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253. *Phenylation with Diazoaminobenzenes.*

By R. L. Hardie and R. H. Thomson.

Pyrolysis of diazoaminobenzene in aromatic solvents at 150—160° generates phenyl and anilino-radicals. The former attack the solvent, giving relatively high yields of diphenyl derivatives and negligible amounts of by-products. Three out of four unsymmetrical diazoaminobenzenes examined gave mixtures of amines and diphenyls which show that these triazens undergo decomposition in both tautomeric forms.

It is well known that diazoaminobenzenes decompose on being heated, with the evolution of nitrogen. This property has been exploited for the production of sponge rubber,[1] but little is known of the fate of the aromatic fragments although it is of interest that the reaction has also been used to initiate polymerisation.[2] Heating diazoaminobenzene at 150°, in sand or paraffin,[3] yields benzene, aniline, diphenyl, diphenylamine, and *o*- or *p*-aminodiphenyl, besides nitrogen, and decomposition in hot aniline [4, 5] gives, in addition, azobenzene and aminoazobenzene. The latter procedure has been recommended for the preparation of the aminodiphenyls.[4, 6] Similar products were obtained on pyrolysis of diazoaminotoluene in *p*-toluidine.[5] Although it is generally assumed [7] that these are homolytic decompositions there is very little direct evidence in the literature. Recent kinetic studies [8] show that radicals are formed on thermal dissociation of alkylaryltriazens

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[1] Guppy, *Trans. Inst. Rubber Ind.*, 1942—3, **18**, 65.
[2] U.S.P. 2,313,233.
[3] Heusler, *Annalen*, 1890, **260**, 227.
[4] Hirsch, *Ber.*, 1892, **25**, 1973.
[5] Morgan and Walls, *J.*, 1930, 1502.
[6] Aeschlimann, Lees, McCleland, and Nicklin, *J.*, 1925, **127**, 66.
[7] Saunders, " The Aromatic Diazo Compounds," Arnold & Co., London, 2nd Edn., 1949, p. 175.
[8] Dolgoplosk, Ugryumov, and Krol, *Doklady Akad. Nauk S.S.S.R.*, 1954, **96**, 757; Dolgoplosk, Erusalimskii, Krol, and Romanov, *Zhur. obshchei Khim.*, 1954, **24**, 1775; Andakushkin, Dolgoplosk, and Radchenko, *ibid.*, 1956, **26**, 2972, 3403; Romanov, Dolgoplosk, and Erusalimskii, *Doklady Akad. Nauk S.S.S.R.*, 1957, **112**, 703.

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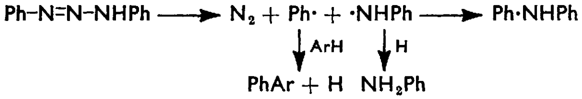
and this is true, of course, in the presence of acid.[9] The present work establishes that diaryltriazens (diazoaminobenzenes) decompose homolytically when heated.

The decompositions were effected by heating 4% solutions of diazoaminobenzene in various aromatic solvents at 150—160° for 40 hr. During this time the initial light yellow solutions darkened appreciably but no tar separated (except from nitrobenzene solution). Primary amines were then removed by acid-extraction and the remaining mixture was fractionated by distillation and chromatography. The products isolated are set out in Table 1. Mixtures of isomeric diphenyls were formed in each case but complete separation was not achieved. Although 2-chlorodiphenyl was the only isomer isolated on pyrolysis of diazoaminobenzene in chlorobenzene, all three isomers were disclosed by infrared analysis,[10] and the isomer ratio is in general agreement with those obtained by other phenylation procedures (see Table 2). From this, and the formation of 2 : 3-dimethyl-2 : 3-diphenylbutane in the decomposition of diazoaminobenzene in *iso*propylbenzene, we conclude that the pyrolysis of diazoaminobenzene generates phenyl radicals which then attack the solvent. The reaction can be represented as follows:

TABLE 1. *Products isolated on pyrolysis of diazoaminobenzene in organic solvents.*

Solvent	Ph_2 derivs.	Amines
Bromobenzenes	2- and 4-Bromo-	NH_2Ph, $NHPh_2$
Chlorobenzene	2-Chloro-	NH_2Ph
Nitrobenzene *	2- and 4-Nitro-	NH_2Ph, $NHPh_2$
*iso*Propylbenzene †	Mixed *iso*propyl-	,,

