169. *The Chemical Effects of γ-Radiation on Organic Systems. Part V.*[1] *The Radiolysis of Bromobenzene.*

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γ-Radiolysis of bromobenzene yields benzene and hydrogen bromide, together with 2-, 3-, and 4-bromobiphenyl in the same ratio as these isomers are formed by the action of chemically generated phenyl radicals on bromobenzene. Small amounts of the dibromobenzenes and other products are also formed. The results are interpreted on the assumption that bromobenzene undergoes radiolysis to give bromine atoms and phenyl radicals.

Little has been published on the radiation chemistry of bromobenzene, although in Part I[2] we discussed the effects of γ-radiation on the systems pyridine–bromobenzene and aniline–bromobenzene. In these, homolysis of bromobenzene apparently occurred, giving phenyl radicals and bromine atoms. Irradiation of bromobenzene in evacuated and sealed flasks yielded hydrogen bromide, the yield of which was linear with respect to dose up to the maximum dose for which measurements were made ($1{\cdot}1 \times 10^{21}$ ev/ml.) [G(HBr) 1·28]. When the irradiations were carried out in glass-stoppered flasks under atmospheric pressure, the rate of formation was initially the same as in a vacuum, but after a dose of $0{\cdot}5 \times 10^{21}$ ev/ml. it fell off. Admixture of bromobenzene with various amines resulted in the formation of hydrogen bromide at a much higher rate on irradiation. Increasing the molecular proportion amine : bromobenzene up to ~1 : 3 caused increasing hydrogen bromide formation, but thereafter the rate of formation was independent of the ratio. Irradiation of a mixture of equal volumes of bromobenzene and benzene gave a higher rate of hydrogen bromide formation than with bromobenzene alone; but addition of hexane to bromobenzene had little effect on the rate, while addition of diethyl ether increased it ~3·3 times.

Distillation of bromobenzene, which had received a dose of 5×10^{21} ev/ml. in an evacuated, sealed flask, yielded benzene (G value, based on yield isolated, 1·2) and a trace of ethyl bromide. Chromatography of the residue left after removal of the unchanged bromobenzene by fractional distillation yielded *p*-dibromobenzene, a liquid which consisted of *o*- and/or *m*-dibromobenzene, biphenyl, 4-bromobiphenyl, a mixture of 2- and 3-bromobiphenyl, and a very small amount of a crystalline compound thought to be *p*-terphenyl. The G values for the isolated *p*-dibromobenzene, *o*- and/or *m*-dibromobenzene, and biphenyl were only ~0·01, 0·015, and 0·02, respectively; but the losses involved in isolating these volatile compounds during the distillation of the excess of bromobenzene were probably considerable. 4-Bromobiphenyl was isolated with a G value of 0·037 and a mixture of the 2- and 3-isomers with $G = 0{\cdot}63$. Similar results were obtained by irradiating bromobenzene in a stoppered vessel under atmospheric pressure (dose $2{\cdot}93 \times 10^{21}$ ev/ml.), although the G values here were slightly lower (benzene, 1·06; 4-bromobiphenyl, 0·033; bromobiphenyl mixture, 0·57).

We attempted to determine the isomer ratio of the bromobiphenyls formed, using Augood, Cadogan, Hey, and Williams's infrared spectroscopic method.[3] However, the only way we found for isolating a material containing nothing but the three bromobiphenyls involved chromatography on alumina and this process almost certainly altered the isomer ratio. On the other hand, chromatography did not give a clear-cut separation, for, although it did enable the 4-isomer to be isolated pure, the 2- and the 3-isomer could not be separated. We were therefore unable to obtain trustworthy results by this method and hence used the isotope-dilution method.

We irradiated uniformly labelled bromo[^{14}C]benzene of specific activity approximately

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[1] Part IV, preceding paper.

[2] Swan and Timmons, *J.*, 1958, 4669.

[3] Augood, Cadogan, Hey, and Williams, *J.*, 1953, 3412.

