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REACTIONS OF RADICALS WITH NUCLEOPHILES: THE NATURE OF THE ARYL RADICAL INTERMEDIATE IN THE AROMATIC S(,RN)1 REACTION

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Reactions of radicals with nucleophiles: The nature of the aryl radical intermediate in the aromatic $S_{RN}1$ reaction

by

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CHAPTER I. A LITERATURE REVIEW OF THE $S_{RN}1$ REACTION (AND RELATED TOPICS)

I. THE GENERALIZED $S_{RN}1$ MECHANISM

Nucleophilic substitution reactions are of paramount importance in the repertoire of organic chemists. A description of the process, as it appeared in a 1959 textbook of organic chemistry, concisely identifies the salient features of the transformation: "A basic reagent, using a pair of its electrons, forms a new bond to the carbon atom under attack, and one of the substituents originally bound at this carbon atom is freed, departing with the pair of electrons comprising the bond that has been broken" (1). This concept is illustrated in Eq. 1, where "N" represents the basic reagent (nucleophile), "R" represents an organic group containing the carbon atom under attack and "X" represents the departing substituent (leaving group).

$$R{:}X + N{:}^- \longrightarrow R{:}N + X{:}^- \qquad (1)$$

Many of the mechanisms by which this transformation can occur are clearly delineated and are core material in virtually any textbook of organic chemistry. Thus, acronyms such as "S_N1" and "S_N2" are familiar descriptions of common mechanisms of nucleophilic substitution at saturated carbon and refer to the rate-determining step in a nucleophilic substitution process.

Nucleophilic substitution can also occur at unsaturated carbon. "Addition-elimination" processes

occur in the carboxylic acid family, as well as in vinylogous substrates. Nucleophilic aromatic substitution has been recently reviewed (2). In addition to the classic "benzyne" mechanism, aromatic substitution processes are also described by several acronyms such as "S_N1", "S_N2", "S_N(ANRORC):, etc....

A common thread running through all the nucleophilic substitution reaction mechanisms discussed up to this point is the presumption that electrons move in pairs. In 1964, Russell, Janzen and Strom laid the foundation for an entirely different approach to organic reactivity by demonstrating that electrons do not always move in pairs (3).

The phenomenon known as single electron transfer is illustrated in Eq. 2, where A^- is an anion (carbanion or nitranion in the original paper), π is an unsaturated system and the products $A\cdot$ and $\pi^{\cdot-}$ are a free radical and radical anion respectively. The important feature of this transformation is that there is a net movement of only one electron.

$$A:^- + \pi \longrightarrow A\cdot + \pi^{\cdot-} \qquad (2)$$

In nucleophilic substitution, the nucleophile (N^-) is usually an anion. Additionally, the substrate (RX) may be able to function as an electron acceptor. Thus, a component of single electron transfer may be

involved in nucleophilic substitution.

In 1966, a chain reaction involving electron transfer steps, as well as free radical and radical anion intermediates, was discovered for nucleophilic substitution at saturated carbon (4,5). This process was later extended to unsaturated carbon and given the name "$S_{RN}1$" (6).

The propagation steps of the $S_{RN}1$ reaction are described by Scheme I.

Scheme I

$$\text{PROPAGATION} \begin{cases} RX^{\cdot -} \longrightarrow R\cdot + X^- & (a) \\ R\cdot + N^- \longrightarrow RN^{\cdot -} & (b) \\ RN^{\cdot -} + RX \longrightarrow RN + RX^{\cdot -} & (c) \end{cases}$$

$$\text{OVERALL REACTION} \quad RX + N^- \longrightarrow RN + X^- \qquad (d)$$

In Scheme I, R represents the organic portion of the substrate, N^- is the nucleophile and X the leaving group. Step (a) represents the dissociation of substrate radical anion ($RX^{\cdot -}$) into the free radical (R·) and leaving group (X^-). The name "$S_{RN}1$" is derived from the similarity between this step of the reaction to the dissociation step of the S_N1 reaction (Eq. 3). The subscript "R" is added to indicate the intermediacy of free radicals. However, the symbol "$S_{RN}1$" does not define the rate determining step in the reaction sequence.

$$R\text{-}X \longrightarrow R^+ + X^- \qquad (3)$$

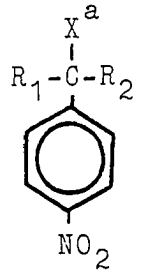
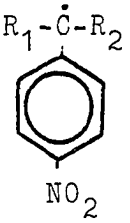
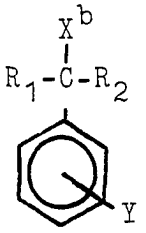
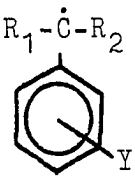
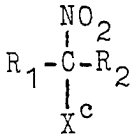
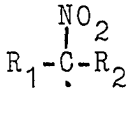
Step (b) of Scheme I involves the coupling of the free radical ($R\cdot$) with the nucleophile (N^-) to form a new radical anion ($RX^{\cdot-}$) which in step (c), the final link of the chain, transfers its extra electron to a molecule of starting material (RX). Steps (a) - (c) sum to yield (d), representing the overall process--nucleophilic substitution.

A. The Nature of Substrate (RX)

Steps (a) - (c) of Scheme I demonstrate an interdependency between the identity of R, X and N. R and X must be chosen such that $RX^{\cdot-}$ will dissociate. N^- must be able to form an adduct ($RN^{\cdot-}$) with $R\cdot$. Finally, $RN^{\cdot-}$ must be able to transfer an electron to RX (i.e., RX should be more easily reduced than RN). Failure to meet any of these criteria result in failure to propagate the chain. For this reason, the subsequent discussion will deal exclusively with substrates and nucleophiles that have been shown to meet this criteria.

Early examples of the aliphatic $S_{RN}1$ reaction involved substrates such as 1, where X is the leaving group and W is an electron withdrawing functionality, usually electron withdrawing by resonance. Some selected examples appear in Table 1.

Table 1. Typical substrates in the aliphatic $S_{RN}1$ reaction yielding stabilized alkyl radicals

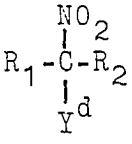
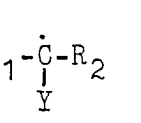
Substrate (RX)	Resultant radical (R·)	Leaving group (X^-)	Reference(s)
		X^-	7, 8, 9
		X^-	7
		X^-	7, 10, 11, 12, 13, 14

[a]Where X = Cl, NO_2, $-SO_2C_6H_5$, N_3, OAr, $\overset{+}{S}Me_2$.

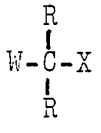
[b]Where X = NO_2 or Cl, and Y = p-CN, p-SO_2Ar, m-NO_2

[c]Where X = Cl, Br, I, NO_2, $ArSO_2$, SCN, SR.

Table 1. (Continued)

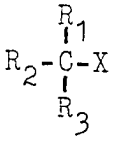
Substrate (RX)	Resultant radical (R·)	Leaving group (X^-)	Reference(s)
		NO_2^-	7, 9, 12, 15
$BrCF_2Cl$	$\cdot CF_2Cl$	Br^-	16

[d]Where Y = CO_2R, CN, C(O)R.



1

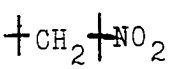
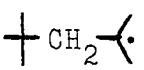
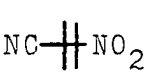
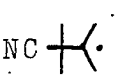
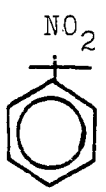
Shortly afterward, substrates such as (2) were found to yield simple alkyl radicals upon dissociation of their radical anions. Specific examples of these appear in Table 2.



R_1, R_2, R_3 = alkyl
X = NO_2, HgCl

2

Table 2. Typical substrates in the aliphatic $S_{RN}1$ reaction yielding simple alkyl radicals

Substrate (RX)	Resultant radical (R·)	Leaving group (X^-)	Reference(s)
$RHgX$[a]	R·	X^-	17
	<u>t</u>-Bu·	NO_2^-	18
		NO_2^-	18
		NO_2^-	18
		NO_2^-	18

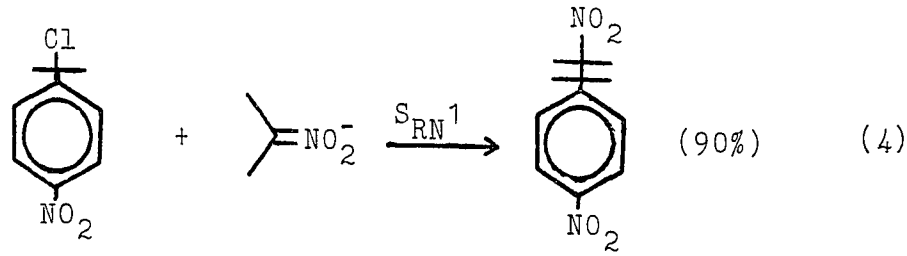
[a]Where R = $PhCH_2$, <u>c</u>-C_6H_{11}, <u>n</u>-C_6H_{13}, <u>i</u>-Pr and X is halogen.

In 1970, with the discovery of the aromatic $S_{RN}1$ reaction, it was found that several aromatic substrates (ArX) also dissociate (after one electron reduction) to Ar• and X^-. Several suitable substrates are listed in Table 3.

B. The Nature of Nucleophiles (N^-)

Table 4 organizes several nucleophiles under the nature of the radicals they can react with. Alkyl radicals have been further subdivided into "simple" and "stabilized." This subdivision is not arbitrary as will become evident shortly.

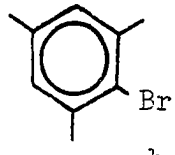
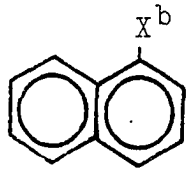
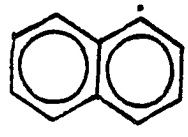
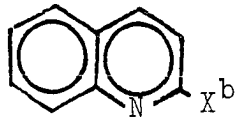
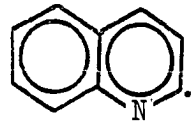
Two features of Table 4 should be pointed out. The first (and more obvious) is that the $S_{RN}1$ reaction provides incredible synthetic potential. A large number of these reactions form carbon-carbon bonds. Many of the products would be difficult (or impossible) to form by any other procedure. Furthermore, it has been pointed out that the $S_{RN}1$ reaction is relatively insensitive to steric effects (19, 20). Consider Eqs. 4 and 5:



(90%) (4)

reference 21

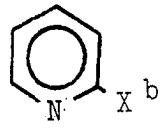
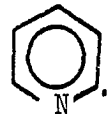
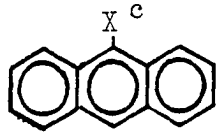
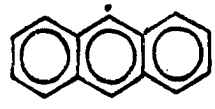
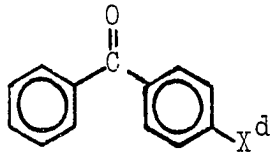
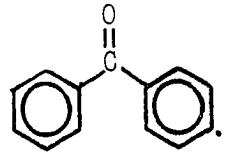
Table 3. Typical substrates in the aromatic $S_{RN}1$ reaction

Substrate (RX)	Resultant radical (R·)	Leaving group (X^-)	Reference(s)
	Ph·	X^-	20
		Br^-	6
		X^-	20, 22, 23
		X^-	20, 22, 23, 24

[a]Where X = I, Br, Cl, F, SPh, $+NMe_3$, $OP(O)(OEt)_2$, SePh, and $+SPh_2$.

[b]Where X = halogen.

Table 3. (Continued)

Substrate (RX)	Resultant radical (R·)	Leaving group (X^-)	Reference(s)
		X^-	20, 23, 24
		X^-	20, 23
		X^-	20, 22
		Cl^-	22

[c]Where X = Br.

[d]Where X = Cl or Br

Table 4. Nucleophiles that trap radicals in the $S_{RN}1$ reaction

Nature of radical (R·)	Nucleophile (N^-)	Isolated product(s)	Reference(s)
stabilized alkyl	$R_1OC(=O)-\underset{-}{C}(R_2)-CO_2R_1$	$R-C(CO_2R_1)_2$	7, 9
$W-\overset{R_1}{\underset{R_2}{C}}\cdot$ where W is an electron withdrawing group	$\overset{R_1}{\underset{R_2}{}}C=NO_2^-$	$R-\overset{R_1}{\underset{R_2}{C}}-NO_2$	4, 5, 7, 9
	$PhSO_2^-$	$R-S(=O)_2-Ph$	7, 19
	NO_2^-	$R-NO_2$	7, 9, 19
	CN^-	R-CN	7
	PhS^-	R-SPh	7, 9
	N_3^-	$R-N_3$	7, 9
	^-OAr	R-OAr	7, 9
	$(EtO)_2PO^-$	$R-P(=O)(OEt)_2$	25, 26
	$CH_3\overset{O^-}{C}=CH_2$	$RCH_2\overset{O}{C}CH_3$	27

Table 4. (Continued)

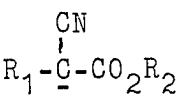
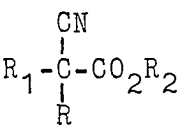
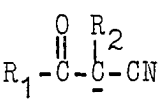
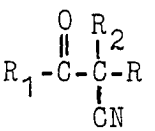
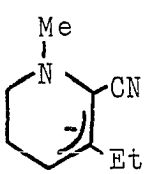
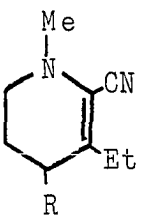
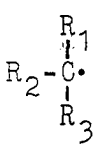
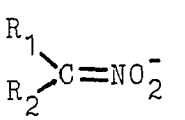
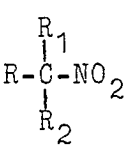
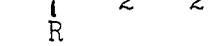
Nature of radical (R·)	Nucleophile (N^-)	Isolated product(s)	Reference(s)
stabilized alkyl (continued)	$(EtO)_2PS^-$	$R-P(OEt)_2$ (=S)	26
			9, 28
			9, 28
			29
simple alkyl  R_1, R_2, R_3 = alkyl or H			17, 18
	$PhC^-(CO_2Et)_2$		30

Table 4. (Continued)

