Phosphoranyl Radicals as Reducing Agents: $S_{RN}1$ Chains with Onium Salts and Neutral Nucleophiles[1]

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Redox radical chain reactions of trivalent organophosphorus compounds (PZ_3) with diaryliodonium (Ar_2I^+) and triarylsulfonium (Ar_3S^+) salts to give arylphosphonium (ArP^+Z_3) salts and iodoarenes (ArI) or diaryl sulfides (Ar_2S) are reported. The key propagation step in these $S_{RN}1$ reactions is a single-electron reduction of the onium salts by intermediate phosphoranyl radicals ($Ar\dot{P}Z_3$). The observation of competitions between solvent molecules and phosphine establishes the intermediacy of free aryl radicals and allows estimates of rate constants for addition of *p*-tolyl radicals to triphenylphosphine ($k \approx 3 \times 10^8$ M^{-1} s^{-1}) and to trimethyl phosphite ($k \approx 2 \times 10^8$ M^{-1} s^{-1}). The intermediate phosphoranyl radicals can also partition between competitive reaction pathways; the aryltributylphosphoranyl radical, $Ar\dot{P}Bu_3$, for example, partitions between unimolecular α-cleavage of butyl radical and chain-propagating electron transfer to diaryliodonium salt. The relative amounts of these two pathways allows an estimate of the rate constant for electron transfer, $k_{SET} \approx 4 \times 10^9$ M^{-1} s^{-1}.

Phosphoranyl radicals ($Z_4P^{\bullet}$) are well-known species, often characterizable by ESR spectroscopy.[2] Most of the work on the reactions of phosphoranyl radicals has focused on the unimolecular pathways for α- and β-scission.[3] However, some phosphoranyl radicals have sufficient lifetimes to permit bimolecular reactions in solution; a few radical–radical[4] and radical–molecule[5] reactions have been recognized. Phosphoranyl radicals have occasionally been generated by reduction of phosphonium cations,[6] but the reverse reaction (eq 1) has received little attention and is not even mentioned in several recent and otherwise

$$Z_4P^{\bullet} \rightarrow Z_4P^+ + e^- \tag{1}$$

comprehensive reviews.[2a,b,d] Nevertheless, several reactions which proceed through an electron-transfer step of exactly this type have been reported in the literature.[7–9] In addition, we have found that certain phosphoranyl radicals are good reducing agents; several examples are reported in this paper.

The photoinitiated arylation of triphenylphosphine by diaryliodonium salts was reported by Reutov and co-workers in 1965.[9] Although the authors were not certain about the arylating species ($Ar_2I^{\bullet}$ or $Ar^{\bullet}$) they were quite clear about the radical chain nature of the reaction and the role of phosphoranyl radicals as one-electron reductants.

Results and Discussion

Di-*p*-tolyliodonium hexafluorophosphate (1) reacts rapidly with triphenylphosphine in acetone-d_6 or acetonitrile-d_3 (Table I) in a reaction stimulated by irradiation at 313 nm (expt 1, Table I) or, more simply, by irradiation with visible light from a 200-W floodlamp (expts 2, 3, Table I) to give *p*-tolyltriphenylphosphonium salt (2) and 4-iodotoluene (3). Although the reaction of iodonium salt with phosphine can be photostimulated, the fundamental process is a free-radical chain reaction since it is also started by the decomposition of di-*tert*-butyl peroxalate (DBPO) at room temperature (expt 4, Table I). When the reaction is initiated by visible light or DBPO, 2 and 3 are formed in a 1:1 ratio throughout the course of the reaction. When shorter wavelength (313 nm) light is used, 2 is formed at

(1) Results presented, in part, at the 203rd National Meeting of the American Chemical Society, San Francisco, CA, April 1992 (Abstract: Kampmeier, J. A.; Nalli, T. W. *Book of Abstracts*, ORGN 319).

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(3) Reference 2a and references therein. See especially (a) Watts, G. B.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* 1972, *94*, 8784–8789. (b) Roberts, B. P.; Scaiano, J. C. *J. Chem. Soc., Perkin Trans. 2* 1981, 905–911. (c) Cooper, J. W.; Roberts, B. P. *Ibid.* 1976, 808–813. (d) Griller, D.; Ingold, K. U.; Patterson, L. K.; Scaiano, J. C.; Small, R. D., Jr. *J. Am. Chem. Soc.* 1979, *101*, 3780–3785.

(4) Reference 3a,c. Also see: (a) Davidson, R. S. *Tetrahedron* 1969, *25*, 3383–3388. (b) Bentrude, W. G. In *Organic Free Radicals*; Pryor, W. A., Ed.; ACS Symposium Series No. 69; American Chemical Society: Washington, DC, 1978; Chapter 20. (c) Bentrude, W. G. *Phosphorus Sulfur* 1977, *3*, 109–130. (d) Howard, J. A.; Tait, J. C. *Can. J. Chem.* 1978, *56*, 2163–2166. (e) Griller, D.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* 1973, 1339–1342. (f) Dennis, R. W.; Roberts, B. P. *Ibid.* 1975, 140–152. (g) Griller, D.; Roberts, B. P. *Ibid.* 1973, 1416–1421.

(5) References 3a and 4d,g. Also see: (a) Mayo, F. R.; Durham, L. J.; Griggs, K. S. *J. Am. Chem. Soc.* 1963, *85*, 3156–3164. (b) Flurry, R. L. Jr.; Boozer, C. E. *J. Org. Chem.* 1966, *31*, 2076–2083. (c) Davies, A. G.; Griller, D.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* 1972, 993–998. (d) Tordo, P.; Boyer, M.; Friedmann, A.; Santero, O.; Pujol, L. *J. Phys. Chem.* 1978, *82*, 1742–1744. (e) Griller, D.; Cooper, J. W.; Ingold, K. U. *J. Am. Chem. Soc.* 1975, *97*, 4269–4275. (f) Grechkin, N. P.; Gubanova, G. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1970, 2803–2804. (g) Wittig, G.; Rieber, M. *Liebigs Ann. Chem.* 1949, *562*, 187–192. (h) Wittig, G.; Geissler, G. *Ibid.* 1953, *580*, 44–57. (i) Razuvaev, G. A.; Osanova, N. A. *Dokl. Akad. Nauk SSSR* 1955, *104*, 552–554. (j) Razuvaev, G. A.; Osanova, N. A. *Zh. Obshch. Khim.* 1956, *26*, 2531–2537. (k) Kawashima, T.; Bentrude, W. G. *J. Am. Chem. Soc.* 1979, *101*, 3981–3982. (l) Bentrude, W. G.; Kawashima, T.; Keys, B. A.; Garroussian, M.; Heide, W.; Wedegaertner, D. A. *Ibid.* 1987, *109*, 1227–1235.

(6) (a) Horner, L.; Fuchs, H.; Winkler, H.; Rapp, A. *Tetrahedron Lett.* 1963, 965–967. (b) Horner, L.; Haufe, J. *Chem. Ber.* 1968, *101*, 2903–2920. (c) Horner, L.; Mentrup, A. *Liebigs Ann. Chem.* 1961, *646*, 65–77. (d) Saveant, J. M.; Binh, S. K. *J. Org. Chem.* 1977, *42*, 1242–1248.

