

Thermal Decomposition of Dibenz[*b,d*]iodolium and 10*H*-Dibenz[*b,e*]-iodinium Halides. Evidence for a Homolytic Pathway from Halogen Scrambling, Hydrogen Transfer, and Trapping¹

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The thermal decomposition of dibenz[*b,d*]iodolium halides and 10*H*-dibenz[*b,e*]iodinium halides has been examined. Observation of products of halogen scrambling and hydrogen transfer suggested a radical mechanism involving 2'-iodobiphenyl-2-yl and 2-(2-iodobenzyl)phenyl radicals. Results of trapping experiments with an acetylenic ester suggested the involvement of a biphenyl diradical.

DIARYLIODONIUM salts undergo ready displacement reactions with a number of organic and inorganic bases and with reducing agents:²⁻⁸



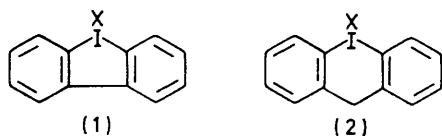
Mechanistic studies have revealed two reaction types: a nucleophilic displacement and a radical-pair process involving an electron transfer.⁹ The catalytic action of metal salts has been explained in terms of a radical mechanism or complex formation.^{3,5,6,10}

Diaryliodonium salts decompose on heating or on u.v. irradiation:¹¹



The reaction has been interpreted in various ways, in terms of both homolytic¹¹ and heterolytic mechanisms.^{11,12} As a support for the radical mechanism, the arylation of metals and pyridine has been quoted.¹¹ Other workers have been suspicious of this since they failed to obtain the expected radical coupling products, such as biaryls.¹¹

No unequivocal evidence as to the nature of the self-decomposition mechanism can be derived from studies of substituted diaryliodonium salts, since the fate of halogen atoms cannot be traced (fragmentation occurs). We have studied the cyclic compounds (1) and (2), and now present evidence for the occurrence of a deep-seated homolytic cleavage process.



Thermal decomposition of the iodide (1; X = I) is known to produce 2,2'-di-iodobiphenyl in good yield.^{11,13}

¹ Preliminary account, T. Sato, S. Shimada, K. Shimizu, and K. Hata, *Bull. Chem. Soc. Japan*, 1970, **43**, 1918.

² D. F. Banks, *Chem. Rev.*, 1966, **66**, 243.

³ F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Amer. Chem. Soc.*, 1953, **75**, 2708.

⁴ F. M. Beringer and E. J. Geering, *J. Amer. Chem. Soc.*, 1955, **77**, 3202.

⁵ F. M. Beringer, E. J. Geering, I. Kuntz, and M. Mausner, *J. Phys. Chem.*, 1956, **60**, 141.

⁶ M. C. Caserio, D. L. Glusker, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1959, **81**, 336.

⁷ D. J. Le Count, *J. Chem. Soc.*, 1967, 1298.

⁸ E. K. Grubbs, R. J. Milligan, and M. H. Goodrow, *J. Org. Chem.*, 1971, **36**, 1780.

⁹ F. M. Beringer and R. A. Falk, *J. Chem. Soc.*, 1964, 4442.

The reaction is of synthetic value.^{1,14,15} Halides (1) were prepared from the hydrogen sulphate (1; X = HSO₄) by an ion-exchange reaction.^{16,17} A vigorous exothermic reaction occurred when these were heated in the solid state under nitrogen.

The iodide (1; X = I) decomposed at 210° giving 2,2'-di-iodobiphenyl (98%) and 2-iodobiphenyl (2%). When the decomposition was carried out in a hydrogen donor solvent the yield of the latter product was increased. For example, decomposition in triethylene glycol at 240–245° gave 2-iodo- and 2,2'-di-iodobiphenyls in the ratio of 1:2, together with a small amount of biphenyl (Tables 1 and 2). The solid-state decomposition of the bromide (1; X = Br) and the chloride (1; X = Cl) occurred at higher temperatures (290 and 295°, respectively). The products, estimated by g.l.c., are shown in Table 1.