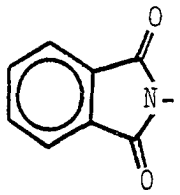
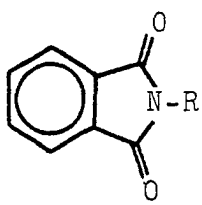
Nature of radical (R·)	Nucleophile (N^-)	Isolated product(s)	Reference(s)
simple alkyl (continued)	NO_2^-	$R\text{-}NO_2$	30
			30
	$Ph_2\bar{C}CN$	$Ph_2C(R)\text{-}CN$ and $Ph_2C{=}C{=}N\text{-}R$	30
	<u>unreactive</u>: $(EtO)_2PO^-$, $PhSO_2^-$		17
aryl	$(EtO)_2PO^-$	$Ar\text{-}P(O)(OEt)_2$	20
	PhS^-	Ar-SPh	20
	$PhTe^-$	ArTePh	23
	Ph_2As^-	Ph_2AsAr	23

Table 4. (Continued)

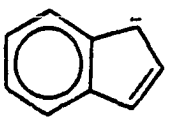
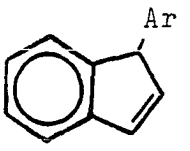
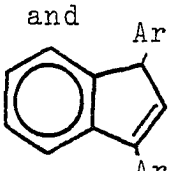
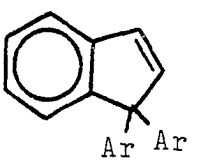
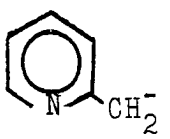
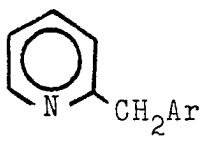
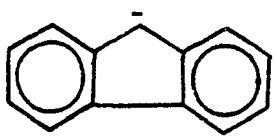
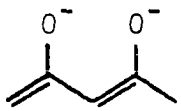
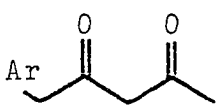
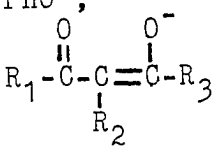
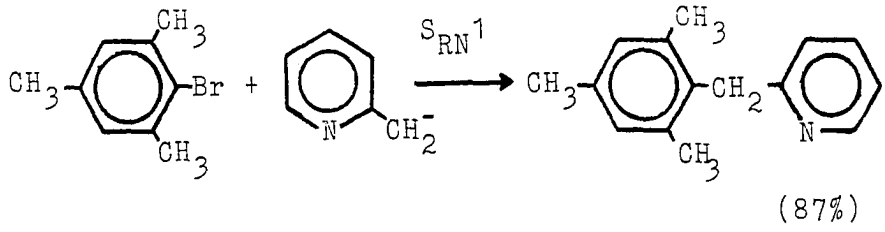
Nature of radical (R·)	Nucleophile (N^-)	Isolated product(s)	Reference(s)
aryl (continued)	Ph_2Sb^-	Ph_2SbAr	23
	$(EtO)_2PS^-$	$ArP(=S)(OEt)_2$	20
	$CH_2{=}C(O^-)\text{-}CH_2R$	$ArCH_2C(=O)CH_2R$ and $Ar_2CHC(=O)CH_2R$	20
	Ph_2P^-	$ArPPh_2$	20
		 and  and 	31

Table 4. (Continued)

Nature of radical (R·)	Nucleophile (N^-)	Isolated product(s)	Reference(s)
aryl (continued)	$^-CH_2CN$	$ArCH_2CN$ and $(ArCH_2)_2$	20
	NH_2^-	$Ar\text{-}NH_2$	6, 20
			20, 32
		9-ArFl	20
			20
	<u>unreactive</u>: $PhSO_2^-$, RO^-, PhO^-, 		20

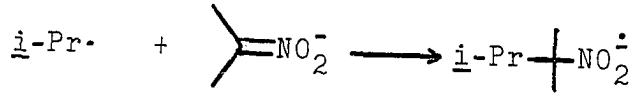


(5)

(87%)

Despite what appears to be severe steric constraint, these reactions none the less provide a high yield of product.

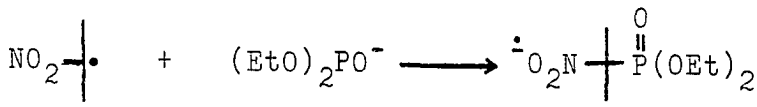
The second important feature of Table 4 is more subtle. All nucleophiles which successfully trap simple alkyl radicals contain substituents that are capable of stabilizing the resultant radical anion. In Eq. 6, it is apparent that the NO_2 functionality, by stabilizing the radical anion, increases the facility of this process. Nucleophiles that are incapable of providing this stabilization (e.g., $(EtO)_2PO^-$) do not trap simple alkyl radicals (17).



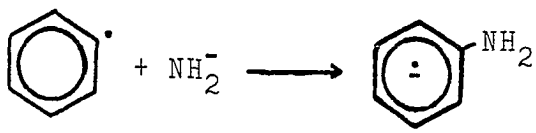
(6)

Such is not the case for aryl radicals or "stabilized" alkyl radicals. In the latter case, the electron withdrawing functionality can provide this stabilization (Eq. 7). In the former case, apparently the π-system plays some role in the reaction, perhaps

by stabilizing the resultant radical anion (Eq. 8) in instances where no other source of stability is present.



(7)



(8)

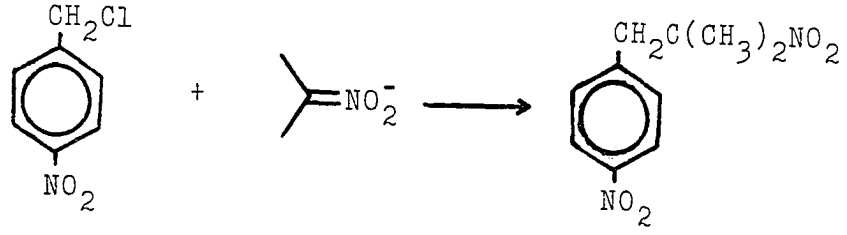
It is tempting to conclude that aryl radicals resemble stabilized alkyl radicals with respect to reactivity towards nucleophilic reagents.

II. EVIDENCE FOR THE $S_{RN}1$ MECHANISM-- DISTINCTION FROM OTHER POSSIBILITIES

A. The Aliphatic $S_{RN}1$ Reaction

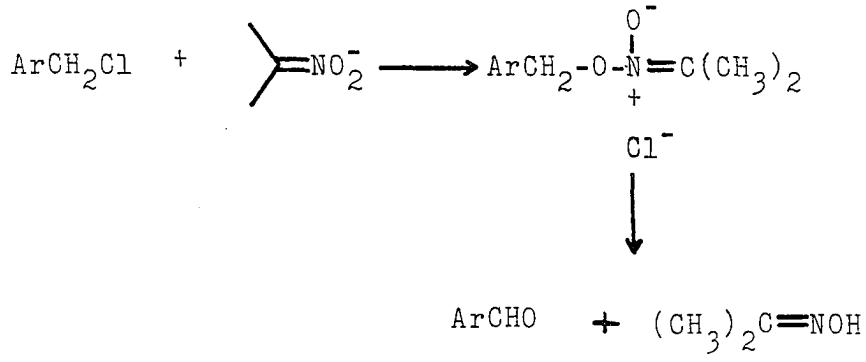
Perhaps the best way to begin this discussion is to review the events that led to the discovery of the aliphatic $S_{RN}1$ reaction.

In 1949, it was reported that the reaction of p-nitrobenzyl chloride with the anion of 2-nitropropane yielded C-alkylated product according to Eq. 9 (33). This result was somewhat unexpected



(9)

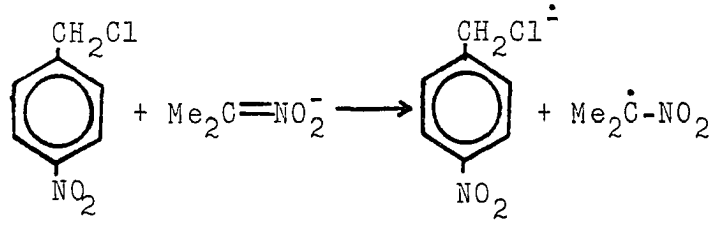
since alkylation of nitronate anions by S_N2 processes result exclusively in the corresponding aldehyde (via O-alkylation) (33). Eq. 10 demonstrates this point.

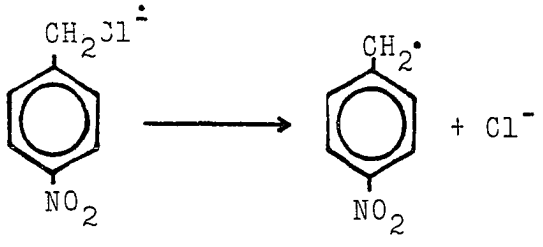


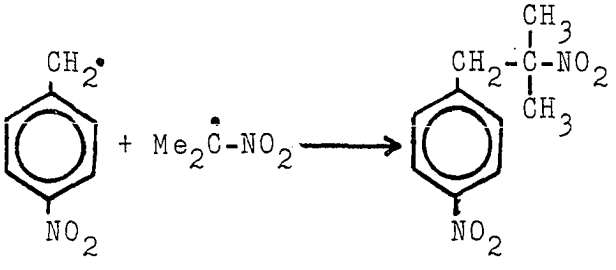
(10)

In 1964, it was proposed that C-alkylation was not occurring by an S_N2 process. A mechanism involving free radicals and radical anion intermediates (Scheme II) was proposed (34).

Scheme II

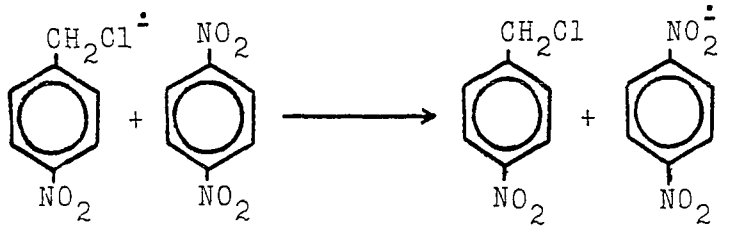






The strongest evidence for Scheme II derives from the effect of added reagents that were known to be easily reduced (e.g., p-dinitrobenzene). Because of interception of the nitrobenzyl chloride anion radical by the electron acceptor (Eq. 11), the process yielding

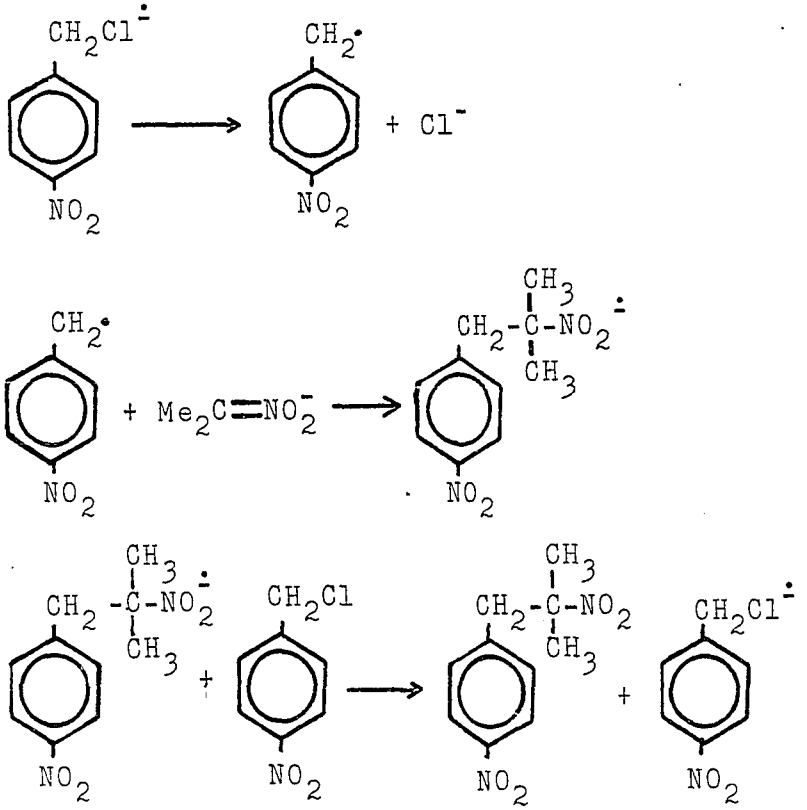
the C-alkylated product could be effectively suppressed (34).



(11)

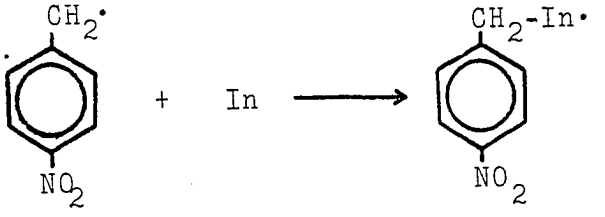
It was soon realized that Scheme II needed modification. In 1966, a free radical chain mechanism was proposed (Scheme III) (4, 5). Scheme III is what is now known as the $S_{RN}1$ reaction.

Scheme III



The key to differentiating between the mechanisms of Schemes II and III was to look at the effect of added reagents (inhibitors) on the rate of the reaction.

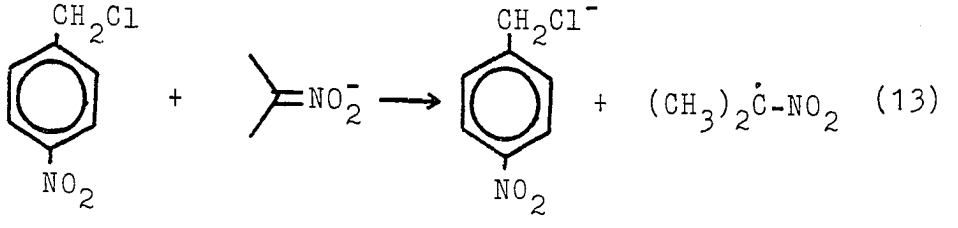
The concept of inhibition can be developed as follows. Suppose a molecule, In, that has the ability to react with a free radical (such as p-nitrobenzyl) as in Eq. 12.



(12)

3

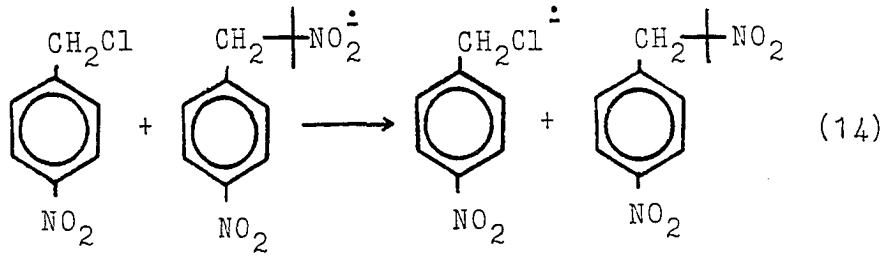
Furthermore, suppose that the product of this reaction (3) is inert, undergoing no further reactions that consume starting material. If the mechanism of Scheme II were operating, the addition of a small quantity of In (typically 5-10 mole %) should have no effect on the rate of dissappearance of starting material, the reason being that the rate of disappearance is governed by Eq. 13.



