23. *Decomposition Reactions of the Aromatic Diazo-compounds. Part I. Evidence for Non-ionic Reaction.*

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Grieve and Hey (J., 1934, 1799, 1966) brought forward strong experimental evidence for the view that the decomposition of the aromatic diazo-compounds was non-ionic in character and gave rise to the transient existence of free aryl radicals. In particular they showed that, in a series of solvents, the rate of decomposition of benzene *iso*(*anti*)-diazoacetate was influenced but slightly by the nature of the solvent, and that, in the preparation of derivatives of diphenyl by the reactions of Bamberger and Gomberg, a substituting phenyl group gave invariably a para-substituted product, not acting therefore either as a kationoid or as an anionoid reagent.

The possibility of this non-ionic decomposition ($Ph{\cdot}N_2{\cdot}X \longrightarrow Ph{\cdot} + N_2 + {\cdot}X$, not $Ph^+ + N_2 + X^-$ (compare Bradley and Robinson, J., 1928, 1312) in many of the familiar diazo-reactions had independently occurred to the author in 1931 (*Proc. Durham Phil. Soc.*, 1932, **8**, 459) when endeavouring to collect information concerning the reactions of the neutral free radicals (compare Waters, "Physical Aspects of Organic Chemistry," 1935, Chap. VII), for it seemed unlikely that the decompositions of benzeneazotriphenylmethyl (Wieland, *Ber.*, 1922, **55**, 1816) and azomethane (Ramsperger, *J. Amer. Chem. Soc.*, 1927, **49**, 912, 1495; Leermakers, *ibid.*, 1933, **55**, 3499) could be unique.

With the concurrence of Dr. Hey the author commenced experimental work to substantiate this hypothesis of non-ionic fission of nitrogen gas from the aromatic diazo-compounds, and, in consequence, a further study has been made of the decomposition of benzene *iso*(*anti*)-diazoacetate, prepared as its labile tautomer *N*-nitrosoacetanilide. It was obvious that, if free neutral phenyl radicals could be produced by the decomposition of a diazo-compound in the liquid phase, one would be dealing with an extremely reactive substance, liable to interact with and decompose the first molecule it encountered. Consequently any reaction occurring in a solvent would be principally an interaction of a phenyl radical with a solvent molecule, no matter what other dissolved substances might be added, and hence but little new information might be drawn from re-examining any earlier work on the decomposition of diazo-compounds in aqueous solution. Dry benzene diazoacetate was therefore prepared and allowed to decompose in a number of anhydrous solvents at room temperature. With all the liquids examined as yet, it reacts vigorously, yielding to the extent of 5—40% a simple aromatic compound, together with a complex tar.

In *n*-hexane and in *cyclo*hexane the diazoacetate was practically insoluble, but nevertheless, decomposition in suspension yielded small quantities of *benzene* in each case. Benzene was also a product of the decomposition in solutions in diethyl ether, dioxan, acetone, ethyl acetate, acetonitrile, and acetic anhydride. With the first four of these solvents acetic acid and an aldehyde were also produced. It therefore appeared that the non-ionic reaction $Ph{\cdot} + H{\cdot}R \longrightarrow Ph{\cdot}H$ was a regular occurrence in hydrogen-containing solvents, and need not necessarily be attributed to the action of a reducing agent, as is customarily done when explaining the decomposition of a benzenediazonium salt in ethyl-alcoholic solution. Moreover the decomposition in acetic anhydride also yielded *carbon dioxide*, which can only be attributed to the transient formation of the neutral acetate radical,

$$ {\cdot}O{\cdot}CO{\cdot}CH_3 \longrightarrow CO_2 + {\cdot}CH_3\ (\longrightarrow CH_3{\cdot}CH_3) $$

since an acetate anion, $(O{\cdot}CO{\cdot}CH_3)^-$, never loses carbon dioxide at room temperature, except on discharge at an anode.

With both methyl and ethyl iodides there was produced iodobenzene; with ethyl bromide and with bromoform there was produced bromobenzene, and with chloroform and carbon tetrachloride there was produced chlorobenzene. Thus the reaction $Ph{\cdot} + Hal{\cdot}R \longrightarrow Ph{\cdot}Hal$ has beeen substantiated. The decomposition in carbon tetrachloride solution again yielded carbon dioxide in quantity.

