Oxygen Effects in the Photolysis of 4-Iodobiphenyl in Benzene

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THE photolysis of iodoaromatic compounds in benzene, under controlled conditions, was previously shown to have general utility for the synthesis of biaryls and substituted biaryls.[1] The free-radical nature of these reactions is supported by several lines of evidence, and especially by the isomer distribution ratios found in the photolysis of iodobenzene in selected aromatic solvents.[1,2]

We now report that in the photolysis of dilute solutions of 4-iodobiphenyl in benzene, using a source of ultraviolet irradiation as previously described,[1] oxygen exerts a marked influence on the product distribution. With more efficient removal of oxygen, by pump–freeze–thaw cycles, the yields of the hydrogen transfer product (*i.e.*, biphenyl in the case of 4-iodobiphenyl) increase at the expense of the arylation product (terphenyl). The increasing ratios of biphenyl:terphenyl, determined by gas chromatography, are shown in the Table. The average for the degassed solutions was 0·50, as against 0·11 for the solutions which were not degassed. Similar results, clearly showing the oxygen effect on the biphenyl:terphenyl ratio, were obtained with solutions which were saturated with pure oxygen rather than with air (*cf.* Table 1, footnote *e*).

The results of the present study complement those of Eliel and his co-workers[3] on the thermal decomposition of benzoyl peroxides in benzene. The explanation suggested by these authors for the improved yields of the phenylation product, when oxygen was present, involved removal of hydrogen from the intermediate phenylcyclohexadienyl radicals. As the latter were thus removed, their dimerizations and disproportionations to form other products became less important.

In the thermal decompositions of *p*-chlorobenzoyl peroxide and *p*-methoxybenzoyl peroxide, in benzene, chlorobenzene and anisole were found as products, in unstated, presumably low yields.[4] These reduction products very likely arise by hydrogen transfer from the intermediate phenylcyclohexadienyl radicals to the aryl radicals. With depletion of oxygen, it may be predicted that the yields of hydrogen-transfer products would increase in the cases of the above peroxides, and also in the thermal decomposition of benzoyl peroxide in benzene.

In the present study, small amounts of 4-hydroxybiphenyl were found in the reaction mixtures in which no attempt was made to deoxygenate the solutions (*cf.* phenol formation[3]); and if the solutions were kept saturated with oxygen during the photolyses, the yield of 4-hydroxybiphenyl, determined by gas chromatography, was increased to 26%. Thus, a second effect of oxygen in these reactions is to trap the aryl radicals, yielding oxygenated products.

Effects of degassing on the biphenyl:terphenyl ratio in the photolysis of 4-iodobiphenyl in benzene

Run	% Photolysis	Biphenyl Ar–H	*p*-Terphenyl Ar–C_6H_5	4-Iodobiphenyl Ar–I	Product Balance	Biphenyl/ Terphenyl
1	35·5	3·1	26·2	64·7	94·0	0·12
2	39·4	3·1	28·8	62·2	94·1	0·11
3	28·1	4·2	29·3	64·6	98·1	0·14
4	35·7	2·6	26·5	66·7	95·8	0·10
5	97·5	6·3	89·8	3·6	99·7	0·07
6	44·0	13·9	33·8	48·9	96·6	0·41
7	31·4	13·1	26·9	58·5	98·5	0·49
8	96·4	32·8	62·0	1·4	96·2	0·53
9	43·3	13·6	24·7	56·4	94·7	0·55
10	31·2	10·0	19·8	62·7	92·5	0·51

[a] The extent of photolysis was ascertained and controlled by measuring the iodine release.

[b] Gas chromatography was carried out in $\frac{1}{8}$-inch diameter columns, five feet in length, on 5% SE-30 on Chromosorb W, using an Aerograph "HY-Fl" chromatograph with hydrogen flame detector and an integrating recorder.

[c] Runs 1—5 were made with ordinary reagent-grade benzene, from a gallon bottle which had been opened and used for these studies in the usual manner. Runs 6—10 were made with the same stock solutions, but after subjecting them to four to five freeze–thaw–pump cycles.

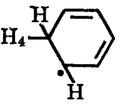
[d] Runs 1, 3, 5, 6, 7 and 8 were made with Mrs. Heidi B. Lewis. Runs 2, 4, 9 and 10 were made independently by R. K. S.

[e] To assure that *oxygen* was the cause for the variations in ratios of biphenyl to terphenyl, experiments were made in which the stock solution was saturated with pure oxygen, rather than with air. The ratios found in two experiments were: *degassed,* 0·43 and 0·39; *not degassed,* 0·04 and 0·04, in good accord with the values shown above.

The decreased ratios of biphenyl: terphenyl in the presence of oxygen, in the photolysis of 4-iodobiphenyl, may be explained in terms of the ability of oxygen to interfere with hydrogen-transfer processes 3 and 5, in the scheme below.

The reversibility of the photolytic step is known from experiments with radioactive iodine in the 2-iodobiphenyl system.[1] However, the suggested route to 4-hydroxybiphenyl *via* the biphenylyl hydroperoxide is speculative at this time.

(1) $C_6H_5\text{–}C_6H_4I \rightleftharpoons C_6H_5\text{–}C_6H_4^{\bullet} + I^{\bullet}\ (\tfrac{1}{2}\,I_2)$

(2) $C_6H_6 + C_6H_5\text{–}C_6H_4^{\bullet} \rightarrow C_6H_5\text{—}C_6H_4$  (A)

(3) $C_6H_5\text{–}C_6H_4^{\bullet} + (A) \rightarrow C_6H_5\text{–}C_6H_5 + C_6H_5\text{–}C_6H_4\text{–}C_6H_5$

(4) $(A) + \tfrac{1}{2}\,I_2 \rightarrow C_6H_5\text{–}C_6H_4\text{–}C_6H_5 + HI$

(5) $C_6H_5\text{–}C_6H_4^{\bullet} + HI \rightarrow C_6H_5\text{–}C_6H_5 + I^{\bullet}$

(6) $2\,I^{\bullet} \rightleftharpoons I^{\bullet}$

(7) $(A) + O_2 \rightarrow C_6H_5\text{–}C_6H_4\text{–}C_6H_5 + HO_2^{\bullet}$

(8) $C_6H_5\text{–}C_6H_4^{\bullet} + O_2 \rightarrow C_6H_5\text{–}C_6H_4\text{–}OO^{\bullet}$

(9) $C_6H_5\text{–}C_6H_4\text{–}OO^{\bullet} + HI \rightarrow C_6H_5\text{–}C_6H_4\text{–}OOH \rightarrow C_6H_5\text{–}C_6H_4\text{–}OH$

(*Received, January 20th,* 1966; *Com.* 040.)

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[1] W. Wolf and N. Kharasch, *J. Org. Chem.*, 1965, **30**, 2493.

[2] N. Kharasch and P. G. Naylor, unpublished work. See also footnote 19 in Reference 1 above.

[3] E. L. Eliel and M. Eberhardt, *J. Org. Chem.* 1962, **27**, 2289.

[4] E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Amer. Chem. Soc.* 1960, **82**, 2936.