(13)

The yield of expected product would be decreased since the p-nitrobenzyl radical is diverted to a different product.

If Scheme III were operating however, a completely different result is expected. The rate of disappearance of starting material is governed primarily by Eq. 14:



(14)

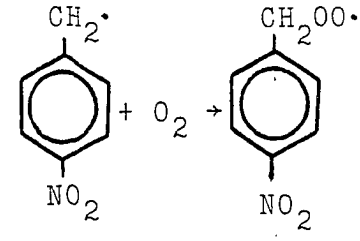
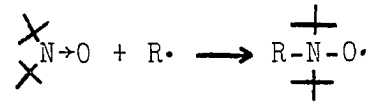
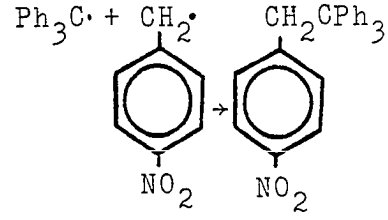
4

Diversion of the p-nitrobenzyl radical by In reduces the steady state concentration of (4). Therefore, the rate of the reaction is profoundly reduced.

This latter situation was shown to prevail in the reaction of p-nitrobenzyl chloride with nitronate ion, thereby providing evidence for Scheme III--the $S_{RN}1$ reaction mechanism (4,5).

Typical inhibitors (In) of the $S_{RN}1$ reaction and the nature of the species they intercept are given in Table 5. The references listed in Tables 1 and 2 provide specific examples of the use of inhibitors in

Table 5. Common inhibitors of the $S_{RN}1$ reaction

Inhibitor	Species intercepted	Example
O_2	free radicals	
<u>m</u>-dinitrobenzene <u>p</u>-dinitrobenzene	radical anions	equation 11
di-<u>tert</u>-butyl nitroxide	free radicals	
hexaphenylethane	free radicals	

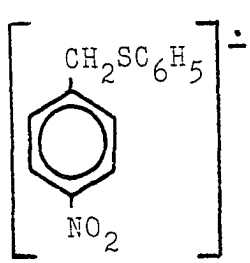
elucidating the $S_{RN}1$ mechanism, and the interested reader is directed in that direction.

Another diagnostic feature of the $S_{RN}1$ reaction is that it can be initiated by light. Presumably a species capable of entering the propagation cycle is generated photochemically. For the reaction of <u>p</u>-nitrobenzyl chloride with nitronate anion, Eq. 15 was suggested

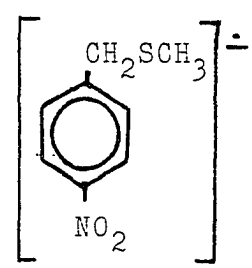
to account for initiation (35).

$$\underline{p}\text{-}ClCH_2C_6H_4NO_2 \xrightarrow[THF]{h\nu} (\underline{p}\text{-}ClCH_2C_6H_4NO_2H\cdot)$$
$$\Big\downarrow B^- \qquad (15)$$
$$\underline{p}\text{-}ClCH_2C_6H_4NO_2^{\cdot-} + BH$$

Additional evidence was provided by the ability of catalytic quantities of one-electron reducing agents (such as naphthalene sodium, NaO_2, Na) to induce the chain reaction (7), as well as the detection of reactive intermediates by esr spectroscopy. In the latter example, it was possible to detect the radical anions of p-nitrobenzyl phenyl sulfide (5) and p-nitrobenzyl methyl sulfide (6) in the respective reactions of p-nitrobenzyl chloride with thiophenoxide and methyl mercaptide ions (8).



5



6

The experimental evidence discussed thus far clearly allow distinction between the mechanism depicted in Scheme II (a non-chain process) and that depicted in Scheme III (a chain process). However, the question must be asked: Is there any other reasonable chain mechanism that can be proposed as an alternative to the $S_{RN}1$ mechanism? The answer is yes, and such a mechanism is presented in Scheme IV.

Scheme IV

PROPAGATION

$$RX^{\cdot -} + N^- \longrightarrow RN^{\cdot -} + X^- \qquad (a)$$

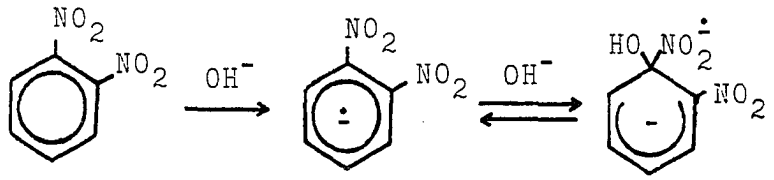
$$RN^{\cdot -} + RX \longrightarrow RN + RX^{\cdot -} \qquad (b)$$

OVERALL REACTION

$$RX + N^- \longrightarrow RN + X^- \qquad (c)$$

The mechanism of Scheme IV supposes that the radical anion ($RX^{\cdot -}$) is attacked by nucleophile (N^-) and in analogy to an S_N2 reaction (where RX is attacked by N^-), the reaction is thus called $S_{RN}2$.

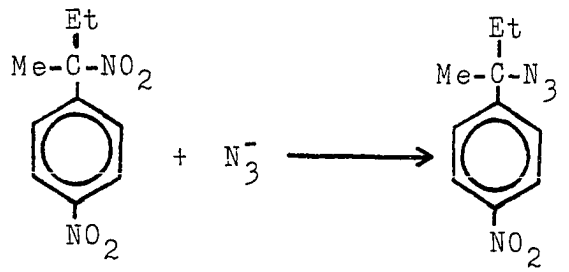
The concept of a negatively charged nucleophile attacking a radical anion may appear counter-intuitive, but it is not without precedent. Reaction of o- or p-dinitrobenzene with hydroxide (producing the corresponding nitrophenols) have been shown to involve such an attack (Eq. 16) (36).



(16)

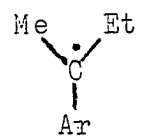
The unambiguous demonstration of the intermediacy of a free radical (R·) provides a basis for ruling out an $S_{RN}2$ reaction. Two useful approaches involve determining the stereochemistry of the reaction and the use of intramolecular rearrangements (radical probes).

Optically active substrate (7), in its reaction with azide ion (Eq. 17), has been shown to produce racemic product (8) consistent with the involvement of the planar radical (9) (7).



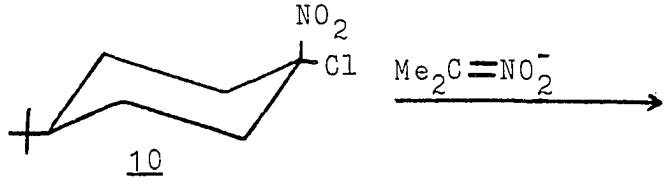
(17)

7 8



9

The analogous reaction of either (10) or (11) with nitronate produced (12) and (13) in nearly the same ratio (Eq. 18), 9:91 and 10:90 respectively (37):



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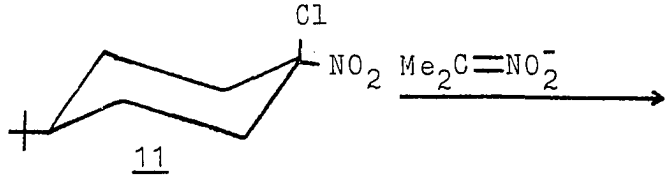
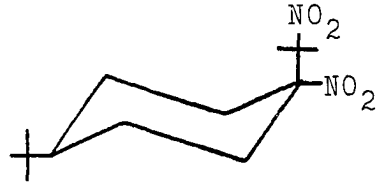
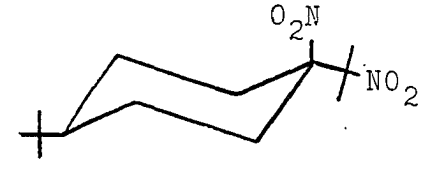


11

12 + 13 (17)



12



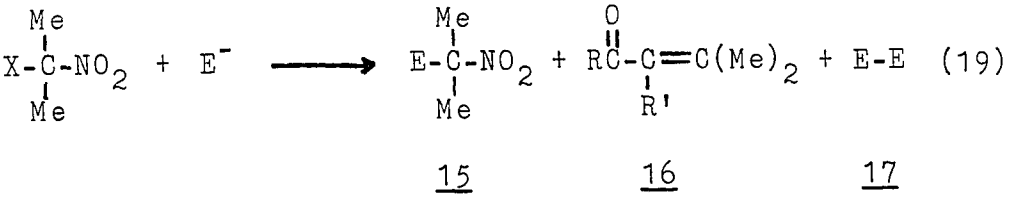
13

The same intermediate (14) is clearly involved in both instances.

14

The relative reactivities of a series of anions towards 2-nitro-2-propyl radical were reported to be constant with respect to three different leaving groups: Cl^-, p-$MePhSO_2^-$ and NO_2^-, inferring the intermediacy of a common free radical (26).

Evidence has been presented for a process which might formally be an $S_{RN}2$ reaction. The reactions of enolates (E^- = $RC(O^-)=CHR'$) with $XCMe_2NO_2$ leads to coupling {(15) and (16)} and dimerization (17) products (Eq. 19) via a free radical chain reaction.

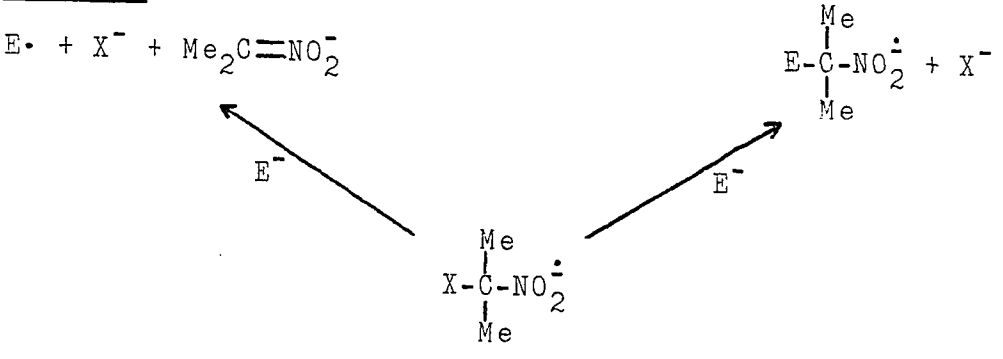


(19)

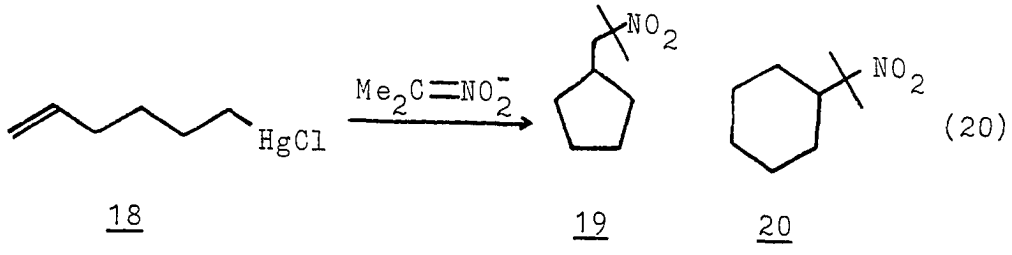
15 16 17

The ratio of {(15) + (16)}/(17) was shown to be dependant on X. It was proposed that enolate reacts at the radical anion stage according to Scheme V (38).

Scheme V



The use of intramolecular rearrangements is nicely illustrated by the reaction of 1-chloromercury-5-hexene (18) with nitronate (Eq. 20).



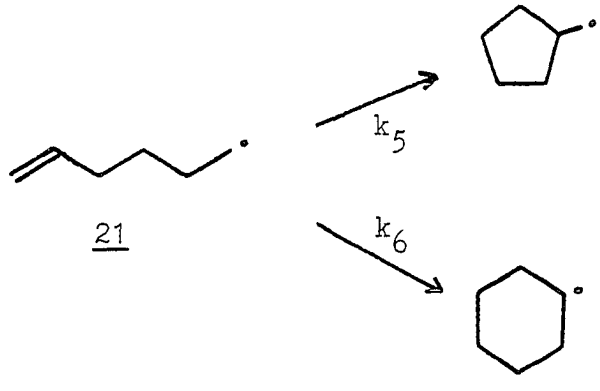
(20)

18 19 20

$+ Hg^0 + Cl^-$

Cyclized products (19) and (20) were obtained. The observed ratio of cyclopentylcarbinyl to cyclohexyl product of 96:4 is exactly as expected for the Δ^5-hexenyl radical (21) in Scheme VI (17).

Scheme VI

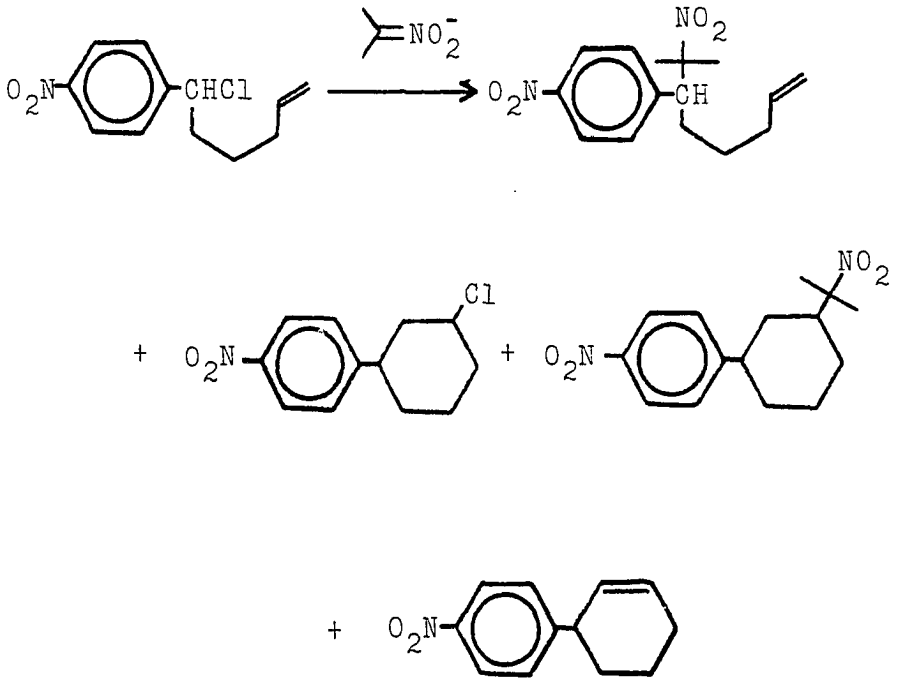


21

$k_5 > k_6$

Intramolecular trapping of a free radical intermediate has also been demonstrated in the p-nitrobenzyl system (Scheme VII) (39).

