365. *Photolytic Formation and Reactions of Aralkyl Radicals.*

By D. H. Hey, D. A. Shingleton, and Gareth H. Williams.

The photochemical decomposition of benzyl iodide, dibenzylmercury, and benzylmercuric iodide in some aromatic solvents has been studied. The decomposition of benzylmercuric iodide provides a convenient source of benzyl radicals: mercurous iodide is formed in quantitative yield and in isopropylbenzene the products consist of bibenzyl, 1,2,3-triphenylpropane, and toluene. Confirmation of the intermediate formation of free radicals was obtained by experiments with diphenylpicrylhydrazyl and by the photodecomposition of an equimolar mixture of benzyl and 4-chlorobenzylmercuric iodide in isopropylbenzene, which gave 4-chlorobibenzyl in high yield.

Although the formation of benzyl and analogous radicals by α-hydrogen abstraction from aromatic side-chains by various radicals is well known, very few reactions of these resonance-stabilised radicals, other than dimerisation, have been recorded. Their reaction in the gas-phase with mercury has been recognised by Hein and Mesee[1] and their reaction in solution with anthracene has been reported by Beckwith, Norman, and Waters.[2] Evidence that hydrogen-abstraction can be effected by aralkyl radicals in solution is, however, not abundant. Studies of the so-called identity reaction (1), where $R = Ph{\cdot}CH_2$, with toluene

$$RH + R\cdot \longrightarrow RH + R\cdot \qquad (1)$$

deuterated in the α-position have indicated that this reaction does not take place to an appreciable extent.[3,4] In these experiments the aralkyl radicals (R·) were formed in the presence of their parent hydrocarbons (RH), and the most conclusive evidence for the occurrence of hydrogen-abstraction by R·, namely, the formation of RH, was not obtainable. In order to obtain this evidence, it is desirable to employ a source of aralkyl radicals such that these radicals are formed directly, without any free-radical precursors. It is also desirable that they should be formed singly, rather than in pairs, so that wastage due to geminate recombination in a solvent-cage is minimised. The second of these conditions was satisfied in the work of Cadogan, Hey, and Sanderson[5] on the thermal decomposition of 9-benzyl-9-fluorenyl peroxide, which gives 9-benzyl-9-fluorenyloxy-radicals as the primary product. The further decomposition of these radicals to fluorenone and benzyl radicals was inferred from the isolation of benzyl derivatives from the reaction in various solvents, although the interpretation of these results is complicated by the presence of radicals other than benzyl. Only in the reaction with γ-picoline is it certain that α-hydrogen abstraction by benzyl radicals occurred, since toluene was formed, but even here the presence of the other product of this process, namely, the γ-picolyl radical, could not be demonstrated.

In the present work, the photolytic decomposition of dibenzylmercury, benzyl iodide, benzylmercuric iodide, and 4-chlorobenzylmercuric iodide has been shown to give benzyl or 4-chlorobenzyl radicals. The aralkylmercuric iodides are by far the most convenient and efficient radical sources of those investigated.

Dibenzylmercury.—The photolysis of dibenzylmercury in γ-picoline gave bibenzyl as the sole organic product. This experiment therefore provides no evidence for the existence of *free* benzyl radicals during this reaction. The analogous reaction in isopropylbenzene, however, gave a little 1,2,3-triphenylpropane (0·057 mole per mole of dibenzylmercury), as well as bibenzyl (0·897 mole per mole of dibenzylmercury). Neither toluene nor bicumyl

---

[1] Hein and Mesee, *Naturwiss.*, 1938, **26**, 715.
[2] Beckwith, Norman, and Waters, *J.*, 1958, 171.
[3] Eliel, Wilken, Fang, and Wilen, *J. Amer. Chem. Soc.*, 1958, **80**, 3303.
[4] Wilen and Eliel, *J. Amer. Chem. Soc.*, 1958, **80**, 3309.
[5] Cadogan, Hey, and Sanderson, *J.*, 1960, 3203.

could be detected among the products, and the excess of isopropylbenzene contained a yellow unsaturated impurity, probably a derivative of fulvene. Fulvene itself has been reported as a product of the photochemical isomerisation of benzene.[6] The formation of 1,2,3-triphenylpropane provides evidence for the existence of, and hydrogen abstraction by, benzyl radicals, since this substance is probably formed by α-hydrogen abstraction from the primary product bibenzyl, followed by combination of benzyl and 1,2-diphenylethyl radicals:

$$\text{Ph·CH}_2\text{·} + \text{Ph·CH}_2\text{·CH}_2\text{Ph} \longrightarrow \text{Ph·CH}_3 + \text{·CHPh·CH}_2\text{Ph} \quad . \; . \; . \; . \; . \; . \quad (2)$$

$$\text{·CHPh·CH}_2\text{Ph} + \text{Ph·CH}_2\text{·} \longrightarrow \text{Ph·CH}_2\text{·CHPh·CH}_2\text{Ph} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

This evidence cannot, however, be regarded as conclusive, since toluene was not identified among the products, possibly as a result of wastage of many of the radicals, which must be formed in pairs. The conclusion that free radicals are formed in this reaction is supported by the rapid decoloration of 1,1-diphenyl-2-picrylhydrazyl, which occurred when a solution of dibenzylmercury in benzene was photolysed in the presence of this reagent.

