Thermal Decomposition of Dibenziodolium Halides. Evidence for a Homolytic Pathway[1]

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The thermal decomposition of dibenziodolium iodides, such as **1**/I;[*1] is an efficient way of preparing 2,2′-diiodobiphenyls.[2,3] Recently, Heaney and Lees[4] reported that the thermal decomposition of dibenziodolium chloride (**1**/Cl) gave 2-chloro-2′-iodobiphenyl as the sole product. We obtained, however, conflicting results which led us to examine a series of dibenziodolium halides (**1**) in details. We here present our findings which are in accord with a radical mechanism.

Contrary to the former report by Heaney and Lees[4] the decomposition of **1**/Cl[5] at 295°C was found to produce a mixture of five halogenobiphenyls as analysed by gas chromatography using XE-60 silicone gum rubber on Chromosorb W column. They were 2-chloro-, 2,2′-dichloro-, 2-iodo-, 2-chloro-2′-iodo-, and 2,2′-diiodobiphenyls (in the order of the retention time), among which three dihalogenobiphenyls constituted major portions (Table 1). The decomposition of bromide **1**/Br occurring at 290°C again afforded five halogenobiphenyls as shown in Table 1.

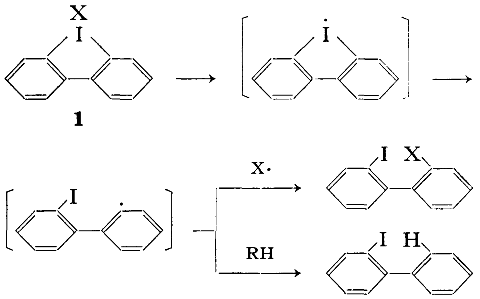
Iodide **1**/I decomposed at a lower temperature of 210°C producing 98% of 2,2′-diiodobiphenyl and 2% of 2-iodobiphenyl, the ratio of which varied markedly when the reaction was performed in solvents. For example, 2-iodo- and 2,2′-diiodobiphenyls were formed in a ratio of 1 : 2 when **1**/I was heated in triethylene glycol at 240—245°C. A small amount of biphenyl was also produced. The decomposition of **1**/Cl and **1**/Br in the same solvent gave 2-iodobiphenyl even in higher yields, 77 and 60% respectively.

TABLE 1. DIHALOGENOBIPHENYLS FROM DIBENZIODOLIUM HALIDES (**1**)[a]

X	Temp. °C	Product ratio, % 2,2′-Di-X	2-X-2′-I	2,2′-Di-I	Total biphenyl yield, %
Cl	295	4	74	22	55[b]
Br	290	10	76	14	72[c]
I	210		98		84[d]

a) Reactions were carried out for 30 min in nitrogen.
b, c, d) In addition, small amounts of 2-chloro-,[b) -bromo-,[c] and -iodobiphenyls[b,c,d] were detected.

Need for high temperatures and the formation of disproportionation and hydrogen transfer products suggest that these decomposition reactions are best interpreted as a radical mechanism. Increasing temperatures for decomposition as going from **1**/I to **1**/Cl seem to reflect increasing bond energies of halogen-iodine bondings. The main route of the reaction leading to 2-halogeno-2′-iodobiphenyl as well as 2-iodobiphenyl is explained in the following way.



To account for the formation of dichloro-, dibromo-, and diiodobiphenyls one must postulate the cleavage of both of the carbon-iodine bonds as a minor process.[6,7] Such a cleavage was further indicated by the reaction of **1**/I in dimethyl acetylenedicarboxylate, which afforded the expected adduct, dimethyl 9,10-phenanthrenedicarboxylate, mp 127—128°C,[8] as one of the products.

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[1] Photo-Aryl Coupling and Related Reactions. V.

[*1] Abbreviation of compound **1** where X=I.

[2] D. F. Banks, *Chem. Rev.*, **66**, 243 (1966).

[3] H. Irving and R. W. Reid, *J. Chem. Soc.*, **1960**, 2078; R. B. Sandin, *J. Org. Chem.*, **34**, 456 (1969) and references cited therein.

[4] H. Heaney and P. Lees, *Tetrahedron* **24**, 3717 (1968).

[5] J. Collette, D. Mcgreer, R. Crawford, F. Chubb, and R. B. Sandin, *J. Amer. Chem. Soc.*, **78**, 3819 (1956).

[6] Existence of a biphenylyl biradical was implied by the electron impact of biphenylene [L. Friedman and D. F. Lindon, *J. Amer. Chem. Soc.*, **90**, 2324 (1968)].

[7] No biphenylene formation was observed possibly due to rapid and efficient trapping of the intermediate with halogen atoms.

[8] A. Jeanes and R. Adams, *J. Amer. Chem. Soc.*, **59**, 2608 (1937).