## Table I
Photostimulated Reactions of Aryl Halides with Thiophenoxide Ion[a] in Liquid Ammonia

Run no.	Substrate	Reaction time, min	Sulfide product	% yield[b]	Other products[c]
1	m-ClC$_6$H$_4$I	150	m-PhSC$_6$H$_4$SPh	91	PhSPh, m-ClC$_6$H$_4$SPh
2	p-ClC$_6$H$_4$I	120	p-PhSC$_6$H$_4$SPh	89[e]	PhSPh, p-ClC$_6$H$_4$SPh
3	m-BrC$_6$H$_4$Br	190	m-PhSC$_6$H$_4$SPh	92	PhSPh
4	m-ClC$_6$H$_4$Br	180	m-PhSC$_6$H$_4$SPh	55[f]	PhSPh, m-ClC$_6$H$_4$SPh
5	p-BrC$_6$H$_4$Br	300	p-PhSC$_6$H$_4$SPh	64[d,g]	
6	p-IC$_6$H$_4$N$^+$Me$_3$I$^-$	180	p-PhSC$_6$H$_4$SPh	95	PhSPh
7	o-ClC$_6$H$_4$I	90	o-PhSC$_6$H$_4$SPh	77[h]	PhSPh, o-ClC$_6$H$_4$SPh
8	m-FC$_6$H$_4$I	100	m-FC$_6$H$_4$SPh	96	

[a] PhS$^-$ supplied by dissolving PhSH in ammonia; irradiation by "350 nm" lamps.[3] [b] Isolated yield unless otherwise indicated. [c] Trace amounts. [d] Glpc yield. [e] After recrystallization. [f] 33% unreacted m-chlorobromobenzene. [g] 26% unreacted p-dibromobenzene. [h] 9% unreacted o-chloroiodobenzene.

Scheme I
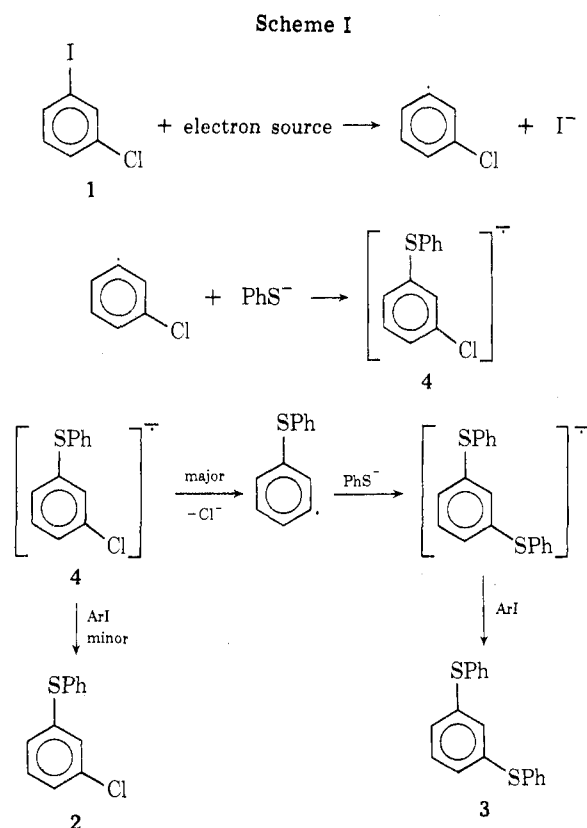
Kinetic analysis of the photostimulated reaction of m-chloroiodobenzene (1) with thiophenoxide ion shows that, except to a minor extent, the monosubstitution product (2) is not an intermediate in formation of bis-sulfide 3. First, in separate reactions with thiophenoxide ion, 1 is more reactive than 2. Thus, during 105 sec irradiation, 1 reacted to the extent of 68% but 2 only to the extent of 15%, both to form predominantly 3. Second, when mixtures of 1 or 2 and iodobenzene were allowed to compete for excess thiophenoxide, iodobenzene was found to be more reactive than 2 but less reactive than 1. Third, in direct competition between 1 and 2 for thiophenoxide ion, 1 was 17.4 times more reactive than 2.