Benzyl Iodide.—Benzyl radicals might be expected to be formed singly by the photolysis of benzyl iodide, since organic iodides exhibit continuous absorption in the range 2500—2600 Å and are readily decomposed by ultraviolet light. The decomposition of benzyl iodide might be expected to be particularly easy, since the dissociation energy of the C–I bond is only ~37 kcal. mole^{-1}.[7] However, with most iodides, the quantum yield for the dissociation is very low, because of the importance of the reverse reaction of recombination.[8,9] The efficiency of the process might, however, be increased by the presence of an iodine-scavenger, and silver powder and mercury were used for this purpose. The photolysis of benzyl iodide in isopropylbenzene gave a little 1,2,3-triphenylpropane (0·040 mole per mole of benzyl iodide) as well as bibenzyl (0·304 mole per mole of benzyl iodide), thus providing some evidence for hydrogen abstraction by benzyl radicals although, again, neither bicumyl nor toluene could be detected among the products.

Aralkylmercuric Iodides.—The photolytic decomposition of benzyl iodide in the presence of mercury is interesting in view of the reported formation of organomercuric iodides from the reactions of the corresponding iodide with mercury in light.[10,11] Maynard [12] prepared benzylmercuric iodide by this method. It therefore appears that, while the C–I bond in organic iodides can be cleaved by light of fairly long wavelength, to which the C–Hg bond in the organomercuric iodides is impervious, the shorter-wavelength ultraviolet radiation used in the present experiments is sufficiently energetic to cleave this C–Hg bond. The photolysis of benzylmercuric iodide under these conditions was shown to give benzyl radicals and mercurous iodide, and to provide a source of benzyl radicals which was ideal for the present purposes.

The formation of free benzyl radicals was demonstrated by the rapid decoloration of diphenylpicrylhydrazyl when benzylmercuric iodide was photolysed in cyclohexane in the presence of this reagent, and also by the formation of the unsymmetrical combination product 4-chlorobibenzyl, as well as of bibenzyl and 4,4′-dichlorobibenzyl, by the photolysis of a mixture of benzylmercuric iodide and 4-chlorobenzylmercuric iodide in isopropylbenzene. The former demonstration was conclusive since control experiments indicated that the decoloration was due neither to hydrogen abstraction by diphenylpicrylhydrazyl nor to its photodecomposition. The interpretation of the results of the latter demonstration is, however, somewhat complicated by the observation that small amounts of 4-chlorobibenzyl and bibenzyl are formed by the photolysis of an isopropylbenzene solution of

---

[6] Blair and Bryce-Smith, *Proc. Chem. Soc.*, 1957, 287.

[7] Szwarc, *Chem. Rev.*, 1950, **47**, 75.

[8] Steacie, " Atomic and Free Radical Reactions," Reinhold Publ. Co., New York, 1954, p. 397.

[9] Olaerts and Jungers, *Discuss. Faraday Soc.*, 1947, **2**, 222.

[10] Frankland, *J.*, 1850, **3**, 322.

[11] Reutov and Nesmeyanov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1953, 655.

[12] Maynard, *J. Amer. Chem. Soc.*, 1932, **54**, 2108.

4-chlorobenzylmercuric iodide alone, presumably as a result of photochemical dechlorination. The high yield of 4-chlorobibenzyl obtained in the photolysis of the mixture of aralkylmercuric iodides (0·214 mole per mole of aralkylmercuric iodide) cannot be accounted for on this basis. It must therefore have been formed by the combination of benzyl and 4-chlorobenzyl radicals.

The hydrogen abstraction by benzyl radicals is clearly established by the products of the photolysis of benzylmercuric iodide in isopropylbenzene and in cyclohexane. The mean yields of these products are given in Table 1. αα-Dimethylbibenzyl is formed in the reaction in isopropylbenzene by α-hydrogen abstraction from the solvent followed by combination of α-cumyl and benzyl radicals. The product of dimerisation of α-cumyl radicals, namely, bicumyl, was not identified, probably because, owing to the very low stationary concentration of α-cumyl compared with that of benzyl radicals, it is formed only in very small amount. Hydrogen abstraction from cyclohexane does not appear to take place to an extent sufficient for its products to be recognised, but hydrogen abstraction from bibenzyl occurs in both solvents. In addition, the formation of toluene in both reactions establishes conclusively the occurrence of hydrogen abstraction by benzyl radicals. Similarly, *p*-chlorotoluene (0·044 mole per mole of aralkylmercuric iodide) was formed in the reactions with 4-chlorobenzylmercuric iodide.

TABLE 1.

Yields of products of photolysis of benzylmercuric iodide (mole per mole of benzylmercuric iodide).

