940. *The Chemical Effects of γ-Radiation on Organic Systems. Part I. The Systems Pyridine–Bromobenzene and Aniline–Bromobenzene.*

By G. A. Swan and P. S. Timmons.

γ-Irradiation of a mixture of pyridine and bromobenzene afforded 2-, 3-, and 4-phenylpyridine, as well as pyridine hydrobromide. From an irradiated mixture of aniline and bromobenzene, 2- and 4-aminodiphenyl, azophenine, and aniline hydrobromide were isolated. These reactions are apparently initiated by homolysis of bromobenzene under the influence of γ-rays.

Although a number of studies of the radiation chemistry of pure organic compounds (as opposed to dilute, aqueous solutions of such compounds) have been carried out, the irradiation products have been isolated and satisfactorily characterised in only a very few cases.[1] In this and subsequent papers we describe some results of work initiated in these laboratories when, about four years ago, a ^{60}Co source of γ-radiation (nominally 100 c) was installed. In a wider fundamental study of the products of γ-irradiation of pure organic compounds and mixtures thereof, one line of work was concerned with mixtures of bromobenzene and various amines. We chose bromobenzene because of the relative inertness of its halogen atom towards most chemical reagents: if radiation activated the halogen, useful reactions might be possible.

It is well known that, particularly in aqueous solutions, oxygen often affects the course of a radiochemical reaction. Although we hope to investigate the effect of oxygen and of temperature on certain of our systems, our irradiations, except when otherwise stated, have hitherto been performed at room temperature in glass vessels stoppered in the normal way, without precautions to exclude air. The bulk of the starting materials were usually recovered unchanged; yields are expressed as G values (the number of molecules of product corresponding to an energy absorption of 100 ev). Where the yield is based only on the weight of product isolated, the G value should be regarded only as a minimum value.

When mixtures of various amines with bromobenzene were irradiated, the crystalline amine hydrobromide generally separated in amount showing linear dependence on the total dose of radiation up to the maximum studied (about 7×10^{20} ev/ml.) (in certain cases the hydrobromide separated only when the mixture was diluted with ether, after irradiation). Thus hydrogen bromide was produced during the irradiation: the rate of its production increased according to the following order of amines: dimethylaniline, diethylaniline, pyridine, ethylaniline, dibenzylamine, benzylamine, aniline, trimethylamine, ethylamine, diethylamine, triethylamine. Very little is known about the action of radiation on any of these components. Bromobenzene [2] has been shown to yield hydrogen bromide when irradiated with X-rays, and pyridine [3,4] and aniline [4,5] are slowly converted into unknown products by other forms of ionising radiation. In this paper some of the products formed in the systems pyridine–bromobenzene and aniline–bromobenzene are reported.

From an equimolecular mixture of pyridine and bromobenzene the weight of the precipitated pyridine hydrobromide showed that $G(\mathrm{HBr}) = 5{\cdot}5$. From the filtrate, a mixture of 2-, 3-, and 4-phenylpyridine was isolated, with $G(\text{phenylpyridines}) = 1{\cdot}2$, apparently in the approximate ratio of $7:2:1$. Although this is somewhat different from the isomer ratios reported in the phenylation of pyridine by benzoyl peroxide

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[1] Cf. Collinson and Swallow, *Quart. Rev.*, 1955, **9**, 311; *Chem. Rev.*, 1956, **56**, 471; Tolbert and Lemmon, *Radiation Res.*, 1955, **3**, 52.

[2] Schuler and Hamill, *J. Amer. Chem. Soc.*, 1952, **74**, 6171.

[3] Rubin, U.S. Atomic Energy Commission Report NP-5135 (1954); *Nuclear Sci. Abs.*, 1954 **8**, No. 3698.

[4] Kailan, *Sitzungsber. Akad. Wiss. Wien*, 1926, IIa, **135**, 611.