(7) (a) Kamai, G.; Kharrasova, F. M. *Zh. Obshch. Khim.* 1957, *27*, 953–960. (b) Ramirez, F.; McKelvie, N. *J. Am. Chem. Soc.* 1957, *79*, 5829–5830. (c) Griffin, C. E. *Chem. Ind.* 1958, 415. (d) Cadogan, J. I. G.; Foster, W. R. *J. Chem. Soc.* 1961, 3071–3076.

(8) Plumb, J. R.; Obrycki, R.; Griffin, C. E. *J. Org. Chem.* 1966, *31*, 2455–2458.

(9) (a) Ptitsyna, O. A.; Pudeeva, M. E.; Reutov, O. A. *Dokl. Akad. Nauk SSSR* 1965, *165*, 582–585. (b) Ptitsyna, O. A.; Pudeeva, M. E.; Bel'kovich, N. A.; Reutov, O. A. *Ibid.* 1965, *163*, 383–385. (c) Ptitsyna, O. A.; Pudeeva, M. E.; Reutov, O. A. *Ibid.* 1966, *168*, 595–598; (d) *Ibid.* 1965, *165*, 838–841.

Table I. Reactions of Di-*p*-tolyliodonium Hexafluorophosphate (1) with Triphenylphosphine[a]

expt	solvent	[1], M	[PPh₃], equiv	method	time, min	yields[b] (%) 2	3	TolD	% conv[c,b]
1	CD₃COCD₃	0.02	8	UV[d]	10	58	42	–	97
					23	60	40	–	99
2	CD₃CN	0.08	5	vis[e]	30	50	50	–	95
3	CD₃COCD₃	0.02	6.5	vis[e]	45	50	50	–	85
4	CD₃COCD₃	0.04	4	DBPO[f]	9	51	49	–	49
					14	51	49	–	64
					32	52	48	–	84
5	CDCl₃	0.05	3	DBPO[f]	4	34	50	16	22
					12	36	49	14	33
					45	39	50	12	39
6	CDCl₃	0.02	3	vis[e]	20	19	50	31	24
7	CDCl₃	0.02	21	vis[e]	20	44	48	7	49
8	THF-d₈	0.02	3.5	UV[d]	1.5	36	51	13	61
9	THF-d₈	0.03	none	UV[d]	1.5	–	–	–	<2[g]

[a] Reactions run at room temperature in NMR tubes. [b] Deduced from ¹H NMR integrals of resonances due to *p*-Me protons. A dash means no peak was detected. [c] Percent conversion of 1 to products. [d] Photolysis at 313 nm. [e] Photolysis with a 200-W flood lamp. [f] Di-*tert*-butyl peroxalate (DBPO) was used as an initiator. Reaction proceeded in the NMR probe in the dark. [g] Estimated limit of detection of 3.
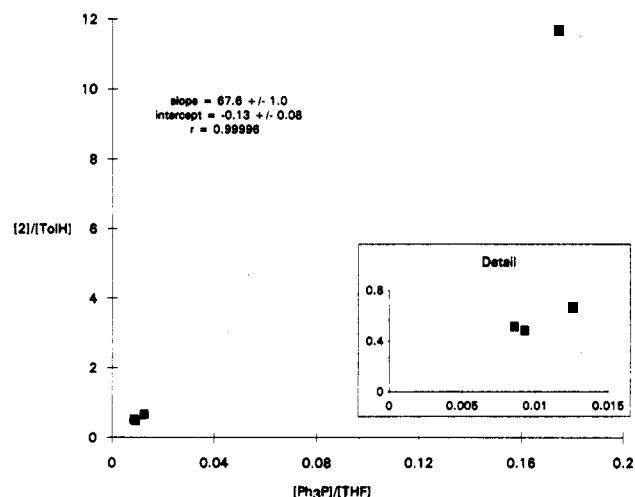

Figure 1. Product ratio [2]/[TolH] vs reactant ratio [Ph₃P]/[THF].

the expense of 3, reflecting secondary photolysis of iodotoluene (3) under the reaction conditions.
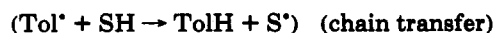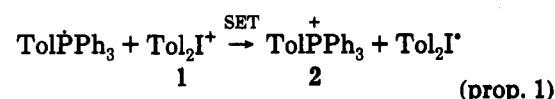
Iodonium salt also reacts with triphenylphosphine in better hydrogen-donor solvents such as chloroform-*d* (expts 5-7, Table I) or tetrahydrofuran-d₈ (expt 8, Table I) but the products are now 2, 3, and 4-deuteriotoluene (TolD). The sum of the yields of deuteriotoluene and 2 equals the yield of 4-iodotoluene (3), and the ratio [2]:[TolD] increases with increasing triphenylphosphine concentration. The phosphonium salt and deuteriotoluene are, therefore, derived from a common, free aryl radical intermediate that is captured competitively by phosphine to give 2 or by solvent to give deuteriotoluene. Direct arylation of phosphine by diaryliodyl radical (Ar₂I·) is ruled out because the competitive dissociation of this species should not be affected by the nature (i.e., H-donating ability) of the solvent. When the reaction was carried out in THF/acetone-d₆ mixtures, the ratio of phosphonium salt to toluene formed ([2]:[TolH]) predictably increased linearly with increasing [Ph₃P]:[THF] (Figure 1). By using the reaction of phenyl radical with THF as a kinetic reference point (k_{THF} = 5 × 10⁶ M⁻¹ s⁻¹ at 298 K),[10] a rate constant for addition of tolyl radical to triphenylphosphine (k_{add}) of ca. 3 × 10⁸ M⁻¹ s⁻¹ can be estimated from the slope of Figure 1.

The reaction of iodonium salt (0.02 M) with triphenylphosphine (0.16 M) in acetone-d₆ is astonishingly fast.

When the reaction is initiated by irradiation at 313 nm, 97% of the iodonium salt 1 is consumed in 10 min (expt 1, Table I). Iodonium salt is also converted to iodoarene and arene in a photoinitiated reaction in THF-d₈ in the absence of phosphine. This is, in contrast, a relatively slow, short redox chain reaction for which we have measured a quantum yield of 14 at 313 nm.[11] When 3.5 equiv of triphenylphosphine is added to an otherwise identical reaction mixture (expts 8, 9, Table I), the iodonium salt is consumed at least 30 times faster than in THF-d₈ alone. Thus, the phosphine chain (in THF) is much longer than the THF chain and must have a quantum yield of on the order of 100 or more. Because some of the intermediate tolyl radicals are diverted to reaction with the solvent (resulting in the formation of toluene) and, hence, do not propagate the phosphine chain in this solvent, the chain must be even longer in a solvent such as acetone.