150 μc/mole at room temperature and then divided it into three portions, to which accurately known weights of each of the three isomers being assayed were added. 4-Bromobiphenyl was readily isolated pure as such, by chromatography on alumina; and the 2-isomer was obtained as a crystalline 4′,5-dinitro-derivative. Isolation of the 3-isomer, however, proved difficult and two different methods were used. In method A, the 3-isomer was isolated as the crystalline 4,4′-dinitro-derivative but this was only possible when a relatively large proportion of carrier was used, otherwise the 2-isomer (formed in greatest amount) interfered. Attempts to isolate 3-bromo-4,4′-dinitrobiphenyl from its mixture with 2-bromo-4′,5-dinitrobiphenyl as a benzotriazole by reaction with hydrazine were unsuccessful (cf. the reaction of *o*-bromonitrobenzene with hydrazine [4]). In method B, a chromatographic fraction, rich in the 3-isomer, was oxidised by chromic acid and the resulting mixture of *m*-bromobenzoic acid, benzoic acid, etc., was subjected to partition chromatography; the *m*-bromobenzoic acid was obtained almost pure (possibly containing a trace of *p*-isomer), but was subsequently further purified through the barium salt. Trial experiments on a mixture of *m*- and *p*-bromobenzoic acid indicated that separation could not be achieved by partition chromatography on phosphate-buffered Celite columns within the range pH 7—8. Sen and Leopold [5] claim to have separated these two acids by paper chromatography but we were unable to do so using propan-2-ol–ammonia. Chromatography on silica gel also failed to separate the two acids. Fractional crystallisation from benzene produced some separation, but the process was too wasteful. Most derivatives of the *p*-bromo-acid have higher melting points and lower solubilities than the corresponding *meta*-derivatives. The phenacyl derivatives were exceptional in that the *para*-isomer had the lower melting point, but also the lower solubility. However, separation was achieved by using the barium salts, that of the *m*-bromo-acid being the less soluble.

The isotope dilution analysis was carried out four times, twice by each method; the results are shown in the accompanying Table. The lower total yield of bromobiphenyl obtained in experiment no. 3 is probably due to the larger total dose. The agreement in *G* values of the 2- and the 4-isomer in the other three experiments is regarded as reasonable; but the results for the 3-isomer obtained by method A are considerably higher than those obtained by method B. We do not regard this discrepancy as being due to impurity of the compounds measured. Nor can it be explained by the presence of 3,3′-dibromobiphenyl in the 3-bromobiphenyl oxidised, as this occurrence would result in a higher value being obtained by method B, whereas it is actually the lower. It seems possible that it may be due to an isotope effect and there appear to be three stages at which this might be involved (bromination of benzene, phenylation of bromobenzene, or oxidation of bromobiphenyl). We are unable to investigate this further at present and regard method A as probably the more reliable. The isomer ratios obtained are in reasonable agreement with those obtained by other workers [3,6] by phenylation of bromobenzene with phenyl radicals derived from benzoyl peroxide, as shown in the Table. The results therefore suggest that the formation of the bromobiphenyls by radiolysis of bromobenzene

Mode of generation of phenyl radicals	Method of isolation of 3-isomer	*G* Values of the isomeric bromobiphenyls			Isomer ratio (%) of the bromobiphenyls		
		2-	3-	4-	2-	3-	4-
Irradiation: (1) $2{\cdot}2 \times 10^{21}$ ev/ml. ...	B	0·406	0·226	0·131	53·2	29·6	17·2
,, (2) $2{\cdot}44 \times 10^{21}$ ev/ml. ...	A	0·387	0·295	0·130	47·7	36·3	16·0
,, (3) $4{\cdot}22 \times 10^{21}$ ev/ml. ...	A	0·303	0·221	0·114	47·5	34·6	17·9
,, (4) $2{\cdot}28 \times 10^{21}$ ev/ml. ...	B	0·367	0·192	0·133	53·0	27·7	19·3
Benzoyl peroxide (ref. 3)					49·3	33·3	17·4
,, ,, (ref. 6)					48·5	33·0	18·5

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[4] Brady and Reynolds, *J.*, 1928, 193.