Previous reports¹⁷ on the decomposition of the halides (1) gave only brief mention of yield and products. We have found that the thermolysis gives a complex mixture of biphenyls. The decomposition of (1; X = Br) also produced an appreciable amount of halogen-scrambling products. The decomposition of (1; X = Cl) and (1; X = Br) in triethylene glycol gave 77 and 60% yields, respectively, of 2-iodobiphenyl (Table 2).

In contrast to the purely ionic fluoroborates, the I-X bond in iodonium halides has been shown to possess some covalent character, as indicated by X-ray data.^{2,18} Increasing temperatures for decomposition in going from the iodide to the bromide and to the chloride parallel the increasing energies of the I-X bond. This observation, coupled with the formation of hydrogen-transfer products, leads one to postulate initial cleavage of the I-X bond.

¹⁰ F. M. Beringer and P. Bodlaender, *J. Org. Chem.*, 1969, **34**, 1981.

¹¹ H. Irving and R. W. Reid, *J. Chem. Soc.*, 1960, 2078 and earlier papers cited.

¹² Y. Yamada and M. Okawara, *Bull. Chem. Soc. Japan*, 1972, **45**, 2515.

¹³ R. B. Sandin, *J. Org. Chem.*, 1969, **34**, 456.

¹⁴ T. Sato, K. Uno, M. Kainosho, *J.C.S. Chem. Comm.*, 1972, 579.

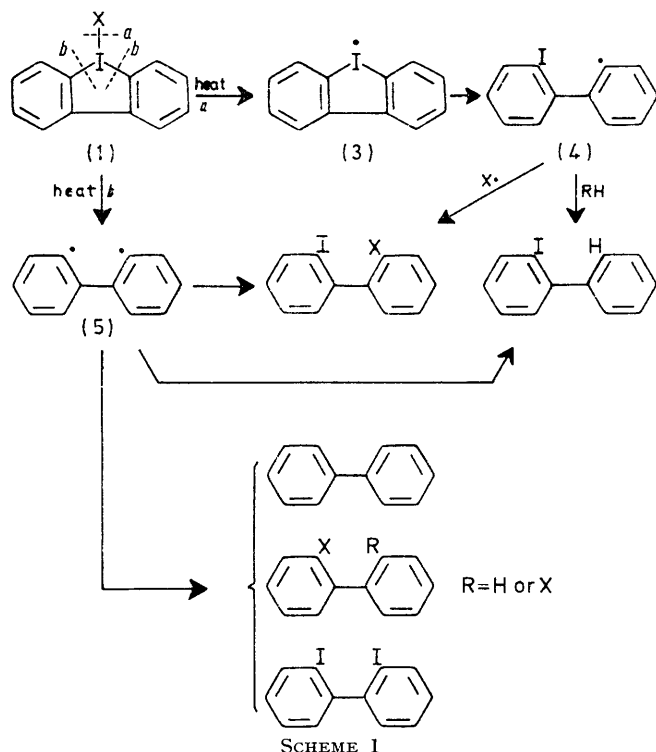
¹⁵ T. Sato and K. Uno, *J.C.S. Perkin I*, 1973, 895.

¹⁶ J. Collette, D. McGreer, R. Crawford, F. Chubb, and R. B. Sandin, *J. Amer. Chem. Soc.*, 1956, **78**, 3819.

¹⁷ H. Heaney and P. Lees, *Tetrahedron*, 1968, **24**, 3717; see also L. Mascarelli and D. Gatti, *Gazzetta*, 1929, **59**, 867.

¹⁸ F. M. Beringer and S. Messing, *J. Org. Chem.*, 1972, **37**, 2484.

