

Photochemistry of Diaryliodonium Salts

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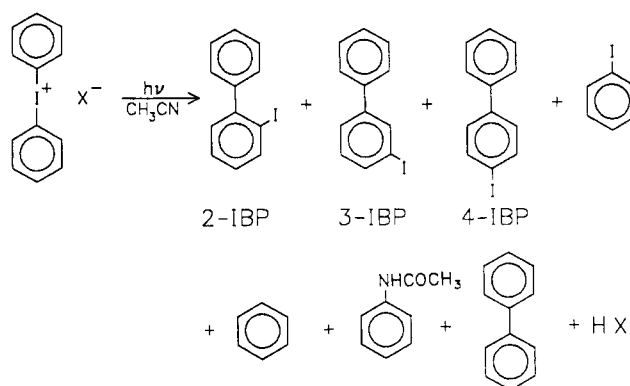
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The photochemistry of diphenyl- and bis(4-methylphenyl)iodonium salts was investigated by product analysis, measurement of acid, and determination of the consumption of the iodonium salts. The primary products formed upon direct and triplet-sensitized irradiation of diphenyliodonium salts are iodobenzene, 2-, 3-, and 4-iodobiphenyl, acetanilide, benzene, and acid. Similarly, iodotoluene, iodobitolyls, 4-methylacetanilide, toluene, and acid are formed from photolysis of bis(4-methylphenyl)iodonium salts. The photolysis products are formed by heterolysis of the diaryliodonium salt to phenyl cation and iodobenzene and also by homolysis to phenyl radical and iodobenzene radical cation. Direct photolysis favors product formation by the heterolytic cleavage pathway, whereas triplet sensitization gives more products from homolytic cleavage. Interconversion between phenyl cation pair and the phenyl radical pair can occur by an electron transfer. Sensitized photodecomposition of the iodonium salt by anthracene gives iodoarene and arylated anthracenes by an electron-transfer mechanism. Electron-transfer quenching and triplet quenching by the iodonium salt are competitive reactions for some sensitizers. The similarities and differences between diaryliodonium and triarylsulfonium photochemistry will be described.

Introduction

Onium salts have found wide application as photoinitiators for acid-catalyzed reactions in polymeric systems.¹ Acid-catalyzed cross-linking of epoxides, deprotection of functionalized polystyrenes, and depolymerization of polyphthalaldehydes can be initiated by irradiation of suitable onium salts.^{2,3} Diaryliodonium and triarylsulfonium salts are most commonly used because they have good thermal stability yet efficiently generate acid upon photolysis. Recently, we have reported on the photochemistry of arylsulfonium salts.⁴ We discovered that the major product formed upon direct irradiation was 2-(phenylthio)biphenyl, along with smaller quantities of 3- and 4-(phenylthio)biphenyl, formed via an in-cage recombination reaction, in addition to diphenyl sulfide, which was previously observed.^{1,5,7} In contrast, no (phenylthio)biphenyl isomers were detected in triplet-sensitized irradiations, and the products were exclusively diphenyl sulfide, benzene, and acid.^{4b} Aryliodonium salts have been reported to have photochemical reactivity similar to that of the arylsulfonium salts.⁵⁻⁷ A recent study of the photochemistry of diphenyliodonium hexafluorophosphate found only two recombination products, 2- and 4-iodobiphenyl, the latter

Scheme I. Products from Irradiation of Diphenyliodonium Salts



being the predominant isomer.⁸ This study found that these recombination products were also formed upon triplet-sensitized excitation. These differences between the photochemistry of sulfonium and iodonium salts prompted us to further investigate some aspects of aryl-iodonium photochemistry. We report here a study on the direct and triplet-sensitized photochemistry and photoinduced electron-transfer reactions of diphenyliodonium and bis(4-methylphenyl)iodonium salts.

Results

Direct Photolysis. Solutions of diphenyliodonium triflate, 0.01 M in argon-purged acetonitrile, were irradiated ($\lambda = 254$ nm) in a Rayonet reactor. The volatile products (Table I, entry 1) were iodobenzene, 2-, 3-, and 4-iodobiphenyl, benzene, acetanilide, and biphenyl. In addition to these products, acid was formed (5.5×10^{-4} M), along with trace quantities of *o*- and *p*-terphenyl (Scheme I). The total of the iodine-containing photoproducts was 4.93×10^{-4} M. The consumption of the iodonium salt was followed spectrophotometrically, via the complex of the iodonium cation and cobalt thiocyanate.⁹ Under these conditions, it was found that 5.33×10^{-4} M of diphenyliodonium triflate was consumed, in excellent quantitative agreement with the formation of acid and volatile iodine-containing photoproducts. Studies on the concentration of photoproducts versus time of irradiation showed that iodobenzene and the iodobiphenyls were primary

(1) (a) Crivello, J. V. *UV Curing: Science and Technology*; Pappas, S. P., Ed.; Technology Marketing Corp.: Stamford, CT, 1978; p 23. (b) Crivello, J. V. *CHEMTECH* 1980, 10, 624. (c) Crivello, J. V. *Polym. Eng. Sci.* 1983, 23, 953. (d) Crivello, J. V. *Adv. Polym. Sci.* 1984, 62, 1. (e) Crivello, J. V. *Makromol. Chem., Macromol. Symp.* 1988, 13/14, 145. (f) Pappas, S. P. *Radiat. Curing* 1981, 8, 28. (g) Pappas, S. P. *Prog. Org. Coat.* 1985, 13, 35. (h) Pappas, S. P. *J. Imaging Technol.* 1985, 11, 146. (i) Yagci, Y.; Schabel, W. R. *Makromol. Chem., Macromol. Symp.* 1988, 13/14, 161.

(2) Crivello, J. V.; Lam, J. H. W.; Volante, N. C. *J. Radiat. Curing* 1977, 4, 2.

(3) (a) Ito, H.; Willson, C. G. *Polym. Eng. Sci.* 1983, 23, 1012. (b) Ito, H.; Willson, C. G. *Polymers in Electronics*; Davidson, T., Ed.; ACS Symposium Series No. 242; American Chemical Society: Washington, DC, 1984; p 11.

(4) (a) Dektar, J. L.; Hacker, N. P. *J. Chem. Soc., Chem. Commun.* 1987, 1591. (b) Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* 1988, 53, 1833. (c) Hacker, N. P.; Dektar, J. L. *Polym. Prepr.* 1988, 29, 524. (d) Dektar, J. L.; Hacker, N. P. *J. Photochem. Photobiol. A* 1989, 46, 233.

(5) (a) Knapzyck, J. W.; McEwen, W. E. *J. Am. Chem. Soc.* 1969, 91, 145. (b) Knapzyck, J. W.; McEwen, W. E. *J. Org. Chem.* 1970, 35, 2539. (c) Knapzyck, J. W.; Lubinkowski, J. J.; McEwen, W. E. *Tetrahedron Lett.* 1971, 3739.

(6) (a) Crivello, J.; Lam, J. H. W. *Macromolecules* 1977, 10, 1307. (b) Crivello, J.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* 1978, 16, 2441. (c) Crivello, J.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* 1979, 17, 3845. (d) Crivello, J.; Lee, J. L. *Polym. Bull.* 1986, 16, 243.

(7) (a) Pappas, S. P.; Jilek, J. H. *Photogr. Sci. Eng.* 1979, 23, 140. (b) Pappas, S. P.; Pappas, B. C.; Gatechair, L. R.; Schnabel, W. R. *J. Polym. Sci., Polym. Chem. Ed.* 1984, 22, 69. (c) Pappas, S. P.; Gatechair, L. R.; Jilek, J. H. *J. Polym. Sci., Polym. Chem. Ed.* 1984, 22, 77. (d) Pappas, S. P.; Pappas, B. C.; Gatechair, L. R.; Jilek, J. H.; Schnabel, W. *Polym. Photochem.* 1984, 5, 1.

(8) Devoe, R. J.; Sahyun, M. R. V.; Serpone, N.; Sharma, D. K. *Can. J. Chem.* 1987, 65, 2342.

(9) Potratz, H. A.; Rosen, J. M. *Anal. Chem.* 1949, 21, 1276.