[5] Sen and Leopold, *Physiol. Plantarum*, 1954, **7**, 98.

[6] Dannley, Gregg, Phelps, and Coleman, *J. Amer. Chem. Soc.*, 1954, **76**, 445.

involves the formation of phenyl radicals, which attack the bromobenzene. We found no evidence for the participation of the unstable diphenylbromonium bromide,[7] although the radiolysis of iodobenzene yields diphenyliodonium iodide.[8]

Addition of amines or diethyl ether increases the radiolytic formation of hydrogen bromide from bromobenzene because these compounds provide a more ready source of hydrogen atoms (from $\colon N{-}CH_2\cdot$ or $\cdot O{-}CH_2\cdot$) than does bromobenzene itself. Phenyl radicals and bromine atoms which do not undergo other reactions will presumably take part in the back-reaction, $Ph\cdot + Br\cdot \longrightarrow PhBr$. Triphenylmethane can react with bromine atoms, yielding triphenylmethyl bromide, which is readily hydrolysed.[9] We therefore irradiated bromobenzene in the presence of small amounts of triphenylmethane, in stoppered flasks with a view to reducing the back-reaction. The yield of hydrogen bromide for a given dose increased with increasing concentration of triphenylmethane up to a certain value, after which no further increase occurred. This presumably represents the quantity of triphenylmethane equivalent to the total production of bromine atoms for that dose (the weights of triphenylmethane and hydrogen bromide correspond quite well). For a fixed concentration of triphenylmethane (1 g. per 100 ml. of bromobenzene), the rate of formation of hydrogen bromide was linear with respect to dose up to the maximum dose for which measurements were made ($9{\cdot}2 \times 10^{20}$ ev/ml.) (G 1·61). Benzene (G 3·3), biphenyl (G 0·01), and the bromobiphenyl isomers (G 1·04) were isolated, but dibromobenzenes were not detected in this case.

In their studies of the liquid-phase photolysis of iodobenzene, most of which were carried out in the presence of silver powder, which reacted with the greater part of the iodine formed, Blair and Bryce-Smith [10] detected the formation of iodobiphenyls, benzene, biphenyl, and only a trace of hydrogen iodide, but the benzene formed was equivalent to only *ca.* 20% of the iodobiphenyl. Our results on the radiolysis of bromobenzene have the opposite difficulty: that the amounts of benzene and hydrogen bromide formed are equivalent (so far as hydrogen is concerned) to more than the amount of bromobiphenyls formed. The amount of bromine appearing as hydrogen bromide is also less than would be equivalent to the bromobiphenyls and benzene formed, but some molecular bromine is probably produced. There is also the possibility of addition of hydrogen bromide either to bromobenzene (we have shown that addition of hydrogen chloride to benzene can be induced by γ-radiation) or to a dihydrobiphenyl or tetrahydroquaterphenyl,[11] radiolytically produced, although we saw little evidence of the presence of such addition compounds. If such addition did occur, it would probably not do so with equal ease to the three isomers, so that the isomer ratio of the bromobiphenyls would probably be altered.

Irradiation of bromobenzene containing benzoyl peroxide led to an increased rate of production of hydrogen bromide and a greatly increased formation of bromobiphenyls (G 8·9). Benzene, biphenyl (G 0·02), and *p*-terphenyl (G 0·008) were also isolated. This suggests that benzoyl peroxide is decomposed by γ-radiation at room temperature, yielding phenyl radicals which result in increased bromobiphenyl formation.[12]

EXPERIMENTAL

Arrangements for the irradiations and dosimetry were as described in Part I.[2] The radioactivity measurements were all made by the gas-counting method on $^{14}CO_2$ as described by Swan.[13] Bromobenzene was purified by being shaken successively with dilute hydrochloric

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[7] Nesmeyanov, Makarova, and Tolstaya, *Tetrahedron*, 1957, **1**, 145.

[8] Parrack, Swan, and Wright, following paper.

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

[10] Blair and Bryce-Smith, *J.*, 1960, 1788.

