J. Org. Chem. **1998,** *63,* 6141−6145

Electron Transfer from a Cyclic Diaryliodine Species to Arenediazonium Salts. Evidence for the Intermediacy of 9−I−2 Structures in Iodine Atom Transfer Reactions[1]

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Received January 22, 1998

2,2′-Diiodobiphenyl (**1**) reacts with arenediazonium hexafluorophosphates ($ArN_2^+PF_6^-$) in acetonitrile to form biphenyleneiodonium salt (**4**) and iodoarenes (ArI) as major products. The reaction follows a free-radical-chain mechanism and involves a cyclic diaryliodine, 9−I−2 species (**3**), which is trapped as the iodonium salt (**4**) by a single-electron transfer (SET) to the diazonium salt. The results show that diaryliodine intermediates formed by the addition of phenyl radicals to iodoarenes can have sufficient lifetimes to allow trapping by bimolecular processes.

Introduction

The field of free-radical chemistry has attained greater significance in recent years due, in part, to its increasing application to complex organic syntheses.[2] Halogen atom transfer reactions are particularly important, forming the basis for several important synthetic methodologies,[2] and are interesting mechanistically because of the possibility that they may proceed through an energy minimum corresponding to a hypervalent 9−X−2 intermediate, $R{-}X^\bullet{-}R'$.[3]

The transfer of iodine from an iodoarene to a phenyl radical is a fast reaction ($k \approx 10^7{-}10^8\ M^{-1}\ s^{-1}$).[4−6] Mechanistically, either the reaction involves the intervention of a 9−I−2, diaryliodine intermediate (eq 1) or it is a concerted process (eq 2).

$$\mathrm{Ph^\bullet + I{-}Ar \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{9{-}I{-}2}{[Ph{-}\dot{I}{-}Ar]} \xrightarrow{k_2} Ph{-}I + Ar^\bullet} \tag{1}$$

$$\mathrm{Ph^\bullet + I{-}Ar \xrightarrow{k_{abs}} Ph{-}I + Ar^\bullet} \tag{2}$$

In an early study, Danen and Saunders[4] measured the relative rates (k_{abs}/k_{Cl}) of reaction of phenyl radicals with a series of iodoarenes versus abstraction of chlorine from CCl_4. A good Hammett correlation ($r = 0.95$) was observed, consistent with both the concerted mechanism (eq 2) and with an irreversible stepwise process (eq 1, $k_2 \gg k_{-1}$). However, Tanner and co-workers[5] subsequently found an unsatisfactory Hammett correlation ($r = 0.82$), suggesting that the iodine atom transfer must involve the reversible formation of a 9−I−2 intermediate (eq 1, $k_2 \approx k_{-1}$). Unfortunately, the later workers' well-conceived attempt to generate the intermediates, measure k_2/k_{-1}, and extract the relative rates of phenylaryliodine formation (k_1/k_{Cl}) from the kinetic data served ultimately to only confuse the issue.[5b]

Sahyun and co-workers[7] detected a short-lived (<0.2 ns) absorption assigned to diphenyliodine ($Ph_2I^\bullet$) in the laser flash photolysis of diphenyliodonium iodide, and several groups have provided CIDNP evidence for diphenyliodine in sensitized diphenyliodonium photolyses.[8] However, the detection of a diphenyliodine intermediate formed by phenyl radical addition to an iodoarene has not been reported in the literature.

Recently, Scaiano and co-workers[9] found a UV absorption with a lifetime of 4.4 ± 0.3 μs in the laser flash photolysis of 1,5-diiodo-1,5-diphenylpentane that was attributed to a cyclic dibenzyliodine 9−I−2 structure. However, the much longer lifetime of the dibenzyliodine