Table I. Product Distributions upon Irradiation of Diphenyliodonium Salts, in Argon-Purged Solution (Concentration $\times 10^{-4}$ M)

	conditions	PhI	Ph ₂	2-IBP	3-IBP	4-IBP
1	CH ₃ CN, 254 nm, 1-Tf	3.76	0.34	0.92	0.13	0.12
2	CH ₃ CN, 254, 1-PF ₆	3.54	0.33	0.91	0.13	0.12
3	CH ₃ CN, 300 nm, 1-Tf	1.49	0.069	0.51	0.063	0.093
4	CH ₃ CN, 350 nm, 1-Tf	0.47	0.061	0.13	0.013	0.025
5	MeOH, 254 nm, 1-Tf ^a	71.4	0.37	0.37	0.034	0.060
6	MeOH, 300 nm, 1-Tf ^b	92.4	0.13	0.18	0.034	0.055
7	acetone, 254 nm, 1-Tf	3.38	0.38	0.88	0.10	0.13
8	acetone, 300 nm, 1-Tf	3.59	0.22	1.08	0.09	0.25
9	acetone, 350 nm, 1-Tf	2.06	0.17	0.33	0.021	0.095
10	25% H ₂ O in MeCN, 254 nm, 1-Cl ^c	1.96	0.061	0.42	0.056	0.061
11	25% H ₂ O in acetone, 300 nm, 1-Cl ^d	1.92	0.012	0.38	0.025	0.075
12	CH ₃ CN, 254 nm, 1-Tf, 0.02 M chlorobenzene ^e	1.65	0.34	0.31	0.042	0.040
13	CH ₃ CN, 300 nm, 1-Tf, 0.02 M chlorobenzene ^f	1.05	0.14	0.35	0.048	0.060
14	CH ₃ CN, 350 nm, 1-Tf, 0.02 M chlorobenzene ^f	0.48	0.058	0.13	0.013	0.024
15	CH ₃ CN, 350 nm, 1-Tf, anthracene ^g	7.27	0.10	0.01	h	h
16	acetone, 350 nm, 1-Tf, anthracene ^g	8.84	h	0.032	h	h
17	CH ₃ CN, 350 nm, 1-Tf, xanthone	5.71	0.04	0.36	0.03	0.02
18	CH ₃ CN, 350 nm, 1-Tf, benzophenone	5.16	0.15	0.467	h	h

^a Anisole, 0.77. ^b Anisole, 0.16. ^c Chlorobenzene, 0.253. ^d Chlorobenzene, 0.243. ^e 2-Chlorobiphenyl, 0.010. ^f 2-Chlorobiphenyl, not detected. ^g Phenylanthracenes, 2.28. ^h Not detected. ⁱ Phenylanthracenes, 2.58.

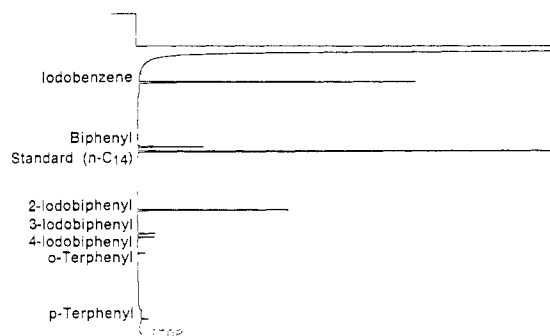


Figure 1. GLC trace of volatile products from a hexanes extract after photolysis of diphenyliodonium triflate in acetonitrile.

photoproducts and that the *o*- and *p*-terphenyls were secondary photoproducts. The designation of biphenyl as a primary or secondary photoproduct is uncertain.

These results differ from the earlier literature. The iodobiphenyls cannot be considered as trace products as reported earlier,⁷ as they form 22% of the iodine-containing products. Our results indicate that the amount of acid formed is about 1.1 times the amount of iodine-containing product formed, showing that acid formation correlates well with product formation. A prior study⁷ reported that acid was formed in 2.1-fold excess over iodobenzene and assumed that iodobenzene formation was the rate of decomposition of the iodonium salt. Additional mechanistic pathways for acid formation were postulated to explain this apparent anomaly. In our studies, while the relative amounts of iodobiphenyl to iodobenzene we found are similar to those recently reported,⁸ our identifications of 2-iodobiphenyl as the major iodobiphenyl isomer, and of the presence of 3-iodobiphenyl are different. The iodobiphenyl isomers produced by photolysis in this study were identified by capillary GLC, against standards (Figure 1). 2- and 4-iodobiphenyl standards were obtained from different commercial sources; 3-iodobiphenyl was prepared from 3-bromobiphenyl. The identity of the three iodobiphenyl isomers was confirmed by ¹H NMR, ¹³C NMR, and ultraviolet spectroscopies. All three isomers were well-resolved under the analysis conditions and eluted in the order 2-, 3-, and 4-iodobiphenyl on a cross-linked poly(methylsiloxane) column. This is the same order observed in our previous studies on triphenylsulfonium photochemistry of the isomeric (phenylthio)biphenyls.⁴ We have observed the same order of elution for the isom-

eric (phenylseleno)biphenyls from photolysis of triphenylselenonium salts and also for the isomeric phenoxybiphenyls, chlorobiphenyls, and bromobiphenyls.¹⁰ Devoe et al. report a 20:80 ratio of 2- to 4-iodobiphenyl. Our results indicate that the ratio of 2- to 3- to 4-iodobiphenyl upon irradiation of the iodonium salt in acetonitrile is 79:11:10. In comparison, the irradiation of triphenylsulfonium triflate produces 2-, 3-, and 4-(phenylthio)biphenyl in a ratio of 77:8:15.⁴ To see if an anion effect was responsible for the difference in product distribution between DeVoe's and our results, the diphenyliodonium hexafluorophosphate and the triflate salts were irradiated in acetonitrile (Table I, entries 1 and 2). No difference was found between the two salts in product distribution.

To examine the effect of a nucleophilic counterion, the photolysis of diphenyliodonium chloride (1-Cl) was conducted in 25% aqueous acetonitrile (water was necessary to solubilize the salt). The product distribution obtained is shown in Table I, entry 10. The relative amount of the escape product iodobenzene is about the same, 78%, as in the photolysis of the triflate and hexafluorophosphate salts in acetonitrile, 76%. The ratios of the isomeric recombination products is also very similar. Of the phenyl moieties that escape, 13% are trapped as chlorobenzene, relative to the other escape product, iodobenzene. Thus, it appears that chloride ion, at these concentrations, does not disturb the photochemistry previously observed and serves to trap phenyl cations.

Irradiation of diphenyliodonium triflate was also conducted in methanol (Table I, entries 5 and 6). A much greater quantity of iodobenzene is formed relative to the acetonitrile solutions, in a similar irradiation time, amounting to nearly complete photolysis of the iodonium salt. Only relatively small amounts of the recombination products are observed, along with small quantities of anisole. These results would indicate that a radical chain reaction is proceeding in this solvent, as previously reported.^{5,11} This is similar to the irradiation of the more strongly oxidizing diazonium salts in methanol, which

(10) Dektar, J. L.; Hacker, N. P., unpublished work.

(11) (a) Ledwith, A.; Al-Kass, S.; Hulme-Lowe, A. In *Cationic Polymerization and Related Processes*; Goethals, E. J., Ed.; Academic Press: New York, 1984; pp 275-287. (b) Ledwith, A.; Sherrington, D. C. In *Reactivity, Mechanism and Structure in Polymer Chemistry*; Jenkins, A. D., Ledwith, A., Eds.; Wiley: London, 1974; pp 244-309. (c) Ledwith, A. *Makromol. Chem., Suppl.* 3 1979, 348. (d) Ledwith, A. *Polymer* 1978, 1217.

Table II. Product Distributions upon Irradiation of Bis(4-methylphenyl)iodonium PF₆, Argon-Purged (Concentrations × 10⁻⁴ M)

	conditions	TolH	<i>p</i> -ITol	2,4'-BT	3,4'-BT	4,4'-BT	2-IBT	3-IBT
1	CH ₃ CN, 254 nm ^a	0.39	1.04	<i>b</i>	0.029	0.088	0.339	0.090
2	acetone, 300 nm	0.410	0.460	<i>b</i>	0.007	0.033	0.124	0.028

^a Also formed, *p*-cresol (0.13), *p*-methylacetanilide (0.47). ^b Not detected.

