Reactions of Halotoluenes with Potassium Diphenylphosphide. Evidence for a Thermally Induced Aromatic $S_{RN}1$ Reaction[1,2]

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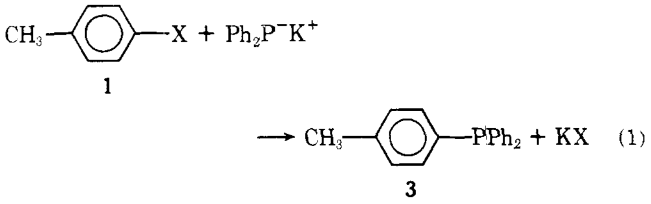
The reaction of *m*- or *p*-iodo- or -bromotoluene with potassium diphenylphosphide in refluxing ammonia or dimethyl sulfoxide at 25 °C gives the corresponding diphenyltolylphosphine in good yield. Reaction occurs in the dark, but is stimulated by irradiation with broad spectrum ultraviolet light. There is no evidence for the formation of an aryne intermediate. Electron acceptors such as *m*-dinitrobenzene and azobenzene inhibit the reaction and suggest a mechanism with electron transfer steps. Entrainment studies indicate a chain mechanism. All data are consistent with the $S_{RN}1$ mechanism of nucleophilic substitution with both thermal and photochemical initiation steps.

The radical chain $S_{RN}1$ mechanism of aromatic nucleophilic substitution was first recognized in 1970.[3] It is now understood as a mechanism of rather wide scope, both as to the nucleophiles and the substrates that participate.[4]

Most aromatic $S_{RN}1$ reactions require stimulation by photons, by solvated electrons, or by electrons from a cathode. However, the initial examples[3] concerning aryl iodides in reaction with KNH_2 involved no intentional stimulation. More recently, it was observed that the enolate ions of acetone and pinacolone react spontaneously with iodobenzene in dimethyl sulfoxide in the dark.[5]

These instances of thermally activated $S_{RN}1$ reactions suggest that there may be more in the same category. In the present study, we consider the reactions of potassium diphenylphosphide with *m*- and *p*-bromo- and -iodotoluenes (eq 1 and 2). These reactions were first reported in 1963 by Aguiar, Greenberg, and Rubenstein,[6] who conducted their studies in tetrahydrofuran (THF) solution.



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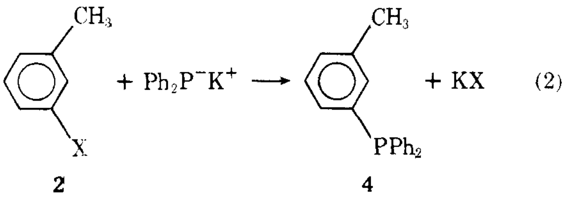


(2)

a, X = Br; b, X = I

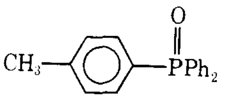
Beyond discovery of these reactions, Aguiar and co-workers made important observations in regard to reaction mechanism. They showed that ipso substitution prevails, without any indication of cine substitution. The possibility of an aryne mechanism was therefore ruled out. They also considered a conceivable double displacement mechanism, along the lines of one recently proposed on good evidence for reactions of trimethylstannylsodium with aryl halides,[7] and argued against it on grounds of product composition especially as related to the order of mixing of the reactants. They suggested that the reaction occurs by a concerted displacement mechanism with a transition state including, besides the aryl halide and $Ph_2P^-Li^+$, a second ion pair (either $Ph_2P^-Li^+$ or Li^+Cl^-).

The $S_{RN}1$ Propagation Cycle. A radical chain mechanism involves initiation, propagation, and termination steps. If the chain is long, most of the reaction occurs in the cycle of propagation steps. The $S_{RN}1$ propagation cycle for reaction 1 or 2 is sketched in Scheme I. Of the three component steps, M1 is fragmentation of the radical anion of the substrate, M2 is combination of the resulting aryl radical with nucleophile Ph_2P^- to form a new covalent bond in radical anion $[ArPPh_2]^{-}\cdot$, and M3 is an electron transfer which regenerates the substrate radical anion.

Results

We conducted our experiments in liquid ammonia or in Me_2SO solution. These solvents are more polar than the THF used by Aguiar et al. and more likely to dissolve salts as free ions rather than ion pairs.

Transformations in the Dark. Potassium diphenylphosphide was found to react with *p*-iodotoluene in ammonia in the dark to form diphenyl-*p*-tolylphosphine in good yield (eq 1). Isolation of the pure triarylphosphine was complicated by unwanted oxidation. Typically, product analyses were conducted by oxidation of the phosphine to the corresponding oxide (**5** or **6**) with ensuing isolation and/or determination by GLC. Results are summarized in Table I. It is noteworthy that diphenyl-*p*-tolylphosphine oxide was isolated in 89% yield after a 5.5-h reaction time. When oxygen was scrupulously excluded from the reaction mixture and a special workup procedure was used (expt 2), diphenyl-*p*-tolylphosphine was obtained as such.



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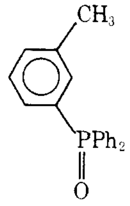

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The reaction was examined for evidence of cine substitution. The reaction of potassium diphenylphosphide with *m*-iodotoluene gave a product with a slightly shorter retention time than diphenyl-*p*-tolylphosphine and gave diphenyl-*m*-tolylphosphine oxide upon oxidation. There was no detectable contamination of the meta or para products by the respective para or meta isomers.

p-Bromotoluene also reacts with potassium diphenylphosphide to give the corresponding tertiary phosphine, albeit much more slowly than the iodo compounds. After a reaction time of 7.5 h, only 2% reaction had taken place.