* Azobenzene was also isolated from this solvent. † 2 : 3-Dimethyl-2 : 3-diphenylbutane was also isolated from this solvent.



$$\begin{tikzcd} Ph{-}N{=}N{-}NHPh \arrow[r] & N_2 + Ph\cdot \arrow[d, "ArH"] & + \cdot NHPh \arrow[d, "H"] \arrow[r] & Ph\cdot NHPh \\ & PhAr + H & NH_2Ph & \end{tikzcd}$$

no benzene was detected (cf. ref. 13). Thus, in the pyrolysis of diazoaminobenzene we have yet another method of phenylation. It has an advantage over other procedures in that the reactions are "clean," yields being relatively high (usually >50%) and the formation of by-products negligible. On the other hand, the method is not applicable to

TABLE 2. *Phenylation of chlorobenzene. Isomer ratios* (%).

Method	*ortho*	*meta*	*para*
Gomberg [10]	64·6	21·7	13·7
Benzoyl peroxide [11]	57·5	26·6	15·9
Silver iodide dibenzoate [12]	60·0	24·0	16·0
Phenylhydrazine–silver oxide [13]	64·9	22·1	13·0
Phenylazotriphenylmethane [11]	58·2	27·9	13·9
Diazoaminobenzene	59·8	23·7	16·5

TABLE 3. *Products obtained on pyrolysis of substituted diazoaminobenzenes in bromobenzene.*

Diazoaminobenzene	Ph_2 derivs.	Amines
4-Bromo-	2- and 4-Bromo-	*p*-Bromoaniline and 4-bromodiphenylamine
4 : 4′-Dibromo-	2 : 4′-, 3 : 4′-, and 4 : 4′-Dibromo-	*p*-Bromoaniline
4-Nitro-	Mixed bromo- and 2-bromo-4′-nitro-	*p*-Nitroaniline
4-Bromo-4′-nitro-	4 : 4′-Dibromo- and 2-bromo-4′-nitro-	*p*-Nitroaniline
4-Methoxy-	Mixed bromo- and 2-, 3-, and 4-bromo-4′-methoxy-	Aniline and *p*-anisidine

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[9] Elks and Hey, *J.*, 1943, 441.
[10] Augood, Hey, and Williams, *J.*, 1953, 45.
[11] Huisgen and Grashey, *Annalen*, 1957, **607**, 46.
[12] Bryce-Smith and Clarke, *J.*, 1956, 2264.
[13] Hardie and Thomson, *J.*, 1957, 2512.

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benzene and a few other low-boiling aromatic solvents. The only other symmetrical diazoaminobenzene examined was the 4 : 4′-dibromo-derivative: in boiling bromobenzene it yielded all three dibromodiphenyls and *p*-bromoaniline (see Table 3).

Since diazoaminobenzenes are tautomeric it would be expected that thermal dissociation of unsymmetrical derivatives would yield two different aryl radicals and two different arylamino-radicals, and so two groups of diphenyl derivatives and two primary amines. In three examples, out of four that we examined (all in bromobenzene), this proved to be the case (see Table 3). We did not succeed in isolating all the expected products but sufficient were obtained to show that both tautomeric forms were present in boiling bromobenzene. This provides novel evidence for the tautomerism of these compounds.

$$\begin{tikzcd}
\mathrm{Ar{-}N{=}N{-}NHAr'} \arrow[r] \arrow[d, shift left] & \mathrm{Ar\cdot + N_2 + \cdot NHAr'} \\
\mathrm{ArNH{-}N{=}NAr'} \arrow[r] \arrow[u, shift left] & \mathrm{Ar'\cdot + N_2 + \cdot NHAr}
\end{tikzcd}$$