These relative reactivity measurements show that 2 is too unreactive to participate as a major reaction intermediate.

That monosubstitution product 2 is, in the main, not an intermediate en route to disubstitution product 3 is a strange result, and constitutes powerful evidence of mechanism. It serves to exclude numerous conceivable mecha-

nisms of substitution. On the other hand, the previously proposed SRN1 mechanism[2,6] not only accommodates this result, but leads to an expectation of it. That mechanism, adapted to the present case, is sketched in Scheme I.

In Scheme I, the fate of radical anion 4 is of central interest. Loss of chloride ion from 4 is the major pathway and leads to disubstitution product 3 without the intervention of 2. Loss of an electron from 4, presumably by transfer to 1, forms 2 but is apparently a minor pathway.

The fact that m-fluoroiodobenzene (run 8) gave only monosubstituted product indicates that the analogous m-fluorophenyl phenyl sulfide radical anion preferentially transfers an electron to aryl iodide. C–F bonds are more difficult to break than C–Cl bonds.

The mechanism of Scheme I is the only one conceivable to us that accommodates the strange result we report. We must, however, add the universal proviso that a presently inconceivable mechanism may also accommodate the evidence.

References and Notes

(1) Research supported in part by the National Science Foundation.
(2) J. F. Bunnett and X. Creary, *J. Org. Chem.*, **39**, 3173 (1974).
(3) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 1407 (1973).
(4) R. A. Rossi and J. F. Bunnett, *J. Amer. Chem. Soc.*, **94**, 683 (1972).
(5) J. F. Bunnett and B. F. Gloor, *J. Org. Chem.*, **39**, 382 (1974).
(6) J. K. Kim and J. F. Bunnett, *J. Amer. Chem. Soc.*, **92**, 7463 (1970).
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Photostimulated Condensation of Aryl Iodides with Potassium Dialkyl Phosphites to Form Dialkyl Arylphosphonates[1]

Summary: Aryl iodides react rapidly with potassium dialkyl phosphites, $(RO)_2PO^-K^+$, in liquid ammonia under "350-nm" irradiation to form dialkyl arylphosphonates in 87–96% yields, probably by the SRN1 mechanism.

Sir: We have found that potassium salts of dialkyl phosphites react rapidly with aryl iodides in liquid ammonia under Pyrex-filtered irradiation to form dialkyl esters of arylphosphonic acids in nearly quantitative yields (Scheme I).

Table I
Photoinitiated Reaction of Potassium Diethyl Phosphite with Aryl Iodides in Liquid Ammonia

Run no.	Aryl iodide	Irradiation time, min	Product[a]	% yield[b]	Other products[c]
1	PhI[d]	50	$PhP(=O)(OCH_3)_2$	93	
2	PhI[e]	60	$PhP(=O)(OCH_2CH_2CH_2CH_3)_2$	88	
3	PhI	45	$PhP(=O)(OEt)_2$	96	
4	$p\text{-}CH_3C_6H_4I$	75	$p\text{-}CH_3C_6H_4P(=O)(OEt)_2$	95	
5	$p\text{-}CH_3OC_6H_4I$	65	$p\text{-}CH_3OC_6H_4P(=O)(OEt)_2$	95	
6	2-Iodo-m-xylene	60	$2,6(CH_3)_2C_6H_3P(=O)(OEt)_2$	87	m-Xylene
7	$m\text{-}CF_3C_6H_4I$	55	$m\text{-}CF_3C_6H_4P(=O)(OEt)_2$	95	
8	1-Iodonaphthalene	130	$C_{10}H_7P(=O)(OEt)_2$	93	Naphthalene
9	$m\text{-}FC_6H_4I$	50	$m\text{-}FC_6H_4P(=O)(OEt)_2$	96	
10	$m\text{-}ClC_6H_4I$	40	$m\text{-}ClC_6H_4P(=O)(OEt)_2$	89	$m\text{-}C_6H_4[P(=O)(OEt)_2]_2$ (4%)
11	$m\text{-}BrC_6H_4I$	60	$m\text{-}C_6H_4[P(=O)(OEt)_2]_2$	87	$m\text{-}BrC_6H_4P(=O)(OEt)_2$
12	$m\text{-}IC_6H_4I$	90	$m\text{-}C_6H_4[P(=O)(OEt)_2]_2$	94	
13	$p\text{-}IC_6H_4I$	205[f]	$p\text{-}C_6H_4[P(=O)(OEt)_2]_2$	87	