Scheme I

$$[ArX]^{-}\cdot \rightarrow Ar\cdot + X^{-} \quad \text{(M1)}$$

$$Ar\cdot + Ph_2P^{-} \rightarrow [ArPPh_2]^{-}\cdot \quad \text{(M2)}$$

$$[ArPPh_2]^{-}\cdot + ArX \rightarrow ArPPh_2 + [ArX]^{-}\cdot \quad \text{(M3)}$$

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Table I. Reactions of Potassium Diphenylphosphide with Halotoluenes

expt no.	ArX	registry no.	solvent	conditions	reaction time, h	% halide ion released	product	GLC yield[a] (as the oxide), %	isolated yield[a] (as the oxide), %
1	p-$IC_6H_4CH_3$	624-31-7	NH_3	dark	5.5	94	**5**		89
2	p-$IC_6H_4CH_3$		NH_3	dark	5.5	80	**3**		40
3	p-$IC_6H_4CH_3$		NH_3	$h\nu$	1	96	**5**		90
4	m-$IC_6H_4CH_3$	625-95-6	NH_3	dark	5.5	96	**6**	*b*	*b*
5	p-$BrC_6H_4CH_3$	106-38-7	NH_3	dark	7.5	2.2	**5**	2.0	
6	p-$BrC_6H_4CH_3$		NH_3	$h\nu$	1.5	70	**5**	57	
7	p-$IC_6H_4CH_3$		Me_2SO	dark	2	96	**5**		78
8	p-$BrC_6H_4CH_3$		Me_2SO	dark	3	13	**5**	6	

[a] After hydrogen peroxide oxidation, except in expt 2. [b] Detected, but not determined quantitatively.

Table II. Photostimulation of Reactions of Potassium Diphenylphosphide with Halobenzenes [a]

expt no.	PhX	registry no.	moles of PhX × 10^4	irradiation time, min	total reaction time, min[b]	moles of X^- × 10^4
9	PhI	591-50-4	20.0	0.0[c]	2.8	2.97
10	PhI		20.0	2.0	2.8	5.28
11	PhBr	108-86-1	90.0	0.0[c]	2.5	0.08
12	PhBr		90.0	2.0	2.5	2.48

[a] Reactions were conducted in the presence of 0.01 mol of $Ph_2P^-K^+$ in 50 mL of refluxing ammonia. [b] Time from addition of the halobenzene to quenching. [c] Kept in dark.

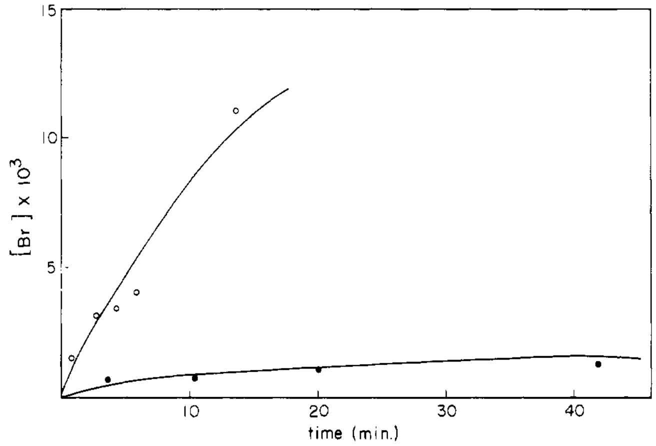


Figure 1. Reaction of p-bromotoluene with potassium diphenylphosphide in Me_2SO. The effect of light: (●) reaction mixture kept in the dark; (○) reaction mixture irradiated with broad spectrum ultraviolet light.

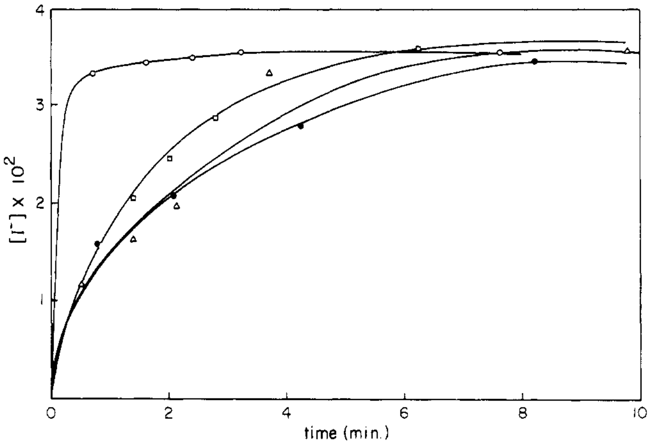


Figure 2. Reaction of p-iodotoluene with potassium diphenylphosphide in Me_2SO in the dark. The effect of added substances: (○) no additive present; (●) 20 mol % of azobenzene added; (□) 20 mol % of m-dinitrobenzene added; (△) 20 mol % of di-*tert*-butyl nitroxide added.

In another solvent, Me_2SO, reactions of potassium diphenylphosphide with p-iodo- or -bromotoluene (expts 7 and 8) likewise gave diphenyl-p-tolylphosphine, again determined as the oxide. There was no detectable contamination by its meta isomer. The reaction of p-iodotoluene was somewhat faster than the corresponding reaction in ammonia. Rate measurements on separate reactions showed p-iodotoluene to be enormously more reactive than p-bromotoluene; thus, 0.2 M $Ph_2P^-K^+$ released 88% of iodide ion from **1b** in 2.4 min but only 0.2% of bromide ion from **1a** in the same period of time.

Effect of Light. Most of the experiments of Table I were run in foil-wrapped flasks to exclude all light. Preparative experience (compare expt 3 with 1, or 6 with 5; Table I) suggested that the reaction of the nucleophile with bromo- or iodotoluene in ammonia was stimulated by irradiation with broad spectrum ultraviolet light. This indication is confirmed by the results in Table II. The reaction of bromobenzene with $Ph_2P^-K^+$ showed a dramatic acceleration when irradiated; 30 times as much bromide was released in 75 min of irradiation (expt 12) as in the dark reaction (expt 11).

In Me_2SO solvent, the reaction of p-bromotoluene with $Ph_2P^-K^+$ is also dramatically accelerated by light, as shown in Figure 1. A 30-fold acceleration is seen here as well. For the reaction of $Ph_2P^-K^+$ with iodobenzene in ammonia, only a 1.8-fold acceleration due to irradiation could be observed (Table II). The thermal reaction of p-iodotoluene in Me_2SO was too fast to permit determination if there was any photostimulation.

Inhibition Studies. The progress of the reaction of p-iodotoluene with $Ph_2P^-K^+$ in the dark in Me_2SO at 25 °C was followed as a function of time. The extent of reaction was determined by removal of small aliquots, quenching, extraction, and titration for iodide ion. It was found that the reaction in the absence of extraneous substances was essentially complete within 1 min. Several experiments were conducted, and the data were found to be reproducible.