All of these observations, along with those of the earlier workers, are adequately described by a radical-initiated chain reaction involving tolyl and phosphoranyl radical intermediates (Scheme I). The key propagation step of

Scheme I

$$\text{TolPPh}_3 + \text{Tol}_2\text{I}^+ \xrightarrow{\text{SET}} \text{Tol}\overset{+}{\text{P}}\text{Ph}_3 + \text{Tol}_2\text{I}^\bullet$$

1   2   (prop. 1)

$$\text{Tol}_2\text{I}^\bullet \rightarrow \text{TolI} + \text{Tol}^\bullet$$
     3   (prop. 2)

$$\text{Tol}^\bullet + \text{PPh}_3 \rightarrow \text{Tol}\overset{\bullet}{\text{P}}\text{Ph}_3$$
      (prop. 3)

$$(\text{Tol}^\bullet + \text{SH} \rightarrow \text{TolH} + \text{S}^\bullet) \quad \text{(chain transfer)}$$

$$\text{SH} \equiv \text{solvent}$$

$$\text{Tol}^\bullet \equiv \text{4-methylphenyl radical}$$

the chain is an electron-transfer step in which the phosphoranyl radical reduces the iodonium salt (eq prop.

(10) (a) Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* 1983, *105*, 3609-3614. We also assumed that the rate constant for the reaction of tolyl radicals with THF is essentially the same as that for the reaction of phenyl radical with THF; see: (b) Pryor, W. A.; Echols, J. T. Jr.; Smith, K. *J. Am. Chem. Soc.* 1966, *88*, 1189-1199.

(11) Nalli, T. W. Ph.D. Dissertation, University of Rochester, 1987.

Table II. Reactions of Unsymmetrical Diaryliodonium Salts, ArI⁺Ar′, with Triphenylphosphine[a]

expt	Ar	Ar′	solvent	time, min	% conv[b,c]	yields[b] (%)				$k_{Ar'}/k_{Ar'}$ [d]
						ArI	Ar′I	ArP⁺Ph₃	Ar′P⁺Ph₃	
10[f]	Tol[e]	Ph	CD₃COCD₃	20	100	54	na	46	na	1.17
11[f]	Tol	Ph	CD₃COCD₃	10–40	50–90	50	na	50	na	1.00 ± 0.04
12	Tol	Ph	CD₃CN	5–30	20–80	54	na	46	na	1.17 ± 0.04
13	An[g]	Ph	CD₃COCD₃	2–23	20–95	62	na	38	na	1.65 ● 0.04
14[f]	An	Ph	CD₃COCD₃	3–50	45–95	63	na	37	na	1.68 ● 0.09
15	An	Ph	CD₃CN	0–30	15–100	60	na	40	na	1.53 ± 0.05
16[h]	An	Tol	CDCl₃	150	100	na	na	44	56	1.27
17	An	Tol	CD₃COCD₃	30–90	75–100	28	23	21	28	1.26 ± 0.06
18	An	Tol	CD₃CN	15–30	60–100	27	23	22	28	1.24 ± 0.07
19	An	Tol	THF mix[i]	30–1800	4–67	na	48	na	52	1.05 ± 0.21
20[j]	An	Tol	THF mix[i]	30–1800	34–96	na	43	na	57	1.35 ± 0.17

[a] The hexafluorophosphate salts were used unless otherwise noted. Initial iodonium salt concentrations, [ArI⁺Ar′], ranged between 0.01 and 0.1 M with no discernable effect on the results. Initial triphenylphosphine concentrations were in the range 2–9 equiv based on [ArI⁺Ar′]. Reaction solutions were irradiated with a 200-W flood lamp at room temperature unless otherwise noted. [b] Relative % yields and conversions were deduced from ¹H NMR integrals of resonances due to p-Me or p-OMe protons; "na" ≡ not analyzed. Where a range of conversions is indicated several measurements were made throughout the progress of the reaction and the results averaged. [c] Conversion of ArI⁺Ar′ to products. For experiments where only two of the four products were analyzed it was assumed that the yields of ArI and Ar′P⁺Ph₃ were equal. Similarly, the yields of Ar′I and ArP⁺Ph₃ were assumed equal. [d] Errors given are the standard error of the mean at the 95% confidence level. [e] Tol ≡ 4-methylphenyl. [f] Di-tert-butyl peroxalate (DBPO) was used as an initiator. Reaction proceeded in the NMR probe in the dark. [g] An ≡ 4-methoxyphenyl. [h] The iodonium bromide salt was used. [i] 3.6 M THF in CD₃COCD₃. [j] Phenylazoisobutyronitrile (PAIBN) was used as a photoinitiator.

Table III. Reactions of Sulfonium Salts (TolS⁺Ar₂)[a] with Trivalent Phosphorus Compounds (PZ₃)[b]

expt	Ar	Z	[TolS⁺Ar₂], M	[PZ₃], equiv	time, min	$\dfrac{[TolSAr]^{c}}{[TolP^{+}Z_{3}]}$	$\dfrac{[TolSPh]^{d}}{[Ph_{2}S]}$	% conv[c,e]
21[f]	Tol	Ph	0.04	3.0	290	0.8		17
22	Ph	Ph	0.03	8.5	110	3.0		42
23[g]	Ph	Ph	0.03	8.5	6	3.35	3.0	100
24[g]	Ph	OMe	0.03	24	44	2.6[h]		52
25[g,i]	Ph	OMe	0.03	88	43	2.7[h]	2.7	80

[a] The hexafluorophosphate salts were used. [b] Acetone-d₆ solutions of the reactants were photolyzed at room temperature with a 200-W flood lamp unless otherwise noted. [c] Deduced from ¹H NMR integrals of resonances due to p-Me protons. [d] Ratio measured by GC. [e] Percent conversion of TolS⁺Ar₂ to products. [f] Simultaneous photolysis of an otherwise identical solution containing iodonium salt (1) instead of sulfonium salt resulted in 97% conversion of 1 to products. [g] Phenylazoisobutyronitrile (PAIBN) was used as a photoinitiator. [h] TolP⁺Z₃ was analyzed as TolP(O)(OMe)₂. [i] CH₃CN was used as solvent.

1). Initiation, whether accomplished photochemically or by thermal decomposition of DBPO, presumably involves addition of a radical (either an aryl radical from photolysis of the iodonium salt or a *tert*-butoxy radical from DBPO[12]) to the phosphine to form a phosphoranyl radical which reduces iodonium salt and starts the chain. The overall process is a previously unrecognized example of the well-known aromatic S_RN1 reaction[13] wherein both the nucleophile and leaving group are neutral (unlike the usual case where both are anionic).

We used this reaction of diaryliodonium salt with triphenylphosphine as a means of probing the effect of substituents on the relative rates of aryl radical departure from the divalent iodine intermediate. The results of reaction employing the unsymmetrical hexafluorophosphate salts of p-tolylphenyliodonium (TolI⁺Ph), p-anisylphenyliodonium (AnI⁺Ph), and p-anisyl-p-tolyliodonium (AnI⁺Tol) cations are given in Table II. The observed cleavage ratios, $k_{Ar'}/k_{Ar'}$, were independent of solvent (acetone, acetonitrile, chloroform), method of initiation (DBPO vs photolysis, expts 11, 14 vs 10, 13, Table II),

counteranion (Br⁻ vs PF₆⁻, expts 16 vs 17, 18, Table II), and extent of reaction. In addition, the chain reaction of iodonium with THF gave the same result for $k_{Tol'}/k_{An'}$ as the phosphine chain (expts 19, 20 vs 17, 18, Table II). These observations, along with the fact that the substituent effect is small,[14] are consistent with a reductive cleavage and rule out mechanisms involving nucleophilic attack on iodonium salt. The results, $k_{Ph'}/k_{Tol'} \approx 1.15$, $k_{Ph'}/k_{An'} \approx 1.5$, $k_{Tol'}/k_{An'} \approx 1.3$, obey the commutative law indicating the absence of secondary substituent effects (effects of Ar substituents on cleavage of Ar′·). Finally, the ratios obtained for the tolylphenyl- and anisylphenyliodonium salts agree closely with the results of Singh and Khanna[16] who reduced the iodonium bromides with 2-nitropropanoate anion in methanol.[17]

