170. *The Chemical Effects of γ-Radiation on Organic Systems. Part VI.*[1] *The Radiolysis of Iodobenzene, 2-Iodobiphenyl, and 2-Bromobiphenyl.*

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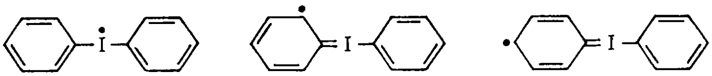
γ-Radiolysis of iodobenzene yields diphenyliodonium tri-iodide, biphenyl, and 4-iodobiphenyl. 2-Iodobiphenyl behaves similarly. Diphenylene was not detected in irradiated 2-iodo- or 2-bromo-biphenyl.

The action of γ-radiation on iodobenzene was studied by Süe and Saeland,[2] who reported the liberation of free iodine (estimated colorimetrically), apparently without investigating the other products formed. Shaw,[3] in a study of some (*n*,γ) effects in iodobenzene, noted the formation of diphenyliodonium iodide as well as of free iodine in pile-irradiated iodobenzene. However, he pointed out that this could not be taken as evidence for the formation of diphenyliodonium radicals by neutron-induced recoils, since the high γ-ray flux, with its associated secondary electrons, might lead to a similar disruption of iodobenzene molecules. We have now shown a similar effect to be produced by the γ-radiation from ^{60}Co. From irradiated iodobenzene we isolated diphenyliodonium tri-iodide ($Ph_2I^+I_3^-$) (*G* 0·75), which we reduced to diphenyliodonium iodide by sulphur dioxide; in addition, hydrogen iodide, biphenyl, 4-iodobiphenyl, and probably 2- and 3-iodobiphenyl were formed.

The mechanism for the formation of diphenyliodonium iodide suggested by Shaw involved the liberation of phenyl radicals and iodine atoms from the iodobenzene, followed by the addition of the former to iodobenzene to form the resonance-stabilised diphenyliodonium radical:



etc.

The latter radical was supposed to react with an iodine atom to give diphenyliodonium iodide. Evidence of the participation of the intermediate diphenyliodonium radical, at any rate under photolytic conditions, was adduced by the ultraviolet irradiation of iodobenzene in the presence of nitric oxide to trap the radical as $Ph_2I{\cdot}NO$, which was subsequently oxidised by hydrogen peroxide and treated with potassium iodide, yielding diphenyliodonium iodide. Further work on the photolysis of iodobenzene has been carried out by Blair and Bryce-Smith,[4] whose experiments were carried out in the presence of silver powder, which removed most of the iodine formed, and by Wolff and Kharasch.[5] A mixture of iodobiphenyls, in the isomer ratio expected of free-radical attack, was obtained and apparently diphenyliodonium iodide was not detected in these experiments. Irving and Reid[6] have, however, shown that diphenyliodonium iodide is decomposed photochemically, although they were unable to prove the participation of free-radical intermediates.

Blair and Bryce-Smith's and Wolff and Kharasch's photolytic results on iodobenzene appeared to correspond to our radiolytic results on bromobenzene, where the formation of phenyl radicals and bromine atoms is postulated. On the other hand, although by radiolysis of iodobenzene we obtained diphenyliodonium iodide, we found no evidence of the formation of the, admittedly unstable, diphenylbromonium bromide by radiolysis of bromobenzene. To test whether iodobenzene could undergo heterolysis (to give I^- and

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[1] Part V, preceding paper.
[2] Süe and Saeland, *Bull. Soc. chim. France*, 1949, 437.
[3] Shaw, *J.*, 1951, 443.
[4] Blair and Bryce-Smith, *J.*, 1960, 1788.
[5] Wolff and Kharasch, *J. Org. Chem.*, 1961, **26**, 283.
[6] Irving and Reid, *J.*, 1960, 2078.

Ph^+, which might react with iodobenzene to give Ph_2I^+) under the influence of γ-radiation, we irradiated mixtures of iodobenzene with diethylamine and triethylamine, respectively. If phenyl cations were produced, then *NN*-diethylaniline and *NN*-diethylaniline ethiodide, respectively, should be formed in these cases. With triethylamine the crystals which separated during the irradiation consisted of almost pure triethylamine hydriodide and, with diethylamine, crystals of diethylamine hydriodide separated. In the latter case, biphenyl and 4-iodobiphenyl were also isolated; there was formed, in addition, some basic material which, judged by its boiling point, might have been *NN*-diethylaniline, but this failed to yield a crystalline picrate or other derivatives, and diethylaniline, if indeed present in it at all, must have constituted only a minor fraction. We also failed to establish the formation of *N*-ethyl-α-methylbenzylamine. We thus found no evidence that radiolysis of iodobenzene yields phenyl cations; but an ion-molecule reaction cannot be excluded.