[11] De Tar and Long, *J. Amer. Chem. Soc.*, 1958, **80**, 4742.

[12] Cf. Krongauz and Bagdasar'yan, *Doklady Akad. Nauk S.S.S.R.*, 1957, **114**, 829.

[13] Swan, *J.*, 1955, 1039.

acid and dilute sodium hydroxide solution; it was then dried ($MgSO_4$) and distilled through a fractionating column.

Investigation of the Formation of Hydrogen Bromide by Irradiation of Bromobenzene.—Bromobenzene was distilled in a high vacuum into 10-ml. flasks, which were sealed off while still under a vacuum. After irradiation the seals were broken under water; the hydrogen bromide formed was extracted with water and titrated with standard sodium hydroxide solution to Bromocresol Purple.

Investigation of the Effect of Added Triphenylmethane.—To portions of bromobenzene (each 10 ml.) in glass-stoppered flasks amounts of triphenylmethane varying from 0 to 200 mg. were added. Each was irradiated for 150 hr. (dose $1{\cdot}46 \times 10^{21}$ ev/ml.), then titrated with standard alkali to Bromocresol Purple. The hydrogen bromide formation was virtually constant at $2{\cdot}6 \times 10^{-5}$ mole per g. of bromobenzene for additions of triphenylmethane greater than 92 mg./10 ml. (*i.e.*, $2{\cdot}5 \times 10^{-5}$ mole per g. of bromobenzene). A similar series of experiments was done with a fixed weight of triphenylmethane (100 mg.) with varying times of irradiation.

Isolation of Products Formed by Irradiation of Bromobenzene.—(*a*) Bromobenzene (275 ml.) was irradiated for 550 hr. in a stoppered vessel (total dose = $8{\cdot}5 \times 10^{23}$ ev). The orange-coloured product was washed first with water, then with 0·1N-sodium hydroxide until free from acid, then again with water. It was dried (Na_2SO_4) and distilled through a fractionating column; apart from a trace of very volatile product, fractions were collected at b. p. 79—85° (800 mg.) and b. p. 85—145° (300 mg.). Refractionation of the former yielded benzene (775 mg.), b. p. 79·5—81°, n_D^{20} 1·4995. The latter contained bromobenzene, and nothing else could be isolated pure from it. The bulk of the unchanged bromobenzene was recovered by distillation under reduced pressure, leaving a residue (6·3 g.) which was chromatographed from light petroleum (b. p. 60—80°) on alumina (300 g.). Light petroleum eluted bromobenzene, followed by the following fractions: (i) An oil (59 mg.), apparently a mixture of *o*-, *m*-, and *p*-dibromobenzene, b. p. 82—85°/0·5 mm., n_D^{20} 1·6103 (Found: C, 30·3; H, 1·85. Calc. for $C_6H_4Br_2$: C, 30·5; H, 1·7%). When kept, this deposited a small amount of the *para*-isomer, which when recrystallised from aqueous methanol had m. p. and mixed m. p. 87·5—89° (22 mg.) (Found: C, 30·4; H, 1·7%). (ii) An oil, which after being distilled solidified and then crystallised from methanol, yielded biphenyl, m. p. 68—69·5°, mixed m. p. 69—70° (25 mg.) (Found: C, 93·7; H, 6·25. Calc. for $C_{12}H_{10}$: C, 93·5; H, 6·5%). (iii) A mixture of mainly 2- and 3-bromobiphenyl, b. p. 117—122°/1 mm., n_D^{20} 1·6326 (1·245 g.) (Found: C, 61·6; H, 3·8. Calc. for $C_{12}H_9Br$: C, 61·8; H, 3·85%). The ultraviolet spectrum of this was quite close to that of synthetic 2-bromobiphenyl, which had $\lambda_{max.}$ 214 and 246 mμ (log ε 4·24 and 4·07), $\lambda_{min.}$ 230 mμ (log ε 3·94), n_D^{20} 1·6263. (iv) A gum (180 mg.) which, after being distilled, solidified and crystallised from methanol, giving 4-bromobiphenyl (73 mg.), m. p. and mixed m. p. 89—90° (Found: C, 61·65; H, 3·85%), $\lambda_{max.}$ 256 mμ (log ε 4·3), $\lambda_{min.}$ 225 mμ (log ε 3·58). Benzene–light petroleum eluted unidentified oils. Benzene eluted a fraction, b. p. 160—185°/0·5 mm., which solidified and then separated from ethanol as crystals (5 mg.), m. p. 198—200°, probably impure *p*-terphenyl, as judged by its ultraviolet spectrum, $\lambda_{max.}$ 278 mμ (log ε 4·46) (Found: C, 93·85; H, 6·4. Calc. for $C_{18}H_{14}$: C, 93·9; H, 6·1%).