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(1) This work was taken, in part, from the senior theses of K.B.G., R.J.T., B.M.G., and D.A.M. (a) Lake, K. B. B.S. Thesis, Purchase College, State University of New York (SUNY), 1990. (b) Taintor, R. J. B.A. Thesis, Purchase College, SUNY, 1992. (c) George, B. M. B.A. Thesis, Purchase College, SUNY, 1993. (d) Wenzel, D. A. B.A. Thesis, Purchase College, SUNY, 1993. Some of our results were presented previously: (e) Lake, K. B.; O'Donoghue, J.; Taintor, R. J.; Nalli, T. W. *Book of Abstracts,* Joint 44th Southeastern-26th Middle Atlantic Regional Meeting of the American Chemical Society, Alexandria, VA, December 1992; American Chemical Society: Washington, DC, 1992; Abstract 224. (f) Lake, K. B.; Taintor, R. J.; George, B. M.; Wenzel, D. A.; O'Donoghue, J.; Nalli, T. W. *Abtracts of Papers, Part 2,* 212th National Meeting of the American Chemical Society, Orlando, FL, Aug 25−29, 1996; American Chemical Society: Washington, DC, 1996; ORGN 366.

(2) For a recent review see; Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1237−1286.

(3) The 9−X−2 designation refers to nine formal valence electrons about a halogen atom with two ligands. See: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Algeria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7754−7759.

(4) Danen, W. C.; Saunders: D. G. *J. Am. Chem. Soc.* **1969**, *91*, 5924−5925. Also see: Danen, W. C. In *Methods in Free-Radical Chemistry*; Huyser, E. S., Ed.; Marcell Dekker: New York, 1974; Vol. 5, Chapter 1.

(5) (a) Tanner, D. D.; Reed, D. W.; Setiloane, B. P. *J. Am. Chem. Soc.* **1982**, *104*, 3917−3923. (b) Tanner, D. D.; Reed, D. W.; Setiloane, B. P. *J. Am. Chem. Soc.* **1983**, *105*, 6768.

(6) Weldon, D.; Holland, S.; Scaiano, J. C. *J. Org. Chem.* **1996**, *61*, 8544−8546.

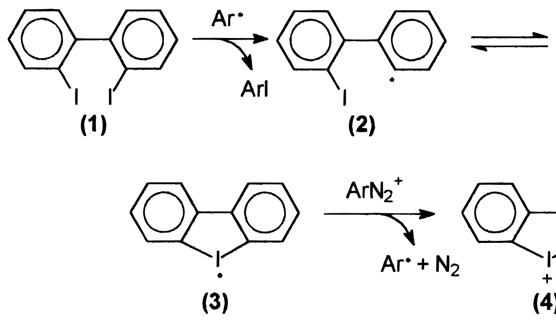
(7) Devoe, R. J.; Sahyun, M. R. V.; Serpone, N.; Sharma, D. K. *Can. J. Chem.* **1987**, *65*, 2342−2349.

(8) (a) Devoe, R. J.; Sahyun, M. R. V.; Schmidt E.; Serpone, N.; Sharma, D. K. *Can. J. Chem.* **1988**, *66*, 319−324. (b) Wang, X. Z.; Wang, E. J. *Chin. Chem. Lett.* **1994**, *5*, 831−834. (c) Eckert, G.; Goez, M.; Maiwald, B.; Mueller, U. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 1191−1198. Also see: Pappas, S. P.; Gatechair, L. R.; Jilek, J. H. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 77−84.

(9) Banks, J. T.; Garcia, H.; Miranda, M. A.; Perez-Prieto, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1995**, *117*, 5049−5054.

S0022-3263(98)00113-3 CCC: $15.00

Scheme 1



structure compared to that of diphenyliodine[7] raises the question of the applicability of these findings to the mechanism of iodine atom transfer between phenyl radicals and iodoarenes.

Bimolecular reactions of free divalent iodine radicals have not been identified in the literature. We thought that an exoergic single-electron transfer from such a radical to a suitable acceptor could be fast enough to compete with C−I bond cleavage. Because the observation of such a reaction would provide strong support for 9−I−2 intermediates in iodine atom abstractions, we set out to generate iodoaryl radical, **2**, in the presence of arenediazonium salts as one-electron acceptors (Scheme 1). We report in this paper that the 9−I−2 species, **3**, does, in fact, have a sufficient lifetime to allow it to be trapped by bimolecular electron transfer.