Irradiation of *o*- and *p*-iodoanisole was also investigated, as it was thought that the electron-releasing methoxyl group might favour heterolysis rather than the homolysis of the C–I bond. However, in these cases, we failed to establish the formation of iodonium salts.

We also investigated the radiolysis of 2-iodo- and 2-bromo-biphenyl, to see whether the resulting aryl radicals could cyclise to give diphenylene. Trial experiments with synthetic diphenylene showed that the latter could be separated from 2-iodo- or 2-bromo-biphenyl by fractional distillation or by chromatography on alumina (the hydrocarbon being more strongly adsorbed). Moreover, the hydrocarbon could be isolated as the picrate, even when mixed with four times its weight of either of the halogen compounds, while in more dilute solutions a scarlet colour was produced. Irradiation of 2-iodobiphenyl led to the precipitation of di-2-biphenylyliodonium tri-iodide (*G* 0·3), which was reduced by sulphur dioxide to the iodide (both apparently new compounds). Biphenyl and what was thought to be a mixture of iodoquaterphenyls were also produced. No biphenylene was detected in this or in irradiated 2-bromobiphenyl, although biphenyl was isolated from the latter.

EXPERIMENTAL

Arrangements for the irradiations and dosimetry were as described in Part I.[7]

Irradiation of Iodobenzene.—Commercial iodobenzene was washed with dilute hydrochloric acid, followed by sodium carbonate solution, dried, and distilled. This product (250 ml.) was irradiated for 120 hr. (total dose $2{\cdot}03 \times 10^{23}$ ev). The resulting purplish-black crystals, m. p. 138° (1·6 g.), were collected and shown by mixed m. p. to be diphenyliodonium tri-iodide.[8] When these crystals were suspended in water and treated with sulphur dioxide, colourless crystals of diphenyliodonium iodide,[9] m. p. and mixed m. p. 176°, were obtained. The irradiated iodobenzene was washed with dilute acid and alkali, dried, and fractionated and the high-boiling residue was distilled in bulbs. When the distillation bulb was kept at 110°/2 mm., a white solid (0·15 g.) slowly sublimed and was shown to be biphenyl by conversion into 4-nitrobiphenyl, m. p. 111—114°, not depressed by admixture with an authentic sample.[10] A fraction of b. p. 150—160° (bath)/2 mm. appeared to consist of a mixture of iodobiphenyls (Found: C, 51·55; H, 3·75. Calc. for $C_{12}H_9I$: C, 51·4; H, 3·2%). The last part of the distillate solidified and when recrystallised from ethanol yielded 4-iodobiphenyl, m. p. 110°, mixed with an authentic sample (m. p. 113·5°), m. p. 112·5°. Light absorption of both samples of 4-iodobiphenyl: $\lambda_{max.}$ 260 mμ (log ε 4·35), $\lambda_{min.}$ 227·5 mμ (log ε 3·62).

Irradiation of a Mixture of Iodobenzene and Triethylamine.—A mixture of triethylamine (5·05 g.) and iodobenzene (10·2 g.) was irradiated for 120 hr. Filtration yielded triethylamine hydriodide (0·39 g.), m. p. 175° (from ethanol) (Found: C, 30·85; H, 7·05. Calc. for $C_6H_{16}IN$: C, 31·45; H, 7·0%).

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[7] Swan and Timmons, *J.*, 1958, 4669.
[8] Hartmann and Meyer, *Ber.*, 1894, **27**, 1592.
[9] Hartmann and Meyer, *Ber.*, 1894, **27**, 502.
[10] Bell, Kenyon, and Robinson, *J.*, 1926, 1239.

Irradiation of a Mixture of Bromobenzene and Iodine.—A solution of iodine (0·25 g.) in bromobenzene (10 ml.) was irradiated for 150 hr., but diphenyliodonium iodide could not be detected in the product.

Irradiation of a Mixture of Iodobenzene and Diethylamine.—An equimolecular mixture of iodobenzene and diethylamine (275 ml.) was irradiated for 120 hr. The unchanged diethylamine was removed by distillation and the residue was diluted with ether; diethylamine hydriodide (3 g.), m. p. 168°, was precipitated. The filtrate was extracted with dilute hydrochloric acid and the acid layer was basified and re-extracted with ether. Distillation of the latter extract yielded a base, b. p. 55—65° (bath)/11 mm. (which gave a red colour with Ehrlich's reagent and contained iodine), together with a second base, b. p. 110—120° (bath)/12 mm. (which failed to give a crystalline picrate or other derivatives). The organic layer which had been extracted with hydrochloric acid was dried and the iodobenzene was removed by distillation. The residue was chromatographed on alumina, yielding biphenyl, m. p. 69·5° (128 mg.), and 4-iodobiphenyl (10 mg.).