	In isopropylbenzene	In cyclohexane
Bibenzyl	0·390	0·420
αα-Dimethylbenzyl	0·014	—
1,2,3-Triphenylpropane	0·041	0·033
Toluene	0·046	0·035

These results show that the reactivities of bibenzyl, isopropylbenzene, and cyclohexane towards hydrogen abstraction by benzyl radicals are in the order: bibenzyl > isopropylbenzene > cyclohexane. Gregg and Mayo[13] have shown that isopropylbenzene is 12·5 times as reactive as cyclohexane towards polystyrene radicals, and this is in accordance with the present results. Kooyman,[14] however, has shown isopropylbenzene to be 1·3 times as reactive as bibenzyl towards trichloromethyl radicals. This discrepancy with the present results is hardly surprising in view of the wide structural differences between the radicals used.

That benzyl radicals can abstract hydrogen from bibenzyl in the gas phase was established by Horrex and Miles,[15] who studied the pyrolysis of bibenzyl in a flow system. Combination of radicals does not occur under these conditions, but disproportionation (4) or decomposition (5) of the 1,2-diphenylethyl radicals leads to the formation of stilbene:

$$2\mathrm{Ph{\cdot}CH_2{\cdot}CHPh{\cdot}} \longrightarrow \mathrm{PhHC{:}CHPh} + \mathrm{Ph{\cdot}CH_2{\cdot}CH_2Ph} \quad . \; . \; . \; . \; . \quad (4)$$

$$\mathrm{Ph{\cdot}CH_2{\cdot}CHPh{\cdot}} \longrightarrow \mathrm{PhHC{:}CHPh} + \mathrm{H{\cdot}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

Bickel and Waters[16] obtained bibenzyl, stilbene, and toluene from the products of decomposition of ωω′-azotoluene in decalin at 200°. Benzyl radicals were considered to be formed, but the stilbene was thought to arise from dimerisation of benzylidene diradicals formed, together with toluene, by disproportionation of benzyl radicals:

$$2\mathrm{Ph{\cdot}CH_2{\cdot}} \longrightarrow \mathrm{Ph{\cdot}CH_3} + \mathrm{Ph{\cdot}CH{:}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

---

[13] Gregg and Mayo, *Discuss. Faraday Soc.*, 1947, **2**, 328.
[14] Kooyman, *Discuss. Faraday Soc.*, 1951, **10**, 163.
[15] Horrex and Miles, *Discuss. Faraday Soc.*, 1951, **10**, 187.
[16] Bickel and Waters, *Rec. Trav. chim.*, 1950, **69**, 312.

In view of Horrex and Miles's results, and those now reported, it is possible that toluene was formed by hydrogen abstraction from bibenzyl, and stilbene by disproportionation of the resulting 1,2-diphenylethyl radicals.

The above results confirm the earlier conclusion [3,4] that the identity reaction of benzyl radicals with toluene occurs only to a very small extent, since the reaction of benzyl radicals with isopropylbenzene is hardly significant compared with the dimerisation of benzyl radicals, and toluene is well known to be only about one-third as reactive as isopropylbenzene in reactions of this type.[17]

EXPERIMENTAL

Apparatus for Photolysis.—The apparatus was similar in principle to that described by Blair, Bryce-Smith, and Pengilly [18] and is shown diagrammatically in Fig. 1. The reaction vessel was constructed by modification of a standard 250-ml. round-bottomed, three-necked flask. Diametrically opposite to, and accurately coaxial with the centre neck was fitted a 1″ bore cylindrical Pyrex-to-quartz graded seal. This was closed at its lower (quartz) end so that it formed a stem terminated by a cylindrical quartz cell, the bottom of which was flat. The two inclined necks carried, respectively, a small mercury–aniline thermoregulator and a water-cooled condenser. Pure nitrogen was introduced through a glass tube down the centre of this condenser. An additional side-arm to the flask was fitted with a B10 ground-glass socket, and carried a thermometer embodying a B10 cone. The contents of the flask were stirred by means of a specially designed stirrer (Fig. 2) whose direction of rotation could be reversed as necessary, and which entered the flask through an airtight gland fitted to the central neck. Glass wool, wound around the spiked lower end of the stirrer, served to rub clean from resinous deposits the inner surface of the quartz cell.

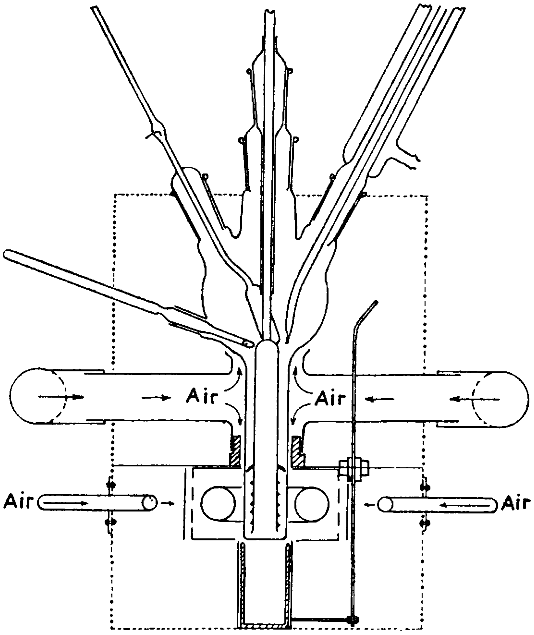

FIG. 1. Apparatus for irradiation.