In similar fashion, the tetraarylphosphoranyl radical reduces triarylsulfonium salts to give diaryl sulfide and

(12) The addition of *tert*-butoxy radical to triphenylphosphine is a fast reaction ($k = 1.9 \times 10^9$ M⁻¹ s⁻¹ at 295 K).[3d] The resultant *tert*-butoxytriphenylphosphoranyl radical undergoes β-cleavage as the chief mode of unimolecular decomposition with a rate constant of only 1.1×10^3 s⁻¹ at 295 K.[3d] Given our estimate of the rate constant for electron transfer from phosphoranyl to iodonium salt, $k_{SET} \approx 4 \times 10^9$ M⁻¹ s⁻¹ (see later discussion), it is likely that electron transfer to iodonium salt from the *tert*-butoxytriphenylphosphoranyl radical competes very well with the unimolecular fragmentation.

(13) For reviews see: (a) Rossi, R. A.; de Rossi, R. H. *ACS Monographs* 1983, No. 178. (b) Bunnett, J. F. *Acc. Chem. Res.* 1978, *11*, 413–420.

(14) The nonselectivity in the direction of the reductive cleavage obviously has synthetic implications. An example may be the recently reported "unexpected" reaction of an alkenylphenyliodonium salt with triphenylphosphine.[15] The reaction gave alkenyl iodide and tetraphenylphosphonium salt in addition to the expected products, iodobenzene and alkenyltriphenylphosphonium salt. The authors proposed a mechanism involving attack by phosphine on iodine to give a 10-I-3 intermediate followed by competitive reductive elimination reactions. Having experience with the photoinitiated reaction of phosphine with diaryliodonium salts (the reactions run even in diffuse room light), it appears likely to us that the reaction was actually an S_RN1 reaction of the type reported here.

(15) Zefirov, N. S.; Koz'min, A. S.; Kaumov, T.; Potekhin, K. A.; Sorokin, V. D.; Brel, V. K.; Abramkin, E. V.; Struchkov, Y. T.; Zhdankin, V. V.; Stang, P. J. *J. Org. Chem.* 1992, *57*, 2433–2437.

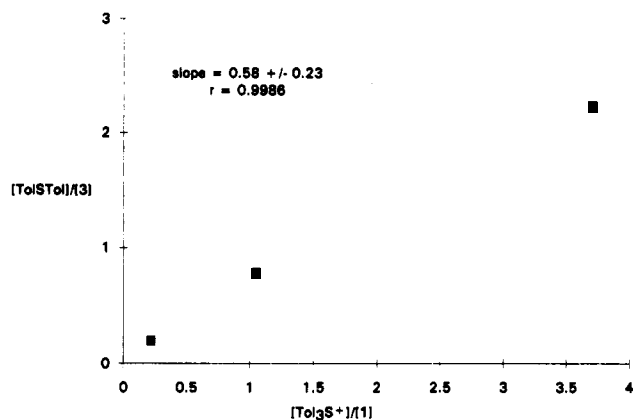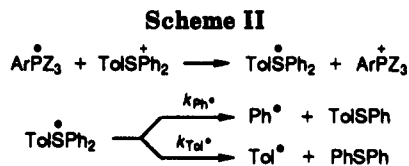(16) Singh, P. R.; Khanna, R. K. *Tetrahedron Lett.* 1982, *23*, 5355–5358.

Scheme II

$$Ar\overset{\bullet}{P}Z_3 + Tol\overset{+}{S}Ph_2 \longrightarrow Tol\overset{\bullet}{S}Ph_2 + Ar\overset{+}{P}Z_3$$

$$Tol\overset{\bullet}{S}Ph_2 \underset{k_{Tol^\bullet}}{\overset{k_{Ph^\bullet}}{\longrightarrow}} \begin{cases} Ph^\bullet + TolSPh \\ Tol^\bullet + PhSPh \end{cases}$$

Figure 2. Product ratio [Tol₂S]/[3] vs reactant ratio [Tol₃S⁺]/[1].

aryl radical (Table III). In side by side experiments, ditolyliodonium (1) and tri-*p*-tolylsulfonium hexafluorophosphates were reacted with triphenylphosphine in acetone-d_6 for 290 min under illumination with visible light to give phosphonium salt 2 in NMR yields of 97% and 17%, respectively (expt 21 and footnote f, Table III). This difference in rate is apparently due to differences in the photoinitiation steps since triphenylphosphine does not form an observable charge-transfer complex with the sulfonium salt in acetone[11] like it does with iodonium salt.[9d] In fact, the reduction of sulfonium salts by triphenylphosphine was dramatically accelerated by the addition of phenylazoisobutyronitrile (PAIBN = PhN=NC(CH₃)₂CN) as a visible-light-sensitive photoinitiator (expts 22, 23, Table III). In addition, when the di-*p*-tolyliodonium and tri-*p*-tolylsulfonium salts were allowed to compete directly for tetraarylphosphoranyl radical they showed more nearly equal reactivities; experiments involving the visible-light photolysis of acetone-d_6 solutions containing the two salts (in varying ratios) gave a good linear correlation ($r = 0.9986$) of the product ratio [Tol₂S]:[TolI] (measured at low conversions) with the reactant ratio [Tol₃S⁺]/[Tol₂I⁺], with a slope of 0.58 ± 0.23 (Figure 2). The sulfonium and iodonium salts are, therefore, reduced by tetraarylphosphoranyl at comparable rates. Both of these SET reactions are substantially exoergic,[19] so it is not surprising that there is little difference in rate.

The reductive cleavage of *p*-tolyldiphenylsulfonium hexafluorophosphate by triphenylphosphine gave both diphenyl sulfide (PhSPh) and *p*-tolyl phenyl sulfide (TolSPh) in a GC ratio of 1:3.0 (expt 23, Table III), corresponding to statistically corrected relative rates of cleavage, $k_{Ph^\bullet}/k_{Tol^\bullet} = 1.5$ (Scheme II).

(17) Our results agree less well with those of McEwen and co-workers[18a] ($k_{Ph^\bullet}/k_{Tol^\bullet} = 0.9$ and $k_{Ph^\bullet}/k_{An^\bullet} = 1.25$) who reduced iodonium with ethoxide in ethanol and disagree markedly with those reported by Tanner and co-workers.[18b] The latter paper claimed to have accomplished single-electron reduction of iodonium by phenoxide ion. The reported results, however, display a sensitivity to substituent ($k_{Ph^\bullet}/k_{Tol^\bullet} = 3.1$ and $k_{Ph^\bullet}/k_{An^\bullet} = 10.8$) which, in our opinion, clearly points to a mechanism involving a nucleophilic attack.

