation through a 30-cm. Dufton column, the dark tarry residue was distilled and the resulting crude mixture of isomeric nitrodiphenyls was redistilled, care being taken to avoid contamination of the nitro-compounds with the last traces of nitrobenzene. The base hydrochlorides were prepared from the mixture of nitro-compounds after a normal stannous chloride reduction. Unless otherwise stated, the above procedure was used in all experiments, and the mixture of bases was not purified by distillation before preparation of the hydrochloride.

Control Determinations.—Numerous control determinations were carried out of which the following examples are typical. (*a*) Mixture of 4-bromo-4′- and -3′-nitrodiphenyls in excess of nitrobenzene. A mixture of 4-bromo-4′-nitrodiphenyl (91·34%) and 4-bromo-3′-nitrodiphenyl (8·66%) was heated to 150° with nitrobenzene (250 ml.) for 2 hours and then subjected to the procedure outlined above. The determination of base hydrochloride by acid–base titration showed 98·5% of amino-4′-bromodiphenyl hydrochloride. Nuclear bromination gave 6·7% of 3-amino-4′-bromodiphenyl hydrochloride.

(*b*) Mixture of 4-methyl-4′-, -3′-, and -2′-nitrodiphenyls in excess of nitrobenzene. A mixture of 4-methyl-4′- and -2′-nitrodiphenyl (88·95%) with 4-methyl-3′-nitrodiphenyl (11·05%) was dissolved in nitrobenzene (250 ml.), heated to 150° for 2 hours, and treated as described above. The determination of base hydrochloride by acid–base titration showed 99·2% of amino-4′-methyldiphenyl hydrochloride. Nuclear bromination gave 15·3% of 3-amino-4′-methyldiphenyl hydrochloride. A mixture of 4-methyl-4′- and -2′-nitrodiphenyl (93·5%) and 4-methyl-3′-nitrodiphenyl (6·5%), subjected to the same procedure as described above, gave base hydrochloride by acid–base titration 98·8%, and 8·8% of 3-amino-4′-methyldiphenyl hydrochloride by nuclear bromination.

Substitution Reactions of Nitrobenzene.

(a) *The Gomberg Reaction* (Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2339; Gomberg and Pernert, *ibid.*, 1926, **48**, 1372).—*The action of sodium* p-*bromobenzenediazoate on nitrobenzene.* (i) A solution of *p*-bromobenzenediazonium chloride was prepared in the usual manner by diazotisation of *p*-bromoaniline (43 g.) in concentrated hydrochloric acid (50 ml.) with 33% aqueous sodium nitrite (36 ml.). Chilled nitrobenzene (400 ml.) was added to the diazonium solution, followed by the slow addition of 5N-aqueous sodium hydroxide (150 ml.). When the addition had been completed, the nitrobenzene layer, which had become deep red, was separated and, on treatment as described above, gave a mixture of isomeric 4′-bromonitrodiphenyls, b. p. 130—175°/3 mm. (11 g., 16%). (ii) A second experiment, using the same procedure as described above, gave the isomeric 4′-bromonitrodiphenyls in 25% yield, b. p. 139—160°/0·5 mm.

The action of sodium p-*toluenediazoate on nitrobenzene.* (i) The diazonium solution, prepared in the normal manner from *p*-toluidine (21 g.) in concentrated hydrochloric acid (50 ml.) and sodium nitrite (20 g.) in water (30 ml.), was allowed to react with nitrobenzene (700 ml.) and worked up as described above. The isomeric 4′-methylnitrodiphenyls (19 g.) were obtained in 45% yield, with b. p. 97—108°/0·015 mm. (ii) In a second experiment the isomeric 4′-methylnitrodiphenyls were obtained, in 27% yield with b. p. 108—110°/0·015 mm., by the same procedure. In this instance the free base was isolated by distillation (b. p. 97—102°/0·02 mm.) before preparation of the hydrochloride. (iii) In a third reaction the isomeric 4′-methylnitrodiphenyls, b. p. 184—192°/9 mm., were obtained in 36% yield. The free base distilled at 175—180°/9 mm.

(b) *The Peroxide Reaction* (Hey and Walker, *J.*, 1948, 2213).—*The action of* p-*bromobenzoyl peroxide on nitrobenzene.* (i) *p*-Bromobenzoyl peroxide (Price, Kell, and Krebs, *J. Amer. Chem. Soc.*, 1942, **64**, 1104) (11·5 g.) was heated with nitrobenzene (140 ml.) at 150—160° for 4 hours. The resulting dark solution was worked up as described in section (a), but because there was a tendency for an emulsion to form when the nitrobenzene solution was being washed with dilute acid, chloroform (150 ml.) was added to aid the separation of the organic layer. The 4′-bromonitrodiphenyls (3·4 g.) were collected at 170—225°/0·2 mm. (ii) By the same procedure as above, 4′-bromonitrodiphenyls (5·0 g.), b. p. 154—170°/0·1 mm., were obtained from *p*-bromobenzoyl peroxide (12 g.).