Results and Discussion

Visible-light irradiation of an acetonitrile solution of 2,2′-diiodobiphenyl (**1**) (0.05 M), *p*-toluenediazonium hexafluorophosphate (0.20 M), and an initiating quantity (0.1 equiv based on **1**) of the visible-light-sensitive radical source, phenylazoisobutyronitrile (PAIBN = PhN=NC-$(CH_3)_2CN$), gives biphenyleneiodonium salt (**4**, isolated as the iodide) and 4-iodotoluene (ArI) as major products (experiment 1, Table 1). Other products are 2-iodobiphenyl (**5**, PhPhI), biphenyl (PhPh), toluene (ArH), iodobenzene (PhI), bitolyls (2,4′-dimethylbiphenyl (**6**) and 3,4′-dimethylbiphenyl (**7**)), iodobitolyls (5-iodo-2,4′-dimethylbiphenyl (**8**) and 2-iodo-5,4′-dimethylbiphenyl) (**9**), and bis(4-methylphenyl)diazene (**10**) (Scheme 2).

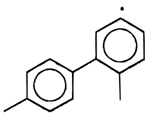
Mass balances on biphenyl-containing compounds (sum of yields of **1**, **4**, **5**, and PhPh) for experiments 1−3 of 75−80% show that most of the starting material (**1**) was accounted for by our analyses. Only trace amounts of 4-fluorotoluene were formed in the product mixtures (Table 1), showing that thermal decomposition of the diazonium hexafluorophosphate was minimal under our reaction conditions.

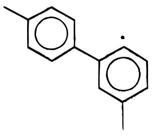
When the radical source, PAIBN, was not included in the reaction solution, the reaction was considerably slower (ca. 8 times slower based on the yield of 4-iodotoluene; compare experiments 3 and 5, Table 1). This observation, along with the formation of trace amounts of iodobenzene in the PAIBN-containing experiments, shows that the function of the azo compound is simply to initiate a free-radical-chain reaction. It does so through its photochemical conversion to phenyl radicals,[10] which abstract iodine from the starting diiodobiphenyl (**1**) to give iodobenzene and the iodoaryl radical (**2**) (eq 3).

$$\mathrm{Ph}^{\bullet} + \mathbf{1} \rightarrow \mathrm{PhI} + \mathbf{2} \qquad (3)$$

Although arenediazonium salts are known to sometimes react via phenyl cation intermediates, 4-methylacetanilide, $ArNHCOCH_3$, the ultimate product of reaction of 4-methylphenyl cation with acetonitrile,[11] was not formed in these reactions. Thus, we rule out the possible role of aryl cation chemistry in the formation of any of the observed products. Instead, the formation of 4-iodotoluene (ArI) clearly points to the presence of 4-methylphenyl radical ($Ar^{\bullet}$) intermediates in the reacting solutions.[12] Accordingly, the iodotoluene is formed chiefly by the reaction of the *p*-tolyl radical with the diiodobiphenyl reactant (**1**) (first step, Scheme 1).

The formation of the diazene (**10**), the bitolyls (**6** and **7**), and the iodobitolyls (**8** and **9**) is also consistent with the involvement of *p*-tolyl radicals, which react with the diazonium salt in the manner recently identified by Minisci and co-workers.[13] Attack on the diazonium group leads to the diazo compound (**10**) while attack on the ring of the arenediazonium salt (preferentially at the 2-position) leads, after loss of N_2 and a proton, to bitolylyl radicals (**11** and **12**), which abstract hydrogen (see later discussion) to give the observed bitolyl products (**6** and **7**) or abstract iodine from **1** to form the iodobitolyls (**8** and **9**).