Small amounts of electron acceptors or free-radical traps were found to retard the reaction in Me_2SO substantially, as represented in Figure 2. Addition of 20 mol % of di-*tert*-butyl nitroxide had a dramatic retardation effect. m-Dinitrobenzene

Table III. Reaction of *p*-Iodotoluene with Potassium Diphenylphosphide in the Dark in Ammonia. Effects of Inhibitors[a]

expt no.	inhibitor	registry no.	amount, mol %	% iodide released[b]
13	none			47
14	*p*-dinitrobenzene	100-25-4	1	11
15	nitrobenzene	98-95-3	3	21
16	nitrobenzene		10	11
17	galvinoxyl	2370-18-5	2	47
18	di-*tert*-butyl nitroxide	2406-25-9	3	41
19	di-*tert*-butyl nitroxide		20	3

[a] Experiments were carried out in the presence of 2.0×10^{-3} mol of iodotoluene and potassium diphenylphosphide in 50 mL of refluxing ammonia for 75 min. [b] Based on iodotoluene.

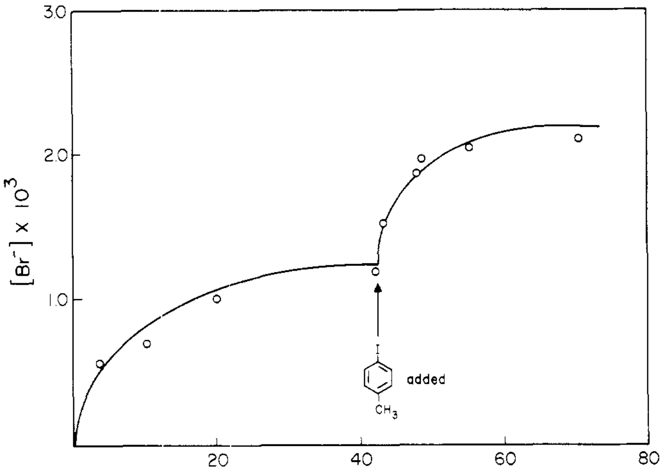


Figure 3. Reaction of *p*-bromotoluene with potassium diphenylphosphide in Me_2SO in the dark. The effect of added *p*-iodotoluene: 33 mol % of *p*-iodotoluene added at 42.6 min.

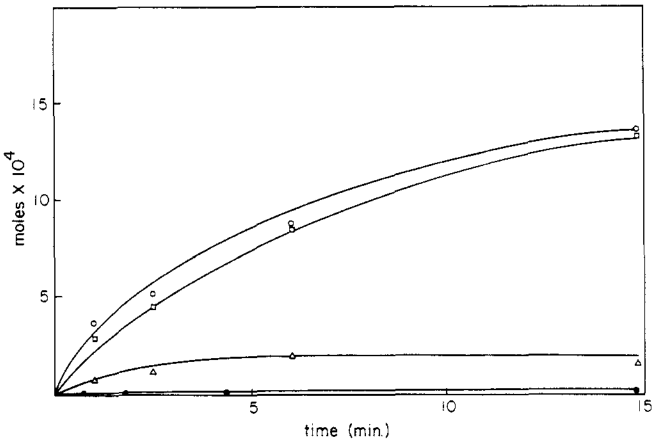


Figure 4. Reaction of *p*-iodotoluene with potassium diethyl phosphite in Me_2SO in the dark. The effect of added potassium diphenylphosphide: (●) yield of I^- with no potassium diphenylphosphide added; (○) yield of I^-, (□) yield of diethyl *p*-tolylphosphonate, and (△) yield of diphenyl-*p*-tolylphosphine with 10 mol % of potassium diphenylphosphide added.

or azobenzene (20 mol %) slowed the reaction almost as much. The rate was only slightly depressed when 10 mol % of 1,1-diphenylethylene or 2 mol % of *p*-dinitrobenzene was added.

A similar study was made of the reaction in ammonia solvent. In this case, reaction mixtures were allowed to stir in the dark for 75 min and then quenched and analyzed. Results are summarized in Table III. Addition of 2 mol % of *p*-dinitrobenzene or of 10 mol % of nitrobenzene reduced the yield of iodide ion by a factor of 4. Galvinoxyl (2 mol %) had no discernible effect. Di-*tert*-butyl nitroxide (3 mol %) did not have much effect, but 20 mol % caused a dramatic 16-fold decrease in the yield of iodide ion.

Entrainment Experiments. The thermal reaction of $Ph_2P^-K^+$ with *p*-bromotoluene in Me_2SO solvent is quite slow. The reaction with iodotoluene, on the other hand, is rapid. A reaction mixture containing *p*-bromotoluene and diphenylphosphide ion was allowed to stir for 1 h, and the release of bromide ion was monitored by analysis of aliquots. *p*-Iodotoluene (33 mol %) was then added. As shown in Figure 3, the addition of *p*-iodotoluene sharply accelerated the release of *bromide ion* from *p*-bromotoluene.

$$PhI + (EtO)_2PO^-K^+ \rightarrow PhPO(OEt)_2 + KI \qquad (3)$$

The $S_{RN}1$ reaction of potassium diethyl phosphite (eq 3) with iodobenzene in Me_2SO is reported to be very slow.[8] A similar observation was made in the present work when *p*-iodotoluene was substituted for iodobenzene. In a further experiment, 10 mol % of potassium diphenylphosphide was an additional component of a reaction mixture otherwise identical with the one containing only diethyl phosphite ion and *p*-iodotoluene. The presence of diphenylphosphide ion dramatically stimulated the formation of *diethyl p-tolylphosphonate.* Results are summarized in Figure 4.

Incidentally, the experiment described above constitutes, in effect, a competition reaction between potassium diphenylphosphide and potassium diethyl phosphite for *p*-iodotoluene. From the data, it can be reckoned that diphenylphosphide nucleophile is 1.7 times as reactive as the diethyl phosphite ion.