Carbon dioxide was also evolved when benzene diazoacetate decomposed in carbon disulphide solution, and in this case the other simple reaction product was diphenyl disulphide, Ph•S•SPh. A solution of iodine in carbon disulphide, however, yielded iodobenzene in 40% yield. This may conceivably be produced by a direct union of free radicals : $2Ph\cdot + I_2 = 2PhI$.

Further it has been shown that, during the decomposition of benzene diazoacetate in the non-polar solvents carbon disulphide and carbon tetrachloride, metallic elements may be attacked. In carbon disulphide solution zinc, iron, copper, lead and antimony all yielded products soluble in water—their acetates principally. Even in the presence of an excess of calcium carbonate, zinc, iron, copper and lead were attacked, so that the solution of the metal is not to be explained as an attack by acetic acid molecules in presence of air. When calcium carbonate was used, however, the aqueous extracts of the decomposition products all contained calcium ions, so that some acetic acid molecules must be produced by the self-interaction of products of the benzene diazoacetate decomposition, *e.g.*,

$$\cdot O\cdot CO\cdot CH_3 + HR \longrightarrow HO\cdot CO\cdot CH_3.$$

Silver foil was not attacked during the decomposition of benzene diazoacetate in a carbon disulphide solution containing calcium carbonate.

In carbon tetrachloride solution tin, copper, mercury and probably bismuth were attacked, giving water-soluble products. The mercury yielded mercurous and mercuric chlorides and also phenylmercuric chloride. In this connection it may be pointed out that McClure and Lowy (*J. Amer. Chem. Soc.*, 1931, **53**, 319) have found that even in aqueous solution benzenediazonium chloride yields this product if allowed to decompose in a solution in which are suspended, by rapid stirring, globules of metallic mercury.

All these reactions with metals, many of which are rather inert, recall in a most striking manner Paneth's tests for the free radicals. Indeed practically without exception the reactions enumerated above are typical of free neutral radicals, and could not occur if a phenyl kation or a phenyl anion was a reaction product. Moreover there has already been recorded one early reaction of this same type which could hardly be attributed to an ionic change. Möhlau and Berger (*Ber.*, 1893, **26**, 1994) allowed dry benzenediazonium chloride to decompose in pyridine and obtained α- and γ-phenylpyridines. Phenyl kation and chloride anion would inevitably have attacked the nitrogen atom of the pyridine and yielded instead phenylpyridinium chloride.

The non-ionic decomposition of benzene diazoacetate may well be typical of all the decomposition reactions of the aromatic diazo-compounds, for a search of the literature does not reveal any contradictory evidence. The hypothesis will greatly amplify, but not in essentials contradict, the theories propounded by Hantzsch, which, in many aspects, remain unproved. Hence it would appear that a careful reinvestigation of the diazo-reactions in the light of the free-radical hypothesis might shed considerable light upon the mechanisms of the reactions of Sandmeyer and Gattermann, in which a copper compound catalytically alters the normal course of decomposition in aqueous solution. Further, the production of neutral aryl radicals, at will, in solutions, is somewhat of a novelty, and in view of their intense reactivity it would now seem possible to extend our knowledge of the chemistry of the free radicals by further studies of decompositions of aryl diazo-compounds in non-aqueous solutions. The experimental work is therefore being continued.

The author wishes to thank Dr. Hey for agreeing to his entry into this field of experimental work so as to search independently for evidence of non-ionic reactions. He has maintained throughout constant communication with Dr. Hey and his results, arrived at in the laboratories at Durham, independently corroborate the work carried out in Manchester. At the author's suggestion Dr. Hey has very kindly repeated and confirmed in his laboratory the critical reactions demonstrating the evolution of carbon dioxide in solutions in acetic anhydride, carbon tetrachloride and carbon disulphide, and also the interactions in carbon disulphide and carbon tetrachloride solutions with metallic zinc, copper, and mercury. In conclusion the author hopes that this friendly interchange of information will continue to be equally fruitful to both investigators in the future.

EXPERIMENTAL.

The benzene *iso*diazoacetate (nitrosoacetanilide) used in the following reactions was prepared as described by Grieve and Hey (*loc. cit.*) and dried for 2 days over calcium chloride in a vacuum desiccator. Specimens kept for a longer time decomposed rapidly, and in one instance exploded.