4-Methoxydiazoaminobenzene gave the most satisfactory results and we were able to isolate a mixture of bromodiphenyls and all three bromo-4′-methoxydiphenyls, together with aniline and *p*-anisidine. From 4-nitro- and 4-bromo-4′-nitro-diazoaminobenzene we isolated at least one diphenyl derivative arising from each of the aryl radicals but only one base (*p*-nitroaniline); however the yield of bromonitrodiphenyl was very small, in both cases, so that the amounts of the second primary amine formed would be smaller still, and escaped detection. Judging from the products isolated, 4-bromodiazoaminobenzene reacts exclusively in one tautomeric form in boiling bromobenzene. The direction of thermal dissociation is presumably controlled by the combined energies of the two radicals liberated, which in turn depends on the relative stabilising influence of the substituents on phenyl and anilino-radicals. No general conclusions can be drawn from these few results but it is of interest that the methoxyl group had the least influence on the course of the decomposition, approximately equal amounts of aniline and *p*-anisidine being obtained (cf. ref. 14).

Benzotriazoles (cyclic triazens) are much more stable than diazoaminobenzenes and many can be distilled without decomposition at normal pressures. However, at very high temperatures, 1-aryl derivatives break up with loss of nitrogen; this must produce a diradical which then rearranges to a carbazole (Graebe's synthesis).

EXPERIMENTAL

Solvents were fractionally distilled through a 50 cm. helix-packed column, and stored over sodium hydroxide pellets. *iso*Propylbenzene was purified by the method of Hey *et al.*[15] and had b. p. 152°/760 mm. Chromatographic separations were done on alumina with light petroleum (b. p. 50—60°) as solvent unless otherwise stated, and products were identified by mixed m. p. determinations.

Pyrolysis of Diazoaminobenzenes in Aromatic Solvents.—General method. A 4% solution of the diazoaminobenzene in an aromatic solvent was boiled under reflux for 40 hr. On cooling, the solution was extracted with dilute hydrochloric acid to obtain the amine(s), and then washed with a 5% solution of sodium hydrogen carbonate, and water, and dried ($MgSO_4$). The solvent was removed by distillation *in vacuo* through a helix-packed column, and the product worked up as indicated below.

Diazoaminobenzene in bromobenzene. From 20 g. of diazoaminobenzene, 5·7 g. of aniline were obtained. Distillation of the crude product gave a light red oil, b. p. 102—125°/0·3 mm., (15·5 g.). Chromatography gave (*a*) mixed bromodiphenyls, b. p. 96—105°/0·3 mm. (11·0 g.) (Found: C, 61·7; H, 4·05; Br, 34·3. Calc. for $C_{12}H_9Br$: C, 61·8; H, 3·85; Br, 34·3%), (*b*) 4-bromodiphenyl (1·8 g.), and (*c*) diphenylamine (0·4 g.). 2-Bromodiphenyl was isolated from (*a*) as its dinitro-derivative by treatment with ethyl nitrate in concentrated sulphuric acid, to give

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[14] Huang and Si-Hoe, *J.*, 1957, 3988.

[15] Hey, Pengilly, and Williams, *J.*, 1956, 1466.

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2-bromo-4′ : 5-dinitrodiphenyl, m. p. 163° (0·8 g.) (cf. ref. 16) (Found: C, 44·4; H, 2·15; N, 8·4. Calc. for $C_{12}H_7O_4N_2Br$: C, 44·5; H, 2·15; N, 8·6%).

Diazoaminobenzene in chlorobenzene. From 10 g. of diazoaminobenzene, 2·8 g. of aniline were obtained. Distillation of the product after removal of the solvent gave a light red oil, b. p. 102—110°/0·5 mm. (6·3 g.) (impure chlorodiphenyls). Purification of this oil for infrared analysis was effected by shaking it in light petroleum with concentrated sulphuric acid until all the colour had passed into the acid layer. The light petroleum solution was then washed with a 5% solution of sodium hydrogen carbonate, and water, and dried ($MgSO_4$). Removal of the solvent and distillation afforded mixed chlorodiphenyls, b. p. 95—102°/0·2 mm. (Found: C, 76·4; H, 4·7. Calc. for $C_{12}H_9Cl$: C, 76·4; H, 4·7%). Chromatography afforded 2-chlorodiphenyl, as a faintly yellow oil which crystallised from aqueous alcohol as prisms, m. p. 34°.