Relative Halogen Mobilities. Relative rates of reaction of aryl iodides and bromides with potassium diphenylphosphide were determined by direct competition, the extents of reaction being determined by halide titration. Results are summarized in Table IV. Iodobenzene reacts about 400 times faster than bromobenzene in the thermal reaction in ammonia. When the reaction mixture is irradiated, the PhI/PhBr rate ratio is about 225. These numbers differ somewhat, but not significantly in view of the experimental error in obtaining the ratios. (The precision in measurement of such large reactivity ratios is not very high due to the large relative error in determination of small bromide ion concentrations.)

In the thermal reactions of *p*-halotoluenes with potassium diphenylphosphide in ammonia, the iodotoluene/bromotoluene rate ratio is roughly 100; see Table IV, expts 30 and 31. For the same reaction in Me_2SO solvent, the ratio (obtained from entrainment experiments previously described) was 140. It should be noted that these ratios for *p*-halotoluenes are fairly close to one another. Possibly the **1b**/**1a** rate ratio is genuinely different from the PhI/PhBr ratio. In principle, it might well differ.

Table IV. Reactions of Potassium Diphenylphosphide with Iodo- and Bromobenzene in Ammonia[a]

expt no.	PhI, mol	PhBr, mol	irradiation time, min	total time, min	iodide, mol	bromide, mol	k_{PhI}/k_{PhBr}
20	2.00×10^{-3}			2.8	2.97×10^{-4}		
21	2.00×10^{-3}		2.0	2.8	5.28×10^{-4}		
22	1.01×10^{-3}		2.0	2.8	5.01×10^{-4}		
23	0.989×10^{-3}			2.0	0.854×10^{-4}		
24	0.998×10^{-3}			2.5	1.64×10^{-4}		
25		9.0×10^{-3}		2.5		0.08×10^{-4}	
26		9.0×10^{-3}	2.0	2.5		2.48×10^{-4}	
27	0.966×10^{-3}	9.0×10^{-3}		2.5	1.81×10^{-4}	0.05×10^{-4}	480
28	1.04×10^{-3}	9.0×10^{-3}		2.5	1.33×10^{-4}	0.04×10^{-4}	350
29	1.03×10^{-3}	9.0×10^{-3}	2.0	2.5	8.80×10^{-4}	0.77×10^{-4}	225
30[b]	3.96×10^{-4}	1.98×10^{-3}		30	3.23×10^{-4}	3.05×10^{-5}	110
31[b]	4.14×10^{-4}	1.99×10^{-3}		6.0	7.18×10^{-5}	3.85×10^{-6}	96

[a] Reactions were conducted in the presence of 0.01 mol of $Ph_2P^-K^+$ in 50 mL of refluxing ammonia. [b] p-Iodotoluene and p-bromotoluene were used in place of iodobenzene and bromobenzene, respectively. Reactions were conducted in the presence of 0.002 mol of $Ph_2P^-K^+$ in 250 mL of ammonia.

Discussion

Several features of these reactions find interpretation in terms of the $S_{RN}1$ mechanism but are inconsistent with conceivable alternative mechanisms.

Inhibition by Electron Acceptors. One of the three steps of the $S_{RN}1$ propagation sequence (step M3, Scheme I) is electron transfer to a substrate molecule. A species that accepts an electron from radical anion $[ArPPh_2]^{-}\cdot$ more rapidly than the substrate does would be expected to interfere with the propagation sequence. The observation of inhibition by good electron acceptors is a characteristic test for the $S_{RN}1$ mechanism.[9] In these terms the observed inhibition by *m*- and *p*-dinitrobenzene, by nitrobenzene, and by azobenzene can be understood. The half-wave reduction potentials of these substances are rather positive as compared with that of iodobenzene.[10] There is precedent for our expectation that electron transfer to substances of more positive reduction potential should be faster than to those of more negative reduction potential.[11]

Inhibition by Radical Scavengers. Di-*tert*-butyl nitroxide is known to combine readily with organic radicals.[12] Inhibition by it has been used as a test for the $S_{RN}1$ mechanism,[13] and was observed again in the present work. The observed inhibition is intelligible in terms of competition with the nucleophile for the radical intermediate. Alternatively, di-*tert*-butyl nitroxide may act as an electron acceptor, interfering as discussed above.

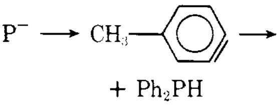
Substrate and Nucleophile Entrainment. In spontaneous (dark) $S_{RN}1$ reactions, initiation is believed to involve electron transfer from nucleophile to substrate, and the rate of initiation, of course, makes an important contribution to overall reactivity. The nucleophile and the substrate are also involved in steps of the propagation sequence (Scheme I). A given nucleophile or substrate may be rather unreactive at initiation, but quite reactive in propagation. In such a case the addition of another nucleophile or substrate, as appropriate, which is more reactive in initiation may serve to generate reactive intermediates and thereby draw into reaction a species which is unreactive in initiation but reactive in propagation.[9] In extreme cases the propagation-reactive reactant may dominate the propagation phase of the reaction (and thus form the predominant product) yet be dependent on the initiation-reactive reactant to start the process.

In the present work, the addition of *p*-iodotoluene accelerates reaction of *p*-bromotoluene with diphenylphosphide ion. This entrainment effect is intelligible in terms of the $S_{RN}1$ mechanism, as just discussed, but it would be difficult to understand in terms of alternative conceivable mechanisms. In this case, *p*-bromotoluene is less reactive than its iodo analogue in initiation, but it is relatively more reactive in propagation.

Diethyl phosphite ion is much less reactive than diphenylphosphide ion with aryl iodides in spontaneous initiation of $S_{RN}1$ reaction, but is nearly as reactive in propagation. Diethyl phosphite ion does not observably react with *p*-iodotoluene in Me_2SO in the dark. Addition of a small amount of diphenylphosphide ion serves to initiate reaction, but the nucleophile predominantly utilized in propagation is diethyl phosphite ion because of its higher concentration, and the main product is diethyl *p*-tolylphosphonate. This striking result is easily interpreted in terms of the $S_{RN}1$ mechanism.

Alternative Mechanisms. Having seen that several observations are readily interpreted in terms of the $S_{RN}1$ mechanism, we now consider some alternative mechanisms, attempting to account for the facts in terms of them.

