645. *Liquid-phase Photolysis. Part I. Variation of Isomer Ratios with Radical Source in the Phenylation of Isopropylbenzene. Photolytic Generation of Phenyl Radicals.*

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Photolysis of iodobenzene in isopropylbenzene gives a mixture of isomeric isopropyldiphenyls in the same ratio as is obtained when dibenzoyl peroxide decomposes in isopropylbenzene. Diphenylmercury and tetraphenyl-lead give a different ratio of these isomers when photolytically decomposed in isopropylbenzene. Variations in the product ratio are briefly discussed. An apparatus useful for the study of solution photolysis is described.

Several groups of workers [1,2,3] found the main products of decomposition of dibenzoyl peroxide in isopropylbenzene to be benzoic acid, benzene, 2,3-dimethyl-2,3-diphenylbutane (" dicumyl "), a mixture of the isomeric isopropyldiphenyls, and a high-boiling residue. They differ, however, in their estimates of product ratios. From the published descriptions of the methods of estimating these, it appears that the results of Hey, Pengilly, and Williams [1] are the most accurate, and their figures are used here for comparison.

It has been found that iodobenzene, diphenylmercury, and tetraphenyl-lead can be photolytically decomposed in isopropylbenzene to give products which show that free phenyl radicals are involved in the reactions. The solvent undergoes both side-chain and nuclear attack, with the production of benzene, 2,3-dimethyl-2,3-diphenylbutane, a mixture of the isomeric isopropyldiphenyls, and a high-boiling residue, together with free

Table 1.

Radical source		Ph_2Hg		Ph_4Pb	PhI		$(BzO)_2$
Expt. no.		1	2	3	4	5	
Temp.		120°	120°	120°	120°	120°	80°
Wt. (g.) of radical source		5·035	4·998	3·698	6·001	6·001	10
Isopropylbenzene (ml.)		41	43	44	43	43	150
Irradiation time (hr.)		6	6	12·5	6	6	—
Decomp. (%)		94	63	43·5	82	97	100
Ph radicals produced (g.)		2·06	1·37	0·96	1·86	2·20	4·08
Benzene produced (g.)		1·06	0·79	0·71	0·95	1·27	2·0
Diphenyl fraction (g.)		1·19	0·83	0·60	0·93	1·31	4·66
Composition (%) of diphenyls: dicumyl fraction	2-	7·7	8·5	5·7	18·1	26·6	
	3-	19·4	17·9	13·2	25·7	36·4	
	4-	9·6	9·5	6·9	15·6	19·7	
	d	63·3	64·2	74·1	40·7	17·3	60·5
Residue (g.)		1·30	0·87	0·38	0·41	0·40	2·29
Ph radicals giving benzene (%)		50·8	56·8	73·1	50·4	57·0	48·4
Ph radicals giving diphenyls (%)		8·33	8·55	6·38	11·65	19·35	17·7
Residue : Ph radicals (w/w)		0·630	0·635	0·390	0·225	0·180	0·560
Benzene accounted for as dicumyl (%)		46·5	44·5	41·0	26·0	11·5	92·5
Yield (%) of dicumyl		23·5	26·0	30·1	13·0	6·5	44·5
Ratios (%) of isopropyldiphenyls:	2-	21·0	23·5	22·0	31·0	32·0	31
	3-	53·0	50·0	51·0	43·0	44·0	42
	4-	26·0	26·5	27·0	26·0	24·0	27

Table 2. *Mol. of principal products per mol. of phenyl radicals.*

Expt. no.	1	2	3	4	5
Benzene	0·51	0·57	0·73	0·50	0·57
Isopropyldiphenyls (*a*)	0·085	0·085	0·065	0·115	0·195
" Dicumyl " (*b*)	0·12	0·13	0·15	0·065	0·035
Mol. of benzene not accounted for by (*a*) and (*b*)	0·185	0·225	0·365	0·255	0·305

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[1] Hey, Pengilly, and Williams, *J.*, 1956, 1463.

[2] Dannley and Zaremsky, *J. Amer. Chem. Soc.*, 1955, **77**, 1588.

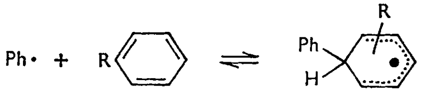
[3] Rondestvedt and Blanchard, *ibid.*, p. 1769.

iodine (fixed as silver iodide), and mercury and lead respectively. In the Tables, experimental details and results are summarized and compared with the results of Hey, Pengilly, and Williams [1] for the decomposition of dibenzoyl peroxide in isopropylbenzene.