[5] Chapiro, *J. Chim. phys.*, 1950, **47**, 764.

decomposing thermally to yield phenyl radicals (54, 32, and 14%, or 58, 28, and 14%)[6, 7] or by the Gomberg reaction (46, 43, and 11% respectively),[6] the quantities of the isomers are in the same order. Under the influence of γ-radiation bromobenzene presumably undergoes homolysis; $PhBr \rightsquigarrow Ph\cdot + Br\cdot$, and the resulting phenyl radicals substitute the pyridine nucleus, hydrogen atoms being removed by the bromine atoms. Since, however, G(HBr) > G(phenylpyridines), other products must also be formed. The other reactions are unknown: they may be concerned with the breakdown of the aromatic or heterocyclic rings, since benzene, when irradiated, gives gaseous and polymeric products.[8]

From an irradiated equimolecular mixture of aniline and bromobenzene, aniline hydrobromide with G(HBr) = 5·9, 2- and 4-aminodiphenyl with G(aminodiphenyls) = 1·7, and azophenine with G value 0·46 (based on slightly impure material) were isolated, and traces of other coloured products were formed. We were unable to detect azophenine in a sample of pure aniline after irradiation and this compound is presumably formed by attack of the radicals derived from the bromobenzene on the amino-group of the aniline, resulting in dehydrogenation. Azophenine has previously been obtained from aniline or its salts by the action of iodic acid,[9] lead dioxide or manganese dioxide,[10] graphitic oxide,[11] or active carbon in the presence of oxygen,[11] as well as by electrolysis[12] and sunlight.[13] If the azophenine is assumed to arise according to the stoicheiometric equation, $5C_6H_5\cdot NH_2 \longrightarrow C_{30}H_{24}N_4 + NH_3 + 8H$, and the liberated hydrogen to react wholly with bromine atoms liberated from bromobenzene to form hydrogen bromide, then this reaction should result in the formation of hydrogen bromide with a G value of $0\cdot46 \times 8 = 3\cdot68$. The reaction, $Ph\cdot NH_2 + PhBr \longrightarrow HBr + Ph\cdot C_6H_4\cdot NH_2$, would result in the liberation of hydrogen bromide with a G value of 1·7, making a total of 5·38, not greatly less than the found value of 5·9. Spectroscopic results suggested that the 2- and 4-aminodiphenyl were present in approximately equal amount, with <1% of the 3-isomer. The literature appears to contain few reliable, quantitative data on reactions such as the phenylation of aniline; but the formation of mainly *ortho*- and *para*-isomers is to be expected in radical substitution in aromatic amines and phenols.[14] Irradiation of a mixture of aniline and bromobenzene in a molecular ratio of 1 : 4 gave the same products with G(HBr) = 6·7 and G(aminodiphenyls) = 1·6.

There thus appears to be no definite evidence against the formation of the observed products in the two systems studied by the radical reactions postulated, although excited-molecule reactions may be possible. If the suggested mechanism is correct, 2-, 3-, and 4-bromodiphenyl should also be produced. In the experiments with pyridine and aniline we did not look for these compounds, as we have shown them to be produced by γ-irradiation of bromobenzene alone. We hope, however, to publish full details of the latter work, together with further discussions of the isomer ratio in a later paper.

EXPERIMENTAL

Arrangements for Irradiations and Dosimetry.—The radiation unit was somewhat similar in design and operation to that described by Gibson and Pearce.[15] The irradiation vessels, of borosilicate glass, varied from test-tubes and small round-bottomed flasks for small samples to annular vessels, made to fit around the source tube, for larger samples. The dose-rate available

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[6] Hey, Stirling, and Williams, *J.*, 1955, 3963.

[7] Dannley and Gregg, *J. Amer. Chem. Soc.*, 1954, **76**, 2997.

[8] Henri, Maxwell, White, and Peterson, *J. Phys. Chem.*, 1952, **56**, 153: Manion and Burton, *ibid.*, p. 560; Gordon, Van Dyken, and Donmini, *ibid.*, 1958, **62**, 20.

[9] Ostrogovich and Silbermann, *Chem. Zentr.*, 1908, I, 266.

[10] Börnstein, *Ber.*, 1901, **34**, 1268.

[11] Carter, Moulds, and Riley, *J.*, 1937, 1305.

[12] Szarvasy, *J.*, 1900, **77**, 207.

[13] Gibbs, *J. Amer. Chem. Soc.*, 1912, **34**, 1190.

[14] Dermer and Edmison, *Chem. Rev.*, 1957, **57**, 77; Augood and Williams, *ibid.*, p. 123.