The action of p-*toluoyl peroxide on nitrobenzene.* (i) *p*-Toluoyl peroxide, m. p. 133—134° (decomp.), was prepared by the procedure described for the preparation of aroyl peroxides by Hey and Walker (*loc. cit.*). Swain, Stockmayer, and Clark (*J. Amer. Chem. Soc.*, 1950, **72**, 5433) record m. p. 136—137° (decomp.). A solution of *p*-toluoyl peroxide (8 g.) in nitrobenzene (300 ml.) was heated at 150° for 4 hours and then left overnight before the dark solution was subjected to the usual working-up procedure. 4′-Methylnitrodiphenyls (5·4 g.), b. p. 106—110°/0·02 mm., were obtained. The free base (b. p. 94—100°/0·09 mm.) was isolated by distillation before preparation of the hydrochloride. (ii) By the same procedure as above, 4′-methylnitrodiphenyls (3·7 g.), b. p. 98—102°/0·05 mm., were obtained from *p*-toluoyl peroxide (6 g.). The base (b. p. 100—108°/0·1 mm.) was isolated by distillation before preparation of the hydrochloride.

(c) *The Acylarylnitrosamine Reaction.*—*The action of* p-*bromo*-N-*nitrosoacetanilide on nitrobenzene.* (i) The method of France, Heilbron, and Hey (*J.*, 1940, 369) was used for the preparation of the anilide, m. p. 87—88° (decomp.). Bamberger and Baudisch (*Ber.*, 1909, **42**, 3590) record m. p. 86—87° (decomp.). A solution of *p*-bromo-N-nitrosoacetanilide (5·9 g.) in nitrobenzene (250 ml.) was maintained at room temperature for 24 hours and was then heated at 150° for 2 hours before the product was subjected to the usual working-up procedure. The 4′-bromonitrodiphenyls (2·4 g.), b. p. 160—174°/1·0 mm., were obtained in 34% yield. (ii) By the procedure described above, a yield of 3·7 g. of 4′-bromonitrodiphenyls (44%) was obtained from the reaction of the nitroso-compound (7 g.) with nitrobenzene (250 ml.).

The action of nitrosoaceto-p-*toluidide on nitrobenzene.* (i) Nitrosoaceto-*p*-toluidide, m. p. 81·5° (decomp.), was prepared by the method described by France, Heilbron, and Hey (*loc. cit.*). Grieve and Hey (*J.*, 1935, 691) record m. p. 80° (decomp.). A solution of this toluidide (10 g.) in nitrobenzene (350 ml.) was maintained at 16° for 12 hours and then heated at 100° for 12 hours before the product was fractionally distilled without further treatment to yield, first, acetic acid, b. p. 20—30°/12 mm., and, secondly, nitrobenzene, b. p. 88°/12 mm. The residue was distilled to yield the 4′-methylnitrodiphenyls (3·8 g., 32%), b. p. 110—115°/0·04 mm. The corresponding base was isolated by distillation, b. p. 98—108°/0·015 mm., before preparation of the base hydrochloride. (ii) The 4′-methylnitrodiphenyls (1·7 g., 28%) were obtained by the decomposition of nitrosoaceto-*p*-toluidide (5 g.) in nitrobenzene (250 ml.), the product being subjected to the normal procedure. The free base, b. p. 91—100°/0·015 mm., was isolated by distillation before preparation of the hydrochloride.