(18) (a) Lubinkowski, J. J.; Arrieche, C. G.; McEwen, W. E. *J. Org. Chem.* **1980**, *45*, 2076-2079. (b) Tanner, D. D.; Reed, D. W.; Setiloane, B. P. *J. Am. Chem. Soc.* **1982**, *104*, 3917-3923; *Ibid.* **1983**, *105*, 6768.

(19) This is based on half-wave reduction potentials (vs SCE) reported in the literature for diphenyliodonium ($E_{1/2} = -0.53$ v),[20a] triphenylsulfonium ($E_{1/2} = -1.2$ v),[20b] and tetraphenylphosphonium ($E_{1/2} = -1.68$ v)[20c] salts.

(20) (a) Beringer, F. M.; Messing, S. *J. Org. Chem.* **1972**, *37*, 2484-2488. (b) Pappas, S. P.; Jilek, J. H. *Photogr. Sci. Eng.* **1979**, *23*, 140-143. (c) Morris, M. D.; Kok, G. L. *Encycl. Electrochem. Elem.* **1979**, *13*, 1-76.

Trimethyl phosphite (TMP) serves as a precursor to another effective reductant of diaryliodonium and triarylsulfonium salts, the aryltrimethoxyphosphoranyl radical, $Ar\overset{\bullet}{P}(OMe)_3$. Reductive cleavage of the unsymmetrical sulfonium salt by trimethyl phosphite (expt 25, Table III) gave a GC ratio of diphenyl to *p*-tolyl phenyl sulfide of 1:2.7, corresponding to a preference for phenyl radical cleavage, $k_{Ph^\bullet}/k_{Tol^\bullet}$, of 1.35. The observation that the cleavage pattern for the unsymmetrical sulfonium salt is independent of the specific phosphoranyl radical reductant is clearly in agreement with a reductive cleavage (Scheme II). Furthermore, a variety of alternative mechanisms requiring the involvement of phosphorus-centered species in the transition state for the cleavage, such as nucleophilic attack by the phosphorus compound on the onium salt, are ruled out.[21]

The other products of these reactions of trimethyl phosphite with triarylsulfonium salt are, interestingly, aryl dimethylphosphonates ($ArPO(OMe)_2$) and methyl dimethylphosphonate ($MePO(OMe)_2$). These products are formed by an initial nucleophilic attack by TMP on the phosphonium salt product of the $S_{RN}1$ chain, $ArP^+(OMe)_3$ (eq 2), and subsequent Arbuzov rearrangement of trimethyl phosphite to methyl dimethylphosphonate by a cationic chain mechanism (eq 3).[23]

$$P(OMe)_3 + Ar\overset{+}{P}(OMe)_3 \rightarrow Me\overset{+}{P}(OMe)_3 + ArPO(OMe)_2 \qquad \mathbf{4} \qquad (2)$$

$$Me\overset{+}{P}(OMe)_3 + P(OMe)_3 \rightarrow MePO(OMe)_2 + Me\overset{+}{P}(OMe)_3 \qquad (3)$$
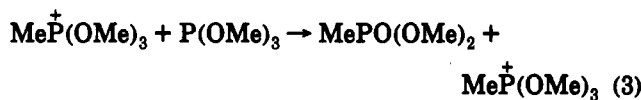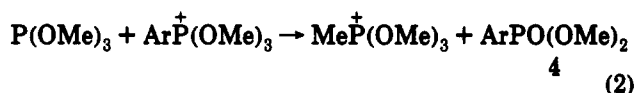
The Arbuzov rearrangement was also observed when trimethyl phosphite was reacted with iodonium salt 1 (Table IV). Rearrangement of the phosphite was slower than the radical-chain reduction of 1 and continued after all of the iodonium salt had been consumed and photolysis had been discontinued, until no phosphite remained. When the bromide of iodonium cation 1 was used as the starting material, the chemistry involving formation of 3 and 4 was unchanged but no rearrangement of the trimethyl phosphite occurred (expts 30, 31, Table IV), a result of the bromide ion competing successfully with TMP for the key cationic intermediates $ArP^+(OMe)_3$ and $MeP^+(OMe)_3$. Resonances attributable to both of these key intermediates were observed as transients in ¹H NMR spectra of reaction solutions that did show rearrangement.[24]

The reaction of iodonium salt 1 with TMP in acetone-d_6 initiated by irradiation with visible light (expt 31, Table

(21) The cleavage ratios reported here not only agree well with each other, they also agree closely with the results of McEwen and co-workers[22] who found that *p*-tolyldiphenylsulfonium iodide reacted with sodium ethoxide by a radical mechanism to give toluene and benzene in a consistent ratio of 1:3.0.

(22) Knapczyk, J. W.; Lai, C. C.; McEwen, W. E.; Calderon, J. L.; Lubinkowski, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 1188-1192.

(23) (a) Colle, K. S.; Lewis, E. S. *J. Org. Chem.* **1978**, *43*, 571-574. (b) Lewis, E. S.; Colle, K. S. *Ibid.* **1981**, *46*, 4369-4372.

Table IV. Reactions of Di-p-tolyliodonium Salts 1[a] with Trimethyl Phosphite (TMP)[b]

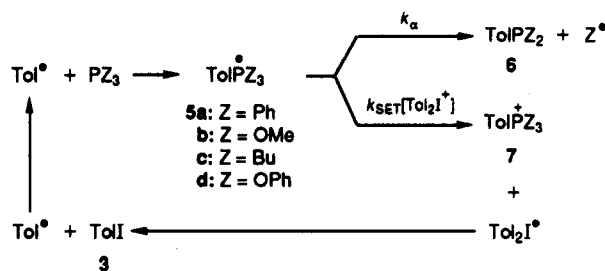| expt | solvent | [1], M | [TMP], equiv | [PAIBN], equiv | time, min | yields[c] (%) | | | % conv[c,d] |
						4	3	TolD	
26[e]	CD3CN	0.08	9	0.3	5			–	≈60
27[e,f]	CD3CN	0.08	9	none	60			–	≈90
28	CDCl3	0.02	14	1.3	10	40	51	9	40
					42	42	49	9	100
29	CDCl3	0.01	22	none	319	34	52	14	62
30[g]	CD3COCD3	0.001	200	9	10	50	50	–	100
31[g]	CD3COCD3	0.001	200	none	10	50	50	–	54

[a] The iodonium hexafluorophosphate was used except where otherwise noted. [b] Reaction solutions were photolyzed at room temperature with a 200-W flood lamp unless otherwise noted. [c] Deduced from ^{1}H NMR integrals of resonances due to p-Me protons. [d] Percent conversion of 1 to products. [e] The resonances of the p-Me protons of 1 and 4 coincided under these conditions so that percent conversion of 1 could only be estimated and the relative yields of 4 and 3 could not be measured. [f] Di-tert-butyl peroxalate (DBPO) was used as an initiator. Reaction proceeded in the NMR probe in the dark. [g] The bromide salt of 1 was used. These were the only cases where reaction of 1 was not accompanied by eventual complete rearrangement of the TMP to methyl dimethylphosphonate.
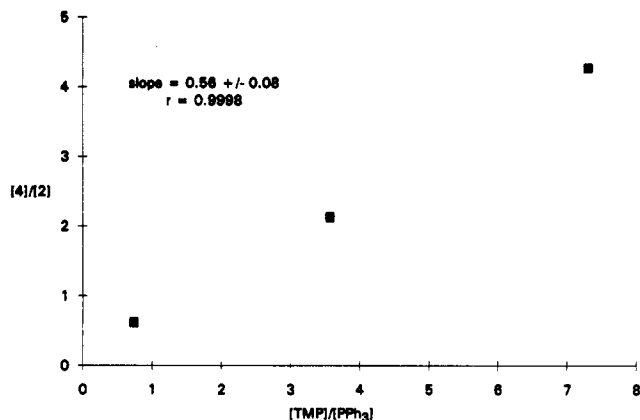
Figure 3. Product ratio [4]/[2] vs reactant ratio [TMP]/[PPh3].

