173. *The Chemical Effects of γ-Radiation on Organic Systems. Part IX.*[1] *The Action of Radiation on* o-*Bromoaniline.*

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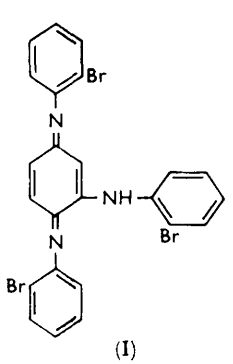
γ-Irradiation of *o*-bromoaniline yields *o*-bromoaniline hydrobromide, a tetrabromoazophenine (III), and two purple compounds.

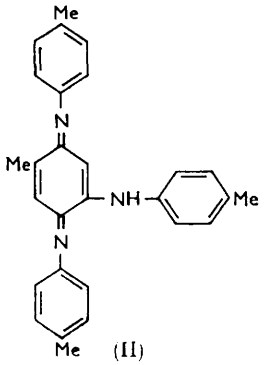
In view of the formation of phenazine when *o*-bromoaniline in nitrobenzene is boiled with potassium carbonate and copper,[2] we irradiated *o*-bromoaniline, but were unable to detect the formation of phenazine although a number of products were isolated. A crystalline precipitate formed, consisted of *o*-bromoaniline hydrobromide, and was the product produced in greatest amount. Next most plentiful was a reddish-purple crystalline compound A, m. p. 233—234°, which was soluble in ether and not extracted from its ethereal solution by 5N-hydrochloric acid. The analytical values obtained from this compound agreed with $C_{24}H_{16}Br_3N_3$, *i.e.* (I), but the spectrum of the compound in chloroform solution [$\lambda_{max.}$ 294 and 394 mμ (log ε 4·46 and 4·31), $\lambda_{min.}$ 348 (log ε 3·87)] was different from that of compound[3] (II) [$\lambda_{max.}$ 306 and 450 mμ (log ε 4·42 and 3·99), $\lambda_{min.}$ 360 mμ (log ε 3·18)], yet so similar to that of azophenine [$\lambda_{max.}$ 295 and 392 mμ (log ε 4·53 and 4·35), $\lambda_{min.}$ 338 mμ (log ε 3·95)] that we formulated it as the tetrabromoazophenine (III). When the compound was dried at 60°/1 mm. it still did not give analytical values corresponding to $C_{30}H_{20}Br_4N_4$ and it seems likely that it contained benzene of crystallisation.

In addition, from irradiated *o*-bromoaniline, two purple compounds, B and C, were isolated, which were insoluble in ether and had m. p. 178—181° and 202—204°, respectively. Both were very weakly basic, although the latter dissolved in 3N-hydrochloric acid. The

[1] Part VIII, preceding paper.
[2] Hillemann, *Ber.*, 1938, **71**, 42.
[3] Perkin, *J.*, 1880, **37**, 546.

spectra of B and C were very similar and, on the assumption that these compounds had formulæ $C_{24}H_{18}Br_2N_4$ and $C_{30}H_{23}Br_2N_5$, respectively, the following characteristics were found: B, $\lambda_{max.}$ 208, 292, and 606 mμ (log ε 4·56, 4·46, and 4·28), $\lambda_{min.}$ 255 and 405 mμ; C, $\lambda_{max.}$ 206, 287, and 590 mμ (log ε 4·56, 4·46, and 4·26), $\lambda_{min.}$ 257 and 392 mμ. The structures


(I)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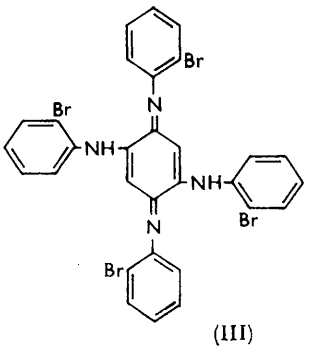
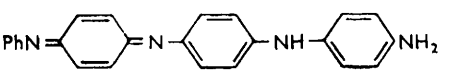

(III)

of these compounds have not been elucidated. They appear not to be induline-like compounds, as their spectra are different from those of 2-anilino-3,5-dihydro-3-imino-5-phenylphenazine (anilinoaposofranine) and 2-amino-3,5-dihydro-5-phenyl-3-phenyliminophenazine,[4] the spectral characteristics of which are recorded in the Experimental section. On the other hand, the spectra of B and C do resemble those of 5,12-dihydro-[5] and of 5,12-dihydro-5,12-diphenyl-quinoxalino[2,3-*b*]phenazine, but the last two compounds show a strong, red fluorescence in solution, and, moreover, the hydrogen values for B and C are too high for such structures.