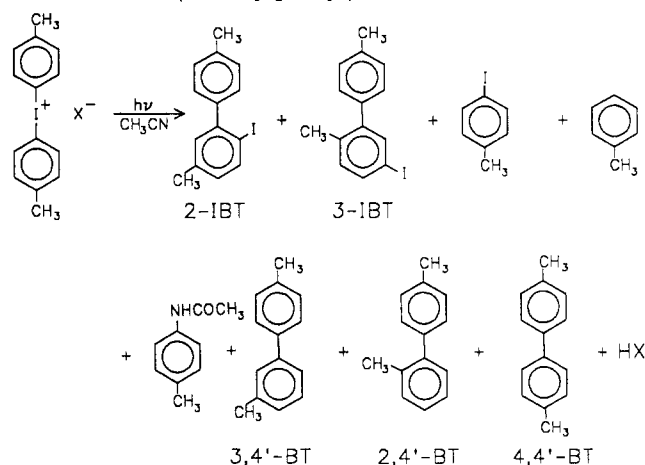
Table III. Product Quantum Yields from Irradiation of Iodonium Salt Solutions in Acetonitrile and Acetone

	conditions	total	ArI	2-IBP	3-IBP	4-IBP
1	CH ₃ CN, 248 nm, 1-Tf ^c	0.54	0.400	0.104	0.018	0.021
2	CH ₃ CN, 248 nm, 2-PF ₆ ^b	0.45	0.320	0.104	0.028	
3	acetone, 300 nm, 1-Tf ^c	0.50	0.393	0.076	0.0051	0.026
4	acetone, 300 nm, 2-PF ₆ ^d	0.42	0.314	0.086	0.019	

^a $\lambda = 248$ nm, 0.01 M iodonium salt, $\Phi(\text{benzene}) = 0.080$, $\Phi(\text{acetanilide}) = 0.312$. ^b $\lambda = 248$ nm, 0.01 M iodonium salt, $\Phi(\text{toluene}) = 0.122$. ^c Limiting Φ at $\lambda = 300$ nm from 0.000972, 0.00303, 0.00749, 0.0148, and 0.0513 M iodonium salt solutions in acetone, $k_q\tau = 994 \pm 15 \text{ M}^{-1}$, $\Phi(\text{benzene}) = 0.197$. ^d Limiting Φ at $\lambda = 300$ nm from 0.00575, 0.00797, 0.0121, and 0.0237 M iodonium salt solutions in acetone, $k_q\tau = 700 \pm 130 \text{ M}^{-1}$, $\Phi(\text{toluene}) = 0.273$.

proceeds by a photochemically initiated chain reaction, in which propagation occurs by oxidation of hydroxymethylene radicals by the diazonium salt.¹²

The irradiation of bis(4-methylphenyl)iodonium hexafluorophosphate was studied. Upon irradiation of an argon-purged 0.01 M solution in acetonitrile ($\lambda = 254$ nm), the following products were formed, in the quantities listed in Table II: toluene, *p*-cresol, *p*-iodotoluene, *p*-methylacetanilide, 2,4', 3,4', and 4,4'-bitolyl, 4',5-dimethyl-2-iodobiphenyl ("o-iodobitolyl", "2-IBT"), and 2,4'-dimethyl-5-iodobiphenyl ("m-iodobitolyl", "3-IBT"; Scheme II). Toluene, which should result from hydrogen abstraction by an intermediate 4-tolyl radical, was formed in 38% yield relative to the formation of 4-iodotoluene. This indicates that at least 38% of the photocleavage escape products are radical derived. The escape product, 4-iodotoluene, forms 71% of the total iodine-containing products, as compared to the photolysis of diphenyliodonium under the same conditions, in which iodobenzene forms 76% of the total iodine-containing products. Thus, the amount of escape products to recombination products in the two iodonium salts is roughly the same. The bis-(4-methylphenyl)iodonium PF₆ salt also shows a preference for the "ortho" product over the "meta" product, although this selectivity is reduced by a factor of 2 relative to diphenyliodonium. Bitolyls were also formed. 3,4'-Bitolyl, which results from secondary photolysis of "o-iodobitolyl", was present, along with the 4,4' isomer. At longer irradiation times the relative yield of 3,4'-bitolyl increased and 2,4'-bitolyl, a secondary photoproduct from "m-iodobitolyl", was detected. It has been previously assumed that the biphenyls formed are a result of coupling between two aryl radicals.^{6,7} This is unlikely under our conditions. The photolysis produces tolyl radicals at an estimated upper limit steady-state concentration of $1 \times 10^{-8} \text{ M s}^{-1}$, figured by the conversion of the iodonium salt per unit time, the volume of solution in which 99% of the light was absorbed, that all photolysis occurs to produce radicals, and that the radicals have a 1-ms lifetime. Coupling would be a bimolecular reaction that would depend on the square of the radical concentration, in this case $1 \times 10^{-16} \text{ M}^2$. Assuming a diffusion-controlled rate constant of 10^{10} , this results in a rate of $1 \times 10^{-6} \text{ M s}^{-1}$. In comparison, the hydrogen abstraction reaction of phenyl radicals occurs with a rate constant of about 10^5 s^{-1} ,¹³ which with the above concentration results in a rate of $1 \times 10^{-3} \text{ M s}^{-1}$, 1000 times faster

Scheme II. Products from Irradiation of Bis(4-methylphenyl)iodonium Salts

than the coupling reaction. However, a 1-ms radical lifetime is probably about a factor of 100 too long, if the hydrogen abstraction reaction from solvent is the fastest reaction open to the phenyl radical, which results in the hydrogen abstraction reaction being overwhelmingly favored. Other systems we have studied confirm this analysis. The triplet-sensitized reaction of triphenylsulfonium to form benzene and diphenyl sulfide proceeds through the intermediacy of phenyl radicals, and only a trace of biphenyl was observed.^{4b} Likewise, the anthracene-sensitized decomposition of diphenyliodonium and triphenylsulfonium salts, which produces phenyl radicals, gave no detectable biphenyl. We conclude that the formation of 4,4'-bitolyl in this reaction does not result from the recombination of two 4-tolyl radicals. Other possible mechanisms for biphenyl formation are coupling of the escape aryl radical with another aromatic species, e.g., the iodonium salt, or by in-cage ipso reaction between the initially formed species after cleavage of the carbon-iodine bond. The former escape reaction should be quenched by the addition of chlorobenzene which can react with the escape phenyl radical to give 2-, 3-, and 4-chlorobiphenyls. Photolysis of 0.01 M diphenyliodonium triflate at 254 nm in the presence of 0.02 M chlorobenzene gave only traces of 2-chlorobiphenyl and did not quench biphenyl formation (Table I, entry 12). No chlorobiphenyls could be detected after irradiation at 300 or 350 nm under similar conditions (Table I, entries 13 and 14). The 2-chlorobiphenyl isolated from photolysis at $\lambda = 254$ nm was less than 5% of the biphenyl formed; thus we conclude that reaction of the escape phenyl fragment with other aromatic species is not

(12) Becker, H. G. O.; Ebisch, R.; Israel, G.; Kroha, G.; Kroha, W.; Brede, O.; Mehnert, R. *J. Prakt. Chem.* 1977, 319, 98.

(13) Galli, C. *Chem. Rev.* 1988, 88, 765.

a significant process and that biphenyl and 4,4'-bitolyl are likely formed by ipso attack.

The quantum yields for direct photolysis ($\lambda = 248$ nm) of the iodonium salts were measured (Table III, entries 1 and 2). The total quantum yield for diphenyliodonium triflate was 0.54, and the escape product, iodobenzene comprised 75% of the total iodine-containing products. The escape phenyl fragments, benzene and acetanilide, accounted for 20% and 78% of the iodobenzene formed, respectively. The total quantum yield for bis(4-methylphenyl)iodonium hexafluorophosphate was 0.45 with 4-iodotoluene accounting for 71% of the iodine-containing products. Toluene was 41% of the iodotoluene formed.

Triplet-Sensitized Photolysis. Originally, it was reported that the triplet state of diphenyliodonium salts was unreactive, and the photolysis of the iodonium salt in the presence of xanthone, acetophenone, and benzophenone proceeded by electron transfer.⁷ Later, it was reported that *m*-(trifluoromethyl)acetophenone sensitized the triplet photolysis of diphenyliodonium salts, since this sensitizer had the same triplet energy as acetophenone but possessed a lower excited-state oxidation potential.⁸ Chloranil (triplet energy 62 kcal mol⁻¹) was found to be ineffective in the sensitized photolysis of diphenyliodonium. Thus, the triplet state of diphenyliodonium could be located between 62 and 73 kcal mol⁻¹, with an estimate of 64 kcal mol⁻¹ being made.⁸

Diphenyliodonium triflate was irradiated in acetone, with 254-nm Rayonet lamps in quartz tubes, and with 300- and 350-nm Rayonet lamps in Pyrex tubes. The iodonium salt should absorb 29% of the light at 254 nm and only 2% at 300 nm, on the basis of the extinction coefficients of acetone and diphenyliodonium triflate. At similar conversion, the products were analyzed by capillary GLC (Table I, entries 7-9). The iodobiphenyls were formed in similar amounts relative to iodobenzene, as in the acetonitrile photolysis. The major difference between the three wavelengths is that at longer wavelengths there is relatively more 4-iodobiphenyl formed at the expense of the 2 and 3 isomers; the ratio of 4- to 3-iodobiphenyl at 254 nm is 1.30, at 300 nm is 2.73, and at 350 nm, 4.52.