The ratios of 2- and 3-isopropyldiphenyl obtained from diphenylmercury and tetraphenyl-lead on one hand, and from iodobenzene and dibenzoyl peroxide on the other, seem to fall into two distinct groups. The differences are 7·5—11% for the 2-isomers and 6—11% for the 3-isomers. The experimental error in the analytical procedure is difficult to assess accurately without many more data; but the internal consistency is *ca.* ±2%, which is a normal range for estimations of this type. The authors accordingly feel it probable that the observed discrepancy, although small, is real. The Tables show that the other product ratios are also subject to variation. About 50% of the phenyl radicals from iodobenzene, diphenylmercury, and dibenzoyl peroxide gave benzene. More than 70% of those from tetraphenyl-lead gave benzene, and this, coupled with an increased yield of 2,3-dimethyl-2,3-diphenylbutane (" dicumyl " in the Table), indicates that phenyl radicals from tetraphenyl-lead preferentially attack the side chain of isopropylbenzene, although the ratio of nuclear isomers was almost identical with that observed when diphenylmercury was the radical source. As judged from the relative rates of decomposition of diphenylmercury and tetraphenyl-lead (see Table 1), the stationary concentration of free phenyl radicals must have been much the lower with tetraphenyl-lead as radical source. Foster and Williams [4] have observed rather similar variations of product ratios with concentration of decomposing dibenzoyl peroxide in isopropylbenzene. The low and variable yield of 2,3-dimethyl-2,3-diphenylbutane from the photolysis of iodobenzene in isopropylbenzene probably has as its cause a reaction between αα-dimethylbenzyl radicals and iodine to give 1-iodo-1-methylethylbenzene. Although the iodine produced in these reactions was absorbed with silver powder, the process was found to be irreproducible. The inevitable variations in the mean concentration of free iodine are reflected in the yields of 2,3-dimethyl-2,3-diphenylbutane. The yield of isopropyldiphenyls was greatest, but again variable, with phenyl radicals from iodobenzene. The yield of high-boiling residue varied and was least with iodobenzene as radical source.

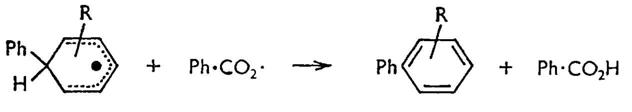
We do not at present propose a full explanation of the variations in ratios of nuclear isomers with the radical source. Several possibilities may, however, be eliminated. First, the ultraviolet radiation itself cannot be a dominating factor since variations in isomer ratios occurred within the group of photolysis experiments. Secondly, the possibility that the " abnormal " ratios involve " hot " phenyl radicals seems unlikely since these ratios are consistent with attack by a rather more selective (*i.e.*, less active) reagent.

A probable mechanism for homolytic aromatic phenylation involves the initial addition of a phenyl radical to the aromatic system, giving a radical analogue of the Wheland intermediate for electrophilic substitution:



· · · · · · · (1) [*]

Abstraction of a hydrogen atom from the radical intermediate by, *e.g.*, a benzoyloxy-radical or dibenzoyl peroxide furnishes the diphenyl derivative; *e.g.*:



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It has recently been shown that the intermediate radicals need not react exclusively in the

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[*] Reaction (1) is written as reversible in view of the lack of contrary evidence.

[4] Foster and Williams, personal communication.

manner of equation (2). For example, Lynch and Pausacker[5] explain the formation of quaterphenyls in terms of dimerization of the intermediate radicals, followed by dehydrogenation. DeTar and Long[6] have identified dihydrodiphenyls among the products from the decomposition of dilute solutions of dibenzoyl peroxide in benzene. Hydrodiphenyls also seem to be formed when diphenylmercury is photolyzed in benzene under nitrogen.[7] Dihydrodiphenyls doubtless arise from disproportionation of the above intermediate radicals, and subsequent dehydrogenation of the former provides an alternative to equation (2) as a route for the production of diphenyls. We consider that under conditions where dehydrogenation is relatively unfavoured, the radical intermediates formed in reaction (1) may reach a higher stationary concentration than is usual. In their subsequent relative tendencies to dimerize or disproportionate, any selectivity between isomers would be reflected in the isomer composition of the substituted diphenyls which are finally isolated.