Diazoaminobenzene in nitrobenzene. The crude product from diazoaminobenzene (10 g.), after removal of aniline (2·6 g.), distilled to a light red oil, b. p. 120—145°/0·7 mm. (6·7 g.). Chromatography afforded (*a*) azobenzene (0·3 g.), (*b*) a light yellow oil (2·9 g.), crystallisation of which from aqueous alcohol gave 2-nitrodiphenyl, (*c*) 4-nitrodiphenyl (1·3 g.), and (*d*) diphenylamine (0·4 g.).

Diazoaminobenzene in iso*propylbenzene.* The crude product from 10 g. of diazoaminobenzene, after extraction of aniline (3 g.), distilled to give an orange oil, b. p. 110—145°/0·6 mm. (3·9 g.), chromatography of which afforded a diaryl fraction (3·2 g.). 2 : 3-Dimethyl-2 : 3-diphenylbutane (0·5 g.) was precipitated from this oil by nitromethane.[14] Mixed *iso*propyldiphenyls were obtained from the nitromethane solution by distillation and had b. p. 95—100°/0·3 mm. (2·2 g.) (Found: C, 91·2; H, 8·4. Calc. for $C_{15}H_{16}$: C, 91·8; H, 8·2%). Further elution of the column with ether–light petroleum (1 : 9) gave diphenylamine (0·3 g.).

4 : 4′-*Dibromodiazoaminobenzene in bromobenzene.* After pyrolysis of 15 g., *p*-bromoaniline (4·5 g.) was extracted with dilute acid. The crude product obtained on removal of the solvent gave two fractions on distillation: (*a*) a light yellow oil, b. p. 135—140°/0·5 mm. (5·3 g.), and (*b*) 4 : 4′-dibromodiphenyl (1·3 g.). Chromatography of (*a*) on Norite (previously washed with distilled water and dried at 150°) from light petroleum (b. p. 60—80°) afforded 2′ : 4-dibromodiphenyl (2·8 g.). Elution with chloroform–light petroleum (1 : 20) gave 3 : 4′-dibromodiphenyl, b. p. 138—140°/0·5 mm. (0·8 g.) (Found: C, 46·5; H, 2·4. Calc. for $C_{12}H_8Br_2$: C, 46·2; H, 2·6%), and more 4 : 4′-dibromodiphenyl (0·3 g.). Authentic 2′ : 4-dibromodiphenyl was prepared as follows:[13] *p*-bromophenylhydrazine (5 g.) was dissolved in bromobenzene (100 ml.) and silver oxide (10 g.) added gradually with stirring. The mixture was left overnight and then boiled under reflux for 30 min. After cooling, the silver residue was filtered off and the filtrate dried ($MgSO_4$) and distilled. The crude product obtained on removal of the solvent gave a light red oil, b. p. 130—138°/0·3 mm. Chromatography afforded 2′ : 4-dibromodiphenyl as colourless needles, m. p. 55° (0·3 g.), and 4 : 4′-dibromodiphenyl, m. p. 162° (0·6 g.).

4-*Bromodiazoaminobenzene in bromobenzene.* Pyrolysis of 10 g. gave *p*-bromoaniline (2·8 g.) by acid-extraction, and distillation of the residual material yielded an orange oil, b. p. 110—140°/0·5 mm. (5·0 g.); chromatography afforded (*a*) a light yellow oil (4·0 g.) and (*b*) 4-bromodiphenylamine. Further chromatography of (*a*) on Norite with light petroleum (b. p. 60—80°) gave mixed bromodiphenyls, b. p. 105—110°/0·5 mm. (2·8 g.) (Found: Br, 33·9. Calc. for $C_{12}H_9Br$: Br, 34·3%), from which 2-bromo-4′ : 5-dinitrodiphenyl was prepared, as above. Further elution of the column with chloroform–light petroleum (1 : 9) afforded 4-bromodiphenyl (0·3 g.).