[a] Structures were verified by mass, ir, and nmr spectra and (for runs 6 and 7) elemental analysis. [b] Isolated yields. [c] Trace amounts unless otherwise indicated. [d] Anion was dimethyl phosphite. [e] Anion was dibutyl phosphite. [f] Long irradiation time required because of low solubility of p-diiodobenzene in liquid ammonia.

Scheme I

$$\text{ArI} + (RO)_2PO^-K^+ \xrightarrow{h\nu} \underset{\underset{OR}{|}}{\overset{\overset{O}{\|}}{Ar\text{P}OR}} + KI$$
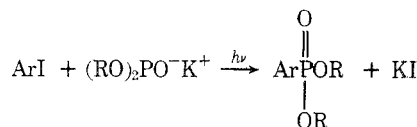
Our principal results are summarized in Table I. This synthesis has been carried out with iodobenzene and 1-iodonaphthalene as well as with iodobenzenes carrying methyl, methoxy, trifluoromethyl, and halogen substituents. Isolated yields range from 87 to 96%. The iodine atom is directly replaced by the phosphonate ester group, without any detectable cine substitution.

The experimental procedure is straightforward. Potassium metal is dissolved in liquid ammonia in a Pyrex flask flushed with nitrogen, the relevant dialkyl phosphonate is added in amount just sufficient to discharge the blue color, the aryl iodide is added (about half a mole per mole of dialkyl phosphonate), a condenser cooled by solid carbon dioxide is affixed, and the mixture is irradiated for about an hour (see Table I) in a Rayonet photochemical reactor equipped with "350-nm" lamps under constant stirring. Conceivably, equally good results could be obtained in shorter reaction times.

With potassium dibutyl phosphite in liquid ammonia for 60 min in the dark, iodobenzene underwent only 4% reaction.

For preparative purposes, this method compares favorably with others to obtain arylphosphonic acids or esters. Of other methods,[2,3] the one most closely related is the photochemical reaction of aryl iodides with trialkyl phosphites.[3] However, that method employs prolonged irradiation (~24 hr) in silica vessels with light from high pressure quartz mercury vapor lamps.

In Table I, it should be noted that, of the four m-haloiodobenzenes, the fluoro compound (run 9) suffered replacement only of iodine whereas the chloro compound (run 10) also underwent 4% replacement of chlorine, the bromo compound (run 11) gave mainly disubstitution with only a trace of m-bromophenylphosphonate ester, and m-diiodobenzene (run 12) as well as its para isomer (run 13) gave entirely disubstitution products.

The reactions of Table I are believed to occur by the SRN1 mechanism[4] which has also been suggested for the facile photostimulated condensations of aryl halides with

Scheme II
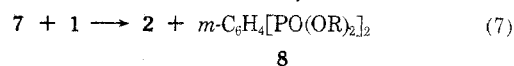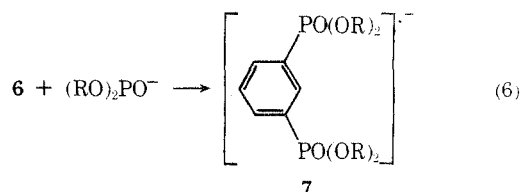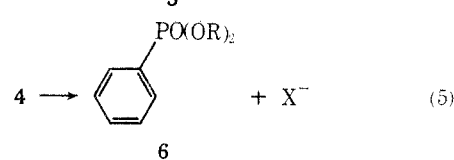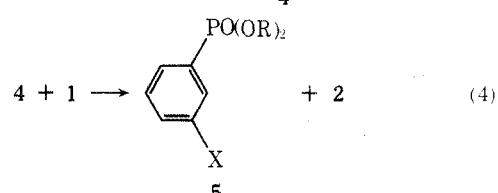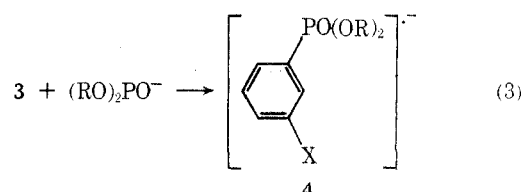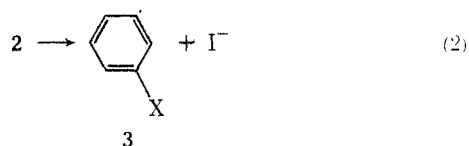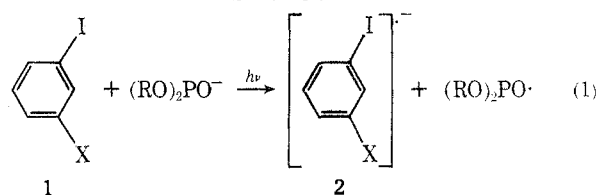
thiolate[5] and carbanion[6] nucleophiles. The SRN1 mechanism for the case of a meta-substituted iodobenzene react-