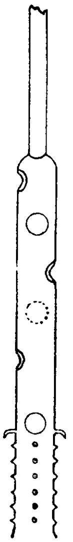

FIG. 2. Stirrer.

Ultraviolet light, and heating, were provided by a Hanovia S.500 high-pressure mercury arc tube. This was U-shaped, mounted in a polished aluminium lamp housing, and situated round the quartz cell of the reaction vessel. Cooling was effected by means of streams of air

---

[17] See, *e.g.*, Brook, *Trans. Faraday Soc.*, 1957, **53**, 327; Johnston and Williams, *J.*, 1960, 1446.
[18] Blair, Bryce-Smith, and Pengilly, *J.*, 1959, 3174.

blown on to the bottom stem of the reaction vessel. The speed of the fan motor was governed by a resistance R_1 in series with it, and was adjusted so that the contents of the reaction vessel reached a temperature slightly above that required. The thermoregulator circuit was thus made, and a second (high) resistance R_2 in parallel with R_1 was introduced into the fan-motor circuit by means of a modified " Sunvic " hotwire vacuum switch (type F102/3) in the thermoregulator circuit. The resulting increased speed of the fan motor was sufficient to reduce the temperature below the required value, so that the thermoregulator circuit was then broken and the process reversed. In this way it was possible automatically to control the reaction temperature to $\pm 0{\cdot}3°$. A copper sleeve could be raised to cover the quartz cell so that the latter could be heated without irradiation. The whole apparatus was mounted in a polished aluminium casing (shown by the broken line in Fig. 1) from which ozone-containing cooling air was removed by two ducts (not shown in the diagram).

Experimental Procedure for Photolysis.—With a tap-funnel in place of the thermoregulator, the apparatus was flushed with dry, oxygen-free nitrogen for 1 hr. A weighed quantity of the radical-source was then washed into the reaction vessel through the tap funnel with 200 ml. of the appropriate solvent. The tap funnel was replaced by the thermoregulator, stirring commenced, and a rapid stream of nitrogen passed through the reaction mixture for 2 hr. and a slower stream overnight. With the light-guard raised into position, the flask was heated by the arc-tube until the required temperature had been reached. The resistances R_1 and R_2 were adjusted so that this temperature was maintained, and then irradiation was commenced by lowering the light-guard. Nitrogen was passed very slowly through the reaction mixture during photolysis, and the direction of stirring was frequently reversed. After irradiation and cooling, the mixture was quantitatively filtered through sintered glass. All components of the apparatus which had been in contact with the reaction mixture were washed with a volatile solvent (usually anhydrous ether), and the washings, after filtration, were added to the reaction mixture. All components contaminated with free metal (when this was formed) were dried at 50° and extracted with 100 ml. of concentrated nitric acid, then with distilled water. These extracts were poured through the sintered glass crucible used for the filtration of the reaction mixture, into a 1-l. graduated flask. The resulting solution, which contained all the liberated metal as its nitrate, was made up with distilled water and analysed as described below.

The solution containing the organic products of photolysis was distilled through a 30 cm. helix-packed column until about 5 ml. remained. The first fraction, consisting of wash-liquid, was discarded. A small forerun (10—20 ml.) to the main fraction was then collected, followed by the bulk of the solvent used. After cooling, the column was washed with anhydrous ether (~50 ml.), and the washings were added to the higher-boiling material remaining in the flask. Ether was removed from this by careful distillation at atmospheric pressure. The higher-boiling products were isolated by distillation *in vacuo* as described by Augood, Hey, and Williams.[19]

Determination of Mercury.—Mercury was determined by titration with ~0·1N-ammonium thiocyanate, which had previously been standardised against a solution of mercuric nitrate prepared from a known weight of mercury [20] and having the same acidity as the solutions to be analysed. Because of the rather high acidity of the solution, titrations were conducted at 0°, at which temperature the influence of the acid concentration is negligible. All volumetric apparatus was calibrated before use.

Photolysis of Dibenzylmercury.—(*a*) *In γ-picoline at* 80°. The residue after removal of solvents, to which the ethereal washings of the column had been added, was extracted with 7N-hydrochloric acid (4 × 20 ml.) and water (20 ml.). The combined extracts were extracted with ether (20 ml.), which was combined with the main organic portion and dried ($MgSO_4$). The acidic portion was made just alkaline with 50% aqueous sodium hydroxide and extracted with chloroform (4 × 20 ml.). Distillation of the dried (K_2CO_3) chloroform extract gave only a small, involatile residue (0·053 g.). Distillation of the main organic portion gave bibenzyl, b. p. 79—81°/0·05 mm., m. p. and mixed m. p. 51—52° (Found: C, 92·6; H, 7·4. Calc. for $C_{14}H_{14}$: C, 92·3; H, 7·7%). The infrared spectrum of this material was identical with that of an authentic specimen. A small residue, which could not be distilled at 200°/0·05 mm., remained.