Scheme 1 shows reaction steps leading to 2-halogeno-2'-iodo- and 2,2'-di-iodobiphenyls. The key intermediate is the 2'-iodobiphenyl-2-yl radical (4), formed *via* the radical (3) following scission *a*. Formation of 2-iodobiphenyl in low yield can be explained by hydrogen abstraction from other biphenyl molecules. The formation of biphenyl, 2'-chloro- and 2-bromobiphenyls, and 2,2'-dichloro- and 2,2'-dibromobiphenyls suggests that the cleavage of the two C-I bonds (scission *b*) to give the biphenyl diradical (5) is occurring. A statistical consideration of the product ratios favours scission *a* as the major process and explains the high yields of 2-halogeno-2'-iodobiphenyls. Product distribution is also determined by the reactivity of halogen atoms towards radical intermediates such as (4) or (5). A low yield of chloro-compounds implies that loss of halogen occurs at higher temperatures. One can estimate that the maximum contribution of the intermediate (5) (*i.e.* path *b*) is about 20% of the total reactions leading to



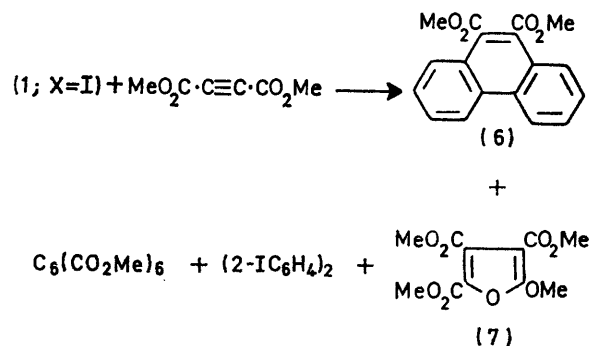
biphenyls, since the yield of 2,2'-di-iodobiphenyl from (1; X = Cl) is 22%.

Whether the diradical (5) is involved as a transient species can not easily be determined. One of the expected products, biphenylene, could not be found,* but this does not prove the non-existence of (5) since rapid recombination with halogens in a 'cage' could occur preferentially. Further, biphenylene, if formed, may be cleaved by halogens.

To prove the involvement of the radical (5), trapping

* The formation of (5) by electron impact on biphenylene has been claimed (L. Friedman and D. F. Linden, *J. Amer. Chem. Soc.*, 1968, **90**, 2324). See also J. M. Gaidis, *J. Org. Chem.*, 1970, **35**, 2811.

with dimethyl acetylenedicarboxylate was attempted. When compound (1; X = I) was decomposed in the presence of the acetylenic ester at 210–230° four products were formed (Scheme 2). In addition to 2,2'-di-iodobiphenyl, dimethyl phenanthrene-9,10-dicarboxylate (6) was isolated in 5.9% yield. The adduct (6) was not formed in control experiments in which

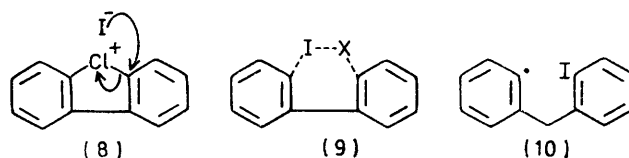


2,2'-di-iodobiphenyl and the acetylenic ester were heated under similar conditions. The two other products were the furan derivative (7) and hexamethyl benzenehexacarboxylate which were formed by dimerisation of the acetylenic ester followed by oxidation in air and loss of CO, and by trimerisation, respectively.

Table 2 summarises the results of decomposition of compound (1; X = I) in various solvents. Hydrogen transfer products were formed in hydrogen donor solvents and chlorine abstraction occurred in hexachloroethane. These are explained in terms of the intermediacy of the radical (4).

Re-examination of the thermal decomposition of 4-methoxydiphenyliodonium iodide showed that the three possible radical recombination products, biphenyl and 4-methoxy- and 4,4'-dimethoxybiphenyls, were obtained, though in low yields. The major products were iodobenzene and 4-iodoanisole, as expected.

Compound (8),¹⁹ isomeric with (1; X = Cl), was also examined. Decomposition at 120° gave 2-chloro-2'-iodobiphenyl selectively. If the decomposition of com-



pounds (1) proceeds through an intermediate such as (9), then (1; X = Cl) and (8) should both give similar products. As this is not the case, the intermediate (9) is unlikely.