ing with a dialkyl phosphite anion is sketched in Scheme II.

Step 1 of the suggested mechanism is a photoactivated electron transfer from dialkyl phosphite anion to aryl iodide, and is the initiation step of an overall chain mechanism. An alternative possibility for initiation is photolysis of the C–I bond,[7] forming an aryl radical which enters the propagation sequence at step 3. Termination steps must also be involved, but are not shown.

Steps 2, 3, and 4 constitute a propagation cycle leading to product **5** in which the iodine atom has been replaced but substituent X survives. If intermediate radical anion **4** expels halide ion (in step 5) instead of transferring an electron (in step 4), steps 6 and 7 can then ensue, leading to disubstitution product **8**. Inasmuch as C–Br and C–I bonds are more readily broken than C–F and C–Cl bonds, it is not surprising that step 5 is favored when X is Br or I while step 4 predominates when X is F or Cl.

It is significant that photostimulated reaction of *m*-chloroiodobenzene with thiophenoxide ion gives mainly disubstitution[5,8] but with diethyl phosphite ion (run 10) principally monosubstitution. This contrasting behavior is probably to be attributed to greater stability for **4** (X = Cl) than for the corresponding intermediate in the reaction with thiophenoxide ion, namely, the *m*-chlorophenyl phenyl sulfide radical anion. Inasmuch as the –PO(OEt)$_2$ substituent is more strongly electron attracting than –SC$_6$H$_5$,[9] such an order of stability would be expected. Greater stability for **4** would enable it to survive long enough to transfer an electron in bimolecular step 4, and thereby form monosubstitution product **5**.

References and Notes

(1) Research supported in part by the National Science Foundation.
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(7) A. Levy, D. Meyerstein, and M. Ottolenghi, *J. Phys. Chem.*, **77**, 3044 (1973).
(8) The photostimulated reaction of *m*-chloroiodobenzene with thiophenoxide ion affords predominantly the distribution product, *m*-di(thiophenoxy)benzene.[5] There is evidence that *m*-chlorophenyl phenyl sulfide is not an intermediate on the main disubstitution reaction pathway. In the present case we have no proof that **5** is not an intermediate in formation of **8**, although that is implied by Scheme II and our discussion.
(9) L. D. Freedman and H. H. Jaffe, *J. Amer. Chem. Soc.*, **77**, 920 (1955); E. N. Tsvetkov, D. I. Lobanov, L. A. Izosenkova, and M. I. Kabachnik, *Zh. Obshch. Khim.*, **39**, 2177 (1969); H. H. Szmant and G. Suld, *J. Amer. Chem. Soc.*, **78**, 3400 (1956).

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Steric Acceleration of Perester Decomposition Leading to Tertiary Alkyl Radicals

Summary. The rate accelerations observed in the formation of some tertiary radicals from crowded peresters are comparable to those in corresponding carbonium ion reactions.