We noticed that the spectrum of compound[6] (IV) in ethanol [$\lambda_{max.}$ 305 and 595 mμ (log ε 4·42 and 4·21), $\lambda_{min.}$ 227 and 415 mμ (log ε 4·03 and 3·35)] resembled those of compounds B and C, although it was changed in acid solution [$\lambda_{max.}$ 297 and 420 mμ (log ε 4·14 and 4·25), $\lambda_{min.}$ 250 and 337 mμ (log ε 3·89 and 3·92)], the compound (IV) being more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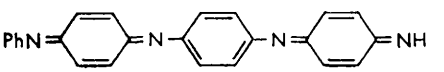
(V)

strongly basic. However, neither B nor C was affected by mild oxidising agents such as transform the imine (IV) into the red compound (V) with $\lambda_{max.}$ 272, 313, and 490 mμ (log ε 4·24, 4·46, and 3·92), $\lambda_{min.}$ 220, 287, and 380 mμ (log ε 3·49, 4·20, and 3·37). Compounds B and C exhibited moderate infrared absorption in the 750 cm.$^{-1}$ region with only very weak absorption in the 700 cm.$^{-1}$ region.

As we required 2-bromodiphenylamine (see below) we carried out an Ullmann reaction between *o*-bromoaniline and bromobenzene. As by-products, we isolated a purple and a blue compound, the visible and ultraviolet spectra of which resembled those of B and C. The infrared spectra of these compounds also resembled those of B and C, except that they showed, in addition, moderately strong absorption in the 695 cm.$^{-1}$ region, which might be due to terminal residues derived from bromobenzene instead of *o*-bromoaniline. Compound C showed an additional peak at 780 mμ (minimum at 665 mμ) and the blue compound from the Ullmann reaction absorbed at 795 mμ (minimum at 653 mμ). This peak was absent from the spectra of compound B and the purple compound from the Ullmann reaction.

[4] Barry, Belton, O'Sullivan, and Twomey, *J.*, 1956, 888.
[5] Badger and Pettit, *J.*, 1951, 3211.
[6] Willstätter and Moore, *Ber.*, 1907, **40**, 2665.

We also synthesised *o*-bromo-*N*-ethylaniline and *o*-bromo-*NN*-diethylaniline and irradiated these. The former yielded a purple product, the ultraviolet spectrum of which was very similar to that of compound B; but the diethyl compound yielded no purple product. The formation of the purple compound from *o*-bromo-*N*-ethylaniline seems to be against structures based on (IV). Irradiation of a mixture of *N*-methyl- or *N*-ethylaniline with bromobenzene yielded the corresponding hydrobromide and a purple product, with similar visible and ultraviolet spectra to the above, whereas irradiation of the *NN*-disubstituted aniline with bromobenzene yielded no purple compound.

Another type of structure which might be possible for the compounds B and C would depend on carbon–carbon coupling of two aniline residues (*e.g.*, yielding a benzidine). We have frequently observed such dimerisation on irradiation of aromatic compounds (*e.g.*, nitrobenzene and anisole [7]). Dehydrogenation could yield a diphenoquinone di-imine, which might react further with the amine. Although such imines are apparently unstable,[8] the oxidation product of benzidine itself has been isolated as the perchlorate.[9]

Irradiation of a mixture of *o*-bromoaniline and bromobenzene gave, in addition to *o*-bromoaniline hydrobromide, aniline, and bromobiphenyl, a number of products which were not identified. One of those was a colourless, crystalline solid, m. p. 66°, which failed to yield an acetyl derivative; this was different from synthetic 4-amino-3-bromobiphenyl, m. p. 66°. Synthetic 2-bromodiphenylamine was an oil.