(*b*) In a similar experiment, bromobenzene (30 ml.) was irradiated in an evacuated and sealed vessel (total dose $1{\cdot}5 \times 10^{23}$ ev). The first 0·5 ml. of distillate was examined by gas-chromatography on a dodecyl phthalate column at 82°. The major constituent was benzene, but a more volatile material was collected in a trap cooled by liquid nitrogen and transferred to the mass spectrometer. This proved to be ethyl bromide. As before, the following were obtained; *p*-dibromobenzene, *o*-dibromobenzene, possibly mixed with *m*-isomer, biphenyl, 4-bromobiphenyl, and 2- and 3-bromobiphenyl.

Irradiation of Bromobenzene Containing Triphenylmethane.—A solution of triphenylmethane (5·5 g.) in bromobenzene (275 ml.) was irradiated for 200 hr. (total dose = $3{\cdot}09 \times 10^{23}$ ev) and worked up as above, yielding benzene (1·32 g.), b. p. 80—82°, n_D^{20} 1·4998. The residue left after distillation of unchanged bromobenzene partly crystallised. The crystals, when recrystallised from light petroleum (b. p. 60—80°), yielded recovered triphenylmethane (2·82 g.), m. p. and mixed m. p. 92—93° (Found: C, 93·3; H, 6·6. Calc. for $C_{19}H_{16}$: C, 93·45; H, 6·55%). The material which was insoluble in light petroleum was recrystallised from ethanol, affording triphenylmethanol (2·18 g.), m. p. and mixed m. p. 158—160° (Found: C, 87·55; H, 6·1. Calc. for $C_{19}H_{16}O$: C, 87·7; H, 6·15%). The material (1·39 g.) which remained in the light petroleum was chromatographed on alumina (100 g.). Elution with light petroleum yielded: (i) An oil, b. p. 110—118°/1·5 mm., which crystallised from methanol, giving biphenyl (8 mg.), m. p. and mixed m. p. 68—69° (Found: C, 93·25; H, 6·65%). (ii) A mixture of bromobiphenyls (1·24 g.), b. p. 120—123°/1 mm., n_D^{18} 1·6343, from which 4-bromobiphenyl (3 mg.), m. p. and mixed m. p. 88—89°, was isolated. (iii) Triphenylmethane (0·43 g.), m. p. and mixed m. p. 92—93° (from methanol).