---

[19] Augood, Hey, and Williams, *J.*, 1952, 2094.

[20] Sutton, " A Systematic Handbook of Volumetric Analysis," 13th edn., Butterworths Scientific Publications, London, 1955.

(*b*) *In isopropylbenzene at* 80°. No acid-extraction was carried out in this case. The excess of isopropylbenzene removed by distillation was pale yellow and decolorised a very small quantity of bromine in carbon tetrachloride. Gas–liquid chromatography failed to reveal any component other than isopropylbenzene. Two fractions were obtained by distillation of the residue. The first fraction (b. p. 90°/0·1 mm.) was bibenzyl, which was characterised as described above. The physical properties of the second fraction (b. p. 140—150°/0·1 mm., n_D^{25} 1·5952) are in agreement with those reported for 1,2,3-triphenylpropane [21,22] (Found: C, 92·0; H, 7·5%; *M*, 260. Calc. for $C_{21}H_{20}$: C, 92·6; H, 7·4%; *M*, 272). The results of these two experiments are summarised in Table 2.

TABLE 2.

Photolysis of dibenzylmercury at 80°.

	Expt. 1. γ-Picoline (200 ml.)	Expt. 2. Isopropylbenzene (200 ml.)
Dibenzylmercury (g.)	4·400	4·201
Period of irradiation (hr.)	8	8
Dibenzylmercury decomposed, as metal (%)	98·2	97·6
Bibenzyl (g.)	1·857	1·790
1,2,3-Triphenylpropane (g.)	0·00	0·171
Total undistilled residue (g.)	0·204	0·168
Dibenzylmercury accounted for by bibenzyl and 1,2,3-triphenylpropane (%)	89	98·2

Photolysis of Benzyl Iodide.—(*a*) *In γ-picoline in the presence of silver powder at* 80°. Owing to the extreme photochemical instability of benzyl iodide, care was taken to shield reaction mixtures containing this compound from daylight until the commencement of photolysis. For similar reasons, the metal used as iodine scavenger was not added until immediately before illumination. All operations in the working-up procedure were carried out away from direct light. The reaction mixture, consisting of γ-picoline (200 ml.), benzyl iodide (4·36 g.), and silver powder (2·59 g.), was photolysed for 8 hr. at 80°. The mixture, after filtration from silver powder, deposited 1-*benzyl*-4-*methylpyridinium iodide* (4·41 g.), m. p. 149—151°, from methanol–ether (Found: I, 41·4; N, 4·4. $C_{13}H_{14}IN$ requires I, 40·8; N, 4·5%). Removal of the excess of γ-picoline by distillation at 12 mm. in nitrogen left a residue from which a further quantity of the quaternary iodide (1·5 g.) was obtained. 1-Benzyl-4-methylpyridinium iodide, m. p. 149—151°, was also formed in quantitative yield by warming a mixture of benzyl iodide and γ-picoline in the dark.

(*b*) *In isopropylbenzene in the presence of silver powder.* Several trial experiments were carried out at 80° and 100° with silver powder in various amounts and for various times, but in no case was complete decomposition of the benzyl iodide achieved. The mixtures after photolysis always contained free iodine and benzyl iodide. The iodine was removed by extraction with sodium thiosulphate solution, but the extreme lachrymatory properties of benzyl iodide, and its gradual decomposition to liberate more iodine when kept or distilled, added greatly to the difficulties of working up. Bibenzyl was isolated from all these mixtures, in varying amounts, but quantitative results could not be obtained.

(*c*) *In isopropylbenzene in the presence of mercury at* 100°. Trial experiments indicated that mercury was a much more satisfactory iodine scavenger than silver. In Expt. 3, a mixture of benzyl iodide (4·50 g.), isopropylbenzene (200 ml.), and mercury (6·21 g.) was photolysed for 8 hr. During photolysis, greenish-yellow mercurous iodide was deposited, together with some red mercuric iodide. The mixture was filtered, and the filtrate extracted with a 10% aqueous solution of potassium iodide and worked up as previously described. The final distillation gave bibenzyl (1·140 g.) and 1,2,3-triphenylpropane (0·224 g.), both of which were characterised as described above, and which together accounted for 73% of the benzyl iodide used. A residue (0·109 g.), which was not volatile at 250°/0·1 mm., was also formed.

Photolysis of Benzylmercuric Iodide in Isopropylbenzene at 80°.—The mixtures obtained from Expts. 4, 5, and 6 after photolysis were very pale yellow. In Expt. 4, the exact amount of mercurous iodide formed was determined by weighing, before and after photolysis, every

---

[21] Farmer and Moore, *J.*, 1951, 131.