Irradiation of a mixture of phenazine and bromobenzene yielded a crystalline precipitate, which gave a deeply coloured solution in ethanol, but when recrystallised afforded phenazine hydrobromide. It appeared therefore that the irradiation had caused some reduction, leading to a semiquinone.

Experimental

Arrangements for the irradiations and dosimetry were as described in Part I.[10]

Irradiation of o-*Bromoaniline.*—Commercial *o*-bromoaniline was recrystallised from light petroleum. The purified material (100 g.) was irradiated for 400 hr. (total dose $2{\cdot}25 \times 10^{23}$ ev) at 40° (carbon-filament lamp). The resulting black liquid was filtered and the crystalline precipitate was washed with ether (100 ml.) and sublimed in a vacuum, yielding *o*-bromoaniline hydrobromide (2·61 g.) as colourless needles, m. p. 211—212° (Found: C, 28·6; H, 3·0. Calc. for $C_6H_7Br_2N$: C, 28·45; H, 2·8%). The mother-liquors, along with the ether washings, were kept in a refrigerator for 3 days. The resulting purple precipitate (214 mg.) was collected, dissolved in chloroform (10 ml.), and chromatographed on alumina, from which chloroform eluted a purple solid (128 mg.). After purification from chloroform–light petroleum this *product*, B had m. p. 178—181° (Found: C, 54·85; H, 4·05; Br, 31·1; N, 9·2. $C_{24}H_{18}Br_2N_4$ requires C, 55·15; H, 3·45; Br, 30·65; N, 10·7%). Methanol eluted a purplish-blue *product* C (54 mg.), m. p. 202—204° (Found: C, 58·9; H, 4·15; N, 10·7. $C_{30}H_{23}Br_2N_5$ requires C, 58·7; H, 3·75; N, 11·4%).

The ethereal filtrate from which the above purple material had been removed, was washed with 5N-hydrochloric acid (5 × 100 ml.), then with water (3 × 100 ml.), and dried and the solvent was removed. The dark, brown, residual gum (300 mg.) in benzene–light petroleum (20 ml., 5 : 1) was chromatographed on alumina, from which light petroleum (b. p. 60—80°) eluted a solid that crystallised from the latter solvent in pale orange needles (4·3 mg.), m. p. 126—127°, $\lambda_{max.}$ (in $CHCl_3$) 246 and 333 mμ. Benzene eluted a dark red material which separated from ether or benzene–light petroleum as reddish-purple plates (A), m. p. 233—234° (176 mg.) (Found: C, 49·6, 48·95, 49·55; H, 2·95, 2·75, 2·8; Br, 41·3; N, 7·4, 7·6. $C_{30}H_{20}Br_4N_4,\frac{1}{3}C_6H_6$ requires C, 49·1; H, 2·9; Br, 40·9; N, 7·15%). This *solvate* was then dried for 4½ hr. at 60°/1 mm. (Found: C, 48·65, 48·5; H, 2·6, 2·95. Calc. for $C_{30}H_{20}Br_4N_4$: C, 47·4; H, 2·65; N, 7·4; Br, 42·3%). Benzene–chloroform eluted a dark gum which, on treatment with benzene–light petroleum, yielded a brick-red solid (42 mg.), of indefinite m. p., resisting purification.

[7] Everard and Swan, *J.*, 1962, 914.
[8] Adams and Holmes, *J. Amer. Chem. Soc.*, 1952, **74**, 3033.
[9] Hünig and Richters, *Chem. Ber.*, 1958, **91**, 442.
[10] Swan and Timmons, *J.*, 1958, 4669.