In the present work, the " abnormal " isomer ratios were observed in experiments with diphenylmercury and tetraphenyl-lead where reactions of type (2) should be relatively unfavoured. With iodobenzene as radical source, the isomer ratios were " normal ": here, free iodine was always present in a varying and irreproducible concentration, despite the addition of silver powder, and would possibly be effective both in dehydrogenating the radical intermediates as in equation (2), and in capturing a proportion of αα-dimethylbenzyl radicals. This suggestion is consistent with the observed evolution of hydrogen iodide, the much higher yield of isopropyldiphenyls, and the variable yields of " dicumyl," when iodobenzene was used as the radical source.

EXPERIMENTAL

The Photolysis Cell.—This was constructed round a Jencon's 1″ quartz/borosilicate-glass graded seal. The quartz end of the seal was closed to give a 2″ quartz tube. The glass end of the seal was joined co-axially to the bottom of a 100 ml. round-bottomed B.24 " Quickfit " flask. A tube at an upward angle joined to the glass part of the extension served to take a thermometer or thermocouple which was sealed in position with a silicone rubber gland. Two B.14 sockets on the flask at a slight angle to the vertical took a water-condenser which was attached to a mercury-trap at its other end, and a hopper for silver powder. Both radiation and heating were provided by a " Hanovia " S 500 mercury-vapour ultraviolet lamp, which was mounted with the semi-torus of the lamp around the quartz part of the cell, allowing a clearance of 2—3 mm. A removable aluminium sheath fitted between the lamp and the cell, preventing irradiation of the cell contents until the desired temperature had been reached. The lamp and the quartz cell were encased in a ventilated aluminium box, the walls of which were coated with magnesium oxide. During irradiation, the inner quartz surface was continually rubbed with glass wool attached to the axially-impelling stirrer to prevent the deposition of polymer films. The stirrer carried small spikes on its shaft to hold the glass wool in position. The direction of rotation was changed periodically to prevent the glass wool from becoming tightly wound round the stirrer. A shaped polyvinyl chloride gland lubricated with a mixture of petroleum jelly and liquid paraffin formed an air-tight seal between the stirrer and the stirrer guide. A side-arm on the stirrer-guide was used as a nitrogen inlet. The temperature of the cell contents during irradiation was controlled by varying the air-flow from a small cooling-fan which blew air through a duct around the upper parts of the cell extension.

A modified cell with a built-in water jacket has also been used. This enables irradiations to be carried out at temperatures down to 45°. In it, the temperature is very simply adjusted by means of a variable-head device attached to the coolant supply.

Purification of Diphenylmercury.—The product supplied by " Lunevale Products Ltd." contained considerable quantities of halogen. This could not be removed by recrystallization from a variety of solvents. The following procedure proved effective. Crude diphenylmercury (10 g.) was dissolved in the minimum quantity of warm ethanol (*ca.* 150 ml.) and was shaken with moist silver oxide (*ca.* 10 g.) for 30 min. The mixture was then heated under reflux for

[5] Lynch and Pausacker, *Austral. J. Chem.*, 1957, **10**, 165.
[6] DeTar and Long, *J. Amer. Chem. Soc.*, 1958, **80**, 4742.
[7] Blair and Bryce-Smith, unpublished work.

30 min. and filtered while hot. The filtrate was concentrated by evaporation to obtain the diphenylmercury. This was recrystallized from benzene, to give halogen-free material, m. p. 125—126°. This procedure converts phenylmercuric halides into phenylmercuric hydroxide, which is much more soluble in alcohol and benzene.

Preparation of Tetraphenyl-lead.—A solution of phenylmagnesium bromide was prepared in the usual manner from magnesium (7 g.) and bromobenzene (42 g.) in ether (100 ml.). Dry lead chloride (20 g.) was added. Stirring and heating under reflux were continued for about 36 hr., then the mixture was cooled. Water was added, followed by dilute hydrochloric acid. The solid material was washed with water and ether, and finally extracted with benzene in a Soxhlet apparatus, with a heating-tape wound round the extractor unit and so adjusted as to maintain the benzene there just below its b. p. Tetraphenyl-lead (10·8 g.) was extracted. Its m. p. (224—226°) was unchanged after recrystallization from xylene (cf. refs. 8 and 9).

