

Thermal Decomposition of Dibenziodolium Halides. Evidence for a Homolytic Pathway¹⁾

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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 Lees⁴⁾ 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 Lees⁴⁾ the decomposition of **1**/Cl⁵⁾ 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.

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.

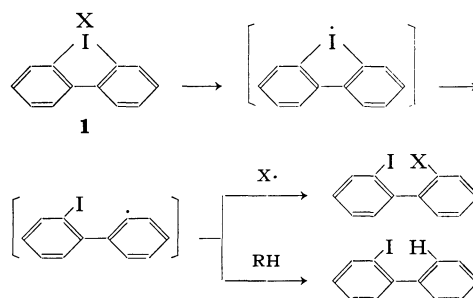


TABLE 1. DIHALOGENOBIPHENYLS FROM DIBENZIODO-
LIUM HALIDES (**1**)^{a)}

X	Temp. °C	Product ratio, %			Total biphenyl yield, %
		2,2'- Di-X	2-X- 2'-I	2,2'- Di-I	
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.

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).

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.

6) Existence of a biphenyl 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).