Ullmann Condensation between o-*Bromoaniline and Bromobenzene.*—A mixture of *o*-bromoaniline (10 g.), bromobenzene (30 ml.), finely powdered potassium carbonate (2·5 g.), and copper bronze (0·25 g.) was refluxed for 15 hr. The excess of bromobenzene was removed in steam and the residue was washed with 3N-hydrochloric acid (3 × 20 ml.). A solution of the residue (890 mg.) in benzene–light petroleum (20 ml.; 4 : 1) was chromatographed on alumina. Light petroleum eluted a pale yellow oil, b. p. 138—141°/2 mm. (570 mg.), which was treated with acetic anhydride in the presence of sulphuric acid and redistilled, yielding 2-*bromodiphenylamine* (525 mg.), b. p. 128—132°/0·5 mm. (Found: C, 58·25; H, 4·35. $C_{12}H_{10}BrN$ requires C, 58·05; H, 4·05%). Benzene–chloroform mixtures eluted a variety of coloured products in very low yields. Chloroform then eluted a purple solid which, after crystallisation from benzene–light petroleum had m. p. 198—199° (165 mg.) (Found: C, 69·5; H, 4·65; Br, 13·8; N, 10·45. $C_{30}H_{23}BrN_4$ requires C, 69·5; H, 4·45; Br, 15·35; N, 10·7%). The hydrogen absorbed by this material in the presence of Adams catalyst was equivalent to 1 mole per 510 g.; the mol. wt. corresponding to $C_{30}H_{23}BrN_4$ is 519. Finally, methanol eluted a blue compound, m. p. 204—206° (32 mg.) (Found: C, 70·7; H, 4·95; N, 8·7%).

Spectra of 2-*Anilino*-3,5-*dihydro*-3-*imino*-5-*phenylphenazine* (X) *and* 2-*Amino*-3,5-*dihydro*-5-*phenyl*-3-*phenyliminophenazine* (Y).—The absorptions given in the Table were recorded for ethanolic solutions of specimens kindly supplied by Dr. V. C. Barry.

	$\lambda_{max.}$	log ε	$\lambda_{min.}$	log ε		$\lambda_{max.}$	log ε	$\lambda_{min.}$	log ε
X as base	272,452	4·51, 4·29	357	3·32	Y as base	276,460	4·89, 4·62	355	3·60
X in 1% HCl	281,496	4·55, 4·34	375	3·15	Y in 1% HCl	282,485	4·92, 4·65	380	3·56
X in 15% HCl	287,530	4·57, 4·48	375	3·33	Y in 15% HCl	286,530	4·79, 4·68	390	3·60

o-*Bromo*-N-*ethylaniline.*—Diethyl phosphorochloridate [11] (20 g.) was added to *o*-bromoaniline (40 g.) with ice-cooling. The mixture was kept overnight at room temperature, boiled with benzene, and filtered from the precipitated *o*-bromoaniline hydrochloride.[12] The benzene was removed from the filtrate under reduced pressure, but the viscous residue failed to crystallise. This diethyl *N*-*o*-bromophenylphosphoramidate was decomposed by heat, yielding a distillate, b. p. 210—225° (20 g.). The infrared spectrum in the 2000—2600 cm.$^{-1}$ region suggested that this contained phosphate. The material was therefore shaken with 10% sodium hydroxide solution and then extracted with ether, and the dried extract was distilled, yielding o-*bromo*-N-*ethylaniline* (17·4 g.), b. p. 109—111°/14 mm., n_D^{18} 1·5847 (Found: C, 48·3; H, 4·85. $C_8H_{10}BrN$ requires C, 48·0; H, 5·0%). This failed to give a picrate.

Alternatively, the crude base (7 g.) could be purified through the benzoyl derivative (6 g.) (Schotten–Baumann), m. p. 100—101° [from light petroleum (b. p. 60—80°)]. This derivative was hydrolysed by boiling with 50% sulphuric acid (50 ml.) for 2·5 hr. Precipitated benzoic acid was filtered off and the filtrate was basified and extracted with ether. Distillation of the dried extract gave the base (3·4 g.), b. p. 118—119°/16 mm., n_D^{18} 1·5851, $\lambda_{max.}$ 214, 246·5, and 302 mμ (log ε 4·01, 4·05, and 3·49), $\lambda_{min.}$ 226 and 273 mμ (log ε 3·56 and 3·02).