Diethyl N-*α-Methylbenzylphosphoramidate.*—Diethyl phosphorochloridate[11] (8·22 g.) was added to a solution of α-methylbenzylamine (11·5 g.) in benzene (8 ml.). The mixture was kept for 2 hr. at room temperature, then diluted with benzene (80 ml.). The precipitated α-methylbenzylamine hydrochloride was removed and the filtrate was washed twice with cold water, dried, and evaporated. The residue, when recrystallised from light petroleum (b. p. 40—60°), afforded the *product*, m. p. 48—51° (Found: C, 55·5; H, 8·05. $C_{12}H_{20}NO_3P$ requires C, 56·05; H, 7·8%).

N-*Ethyl-α-methylbenzylamine Picrate.*—The above phosphoramidate (11 g.) decomposed at 280° to a colourless liquid (cf. Gerrard and Jeacocke[12]), distillation of which yielded fractions of b. p. 58°/30 mm. (2 g.) and 104°/30 mm. (3 g.). The b. p. of the latter fraction agrees with that of *N*-ethyl-α-methylbenzylamine, but the product was impure and failed to give a pure hydrochloride. The pure base was, however, obtained by Novelli's method[13] and yielded a hydrochloride, m. p. 200°, and a *picrate*, separating from ethanol as orange prisms, m. p. 167° (Found: C, 51·2; H, 5·1. $C_{16}H_{18}N_4O_7$ requires C, 50·8; H, 4·75%).

Irradiation of o-*Iodoanisole.*—*o*-Iodoanisole (10 ml.) was irradiated for 162 hr., then diluted with ether and kept at 0°. A very small amount of a mixture of black and colourless crystals separated, having m. p. 136°.

Irradiation of p-*Iodoanisole.*—*p*-Iodoanisole (10 ml.) was kept molten by means of a carbon-filament lamp while it was irradiated. It was then diluted with ether and kept at 0°, but no solid separated.

Irradiation of 2-Iodobiphenyl.—2-Iodobiphenyl, prepared from commercial 2-aminobiphenyl by the Sandmeyer reaction, was washed with sodium thiosulphate solution, dilute acid, and dilute alkali, then dried and distilled (b. p. 125—126°/1 mm.; yield, 68%). It (100 g.) was irradiated for 525 hr. (total dose = $3·23 \times 10^{23}$ ev). The resulting purplish-black crystals of *di-2-biphenylyliodonium tri-iodide* were collected and after being washed with ethanol had m. p. 181—182° (1·33 g.) (Found: C, 35·45; H, 2·45. $C_{24}H_{18}I_4$ requires C, 35·4; H, 2·2%). Treatment of this tri-iodide with sulphur dioxide in ethanol yielded the corresponding *iodide*, m. p. 164—165° (from chloroform–ether) (Found: C, 51·75; H, 3·7. $C_{24}H_{18}I_2$ requires C, 51·45; H, 3·2%). Dilution of the irradiated mixture with ether caused no further precipitation. The mixture was shaken with dilute sodium hydroxide solution, then with water, dried, and distilled through a fractionating column. The bulk of the distillate consisted of 2-iodobiphenyl, but small " head " and " tail " fractions were collected separately. Chromatography of the " head " fraction on alumina yielded biphenyl (8 mg.) (from methanol), m. p. and mixed m. p. 72—73°. Similar chromatography of the " tail " fraction yielded a glass (eluted by benzene), b. p. 186—190°/0·3 mm. (0·85 g.), presumably consisting of a mixture of iodoquaterphenyls (Found: C, 66·75; H, 4·2. Calc. for $C_{24}H_{17}I$: C, 66·65; H, 3·95%).

Irradiation of 2-Bromobiphenyl.—2-Bromobiphenyl was prepared and purified in a similar way to 2-iodobiphenyl. This (30 g.) was irradiated for 825 hr. (total dose = $1·5 \times 10^{23}$ ev), then washed with dilute sodium hydroxide solution and water, dried, and chromatographed on alumina. Light petroleum eluted 2-bromobiphenyl (28·8 g.), followed by a gum. The latter

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[11] McCombie, Saunders, and Stacey, *J.*, 1945, 380.
[12] Gerrard and Jeacocke, *Chem. and Ind.*, 1954, 1538.
[13] Novelli, *J. Amer. Chem. Soc.*, 1939, **61**, 520.

solidified when treated with methanol; when recrystallised from benzene it yielded 4-bromobiphenyl (5 mg.), m. p. 87—88° and mixed m. p. 89°. This is assumed to have been present as an impurity in the original 2-bromobiphenyl. Benzene–light petroleum eluted biphenyl (115 mg.), m. p. and mixed m. p. 72° (from methanol). Benzene–chloroform eluted a crystalline compound (3 mg.), m. p. 207—211°, the ultraviolet spectrum of which suggested that it was a quaterphenyl.

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