[15] Gibson and Pearce, *Chem. and Ind.*, 1957, 613.

for each type of irradiation vessel was determined by use of the ferrous–ferric system, the concentration of the ferric ion in the irradiated solution being estimated by measurement of the optical density at 3050 Å, using a Hilger Uvispec Spectrophotometer, and a *G* value of 16·0 for the oxidation. The dose received by an organic system was taken as that absorbed by an equal volume of the aqueous dosimeter in the same vessel multiplied by the specific gravity of the organic liquid. The electron-density of the medium was not taken into account, as this is unnecessary for γ-radiation unless high accuracy is required.

Compounds to be irradiated were purified before use.

Irradiation of an Equimolecular Mixture of Pyridine and Bromobenzene.—A mixture of pyridine (126 g.) and bromobenzene (250 g.) was irradiated for 117 hr. (total dose $1\cdot84 \times 10^{23}$ ev), then diluted with ether. The precipitated pyridine hydrobromide (2·67 g.) was filtered off, the filtrate was washed with water and dried, and the bulk of the pyridine and bromobenzene were removed by distillation under reduced pressure. The residue was extracted with 17% hydrochloric acid, and the extract was basified and extracted with ether. The latter extract was dried and distilled, giving a mixture of phenylpyridines, b. p. 150°/10 mm. (0·55 g.). By fractional crystallisation (Haworth, Heilbron, and Hey's method [16]) the mixed picrates derived from this base yielded (*a*) yellow, rhombic prisms, m. p. 175—176°, (*b*) yellow needles, m. p. 159—160°, and (*c*) orange needles, m. p. 195—196°, which were shown, by mixed m. p. determinations, to be identical with samples of the picrates of 2-, 3-, and 4-phenylpyridine, respectively, prepared by Haworth, Heilbron, and Hey's method. Spectroscopic determination [6, 17] of the composition of the base mixture, on the assumption that it contained only 2-, 3-, and 4-phenylpyridine, showed these isomers to be present in the approximate ratios of 7 : 2 : 1. The phenylpyridine mixture was slightly impure (Found: C, 83·7; H, 6·0. Calc. for $C_{11}H_9N$: C, 85·15; H, 5·8%), the amount being small, so the accuracy of the result is uncertain. In particular, traces of dipyridyls might be present.

Irradiation of an Equimolecular Mixture of Aniline and Bromobenzene.—A mixture of aniline (128 g.) and bromobenzene (216 g.) was irradiated for 136 hr. (total dose $1\cdot83 \times 10^{23}$ ev) during which precipitation of aniline hydrobromide (3·14 g.) began and this was completed by the addition of dry ether (1 l.) after the irradiation. The nature of the precipitate was confirmed by conversion into aniline picrate (mixed m. p.). The ethereal filtrate was washed with water and dried, and the ether and the bulk of the aniline and bromobenzene were removed by distillation (water-bath/reduced pressure). An ethereal solution of the residue was extracted several times with 17% hydrochloric acid (total volume 200 ml.). The combined acid extracts were diluted with water and the resulting dark precipitate A (0·52 g.) was collected, washed with water, and dried in a vacuum-desiccator. The filtrate was basified with 40% sodium hydroxide solution and extracted with ether. The ether was removed from the dried (Na_2SO_4) extract, and the residue was heated at 100°/15 mm. to free it from volatile material. A solution of the resulting brown oil (6·35 g.) in light petroleum (b. p. 40—60°)–benzene (3 : 2) was chromatographed on Peter Spence Grade 0 alumina (160 g.). Development with light petroleum (b. p. 40—60°)–benzene (1 : 1) yielded a red oil which, on distillation, gave aniline, b. p. 100° (bath-temp.)/15 mm., followed by a base B (0·9 g.), b. p. 145° (bath-temp.)/0·5 mm., which slowly crystallised. Further development with benzene yielded more aniline. Development with chloroform yielded, on one occasion, an oil (0·3 g.), b. p. 145° (bath-temp.)/15 mm. (Found: C, 77·5; H, 7·65%). The latter figures are close to those required by aniline, but the b. p. did not agree and no picrate or hydrochloride could be obtained from the oil, the light absorption of which was weaker than that of aniline. Unfortunately we were unable to isolate the oil in subsequent experiments.