Diphenyliodonium chloride was irradiated in 25% aqueous acetone, at 300 nm (Table I, entry 11). Similar results were obtained to the sensitization of diphenyliodonium triflate by acetone. The amount of escape product, iodobenzene, increased to 80% of the iodine-containing products, relative to 72% in the triflate irradiation. The ratios of the isomeric iodobiphenyls were almost the same. Chlorobenzene was formed in 12.7% yield relative to iodobenzene, which indicates the involvement of phenyl cation in the triplet-sensitized photolysis of diphenyliodonium salts.

The triplet-sensitized reaction of bis(4-methylphenyl)iodonium PF₆ was also studied (Table II, entry 2). Similar products were formed as in the direct irradiation (cf. entry 1). However, 90% of the tolyl moieties cleaved from the iodonium salt appear as toluene, as judged by the ratio of toluene to iodotoluene. This contrasts with the direct irradiation where only 38% of the tolyl moieties appear as toluene. The triplet-sensitized reaction results in more radical-derived escape products than the direct photolysis. The fraction of escape product relative to recombination products increases slightly compared to the direct photolysis, from 71% to 75%. This agrees with the diphenyliodonium salt photolysis, where the sensitized escape ratio was 72%, compared with the direct 76%. Finally, the ratio of the ortho to the meta rearranged product increases in the bis(4-methylphenyl)iodonium system, where this ratio

increased from 7.1 in the direct photolysis to 13 upon triplet sensitization.

Limiting quantum yields for acetone triplet-sensitized decomposition of diphenyliodonium triflate and bis(4-methylphenyl)iodonium hexafluoroantimonate were obtained from double-reciprocal plots at four concentrations of iodonium salts (Table III, entries 3 and 4). The Stern-Volmer slope $k_q\tau$ was obtained from the ratio of the intercept of the plot to the slope. The limiting quantum yields were 0.50 and 0.42, and the $k_q\tau$ values were 994 and 700 M⁻¹, respectively, for the diphenyl- and bis(4-methylphenyl)iodonium salts. This gives a quenching rate constant of about 10⁹ s⁻¹ assuming the lifetime of the acetone triplet is 0.9 × 10⁻⁶ s⁻¹. This about 10 times smaller than the diffusion-controlled rate constant and may be the result of competitive quenching by impurities such as oxygen or mesityl oxide.

Sensitization by Photoinduced Electron Transfer.

We investigated the sensitization of diphenyliodonium triflate by anthracene to provide an example of a pure electron-transfer reaction to compare with other sensitizers.¹⁴ It was previously reported that iodonium salts quenched the singlet excited state of anthracene and that photodecomposition occurred by an electron-transfer reaction.^{7,14} When a solution of anthracene (2.5 × 10⁻³ M) and diphenyliodonium triflate (1.0 × 10⁻² M) is irradiated ($\lambda = 350$ nm) in acetonitrile, the product distribution (Table I, entry 15) shows only trace quantities of the recombination product, 2-iodobiphenyl. The anthracene-photosensitized reaction produces iodobenzene as over 99% of the iodine-containing products. The trace amount of 2-iodobiphenyl formed may be the result of phenyl radical attack on iodobenzene. A similar experiment conducted in acetone solvent also gave only traces of 2-iodobiphenyl (Table I, entry 16). Under these conditions anthracene absorbs 99% of the incident light (350 nm), and so the reaction proceeds by electron transfer rather than the triplet energy transfer observed in acetone at 300 and 350 nm in the absence of anthracene. About 31% of the phenyl radicals formed are trapped by anthracene radical cation to produce phenylanthracenes. This result is similar to those obtained upon electron-transfer sensitization of triphenylsulfonium salts with anthracene and argues that the lifetime of the diphenyliodine radical is shorter than diffusion of the reactive species out of the solvent cage.^{4d,14} Earlier workers reported that the loss of iodonium was equivalent to anthracene consumption.¹⁴ These workers also found that of the anthracene lost, 55% could be accounted for by formation of phenylanthracenes. We found, in a concentration against time study, at an anthracene concentration of 2.5 × 10⁻³ M and a diphenyliodonium triflate concentration of 1.00 × 10⁻² M and at low consumption of diphenyliodonium triflate, (less than 5%), that consumption of anthracene, formation of iodobenzene (both measured by GLC), and consumption of diphenyliodonium (measured with the cobalt complex) were equivalent within experimental error. At this conversion, only 12% of the anthracene lost appeared as 9-phenylanthracene, and the total of the phenylanthracenes (identified by GC MS), assuming equal response ratios to 9-phenylanthracene, amounted to only 31% of the anthracene consumed. At higher conversion of the iodonium salt (14%), iodonium consumption again agreed well with the formation of iodobenzene. However, anthracene consumption amounted only to ca. 60% of the iodonium consumption, and the phenylanthracenes now accounted

(14) DeVoe, R. J.; Sahyun, M. R. V.; Schmidt, E.; Serpone, D. K. *Can. J. Chem.* 1988, 66, 319.

for only 25% of the anthracene consumed. The phenylanthracenes can also act as electron donors toward diphenyliodonium triflate, and as the anthracene is consumed, the phenylanthracenes will absorb a greater fraction of the incident light and be consumed themselves. Presumably, polyphenylanthracenes are formed to some extent. These results also show that the products of the photoelectron transfer, anthracene radical cation and diphenyliodonium radical, undergo irreversible reactions. Diphenyliodonium radical decomposes to phenyl radical and iodobenzene, while anthracene radical cation can react with phenyl radical, followed by proton loss, to generate phenylanthracenes and acid, or the anthracene radical cation can undergo undetermined reactions. Reactions that regenerate anthracene by reduction of the radical cation do not occur, as shown by the equivalence of anthracene consumption and iodonium consumption at low conversion. We consider these results to be reliable, as the only assumption made in obtaining them was the equal response ratio assumption, which our experience has shown to be reasonable for isomeric compounds. The previous workers quantified the anthracene consumption by UV spectroscopy and implicitly assumed that the UV spectra of the three phenylanthracenes are the same and that no other compound present in the photolysis mixture absorbs in the same spectral region.¹⁴ In addition, as both these workers and ourselves cannot account for all of the anthracene lost in products formed, it is likely that some of these products will absorb in this spectral region, particularly the polyphenylanthracenes. Thus, we consider our results to be reliable.

Duality of Triplet Energy Transfer and Photoinduced Electron Transfer. The fact that triplet energy transfer and electron transfer can occur in sensitized photolysis of diaryliodonium salts is another interesting facet of aryliodonium photochemistry. Some sensitizers may be capable of both exergonic electron transfer and triplet energy transfer, and it would be of interest to investigate the relative importance of the two processes. Since the electron-transfer-sensitized decomposition of diphenyliodonium triflate does not produce recombination products and the triplet energy transfer reaction does produce recombination products, it should be possible to evaluate whether a particular sensitizer operates through a triplet or an electron-transfer path, in cases where both energy and electron transfer are energetically feasible.

When a solution of diphenyliodonium triflate (1.0×10^{-2} M) and xanthone (1.0×10^{-2} M) in argon-purged acetonitrile is irradiated, a different product distribution from the anthracene product distribution was obtained (Table I, entry 17). Significant quantities of the iodobiphenyl recombination products are produced, with an iodobiphenyl isomer distribution similar to that observed in the acetone-sensitized irradiations. In acetone at $\lambda = 300$ nm, the iodobiphenyls are about 25% of the iodine-containing photoproducts. In the xanthone irradiation, the iodobiphenyls make up about 7% of the iodine-containing photoproducts. Xanthone has been previously reported to photosensitize the decomposition of diphenyliodonium PF₆ by an electron-transfer mechanism.⁷ Our results here indicate that the reaction occurs partially by electron transfer and partially by triplet energy transfer, as indicated by the fraction of recombination products to escape products. If the ratio of recombination products to iodobenzene is approximately unaffected by solvent (acetone to acetonitrile), then the fraction of triplet-derived products in this reaction is about 25%. It is unlikely that the triplet state of the diphenyliodonium salt is generated by

back electron transfer to the xanthone radical cation. If the oxidation potential of xanthone is taken to be 1.8 V vs SCE as previously calculated⁷ and the reduction potential for diphenyliodonium is taken to be either -0.2 V¹⁵ or -0.7 V vs SCE⁸ in acetonitrile, then the energy available in the back electron transfer would be a maximum of about 58 kcal mol⁻¹. The triplet state of diphenyliodonium has been shown to be about 64 kcal mol⁻¹ in energy and definitely greater than 62 kcal mol⁻¹. Thus, there is not sufficient energy to efficiently populate the iodonium triplet state by back electron transfer from the xanthone radical cation-diphenyliodonium pair.

