421. *The Photochemical Decomposition of Diphenyliodonium Iodide.*

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Photochemical decomposition of solutions of diphenyliodonium iodide in chloroform yields iodobenzene, iodine, diphenyliodonium tri-iodide, and benzene as major products (but less readily in a number of other solvents). The mechanism is discussed. A similar photodecomposition of di-*p*-fluorophenyliodonium iodide and of diphenyleneiodonium iodide is noted.

During a preliminary study of the solvent extraction of anions as salts with diaryliodonium cations, Williams[1] noted that solutions of diphenyliodonium iodide, $Ph_2I^+I^-$, in chloroform decomposed readily when exposed to laboratory fluorescent lighting. Iodine was identified in the violet solution obtained initially. On prolonged irradiation of the solution, the colour disappeared and a solid, thought to be impure 2,2′-di-iodobiphenyl, was obtained. Only 25% of the starting material could be accounted for.

We now find that a solution of diphenyliodonium iodide (0·1 g.) in chloroform (100 ml.) remains unchanged indefinitely in the dark, but becomes pink after one hour's exposure to laboratory fluorescent lighting, and colourless after a further 10—14 hours. If, however, the solution is placed in a quartz vessel and exposed to ultraviolet light from a 125 w high-pressure mercury-vapour lamp with a quartz envelope a pink coloration develops within 5 min. and decolorisation is complete in 2—3 hr.; still longer irradiation produces a yellow solution. By evaporation of portions of the pink or of the nearly colourless solutions produced at various stages in the irradiation, mixtures not readily separated by chromatography were obtained.

In experiments intended to yield higher concentrations of products a small quantity of diphenyliodonium tri-iodide[2] was deposited and the filtrate contained diphenyliodonium iodide and free iodine. 2,2′-Di-iodobiphenyl was not detected during a large number of photodecompositions carried out under widely different conditions. When accumulation of iodine was prevented (by carrying out the decomposition in contact with aqueous thiosulphate) iodobenzene, iodine, and benzene were obtained, corresponding to over 80% of the starting material.

Experimental

Preparation of Diaryliodonium Salts.—These were prepared essentially by Beringer's procedure,[3] with certain important modifications which are illustrated by the following preparation.

*Di-*p*-fluorophenyliodonium chloride.* A cold solution of acetic anhydride (100 ml.) and concentrated sulphuric acid (225 ml.), prepared by slowly mixing the well-chilled components during 1—2 hr., was slowly added (1 drop/3 sec.) to a vigorously stirred mixture of very finely

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[1] Williams, Part II Thesis, Oxford, 1955.

[2] Meyer and Hartmann, *Ber.*, 1894, **27**, 502, 1592.

[3] Beringer, Drexler, Gindler, and Lumpkin, *J. Amer. Chem. Soc.*, 1953, **75**, 2705.

powdered potassium iodate (107 g.), fluorobenzene (97 g.), and acetic anhydride (200 ml.) kept below 5°. When addition was completed (8—12 hr.) the stirred mixture was allowed to warm slowly to room temperature. From time to time a portion was removed and shaken with aqueous potassium iodide and a few ml. of chloroform. Reaction was considered to be complete when free iodine no longer coloured the organic phase (about 20 hr.).

After inorganic salts had been filtered off (suction) through sintered glass, the viscous product was poured slowly on crushed ice (400 g.) and the resulting solution extracted with ether (3 × 200 ml.). The aqueous phase was then shaken (4 hr.) with animal charcoal (100 g.), dissolved ether being allowed to escape. This decolorisation could be omitted (with some decrease in yield) if the precipitated salt was very thoroughly washed with ice-cold water.

To avoid violent exothermic decomposition, the solution was at once filtered through sintered glass, mixed with hydrochloric acid (60 ml.), and placed in an ice-chest overnight. *Di-*p*-fluorophenyliodonium chloride* (58 g.) separated and after three recrystallisations from boiling methanol formed almost colourless crystals, m. p. 232° [Found: Cl (Volhard method), 10·0. $C_{12}H_8ClF_2I$ requires Cl, 10·1%].

*Di-*p*-fluorophenyliodonium chloride* prepared by the addition of potassium iodide to a concentrated aqueous solution of the chloride, crystallised from methanol in pale yellow needles, m. p. 172° {Found: $[(C_6H_4F)_2I^+$, 71·0. $C_{12}H_8F_2I_2$ requires $[(C_6H_4F)_2I]^+$, 71·4%)}.

Purification and Analysis.—The total solubility [2] and the temperature gradient of diphenyliodonium iodide are too low to permit use of hexane, carbon tetrachloride, ether, or acetone for crystallisation. Dimethylformamide gave good crystals at $<60°$; redistilled nitromethane was also effective although the solubility was rather low. Although the iodide was more soluble in hot pyridine,[4] the thermal decomposition which ensued in this solvent and in boiling aqueous acetic acid invariably led to yellowish products, due probably to traces of the tri-iodide. The purity did not then exceed 97%. Rapid recrystallisation from boiling methanol, as recommended by Beringer,[3] could not be improved upon. Cooling in acetone–solid carbon dioxide a solution in chloroform saturated at room temperature is also effective if photochemical decomposition is prevented.