The aryne mechanism was considered by Aguiar et al.[6] and was dismissed by them because the entering diphenylphosphino group took exactly the position vacated by the departing halogen. Were *p*-iodotoluene reacting by the aryne mechanism, the course of reaction might be represented as in eq 4. Inasmuch as nucleophiles add preferentially meta to the methyl group of 4-methylbenzyne,[14] *m*-tolyldiphenylphosphine (4) ought to be the main product via the aryne mechanism, but no 4 was found. Our work likewise shows that strict ipso substitution prevails and firmly supports their dismissal of the aryne mechanism.

1b + Ph_2P^- ⟶  ⟶ **3** + **4** (4)

+ Ph_2PH

The double displacement mechanism which appears to obtain for the reactions of trimethylstannylsodium with aryl halides[7] would, when applied to the present reactions, be written as in Scheme II. Although this mechanism would be consistent with the observation of strict ipso substitution, it is incompatible with other observations. Ammonia is sufficiently strong as a proton donor to protonate the aryl anion formed in step M4 and divert the reaction of ArH. Indeed, the reaction of Me_3SnNa with bromobenzene in ammonia gives mainly benzene.[7] Dimethyl sulfoxide also has proton donation capability and should likewise interfere.

Scheme II

$Ph_2P^-K^+ + ArX \rightarrow Ph_2PX + Ar^-K^+$ (M4)

$Ar^-K^+ + Ph_2PX \rightarrow ArPPh_2 + KX$ (M5)

One could perhaps construct a set of ad hoc explanations to account for inhibition by nitrobenzene, dinitrobenzenes, azobenzene, and di-*tert*-butyl nitroxide in terms of the mechanism of Scheme II. No doubt such explanations would have difficulty in accounting for facts such as that 10 mol % of nitrobenzene reduces the rate not by 10% but rather by 76% (expt 16, Table III). The double displacement mechanism would, however, fail utterly in seeking to account for the observed entrainment effects. Thus, several types of evidence require its exclusion.

The familiar S_NAr mechanism[15] and the unusual direct displacement mechanism advocated by Aguiar et al.[6] likewise give no rational account of the observed inhibition and entrainment effects. They also must be rejected.

$S_{RN}1$ Reactivity Studies. In step M3 of the $S_{RN}1$ propagation cycle (Scheme I), the arylated nucleophile radical anion transfers an electron to an aryl halide. When two aryl halides are present, they compete for electrons in this step. The outcome of the competition determines the relative rates of consumption of the two aryl halides. (Here some assumptions are made. One is that the chain length is long and that only propagation, not initiation, steps consume significant quantities of aryl halides. Another is that step M1 is much faster than any alternative reaction of $[ArX]^{-}\cdot$.) Iodobenzene reacts roughly 300 times faster than bromobenzene in both the dark and photoinitiated reactions in ammonia. This is consistent with the fact that iodobenzene is more easily reduced than bromobenzene, both kinetically[16] and in polarography.[10] The same order is seen, although the ratio is about 120, for the thermal reactions of *p*-iodotoluene and *p*-bromotoluene with $Ph_2P^-K^+$ in ammonia or Me_2SO solvent.

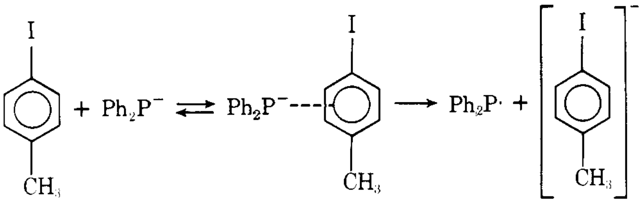
The relative rate of reaction of potassium diphenylphosphide to potassium diethyl phosphite is 1.7 as determined by direct competition. The less than twofold difference in nucleophilicity of these two anions is remarkably low in view of the fact that diphenylphosphide ion is about ten million times stronger as a base. Approximately, the pK_a for Ph_2PH is 22,[17] and for $(EtO)_2PHO$ it is 15.[18] The $S_{RN}1$ mechanism calls for the two nucleophiles to compete in steps of type M2, Scheme I. Possibly with both nucleophiles the rate constants for these steps are close to the diffusion-controlled limit, so that little selectivity is possible.

The Mechanism of Initiation. At present nothing is known about either the initiation or termination steps of the mechanism for the diphenylphosphide ion reactions. We noticed that the red color of the potassium diphenylphosphide–Me_2SO solution became more intense and more bluish when *p*-iodotoluene was added. This change is perhaps due to charge transfer complex formation, as depicted in Scheme III. The second step in Scheme III is decomposition of the charge transfer complex to form the iodotoluene radical anion and the diphenylphosphino radical. Inasmuch as the iodotoluene radical anion is a reactive intermediate involved in step M1 of the propagation cycle, the process in Scheme III would serve to initiate reaction.

Irradiation possibly increases the rate of transfer of an electron from the phosphide ion to the aryl halide moiety of the charge transfer complex of Scheme III, and thereby the rate of formation of the iodotoluene radical anion reactive intermediate.

As for termination steps, one strong possibility is scission of the diphenyltolylphosphine radical anion, formed in step M2, to aryl anion and diarylphosphino radical as for example in step M6. There is evidence that scission does occur in the indicated sense.[19] Step M6 is actually a pre-termination step, inasmuch as it does not actually destroy radicals. However, once it occurs termination is foreordained, for the sluggish diarylphosphino radical is unable to continue or revive the propagation sequence and can only engage in termination.

Scheme III



$$[ArPPh_2]^{-}\cdot \rightarrow Ph^{-}: + ArPhP\cdot \qquad (M6)$$

Some Curious Observations. In $S_{RN}1$ chemistry, *p*-dinitrobenzene is esteemed as an inhibitor par excellence.[5,9] In the present work, it significantly depressed the rate of reaction of $Ph_2P^-K^+$ with *p*-iodotoluene in ammonia (Table III) but had little effect on the same reaction in Me_2SO. On the other hand, *m*-dinitrobenzene acted as a strong inhibitor in Me_2SO.

p-Dinitrobenzene is well-known to be reactive with nucleophiles, undergoing replacement of a nitro group and forming *p*-nitrophenyl derivatives of the nucleophiles.[15,20] We suspect that the ineffectiveness of *p*-dinitrobenzene in Me_2SO stems from interference by such a reaction. The complicating reaction with $Ph_2P^-K^+$ may be much slower in ammonia, in part because the temperature is 58 °C lower.