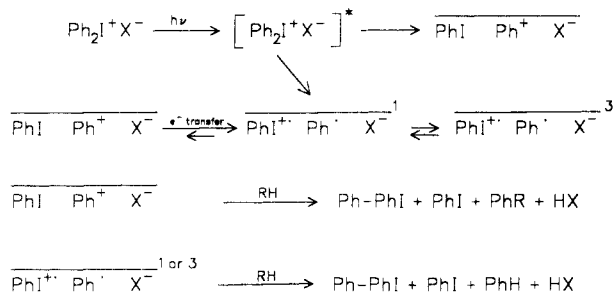
The irradiation of benzophenone (1.0×10^{-2} M) and diphenyliodonium triflate (1.0×10^{-2} M) was also examined. Irradiation in acetonitrile produced both iodobenzene and 2-iodobiphenyl (Table I, entry 18). If the same argument as stated above is applied to this system, then about 30% of this reaction occurs by triplet energy transfer and 70% by electron transfer. The triplet energy of benzophenone is 5 kcal mol⁻¹ lower than xanthone, being 69 kcal mol⁻¹.¹⁶ The energy for electron transfer can be calculated by using the value of 2.7 V for the oxidation potential of benzophenone,⁷ -0.2 V¹⁵ or -0.7 V⁸ for diphenyliodonium triflate, and the triplet state energy of 69 kcal mol⁻¹ for benzophenone. Through the Rehm-Weller equation, this leads to a value of either -2 kcal mol⁻¹ or $+9$ kcal mol⁻¹. Since the electron transfer is clearly occurring, this observation would tend to support the more positive value for the reduction potential of the iodonium salt. Also, the calculated result of an almost thermoneutral electron transfer would predict a reduced rate of electron transfer. This would explain why the triplet reaction is a greater fraction of the total reaction compared to the xanthone reaction, despite the lower triplet energy of benzophenone relative to xanthone.

Discussion

These results, taken in conjunction with the other recent reports on iodonium and sulfonium photochemistry, allow a complete picture of iodonium photoreactivity. For sulfonium salts, the mechanism we propose for direct photolysis is based, in part, on the mechanism originally proposed by McEwen.⁵ Heterolysis of the excited state occurs to form diphenyl sulfide and phenyl cation. The phenyl cation could be trapped by solvent (methanol and acetonitrile), oxidize the diphenyl sulfide to form diphenylsulfinyl radical cation and phenyl radical, recombine to reform the sulfonium salt, and undergo electrophilic attack on the diphenyl sulfide to yield, ultimately, (phenylthio)biphenyls, the observed recombination product.⁴ The phenyl radical-diphenylsulfinyl radical cation pair could also undergo recombination to form (phenylthio)biphenyls or escape to form the reduced arene and diphenyl sulfide. In contrast, the triplet-sensitized irradiation of triphenylsulfonium cation in methanol with 1-indanone yielded no trace of anisole or of the (phenylthio)biphenyls, yielding only benzene, diphenyl sulfide, and acid as products.^{4b} This indicated that the reaction proceeded only by homolysis of the triplet excited state, and the fate of the initially formed triplet radical pair was only escape from, or reaction with, the solvent cage. For aryliodonium salts, the most recent mechanism for photolysis proposed the homolytic cleavage of the iodonium salt to phenyl radical and iodobenzene radical cation,

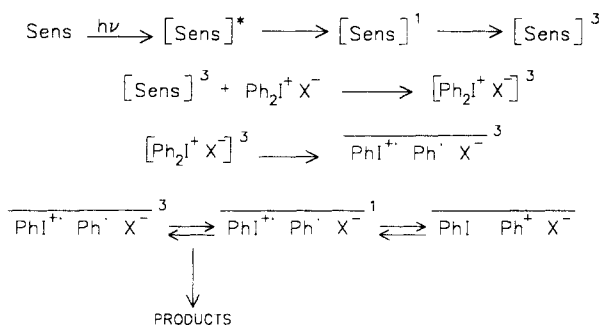
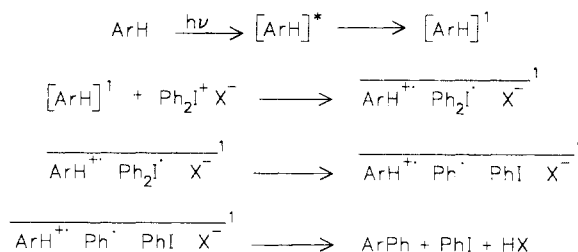
(15) Bachofner, H. E.; Beringer, F. M.; Meites, L. M. *J. Am. Chem. Soc.* **1958**, *80*, 4269.

(16) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

Scheme III. Mechanism for Product Formation from Direct Photolysis of Diaryliodonium Salts


which then formed the observed products, iodobenzene, acetanilide, biphenyl, and 4-iodobiphenyl.⁸ The difference in chemistry between the iodonium and sulfonium systems should be related to the thermodynamics of the photolytic fragments and the influence of the iodine atom on inter-system crossing. At least some of the photolysis of the diphenyliodonium salt occurs by a homolytic pathway, as many recent studies propose, to form iodobenzene radical cation and phenyl radical. Iodobenzene radical cation has been observed by flash photolysis of iodonium salts.^{7,8,17} A heterolytic cleavage must also occur, leading to iodobenzene and phenyl cation. This path is indicated by the formation of acetanilide and chlorobenzene from photolysis of diphenyliodonium salts in acetonitrile and observation of 4-methylacetanilide and *p*-cresol from photolysis of bis(4-methylphenyl)iodonium salts in acetonitrile. These products are not formed in phenyl radical reactions. Previously, a transient in the photolysis of diphenyliodonium⁸ and bis(4-*tert*-butylphenyl)iodonium¹⁷ with a maximum near 400 nm has been assigned to phenyl cation. This transient had a 2- μ s lifetime, which is too long for phenyl cation in the solvents studied.⁸ However, the assignment was based on a literature reference that deals with benzyl, not phenyl, cations.¹⁸ Attempts to observe the phenyl cation in solution have been made with no success.¹⁹ Thus, we believe the assignment of this transient to phenyl cation is unwarranted based only on this reference,¹⁸ without any other corroborating data, but phenyl cation does seem to be present.

The experimental observations of diphenyliodonium photochemistry require that both the phenyl cation-iodobenzene pair and the phenyl radical-iodobenzene radical cation pair be present in any mechanism. Since the iodonium excited state has a greater energy than either pair, the direct formation of both pairs from the excited state is thermodynamically permitted. However, since these pairs are related by an electron transfer, formation of the less stable pair from the excited state may be followed by an electron transfer to yield the more stable intermediate pair. The relative energetics of iodobenzene radical cation-phenyl radical and iodobenzene-phenyl cation can be determined by use of the measured half-wave potential of iodobenzene (2.07 V vs SCE in CH₃CN)²⁰ and the vertical ionization potential of phenyl radical (9.20 V)²¹ in combination with a correlation of IP and half-wave potential.²² This leads to a prediction that the iodo-