The diphenyliodonium iodide used was recrystallised three times from boiling methanol and dried *in vacuo* at 60°; it then had m. p. 181—183°. The purity, as determined (*a*) by argentometric titration with phenosafranine as indicator,[1] (*b*) by the Volhard method, and (*c*) by neutralisation with standard acid of the strongly basic diphenyliodonium hydroxide prepared quantitatively with the aid of excess of Amberlite IRA-400 (OH) resin, varied from 99·5 to 99·9%.

Phenyleneiodonium iodide [m. p. 212° (decomp.), from pyridine] was prepared from diazotised 2,2′-diaminobiphenyl and potassium iodide,[5,6] and was decomposed thermally to give an authentic specimen of 2,2′-di-iodobiphenyl.[6]

Catalytic Reduction of 2,2′-Dinitrobiphenyl.—A solution of 2,2′-dinitrobiphenyl (10 g.) in ethanol (100 ml.) was hydrogenated in the presence of Raney nickel (1·5 g.). When no more hydrogen was absorbed the catalyst was removed and the solution concentrated. 7,8-Benzocinnoline (6·6 g., 90%) formed fine yellow crystals, m. p. 156·5°, from boiling ethanol [7] (Found: N, 15·5. Calc. for $C_{12}H_8N_2$: N, 15·6%).

Photodecompositions.—To provide a higher concentration of products than was obtained in the preliminary experiment already described, a suspension of diphenyliodonium iodide (2 g.) in chloroform (250 ml.) was irradiated by laboratory fluorescent lighting for 24 hr. The iodide dissolved completely and the resulting deep violet-coloured solution deposited a small quantity of very dark-red crystals (m. p. 136—137°; from methanol). These were shown to be diphenyliodonium tri-iodide (Found: I, 76·4. Calc. for $Ph_2I^+I_3^-$: I, 76·7%) by comparison with an authentic specimen,[2] by mixed melting point (136°), and by titration with standard sodium thiosulphate. This tri-iodide, which Foster and Schaeppi also obtained indirectly,[8] yields diphenyliodonium iodide and sodium tetrathionate quantitatively when treated with sodium thiosulphate. We failed to detect any trace of 2,2′-di-iodobiphenyl during a large number of photodecompositions carried out under widely different conditions.

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[4] Büchner, *Proc. k. ned. Akad. Wetenschap.*, 1903, **5**, 646.

[5] Sandin and Hay, *J. Amer. Chem. Soc.*, 1952, **74**, 274.

[6] Mascarelli and Benati, *Gazzetta*, 1908, **38**, 619.

[7] Täubner, *Ber.*, 1891, **24**, 3081.

[8] Foster and Schaeppi, *J.*, 1912, 382.

The absorption spectrum (at 510 mμ) of the violet chloroform solution from which diphenyliodonium tri-iodide had separated established the presence of free iodine. This was at once removed on treatment with aqueous sodium thiosulphate, leaving a colourless solution from which diphenyliodonium iodide (m. p. and mixed m. p. 175°; from methanol) separated on removal of the organic solvent. The amount of iodine liberated during 2 hours' irradiation was 10—15% by weight of the starting material.

As the course of reaction might be simplified if iodine was not allowed to accumulate, a suspension of diphenyliodonium iodide in a mixture of chloroform and aqueous sodium thiosulphate was irradiated by ultraviolet light. At intervals the quartz container was shaken whereupon the iodine colour was bleached, only to return on further irradiation. After 48 hr. the complete absence of colour in the organic phase showed that all the diphenyliodonium iodide had reacted. Distillation of the dried organic solution gave nine fractions of b. p. 61·5—62·0°/760 mm., a fraction of b. p. 67°/10 mm. (187°/760 mm.) identified as iodobenzene, and a minute residue which was not further examined. Each of the low-boiling chloroform fractions showed $\lambda_{\text{max.}}$ 244·0, 249·5, 255·5, and 261·5 mμ, characteristic of a solution of benzene.

In a roughly quantitative experiment with 4·6 g. of diphenyliodonium iodide, 3·17 g. of iodobenzene, 0·44 g. of iodine, and 0·18 g. of benzene were identified. This corresponds to over 80% of the starting material. The deficiency will have been due in part to unidentified products but mainly to losses of iodine, benzene, and other volatile products during irradiation.