Scheme VII



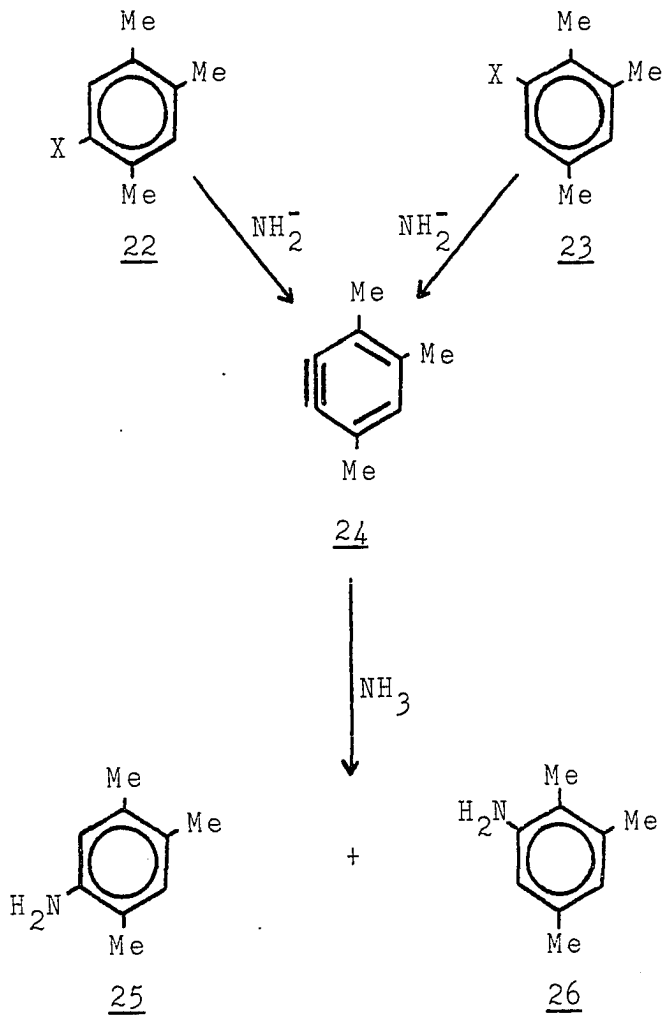
Thus, inhibition experiments, catalysis by light, catalysis by one-electron reducing agents, reaction stereochemistry and radical probes have all been employed in the formulation of the aliphatic $S_{RN}1$ reaction.

B. The Aromatic $S_{RN}1$ Reaction

The aromatic $S_{RN}1$ reaction, like its aliphatic counterpart, was proposed to explain results that were otherwise inexplicable by conventional mechanisms of

nucleophilic substitution. In studying substitution reactions of 5-halo and 6-halopseudocumenes, (22) and (23) respectively, by NH_2^- in ammonia, an unexpected result was obtained. The aryne mechanism (Scheme VIII) was anticipated.

Scheme VIII



Since the same aryne intermediate (24) was expected to be involved in either the reaction of (22) or (23), the ratio of 6-amino- to 5-aminopseudocumene, (26)/(25), should be the same. Such indeed was the case for X = Cl or X = Br, where in all cases the ratio was 1.46 (6, 20).

When X = I however, the ratio (26)/(25) was 0.63 and 5.9 from 5- and 6-iodopseudocumene respectively, indicating substitution was occurring to a significant extent without rearrangement (6,20).

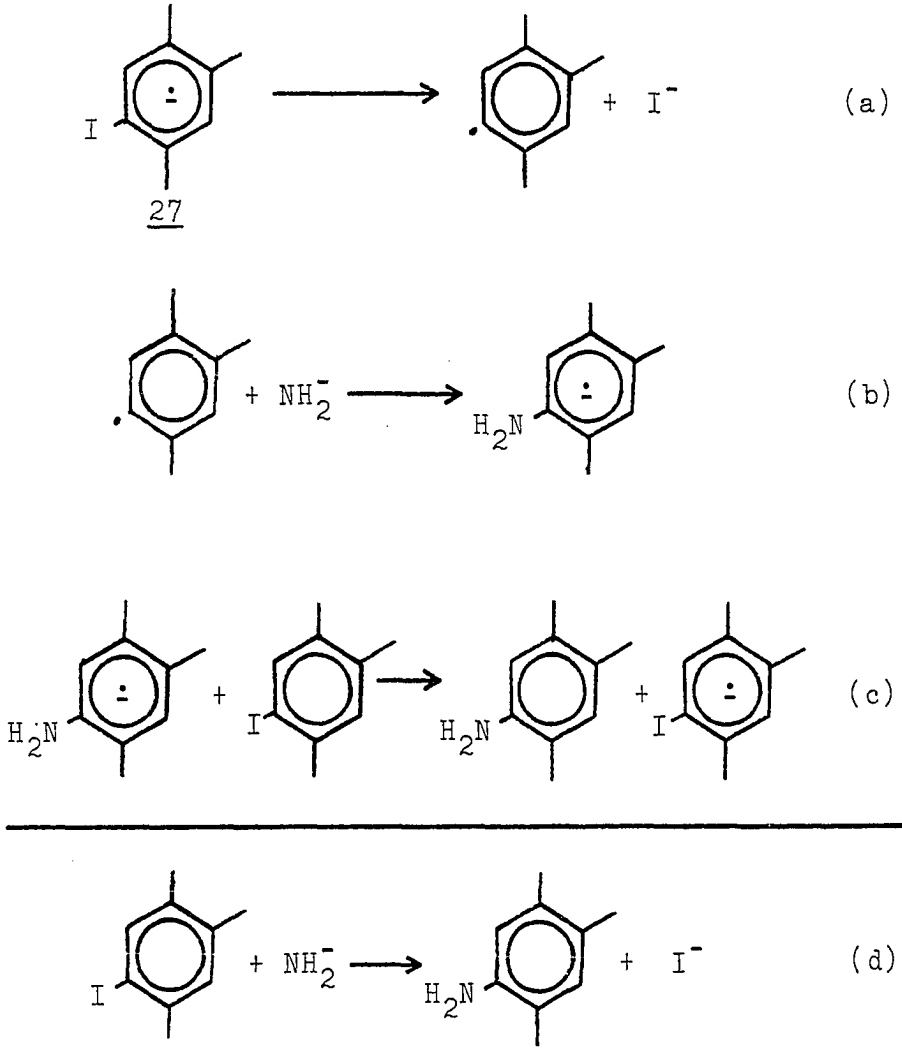
A radical scavenger (tetraphenylhydrazine) brought the ratio (26)/(25) closer to the value expected for an aryne mechanism. Furthermore, potassium metal (a source of solvated electrons in liquid ammonia) when added to the reaction mixture resulted in exclusively unrearranged products. Thus, it was proposed that the unrearranged products were the result of a reaction mechanism involving free radicals and radical anions--the aromatic $S_{RN}1$ reaction (Scheme IX) (6,20).

The effect of added potassium produces $ArX^{\cdot-}$ {(27) in Scheme IX} which can enter the propagation sequence at step (a).

In addition to catalysis by solvated electrons (K in NH_3), the aromatic $S_{RN}1$ reaction can be initiated photochemically, electrochemically of by the addition of one-electron reducing reagents--all indicating the

intermediacy of radical anions (20).

Scheme IX

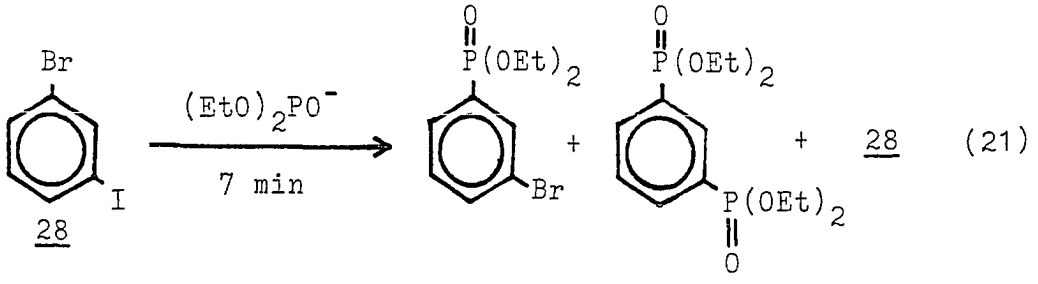


That the reaction was in fact a chain mechanism (as in the case of the aliphatic $S_{RN}1$ reaction) was demonstrated by the addition of small quantities of inhibitors. Tetraphenylhydrazine was mentioned earlier. Other inhibitors include dioxygen, di-tert-butyl nitroxide,

m-dinitrobenzene, etc... (20).

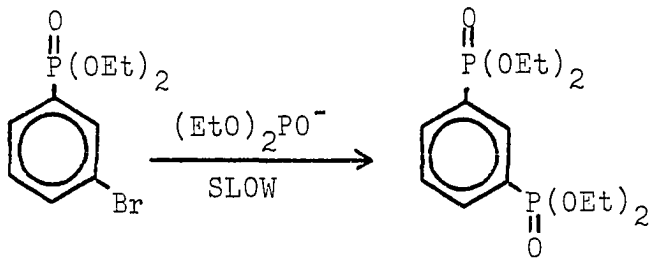
The photostimulated $S_{RN}1$ reaction of iodobenzene with the anion of diethyl phosphite was studied quantitatively. Quantum yields were found to exceed unity, falling between 20 and 50 (40). This result indicated that although the initiation was photochemical, the propagation steps were not. Electrochemically stimulated, 100% conversion can be achieved with a fraction of an electron per molecule of substrate (22).

The reactions of dihalobenzenes provide unique insight into the $S_{RN}1$ mechanism. In the reaction of m-bromoiodobenzene with diethyl phosphite anion, if the reaction is quenched after seven minutes, the following is observed (Eq. 21) (20):



(21)

Furthermore, the conversion of (29) to (30), Eq. 22, is slower than the conversion (28) to (30) (20).



(22)

29 30

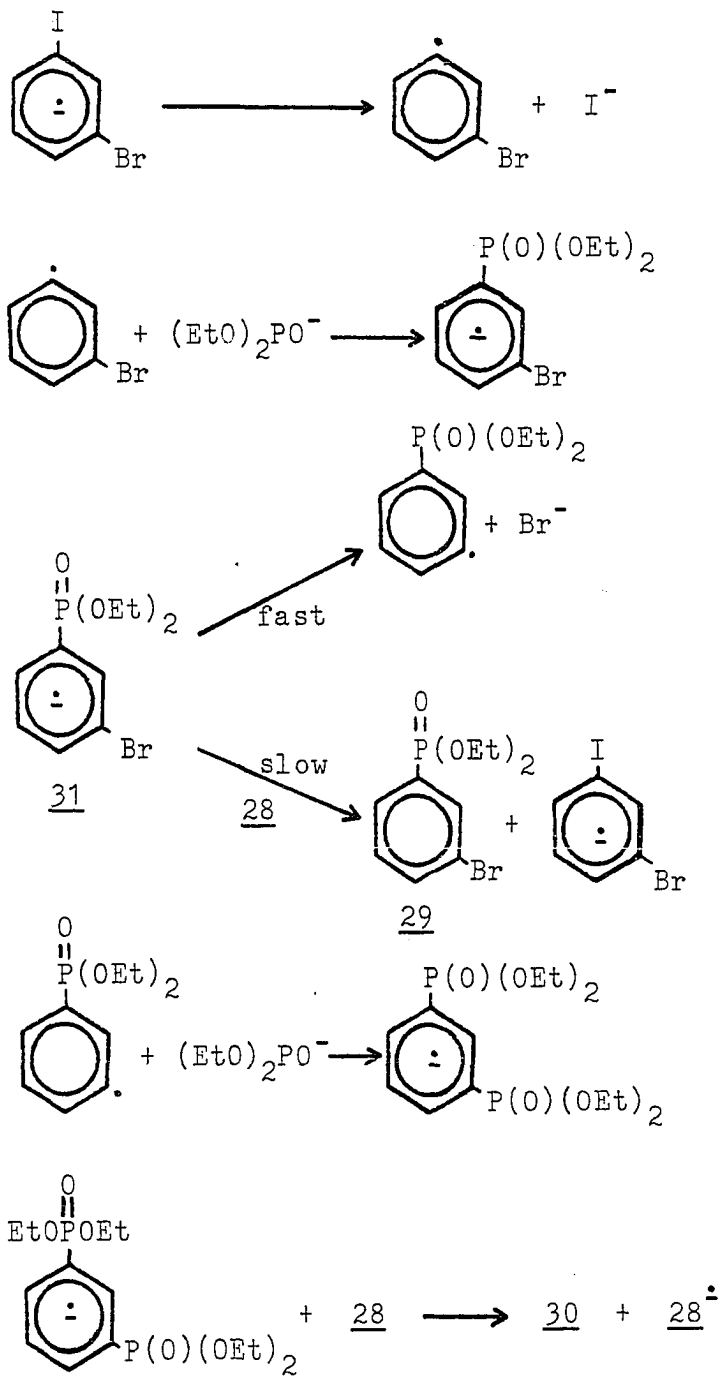
The former result suggests that if (29) is an intermediate in the conversion of (28) to (30), then it must react faster with diethyl phosphite anion than (28). The latter result shows that such is simply not the case. A modified $S_{RN}1$ reaction (Scheme X) readily explains these observations (20).

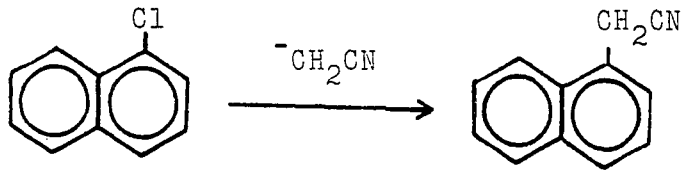
Thus, unimolecular decomposition of intermediate radical anion (31) being faster than bimolecular electron transfer to starting material (28) circumvents formation of mono-substituted product (29) in the reaction.