Scheme IV. Mechanisms for Sensitization of Diaryliodonium Salts by Triplet Energy Transfer and Electron Transfer
a. Triplet Energy Transfer

b. Electron Transfer


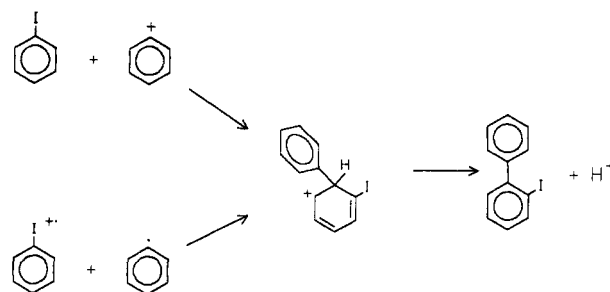
benzene radical cation-phenyl radical pair is more stable by 8.7 kcal mol⁻¹. Recently, a combined theoretical and ultraviolet photoelectron spectroscopy study of the phenyl radical concluded that the UPS peak observed corresponded to the adiabatic ionization of the phenyl radical to the first excited state of the phenyl cation, a triplet configuration, and that the ionization to the ground state of phenyl cation was weak and consequently not observed.²³ From their calculations, they predicted the adiabatic ionization to the phenyl cation ground state to occur at 7.92 eV and the vertical ionization potential to be at 8.79 eV. Using this value of the vertical ionization potential, the phenyl radical pair is predicted to be more stable by 0.3 kcal mol⁻¹. This analysis indicates that phenyl cation-iodobenzene pair and the phenyl radical-iodobenzene radical cation pair are of comparable thermodynamic stability, with the phenyl radical pair being somewhat more stable. Thus, electron transfer to and from each pair should be possible. A similar treatment for bis(4-methylphenyl)iodonium, using the vertical ionization potential for 4-iodotoluene of 8.50 eV²⁴ and assuming that the methyl group has little influence on the ionization of 4-tolyl radical, leads to the conclusion that the 4-tolyl radical-4-iodotoluene radical cation pair is more stable by 6 kcal mol⁻¹ than the 4-tolyl cation-4-iodotoluene pair. This difference in stability between the diphenyl and bis(4-methylphenyl)iodonium systems is manifested in the photochemistry. For diphenyliodonium chloride, similar amounts of chlorobenzene, a phenyl cation trapping product, were formed upon direct irradiation and triplet-sensitized irradiation, at similar chloride concentrations. However, for bis(4-methylphenyl)iodonium, the amount of toluene, a radical-derived product, increases from 38% in the direct photolysis to 90% in the sensitized photolysis. It appears that the first formed radical pair in the triplet

(17) Klemm, E.; Riesenberger, E.; Graness, A. *Z. Chem.* **1983**, *23*, 222.(18) Pask, S. D.; Plesch, P. H. *Eur. Polym. J.* **1982**, *18*, 939.(19) Scaiano, J. C.; Kim-Thuan, N. *J. Photochem.* **1983**, *23*, 269.(20) Neikam, W. C.; Dimeler, G. R.; Desmond, M. M. *J. Electrochem. Soc.* **1964**, *111*, 1190.(21) Fisher, I. P.; Palmer, T. F.; Lossing, F. P. *J. Am. Chem. Soc.* **1964**, *86*, 2742.(22) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916.(23) Butcher, V.; Costa, M. L.; Dyke, J. M.; Ellis, A. R.; Morris, A. *Chem. Phys.* **1987**, *115*, 261.(24) Baidin, V. N.; Misharev, A. D.; Takhistov, V. V. *Zh. Org. Khim.* **1985**, *21*, 817.

reaction does not undergo efficient electron transfer to form the tolyl cation-iodotoluene pair. We cannot determine if, in fact, this electron transfer is occurring. The electron transfer should be facilitated by the preorganization of the two moieties and should be impeded by the low thermodynamic driving force for the reaction, by the solvent reorganization energy, and by the geometry change between phenyl cation and phenyl radical that results in the low Franck-Condon factors which caused the low ionization cross-section.²³ However, the fact that both heterolytic and homolytic type products result from irradiation suggests that this process occurs or that the homolysis and heterolysis both occur from the iodonium excited state, or that both pathways operate. A feature of diphenyliodonium photochemistry that differs from triphenylsulfonium photochemistry is that the triplet-sensitized irradiation of diphenyliodonium yields recombination products.⁸ We found that triphenylsulfonium upon triplet sensitization produces no recombination products.^{4b} We used acetone as a triplet sensitizer. It is unlikely that acetone acted as an electron donor in the photolysis reported here, as the anthracene-sensitized photolysis of diphenyliodonium triflate resulted only in iodobenzene formation. Anthracene has been reported to photosensitize the decomposition of diphenyliodonium through an electron-transfer mechanism.⁷ The product ratios determined in the acetone-sensitized photolysis show a ratio of iodobenzene to iodobiphenyls that is slightly lower than that found in the acetonitrile photolysis. Thus, by this product criteria, electron transfer does not seem to be occurring. Comparison of the product distributions in acetone at the wavelengths used, which should compare the triplet-sensitized reaction with the direct photolysis, indicated little difference between the methods of generating an iodonium excited state. This could be interpreted in terms of rapid conversion of the initial iodonium singlet to the triplet excited state or additionally in terms of the interconversion of the phenyl radical-iodobenzene radical cation triplet and singlet radical pairs. This intersystem crossing would necessarily have to occur faster than the reaction of phenyl radical with the solvent cage walls. The rapid interconversion could occur by two mechanisms, the heavy-atom effect (spin-orbit coupling) or, as recently proposed for some other onium salts, by hyperfine coupling of the nuclear spin of iodine-127 (5/2), the major natural isotope, with the odd electron.²⁵ There is not enough information to decide between these paths.

The different recombination product distribution observed upon triplet and singlet photolysis shows that there must be two paths to form these products. The small but significant increase in the 4-iodobiphenyl amount at 300 nm is probably due to the triplet-sensitized recombination products arising from a phenyl radical reacting with iodobenzene radical cation. Reaction should occur in the aromatic ring where the odd-electron density is highest, the 2- and 4-positions. The relatively greater formation of 3-iodobiphenyl upon direct photolysis can be explained, in that the direct photolysis proceeds through heterolysis to form phenyl cation, which less selectively attacks iodobenzene to form recombination products. The high similarity between the product distributions upon direct irradiation and acetone-sensitized photolysis suggests that the proposed set of intermediates, phenyl cation-iodobenzene, singlet phenyl radical iodobenzene radical cation, and triplet phenyl radical-iodobenzene radical cation, are able to interconvert somewhat faster than the time scale

Scheme V. Acid Generation from Formation of Rearrangement Products



of the product forming reactions. This interconversion might approach equilibrium, but as indicated by the change in regioselectivity indicated in the iodobiphenyls, some memory of the method of generating these intermediate pairs is retained. Phenyl cation involvement is also indicated by the formation of acetanilides and chlorobenzene. It was suggested that acetanilide formation occurs by attack of phenyl cation or phenyl radical on acetonitrile.⁸ We have never observed the formation of acetanilide in phenyl radical reactions in acetonitrile.

The differences between triphenylsulfonium and diphenyliodonium photochemistry can be attributed to the "heavy-atom" or nuclear spin properties of iodine and the difference in stability between the various sets of intermediates formed in the photolysis. Sulfur is a relatively light atom with the major natural isotope possessing no nuclear spin. Sulfur does not, in the initially formed radical pair, increase the intersystem crossing rate enough to compete with diffusion and the solvent reactions of the triplet radical pair. Iodine, in contrast, strongly increases the rate of ISC over that of the other reactions. Thus, recombination products are obtained. In addition, the triplet-sensitized reaction of triphenylsulfonium in methanol gave no anisole, indicating that phenyl cation is not present upon triplet-sensitized photolysis.^{4b} Diphenyliodonium has been reported to form acetanilide upon triplet-sensitized photolysis.⁸ Two steps must occur after triplet sensitization for phenyl cation formation from the onium salts. The first is intersystem crossing within the radical pair, and the second is the electron transfer from phenyl radical to iodobenzene radical cation. In the iodonium salt chemistry, the iodine atom facilitates the intersystem crossing, and the near equal energy of the phenyl cation pair and the phenyl radical pair thermodynamically permits the electron transfer. In the sulfonium salt, sulfur is not efficient at causing intersystem crossing, in this reaction, and the phenyl cation pair is much higher in energy than the phenyl radical pair. This accounts for the different chemistry upon triplet excitation of the diphenyliodonium and the triphenylsulfonium salts.