Irradiation of Bromobenzene Containing Benzoyl Peroxide.—Bromobenzene (275 ml.) containing benzoyl peroxide (5·5 g., estimated on available oxygen) was irradiated for 93 hr. (total dose = $1·34 \times 10^{23}$ ev). It was then shaken with 0·1N-sodium hydroxide and kept overnight with ferrous sulphate, washed with water, dried, and fractionated, yielding: (*a*) A liquid, b. p. <74° (250 mg.), which smelt like acetaldehyde, gave a slight precipitate with Brady's reagent, and was removed from ethereal solution by concentrated alkali. (*b*) A liquid which on refractionation yielded benzene (53 mg.), b. p. 80—81·5°, n_D^{20} 1·4993. The bulk of the bromobenzene was then removed under reduced pressure and the residue (4·3 g.) was chromatographed on alumina (200 g.) from light petroleum (b. p. 60—80°). Light petroleum eluted: (i) An unidentified oil (33 mg.), b. p. 105—107°/4 mm., n_D^{18} 1·6268. (ii) Biphenyl (16 mg.) (from methanol), m. p. 68—70°, mixed m. p. 69—70° (Found: C, 93·65; H, 6·45%). (iii) A mixture of 2- and 3-bromobiphenyl (3·25 g.), b. p. 120—123°/1·5 mm., n_D^{18} 1·6345 (Found: C, 61·7; H, 3·95%). (iv) 4-Bromobiphenyl (25 mg.) (from methanol), m. p. and mixed m. p. 88—89° (Found: C, 61·7; H, 3·65%), $\lambda_{max.}$ 256 mμ (log ε 4·29), $\lambda_{min.}$ 225 mμ (log ε 3·55). Benzene then eluted: (v) A solid (4 mg.), separating from ethanol as needles, m. p. 162—164°, probably 4,4'-dibromobiphenyl [$\lambda_{max.}$ 211 and 277 mμ (log ε 4·56 and 4·41), $\lambda_{min.}$ 242 mμ (log ε 3·88)]. (vi) A solid (3 mg.), separating from ethanol as plates, m. p. 204—206°, probably *p*-terphenyl [$\lambda_{max.}$ 278 mμ (log ε 4·48)]. Finally methanol eluted a phenolic fraction, b. p. 75—80°/15 mm.

Separation of a Mixture of o- *and* m-*Bromobenzoic Acid.*—A mixture of Celite (16 g.) and M/15-phosphate buffer of pH 7 (9·6 ml.) was packed into a column filled with benzene, previously equilibrated with the buffer solution. A solution of *o*- (20 mg.) and *m*-bromobenzoic acid (20 mg.) in benzene was run on to the column. Elution with benzene (500 ml.), previously equilibrated with the buffer, removed the *m*-bromobenzoic acid. The *o*-bromo-acid was recovered from the column by acidification and extraction with ether.

Irradiation of Bromo[^{14}C]*benzene.*—(1) Bromo[^{14}C]benzene of specific activity 90 μc/mole (279 ml.) was irradiated for 360 hr. (total dose $6·14 \times 10^{23}$ ev), then divided into three approximately equal portions:

(*a*) A portion (92 ml.) was mixed with pure, inactive 2-bromobiphenyl (505 mg.), washed with 0·1N-sodium hydroxide solution until free from acid, then with water, and dried ($MgSO_4$) and the unchanged bromobenzene was recovered by distillation in a vacuum. The residue (1·9 g.) in light petroleum (b. p. 40—60°) was chromatographed on alumina (100 g.), the eluted fractions being evaporated, and the refractive index of each residue was determined to locate the 2-bromobiphenyl. An appropriate fraction (600 mg.) was nitrated with ethyl nitrate (2 mol.) according to Case's method [14] and the product was recrystallised from acetone–ethanol, affording 2-bromo-4',5-dinitrobiphenyl as needles, m. p. 167° (97 mg.) (Found: C, 44·35; H, 2·55. Calc. for $C_{12}H_7BrN_2O_4$: C, 44·6; H, 2·15%), used for radioactivity measurements.

(*b*) A portion (92 ml.) was mixed with pure, inactive 3-bromobiphenyl (503 mg.), washed, distilled, and chromatographed as in (*a*). A fraction of appropriate refractive index (1·1 g.) in acetic acid (11 ml.) was added gradually to a solution of chromium trioxide (8·8 g.) in water (5·5 ml.) and acetic acid (33 ml.) with shaking. The mixture was kept at 60° with occasional shaking for 4 hr., then poured into water and extracted with ether. The extract was washed with water, then extracted with sodium carbonate solution, and the alkaline extract was acidified with hydrochloric acid. The resulting precipitate was collected, washed with water, and dried (106 mg.; m. p. 130—140°). This was subjected to partition chromatography from ethereal solution, with a phosphate buffer of pH 7 on a Celite column, yielding crystals (68 mg., m. p. 140—143°), which were boiled with water (20 ml.) and barium carbonate (50 mg.) and filtered hot. The crystals which separated on cooling were recrystallised three times from hot water. A solution of the resulting, purified barium salt in hot water was acidified with hydrochloric acid, and the precipitated *m*-bromobenzoic acid was recrystallised from hot water, yielding needles, m. p. 157° (18 mg.), which were used for radioactivity measurements.