(11)


(12)

The presence of free aryl radicals in the reacting solutions indicates that the arenediazonium salt undergoes a one-electron reduction to give an aryl radical and N_2.[14] In addition, the production of the iodonium salt (**4**) implicates the diaryliodine radical (**3**) as a one-electron reductant. Accordingly, we propose a single-electron transfer from the 9−I−2 structure (**3**) to the arenediazonium salt (third step, Scheme 1) as a key step in the mechanism of the reactions summarized in Table 1.[15] The 9−I−2 intermediate (**3**) is formed by cyclization of the 2-iodobiphenyl-2′-yl radical (**2**) (second step, Scheme 1). The sequence amounts to a free-radical-chain reaction

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(10) (a) Ford, M. C.; Rust, R. A. *J. Chem. Soc.* **1958**, 1297−1298. (b) Bleha, M.; Lim, D. *J. Polym. Sci., Part C* **1968**, *23*, 15−20.

(11) Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1990**, *55*, 639−647.

(12) Wassmundt, F. W.; Kiesman, W. F. *J. Org. Chem.* **1997**, *62*, 8304−8308.

(13) Minisci, F.; Coppa, F.; Fontana, F.; Pianese, G.; Zhao, L. *J. Org. Chem.* **1992**, *57*, 3929−3933.

(14) The initially formed diazenyl radical ($ArN_2^{\bullet}$) quickly fragments to give the aryl radical and N_2. For a review of single-electron transfer to arenediazonium salts to give aryl radicals, see; Galli, C. *Chem. Rev.* **1988**, *88*, 765−792.

(15) The proposed electron transfer is substantially exoergic. This is based on half-wave reduction potentials (vs SCE) reported in the literature of $E_{1/2} = -0.7$ V for diphenyliodonium salts[7]) and $E_{1/2} = +0.25$ V for *p*-toluenediazonium salts[16] corresponding to $\Delta G° = -22$ kcal/mol.

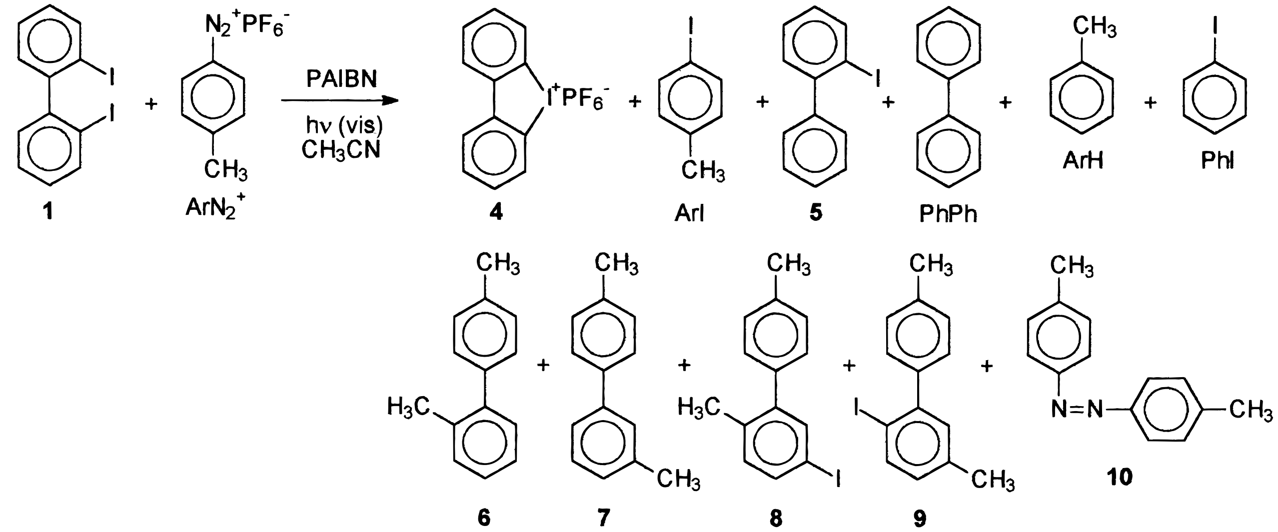
(16) Elofson, R. M.; Gadallah, F. F. *J. Org. Chem.* **1969**, *34*, 854−857.