Other fragmentations of radical anion intermediates in the aromatic $S_{RN}1$ reaction have received great attention (23). A classic example involves the reactions of cyanomethyl anion with 1-chloronaphthalene and bromobenzene, Eqs. 23 and 24 respectively.

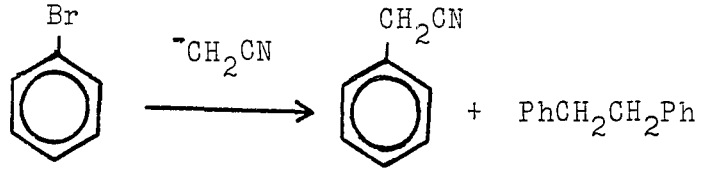
The formation of bibenzyl in Eq. 24 is reckoned as being the direct result of intermediate radical anion

Scheme X





(89%) (23)



(8%) (18%) (24)

fragmentation as per Scheme XI (23).

Scheme XI

$$Ar\text{-}X^{\cdot-} \longrightarrow Ar\cdot + X^-$$

$$Ar\cdot + {}^-CH_2CN \longrightarrow ArCH_2CN^{\cdot-}$$

$$ArCH_2CN^{\cdot-} \xrightarrow{k_d} ArCH_2\cdot + CN^-$$

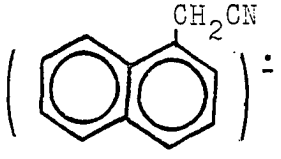
$$ArCH_2\cdot \longrightarrow ArCH_2CH_2Ar$$

$$ArCH_2CN^{\cdot-} + Ar\text{-}X \xrightarrow{k_{et}} Ar\text{-}X^{\cdot-} + ArCH_2CN$$

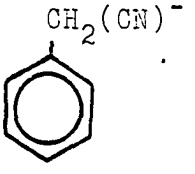
Thus if $k_d > k_{et}(ArX)$, fragmentation is observed (as when bromobenzene is the substrate) and if $k_d < k_{et}(ArX)$, normal substitution is observed (as when 1-chloronaphthalene is the substrate).

The difference in fragmentation rates (Ar = 1-naphthyl versus Ar = Ph) is rationalized by considering the structure of the radical anion based upon the LUMO (lowest unoccupied molecular orbital) of each parent molecule.

Thus, (33) is more likely to dissociate into Ar· + CN^- than (32) (23).



32



33

Nucleophiles that lead to fragmentation during aromatic $S_{RN}1$ reactions include ArS^-, $ArTe^-$, Ar_2As^-, Ar_2Sb^-, and others (23).

As with the aliphatic $S_{RN}1$ reaction mechanism, an alternative to the aromatic $S_{RN}1$ reaction would be an aromatic $S_{RN}2$ reaction. However, unlike its aliphatic counterpart, stereochemistry of substitution cannot be used as a criterion for distinguishing the mechanisms since sp^2 carbons <u>have</u> no stereochemistry.

The best evidence to date comes from competition experiments. Consider Scheme XII.

Scheme XII

$$Ar\text{-}X^{\cdot-} \longrightarrow Ar\cdot + X^- \qquad (a)$$

$$Ar\cdot + A^- \xrightarrow{k_A} Ar\text{-}A^{\cdot-} \qquad (b)$$

$$Ar\cdot + B^- \xrightarrow{k_B} Ar\text{-}B^{\cdot-} \qquad (c)$$

$$Ar\text{-}A^{\cdot-} + Ar\text{-}X \xrightarrow{fast} Ar\text{-}A + Ar\text{-}X^{\cdot-} \qquad (d)$$

$$Ar\text{-}B^{\cdot-} + Ar\text{-}X \xrightarrow{fast} Ar\text{-}B + Ar\text{-}X^{\cdot-} \qquad (e)$$

If subsequent electron transfer steps are fast (steps (d) and (e) in Scheme XII), and if $(A^-)_i$, $(B^-)_i > (ArX)_i$, Eq. 25 expresses a relationship between product yields, initial concentrations of the anions and the rate constant ratio k_A/k_B.

$$\frac{(ArA)}{(ArB)} = \frac{k_A(B)_i}{k_B(A)_i} \qquad (25)$$

Now the critical point: If free Ar· is truly the intermediate, k_A/k_B will be independent of the identity of X. These experiments were in fact performed, and the results are presented in Table 6 (41).

The constancy of k_P/k_E irrespective of substrate is consistent with the involvement of a "free" phenyl radical. Unfortunately, although this observation is a necessary condition for the $S_{RN}1$ mechanism, it is not a sufficient condition and therefore these results do not constitute absolute proof.

Table 6. Relative reactivities of diethyl phosphite anion and pinacolone enolate (k_P/k_E) as a function of leaving group

Substrate	Relative reactivity (k_P/k_E)[a]
PhI	1.33
PhBr	1.38
PhCl	1.47
PhF	1.38
Ph_2S	1.46
$PhN^+Me_3I^-$	1.25

[a]In liquid ammonia at 40 C.

III. AN IN-DEPTH DISCUSSION OF THE KEY STEPS OF THE $S_{RN}1$ REACTION

The focus of this discussion will now shift to a detailed examination of the individual steps of the $S_{RN}1$ reaction from both a theoretical and experimental perspective. Due to the development of techniques such as cyclic voltammetry and pulse radiolysis, it is frequently possible to study an individual step of the reaction even when the $S_{RN}1$ chain mechanism is not operating.

A. The Dissociation of Radical Anions

1. Experimental approaches

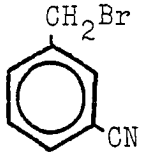
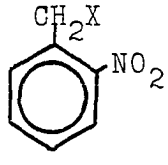
The rates of dissociation of several organic halide radical anions (Eq. 26) have been extensively studied by pulse radiolytic and electrochemical techniques.

$$R\text{-}X^{\cdot -} \longrightarrow R\cdot + X^- \qquad (26)$$

Table 7 surveys these results for benzylic halides, and Table 8 for aryl halides.

Several features of Table 7 are noteworthy. For the dissociation of benzylic halide radical anions, there is an unmistakable dependence on halogen (or

Table 7. Rates of dissociation of benzylic halide radical anions as determined by cyclic voltammetry and pulse radiolysis

Substrate	k (s^{-1})	Solvent	Method[a]	Reference(s)
	1.3×10^7	H_2O	P	42
				
X = Cl	$>3.0 \times 10^7$ (10^9)	H_2O	P	42
Br	$>6.0 \times 10^7$ (10^{10})	H_2O	P	42
				
X = Cl	1.0×10^4	H_2O	P	43
Cl	6.0×10^5	CH_3CN	E	44
Br	4.0×10^5	H_2O	P	43
Br	2.0×10^9	CH_3CN	E	44

[a] P = pulse radiolysis and E = electrochemical.

Table 7. (Continued)

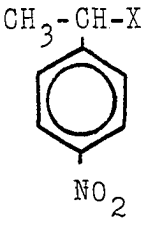
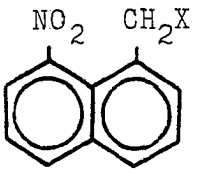
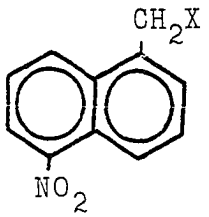
Substrate	k (s^{-1})	Solvent	Method[a]	Reference(s)
				
X = Cl	9.7×10^4	H_2O	P	45
Br	3.5×10^6	H_2O	P	45
OTs	8.0×10^4	H_2O	P	45
				
X = Cl	4.0×10^2	H_2O	P	45
Br	2.4×10^3	H_2O	P	45
				
X = Cl	1.0×10^1	H_2O	P	45
Br	5.8×10^2	H_2O	P	45

Table 7. (Continued)

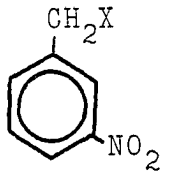
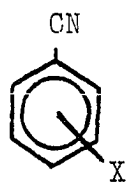
Substrate	k (s^{-1})	Solvent	Method[a]	Reference(s)
				
X = Cl	<5	H_2O	P	43, 45
Cl	2.5	CH_3CN	E	44
Br	6.0×10^1	H_2O	P	43, 45
Br	3.5×10^1	CH_3CN	E	44
I	3.0×10^3	H_2O	P	43
				
X = Cl	4.0×10^3	H_2O	P	43, 45
Cl	2.0×10^4	CH_3CN	E	44
Br	1.7×10^5	H_2O	P	43, 45
Br	6.0×10^8	CH_3CN	E	44
I	5.7×10^5	H_2O	P	43
OTs	$\sim 1.0 \times 10^2$	H_2O	P	45

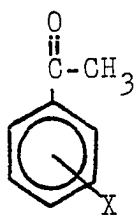
Table 8. Rates of dissociation of aryl halide radical anions as determined by cyclic voltammetry and pulse radiolysis

Substrate	k (s^{-1})	Solvent	Method[a]	Reference(s)
C_6H_5Cl	1.0×10^7	DMF	E	46
p-PhC_6H_4Cl	7.5×10^7	H_2O	P	47
				
X = F	6.0×10^5	H_2O	P	48
Cl	4.0×10^7	H_2O	P	48
				
X = m-F[b]	$\sim 10^3$	DMF	E	49
p-F	6.5×10^5	H_2O	P	42
p-F	1.1×10^1	DMF	E	49
o-Cl	9.0×10^6	H_2O	P	42

[a] P = pulse radiolysis and E = electrochemical.

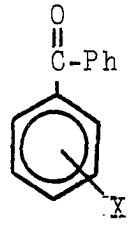
[b] Loss of F^-.

Table 8. (Continued)

Substrate	k (s^{-1})	Solvent	Method[a]	Reference(s)
m-Cl	$\sim 10^{10}$	DMF	E	50
m-Cl	4.2×10^{4}	H_2O	P	42
p-Cl	$\sim 10^{10}$	DMF	E	50
p-Cl[c]	9.0×10^{8}	NH_3	E	51
p-Cl	5.0×10^{6}	H_2O	P	42
m-Br	8.0×10^{6}	H_2O	P	42
m-Br	$\sim 10^{10}$	DMF	E	50
p-Br	$\sim 10^{10}$	DMF	E	50
p-Br	$>3.0 \times 10^{7}$	H_2O	P	42
m-I	$\sim 10^{10}$	DMF	E	50
p-I	$\sim 10^{10}$	DMF	E	50
				
X = o-Cl	1.5×10^{3}	H_2O	P	48
m-Cl	1.0×10^{1}	DMF	E	52
p-Cl	$\sim 10^{5}$	DMF	E	52
p-Cl	$\sim 10^{2}$	H_2O	P	48

[c]Temperature = -40 C.

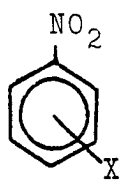
Table 8. (Continued)

Substrate	k (s^{-1})	Solvent	Method[a]	Reference(s)
<u>o</u>-Br	5.0×10^{5}	H_2O	P	48
<u>m</u>-Br	$\sim 10^{2}$	H_2O	P	48
<u>p</u>-Br	5.0×10^{3}	H_2O	P	48
<u>p</u>-I	1.4×10^{5}	H_2O	P	48
	$4.0 \quad 10^{2}$	H_2O	P	48
				
X = <u>m</u>-Cl	1.0×10^{-1}	DMF	E	52, 53
<u>p</u>-Cl[d]	1.0×10^{1}	DMF	E	52, 53
<u>p</u>-Cl[e]	3.4×10^{1}	CH_3CN	E	54
<u>p</u>-Cl[e]	5.1×10^{1}	DMF	E	55
<u>m</u>-Br[d]	9.0	CH_3CN	E	54
<u>m</u>-Br[d]	3.0×10^{1}	Me_2CHCN	E	54

[d]Temperature = 20 C.

[e]Temperature = 25 C.

Table 8. (Continued)

Substrate	k (s^{-1})	Solvent	Method[a]	Reference(s)
m-Br[d]	7.4×10^{2}	DMF	E	54
p-Br[e]	2.2×10^{4}	CH_3CN	E	55
p-Br[d]	2.4×10^{3}	CH_3CN	E	54
p-Br[d]	6.8×10^{3}	Me_2CHCN	E	54
p-Br[d]	8.0×10^{4}	DMF	E	54
p-Br	<7	H_2O	P	48
				
X = m-F	2.0×10^{-1}	CH_3CN	E	56
p-F	3.0×10^{-3}	CH_3CN	E	56
p-F[e]	1.4×10^{-2}	CH_3CN	E	57
o-Cl[f]	1.0×10^{-2}	DMF	E	58
m-Cl	$<10^{-3}$	DMF	E	52
m-Cl	3.0×10^{-3}	CH_3CN	E	56
p-Cl[f]	$\times 10^{-2}$	DMF	E	58
p-Cl	1.4×10^{-2}	DMF	E	59
p-Cl[f]	1.0×10^{-6}	DMF	E	60

[f] Temperature = 22 C.

Table 8. (Continued)

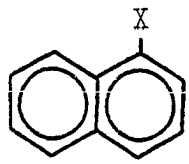
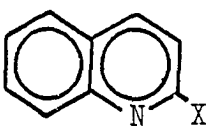
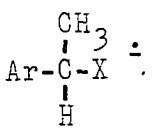
Substrate	k (s^{-1})	Solvent	Method[a]	Reference(s)
<u>o</u>-Br[f]	1.1×10^{2}	DMF	E	58
<u>m</u>-Br	5.0×10^{-3}	CH_3CN	E	56
<u>p</u>-Br[f]	4.0×10^{-3}	DMF	E	58
<u>p</u>-Br[f]	1.4×10^{-3}	DMF	E	60
<u>p</u>-Br	1.2×10^{-2}	CH_3CN	E	56
<u>o</u>-I[f]	8.0×10^{4}	DMF	E	58
<u>m</u>-I[f]	3.1×10^{-1}	DMF	E	58
<u>p</u>-I[f]	9.0×10^{-1}	DMF	E	58
<u>p</u>-I[f]	6.7	DMF	E	60, 61
<u>p</u>-I	6.4×10^{-1}	CH_3CN	E	56
				
X = Cl[c]	1.5×10^{4}	NH_3	E	62
Cl	5.0×10^{7}	Me_2SO	E	63
Br	3.0×10^{8}	Me_2SO	E	63
I	$\sim 6.0 \times 10^{8}$	Me_2SO	E	63

Table 8. (Continued)

Substrate	k (s^{-1})	Solvent	Method[a]	Reference(s)
				
X = Br[c]	1.7×10^4	NH_3	E	62
Cl[c]	1.3×10^5	NH_3	E	62
I[c]	3.0×10^6	NH_3	E	62

pseudohalogen): I > Br > Cl > OTs. Furthermore, electron withdrawing groups in the ring clearly retard the rate: $\underline{p}$-$O_2NC_6H_4CH_2$ > $\underline{p}$-$NCC_6H_4CH_2$, and the rate is dependant on the position of the group: ortho > para >> meta. Finally, increased bulkiness at the benzylic position enhances the rate. Thus, (34) decomposes faster than (35).