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

(*c*) A portion (95 ml.) was mixed with pure, inactive 4-bromobiphenyl (403 mg.), washed, distilled, and chromatographed as in (*a*). Development with light petroleum (b. p. 40—60°) yielded several liquid fractions, but later fractions tended to crystallise. Repeated recrystallisation of the resulting solid from ethanol yielded colourless plates of 4-bromobiphenyl, m. p. 91° (84 mg.), which was sublimed in a vacuum for radioactivity measurements.

(2) Bromo[^{14}C]benzene of specific activity 150 μc/mole (251 ml.) was irradiated for 408 hr. (total dose $6{\cdot}13 \times 10^{23}$ ev), then divided into three portions. (*a*) A portion (83 ml.) was mixed with 2-bromobiphenyl (520 mg.) and yielded, as before, 2-bromo-4′,5-dinitrobiphenyl, m. p. 167° (107 mg.). (*b*) A portion (85 ml.) was mixed with 3-bromobiphenyl (1 g.), washed, distilled, and chromatographed as before. Appropriate fractions were nitrated with ethyl nitrate (1 mol.) according to Case's method [15] and the product was recrystallised many times from acetone–ethanol, yielding 3-bromo-4,4′-dinitrobiphenyl, m. p. and mixed m. p. 204—205° (15 mg.), used for radioactivity measurements. (*c*) A portion (83 ml.) was mixed with 4-bromobiphenyl (400 mg.) and yielded, as before, 4-bromobiphenyl, m. p. 91° (100 mg.), which was sublimed and used for radioactivity measurements.

(3) Bromo[^{14}C]benzene of specific activity 150 μc/mole (279 ml.) was irradiated for 720 hr. (total dose $11{\cdot}76 \times 10^{23}$ ev), then divided into three portions: (*a*) A portion (47 ml.) was mixed with 2-bromobiphenyl (508·5 mg.) and, as before, this yielded 2-bromo-4′,5-dinitrobiphenyl, m. p. 167° (68 mg.). (*b*) A portion (180 ml.) was mixed with 3-bromobiphenyl (3499 mg.) and worked up as in (2). A number of chromatographic fractions were nitrated separately and the product from each was checked as 3-bromo-4,4′-dinitrobiphenyl by mixed m. p. before these were combined and further recrystallised from acetone–ethanol, yielding pale yellow crystals, m. p. and mixed m. p. 204—205° (25 mg.). (*c*) A portion (52 ml.) was mixed with 4-bromobiphenyl (389·4 mg.) and yielded, as before, 4-bromobiphenyl, m. p. 91° (53 mg.).

(4) Bromo[^{14}C]benzene of specific activity 150 μc/mole (261 ml.) was irradiated for 401 hr. (total dose $5{\cdot}95 \times 10^{23}$ ev), then divided into three portions: (*a*) A portion (61 ml.) was mixed with 2-bromobiphenyl (343·5 mg.) and, as before, yielded 2-bromo-4′,5-dinitrobiphenyl, m. p. 167° (44 mg.). (*b*) A portion (140 ml.) was mixed with 3-bromobiphenyl (899·6 mg.) and worked up as in (1) (*b*). The crude *m*-bromobenzoic acid had m. p. 136—146° (201 mg.) and after partition chromatography m. p. 157° (81 mg.). Part of the latter product was used as such for radioactivity measurements, and the remainder was converted into the barium salt which was recrystallised three times from water, before recovery of the acid, which had m. p. 157° and the same specific radioactivity. (*c*) A portion (60 ml.) was mixed with 4-bromobiphenyl (251·7 mg.) and as before yielded 4-bromobiphenyl, m. p. 91° (51 mg.).

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[15] Case, *J. Amer. Chem. Soc.*, 1945, **67**, 116.