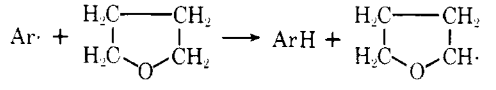
It is also noteworthy that 1,1-diphenylethene failed to inhibit the reaction of $Ph_2P^-K^+$ with **1b** in Me_2SO. Elsewhere, this olefin has served well to inhibit reactions involving aryl radical intermediates, notably in alkaline alcoholic solvents.[21] Inhibition is attributed to addition of a radical to C-2 (eq M7), forming a lethargic benzhydryl-type radical.

$$R\cdot + Ph_2C{=}CH_2 \rightarrow Ph_2\dot{C}{-}CH_2R \qquad (M7)$$

In the present system, it is conceivable that 1,1-diphenylethene undergoes addition of the elements of diphenylphosphine to form diphenyl(2,2-diphenylethyl)phosphine. Such reaction would not consume enough of the nucleophile significantly to affect the reaction rate. Alternatively, the combination of phenyl radicals with diphenylphosphide ion (step M2, Scheme I) may be so fast that the competing reaction with 1,1-diphenylethene may not be able to interfere.

Aguiar, Greenberg, and Rubenstein[6] observed that high yields of aryldiphenylphosphines were obtained when a solution of the aryl halide in THF was added dropwise to a solution of $Ph_2P^-Li^+$ in THF, but that yields were usually much lower when the addition was performed in inverse order. However, when a solution of $Ph_2P^-Li^+$ was added to one of the aryl halide in THF containing also LiCl, much better yields were obtained than in plain inverse addition.

How can one account for such phenomena in terms of the $S_{RN}1$ mechanism? We suggest that abstraction of hydrogen atoms from α positions of THF by aryl radicals (eq M8) is a serious side reaction that consumes them unproductively. This side reaction is in competition with step M2, Scheme I. In normal addition (ArX to $Ph_2P^-Li^+$), the nucleophile is in excess and there is little effective competition by THF. In inverse addition ($Ph_2P^-Li^+$ to ArX), only a low concentration of nucleophile is present at any time, and reaction of aryl radicals with THF (eq M8) predominates.



(M8)

In this connection, we call attention to other experiments in this laboratory which indicate ether solvents to be somewhat unfavorable for aromatic $S_{RN}1$ reactions. Reactions of *m*-dibromobenzene with diethyl phosphite ion, photostimulated, gave poorer yields of substitution product in 20%

THF–80% ammonia than in neat ammonia.[22] Also, prolonged irradiation of iodobenzene and potassium diethyl phosphite in glyme gave indifferent yields of $PhPO(OEt)_2$ and iodide ion.[23]

What about the effect of LiCl? It is possible that LiCl and $Ph_2P^-Li^+$ interact to form $(Li^+)_2Cl^-$ triple ions plus free Ph_2P^- (eq M9), or that a parallel reaction involving larger ion aggregates than Li^+Cl^- may obtain.[24] The effect of triple ion formation as in eq M9 is to release diphenylphosphide ion from ion pairing with lithium ion, and thereby to increase the concentration of nucleophile in the form most reactive with aryl radical. The actual rate of step M2 is thereby increased.

$$Li^+Cl^- + Ph_2P^-Li^+ \rightleftharpoons Ph_2P^- + (Li^+)_2Cl^- \qquad (M9)$$

Experimental Section

General. Gas–liquid chromatography was conducted on a Hewlett-Packard Model 5751B chromatograph equipped with a flame ionization detector. Analyses were done using a 5% SE-30 on 60–80 mesh Chromosorb W, 1.52 m × 3.2 mm column operating at 220–240 °C, except as otherwise noted. Yields of products were determined by the usual methods with the use of biphenyl, triphenylphosphine, and triphenylphosphine oxide as internal standards. In all cases, the areas were corrected for molar response as determined from standard solutions of the products and the internal standard.

Irradiations were conducted in a Rayonet Model RPR-100 photochemical reactor equipped with 16 lamps emitting maximally at 350 nm.

Infrared spectra were recorded on a Perkin-Elmer Model 237 or 337 grating spectrophotometer, NMR spectra on a Jeolco Minimar (60 MHz) instrument, and mass spectra on a Hitachi RMU-6E mass spectrometer or a Finnigan Model 4000 GC/MS system.

Rate ratios were calculated by means of eq 5.[25]

$$\frac{k_{ArI}}{k_{ArBr}} = \frac{[ArBr]_0 \ln [[ArI]_0/([ArI]_0 - [I^-]_t)]}{[Br^-]_t} \qquad (5)$$

Materials. Me_2SO was purified by the method of Skinner and Ritchie,[26] except that distillation was from calcium hydride and sodium amide. It was stored under argon in a foil-wrapped flask fitted with a three-way stopcock. Transfer was carried out by withdrawal through the stopcock using a long needle syringe with argon flowing through the stopcock via the side arm. Anhydrous ammonia was distilled from sodium prior to use. Potassium *tert*-butoxide (*t*-BuOK) (Alfa Inorganics) was sublimed immediately prior to use, quickly weighed, and transferred to the reaction flask. Aryl halides and diethyl phosphonate were purchased from commercial sources, distilled from calcium hydride prior to use, and stored in foil-wrapped bottles. Diphenylphosphine was synthesized by the method of Gee, Shaw, and Smith,[27] except that the triphenylphosphine was added as an ether solution to the ammonia. The diphenylphosphine was stored and transferred in the same manner as for Me_2SO. Triphenylphosphine was recrystallized from diethyl ether prior to use.