By fractional crystallisation of the hydrochloride of base B from benzene, two compounds were obtained:

(i) The less soluble fraction (which could also be sublimed out of the mixture) consisted of 4-aminodiphenyl hydrochloride, and basification yielded 4-aminodiphenyl which, when recrystallised from light petroleum (b. p. 40—60°), had m. p. 53° (Found: C, 85·1; H, 6·6. Calc. for $C_{12}H_{11}N$: C, 85·2; H, 6·5%) and afforded an acetyl derivative, m. p. 170° (Found: C, 79·25; H, 6 55. Calc. for $C_{14}H_{13}ON$: C, 79·6; H, 6·15%).

(ii) The more soluble fraction consisted of 2-aminodiphenyl hydrochloride, m. p. 180°, and

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[16] Haworth, Heilbron, and Hey, *J.*, 1940, 349.

[17] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1951, p. 29; Cadogan, Hey, and Williams, *J.*, 1954, 794.

on basification yielded 2-aminodiphenyl, m. p. 49° (Found: C, 85·4; H, 6·4%), which gave an acetyl derivative, m. p. 120° (Found: C, 79·35; H, 6·45%).

These compounds were identified by direct comparison of m. p. and of ultraviolet spectra with authentic samples, the spectroscopic constants being tabulated.

	$\lambda_{max.}$ (Å)	ε	$\lambda_{min.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε
2-Aminodiphenyl (authentic)	2300	10,360	2750	1861	3000	3738
,, (from irradiation)	2300	10,320	2750	1840	3000	3654
4-Aminodiphenyl (authentic)	2175	9311	2375	2317	2800	13,930
,, (from irradiation)	2175	9265	2375	2265	2800	13,470

We were unable to isolate 3-aminodiphenyl from material B, but, on the assumption that the latter contained only the three isomeric aminodiphenyls, its composition was determined spectroscopically, following the general methods described by Cadogan, Hey, and Williams, and Friedel and Orchin,[17] to be 50·5, 1·0, and 48·5% of 2-, 3-, and 4-aminodiphenyl respectively.

A solution of the precipitate A in benzene–chloroform (1 : 1) was chromatographed on alumina. The first material to be eluted crystallised from ethyl acetate as red plates with a purplish iridescence, m. p. 253° [Found: C, 81·65; H, 5·25; N, 12·35%; *M* (Rast), 409. Calc. for $C_{30}H_{24}N_4$: C, 81·8; H, 5·45; N, 12·75%; *M*, 440]. The identity of this with azophenine (m. p. 253°) was shown by a mixed m. p. (253°) and by comparison of its spectrum (in ethyl acetate) with that of azophenine prepared by Ruggli and Buchmeier's method,[18] the following values being obtained:

	$\lambda_{max.}$ (Å)	ε	$\lambda_{min.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε
Azophenine (from irradiation)	2900	25,770	3300	7026	3800	16,820
,, (authentic)	2900	25,690	3300	7008	3800	16,800

The material dissolved in concentrated sulphuric acid to a deep purple solution, which became red on dilution or deep blue when heated. Further development with chloroform eluted the bulk of the original material, but the product was darker than, although otherwise indistinguishable from, the initial eluate.

Irradiation of a 1 : 4 *Molar Mixture of Aniline and Bromobenzene*.—A mixture of aniline (48 g.) and bromobenzene (337 g.) when irradiated for 160 hr. (total dose $2·15 \times 10^{23}$ ev) gave aniline hydrobromide (4·15 g.). 2- and 4-Aminodiphenyl (0·74 and 0·25 g., respectively) were isolated by chromatography on alumina, the former being eluted first (along with aniline) by light petroleum–benzene (7 : 3).

We thank the United Kingdom Atomic Energy Authority (Research Group, Harwell) for financial support, including the provision of a research assistantship (to P. S. T.), and for permission to publish this paper; also Professor G. R. Clemo, F.R.S., Dr. W. Wild, and Mr. J. Wright for their interest and help in the initiation of this work.

DEPARTMENT OF CHEMISTRY, KING'S COLLEGE (UNIVERSITY OF DURHAM),
NEWCASTLE UPON TYNE, 1.
[*Received, May 27th*, 1958.]

[18] Ruggli and Buchmeier, *Helv. Chim. Acta*, 1945, **28**, 850.