(I) *Decomposition in Liquids containing Hydrogen.*—(i) n-*Hexane.* Gases were gradually evolved at room temperature from benzene diazoacetate (7 g.) covered with *n*-hexane (15 g., B. D. H. " pure for spectroscopy ") in a water-cooled flask. After 6 days the hexane was distilled on the water-bath and shown to contain benzene by (*a*) nitration, which yielded some *m*-dinitrobenzene, m. p. and mixed m. p. 91°, and (*b*) by a very sensitive conversion into diphenyliodonium iodide recently discovered in these laboratories by Professor Irvine Masson.* The residue was distilled in steam, but yielded no diphenyl.

(ii) cyclo*Hexane.* The above reaction was repeated with *cyclo*hexane free from benzene. After 8 days the portion distilling below 100° gave positive tests for benzene by both reactions.

(iii) *Diethyl ether.* Gases were evolved immediately from benzene diazoacetate (6 g.) dissolved in sodium-dried ether (50 c.c.) in a water-cooled flask under a reflux condenser and the smell of acetaldehyde was soon noticeable. After a day, since reaction had ceased, benzene-free hexane (20 c.c.) was added as a vehicle for the collection of any benzene, and the mixture was distilled on the water-bath. The distillate gave a very strong reaction with Schiff's reagent, a positive iodoform test, and reacted with 2 : 4-dinitrophenylhydrazine. The hydrocarbon layer remaining after repeated washing with water gave strong positive tests for the presence of benzene by both reactions (*a*) and (*b*) above.

(iv) *Dioxan.* A solution of benzene diazoacetate in dioxan was allowed to decompose for 4 days and then, by addition of hexane, distillation, etc., as in (iii) above, was shown to contain a considerable quantity of benzene.

(v) *Acetone.* A solution of benzene diazoacetate in A.R. acetone was allowed to decompose for a week. After addition of hexane the distillate below 100° gave a positive test with Schiff's reagent, and the hydrocarbon fraction, after washing with sodium bisulphite solution, contained benzene, which had been produced in not less than 50% yield.

(vi) *Acetonitrile.* In this solvent again benzene formed the principal reaction product. There was no evidence of the formation of benzonitrile.

(vii) *Ethyl acetate* (compare Grieve and Hey, *loc. cit.*). Benzene diazoacetate on decomposition in dry ethyl acetate solution soon produced acetaldehyde. After addition of hexane the distillate below 100° gave a positive reaction with Schiff's reagent, and the hydrocarbon layer contained benzene, produced in about 50% yield. The residue not volatile at 100° was distilled in steam and yielded acetic acid and traces of phenol, but neither phenyl acetate nor diphenyl.

(viii) *Acetic anhydride.* Benzene diazoacetate (6 g.), dissolved in acetic anhydride (30 g.), was allowed to decompose in a water-cooled flask fitted with a reflux condenser, from which the evolved gases were led through a fresh solution of baryta. A thick precipitate of barium carbonate soon indicated the presence of carbon dioxide as a reaction product.** After a week hexane (20 c.c.) was added, and the mixture distilled on the water-bath. The distillate gave positive tests for the presence of benzene by both reactions (*a*) and (*b*) above.

(II) *Decomposition in Liquids containing Halogens.*—(i) *Methyl iodide.* Benzene diazoacetate (6 g.) was allowed to decompose in methyl iodide (20 g.) in a water-cooled flask, and after 3 days the excess of solvent was removed by distillation. On distilling the residue in steam there was obtained iodobenzene (0·8 g.), b. p. 187°, identified by conversion into *p*-iodonitrobenzene, m. p. 173—174° alone or mixed with an authentic specimen.

(ii) *Ethyl iodide.* The same quantities being used as in the preceding experiment, from ethyl iodide there was obtained 0·3 g. of iodobenzene, which was identified in a similar manner.

(iii) *Ethyl bromide.* Benzene diazoacetate (7 g.) when decomposed in ethyl bromide (30 g.) gave bromobenzene (0·3 g.), which was separated by steam distillation and identified by conversion into *p*-bromonitrobenzene, m. p. and mixed m. p. 126°.