(Figure 3: plot with slope = 0.56 +/- 0.08, r = 0.9998; y-axis [4]/[2], x-axis [TMP]/[PPh3])

IV) gave equal amounts of p-tolyl dimethylphosphonate (4) and 4-iodotoluene (3). In addition, the rate of reaction was accelerated by PAIBN (expt 30, Table IV). The reaction in acetonitrile-d_3 could be initiated both by photolysis of PAIBN (expt 26, Table IV) and by room-temperature decomposition of DBPO (expt 27, Table IV). When chloroform-d was used as the solvent for the light-initiated reaction, deuteriotoluene (TolD) was formed at the expense of 4 (expts 28, 29, Table IV). The sum of the yields of these two products equalled the yield of 3 and the ratio, [4]:[TolD] increased with increasing [TMP]. Thus, the aryl radical is trapped competitively by trimethyl phosphite and solvent.

Visible-light irradiation of acetone-d_6 solutions containing both triphenylphosphine and trimethyl phosphite (in varying ratios) and 1 allowed the observation of a competition between the two phosphorus compounds for tolyl radical. As expected, the product ratio [4]:[2] increased linearly with the starting phosphine ratio [TMP]:[Ph3P] (Figure 3). The slope of the line, 0.56 ± 0.08, corresponds to the relative rate of reaction of the aryl radical with TMP vs phosphine. Our estimate of the rate constant for the phosphine reaction allows extraction of a rate constant for the reaction with TMP (k_{TMP}) of ca. 2×10^8 M^{-1}s^{-1}. The agreement of this value with a previous estimate, k_{TMP} = ca. 3.5×10^8 M^{-1} s^{-1} at 45 °C,[25] is quite good.

(24) MeP$^+$(OMe)3: ^{1}H NMR δ 4.13 (d, J = 11.5 Hz), 2.15 (d, J = 17.2 Hz) (lit.[23a] ^{1}H NMR (CCl4) δ 4.05 (d, J = 11 Hz), 2.18 (d, J = 17 Hz)). TolP$^+$(OMe)3: δ 4.15 (d, J ≈ 12 Hz), 7.6 (d, J ≈ 8 Hz), 7.8 (dd, J ≈ 15 Hz, J' ≈ 8 Hz).
(25) (a) Kryger, R. G.; Lorand, J. P.; Stevens, N. R.; Herron, N. R. *J. Am. Chem. Soc.* 1977, 99, 7589–7600. (b) Fu, J.-J. L.; Bentrude, W. G.; Griffin, C. E. *Ibid.* 1972, 94, 7717–7722.
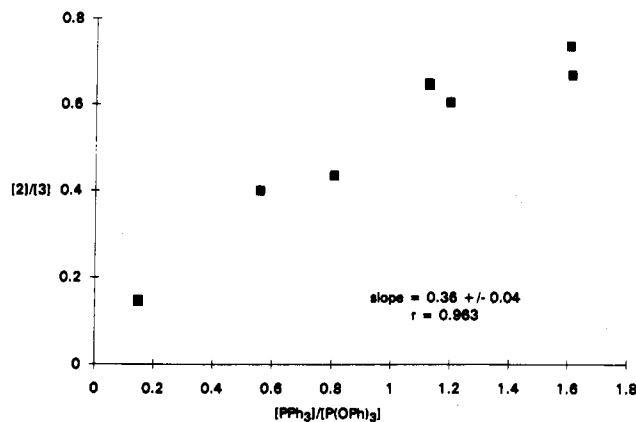
Scheme III

Tol• + PZ3 → Tol·PZ3•

  → k_α → TolPZ2 + Z• (6)

  → k_{SET}[Tol2I$^+$] → TolP·Z3$^+$ (7)

5a: Z = Ph
b: Z = OMe
c: Z = Bu
d: Z = OPh

Tol• + TolI ← Tol2I• (3)

Both the tetraaryl- and aryltrimethoxyphosphoranyl radicals (5a and 5b, respectively) reduce iodonium salt at rates sufficiently fast to compete effectively with bimolecular termination processes and with unimolecular reactions (i.e., α-scission) of the phosphoranyl radical intermediates (Scheme III).

Tributylphosphine also reacts rapidly with ditolyliodonium salt 1 in acetone-d_6 solution under irradiation with visible light. The reaction gives 55% conversion of 1 after only 20 min to iodotoluene, 3, p-tolyltributylphosphonium cation, 7c, and a new type of product, p-tolyldibutylphosphine, 6c. The sum of the yields of 6c and 7c equals the yield of 3 accounting for all of the tolyl radicals formed from the reduction of 1. Since all tolyl radicals in acetone-d_6 react with the phosphine, it must be that phosphoranyl radical 5c has two possible fates. Phosphoranyl 5c, unlike 5a and 5b, undergoes electron transfer to the iodonium salt *in competition with* unimolecular decay via α-scission to give phosphine 6c. The relative amounts of these two pathways was approximately 1:1 under the conditions employed here ([1]$_0$ = 0.07 M). α-Cleavage of butyl from other phosphoranyl radicals is known to be a fast process; cleavage of butyl from tert-butoxytributylphosphoranyl, for example, occurs with a rate constant of 2.7×10^7 s^{-1} at 25 °C.[3b] If it is assumed that the rate of α-scission of butyl from a tributylphosphoranyl radical is not greatly affected by the identity of the fourth ligand (t-BuO or p-Tol), then the relative yields of 6c and 7c, the concentration of 1, and the literature rate constant for α-cleavage of butyl give k_{SET} ≈ 4×10^9 M^{-1} s^{-1}.

The fact that the reaction of tributylphosphine with iodonium salt is fast (see above), even though ca. 50% of the intermediate tolyltributylphosphoranyl radicals (5c) do not directly propagate the redox chain by electron transfer, indicates that the butyl radical formed by the competing α-scission reaction must also propagate a chain for destruction of 1. It does so by adding to tributylphosphine to form a tetrabutylphosphoranyl radical (Bu4P•), which then reduces the onium salt. A characteristic

Figure 4. Product ratio [2]/[3] vs reactant ratio [PPh₃]/[P(OPh)₃].

resonance (δ 2.40, m) due to the α protons of the resulting tetrabutylphosphonium salt, Bu_4P^+, was, in fact, observable in the ¹H NMR spectra of the product mixtures.