Table 1. Reactions of 2,2′-Diiodobiphenyl (1) with *p*-Toluenediazonium Hexafluorophosphate (ArN_2^+)[a]

					GC yields[b]								
expt	[**1**], M	[ArN_2+], M	[PAIBN], mM	solvent	ArI	PhI	5	PhPh	ArH	7	ArF	**1**[c]	**4**[d]
1	0.05	0.20	6	CH_3CN	94	0.60	9.6	19	21	6.0	na	14	42
2	0.05	0.05	6	CH_3CN	6.7	0.27	0.95	nd	1.6	nd	0.07	76	0
3	0.10	0.10	6	CH_3CN	40	0.53	9.7	6.0	8.6	0.50	0.14	55	6
4	0.05	0.20	6	CD_3CN	98	0.54	2.8[f]	5.0[f]	8.8[f]	5.1[f]	0.26	7.0	na[e]
5	0.10	0.10	0	CH_3CN	5.3	nd	0.48	nd	1.1	nd	0.15	66	0

[a] Reaction solutions contained the photoinitiator, phenylazoisobutyronitrile (PAIBN), and were irradiated with a 150-W flood lamp at approximately 15 °C for 16.5 h. [b] Percent yields based on **1**; "nd" means not detected, and "na" means not analyzed. [c] Unchanged starting material. [d] Percent yield of iodonium salt, **4**, isolated as the iodide. [e] A different workup procedure was used and was unsuccessful. [f] These products showed significant deuterium incorporation by GC/MS. See Table 2.

Scheme 2



of diiodobiphenyl (**1**) with ArN_2^+ to form iodonium salt (**4**), iodoarene (ArI), and N_2 (eq 4).[17]

$$\mathbf{1} + ArN_2^+ \rightarrow \mathbf{4} + ArI + N_2 \qquad (4)$$

The formation of toluene (ArH) and 2-iodobiphenyl (**5**), the respective products of hydrogen donation to *p*-tolyl radical ($Ar^•$) and radical **2** (eqs 5 and 6), highlights a competitive pathway available to intermediate free radicals in the reaction solution. The use of acetonitrile-d_3 as solvent (experiment 4, Table 1) led to significantly decreased yields of these reduced products (compare experiment 4 to experiment 1, Table 1). Thus, acetonitrile is an important source of hydrogen in these reactions with eqs 5 and 6 being slower for CD_3CN because of the primary deuterium isotope effect.

$$Ar^• + Don{-}H \rightarrow ArH + Don^• \qquad (5)$$

$$\mathbf{2} + Don{-}H \rightarrow \mathbf{5} + Don^• \qquad (6)$$

Table 2. Deuterium Content of Products of Reaction of 1 with *p*-Toluenediazonium Salt in CD_3CN (expt 4)

product	%d[a]	product	%d[a]
ArI	−2.2 ± 5.5	3,4′-ArAr (**7**)	25.4 ± 2.7
PhI	−0.5 ± 2.8	3,4′-ArArI (**9**)	−0.3 ± 1.8
PhPhI (**5**)	18.1 ± 1.5	ArN=NAr (**10**)	4.6 ± 3.4
PhPh	38.8 ± 0.5 (32.7% d_1, 3.0% d_2)	ArF	7.6 ± 9.0
ArH	41.7 ± 0.9 (39.5% d_1, 1.1% d_2)		

[a] Deuterium incorporation calculated from relative abundances in molecular ion clusters of mass spectra averaged over the duration of GC peaks. A variety of calculation methods was used, and the averages of those most appropriate for each compound are given in the table. Errors given are 1 standard deviation of the mean.

The mass spectra of the reduction products in CD_3CN revealed significant deuterium incorporations of 42% for toluene and 18% for **5** (Table 2). Assuming $k_H/k_D \approx 5$ leads to the conclusion that ca. 80% of the toluene formed in the nondeuteriated solvent (experiment 1) resulted from the reaction of tolyl radicals with the solvent. Therefore, it can generally be concluded that the bulk of hydrogen donation observed in the nondeuteriated solvent was from the solvent molecules. In addition, the 25% deuterium incorporation observed for the 3,4′-biaryl product (**7**) in experiment 4 demonstrates its formation from the 5,4′-dimethylbiphenyl-2-yl radical (**12**), as discussed previously.