(iv) *Bromoform.* Benzene diazoacetate (6 g.) was decomposed in bromoform (30 g.) which had been shaken with concentrated sulphuric acid and then freshly distilled. The product from steam distillation was saponified with alcoholic potash, and the unattacked residue of bromobenzene (0·6 g.) identified by conversion into *p*-bromonitrobenzene.

(v) *Chloroform.* Benzene diazoacetate (7 g.) after decomposition in 50 c.c. of chloroform, purified by shaking with concentrated sulphuric acid and distillation, gave 0·7 g. of a colourless oil, b. p. *ca.* 143°, which smelt strongly of chlorobenzene and on nitration, gave a gummy product which reacted with piperidine.

(iv) *Carbon tetrachloride.* Decomposition of 8 g. of benzene diazoacetate in 80 g. of carbon

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* To be published shortly.

tetrachloride gave 1·5 c.c. of a liquid, b. p. 130—160°, containing chlorobenzene. This was nitrated, giving a product, m. p. 46—47° (after crystallisation from methyl alcohol), raised slightly in admixture with authentic 2 : 4-dinitrochlorobenzene. The crude nitration product reacted with piperidine, and, with aniline, it gave 2 : 4-dinitrodiphenylamine, m. p. and mixed m. p. 156—157°. Another portion of benzene diazoacetate on decomposition in carbon tetrachloride was shown to give carbon dioxide in quantity by passing the evolved gases through a fresh baryta solution, from which barium carbonate was soon deposited.** From this reaction mixture the excess of carbon tetrachloride was removed by distillation on the water-bath, and the residue was then hydrolysed for 3 hours with alcoholic potash. The alkaline product was examined for the presence of benzoic acid, but none could be found. Hence benzotrichloride does not seem to be a reaction product.

(vii) *Phosphorus trichloride.* Benzene diazoacetate was slowly added in very small portions to phosphorus trichloride in a basin. It reacted at once, giving initially a white precipitate, which was presumably benzenediazonium chloride, since it gave an azo-dye with β-naphthol. Eventually a tarry mass was formed, which, after treatment with water, yielded acetanilide, m. p. 114°. Chlorobenzene did not appear to be formed.

(III) *Decomposition in Carbon Disulphide.*—40 G. of benzene diazoacetate were dissolved in 300 c.c. of carbon disulphide (which had been purified by shaking with anhydrous copper sulphate and distillation) in a water-cooled flask fitted with a reflux condenser, from which the evolved gases were led through a fresh solution of baryta protected from the air by a guard tube. Formation of carbon dioxide was apparent after 15 minutes,** and soon there was a thick deposit of barium carbonate. After a week reaction had ceased, and the excess of solvent was then distilled off on the water-bath. The red tarry residue was extracted four times with successive portions (300 c.c. each) of light petroleum (b. p. 60—80°) and these solutions were evaporated as far as possible on the water-bath. The residue thus obtained was similarly extracted with light petroleum (b. p. 40—60°), and this solution after concentration gave an orange-red gum which solidified almost completely on freezing. This, crystallised repeatedly from methyl alcohol–ether and finally from methyl alcohol alone, gave 8 g. of colourless needles, m. p. 61·5°, which were proved to be diphenyl disulphide (Found : S, 29·7. Calc., 29·4%). A portion of the product was boiled with alcoholic potash, and the solution after acidification yielded thiophenol on steam distillation, from which were prepared lead, copper, mercury, and silver salts. Diphenyl disulphide was also synthesised from thiophenol, and the specimen thus obtained had a melting point unaltered by admixture with the specimen from the decomposition of the benzene diazoacetate.

No other reaction product could be isolated in appreciable quantity from the tarry residue by extraction with other solvents.

Decomposition of benzene diazoacetate in a solution of sulphur in carbon disulphide yielded no reaction product other than that isolated from the pure solvent.

(IV) *Reaction with Iodine in Carbon Disulphide.*—8 G. of benzene diazoacetate and 8 g. of iodine were dissolved in 50 c.c. of purified carbon disulphide, and the mixture was allowed to decompose in a water-cooled flask under a reflux condenser. After 6 days the carbon disulphide was distilled off on the water-bath, and the residue treated with water and steam distilled. After the distillate had been decolourised with sodium sulphite, the remaining heavy oil was extracted with ether, dried, and fractionated. 3·3 G. of iodobenzene, b. p. 186—191°, were thus obtained, and identified by conversion into *p*-iodonitrobenzene, m. p. and mixed m. p. 173°.