Reaction of *p*-Iodotoluene with Potassium Diphenylphosphide in Ammonia in the Dark. Into a three-neck, 500-mL round-bottom flask equipped with a cold finger condenser charged with solid CO_2 and 2-propanol, nitrogen inlet, and magnetic stirrer was condensed ~250 mL of ammonia. To the ammonia was added *t*-BuOK (1.18 g, 0.0105 mol) and diphenylphosphine (1.86 g, 0.01 mol). *p*-Iodotoluene (2.18 g, 0.01 mol) was added, the flask wrapped with aluminum foil, and the mixture stirred for 5.5 h. Solid ammonium nitrate was added to acidify the reaction mixture, and diethyl ether (100 mL) was added. The solid CO_2 was removed from the condenser and the ammonia allowed to evaporate. Water (100 mL) was added, and the layers were separated. The water layer was extracted with diethyl ether (3 × 75 mL), and the combined ether extracts were dried with $MgSO_4$. Potentiometric titration of the water phase with $AgNO_3$ indicated that 93.8% of iodide ion was released.

The ether extracts were diluted to 500 mL. GLC analysis of a 5-mL aliquot showed a peak with a slightly longer retention time than Ph_3P and another with a slightly longer retention time than Ph_3PO. The ether was evaporated from the aliquot, and 5 mL of CH_2Cl_2 was added. The solution was washed with 5% H_2O_2 (2 × 5 mL), 10% NaOH (2 × 5 mL), and water (1 × 5 mL). Triphenylphosphine oxide was added as a standard, and the mixture was analyzed by GLC. The yield of diphenyl-*p*-tolylphosphine oxide was 79%.

The ether was evaporated from the main fraction of the reaction mixture, the residue dissolved in 50 mL of CH_2Cl_2, and the solution washed with 5% H_2O_2 (2 × 50 mL), 10% NaOH (2 × 50 mL), and water (1 × 50 mL). The solution was dried over $MgSO_4$ and evaporated to give 2.59 g (89%) of diphenyl-*p*-tolylphosphine oxide, mp 121–124 °C. One recrystallization from diethyl ether and petroleum ether give 1.33 g: mp 129.5–130 °C (lit.[28] mp 129–130 °C); NMR ($CDCl_3$) δ 8.07–7.23 (m, 14 H), 2.40 (s, 3 H); IR (KBr pellet) 3050, 2990 (C–H), 1180 (P=O), 818 (para-disubstituted benzene), 750, 698 (monosubstituted benzene) cm^{-1}; MS *m/e* 292, 291, 215, 213, 199, 183, 165, 152.

Another experiment was conducted on the same scale and by the same procedure, except that the atmosphere was deoxygenated argon instead of N_2, through the addition of NH_4NO_3 to acidify the reaction mixture. At that point, degassed ether (100 mL) was added. The solid CO_2 was removed from the condenser and the ammonia allowed to evaporate under an argon atmosphere. Degassed water (75 mL) was added and the reaction mixture transferred to a nitrogen-filled glovebox. The mixture was transferred to a separatory funnel, and the layers were separated. The water phase was extracted with ether (3 × 100 mL). The combined organic extracts were dried with $MgSO_4$ and evaporated under an inert atmosphere. The resulting oil was transferred, under argon, to a short-path distillation apparatus and heated to 100 °C under reduced pressure (0.1 mm) for 3 h. The oil was cooled, and 2–3 mL of dried, degassed methanol was added. The mixture was swirled and dipped in a solid CO_2–acetone bath. The white solid which crystallized was collected and dried in a Schlenk filter to give diphenyl-*p*-tolylphosphine (1.11 g, 40.2%), mp 63.5–65 °C (lit.[29] mp 68–69 °C). IR and NMR spectra were in excellent agreement with literature spectra:[28] NMR ($CDCl_3$) δ 8.13–6.83 (m), 2.83 (s); IR (KBr pellet) 3025 (C–H), 1455, 1420 (Ph–P), 805 (para-substituted benzene) cm^{-1}; MS *m/e* 276, 199, 197, 183, 108.

Titration of the aqueous phase with 0.07 M $AgNO_3$ indicated that 80.5% of iodide ion was released.

Reaction of *m*-Iodotoluene with Potassium Diphenylphosphide in Ammonia in the Dark. The procedure was identical with that used for the reaction of *p*-iodotoluene with potassium diphenylphosphide in ammonia. Oxidation of the product gave diphenyl-*m*-tolylphosphine oxide which was recrystallized from diethyl ether and petroleum ether: mp 123.5–125 °C (lit.[28] mp 123–124 °C); NMR ($CDCl_3$) δ 7.92–7.8 (m, 14 H), 2.30 (s, 3 H); IR (KBr pellet) 3060, 2930 (C–H), 1182 (P=O), 865, 795, 698 (meta-disubstituted benzene), 752, 705 (monosubstituted benzene) cm^{-1}; MS *m/e* 292, 215, 213, 199, 183, 165, 152.

Reaction of Potassium Diphenylphosphide with *p*-Iodotoluene in Dimethyl Sulfoxide in the Dark. To a 300-mL round-bottom flask equipped with an argon inlet and magnetic stirrer was added 200 mL of Me_2SO, 2.36 g (0.0210 mol) of *t*-BuOK, and 3.72 g (0.02 mol) of diphenylphosphine. The mixture was stirred and equilibrated at 25 °C, and the flask was wrapped with aluminum foil to exclude light. *p*-Iodotoluene (2.18 g, 0.01 mol) was added, and the mixture was stirred and returned to the temperature bath. Aliquots (5 mL) were removed, diluted with 25 mL of water, extracted with ether (3 × 30 mL), and titrated for iodide ion with 0.07 M $AgNO_3$. At 65 min, 94.2% of iodide ion had been released and at 115 min, 96.3%. At 120 min, the reaction mixture was added to 600 mL of water and extracted with ether (3 × 150 mL). The combined ether extracts were washed with 100 mL of water and diluted to 500 mL with ether. A 5-mL aliquot was removed for GLC analysis as described above. The crude reaction mixture contained a mixture (~3:1) of diphenyl-*p*-tolylphosphine and its oxide. Oxidation and quantitative determination by GLC showed a 63% yield of the phosphine oxide.

The ether extract was dried over $MgSO_4$ and evaporated. The residue was dissolved in 50 mL of CH_2Cl_2 and oxidized as described previously. Evaporation of the solvent gave 2.28 g (78.1%) of diphenyl-*p*-tolylphosphine oxide, mp 110–115 °C. Recrystallization from petroleum ether and diethyl ether gave 1.50 g, mp 126–127 °C.