The mechanism that is suggested by these results is that the diphenyliodonium salt absorbs a photon to form an excited state. This excited state may undergo heterolysis to form iodobenzene and phenyl cation, homolysis to form iodobenzene radical cation and phenyl radical, or ISC to the triplet state, which probably can compete with the cleavage reactions because of the iodine heavy-atom enhancement of the ISC rate. The triplet state can undergo homolysis to form a triplet radical pair, phenyl radical, and iodobenzene radical cation. The phenyl cation-iodobenzene pair can recombine to form a cyclohexadienyl cation (Scheme V), recombine to form the iodonium salt starting material, undergo reaction with solvent, which would produce acetanilide and iodobenzene, or undergo electron transfer to form a singlet radical pair, phenyl

radical-iodobenzene radical cation. The singlet radical pair could undergo recombination to form a cyclohexadienyl cation which leads to the iodobiphenyls, recombination to form starting iodonium salt, reaction with solvent, electron transfer to form the phenyl cation pair, or ISC to form the triplet radical pair. The triplet radical pair can undergo only diffusion or ISC back to singlet pair. It seems that ISC and the electron transfer occur at faster rates than the solvent reaction and recombination steps. This mechanism is consistent with all observations made of the photochemistry of diphenyliodonium salts.

Conclusions

Direct photolysis of diaryliodonium salts leads to formation of iodobenzene as the major iodine-containing product, with the in-cage recombination products 2-iodobiphenyl and the other iodobiphenyl isomers forming a significant fraction of the products. A similar product distribution was obtained upon triplet-sensitized irradiation. These products are derived from three pairs of intermediates that may interconvert: phenyl cation-iodobenzene, singlet phenyl radical-iodobenzene radical cation, and triplet phenyl radical-iodobenzene radical cation. This occurs because of comparable stability of the pairs of intermediates and the enhancement of ISC due to the iodine atom.

Our results on the anthracene sensitization of diphenyliodonium photolysis are consistent with the scheme presented recently.¹⁴ We have shown that the photoelectron transfer, aside from any back electron transfer, stoichiometrically consumes one anthracene and one diphenyliodonium for every iodobenzene produced. This implies that anthracene radical cation does not act as an oxidizing agent for intermediate odd-electron species in this reaction under our conditions but instead undergoes irreversible reactions with phenyl radical in-cage to produce phenylanthracenes and other, undetermined reactions. We have also shown that some of the molecules that had been reported to sensitize the decomposition of diphenyliodonium by an electron-transfer mechanism also can and do act through a triplet energy-transfer mechanism. An electron-transfer chain mechanism is indicated for the direct irradiation of diphenyliodonium triflate in methanol.

Experimental Section

General Procedures. ¹H NMR spectra were determined on an IBM-250 (250 MHz). ¹³C NMR spectra were determined on the IBM-250 at 63 MHz. Chemical shifts are reported in ppm downfield relative to internal TMS. Ultraviolet spectra were measured on a Hewlett-Packard 8451 spectrometer. Infrared spectra were measured on an IBM Instruments IR-44. Melting points were determined in open capillaries, on a Mel-Temp apparatus (Laboratory Devices). Capillary GLC analysis was performed on a Hewlett-Packard 5890 chromatograph equipped with flame ionization detector, using a Shimadzu Chromatopac C-R1B integrator/recorder. Quantitative analysis was accomplished using known quantities of the photoproducts to calibrate the integrator. The column was a J & W Scientific DB-1 (cross-linked methylsilicone) 0.4 μm by 0.18 mm by 20 m.

Materials. Diphenyliodonium chloride was prepared according to the literature.²⁶ Trifluoromethanesulfonic acid, 4-iodobiphenyl, biphenyl, *o*-terphenyl, *p*-terphenyl, and anthracene were obtained from Kodak Organic Chemicals. 9-Phenylanthracene was obtained from Pfaltz & Bauer. 2-Iodobiphenyl was obtained from Lancaster Synthesis. 3-Iodobiphenyl was obtained by the reaction of iodine with the Grignard reagent from 3-bromobiphenyl, obtained from Columbia Organics. Iodobenzene and xanthone were obtained

from Aldrich Chemical Co., and acetonitrile, methanol, and acetone were obtained from American Burdick & Jackson and were used as received. Diphenyliodonium PF₆ was prepared according to the literature.^{6a,26}

Diphenyliodonium Trifluoromethanesulfonate. Diphenyliodonium chloride²⁶ (17.0 gm, 53.7 mmol) was suspended in 150 mL of dry dichloromethane. Trifluoromethanesulfonic acid (5.0 mL, 8.5 g, 56.5 mmol) was added in one portion. The suspension was heated to reflux for 1 h in a fume hood and evolved HCl fumes. The suspension was then cooled, and the white solid filtered. The solid was washed with ether and with hexane, and the residual solvent was removed under vacuum, to give 23.08 g (53.6 mmol, 99%) of the title compound: mp 178–80 °C; UV (CH₃CN) λ_{max} 230 nm (ε 14 900 M⁻¹ cm⁻¹); IR (KBr pellet) 1471, 1438, 1263, 1179, 1033, 1028, 989, 743, 738, 680, 653, 648 cm⁻¹; ¹H NMR (acetone-*d*₆) δ 8.33 (m, 4 H), 7.73 (m, 2 H), 7.57 (m, 2 H); ¹³C NMR (acetone-*d*₆) δ 136.58, 133.52, 133.04, 122.35 (q), 115.50.

Bis(4-methylphenyl)iodonium Trifluoromethanesulfonate. Bis(4-methylphenyl)iodonium chloride²⁶ (5.0 g, 14.5 mmol) was dissolved in 100 mL of dry dichloromethane. Trifluoromethanesulfonic acid (1.3 mL, 2.2 gm, 14.7 mmol) was added in one portion, and the solution was heated to reflux and evolved HCl fumes. After 1 h, the solution was cooled and washed with 50 mL of saturated aqueous sodium bicarbonate solution and with 50 mL of brine. The dichloromethane solution was dried with MgSO₄, and the solvent was removed with a rotary evaporator to give 6.58 g of white powder, 99%: mp 145–8 °C; UV (CH₃CN) λ_{max} 242 nm (22 800 M⁻¹ cm⁻¹); IR (KBr pellet) 1483, 1453, 1271, 1224, 1209, 1183, 1156, 1031, 996, 799, 697, 639 cm⁻¹; ¹H NMR (acetone-*d*₆) δ 7.85 (d, 4 H), 7.11 (d, 4 H), 2.31 (s, 6 H); ¹³C NMR (acetone-*d*₆) δ 142.46, 135.00, 132.56, 122.35 (q), 114.62, 21.35.

3-Iodobiphenyl. The Grignard reagent from 3-bromobiphenyl in ether was added to the equivalent amount of iodine in ether at 0 °C. After stirring 2 h, the solution was allowed to warm to room temperature, and a solution of sodium thiosulfate in water was added until the two-phase mixture showed no iodine color. The layers were separated, and the ether layer was washed with water and brine and dried over MgSO₄, and the ether was removed with a rotary evaporator. The residue was further purified by preparative GLC (Shimadzu GC-8A, 10 ft × 0.25 in. 5% SE-30 on Chromosorb G, AW-DMCS, 60–80 mesh, temperature program 260 °C for 1 min, then 3 °C min⁻¹ to 310 °C); UV (CH₃CN) λ_{max} 206 nm (ε 35 000 M⁻¹ cm⁻¹), 232 nm (29 000), 252 nm (18 900); ¹H NMR (chloroform-*d*) δ 7.93 (approx s, 1 H), 7.64 (dt, 1 H), 7.53–7.34 (m, 6 H), 7.14 (t, 1 H); ¹³C NMR (chloroform-*d*) δ 143.6, 139.5, 136.1, 130.1, 128.8, 127.8, 127.0, 126.4, 94.9 (only lines observed).

Spectra of 2- and 4-Iodobiphenyl. 2-Iodobiphenyl (Lancaster Synthesis): ¹H NMR (chloroform-*d*) δ 7.91 (d, 1 H), 7.38–7.24 (m, 7 H), 6.96 (td, 1 H); ¹³C NMR (chloroform-*d*) δ 146.80, 144.39, 139.72, 130.32, 129.31, 129.03, 128.36, 128.20, 127.87, 98.94. 4-Iodobiphenyl (Eastman Organic Chemicals): ¹H NMR (chloroform-*d*) δ 7.72 (d, 2 H), 7.50 (d, 2 H), 7.44–7.26 (m, 5 H); ¹³C NMR (chloroform-*d*) 140.50, 140.02, 137.86, 129.01, 128.94, 127.72, 126.90, 93.14 ppm.

