354. *Liquid-phase Photolysis. Part II.*[1] *Iodobenzene.*

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Ultraviolet irradiation of liquid iodobenzene in the presence of silver powder gives iodobiphenyls, benzene, biphenyl, hydrogen iodide, and hydrogen, together with silver iodide, as the main identified products. The course of the process is discussed in terms of free-radical intermediates.

In Part I,[1] the photolysis of diphenylmercury, tetraphenyl-lead, and iodobenzene in isopropylbenzene was used to provide information regarding the mechanism of homolytic phenylation. Photolysis of pure iodobenzene seemed likely to be particularly simple, since this compound can act as both radical source and substrate; yet, in fact, it proved complex.

In preliminary experiments we observed that, when iodobenzene was exposed in silica tubes to ultraviolet radiation, the initial rapid decomposition to give free iodine soon ceased. Addition of silver powder to remove free iodine led to some improvement, but a satisfactory degree of decomposition was obtained only by use of the apparatus described in Part I.[1] Under such conditions a convenient 5% decomposition occurred in 2—3 hr. Greater degrees of decomposition were avoided in order to minimise effects due to secondary photodecomposition of iodine-containing products. The products generally identified were a mixture of the three isomeric iodobiphenyls, benzene, biphenyl, hydrogen, and hydrogen iodide (trace). The formation of hydrogen was most marked at the higher temperatures, and neither hydrogen nor hydrogen iodide was evolved to a significant extent during a photolysis at 47°. No marked variation in ratios of isomers with temperature was observed: the isomeric composition of the iodobiphenyls from an experiment at 125° was 2-, 56·5; 3-, 29·5; 4-, 14%. These values are in approximate agreement with those reported by Augood, Cadogan, Hey, and Williams[2] for the decomposition of dibenzoyl peroxide in iodobenzene (2-, 51·7; 3-, 31·6; 4-, 16·7%). In both cases the precision of the spectrophotometric analytical procedure was not high—certainly not high enough to justify suspicion that the small differences observed have real significance. Photodecomposition of the iodobiphenyls may account for the formation of traces of biphenyl, but is unlikely to have been appreciable at such low concentrations, or markedly selective between isomers. We conclude that free phenyl radicals were formed and led to phenylation of the iodobenzene, in agreement with the results reported in Part I.[1]

In phenylations with dibenzoyl peroxide as the radical source, it had been concluded that the displaced hydrogen atom appears largely as benzoic acid, *e.g.*, through abstraction from an intermediate by dibenzoyl peroxide or a benzoyloxy-radical.[3] On this basis, displaced hydrogen in the present case might have been expected to appear as benzene. In fact, the benzene formed was equivalent to only *ca.* 20% of the iodobiphenyls. Although traces of hydrogen iodide and a little hydrogen were evolved, particularly in photolyses above 100°, these were insufficient to account for the deficiency.

Hydrogen iodide could result from dehydrogenation of an intermediate radical (I) by iodine. The failure to account for the displaced hydrogen largely as benzene may be explained by the very high reactivity of phenyl in comparison with (say) benzoyloxy-radicals, so that the stationary concentration of the former in an aromatic solvent tends

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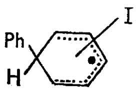
[1] Part I, Blair, Bryce-Smith, and Pengilly, *J.*, 1959, 3174.
[2] Augood, Cadogan, Hey, and Williams, *J.*, 1953, 3412.
[3] Augood and Williams, *Chem. Rev.*, 1957, **57**, 123.

to be particularly low, and addition to the solvent is preferred to abstraction of a hydrogen atom from another species also at a low concentration. The considerations raised in Part I[1] suggest that dihydroiodobiphenyls might well be formed under the present conditions after disproportionation of the intermediate radicals (I). Attempts to isolate dihydroiodobiphenyls failed, although there were indications of their presence. Thus, distillation under reduced pressure was invariably accompanied by the evolution of hydrogen iodide and the liberation of free iodine, this being most marked with the materials from photolyses at lower temperatures: the products isolated were iodobiphenyls and a little biphenyl. It may be noted that hydrogen iodide formed *during* the photolysis would not necessarily all be evolved at this time in the presence of unsaturated reaction products such as dihydroiodobiphenyls, but might well appear during subsequent distillation.