o-*Bromo*-NN-*diethylaniline.*—A mixture of *o*-bromoaniline (52 g.), ethyl iodide (184 g.), sodium carbonate (112 g.), and water (1320 ml.) was refluxed for 16 hr., then distilled in steam. The steam-distillate was extracted with ether, the extract dried, and the ether removed. The residue was kept overnight in the presence of acetic anhydride (40 g.), then diluted with water and distilled in steam. The distillate was extracted with ether, and the dried extract was distilled, giving fractions: (i) 3·6 g., b. p. 110—112°/15 mm.; (ii) 12·55 g., b. p. 113—118°/15 mm.; and (iii) 3·85 g., b. p. 146—150°/15 mm. Redistillation of fraction (ii) yielded the *base* (12·2 g.), b. p. 115—118°/15 mm., n_D^{16} 1·5519 (Found: C, 53·0; H, 6·3. $C_{10}H_{14}BrN$ requires C, 52·65; H, 6·1%); $\lambda_{max.}$ 219 and 260 mμ (log ε 3·83 and 3·52), $\lambda_{min.}$ 240 mμ (log ε 3·40). The picrate had m. p. 154—155° [from ethanol–light petroleum (b. p. 60—80°)].

Irradiation of a Mixture of o-*Bromoaniline and Bromobenzene.*—A solution of *o*-bromoaniline (54·3 g.) in bromobenzene (365 g.) was irradiated for 93 hr. The precipitated *o*-bromoaniline hydrobromide (3·3 g.) was filtered off and identified by conversion into *o*-bromoacetanilide, m. p. and mixed m. p. 99°. Bromobenzene was removed from the filtrate by distillation under reduced pressure and the residue was diluted with ether, giving a purple precipitate (2·5 g.), which was filtered off. The purple solid was shaken with chloroform and water. The reddish-

[11] McCombie, Saunders, and Stacey, *J.*, 1945, 380.
[12] Gerrard and Jeacocke, *Chem. and Ind.*, 1954, 1538.

purple aqueous layer was basified with 10% aqueous sodium hydroxide and extracted with ether, giving a pale yellow extract which, on distillation, yielded aniline (0·97 g.), b. p. 90—92°/12 mm. (Found: C, 77·65; H, 7·2. Calc. for C_6H_7N: C, 77·4; H, 7·55%) (acetyl derivative, m. p. 114°).

The red chloroform layer, on evaporation, yielded a dark brown gum (0·95 g.) which was chromatographed in benzene–chloroform (1 : 1, 20 ml.) on alumina. Chloroform eluted a deep reddish-violet material (5 mg.) with absorption maxima at 298 and 507 mμ (in chloroform), followed by a yellowish-brown strongly fluorescent material (15 mg.) absorbing at 257, 296, and 448 mμ. The bulk of the material was eluted with methanol, but resisted purification. No trace of an azophenine was detected.

The solvent was removed from the above-mentioned ethereal solution and the unchanged *o*-bromoaniline was distilled off under reduced pressure. The residue (6·7 g.) was shaken with ether and 17% hydrochloric acid. The material left undissolved was shaken with chloroform and sodium carbonate solution, and the chloroform extract was evaporated to dryness; the residue was chromatographed in benzene on alumina. Elution with light petroleum (b. p. 40—60°) containing benzene (30%) (total volume 300 ml.) gave a reddish oil (1·33 g.) which on distillation yielded a liquid, b. p. 140—145° (bath-temp.)/1 mm. (1·12 g.), that reddened. A solution of it in benzene was shaken with concentrated sulphuric acid until the benzene layer was colourless and this was then washed with water, dried, and distilled, giving a colourless oil (1·01 g.), mainly 2-bromobiphenyl, b. p. 120—122° (bath-temp.)/0·5 mm. (Found: C, 62·15; H, 4·2. Calc. for $C_{12}H_9Br$: C, 61·8; H, 3·85%), $\lambda_{max.}$ 215 and 246 mμ (log ε 4·09 and 3·99), $\lambda_{min.}$ 230 mμ (log ε 3·89) [2-bromobiphenyl in ethanol had $\lambda_{max.}$ 247 mμ (log ε 4·0), $\lambda_{min.}$ 229 mμ (log ε 3·88)]. On oxidation with chromium trioxide in acetic acid this yielded *o*-bromobenzoic acid, m. p. and mixed m. p. 142°.