DISCUSSION

The principal products of the photochemical decomposition of diphenyliodonium iodide in chloroform appear to be iodobenzene, iodine, and benzene. If the iodine is allowed to accumulate, diphenyliodonium tri-iodide separates intermediately. The rate of reaction, slow at first, increases rapidly in the later stages, and large amounts of the sparingly soluble diphenyliodonium iodide can be made to dissolve in a small volume of chloroform. These observations complement those of Fletcher and Hinshelwood [9] that the thermal decomposition of diphenyliodonium iodide may be autocatalytic and that the reaction rate increases as diphenyliodonium iodide dissolves in the iodobenzene formed. Beringer *et al.* have shown that the thermal decomposition of diphenyliodonium iodide in dimethylformamide follows first-order kinetics.[10] Lucas and his co-workers suggest an ionic mechanism for this rearrangement because they found that di-*o*-tolyliodonium iodide decomposed at 155° to give *o*-iodotoluene almost exclusively, with less than 1% of iodine and bitolyl.[11]

Sandin, Kulka, and McCready studied the thermal decomposition of *p*-methoxydiphenyliodonium iodide at 175° and identified iodobenzene and *p*-iodoanisole as the principal products.[12] In this case 4·2% of the total iodine was liberated and the following side-reaction was postulated

$$2[p\text{-MeO}{\cdot}C_6H_4{\cdot}I{\cdot}C_6H_5]^+I^- \longrightarrow I_2 + C_6H_5{\cdot}C_6H_5 + p\text{-MeO}{\cdot}C_6H_4{\cdot}I$$

although the formation of biphenyl was not established experimentally.

American workers have produced much evidence for the formation of phenyl radicals in the thermal decomposition of diphenyliodonium halides and have demonstrated their use for the phenylation of mercury and tellurium,[13] of pyridine (in which case 2-, 3-, and 4-isomers are formed),[14] and of various organic and inorganic bases.[15] Extensive studies by Russian workers indicate that either phenyl radicals or phenyl cations can participate

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[9] Fletcher and Hinshelwood, *J.*, 1935, 596.

[10] Beringer, Geering, Kuntz, and Mausner, *J. Chem. Phys.*, 1956, **60**, 141.

[11] Lucas, Kennedy, and Wilmot, *J. Amer. Chem. Soc.*, 1936, **58**, 157.

[12] Sandin, Kulka, and McCready, *J. Amer. Chem. Soc.*, 1937, **59**, 2014.

[13] Sandin, McClure, and Irwin, *J. Amer. Chem. Soc.*, 1939, **61**, 2944.

[14] Sandin and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 2253.

[15] Beringer, Brierley, Drexler, Gindler, and Lumpkin, *J. Amer. Chem. Soc.*, 1953, **75**, 2708.

in such reactions, heterolysis being predominant in the thermal decomposition of diaryliodonium borofluorides.[16,17,18]

The increased formation of iodine and especially the formation of benzene are the most striking features which distinguish the photochemical decomposition of diphenyliodonium iodide in chloroform from its thermal decomposition. The hydrogen required for the production of benzene may be provided by the chloroform or by the dehydrogenation of other aromatic groups present. It is significant that a solution of diphenyliodonium iodide in benzene decomposes photochemically in much the same way as in chloroform: a yellow colour quickly develops and soon changes to violet because of free iodine. On the other hand, photochemical reactions in hexane, carbon tetrachloride, and ether are negligible under comparable conditions although saturated solutions of diphenyliodonium iodide in methanol, aqueous acetic acid, and acetone become pale-yellow, yellowish-brown, and greenish-yellow, respectively, when exposed to daylight for some time.

That chloroform can serve as a source of hydrogen atoms was established by Böeseken and Gelissen who showed that benzene, ω-trichloro-*p*-toluic acid and carbonyl chloride were formed, with traces of biphenyl and hexachloroethane, when a solution of dibenzoyl peroxide in chloroform was heated to the boiling point.[19]

We have not obtained direct evidence of the presence of phenyl radicals during the photodecomposition of diphenyliodonium iodide, and the result, *e.g.*, of irradiating 0·05 g. of this substance dissolved in 100 ml. of chloroform containing a few ml. of methyl methacrylate were inconclusive. At the same time we have not detected any by-product which could be attributed to the formation of trichloromethyl radicals. It is clear that a more detailed analysis of minor reaction products is called for, both in this case and in the general study of the thermal decomposition of iodonium salts.

The behaviour of solutions of di-*p*-fluorophenyliodonium iodide and of phenyleneiodonium iodide in chloroform on prolonged exposure to daylight or on irradiation by ultraviolet light resembles that recorded above for diphenyliodonium iodide. Detailed studies of the reaction products were not carried out. Under comparable conditions the photodecomposition of the corresponding bromides, chlorides, or fluorides is barely detectable. This suggests that a reaction of the type

$$[Ar_2I]^+I^- \longrightarrow Ar_2I{-}I \longrightarrow ArI + Ar\cdot + I\cdot$$

may be significant with the readily deformable iodide ion. However, examination of the spectra of diphenyliodonium salts has provided no evidence for any marked charge-transfer effects.[20]

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[16] Makarova and Nesmeyanov, *Bull. Acad. Sci. U.S.S.R.*, 1945, 617.

[17] Makarova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1951, 741.

[18] Nesmeyanov, Makarova, and Tolstoya, *Tetrahedron*, 1957, **1**, 145.

[19] Böeseken and Gelissen, *Rec. Trav. chim.*, 1924, **43**, 869.

[20] Irving, Turner, and Reid, following paper.