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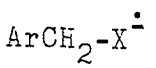

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From Table 8, several trends in the dissociation rate of aryl halide radical anions can be extracted. There is an unambiguous dependence of rate on the identity of the leaving group: I > Br > Cl > F. Substitution by electron withdrawing groups retards the rate of dehalogenation. The following reactivity pattern is revealed: C_6H_5 > PhC_6H_4 > $^-O_2CC_6H_4$ > NCC_6H_4 > $CH_3COC_6H_4$ > $HCOC_6H_4$ > $PhCOC_6H_4$ >> $O_2NC_6H_4$.

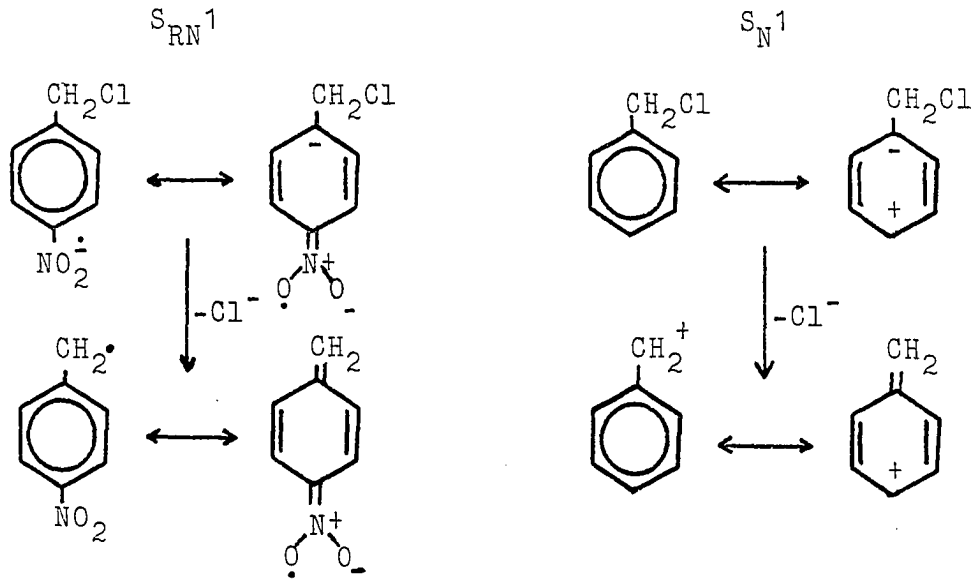
Position of the substituent relative to halogen appears to also effect the rate: ortho > para > meta. The nature of the aryl group is also important. Thus, phenyl ≈ 1-naphthyl > 2-quinoline.

It is interesting to note, that in cases where a particular radical anion was studied by both cyclic voltammetry and pulse radiolysis, the value of the rate constant obtained by cyclic voltammetry was inevitably 100 - 1000 times greater.

2. Theoretical approaches

a. Stabilized alkyl-type radicals The dehalogenation of a radical anion such as that of p-nitrobenzyl chloride has been discussed in analogy to the S_N1 reaction of a benzyl halide (7). This concept is depicted in Scheme XIII.

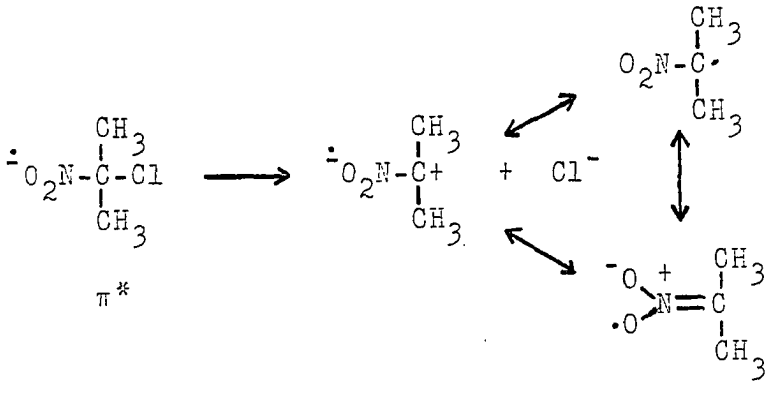
Scheme XIII



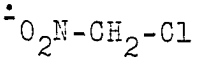
The p-nitrobenzyl chloride radical anion is expected to be π^*, the excess electron being accomodated in the π-system. Additionally, p-nitrobenzyl radical is expected to be a π-radical. Thus, the symmetry of the unpaired electron is preserved in the dehalogenation of the radical anion.

Similar considerations are appropriate for the dehalogenation of 1-chloro-2-nitropropyl radical anion and related species (Scheme XIV).

Scheme XIV



The aliphatic $S_{RN}1$ reaction has been studied using ab initio methods (64). Two points regarding the dissociation of chloronitromethane radical anion (36) are pertinent.



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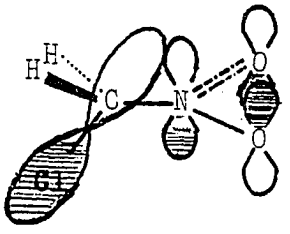
Chloronitromethane radical anion is not a stable species, but dissociates spontaneously to nitromethyl radical and chloride ion (64).

The second point is that the expulsion of chloride occurs under stereoelectronic control: (37) represents the conformation whereby chloride expulsion is most favorable. Note the antibonding orbital on carbon is in phase with the orbital containing the unpaired electron (64).



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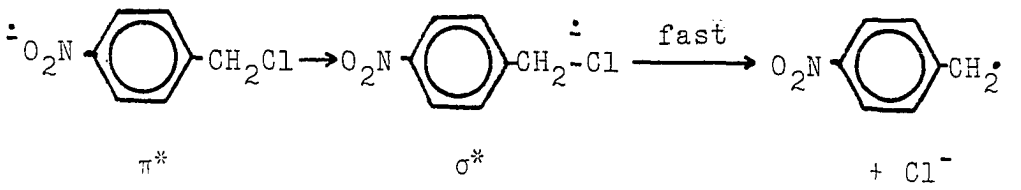
Thus, chloride departure occurring perpendicular to the plane containing the nitro group is consistent with the formation of a π-nitromethyl radical from a π*-chloronitromethane radical anion (64).

It is becoming increasingly popular to describe the dehalogenation of radical anions as "intramolecular electron transfer" (42, 43, 45, 47, 48). Expulsion of halide is rationalized as initial addition of the electron to the π-system and subsequent intramolecular electron transfer to the C-X σ*-bond to form halide and a carbon centered radical. The degree of overlap between the π-system and the σ-bond is then responsible for the

observed rate (Scheme XV) (42, 43, 45, 47, 48).

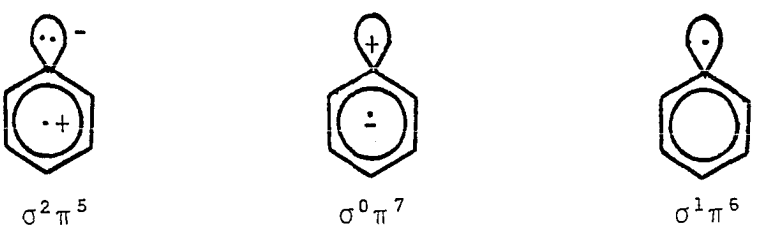
Scheme XV



b. Aryl radicals The decomposition of aryl halide radical anions (Eq. 27) is more complicated from a theoretical viewpoint than the analogous reaction of the alkyl halides just discussed.

$$Ar\text{-}X^{\cdot -} \longrightarrow Ar\cdot + X^{-} \qquad (27)$$

Figure 1 depicts the possible electronic states of phenyl radical (65).



38 39 40

Figure 1. Electronic states of phenyl radical

ESR spectroscopy of phenyl radical (Table 9) has clearly demonstrated that the ground state of phenyl radical is the $\sigma^1\pi^6$ state (40) (66, 67). The unpaired electron occupies the sp^2 (σ) orbital in the nodal plane of the π-system.

Table 9. ESR data for phenyl radical[a]

	Observed (Gauss)	Calculated (Gauss)[b]
a_H, ortho	+17.4	18.7
a_H, meta	+5.9	6.1
a_H, para	+1.9	3.9
$a_{C_1^{13}}$	+129	

[a]References 66 and 67.

[b]Assuming $\sigma^1\pi^6$ structure and calculated by SCF-INDO.

The observed hyperfine in the σ-phenyl radical has been explained as a combination of delocalization of electron spin density into the σ-framework and spin induced polarization (68). The contribution of spin induced polarization decreases with increasing distance from the radical site. Figure 2 depicts the relative signs of these two effects (68).

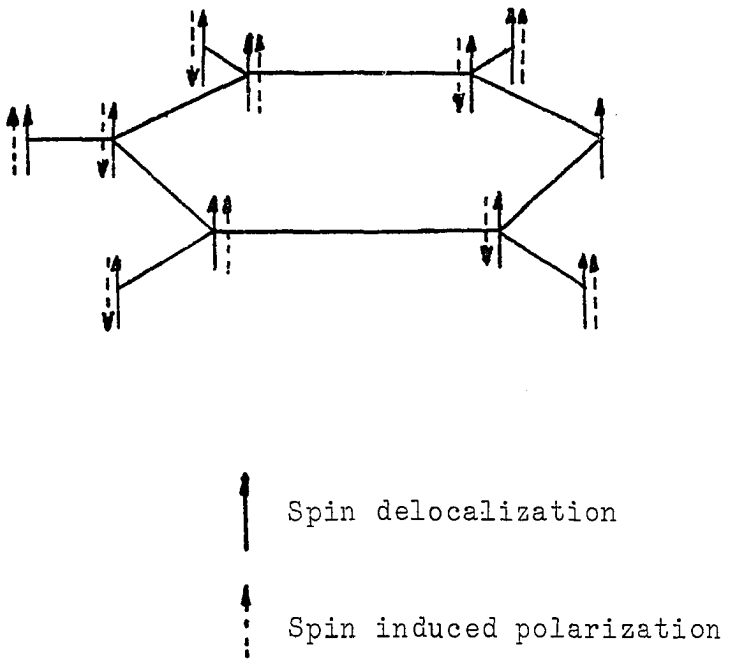


Figure 2. Relative signs of the contributions of spin delocalization and spin induced polarization in the σ-phenyl radical to the observed hyperfine splitting

The electronic structure of $ArX^{\cdot-}$ is less certain, at least when Ar = Ph. Electron transmission spectroscopy has demonstrated the excess electron in halobenzene radical anions occupies a π*-orbital (Eq. 28) (69).

$$\text{Ph-X} \xrightarrow{e^-} \pi^*\text{-Ph-X}^{\cdot-} \qquad (28)$$

X = H, NH_2, OH, OMe, F, Cl, Br

In one study (70), Namiki has detected fluorobenzene radical anion, produced by gamma irradiation in ethanol at 4 K. Optical absorption and ESR spectroscopies have indicated fluorobenzene to form a π^*-radical anion. Furthermore chloro- and bromonaphthalene radical anions were also determined to be π^*. However, gamma irradiation applied to chloro-, bromo-, or iodobenzene in ethanol at 4 K produced species shown not to be their respective π^*- or σ^*-radical anions. It was speculated that these species were phenyl radical-halide charge transfer complexes (70).

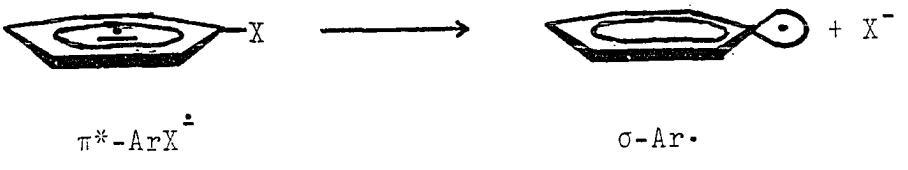
Symons has exposed several halogenated benzenes to ionizing irradiation (^{60}Co γ-rays) in methyltetrahydrofuran at 77 K. In one paper, it is reported that iodobenzene gave "what appear(s) to be π^*-radicals on electron attachment..." although no details were reported (71). In a later paper, Mishra and Symons report that under the same conditions bromo- and iodobenzene gave σ^*-radical anions, the excess electron being in the C-X σ^*-antibonding orbital (72). Poorly resolved ESR spectra showing large hyperfine coupling to halogen were presented. Furthermore, it was argued that the spectra observed by Namiki were actually σ^*-radical anions (72), although this latter proposal was considered and rejected by Namiki, who found irradiated chloro- or iodobenzene solutions in ethanol

at 4 K gave only esr spectra attributable to phenyl radical (70).

Molecular orbital calculations at the CNDO/2 level reveal that chlorobenzene radical anion is σ* (73, 74). This result is especially surprising as it directly contradicts the gas phase experimental results obtained by electron transmission spectroscopy.

Thus, the decomposition mechanism of aryl halide radical anions is complicated because the C-X σ-bond formally broken in Eq. 27 is orthogonal to the π-system potentially containing the excess electron in $ArX^{\cdot -}$ and this orthogonality, unlike the case for alkyl systems, cannot be removed by rotation about a bond.

Most mechanisms proposed for this dissociation assume stretching of the C-X bond in the plane of the benzene ring during decomposition (Figure 3).



π^*-$ArX^{\cdot -}$ σ-Ar·

Figure 3. Dissociation of halobenzene radical anion via C-X bond stretching

Early approaches to the mechanism were sensitive to the electronic symmetry of the initial and final

state. The dissociation was rationalized by the superimposition of three potential energy curves (Figure 4) (75).