[22] Fuson, *J. Amer. Chem. Soc.*, 1926, **48**, 2937.

component of the apparatus on which mercurous iodide was deposited. No errors arising from the detachment of fragments of glass wool from the stirrer were incurred, as these fragments were weighed together with mercurous iodide in the sintered-glass crucible through which the mixture was filtered after photolysis. Dissolved mercurous iodide was estimated by weighing the mixture of organic products obtained after removal of solvents before and after extraction with 10% aqueous potassium iodide. In this experiment, bibenzyl and 1,2,3-triphenylpropane were separated by distillation as previously described. In Expts. 5 and 6, a forerun (∼10 g.) to the bulk of the solvent was collected in the initial distillation, after removal of ether. This forerun was analysed for toluene by gas–liquid chromatography with a Perkin-Elmer model 116 vapour fractometer. A calibration curve of peak height against toluene content was constructed by the analysis of mixtures of toluene and isopropylbenzene of known composition under conditions identical with those used for the experimental mixtures. Samples (20 μl.) were introduced by means of a precision capillary pipette.

The mixture of products obtained by distillation, after extraction with potassium iodide solution, was separated into two fractions by chromatography on alumina. The first (binuclear) fraction (m. p. 48—49°), which was eluted with light petroleum (b. p. 40—60°), was analysed by gas–liquid chromatography. Samples (2—5 μl.) were injected in the fused state by preheated syringes, sometimes after addition of a known quantity of another compound of similar volatility and of known and sufficiently different retention time (*e.g.*, biphenyl) to depress the m. p. The method of internal normalisation was shown by the analysis of synthetic mixtures of known composition to be suitable for the quantitative analysis of these mixtures, which were thus shown to contain bibenzyl and αα-dimethylbibenzyl only. The second fraction obtained by chromatography, which was eluted with methylene chloride or ether, consisted of 1,2,3-triphenylpropane, which was characterised as previously described. The results of these experiments are given in Table 3.

TABLE 3.

Photolysis of benzylmercuric iodide in isopropylbenzene at 80°.

Expt.:	4	5	6
Isopropylbenzene (ml.)	200	200	200
Benzylmercuric iodide (g.)	9·000	6·000	6·000
Period of irradiation (hr.)	5	4	5
Mercurous iodide (g.)	6·93	—	—
Mercurous iodide (% of theoretical)	98·4	—	—
Binuclear fraction (g.)	1·538	1·053	1·086
Bibenzyl in binuclear fraction (%)	96·2	96·2	96·0
αα-Dimethylbibenzyl in binuclear fraction (%)	3·8	3·8	4·0
1,2,3-Triphenylpropane (g.)	0·239	0·157	0·159
Toluene (g.)	—	0·058	0·061
Undistilled residue (g.)	0·104	0·066	0·070
Benzylmercuric iodide accounted for by identified products (%)	89·2	95·5	96·7
Toluene (% of theoretical)	—	83·0	83·9

Photolysis of Benzylmercuric Iodide in Cyclohexane at 80°.—The pale yellow mixture after photolysis (Expt. 7) was worked up by the procedure used in Expt. 4 for the estimation of mercurous iodide. Not all the benzylmercuric iodide was dissolved at the beginning of the photolysis, which was, however, complete after 2 hr. The organic products were isolated and analysed as described for Expts. 5 and 6, except that the toluene was present in an " after-run " to the bulk of the solvent. This after-run was analysed by gas–liquid chromatography. The results of this analysis are, however, less accurate than those described above, owing to overlapping of the cyclohexane and toluene peaks. This resulted from extensive " tailing " of the cyclohexane peak, due to overloading of the column, which was unavoidable since the toluene content of the mixtures was very small. The yield of toluene which is given, together with the other results of this experiment, in Table 4, is therefore a *minimum* value.

Photolysis of 4-*Chlorobenzylmercuric Iodide in Isopropylbenzene at* 100°.—The pale yellow reaction mixture after photolysis (Expt. 8) was worked up and the various fractions analysed as described for Expt. 7. *p*-Chlorotoluene occurred in an after-run to the bulk of solvent, and the yield, which is given, together with the other results of this experiment, in Table 5, is a minimum value. The presence of a trace of α-methylstyrene in the after-run was also detected. The binuclear fraction, which was separated from the trinuclear fraction by distillation *in vacuo*, was analysed by gas–liquid chromatography. The trinuclear fraction was a pale yellow semi-solid (b. p. 188—200°/0·005 mm.). A white solid (0·08 g.), m. p. 149—153° (Found: C, 81·9; H, 7·1; Cl, 11·1%; *M*, 312. Calc. for $C_{21}H_{19}Cl$: C, 82·2; H, 6·3; Cl, 11·5%; *M*, 307), was obtained by precipitation with light petroleum (b. p. 40—60°) from a cold chloroform solution of the semi-solid. The analysis suggests a dehydrogeno-trimer which has, however, only one-third of the expected chlorine content. Evaporation of the mother-liquors gave an oil (0·32 g.) (Found: C, 79·5; H, 6·8; Cl, 14·1%), which was assumed to be a mixture of dehydrogeno-trimers containing, severally, one, two, and three atoms of chlorine.