(d) *The Triazen Reaction* (Elks and Hey, *J.*, 1943, 441).—*The action of* 1-p-*bromophenyl*-3 : 3-*dimethyltriazen on nitrobenzene.* (i) A solution of the triazen (17 g.) (specimen provided by Dr. J. M. Osbond) in nitrobenzene (200 ml.) was heated at 120° while dry hydrogen chloride was passed into the solution for 1 hour; the solution had then become deep red, and heating was discontinued. There was no precipitate of dimethylamine hydrochloride, even after the mixture had been kept overnight. The mixture was subjected to the usual procedure and the emulsion which had formed in the washing process was broken by the addition of an equal volume of chloroform. Distillation of the residue which remained after the solvents had been removed gave an orange-coloured liquid (11·2 g.), b. p. 130—164°/0·2 mm., which showed less tendency to crystallise than had previous products. (ii) A slow stream of hydrogen chloride was passed for 4 hours through a solution of 1-*p*-bromophenyl-3 : 3-dimethyltriazen (7·0 g.) in nitrobenzene (250 ml.) at 160°. The reaction product, an orange-coloured oil (4·6 g.), b. p. 116—148°/0·18 mm., was obtained from the nitrobenzene solution as in the previous reaction. Both products were shown on reduction and analysis of the base hydrochlorides to contain an impurity. A sample of the free base from reaction (ii) was regenerated from the hydrochloride with aqueous sodium hydroxide, extracted with ether, and dried over sodium hydroxide to ensure removal of traces of hydrogen chloride. The base, which distilled at 130—135°/0·13 mm., was found by sodium fusion to contain both bromine and chlorine. (iii) Prolonged passage of hydrogen chloride (9 hours) through a solution of 1-*p*-bromophenyl-3 : 3-dimethyltriazen (5 g.) in nitrobenzene (250 ml.) at 150°, followed by the normal working-up procedure, afforded a mixture of nitro-compounds (1·88 g.), b. p. 110—132°/0·05 mm. The corresponding mixture of free bases was isolated by distillation at 97—110°/0·015 mm. and found to contain both bromine and chlorine.

The anomalous results obtained by the volumetric determination of the samples of base hydrochlorides obtained from the three reaction products are due to a partial interchange of nuclear bromine and chlorine which takes place in the presence of the excess of hydrogen chloride necessary for the decomposition of the triazen.

The action of 3 : 3-*dimethyl*-1-p-*tolyltriazen on nitrobenzene.* (i) A current of dry hydrogen chloride was passed into a solution of 3 : 3-dimethyl-1-*p*-tolyltriazen (10 g.) (Hunter, *J.*, 1937, 324) in nitrobenzene (300 ml.) at 150° for 8 hours. The black reaction product was kept overnight before it was subjected to the usual working-up procedure. The isomeric 4′-methylnitrodiphenyls (7·1 g.), b. p. 104—110°/0·015 mm., were obtained in 54% yield. (ii) The isomeric 4′-methylnitrodiphenyls (3·3 g., 50%), b. p. 99—100°/0·012 mm., were obtained from the triazen (5 g.) by a method similar to that described above. The free base was isolated by distillation (b. p. 92—106°/0·07 mm.) before preparation of the hydrochloride.

The quantitative results obtained from the analysis of the products of the above reactions with nitrobenzene are summarised in the following table.

TABLE I.

Reaction of $R{\cdot}C_6H_4{\cdot}$ *on nitrobenzene.*

Reaction	R = Br		R = Me	
	Acid–base titration : base hydrochloride, %	Nuclear bromination : 3-aminodiphenyl, %	Acid–base titration : base hydrochloride, %	Nuclear bromination : 3-aminodiphenyl, %
Sodium diazoate	99·2	12·5	—	—
	98·4	12·3	—	—
	—	—	98·3	9·4
	—	—	98·3	8·3
	—	—	98·7	9·1
Acyl peroxide	98·1	11·8	—	—
	99·5	11·6	—	—
	—	—	98·7	9·5
	—	—	98·1	9·2
Acylarylnitrosamine	98·8	11·9	—	—
	100·0	12·7	—	—
	—	—	100·0	8·7
	—	—	99·3	8·0
1-Aryl-3 : 3-dimethyltriazen	[104·5]	[21·7]	—	—
	[104·8]	[28·6]	—	—
	[109·7]	[24·5]	—	—
	—	—	96·7	7·0
	—	—	96·1	8·5
		Average 12·1%		Average 8·6%

The action of 3 : 3-*dimethyl*-1-o-*nitrophenyltriazen on benzene.* This *triazen*, prepared by the method of Elks and Hey (*loc. cit.*), crystallised from light petroleum (b. p. 40—60°) in slender yellow needles, m. p. 32° (Found : C, 49·45; H, 5·4. $C_8H_{10}O_2N_4$ requires C, 49·45; H, 5·15%). Hydrogen chloride was passed for 3 hours through a solution of the triazen (24 g.) in boiling benzene (200 ml.). The benzene solution was then washed with water and dried ($CaCl_2$). Evaporation of the benzene left a residue, which on distillation gave (*a*) a pale yellow liquid (5 g.), b. p. 110—135°/12 mm., and (*b*) a yellow liquid (6·4 g.), b. p. 135—170°/12 mm. Fraction (*a*) partly crystallised during 2 years at room temperature in a sealed tube, and further crystallisation from light petroleum (b. p. 40—60°) gave 2-chlorodiphenyl in colourless prisms, m. p. 31·5—32°, undepressed on admixture with an authentic specimen, m. p. 30—31°. Fraction (*b*) gave after redistillation *o*-chloronitrobenzene (1·5 g.), m. p. 31·5—32°, 2-chlorodiphenyl (2·4 g.), m. p. 31°, and 3 : 3-dimethyl-1-*o*-nitrophenyltriazen (1·7 g.), m. p. 30—32°. No 2-nitrodiphenyl was found in any of the fractions.