Purification of Iodobenzene.—Commercial material was decolorized by being shaken with aqueous sodium thiosulphate, washed with water, dried ($CaCl_2$), and fractionally distilled under reduced pressure. The fraction boiling at 114°/92 mm. was collected and stored over a little silver powder and calcium chloride.

Isopropylbenzene was purified and stored as previously described.[10]

Photolysis of Diphenylmercury, Tetraphenyl-lead, and Iodobenzene in Isopropylbenzene.—Sufficient diphenylmercury, tetraphenyl-lead or iodobenzene to produce about 2·5 g. of phenyl radicals was irradiated in isopropylbenzene in the cell described for ~6 hr. at 120° ± 10° under nitrogen. With iodobenzene, about 2½ times the theoretical quantity of silver powder was added to absorb the iodine which was set free. Hydrogen iodide was evolved during these photolyses. Sometimes extra silver powder had to be added during the photolyses, so air could not be strictly excluded. After irradiation, the contents of the cell were filtered into a distilling flask. The cell and filter were washed with a little isopropylbenzene, and the washings were added to the mixture in the distilling flask. The mercury liberated from diphenylmercury, and the lead liberated from tetraphenyl-lead, were determined by standard methods to measure the extent of decomposition. The benzene formed during the photolysis was removed with added carbon tetrachloride by fractional distillation and estimated as *m*-dinitrobenzene. The first runnings from this distillation were usually cloudy despite efforts to maintain anhydrous conditions. Most of the isopropylbenzene was removed by fractional distillation. The column was washed down into the flask with light petroleum. Unchanged diphenylmercury was converted into phenylmercuric chloride by heating the residue from the fractional distillation under reflux with a little concentrated hydrochloric acid for 30 min. Insoluble phenylmercuric chloride was filtered off, and the mixture was washed with water and dried. Tetraphenyl-lead remaining unchanged after the photolysis crystallized almost quantitatively, part on cooling of the cell-contents, and the rest as a residue after the fractional distillation. The residual liquid was transferred quantitatively to a small distillation unit, and the distillation continued. Light petroleum, isopropylbenzene, and always some acetophenone,[1] distilled. In the iodobenzene runs the last runnings were added to the forerun of the diphenyl fraction and analyzed for iodine to give an estimate of the iodobenzene remaining unchanged after photolysis and hence of the extent of decomposition. Hydrogen iodide was evolved during the distillation procedure in the iodobenzene runs. The fraction containing the isopropyldiphenyls and 2,3-dimethyl-2,3-diphenylbutane was collected at 75—120°/0·1—0·3 mm. It was always redistilled to remove traces of forerun and terphenyls.* The mixture was analyzed for the four components by the standard infrared spectrographic method described by Hey, Pengilly, and Williams,[1] except that dimethylformamide was used as a solvent in place of nitromethane. 2,3-Dimethyl-2,3-diphenylbutane is sufficiently soluble in dimethylformamide to make unnecessary its prior separation from the mixture of isomeric isopropyldiphenyls.

Control Experiments.—(1) No detectable amount of 2,3-dimethyl-2,3-diphenylbutane was formed when isopropylbenzene was irradiated alone under the conditions of the present experiments. Very small quantities of isopropylfulvenes were formed (cf. ref. 11).

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* As judged from iodine analyses, the isopropyldiphenyls obtained by using iodobenzene as radical source consistently contained 1·1—1·3% of iododiphenyls: the latter would be expected to co-distil with isopropyldiphenyls.

[8] Pfeiffer and Truskier, *Ber.*, 1904, **37**, 1125.

[9] Setzer, Leeper, and Gilman, *J. Amer. Chem. Soc.*, 1939, **61**, 1609.

[10] Bryce-Smith, *J.*, 1956, 1603.

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

(2) 2,3-Dimethyl-2,3-diphenylbutane was recovered quantitatively after irradiation of a solution in isopropylbenzene.

(3) No detectable amount of 2,3-dimethyl-2,3-diphenylbutane was formed when a solution of iodine in isopropylbenzene was irradiated, although a reaction to give a high-boiling oil did take place.

(4) 2,3-Dimethyl-2,3-diphenylbutane was recovered nearly quantitatively when irradiated in isopropylbenzene containing iodine. Some was probably retained in the oil mentioned in paragraph (3).

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