Further elution of the chromatogram with benzene yielded a material (0·34 g.), b. p. 120° (bath-temp.)/0·2 mm., which separated from light petroleum (b. p. 40—60°) as colourless crystals, m. p. 66° (Found: C, 60·05; H, 5·05; N, 6·5%). 4-Amino-3-bromobiphenyl, m. p. 66° (acetyl derivative, m. p. 161°), was synthesised by Kenyon and Robinson's method [13] except that the final hydrolysis was carried out with ethanolic hydrogen chloride instead of sulphuric acid; when mixed with the above compound it had m. p. 47°. Also the ultraviolet spectra were different. Light absorption of 4-amino-3-bromobiphenyl in ethanol: max. at 220 and 290 mμ (log ε 3·96 and 4·00), min. at 245 mμ (log ε 3·27).

Irradiation of a Mixture of Phenazine and Bromobenzene.—A solution of phenazine (1 g.) in bromobenzene (20 ml.) was irradiated for 110 hr. The resulting dark green-brown liquid was filtered from a crystalline precipitate. The latter was washed with ether and dissolved in ethanol, affording a solution which showed $\lambda_{max.}$ 249, 348, and 373 mμ, $\lambda_{min.}$ 238, 301, and 363 mμ. When recrystallised from ethanol–ether it afforded phenazine hydrobromide (682 mg.) as pale brown needles, m. p. 190—191° (Found: C, 55·05; H, 3·4. Calc. for $C_{12}H_9BrN_2$: C, 55·15; H, 3·45%).

3,3′-Dibromo-4,4′-dinitrobiphenyl.—A hot solution of 4,4′-diamino-3,3′-dibromobiphenyl [14] (2·1 g.) in a mixture of water (40 ml.) and concentrated sulphuric acid (1·8 ml.) was cooled rapidly with stirring and diazotised at 0° with sodium nitrite (0·84 g.) in water (2 ml.). The resulting solution was neutralised with barium carbonate, centrifuged, and added gradually with stirring to a solution of sodium nitrite (7·2 g.) in water (12 ml.) to which Chevreul's salt (2·4 g.) had been added with stirring (cf. ref. 15). The mixture was kept overnight at room temperature, then filtered. The resulting solid was washed with water and stirred with concentrated hydrochloric acid, and the mixture was diluted with water and filtered. The solid was dried in a vacuum-desiccator and recrystallised from chloroform, yielding the *product* (1·38 g.) as a pale brown solid, m. p. 239—240° (Found: C, 35·4; H, 1·55. $C_{12}H_6Br_2N_2O_4$ requires C, 35·8; H, 1·5%).

4,4′-Diamino-3,3′-dianilinobiphenyl.—The above compound (0·95 g.) was refluxed for 17 hr. with aniline (6 ml.) and fused sodium acetate (0·45 g.). The black solid remaining after distillation in steam was washed with water, dried in a vacuum-desiccator, and chromatographed from chloroform solution on alumina (30 g.). The chloroform eluate was concentrated to a small volume and diluted with hot ethanol. The resulting solid was recrystallised from chloroform–

[13] Kenyon and Robinson, *J.*, 1926, 3050.
[14] Snyder, Weaver, and Marshall, *J. Amer. Chem. Soc.*, 1949, **71**, 289.
[15] Topeijev, *Compt. rend. Acad. Sci. U.R.S.S.*, 1935, **4**, 201.

ethanol, yielding 3,3'-*dianilino*-4,4'-*dinitrobiphenyl*, dark reddish-brown needles, m. p. 220—222° (Found: C, 65·15; H, 4·55. $C_{24}H_{18}N_4O_4$ requires C, 67·6; H, 4·25%). A solution of this in acetic acid was warmed on the water-bath with zinc dust for 1½ hr., after which dilute hydrochloric acid and further zinc dust were gradually added. When the solution was almost colourless, it was cooled, treated with an excess of aqueous ammonia, and extracted with ether. The residue left by evaporation of the dried (K_2CO_3) extract was recrystallised from ethanol (charcoal), affording the *tetra-amine* as an almost colourless solid, m. p. 242—243° (Found: C, 78·1; H, 6·25. $C_{24}H_{22}N_4$ requires C, 78·7; H, 6·0%). This appeared to be comparatively stable to oxidation and we saw no evidence of the oxidation, yielding products such as B or C.

We thank the United Kingdom Atomic Energy Authority (Research Group, Harwell) for financial support, including the provision of research assistantships (to J. D. P. and P. S. T.).

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Newcastle upon Tyne, 1. [*Received, June 30th*, 1961.]