In contrast to the results obtained with the other three phosphorus compounds, visible irradiation of an acetone-d_6 solution of triphenyl phosphite (0.3 M) and 1 (0.07 M) for 222 min led to no detectable formation of products (less than 5% conversion of 1). The possibility that inefficient initiation was somehow responsible for the slow reaction is ruled out by the results of an otherwise identical experiment which included PAIBN as a photoinitiator; this experiment showed only 10% conversion of 1 to 3 after 222 min. Compared to the reactions of 1 with other PZ_3, the reaction with triphenyl phosphite is clearly very slow. This cannot be due to an inability of phenyl radical to react with triphenyl phosphite because triphenyl phosphite is nearly as reactive toward phenyl radical as is triphenylphosphine. When iodonium salt 1 was allowed to react with triphenylphosphine in the presence of added triphenyl phosphite, the product ratio [2]:[3] decreased, responding linearly with respect to the ratio of the starting organophosphorus compounds [PPh₃]:[P(OPh)₃] (Figure 4). Clearly the presence of triphenyl phosphite (in concentrations similar to [PPh₃]) in the reaction solutions leads to the diversion of tolyl radicals from reaction with triphenylphosphine. Triphenyl phosphite is, like the other organophosphorus compounds used in this study, an excellent phenyl radical scavenger.

Since phenyl radical does react with triphenyl phosphite and since there is no reason to expect that the *p*-tolyltriphenoxyphosphoranyl radical, **5d**, has less reducing power than other phosphoranyls (trimethoxyphosphoranyl, **5b**, for example) we conclude that α-cleavage of phenoxyl from **5d** is faster than chain-propagating electron transfer and that phenoxyl radical does not propagate a chain reaction of 1; i.e., α-cleavage of **5d** is a termination step.[26] α-Scission of phenoxyl from **5d** must be a significantly faster reaction than α-scission of butyl from **5c**, as expected from the stabilities of the departing radicals. The literature supports this idea; in contrast to *tert*-butoxytributylphosphoranyl radical, *tert*-butoxytriphenoxyphosphoranyl, for example, has such a fleeting

existence that its ESR spectrum can be observed only at low temperatures (i.e., 173 K).[27]

In conclusion, the reactions of diaryliodonium salts with various trivalent phosphorus compounds are summarized in Schemes I and III. In addition, strictly analogous $S_{RN}1$ chains of triarylsulfonium salts have been observed. For the purposes of this paper, the central mechanistic feature is the behavior of the intermediate phosphoranyl radicals. In particular, the chain-propagating SET step occurs in competition with α-cleavage to varying degrees depending on the structure of the phosphoranyl radical. In addition, there are secondary competitions governing the direction of cleavage in the reductive fragmentation of unsymmetrical triarylsulfonium salts (Scheme II) and analogously of unsymmetrical diaryliodonium salts. Finally, free aryl radical intermediates partition between chain-propagating capture by phosphorus and chain transfer reactions with solvent.

Experimental Section

¹H NMR spectra were recorded at 400 MHz unless otherwise noted. Spectral data obtained using CD_3COCD_3, CD_3CN, or THF-d_8 as solvent are normalized to the residual proton resonances of the respective solvent (CD_2HCOCD_3, δ 2.04; CD_2HCN, δ 1.93; β-protioTHF-d_7, δ 1.73). ³¹P NMR spectra were recorded at 121 MHz and were referenced to H_3PO_4 as an external standard. Proton-decoupled ¹³C NMR spectra were recorded at 75.5 MHz and referenced to solvent peaks.

Melting points are uncorrected. Analytical GC was carried out using thermal conductivity detectors with helium as the carrier gas. The column used was 3-ft × ¼-in. 17% Apiezon L on Gas Chrom Z. Peaks were integrated by triangulation and peak identities confirmed through collection and ¹H NMR or MS analysis. Elemental analysis was carried out by Galbraith Laboratories, Knoxville, TN.

Chloroform-d (99.8 atom % D), acetone-d_6 (99.5 atom % D), acetonitrile-d_3 (99 atom % D), and THF-d_8 (99.5 atom % D) were supplied by Aldrich and used as received. THF was distilled from the benzophenone ketyl before use. Acetonitrile was unpurified spectroscopic grade. Iodotoluene, methyl dimethylphosphonate, and tetrabutylphosphonium bromide were obtained from commercial sources and not purified. Triphenylphosphine was crystallized from methanol and stored under nitrogen. Trimethyl phosphite and tributylphosphine were fractionated before use. Triphenyl phosphite in ether solution was washed with 10% NaOH, dried over Na_2SO_4 and distilled after removal of the solvent. Triphenyl phosphite was further purified by flash chromatography on silica gel using pentane as eluant. Di-*tert*-butyl peroxalate (DBPO),[28] phenylazoisobutyronitrile (PAIBN),[29] *p*-tolyltriphenylphosphonium chloride,[30] *p*-tolyltributylphosphonium bromide,[31] *p*-tolylphenyliodonium bromide,[32] *p*-anisylphenyliodonium bromide,[33] *p*-iodosotoluene,[34] and *p*-tolyl dimethylphosphonate[35] were prepared by literature procedures. Di-*p*-tolyliodonium hexafluorophosphate (1) was also prepared according to a literature procedure[33] but was found to be contaminated by about 10% of the isomeric impurity, di-*o,p*-tolyliodonium hexafluorophosphate. It was purified by repeated crystallizations from water to >98% isomeric purity by

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(26) Similarly, a rapid α-cleavage of phenoxy radical from a triphenoxyphosphoranyl radical intermediate, which leads to chain termination, has been cited as the reason for the failure of triphenyl phosphite to undergo facile autoxidation; see: Bentrude, W. G. *Tetrahedron Lett.* **1965**, 3543–3548.

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¹H NMR. p-Tolyldiphenylsulfonium and tri-p-tolylsulfonium hexafluorophosphates were prepared from 1 using published procedures.[36,37] p-Tolyldibutylphosphine[38] was prepared by reduction of p-tolyltributylphosphonium bromide with 29% potassium in graphite (Alfa).

p-Anisyl-p-tolyliodonium Bromide. An adaptation of a literature procedure was used.[32] Concentrated H_2SO_4 (0.7 mL) was added dropwise at 0 °C to a solution of p-iodosotoluene (2.6 g, 11 mmol), anisole (1.2 mL, 11 mmol), and acetic anhydride (6.25 mL, 66 mmol) in acetic acid (72.5 mL). After the solution was warmed to room temperature, 10 g of NaBr in 40 mL of H_2O was added and the solution extracted with $CHCl_3$. Concentration of the extract yielded an oil which was stirred with ether for 24 h to give an off-white solid (1.15 g, 26%) which was collected. The crude solid was crystallized from 95% EtOH yielding 0.85 g (21%) of pure iodonium salt: ¹H NMR ($CDCl_3$) δ 2.31 (s, 3 H), 3.76 (s, 3 H), 6.82 (d, 2 H, J = 8.8 Hz), 7.10 (d, 2 H, J = 8.1 Hz), 7.81 (d, 2 H, J = 8.2 Hz), 7.85 (d, 2 H, J = 8.8 Hz).