The rate constant for the reaction of phenyl radicals with acetonitrile has been reported in the literature, $k_{MeCN} = 1.0 \times 10^5\ M^{-1}\ s^{-1}$.[18] We were able to use a competitive method to measure the rate of reaction of

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(17) We also subjected 2,2′-diiododiphenylmethane (**13**) to reaction conditions which led to the transformation of **1** to **4** (i.e. same conditions as experiment 1, Table 1) but, interestingly, found no evidence for the formation of the six-member ring iodonium salt analogous to **4**. This may be due to a failure of the 2-iododiphenylmethane-2′-yl radical to cyclize or to a failure of the electron transfer from the cyclized diaryliodine to the diazonium salt. The first possibility seems more likely because abstraction of the doubly benzylic hydrogens of the diiodide (**13**) is an additional competitive pathway available to the uncyclized iodoaryl radical in this system. Another factor may be that **4** is more stable than the corresponding six-member ring iodonium salt because of the potential participation of the iodine atom in the delocalized bonding of a 14-electron aromatic ring system. We thank a reviewer for pointing out the potential aromaticity of **4**.

Table 3. Reactions of 2,2′-Diiodobiphenyl (1) with *p*-Nitrobenzenediazonium Hexafluorophosphate ($Ar'N_2^+$).[a]

					GC yields[b]							
expt	[**1**], M	[$Ar'N_2^+$], M	[PAIBN], mM	conditions	Ar′I	PhI	5	PhPh	Ar′H	PAIBN[c]	**1**[c]	4[d]
6	0.05	0.10	6	vis,[e] 17 h	74	0.1	2.6	0.9	28	1.7	21	90
7	0.05	0.10	0	vis,[e] 17 h	62	nd	2.4	0.4	27	nd	21	100
8	0.05	0.05	0	$h\nu$(UV),[f] 2 h	40	nd	3.8	0.7	15	nd	43	15
9	0.05	0.05	0	dark, 48 h	nd	nd	nd	nd	nd	nd	107	na

[a] Acetonitrile solutions. [b] Percent yields based on **1**; "nd" means not detected, and "na" means not analyzed. [c] Unchanged starting material. [d] Percent yield of iodonium salt, **4**, isolated as the iodide. [e] Reaction mixture was irradiated with a 500-W halogen flood lamp at 27 °C. [f] Irradiation with a 450-W Hg arc.

phenyl radicals with 2,2′-diiodobiphenyl (**1**), $k_{abs} = 1.25 \times 10^8\ M^{-1}\ s^{-1}$.[19] Assuming tolyl radicals undergo a simple competition between iodine abstraction from **1** and hydrogen abstraction from CH_3CN (and using $[CH_3CN]_{neat} = 19$ M and [**1**] = 0.05 M), one could predict a product ratio of [ArI]:[ArH] ≈ 3.3 for experiments 1 and 2.[20] The observed product ratios, experiment 1 [ArI]:[ArH] = 4.5 and experiment 2 [ArI]:[ArH] = 4.1 agree well with the predicted value, lending further support for the role of *p*-tolyl radicals in these reactions and for the role of CH_3CN as the primary hydrogen donor.

As the reaction proceeds and the concentration of the side product, 2-iodobiphenyl (**5**), builds up, it begins to serve as an iodine donor[21] with intermediate radicals (i.e. $Ar^{\bullet}$ (eq 7), $Ph^{\bullet}$, **11**, **12**) forming the biphenyl-2-yl radical

$$Ar^{\bullet} + \mathbf{5a} \rightarrow ArI + Ph{-}Ph^{\bullet} \qquad (7)$$

$$Ph\text{-}Ph^{\bullet} + CH_3CN \rightarrow PhPh + {}^{\bullet}CH_2CN \qquad (8)$$

($Ph{-}Ph^{\bullet}$), which abstracts hydrogen (eq 8) to form biphenyl. Accordingly, the biphenyl product formed when CD_3CN was the solvent (experiment 4, Table 1) was 33% d_1 and 3% d_2 (Table 2), exactly the statistical distribution expected for sequential deuteriation steps proceeding with 18% efficiency (the percent deuteriation of 2-iodobiphenyl (**5**)).