Sir: The reactivity of organic peresters has been the subject of intense study, justified by the practical and theo-

Table I
Decomposition of Peresters in Cumene[a]

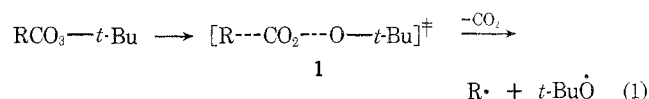|	T, °C	k_1, sec^{-1} [c]	k_{rel}	ΔH*, kcal/mol	ΔS*, eu
i-Pr$_3$CCO$_3$-	24.8	5.32×10^{-6}		26.6	6.7
t-Bu (2)	25.0^b	5.67×10^{-6}	32		
	41.6	6.84×10^{-5}			
	55.2	3.78×10^{-4}			
	60.0^b	7.08×10^{-4}	24		
NpMe$_2$CCO$_3$-	25.0^b	6.13×10^{-7}	3.5	26.5	2.0
t-Bu (3)	40.8	6.15×10^{-6}			
	54.7	3.82×10^{-5}			
	60.0^b	7.55×10^{-5}	2.6		
	70.7	2.73×10^{-4}			
t-BuMe$_2$CCO$_3$-	25.0^b	7.18×10^{-7}	4.1	27.2	4.6
t-Bu (4)	42.2	8.76×10^{-6}			
	54.9	5.84×10^{-5}			
	60.0^b	1.00×10^{-4}	3.4		
	70.3	3.36×10^{-4}			
t-BuCO$_3$-	25.0^d	1.75×10^{-7}	1.0	28.3	5.3
t-Bu	60.0^d	2.93×10^{-5}	1.0		
	70.3	1.11×10^{-4}			

[a] Np = neopentyl. [b] Calculated value. [c] Average of duplicate runs except as noted; maximum deviation ±5%. [d] Calculated from literature values at six temperatures plus one run reported here: J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *J. Amer. Chem. Soc.*, **90**, 5266 (1968); R. C. Fort, Jr., and R. E. Franklin, *ibid.*, **90**, 5267 (1968).

Table II
Comparison of Rates of Formation of Radicals and Cations

	Radicals		Cations
R	RCO$_3$-t-Bu^a	RN=NR^b	RX
i-Pr$_3$C	32	206	49.0,^{c} 109^d
NpMe$_2$C	3.5	247	21,^{e} 6.4^c
t-BuMe$_2$C	4.1	5.3	4.4,^{f} 2.5,^{g} 1.2^h
t-Bu	1.0	1.0	1.0

[a] This work, 25°. [b] In ethylbenzene at 180°, ref 3f. [c] Direct comparison of *p*-nitrobenzoates at 100° in 60% dioxane, ref 3f. [d] Direct comparison of *p*-nitrobenzoates at 100° in 70% acetone: C. F. Wilcox, Jr., and M. E. Mesirov, *J. Amer. Chem. Soc.*, **84**, 2757 (1962). Extrapolation of data from other temperatures gives a calculated rate of 650 at 25° in 80% dioxane: P. D. Bartlett and T. T. Tidwell, *ibid.*, **90**, 4421 (1968); P. D. Bartlett and M. Stiles, *ibid.*, **77**, 2806 (1955). [e] Chlorides at 25°: H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953). [f] *p*-Nitrobenzoates at 25°: H. C. Brown and E. N. Peters, *ibid.*, **95**, 2400 (1973). [g] Chlorides at 25°: P. D. Bartlett and M. S. Swain, *ibid.*, **77**, 2801 (1955). [h] Chlorides at 25°: H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).

retical importance of these compounds.[1] From these studies the mechanism that has emerged for peresters RCO$_3$-*t*-Bu, where R is a tertiary or similarly stabilized radical, involves concerted breaking of two bonds and formation of the R radical, carbon dioxide, and the *tert*-butoxy radical (eq 1).[1]

$$RCO_3 - t\text{-}Bu \longrightarrow [R\text{---}CO_2\text{---}O\text{---}t\text{-}Bu]^{\ddagger} \xrightarrow{-CO_2}$$
$$\mathbf{1}$$
$$R\cdot + t\text{-}Bu\dot{O} \quad (1)$$

This report deals with the examination of the structure of the transition state **1** through study of the reactivity of peresters where R contains bulky alkyl groups. The influence of steric crowding on the rates of solvolysis reactions