The thermal decomposition of the higher homologues (2) was also examined. Table 3 summarises the results. Both halogen scrambling and hydrogen transfer occur

¹⁹ R. B. Sandin and A. S. Hey, *J. Amer. Chem. Soc.*, 1952, **74**, 274.

with (2; X = Cl). Decomposition of (2; X = I) is a good route to bis-(2-iodophenyl)methane.¹⁵

The cleavage of (2) must be closely related to that of compounds (1). Product distribution, however, suggests that the major route involves the iodo-radical (10). Products derived from a hypothetical diphenylmethane diradical analogous to (5) are negligible. This may indicate the importance of biphenyl conjugation for the transient formation of (5).

EXPERIMENTAL

Dibenz[b,d]iodolium Halides (1).—2-Iodosylbiphenyl was obtained by oxidation of 2-iodobiphenyl with peracetic acid in acetic anhydride. To the product was added concentrated sulphuric acid below 10° to give dibenz[b,d]iodolium hydrogen sulphate (1; X = HSO₄), which was converted into the corresponding halides (1; X = Cl, Br, or I) by anion exchange reactions with sodium chloride, sodium bromide, and potassium iodide; (1; X = Cl) had m.p. 248—253° (decomp.)¹⁶ (1; X = Br), m.p. 237—242° (decomp.),¹⁶ and (1; X = I), m.p. 200° (decomp.).¹¹

Thermal Decomposition of the Iodolium Halides (1).—The reactions were carried out in nitrogen for 30 min at the following temperatures: X = Cl, 295°; X = Br, 290°; X = I, 200°. The mixture was analysed by g.l.c. (1 m XE-60 silicone gum-rubber on Chromosorb W). Materials were identified by comparison of retention times with those of authentic materials. Representative results are shown in Table 1.

TABLE 1

Halogenobiphenyls from dibenz[b,d]iodolium halides (1)

X	Temp. (°C)	Proportions (%) of product biphenyls					Total biphenyls (%)
		2-X	2-I	2,2'-X ₂	2,2'-I	2,2'-I ₂	
Cl	295	ca. 1	ca. 1	4	74	22	55
Br	290	ca. 1	ca. 1	10	76	14	72
I	210		2			98	84

TABLE 2

Decomposition of dibenz[b,d]iodolium halides (1) in solvents

Solvent	X	Temp. (°C)	Proportions (%) of product biphenyls				Total biphenyls (%)
			Ph ₂	2-I	2,2'-I	2,2'-I ₂	
TEG ^a	Cl	220—230	1	77	21	1	76
	Br	225—240	1	60	38	1	94
	I	240—245	1	35	64		100
C ₉ H ₅ N ^b	Cl	200—220		21	38	41	29
	Br	210—220		28	22	50	18
	I	210		12		88	40
Me ₂ SO	I	145—160		30		70	46
o-Cl ₂ C ₆ H ₄	I	185—200		3		97	94
PhNO ₂	I	220		2		98	100
(CCl ₃) ₂	I	220—230		1	7 ^b	92	100

^a Triethylene glycol. ^b Quinoline. ^c A chlorine atom comes from hexachlorethane solvent.

Reactions carried out in various solvents are summarised in Table 2.

Dibenzochlorolium Iodide (8) and its Thermal Decomposition.—2-Amino-2'-chlorobiphenyl hydrochloride was

²⁰ E. H. Huntress, T. E. Lesslie, and J. Bornstein, *Org. Synth.*, 1963, **4**, 329.

²¹ A. Jeanes and R. Adams, *J. Amer. Chem. Soc.*, 1937, **59**, 2608.

diazotised in the usual manner and was converted into dibenzochlorolium chloride by warming, which, on treatment with potassium iodide solution, gave compound (8),¹⁹ yellow needles, m.p. 113—115°.