(V) *Reaction with Metals in Carbon Disulphide Solution.*—To separate portions (6 g.) of benzene diazoacetate, dissolved in dry carbon disulphide (30 c.c.) were added : (*a*) 10 g. of iron filings, (*b*) 10 g. of zinc dust,** (*c*) 10 g. of copper powder,** (*d*) 20 g. of lead filings, (*e*) 15 g. of powdered antimony, (*f*) 20 g. of mercury. The mixtures were allowed to decompose for 2 days in water-cooled flasks under reflux condensers, and were shaken frequently. The excess of solvent was then evaporated from each solution on the water-bath, and the residues were shaken for 2 minutes with cold water and filtered. The clear aqueous extracts in each instance contained acetate ions in quantity. In addition the solution from (*a*) contained much ferrous and some ferric ions, from (*b*) zinc ions,** from (*c*) cupric ions,** from (*d*) lead ions, produced in considerable quantity in every case. From (*e*) the aqueous extract contained no antimony compound, but when the residue was warmed for 2 minutes with aqueous ammonium tartrate and filtered, the colourless filtrate gave with hydrogen sulphide a heavy black precipitate containing antimony, verified by positive Marsh and Gutzeit tests, and by the formation of a metallic bead on fusion. From mixture (*f*) no mercury salts were obtained.

Since it was possible in some cases that the metal had been attacked by acetic acid—a likely product of self-decomposition of benzene diazoacetate—rather than by free radicals, the reactions (*a*) to (*d*) were repeated with the addition of 6 g. of dry precipitated chalk to each mixture. Strong positive tests for ferrous, ferric, zinc, cupric, lead, and acetate ions were still given by the cold aqueous extracts. In addition, however, each solution contained calcium ions, showing that acetic acid also must be a reaction product.

A mixture of 6 g. of benzene diazoacetate, 6 g. of precipitated chalk, 30 c.c. of carbon disulphide, and 4 g. of pure silver foil was also allowed to decompose. After treatment as described above, the aqueous extract contained calcium and acetate ions in quantity but no silver ions, and the recovered foil showed no signs of attack.

(VI) *Reaction with Metals in Carbon Tetrachloride Solution.*—To separate portions of benzene diazoacetate (6 g.), dissolved in carbon tetrachloride (20 c.c.), were added: (*a*) 6 g. of copper** powder, (*b*) 12 g. of tin powder, (*c*) 12 g. of powdered bismuth, and (*d*) 20 g. of mercury.** The mixtures were allowed to decompose for 2 days in water-cooled flasks under reflux condensers and were shaken frequently. Mixture (*d*) soon became turbid owing to the formation of an insoluble white substance. After removal of the excess of solvent by distillation on the water-bath each mixture was shaken for 2 minutes with warm water and filtered. From (*a*) the extract contained cupric,** chloride, and acetate ions; from (*b*) stannous and chloride ions, and from (*d*) chloride ions in quantity together with a trace of mercuric ions. From (*c*) no metallic ions were found in the aqueous extract, but the residue, after warming for 2 minutes with 2*N*-hydrochloric acid, yielded a colourless solution containing bismuth ions in quantity. Another portion of bismuth metal was warmed with 2*N*-hydrochloric acid for the same length of time and only a faint trace of the metal was dissolved by the acid.

The reaction mixture (*d*) was treated with successive portions of warm rectified spirit on a filter-paper, and eventually there remained globules of mercury and a white insoluble powder. This was extracted with hot benzene until no more would dissolve. The white powder then remaining blackened instantly on treatment with ammonia and dissolved in aqua regia to give a solution containing mercuric ions. It was thus presumed to be mercurous chloride. The benzene extract was concentrated to small bulk; colourless plates then crystallised. After further crystallisation they melted at 252°, burnt with a smoky flame, and were found to contain both mercury and chlorine. Hence they must consist of phenylmercuric chloride (m. p. recorded 251°).**

The experiments marked ** have been repeated by Dr. D. H. Hey in his laboratory at Manchester, and the results confirmed in all details.

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