4',5-Dimethyl-2-iodobiphenyl and 2,4'-Dimethyl-5-iodobiphenyl. These compounds were prepared by a modified Gomberg-Bachmann reaction.²⁷ 4-Iodotoluene (30 gm) was heated to melting, and 3.7 g of potassium acetate, 50 μL of acetonitrile, and 5.0 g (18.9 mmol) of 4-methylbenzenediazonium-PF₆ was added. The mixture was stirred for 2 h at 50 °C. The mixture was then diluted with 100 mL of ether and was washed with aqueous sodium bicarbonate and with brine. The ether layer was dried with MgSO₄, and the solvent removed with a rotary evaporator. The residue was distilled under vacuum to remove the excess 4-iodotoluene by using an air condenser to avoid solidification in the condenser. The pot residue was then further purified by preparative GLC. (Shimadzu GC-8A, column 10 ft × 0.25 in. 5% SE-30 on Chromosorb G, AW-DMCS, 60–80 mesh; column temperature program 220 °C for 1 min, then 2 °C min⁻¹ to 280 °C). 4',5-Dimethyl-2-iodobiphenyl: UV (CH₃CN) λ_{max} 230 nm (ε 10 900 M⁻¹ cm⁻¹), 330 (510); ¹H NMR (chloroform-*d*) δ 7.79

(26) Beringer, F. M.; Falk, R. A.; Karniol, M.; Lillien, I.; Masullo, G.; Mausner, M.; Sommer, E. *J. Am. Chem. Soc.* 1959, 81, 342.

(27) Beadle, J. R.; Korzeniowski, S. H.; Rosenberg, D. E.; Garcia-Slanga, B. J.; Gokel, G. W. *J. Org. Chem.* 1984, 49, 1594.

(d, 1 H), 7.31-7.11 (m, 5 H), 6.83 (dd, 1 H) 2.41 (s, 3 H) 2.32 (s, 3 H). 2,4'-Dimethyl-5-iodobiphenyl: UV (CH₃CN) λ_{\max} 230 nm (ϵ 28400). ¹H NMR (chloroform-*d*) δ 7.64-6.97 (m, 7 H), 2.39 (s, 3 H), 2.19 (s, 3 H).

The structures were further confirmed by irradiation of the iodobiphenyls in acetonitrile with 254-nm light. This causes the photolysis of the iodine atom, which leads to the dimethylbiphenyl. 4',5-Dimethyl-2-iodobiphenyl produced 3,4'-dimethylbiphenyl, and 2,4'-dimethyl-5-iodobiphenyl produced 2,4'-dimethylbiphenyl, as determined by capillary GLC against authentic samples of the dimethylbiphenyls.

Photolysis Experiments. Solutions of the appropriate salt were prepared in methanol, acetone, or acetonitrile. In all cases, the concentration of the iodonium salt was 1.0×10^{-2} M. The anthracene concentration was 2.65×10^{-3} M, and the xanthone concentration was 1.07×10^{-2} M. Aliquots of the solutions were placed in quartz tubes (for 254-nm photolysis) or Pyrex tubes (for 300- and 350-nm photolysis). The tubes were sealed with rubber septa, and purged with solvent-saturated argon for 10 min prior to irradiation. The samples then were irradiated in a Rayonet photochemical reactor equipped with four bulbs emitting the desired wavelengths, in a carousel. Samples of the irradiated solutions were then diluted with water and extracted with hexanes containing *n*-tetradecane internal standard. The hexanes phase was then analyzed by capillary GLC. Quantification was accomplished by using known concentrations of authentic samples of the photoproducts, extracted in the same way as the photolysis samples. In the sensitized irradiations, the sensitizer absorbed at least 98% of the incident radiation. Measurement of the diphenyliodonium concentration was accomplished using the cobalt thiocyanate complex.⁹ A 2.00-mL aliquot of the irradiated diphenyliodonium solution was diluted to 25.0 mL with chloroform. A 10.00-mL aliquot of this solution was mixed with 10.00 mL of an aqueous 0.1 M CoCl₂ and 0.5 M NH₄SCN solution. The two-phase mixture was shaken and allowed to stand overnight. The absorbance of the chloroform phase was measured at 624 nm, and the concentration of diphenyliodonium determined from a calibration curve determined from known concentrations of the same salt. Acid was determined by using sodium 4-nitrophen-

oxide. Photolysis solution (1.00 mL) was added to 5.00 mL of saturated phenoxide in acetonitrile and diluted to 25 mL. The absorbance was then measured and was converted to concentration by use of a standard absorbance curve determined from freshly prepared trifluoromethanesulfonic acid solutions in acetonitrile, whose absorbance was measured in the same way as the unknowns.

Quantum Yields. Quantum yields were determined by using a modified PTI Quantacount. Solutions were 0.01 M for direct irradiation or 0.005-0.03 M for acetone-sensitized irradiation. Three 3.00-mL aliquots were placed in Suprasil cuvettes, sealed with a rubber septum, and purged with argon for 8 min immediately prior to irradiation. The samples were then irradiated in the Quantacount, which was previously calibrated by using potassium ferrioxalate actinometry. After irradiation, the samples were transferred to tubes containing 1.00 mL of hexanes containing a small amount of *n*-tetradecane as internal standard and 10.00 mL of 0.5 M aqueous NaH₂PO₄. The tubes were stoppered and thoroughly mixed. After standing for 4 h, the hexane layer was removed and analyzed by capillary GLC. The integrator was calibrated against similar concentrations of authentic samples of the photoproducts, which were treated to a similar workup as the photolysis solutions. Benzene was quantified by irradiation of a 3.00-mL aliquot, which was transferred with an additional 1.00 mL of solvent to a tube containing 2.00 mL of *n*-pentane, 10.00 mL of 0.5 M aqueous NaH₂PO₄, and *n*-octane as an internal standard. The contents of the tube were vigorously mixed, and the tube was allowed to stand for 4 h. The pentane layer was separated and analyzed by capillary GLC. Acetanilide was analyzed in the same way, with the exception of the use of methyl *tert*-butyl ether as the extracting solvent and *n*-tetradecane as the internal standard.

Registry No. Diphenyliodonium triflate, 66003-76-7; diphenyliodonium hexafluorophosphate, 58109-40-3; bis(4-methylphenyl)iodonium hexafluorophosphate, 60565-88-0; bis(4-methylphenyl)iodonium trifluoromethanesulfonate, 123726-16-9; 3-iodobiphenyl, 20442-79-9; 2-iodobiphenyl, 2113-51-1; 4-iodobiphenyl, 1591-31-7; 4',5-dimethyl-2-iodobiphenyl, 123726-17-0; 2,4'-dimethyl-5-iodobiphenyl, 123726-18-1.

Behavior of Pyridinium Salts Obtained from Derivatives of Pyridinedicarboxylic Acids in Basic Solutions. Addition of Hydroxide or Alkoxide To Form 1,2-Dihydropyridine Intermediates

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The *N*-alkylated pyridinium salts obtained from the diethyl esters, *N*-ethyl amides, and *N,N*-diethyl amides of pyridine-3,5-dicarboxylic acid exhibit ultraviolet absorptions of moderate intensity in the region of 350 nm when dissolved in 95% ethanol. This absorption increases in intensity on addition of base and disappears on acidification of the solutions. It is not observed in rigorously dried solvents like chloroform or methylene chloride. By ¹H NMR spectroscopy it has been shown that a 1,2-dihydropyridine is formed reversibly by addition of hydroxide (or methoxide) to the 2-position of the pyridinium salts. Concurrently with the formation of these intermediates, proton-deuterium exchange (in deuterated solvents) occurs, possibly via betaines formed by base-induced deprotonation at the 2-position of the pyridinium salts. The corresponding derivatives of pyridine-2,5- and -3,5-dicarboxylic acids do not display this behavior.

Introduction

In the course of examination of the circular dichroism (CD) spectra of chiral bridged pyridines (1)¹ a CD effect at about 350 nm was observed for pyridinium salts (1b)

in spectral grade 95% ethanol.¹ This Cotton effect was obviously associated with an ultraviolet absorption of modest intensity at the same wavelength. However, an absorption at such a long wavelength seems inconsistent with the electronic structure of these pyridinium salts.²

(1) (a) Speelman, J. C.; Talma, A. G.; Kellogg, R. M.; Meetsma, A.; de Boer, J. L.; Beurskens, P. T.; Bosman, W. P. *J. Org. Chem.* 1989, 54, 1055. (b) Schipper, P.; Kellogg, R. M. *J. Am. Chem. Soc.*, in press.

(2) On the basis of experience with pyridinium salts of esters of pyridine-3,5-dicarboxylic acid [Van Bergen, T. J.; Kellogg, R. M. *J. Am. Chem. Soc.* 1972, 94, 8451] we expected the maximum at about 271 nm.