The decomposition was carried out at 117—120° for 1 h and the products were examined by g.l.c. 2-Chloro-2'-iodobiphenyl (55.2%) and 2,2'-di-iodobiphenyl (1.4%) were identified. A previous report also indicated the preferential formation of 2-chloro-2'-iodobiphenyl.¹⁷

Reaction of the Iodolium Iodide (1; X = I) with Dimethyl Acetylenedicarboxylate.—A mixture of the iodide (1.1 g, 2.7 mmol) and the ester (3.5 g, 25 mmol)²⁰ was heated at 210—230° for 1 h, then passed through an alumina column (Woelm neutral; activity III), with n-hexane containing increasing amounts of benzene as eluant. Four components were successively eluted as follows: 2,2'-di-iodobiphenyl (100% hexane) (603 mg), dimethyl phenanthrene-9,10-dicarboxylate (6) (9:1 hexane-benzene) (46 mg), trimethyl 2-methoxyfuran-3,4,5-tricarboxylate (7) (1:1 solvent mixture) (111 mg), and hexamethyl benzenehexacarboxylate (1:2 mixture) (8.3 mg).

Compound (6) was obtained as plates (5.9%), m.p. 127—128°²¹ (Found: C, 73.7; H, 4.8. Calc. for C₁₈H₁₄O₄: C, 73.45; H, 4.8%). Compound (7) was obtained as needles, m.p. 116—116.5°²² (from hexane-benzene); ν_{\max} (KBr) 1750, 1725, 1710, 1600, 1580, 1150, 1100, and 1060 cm⁻¹; δ (CDCl₃) 3.78, 3.83, 3.93, and 4.23 (all s); m/e 272 (M^+), 241, 229, 198, 185, 157, 140, 111, 99, and 80 (Found: C, 48.2; H, 4.35. Calc. for C₁₁H₁₂O₈: C, 48.55; H, 4.4%). The benzene hexaester was isolated as needles, m.p. 183—185°²³ (from hexane-benzene); ν_{\max} (KBr) 1740, 1360, and 1230 cm⁻¹; δ (CDCl₃) 3.87 (s); m/e 426 (M^+) (Found: C, 51.25; H, 4.95. Calc. for C₁₈H₁₈O₁₂: C, 50.7; H, 4.25%).

No phenanthrene formation was noticed in a control experiment in which 2,2'-di-iodobiphenyl and dimethyl acetylenedicarboxylate were heated at 210—230°.

Thermal Decomposition of 4-Methoxyphenylphenyliodonium Iodide.—The iodide²⁴ was decomposed at 160°. G.l.c. showed the products to be iodobenzene (50%) and 4-iodoanisole (50%), together with small amounts of the three possible biphenyls.

Thermal Decomposition of the Dibenz[b,e]iodinium Halides (2).—The preparation of the chloride and iodide has been described earlier,^{15,16} as has the thermal decomposition of the iodide.¹⁵ The chloride (0.70 g, 2.12 mmol) was heated at 245—255° for 30 min. The results are shown in Table 3.

TABLE 3

Decomposition of 10H-dibenz[b,e]iodinium halides (2)^a

X	Temp. (°C)	Proportions (%) of product diphenylmethanes					Ph ₂ CH ₂
		2-Cl	2-I	2-Cl, 2'-I	2,2'-I ₂	6	
Cl	245—255	1		93		6	Trace
I	190—200		Trace			56 ^b	Trace

^a Reaction time 30 min. ^b In a preparative study, the diiodide was obtained in 88% yield (ref. 15).

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²² E. Winterfeldt and G. Giesler, *Angew. Chem. Internat. Edn.*, 1966, **5**, 579; C. F. Heubner, E. Donoghue, L. Foriman, F. A. Stuber, N. Danieli, and E. Wenkert, *Tetrahedron Letters*, 1966, 1185.

²³ H. v. Pechman, *Ber.*, 1898, **31**, 502.

²⁴ F. M. Beringer, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Amer. Chem. Soc.*, 1953, **75**, 2705.