Reaction of Potassium Diphenylphosphide with *p*-Iodotoluene in Dimethyl Sulfoxide in the Dark at 25 °C. Rate Measurements. The apparatus consisted of a 100-mL round-bottom flask with a gas inlet side arm equipped with a short condenser topped with a ground glass stopper. The condenser and top half of the flask were wrapped in black plastic tape. The flask was flushed with argon and kept under a positive argon pressure. Diphenylphosphine (1.86 g, 0.01 mol), Me_2SO (50 mL), and *t*-BuOK (1.18 g, 0.0105 mol) were introduced through the top of the flask. The solution was stirred with a magnetic stirrer until the *t*-BuOK dissolved, and the flask was completely wrapped in aluminum foil and equilibrated in a 25.0 °C water bath. The flask was removed from the bath and returned to the stirrer, where the additive, if any, was added followed by *p*-iodotoluene (0.44 g, 0.002 mol). The mixture was stirred for a few seconds and returned to the water bath. Aliquots were removed from the flask with a 5-mL volumetric pipet and added to 25 mL of water. Each aliquot was extracted with diethyl ether (2 × 35 mL), acidified with dilute HNO_3, and titrated with 0.07 M $AgNO_3$.

In an experiment with **1a** and $Ph_2P^-K^+$ at initial concentrations of 0.04 and 0.2 M, respectively, bromide ion concentration was determined to be 0.091×10^{-3} M at 2.4 min, 0.203×10^{-3} M at 21.8 min, 0.378×10^{-3} M at 61.6 min, and 1.51×10^{-3} M at 372 min.

Reaction of Potassium Diethyl Phosphite with *p*-Iodotoluene in Dimethyl Sulfoxide in the Dark. The apparatus consisted of a 100-mL round-bottom flask with a gas inlet side arm, equipped with a short condenser topped with a ground glass stopper. The condenser and top half of the flask were wrapped in black plastic tape. The flask was flushed with argon and kept under a positive argon pressure. Me_2SO (50 mL), *t*-BuOK (1.34 g, 0.012 mol), and diethyl phosphonate (1.38 g, 0.01 mole) were added and stirred. The mixture was equilibrated in a 25 °C bath and *p*-iodotoluene (0.44 g, 0.002 mol) added. The mixture was stirred and returned to the water bath. Aliquots (5 mL) were withdrawn and added to 25 mL of water to quench the reaction. The samples were extracted with ether (3 × 25 mL), and the aqueous phase was titrated for iodide ion with 0.07 M $AgNO_3$.

Biphenyl was added to the ether extracts as an internal standard, and the amount of diethyl phenylphosphonate was determined by GLC (5% SE-30, 1.52 m × 3.2 mm, 135 °C).

In a second reaction, the procedure used was identical, but diphenylphosphine (0.1967 g, 0.00106 mol) was added with the diethyl phosphonate. The analysis was identical, but after the diethyl phenylphosphonate was determined the ether phase was oxidized as previously described and the amount of diphenyl-*p*-tolylphosphine oxide was determined by GLC with use of triphenylphosphine oxide as internal standard.

Entrainment of 1a by Addition of 1b, and 1b/1a Reactivity Ratio in Me_2SO. The initial concentrations were 0.04 M in **1a** and 0.20 M in $Ph_2P^-K^+$, and the general procedure described for rate measurements was followed. Aliquots taken at 3.7, 10.3, 19.9, and 42.0 min were analyzed for Br^- by potentiometric titration with $AgNO_3$. At 42.6 min, 0.2 mL of a 2 M solution of **1b** in Me_2SO was added (to achieve a **1b** concentration of 0.0133 M), and subsequent aliquots were analyzed with observation of both the I^- and the Br^- end points. The amount of bromide ion released is plotted in Figure 3; the amount of iodide ion released was about 13 times the increment of bromide ion release after addition of **1b**. By means of eq 5, the reactivity ratio, k_{1b}/k_{1a}, was reckoned to be 240 at 43.2 min, 130 at 44.0 min, 140 at 44.6 min, 150 at 55.2 min, and 120 at 70.3 min. In a similar experiment with result like that shown in Figure 3, **1b** to 0.016 M was added at 63.2 min, and k_{1b}/k_{1a} was reckoned as 110 at 64.0 and 130 at 64.8 min.

Effects of Additives on Reactions of 1b in Me_2SO. Initial concentrations were 0.04 M for **1b** and 0.20 M for $Ph_2P^-K^+$, and the general procedure described for rate measurements was followed. The results for reaction with no additive, with 0.0083 M *m*-dinitrobenzene, with 0.0081 M azobenzene, and with 0.0080 M di-*tert*-butyl nitroxide are plotted in Figure 2. Another experiment (not plotted) with 0.0084 M *m*-dinitrobenzene showed much stronger deceleration, to about three-fifths the amount of reaction shown in Figure 2 for aliquots within the first 3 min. With 0.0042 M 1,1-diphenylethene or 0.0086 M *p*-dinitrobenzene, iodide ion release within the first 2 min was nearly as great as in the absence of additives.

Registry No.—**3,** 1031-93-2; **5,** 6840-28-4; **6,** 6840-27-3; potassium diphenylphosphide, 15475-27-1; diphenylphosphine, 829-85-6.

References and Notes

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Mechanism of the α-Chlorination of Propylbenzene by Chromyl Chloride

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Optically active α-deuteriopropylbenzene has been treated with chromyl chloride and gives optically active 1-chloro-1-phenylpropane in 35–40% yield. This reaction proceeds with net overall retention of configuration (about 35%) accompanied by considerable racemization (65%), even at early reaction times. Product chloride itself racemizes during the reaction as well. A radical pair mechanism is supported by the data.

We wish to report the results of our study of the α-chlorination of propylbenzene (**1**) by chromyl chloride. These results support a radical pair mechanism for the chlorination and are not consistent with concerted or radical chain formulations of this reaction.

$$\underset{\textbf{1}}{C_6H_5CH_2CH_2CH_3} + CrO_2Cl_2 \rightarrow \underset{\textbf{2}}{C_6H_5CH(Cl)CH_2CH_3}$$

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