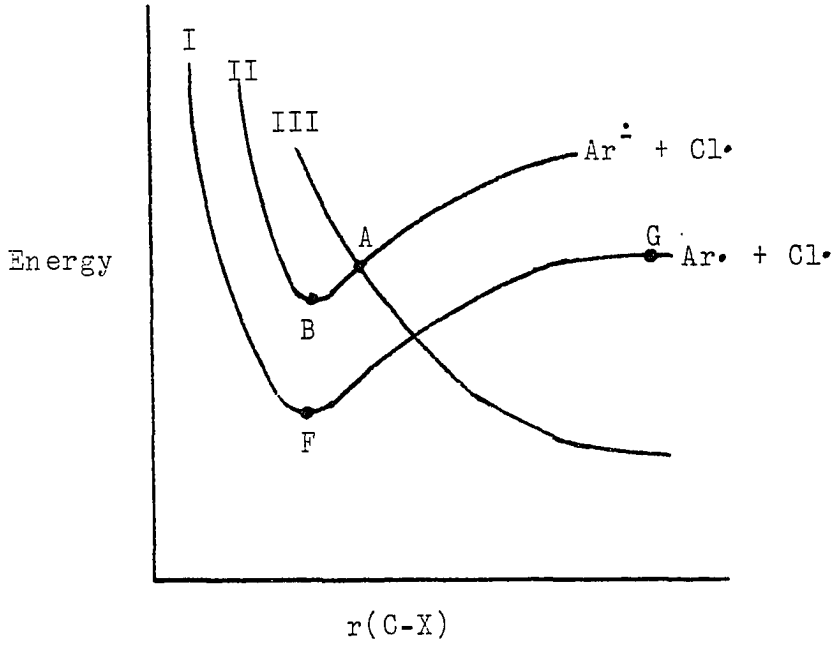
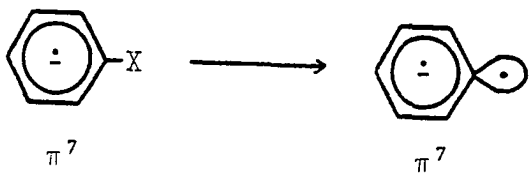


Figure 4. Potential energy curves pertinent to the dissociation of halobenzene radical anions

The reaction coordinate is taken to be along the C-X bond axis in ArX, as in Figure 3. Curve I represents the potential energy curve for neutral ArX, point F being the equilibrium bond length of the C-X σ-bond, and the energy difference between F and G representing its bond dissociation energy (75).

Curve II represents the potential energy curve for $ArX^{\dot{-}}$. The excess electron is presumed to be accommodated in the π-system. Curve II is raised with respect to curve I because of the energy required to put an electron into neutral ArX, its electron affinity. Furthermore, it is assumed that curve II is roughly parallel to curve I. The crucial feature of curve II however is that symmetry is preserved along the reaction coordinate. Thus the π^7-$ArX^{\dot{-}}$ does not dissociate spontaneously into π^6-Ar· + X^-. Curve II represents the homolysis of the C-X bond according to Eq. 29.



(29)

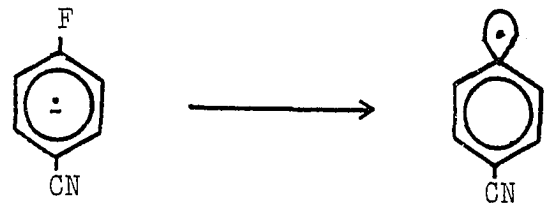
Finally, curve III represents the interaction of neutral phenyl radical with chloride ion. This interaction is considered repulsive at all values of r (75).

Now the mechanism of dissociation of $ArX^{\dot{-}}$ can be described. Neutral ArX (point F) must gain an electron to form $ArX^{\dot{-}}$ (point B). The energy required for this process is $E_B - E_F$. The $ArX^{\dot{-}}$ initially formed cannot dissociate because of symmetry restrictions

into Ar• and X^-. A change of symmetry from π^7 to π^6 is required. Energy is required to reach point A, where curves II and III intersect and some mechanism is required to jump from curve II to curve III, perhaps a collision (75).

An analogous, but essentially equivalent approach to the mechanism involves transferring the odd π^*-electron in $ArX^{\cdot-}$ to a σ^*-molecular orbital, and allowing the dissociation to proceed from the σ^*-state (76).

Consider the dissociation of p-fluorobenzonitrile radical anion (Eq. 30).



$$+ \ F^- \qquad (30)$$

The energies of the frontier orbitals of p-fluorobenzonitrile, as calculated by the INDO method, are presented in Figure 5 (76).

In Figure 5, the arrow indicates the orbital crossing point (π^* - σ^*) in the reaction coordinate. It is assumed at this point that the odd electron in π^* can transfer into the σ^*-orbital (76). Such a crossing is popularly referred to as intramolecular electron transfer (42, 43, 45, 47, 48). It is assumed that

an out of plane vibration is coupled with the C-X stretching to temporarily distort the symmetry and allow electron transfer. It is estimated that an increase in the activation energy of about 5 kcal/mol is required for each degree the bond is lifted from the molecular plane. The fragmentation rate can be correlated with the location of the crossing point from the equilibrium bond length in $ArX^{\cdot-}$ (76).

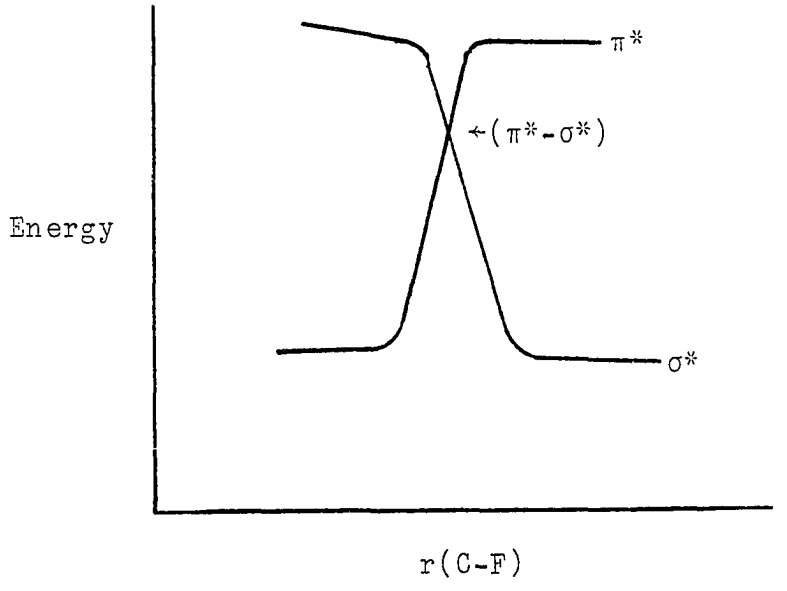


Figure 5. Energies of frontier molecular orbitals of p-fluorobenzonitrile radical anion as a function of C-F bond length

Finally, in this treatment the dissociation of chlorobenzene radical anion is presumed to proceed

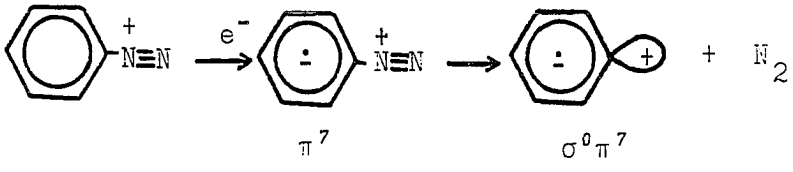
from a ground state chlorobenzene σ*-radical anion (74). As pointed out before however, the assumption of a σ*-ground state for $PhCl^{\cdot -}$ does not appear to be in accordance with all of the experimental results.

Since charge transfer complexes between phenyl radical and halide have been detected in the decomposition of halobenzene radical anions, such charge transfer complexes (CTC) have been proposed as intermediates (Eq. 31) (70).

$$PhX^{\cdot -} \longrightarrow (Ph\cdot X^{-})_{CTC} \longrightarrow Ph\cdot + X^{-} \qquad (31)$$

The lifetime of the charge transfer complex is approximately 1 μs at 100 K (70).

The electron transfer induced decompositions of benzenediazonium salts is analogous to that of halobenzenes. The decomposition was proposed to produce an excited state $\sigma^0\pi^7$-phenyl radical (Eq. 32) (77).

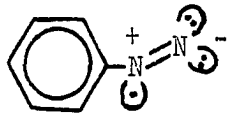


(32)

Thus in Eq. 32, symmetry is preserved.

However, diazenyl radical has been shown to be

a ground state σ-radical, structure (41) (78). Therefore, the diazenyl radical in Eq. 32 must also be an excited state if this proposition is correct.



π^6

41

B. The Coupling of Radicals and Nucleophiles

The coupling reaction of radicals and nucleophiles (Eq. 33) is the formal reverse of the dissociation of radical anions $RX^{\cdot-}$ (Eq. 34) when X = N.

$$R\cdot + N^- \longrightarrow R\text{-}N^{\cdot-} \qquad (33)$$

$$R\text{-}X^{\cdot-} \longrightarrow R\cdot + X^- \qquad (34)$$

Thus, many of the points addressed in the previous section have applicability.

1. Experimental Approaches

Table 4 lists several examples of radicals and nucleophiles that successfully couple under $S_{RN}1$ conditions. It is frequently possible to independently generate a radical (R·) in a solution containing a

nucleophile (N^-) and detect the coupling product ($RN^{\cdot -}$). The detection method is usually electrochemical, spectroscopic or by the isolation of the products of the reaction. Table 10 lists several examples of radicals that couple successfully with nucleophiles under conditions where the $S_{RN}1$ reaction does not operate.

Relatively few absolute rate constants for the coupling reactions of nucleophiles and radicals have been reported. Table 11 summarizes several of these.

The relative reactivities of several nucleophiles have been determined using the competitive $S_{RN}1$ techniques described previously. Table 12 lists the relative reactivities of several nucleophiles towards the phenyl radical intermediate in the $S_{RN}1$ reaction (41).

Except for PhS^-, the relative reactivities towards phenyl radical differed by no more than a factor of ten. The suggestion was made that the coupling of aryl radical with nucleophiles occurs at a diffusion controlled rate (41).

Ion-pairing and solvent play a critical role in the relative reactivity of nucleophiles in the $S_{RN}1$ reaction. Table 13 presents the relative reactivity of several anions toward 2-nitro-propyl radical as a function of counter-ion (26).

Table 10. Generation of radicals in the presence of anions

Radical	Nucleophile	Product	Detection[a] method	Reference
$Ph\cdot$[b]	NO_2^-	$PhNO_2$	I	79
$Ph\cdot$[c]	NO_2^-	$PhNO_2^{\cdot-}$	ESR	80
$\underline{p}\text{-}NO_2Ph\cdot$[d]	CN^-	$\underline{p}\text{-}NO_2C_6H_4CN^{\cdot-}$	ESR, CV	79
$\underline{p}\text{-}NO_2Ph\cdot$[d]	NO_2^-	$\underline{p}\text{-}C_6H_4(NO_2)_2^{\cdot-}$	CV	79
$Ar\cdot$[e]	$CH_2{=}NO_2^-$	$ArCH_2NO_2^{\cdot-}$	ESR	81
$Ar\cdot$[e]	$MeCH{=}NO_2^-$	$ArCH(NO_2)Me^{\cdot-}$	ESR	81
$Ar\cdot$[e]	$EtCH{=}NO_2^-$	$ArCH(NO_2)Et^{\cdot-}$	ESR	81
$Ar\cdot$[e]	$Me_2C{=}NO_2^-$	$ArC(NO_2)Me_2^{\cdot-}$	ESR	81
$\underline{p}\text{-}NO_2Ph\cdot$[c]	I^-	$\underline{p}\text{-}NO_2C_6H_4\text{-}I$	I	60
$\underline{p}\text{-}NO_2Ph\cdot$[c]	Br^-	$\underline{p}\text{-}NO_2C_6H_4Br$	I	60
$\underline{p}\text{-}NO_2Ph\cdot$[c]	Cl^-	$\underline{p}\text{-}NO_2C_6H_4Cl$	I	60

[a]ESR = electron spin resonance, CV = cyclic voltammetry and I = isolated product.

[b]From PhN_2CPh_3 (PAT).

[c]From reduction of ArN_2^+.

[d]From reduction of $\underline{p}\text{-}IC_6H_4NO_2$.

[e]Where Ar = Ph, $\underline{m}$- and $\underline{p}\text{-}(^-O_2C)C_6H_4$ and $\underline{p}\text{-}MeOC_6H_4$, generated from reduction of ArN_2^+.

Table 11. Absolute rate constants for the coupling of radicals and nucleophiles

Radical	Nucleophile	Solvent	k ($M^{-1}s^{-1}$)	Ref.
Δ^5-hexenyl	$Me_2C{=}NO_2^{-a}$	Me_2SO^d	3.0×10^4	82
Δ^5-hexenyl	$Me_2C{=}NO_2^{-b}$	Me_2SO^d	1.4×10^5	82
Δ^5-hexenyl	$Me_2C{=}NO_2^{-c}$	Me_2SO^d	8.9×10^4	82
Δ^5-hexenyl	$Me_2C{=}NO_2^{-a}$	$HMPA^d$	3.6×10^4	82
Δ^5-hexenyl	$Me_2C{=}NO_2^{-c}$	$HMPA^d$	7.5×10^5	82
$\underline{p}$-CNC_6H_4	$(EtO_2PO^{-b}$	$NH_3{}^e$	1.5×10^9	51
$\underline{p}$-$NO_2C_6H_4$	I^{-c}	DMF^f	2.5×10^9	60
$\underline{p}$-$NO_2C_6H_4$	Br^{-c}	DMF^f	1.6×10^8	60
$\underline{p}$-$NO_2C_6H_4$	Cl^{-c}	DMF^f	1.8×10^7	60

[a] Li^+ counter-ion.

[b] K^+ counter-ion.

[c] $\underline{n}$-Bu_4N^+ counter-ion.

[d] Temperature = 40 C.

[e] Temperature = -40 C.

[f] Temperature = 22 C.

Table 11. (Continued)

Radical	Nucleophile	Solvent	k ($M^{-1}s^{-1}$)	Ref.
1-naphthyl	PhS^-	NH_3[e]	2.3×10^7	62
1-naphthyl	PhS^-	Me_2SO[g]	1.7×10^8	83
2-quinolinyl	PhS^-[b]	NH_3[e]	1.4×10^7	62
2-quinolinyl	$4\text{-}ClC_6H_4S^-$[b]	NH_3[e]	6.0×10^6	62
2-quinolinyl	$(EtO)_2PO^-$[b]	NH_3[e]	1.8×10^7	62

[g]Temperature = 20 C.