4-*Nitrodiazoaminobenzene in bromobenzene.* From 15 g. of the diazoamino-compound, 4 g. of *p*-nitroaniline were obtained and the residue, after removal of the solvent, was distilled, giving (*a*) a light red oil, b. p. 105—125°/0·5 mm. (6·7 g.), and (*b*) a dark red oil, b. p. 155—160°/0·5 mm. (0·6 g.). Chromatography of (*a*) gave mixed bromodiphenyls, b. p. 105—110°/0·5 mm. (5·7 g.) (Found: C, 62·1; H, 4·0. Calc. for $C_{12}H_9Br$: C, 61·8; H, 3·85%), from which 2-bromo-4′ : 5-dinitrodiphenyl was prepared as before. 4-Bromodiphenyl (0·2 g.) was obtained by further elution of the column. Trituration of (*b*) with light petroleum precipitated the insoluble *p*-nitroaniline (0·1 g.) and chromatography of the light petroleum solution on Norite yielded 2-bromo-4′-nitrodiphenyl, m. p. 83° (0·3 g.).

4-*Methoxydiazoaminobenzene in bromobenzene.* Acid-extraction of the solution after pyrolysis of 10 g. gave 3 g. of basic material. Chromatography with ether–light petroleum (3 : 7) gave aniline (1·1 g.) and *p*-anisidine (0·7 g.). The product obtained on removal of the bromo-

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[16] Case, *J. Amer. Chem. Soc.*, 1943, **65**, 2137.

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benzene was distilled, giving (*a*) an oil, b. p. 125—140°/0·5 mm. (3·8 g.), and (*b*) a fraction, b. p. 145—148°/0·5 mm., which solidified. Crystallised from light petroleum it had m. p. 144° (1·5 g.) and was 4-bromo-4′-methoxydiphenyl. Chromatography of (*a*) gave an oil consisting of a mixture of bromo-4′-methoxydiphenyls and bromodiphenyls, and a solid which crystallised from light petroleum as prisms, m. p. 55° (1·0 g.) (Found: C, 58·6; H, 4·0; Br, 30·3. $C_{13}H_{11}OBr$ requires C, 59·3; H, 4·2; Br, 30·4%). This is 2(or 3)-*bromo-4′-methoxydiphenyl.* The bromodiphenyls and bromomethoxydiphenyls were separated as follows: the crude product (2·3 g.) (after removal of bromobenzene), in glacial acetic acid (25 ml.) and hydrobromic acid (*d* 1·5; 30 ml.), was boiled under reflux for 2 hr. On cooling, the mixture was added to a large excess of sulphurous acid and extracted with ether. The extract was shaken with 5% aqueous sodium hydrogen carbonate and then with 2N-sodium hydroxide. Acidification of the latter and ether-extraction gave a phenolic oil (0·5 g.; equiv. to 0·53 g. of bromo-4′-methoxydiphenyls), which formed a *benzoate,* m. p. 105° (Found: C, 64·5; H, 4·0; Br, 22·3. $C_{19}H_{13}O_2Br$ requires C, 64·6; H, 3·7; Br, 22·7%). Distillation of the ether solution gave mixed bromodiphenyls, b. p. 108—110°/0·6 mm. (1·4 g.) (Found: C, 61·7; H, 4·05. Calc. for $C_{12}H_9Br$: C, 61·8; H, 3·85%). (From a Gomberg reaction with diazotised *p*-anisidine in bromobenzene we isolated 4-bromo-4′-methoxydiphenyl and an oil, b. p. 138—140°/0·5 mm.; the phenol obtained by demethylation of the latter formed a benzoate, m. p. 105°, identical with that described above.)

4-Bromo-4′-nitrodiazoaminobenzene in bromobenzene. Pyrolysis of 8 g. followed by acid-extraction gave basic material (2·5 g.). Chromatography with chloroform–light petroleum (7 : 3) gave *p*-nitroaniline (1·9 g.). Distillation of the residue, after removal of the solvent, yielded a light red oil, b. p. 140—162°/0·3 mm. (5·0 g.). Chromatography afforded mixed dibromodiphenyls as a faintly yellow semi-solid (2·5 g.), trituration of which with light petroleum gave 4 : 4′-dibromodiphenyl (0·5 g.). Removal of the light petroleum and distillation gave mixed dibromodiphenyls, b. p. 136—138°/0·5 mm. (1·2 g.) (Found: Br, 51·5. Calc. for $C_{12}H_8Br_2$: Br, 51·2%). Further elution of the column gave 2-bromo-4′-nitrodiphenyl (0·3 g.).

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The University, Old Aberdeen, Scotland. [*Received, November* 21*st*, 1957.]