Unsymmetrical Iodonium Hexafluorophosphates. The hexafluorophosphate salts were prepared from the corresponding bromides by ion metathesis. The anisyl bromides (AnI⁺Ph and AnI⁺Tol) were treated with Ag_2O and $NaPF_6$ according to a literature procedure.[33] The other unsymmetrical iodonium bromide (TolI⁺Ph) was dissolved in 1:1 $CH_3OH–H_2O$ and treated with excess $NH_4^+PF_6^-$ (aq). The precipitate was collected and dried under vacuum.

p-Anisyl-p-tolyliodonium hexafluorophosphate: mp 166–168 °C; ¹H NMR (CD_3COCD_3) δ 2.39 (s, 3 H), 3.86 (s, 3 H), 7.10 (d, 2 H, J = 9.2 Hz), 7.38 (d, 2 H, J = 8.0 Hz), 8.12 (d, 2 H, J = 8.4 Hz), 8.19 (d, 2 H, J = 9.1 Hz).

p-Anisylphenyliodonium hexafluorophosphate: mp 113–114 °C; ¹H NMR ($CDCl_3$) δ 3.83 (s, 3 H), 6.97 (d, 2 H, J = 9.3 Hz), 7.46 (t, 2 H, J = 7.9 Hz), 7.62 (t, 1 H, J = 7.5 Hz), 7.97 (d, 2 H, J = 9.3 Hz), 7.97 (d, 2 H, J = 7.2 Hz).

p-Tolylphenyliodonium hexafluorophosphate: mp 148–151 °C; ¹H NMR ($CDCl_3$) δ 2.38 (s, 3 H), 7.22 (d, 2 H, J = 8.3 Hz), 7.41 (t, 2 H, J = 7.8 Hz), 7.56 (t, 1 H, J = 6.8 Hz), 7.85 (d, 2 H, J = 8.4 Hz), 7.95 (d, 2 H, J = 7.8 Hz).

Phosphonium Hexafluorophosphates. Aqueous solutions of the corresponding halides were treated with excess $NH_4^+PF_6^-$ (aq). The precipitates were collected and dried under vacuum.

p-Tolyltriphenylphosphonium hexafluorophosphate (2): ¹H NMR ($CDCl_3$) δ 2.50 (s, 3 H), 7.46 (dd, 2 H, J = 3.6, 8.2 Hz), 7.53 (dd, 2 H, J = 12.6 and 8.4 Hz), 7.58 (dd, 6 H, J = 13.1, 7.4 Hz), 7.72 (dt, 6 H, J = 3.6, 7.8 Hz), 7.83 (dt, 3 H, J = 1.4, 8.5 Hz); ¹³C NMR (CD_3COCD_3) δ 20.9 (s), 114.0 (s), 119.2 (s), 130.5 (d, J = 11 Hz), 131.3 (d, J = 13 Hz), 134.8 (d, J = 11 Hz), 135.5 (s), 147.2 (s); MS m/z 353 (M⁺), 276, 262. Anal. Calcd for $C_{25}H_{22}P_2F_6$: C, 60.25; H, 4.45; F, 22.87; P, 12.43. Found: C, 60.17; H, 4.42; F, 22.65; P, 12.47.

p-Tolyltributylphosphonium hexafluorophosphate: ¹H NMR (300 MHz, CD_3COCD_3, shifts referenced to TMS) δ 0.93 (t, 9 H, J = 7.3 Hz), 1.4–1.7 (m, 12 H), 2.49 (s, 3 H), 2.75 (m, 6

H), 7.60 (dd, 2 H, J_{PH} = 2 Hz, J_{HH} = 8 Hz), 7.93 (dd, 2 H, J_{PH} = 11.8 Hz, J_{HH} = 8.3 Hz); ³¹P NMR ($CDCl_3$) δ 30.0 (s), 269.4 (septet, J = 709 Hz).

Tetrabutylphosphonium hexafluorophosphate: ¹H NMR (300 MHz, CD_3COCD_3) δ 0.94 (t, 9 H, J = 7.3 Hz), 1.51 (sextet, 6 H, J = 7.3 Hz), 1.68 (m, 6 H), 2.40 (m, 6 H).

General Experimental Procedures. In general, reactions were carried out in oven-dried NMR tubes equipped with plastic caps. Usually the reactants were weighed into a vial, 1.0 mL of solvent was added, and the resulting solution was split between two NMR tubes, one of which contained a weighed amount of initiator (PAIBN). Sometimes the reactants were weighed directly into the NMR tube and an appropriate amount of solvent (about 0.7 mL) added. Irradiation at 313 nm was accomplished using a Hanovia SH model medium-pressure Hg arc in conjunction with a 0.002 M K_2CrO_4 in 1% K_2CO_3 (aq) filter solution.[39] A Rayonet Model MGR-500 merry-go-round which rotated samples about the central light source at a rate of 5 rpm was use for simultaneous photolyses at 313 nm. Irradiation with visible light was carried out using a GE 200-W industrial flood lamp at a distance of 2–3 cm from the NMR tubes. Tubes were held side by side equidistant from the light source for simultaneous photolyses. Cooling was provided by directing a vigorous stream of room temperature air directly on the tubes. Before beginning irradiation of reaction solutions, t = 0 NMR spectra were recorded. Spectra were then recorded immediately following each period of photolysis. Experiments using DBPO as a nonphotochemical initiator were carried out by weighing a small amount of the DBPO into the tube containing the reaction solution. This solid stuck to the top of the tube and was not washed down until after weighing. The capped tube was then inverted and the time was recorded and taken as t = 0. The NMR spectrum was then acquired as soon as possible. Spectra were then acquired continuously noting the times of completion of the 8th pulse of 16 total pulses acquired for each FID.

Integration of the 400-MHz ¹H NMR spectra from 2.2–4.0 ppm gave the yields and percent conversions listed in the tables. The resonances in this region of the spectra were due to p-methyl protons (of the tolyl moieties) and p-methoxy protons (of the anisyl moieties) of products or starting onium salts. The positions of these resonances for the various compounds analyzed for in these studies are listed here. **p-Methyl protons:** Tol₂I⁺PF₆⁻ (1) δ 2.36–2.42; TolP⁺Ph₃ PF₆⁻ (2) δ 2.49–2.53; TolI (3) δ 2.26–2.29; TolH(D) δ 2.34–2.36; TolI⁺Ph PF₆⁻ δ 2.29–2.33; AnI⁺Tol PF₆⁻ δ 2.33; AnI⁺Tol PF₆⁻ δ 2.31–2.39; TolS⁺Ph₂ PF₆⁻ δ 2.49–2.50; TolSPh δ 2.31–2.32; Tol₃S⁺PF₆⁻ δ 2.48; Tol₂S δ 2.29; TolPO(OMe)₂ δ 2.39–2.41; TolP⁺Bu₃ PF₆⁻ δ 2.47; TolPBu₂ δ 2.31. **p-Methoxy protons:** AnI⁺Tol Br⁻ δ 3.78; AnI⁺Tol PF₆⁻ δ 3.76–3.85; AnI⁺Ph PF₆⁻ δ 3.80–3.86; AnI δ 3.73–3.80; AnP⁺Ph₃ PF₆⁻ δ 3.90–4.02. Peak identities were verified when necessary by partial separation of reaction mixtures by small scale column chromatography on alumina followed by GC or NMR analysis.[40]

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(40) For complete experimental details and data for each experiment see ref 11.