TABLE 4.

Photolysis of benzylmercuric iodide in cyclohexane at 80°.

	Expt. 7
Cyclohexane (ml.)	200
Benzylmercuric iodide (g.)	9·00
Period of irradiation (hr.)	2
Mercurous iodide (g.)	7·02
Mercurous iodide (% of theoretical)	99·7
Bibenzyl (g.)	1·650
1,2,3-Triphenylpropane (g.)	0·194
Toluene (g.)	0·07
Undistilled residue (g.)	0·051
Benzylmercuric iodide accounted for by identified products (%)	97·4

TABLE 5.

Photolysis of 4-chlorobenzylmercuric iodide and of an equimolar mixture of benzylmercuric iodide and 4-chlorobenzylmercuric iodide in isopropylbenzene at 100°.

Expt.:	8	9
Isopropylbenzene (ml.)	200	200
Benzylmercuric iodide (g.)	0·00	3·140
4-Chlorobenzylmercuric iodide (g.)	6·500	3·398
Period of irradiation (hr.)	5	5
Toluene (g.)	0·0	0·020
p-Chlorotoluene (g.)	0·079	0·048
Binuclear fraction (g.)	1·281	1·319
4,4'-Dichlorobibenzyl in binuclear fraction (%)	84·1	15·9
4-Chlorobibenzyl in binuclear fraction (%)	15·1	52·6
Bibenzyl in binuclear fraction (%)	0·8	31·5
Trinuclear fraction (g.)	0·517	0·370
Undistilled residue (g.)	0·232	0·098
Radical-source accounted for (%) *	90·8	100

* Calc. from yields of binuclear products, toluene, and *p*-chlorotoluene.

Photolysis of an Equimolar Mixture of Benzylmercuric Iodide and 4-Chlorobenzylmercuric Iodide in Isopropylbenzene at 100°.—Expt. 9 was conducted by the procedure described for Expt. 8, except that the binuclear and trinuclear fractions were separated by chromatography on an alumina column. A solid trimeric compound (0·024 g.), m. p. 148—153°, identical with that isolated from Expt. 8, was obtained from the trinuclear fraction. The results are given in Table 5.

Photolysis of Dibenzylmercury in Benzene in the Presence of Diphenylpicrylhydrazyl.—In Expt. 10, a solution of diphenylpicrylhydrazyl (0·01 g., $2·5 \times 10^{-5}$ mole) and dibenzylmercury (1·00 g., $2·6 \times 10^{-3}$ mole) in benzene (200 ml.) was heated to 80° in the dark in the photolysis apparatus. The dark violet solution was instantly decolorised when suddenly exposed to ultraviolet light by lowering of the light-guard. In Expt. 11, a solution containing only diphenylpicrylhydrazyl (0·01 g.) in benzene (200 ml.) when similarly treated required 6 min. for decoloration. Both experiments were carried out in an atmosphere of nitrogen.

Photolysis of Benzylmercuric Iodide in Cyclohexane in the Presence of Diphenylpicrylhydrazyl.—In Expt. 12, two solutions *A* and *B* were made up under nitrogen in stoppered Pyrex flasks. Solution *A* contained diphenylpicrylhydrazyl (0·004 g., 10^{-5} mole) and benzylmercuric iodide (0·042 g., 10^{-4} mole), and solution *B* diphenylpicrylhydrazyl (0·004 g.) (only) in cyclohexane

(100 ml.). Both solutions were placed about 5 cm. from a 125-w high-pressure mercury discharge tube. Both solutions were initially deep violet, but, whereas *A* was decolorised after 33 min., *B* was unchanged after 90 min. The temperature of the solutions was 35°. In a control experiment two solutions *C* and *D*, identical with *A* and *B*, respectively, were stored in the dark for one week at room temperature. The appearance of both solutions was unchanged at the end of this time. Irradiation of these solutions as described above resulted in the decoloration of *C* after 28 min., while the appearance of *D* was unaffected.

Preparation and Purification of Reagents.—Cyclohexane ("AnalaR") was fractionally distilled from sodium (b. p. 80°/760 mm.). It was stored over sodium and again fractionally distilled immediately before use. Its purity was checked by gas–liquid chromatography. Benzene, toluene, and isopropylbenzene (Hopkin and Williams) were shaken repeatedly with concentrated sulphuric acid until the washings were colourless, then with saturated aqueous sodium hydrogen carbonate and water, and dried ($CaCl_2$). They were then fractionally distilled from sodium (b. p. 80°/760 mm., 110°/760 mm., and 152°/760 mm., respectively). They were stored over sodium, and again fractionally distilled and subjected to gas–liquid chromatography to check their purity before use. Gas–liquid chromatography showed that isopropylbenzene required very careful fractionation to remove ethylbenzene, and a large head-fraction was discarded. γ-Picoline (B.D.H.) was dried (KOH) and fractionally distilled from barium oxide (b. p. 145°/760 mm.). Immediately before use it was again fractionally distilled and its purity checked by gas–liquid chromatography.