(I)

A feasible explanation of the liberation of free hydrogen is that this arises from photolysis of hydrogen iodide. In support of this, no hydrogen has been detected when iodine-free radical sources have been employed with benzene and isopropylbenzene as substrates.[1]

EXPERIMENTAL

Photolysis of Iodobenzene.—Iodobenzene, purified as in Part I,[1] was irradiated in the presence of silver powder, under oxygen-free nitrogen by using the cells described in Part I.[1] Five runs at temperatures ranging from 47° to 135° were conducted. The water-cooled cell was used for the run at 47°, and the air-cooled cell at higher temperatures. One representative experiment is described in detail. The results of other experiments are summarised in the Table.

Products from the photolysis of iodobenzene in the presence of silver.

Expt. No.		1	2	3	4	5
Wt. of PhI (g.)		65	70	67	96	156
Irradiation temp.		135°	130°	125°	100°	47°
Irradiation time (hr.)		2·5	2·5	2·7	6	5
Benzene produced (g.)		0·21	0·11	0·18	*	*
H_2 evolved (ml. at N.T.P.)		25	*	15	*	Trace
Iodobiphenyls (g.)		3·15	3·25	3·59	4·01	3·22
Residue (g.)		1·27	0·66	0·91	1·22	1·25
Ratios (%) of iodobiphenyls	2-	56·5	53·3	56·5	58·5	*
	3-	29·0	31·3	29·5	28·5	*
	4-	14·5	15·4	14·0	13·0	*

* Not determined.

Nitrogen was very slowly passed over iodobenzene (65 g.) in the air-cooled cell. The cell was shielded from ultraviolet radiation until the working temperature (135°) had been reached. Silver powder (5 g.) was added from a hopper at intervals as required. Irradiation was continued for 2½ hr. at 135°.

25 Ml. (20% of theoretical based on iodobiphenyls) of hydrogen were evolved. In this experiment hydrogen was estimated by sparking with oxygen the gas retained by a tapped vessel isolated from the cell by a liquid-nitrogen trap and from the atmosphere by a gas-reservoir. In other experiments the hydrogen was estimated by use of a palladium leak. Traces of hydrogen iodide were qualitatively detected. After irradiation the mixture was allowed to cool and was filtered. Benzene formed during irradiation was removed by fractional distillation with added carbon tetrachloride, and was estimated as *m*-dinitrobenzene by the procedure described in Part I:[1] 0·21 g. of benzene was found.

Fractional distillation of the cell contents was continued under reduced pressure until most of the iodobenzene had been removed. The contents of the distilling flask were then transferred to a small distillation unit, and distillation was continued under a high vacuum. A small quantity of biphenyl (*ca.* 0·1 g.) distilled with the last runnings of iodobenzene. It had m. p. 60—64° and mixed m. p. 66—69°, having the correct infrared spectrum in carbon disulphide. The iodobiphenyl fraction (3·4 g.), collected at 85—105°/0·2 mm., was redistilled to remove traces of impurities; analysis for the three isomers by the standard infrared method,[2] dimethylformamide being used as solvent, as in Part I [1] gave: 2-, 56·5; 3-, 29·0; 4-, 14·5%. A synthetic mixture of the three iodobiphenyls (kindly provided by Dr. J. I. G. Cadogan) (2-, 46·7; 3-, 34·1; 4-, 19·2%) which was analysed by the same technique gave 2-, 50·5; 3-, 30·8; 4-, 18·7%. Elemental analysis of the iodobiphenyl fractions was consistent with the presence of a trace of biphenyl (Found: C, 52·7; H, 3·3; I, 43·9. Calc. for $C_{12}H_9I$: C, 51·4; H, 3·2; I, 45·4%. Calc. for a mixture of iodobiphenyls with 3·3% of biphenyl: C, 52·7; H, 3·3; I, 43·8%). The presence of biphenyl introduces an error. Biphenyl does not absorb significantly at the wavelengths used for measurements, and would tend to increase the apparent proportion of 2-iodobiphenyl, for this must be obtained by difference. 0·91 g. of high-boiling residue remained in the flask after the high-vacuum distillation.

Small quantities of an acidic substance were isolated from several experiments. This was deposited on cool glass at the top of the fractionating column during distillation of the iodobenzene. It formed colourless crystals, readily soluble in ethanol and water and giving an aqueous solution of pH 3. It was insoluble in ether, acetone, and iodobenzene. When suddenly heated it volatilised completely; but when slowly heated it decomposed without melting but with slight sublimation at 200°, becoming black, and free iodine was liberated at 200—210° (Found: C, 32·1; H, 3·7). These properties appear to suggest an unusual structure, and the *substance* is being further investigated.

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