We finally note that *p*-nitrobenzenediazonium hexafluorophosphate ($Ar'N_2^+$) undergoes a radical-chain reaction with **1** in a fashion similar to the methyl-substituted diazonium salt whose reactions have been the main focus of this paper (Table 3). Moreover, the nitrodiazonium salt gives a much cleaner 9−I−2 trapping reaction, with high yields of cyclic iodonium salt (**4**) and only trace amounts of the reduction products, biphenyl and 2-iodobiphenyl (**5**) (experiments 6 and 7, Table 3). In this case the presence of the photoinitiator (PAIBN) does not affect the product yields (compare experiment 6 to experiment 7, Table 3), presumably because of the ability of the diazonium salt to absorb visible light. The low yield of reduced products might reflect a faster electron transfer from the 9−I−2 structure (**3**) to the *p*-nitrobenzenediazonium salt than to *p*-toluenediazonium salt.[22] Presumably, radicals **2** and **3** rapidly interconvert, and the relative yields of reduced biphenyls and the 9−I−2 trapping product (**4**) are, therefore, simply determined by the relative rates of hydrogen abstraction by **2** and electron transfer from **3** to diazonium salt (Curtin−Hammett Principle).

Conclusion

The observations reported in this paper are consistent with the central role of a redox radical chain reaction of diiodobiphenyl (**1**) with arenediazonium salts as represented in Scheme 1. By far, the most important feature of this chemistry is the ability of the cyclic diaryliodine species (**3**) to act as a single-electron reductant of the diazonium salts. This conclusion means that diaryliodine intermediates formed by the addition of phenyl radicals to iodoarenes can have sufficient lifetimes to be trapped by bimolecular processes. Hence, our work provides support for the role of diaryliodine intermediates in iodine atom transfer reactions.

Experimental Section

^{1}H NMR spectral data are reported in parts per million relative to tetramethylsilane as an internal standard. Gas chromatography was carried out with helium as the carrier gas and the column temperature ramped from 60 to 300 °C at a rate of 10 °C/min. For quantitation of reaction solutions, flame ionization detection and split injection mode were used. The column was a standard nonpolar (HP-1 or DB-1) capillary column, and peak areas were corrected using response factors generated from mixtures of pure compounds. GC-MS analysis used an HP Model 5890/5971 system, splitless injection mode, and a 25-m × 0.32-mm HP-5 column. Melting points are uncorrected.

All compounds not described below were obtained from commercial sources and not purified. *p*-Toluenediazonium hexafluorophosphate[23] and phenylazoisobutyronitrile (PAIBN)[10] were prepared by literature procedures.

2,2′-Diiodobiphenyl (**1**) and 2,2′-diiododiphenylmethane (**13**) were prepared by thermolysis of the corresponding cyclic iodonium iodides[24] and were purified to >99.9% GC purity by recrystallization from ethanol.

Compound 1: Mp 106.3−106.5 °C (lit. mp 109−110 °C).[25] ^{1}H NMR (60 MHz, CCl_4): δ 7.9 (d, 2H), 7.2 (m, 6H). MS: *m*/*z* 406, 279, 152, 127.

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(18) Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609−3614.

(19) This was accomplished by allowing phenyl radicals from the visible-light photolysis of PAIBN to react with **1** in CCl_4 solution and measuring the product ratio, [PhI]:[PhCl]. The relative rate constant that we measured, $k_{abs}/k_{Cl} = 59$ at 20 °C, together with the value for k_{Cl} recently reported by Scaiano and co-workers[6] ($k_{Cl} = 2.3 \times 10^6\ M^{-1}\ s^{-1}$), gives $k_{abs} = 1.25 \times 10^8\ M^{-1}\ s^{-1}$.

(20) We also assumed that rate constants for tolyl radical reactions are essentially the same as those for the corresponding phenyl radical reactions; see: Pryor, W. A.; Echols, J. T., Jr.; Smith, K. *J. Am. Chem. Soc.* **1966**, *88*, 1189−1199.