Biphenyl (B.D.H.) was recrystallised twice from ethanol (m. p. 70°) and bibenzyl (Judex) from methanol (m. p. 51—52°). Bicumyl (m. p. 118°) and 4,4′-dichlorobibenzyl (m. p. 101°) were prepared by Johnston and Williams's method.[23] Specimens of 4-chlorobibenzyl (m. p. 42°) and $\alpha\alpha$-dimethylbibenzyl (b. p. 75—77°/0·02 mm., n_D^{19} 1·5591) were kindly given by Dr. K. M. Johnston. The silver powder used was the B.D.H. "precipitated" metal. Mercury was redistilled before use. 1,1-Diphenyl-2-picrylhydrazyl was prepared by Poirier, Kahler, and Benington's method [24] and had m. p. 129—130° (decomp.).

Benzyl iodide was prepared in a darkened fume cupboard. An ethanolic solution of equimolar quantities of benzyl chloride and potassium iodide was heated at 70° for 0·5 hr. After cooling in ice, water was added, and the crude benzyl iodide collected by filtration, recrystallised to constant m. p. (24°), and stored under nitrogen at 0° in darkness. Benzylmercuric chloride and dibenzylmercury (m. p. 111°) were prepared by Jones and Werner's method.[25] 4-Chlorobenzylmercuric chloride was similarly prepared from 4-chlorobenzylmagnesium chloride [from 4-chlorobenzyl chloride (40·3 g.) and magnesium (6·1 g.) in anhydrous ether (300 ml.)] and mercuric chloride (67·9 g.) in anhydrous ether (300 ml.); it was obtained in 71% yield as white crystals, m. p. 149·5° (Found: C, 23·8; H, 1·6. Calc. for $C_7H_6Cl_2Hg$: C, 23·3; H, 1·7%); Kharasch, Pines, and Levine [26] reported m. p. 141° for this compound, which they prepared from 4-chlorobenzylmagnesium bromide. *Di-4-chlorobenzylmercury* was prepared in 63% yield by Jones and Werner's method [25] from 4-chlorobenzylmercuric chloride (0·05 mole) and 4-chlorobenzylmagnesium chloride (0·06 mole). Crystallisation from chloroform gave di-4-chlorobenzylmercury as white crystals m. p. 169—170° (decomp.) (Found: C, 36·9; H, 2·8. $C_{14}H_{12}Cl_2Hg$ requires C, 37·2; H, 2·7%).

Benzylmercuric iodide and 4-chlorobenzylmercuric iodide were prepared from the appropriate disubstituted mercurial and mercuric iodide. The preparations were carried out in almost complete darkness, only the minimum of indirect light being used for the manipulations. A solution of dibenzylmercury (or di-4-chlorobenzylmercury) (0·050 mole) in the minimum quantity of tetrahydrofuran was quickly added to a refluxing solution of mercuric iodide (0·050 mole) in methanol (500 ml.). A copious precipitate was immediately formed. The mixture was boiled under reflux for 1·5 hr., and about one-quarter of the solvent was removed by distillation. The organomercuric iodide, which was deposited when the mixture was cooled, was filtered off and dried in a vacuum-oven at 70°. Yields were above 90% and, provided that the compounds were not exposed to light, further crystallisation resulted in no change in m. p. Benzylmercuric iodide had m. p. 117° in the dark [111—113° (decomp.) in light]. Wolff [27]

---

[23] Johnston and Williams, *J.*, 1960, 1168.

[24] Poirier, Kahler, and Benington, *J. Org. Chem.*, 1952, **17**, 1437.

[25] Jones and Werner, *J. Amer. Chem. Soc.*, 1918, **40**, 1266.

[26] Kharasch, Pines, and Levine, *J. Org. Chem.*, 1938, **3**, 347.

[27] Wolff, *Ber.*, 1913, **46**, 64.

reported m. p. 117°. 4-Chlorobenzylmercuric iodide had m. p. 149° (decomp.) in the dark [144—145° (decomp.) in light]. In 3 × 10^{-5}M-solution in ethanol benzylmercuric iodide showed an absorption maximum at 264 mμ ($\varepsilon_{max.}$ 28,200), and 4-chlorobenzylmercuric iodide at 265 mμ ($\varepsilon_{max.}$ 33,400).

The authors thank the Ministry of Education for the award of a grant to D. A. S.

DEPARTMENT OF CHEMISTRY, KING'S COLLEGE (UNIVERSITY OF LONDON),
STRAND, LONDON, W.C.2.
BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
MALET STREET, LONDON, W.C.1.

[*Received, July 6th*, 1962.]