The action of 3 : 3-*dimethyl*-1-m-*nitrophenyltriazen on toluene.* The triazen, prepared by the general method of Elks and Hey (*loc. cit.*), was obtained in deep red tufts of prisms, m. p. 100°, which showed no depression of the m. p. on admixture with an authentic specimen (yellow needles, m. p. 99·5°). A second preparation afforded this triazen in yellow needles, m. p. 100°, with no trace of the red crystalline form. Both crystalline forms of this triazen showed remarkable stability towards hydrogen chloride in boiling toluene. Passage of hydrogen chloride through a boiling toluene solution of the triazen (red prisms) resulted in 50% recovery of the starting material in yellow needles. Prolonged passage of hydrogen chloride (24 hours) through a boiling toluene solution of the triazen afforded *m*-chloronitrobenzene (10%), unchanged triazen (20%), and a mixture of isomeric methyl-3′-nitrodiphenyls from which 2-methy-3′-nitrodiphenyl, m. p. 72·5—73°, was isolated (see above).

The Action of Benzoyl Peroxide on Nitrobenzene and the Isolation of 3-*Nitrodiphenyl.*—A solution of benzoyl peroxide (120 g.) in nitrobenzene (1·5 l.) was kept at 140° for 4 hours. Nitrobenzene (500 ml.) was distilled from the resulting dark solution and the residue was subjected to the normal working-up procedure. After distillation of the remaining nitrobenzene, the following six fractions were collected from the residue, which was distilled through a vacuum-jacketed column (50 cm., packed with metal gauze) kindly lent by Dr. G. H. Williams. Unless otherwise stated, the column was allowed to attain equilibrium for 5 minutes before samples of distillate were removed :

Fraction	Weight, g.	B. p.	Pressure, mm.	Remarks
i	18·0	150—161°	6	Yellow oil removed continuously
ii	17·2	158—163	7	
iii	3·0	162—166	5	Reflux ratio : 1 : 8
iv	2·6	165—169	5	Dark yellow oil
v	14·5	135—140	0·7	Residue from fractionation distilled without column
vi	3·1	170—200	0·1	

Fractions (i) and (ii) were crystallised (light petroleum, b. p. 40—60°), and the non-crystalline residues subjected to refractionation to yield 2-nitrodiphenyl (15 g.), m. p. 37·5°, 4-nitrodiphenyl (1·4 g.), m. p.

112—113°, and diphenyl (0·1 g.), m. p. and mixed m. p. 69° (cf. DeTar, *J. Amer. Chem. Soc.*, 1950, **72**, 1028). The remaining non-crystalline residues from fractions (i) and (ii) were reduced with stannous chloride and acetylated with acetic anhydride. Crystallisation from ethanol gave impure specimens of 2-acetamidodiphenyl, m. p. 116—117°, and 4-acetamidophenyl, m. p. 167—169°. Fractions (iii) and (iv) were crystallised (light petroleum, b. p. 40—60°) and gave 4-nitrodiphenyl (4·1 g.), m. p. 113°, and 2-nitrodiphenyl (0·7 g.), m. p. 36°. The non-crystalline residues, on reduction and acetylation, yielded mixtures of 2- and 4-acetamidophenyl only. Fraction (v) crystallised from ethanol in orange needles, m. p. 108—111° (impure 4-nitrodiphenyl; 12·4 g.). The residual oil from this crystallisation slowly deposited a semi-solid mass, which was separated and recrystallised first from ethanol and then from light petroleum (b. p. 40—60°), giving 3-nitrodiphenyl (0·25 g.) in buff plates, m. p. 57·5—58·5° undepressed on admixture with an authentic specimen, m. p. 58°. The identity of the 3-nitrodiphenyl thus obtained was further confirmed by reduction and acetylation to give 3-acetamidodiphenyl in white needles, m. p. and mixed m. p. 147·5°.

The authors express their thanks to Dr. W. C. Price, Sc.D., F.R.I.C., for valuable discussions and assistance on the infra-red spectroscopic work. Thanks are also accorded to the Department of Scientific and Industrial Research for a Maintenance Grant awarded to one of them (T. S. R.).

King's College, University of London,
Strand, London, W.C.2.

[*Received, May 28th*, 1951.]