(21) We also measured k_{abs}/k_{Cl} for this iodoarene. The value obtained, $k_{abs}/k_{Cl} = 41$, corresponds to $k_{abs} = 8.0 \times 10^7\ M^{-1}\ s^{-1}$ at 20 °C.

(22) This is not surprising since the electron transfer to *p*-nitrobenzenediazonium salt is 5 kcal/mol more exoergic than electron transfer to *p*-toluenediazonium salt. This is based on the half-wave reduction potential (vs SCE) reported in the literature of +0.45 V for *p*-nitrobenzenediazonium salts[16] corresponding to $\Delta G° \approx -27$ kcal/mol. (See ref 15.)

(23) Rutherford, K.; Redmond, W.; Rigamonti, J. *J. Org. Chem.* **1961**, *26*, 5149−5152.

(24) Sato, T.; Shimizu, K.; Moriya, H. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1537−1539.

(25) Sandin, R. B. *J. Org. Chem.* **1969**, *34*, 456−457.

Compound 13: mp 79−81 °C (lit. mp 79−80 °C).[26] ^{1}H NMR (60 MHz, $CDCl_3$): δ 8.0 (d, 2H), 7.4 (m, 6H), 4.2 (s, 2H). MS: *m*/*z* 420, 293, 166, 165.

The iodonium iodide precursors to **1** and **13** were prepared from 2-iodobiphenyl (**5**) and 2-iododiphenylmethane (**14**) respectively using a literature procedure.[27] Iodoarenes **5** and **14** were prepared by diazotization of the corresponding aminoarenes followed by KI treatment. Hexane solutions of the crude iodoarenes were washed with 3 M HCl(aq) and 6 M NaOH(aq), the solvent was removed, and the residue was vacuum distilled.

Compound 5: Bp 110 °C (0.25 Torr) (lit. bp 125−126 °C (1 Torr),[28] 108−115 °C (0.8 Torr)).[29] ^{1}H NMR (60 MHz, CH_2Cl_2): δ 8.4 (d, 1H, *J* = 7 Hz), 7.0−8.0 (m, 8H). MS: *m*/*z* 280, 153, 152, 127.

Compound 14: bp 94−114 °C (0.1 Torr) (lit. bp 182 °C (11 Torr)).[27] ^{1}H NMR (60 MHz, $CDCl_3$): δ 7.8 (dd, 1H, *J* = 8 Hz, *J*′ ≈ 1 Hz), 6.8−7.6 (m, 8H), 4.3 (s, 2H). MS: *m*/*z* 294, 167, 165, 152, 127.

General Experimental Procedures. Dry Pyrex tubes sealed with rubber septa were used as reaction vessels. Reaction tubes were placed inside a Pyrex circulating-water cooling jacket and placed 1.5 cm from a 150-W incandescent flood lamp (Table 1) or 6 cm from a 500-W halogen lamp (Table 3). After irradiation, solutions were poured into water and extracted with hexane. Octadecane internal standard was added to the extracts, which were then dried and GC analyzed.

The aqueous layers were treated with KI(aq) or NaI(aq) in order to precipitate the product iodonium salt (**4**) as the iodide. The solid was washed thoroughly with acetone and air-dried: mp 208 °C (dec.) (lit. mp 210 °C (dec.),[24] 215 °C (dec.)[30]). ^{1}H NMR (270 MHz, Me_2SO-d_6): δ 8.47 (d, 2H, *J* = 9 Hz), 8.30 (d, 2H, *J* = 8.5 Hz), 7.85 (t, 2H, *J* = 8 Hz), 7.70 (t, 2H, *J* = 8 Hz). The thermal decomposition of the solid gave 2,2′-diiodobiphenyl as the only product detectable by GC-MS.[24]

Acknowledgment. We thank Mr. John O'Donoghue for the preparation of PAIBN. We also thank Dr. Jack A. Kampmeier for helpful discussions and encouragement. This research was supported, in part, by Ciba-Geigy Undergraduate Research Awards to K.B.G., R.J.T., B.M.G., and D.A.M.

JO980113P

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