Table 12. Relative reactivity of nucleophiles towards phenyl radical in the aromatic $S_{RN}1$ reaction in NH_3(l).

Nucleophile[a]	Relative reactivity[b]
Ph_2P^-	5.9
Ph_2PO^-	2.7
$(EtO)_2PO^-$	1.4
$Me_3CC(O)CH_2^-$	1.00
PhS^-	0.08
$\underline{t}\text{-}BuO^-$	0.0

[a]K^+ counter-ion.

[b]Temperature = -40 C.

Table 13. Relative reactivity of several anions toward 2-nitro-2-propyl radical in Me_2SO at 25 C

Anion	Relative Reactivity[a] in the absense of ion-pairing	Relative Reactivity in the presence of 0.2 M Li^+	1.0 M Li^+
$(EtO_2C)_2CMe^-$	10	0.24	0.44
$(EtO_2C)_2CH^-$	6	0.47	0.95
$Me_2C{=}NO_2^-$	1	1	1
$(EtO)_2PO^-$	0.54	0	0
$(EtO)_2PS^-$	0.90	1.2	0.82

[a]Counter-ion is K^+(2.2.2)-cryptand.

The relative reactivities of diethyl phosphite and nitronate anions are comparable, 0.54:1, when ion-pairing is unimportant (cryptand added), but ion-pairing to Li^+ destroys the reactivity of diethyl phosphite anion relative to nitronate anion (26).

Table 14 demonstrates a change in the relative reactivity of diethyl methylmalonate versus nitronate anions as a function of solvent polarity (26). As the solvent becomes increasingly less polar, diethyl methylmalonate becomes increasingly more reactive relative to nitronate--presumably due to increased

Table 14. Relative reactivity (k_A/k_B) of anions of diethyl methylmalonate(A) and 2-nitropropane (B) in different solvents at 25 C

Counter-ion, concentration (M)	Solvent	k_A/k_B
Li^+, 0.2	HMPA	0.22
Li^+, 0.2	Me_2SO	0.26
Li^+, 0.2	DMF	1.3
Li^+, 0.2	THF/DMF (50:50)[a]	1.9
Li^+, 0.2	THF/DMF (90:10)[a]	18
Li^+, 0.2	THF	>70
Li^+/12-crown-4,[b] 0.2	THF	20
K^+/(2.2.2)-cryptand,[c] 0.15	Me_2SO	11
K^+/(2.2.2)-cryptand, 0.15	THF/Me_2SO (90:10)[a]	1.6
K^+/(2.2.2)-cryptand, 0.15	THF	0.39

[a](v:v).

[b]Crown ether specific for Li^+.

[c]Cryptand specific for K^+.

ion-pairing in the less polar solvent. The addition of complexing agent (crown ether or cryptand) diminishes ion-pairing, thus restoring the reactivity of nitronate ion--even in the least polar solvent (26).

It is intriguing to speculate on the factors responsible for determining whether a given nucleophile and a given radical will react.

An important criterion appears to be the stability of the resultant radical anion (19). This notion was often advanced to explain the necessity of a nitro group, in either the radical or anion, in the first documented examples of the aliphatic $S_{RN}1$ reaction. However, consider Eq. 35 (17):

$$PhCH_2HgCl + Me_2C{=}NO_2^- + NO_2^- \xrightarrow[S_{RN}1]{} PhCH_2NO_2 + PhCH_2CMe_2NO_2 + Hg^0 + Cl^- \quad (35)$$

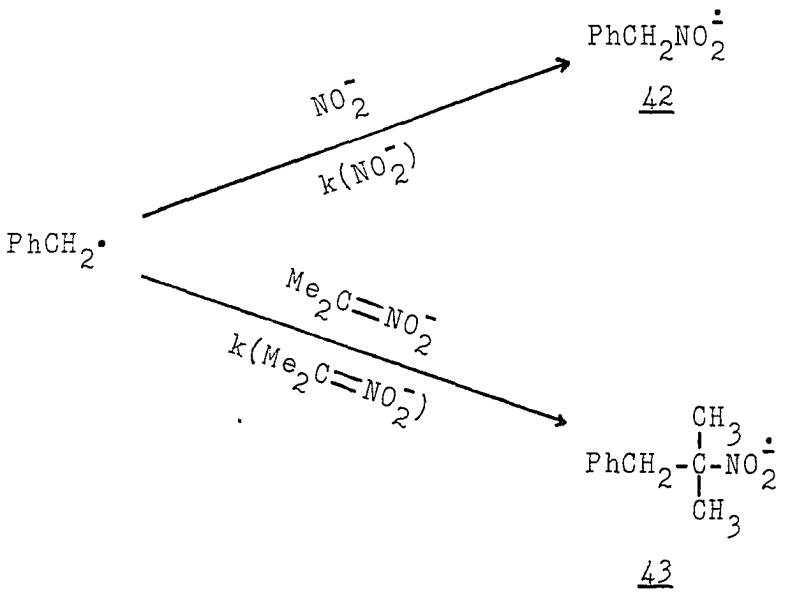
0% 91%

The observed results suggest that in Scheme XVI, $k(NO_2^-) < k(Me_2C{=}NO_2^-)$.

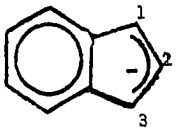
It is unreasonable to expect (43) possesses any greater degree of stability than (42). Clearly, some other factor must be responsible.

Another approach to this problem involves PMO (Perturbated Molecular Orbital) theory (84). In an ambident anion such as indene (44), the coefficent of the highest occupied molecular orbital (HOMO) at C-1 is larger than at C-2. Hence, coupling of phenyl

Scheme XVI



radical occurs at C-1 (Eq. 36) (84).



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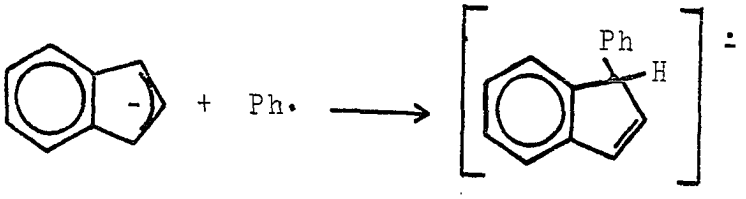
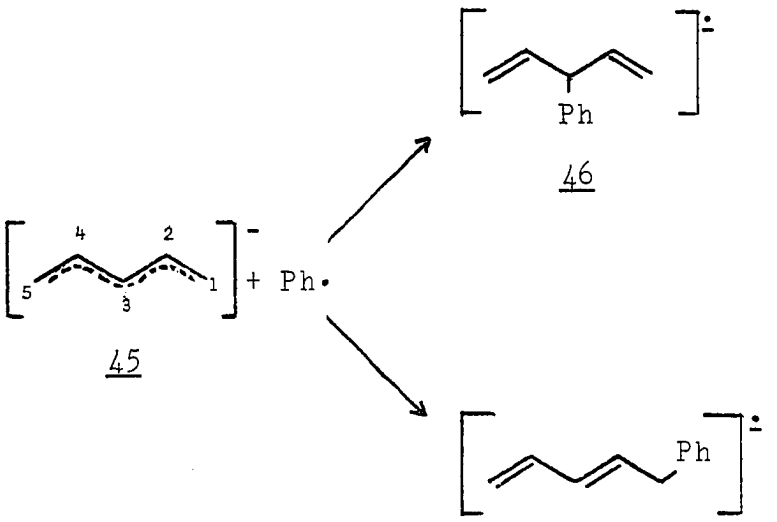


(36)

In cases where the coefficents of the HOMO of an ambident nucleophile are the same, then radical anion

stability determines the product. Thus for pentadienide anion (45), the coefficents are identical for C-1, C-3 and C-5. However in Scheme XVII, (47) is expected to be more stable than (46) (84).

Scheme XVII



46

45

47

Hence, the observed product is (48) (84).

$$PhCH_2CH{=}CH\text{-}CH{=}CH_2$$

48

Another argument advanced to explain regioselectivity in ambident anions is basicity (31).

In Eq. 37, the fact that alkylation occurs preferentially at C-1 is explained by the fact that

C-1 is the most basic site, see Table 15 (31, 85).

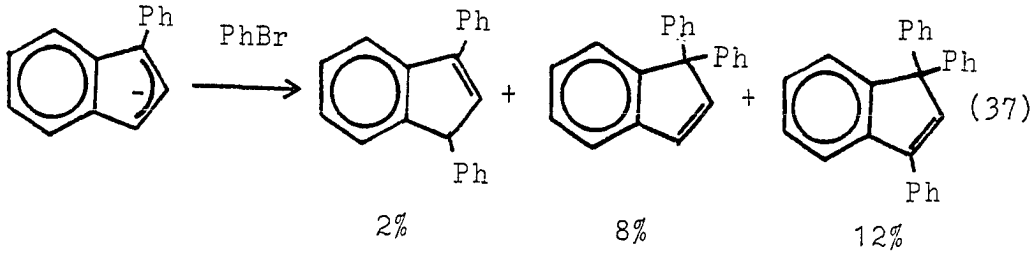
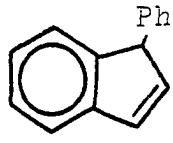
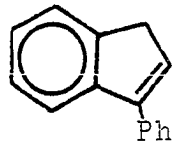
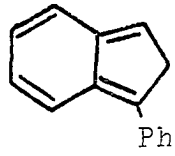
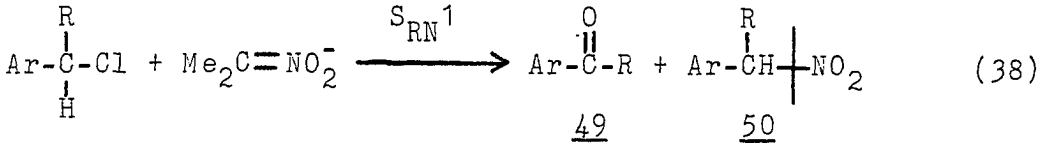


Table 15. Acidities of phenyl indene isomers

Compound	pKa
	17
	<15
	<<15

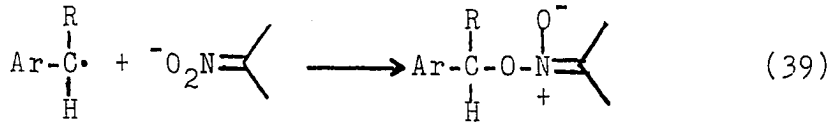
It has been claimed that under severe steric constraint, anions (such as nitronate) will couple with radicals through oxygen (86). Furthermore, it

was proposed the the C/O alkylation ratio decreases with increasing substitution at the β-carbon (86).



(38)

Thus in Eq. 38, ketone (49) is proposed to arise from attack of nitronate on (51) through oxygen (Eq. 39) (86).



(39)

51 R = i-Pr, t-Bu

It was argued that ketone (49) was the result of an $S_{RN}1$ reaction since the reaction was slower in the dark than when illuminated, the reaction occurred only when Ar = p-NO_2Ph, and p-dinitrobenzene inhibits the reaction (86).

These results have been criticized. The system was considered "ambiguous" and "complicated by S_N2 reactions," which produce the O-alkylation product thereby affecting the observed C/O alkylation ratio (19). Nonetheless, it was conceded that under

severe steric constraint, O-alkylation may be possible in the $S_{RN}1$ reaction (19).

It must be interjected however, that the evidence for O-alkylation in this system is extremely weak.

The reaction times for R = i-Pr or t-Bu are unusually long, 24 - 50 hours for 100% conversion. What is claimed to be "inhibition" by p-dinitrobenzene for R = i-Pr, is actually just a decrease in yield from 56% to 35%, and 100 mole % of inhibitor is required (86). Oxygen is found to have no effect on the yield or the rate, this latter point being addressed as O_2 scavenging intermediate radical (51) according to Eq. 40, resulting in the formation of ketone (49) (86).

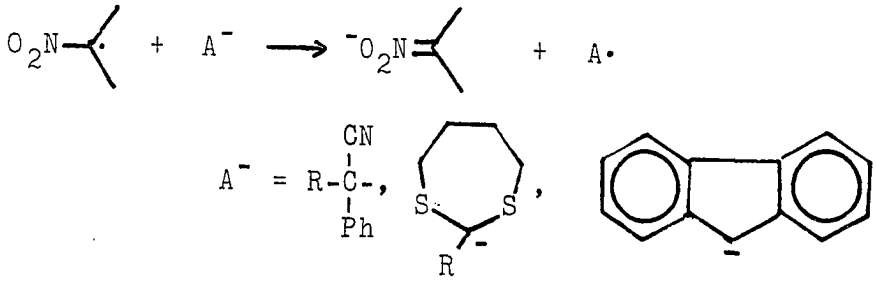
$$\underset{51}{Ar\text{-}\dot{C}HR} + O_2 \longrightarrow Ar\text{-}CHR(O\text{-}O\cdot) \longrightarrow \longrightarrow Ar\text{-}C(=O)\text{-}R \quad (40)$$

While Eq. 40 may explain the formation of product, it is nonetheless a chain terminating event.

It is highly unlikely therefore that the ketone produced in Eq. 38 is the result of a chain process. Thus, there is no evidence for the coupling occurring through oxygen as in Eq. 39.

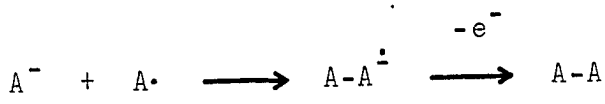
In addition to the coupling reaction of a radical and nucleophile, other processes are possible. Electron

transfer from the nucleophile to the radical (Eq. 41) is one possibility (38).



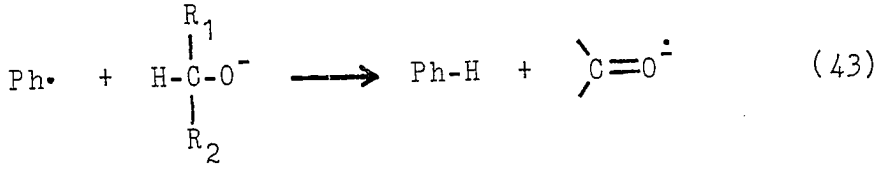
(41)

The observed product (A-A) is thus the result of oxidative dimerization, presumably via Eq. 42 (38):



(42)

Another alternative to coupling is that one of the atoms in the nucleophile can be abstracted by the radical. Eq. 43 provides an example of a H-atom abstraction (87, 88).



(43)

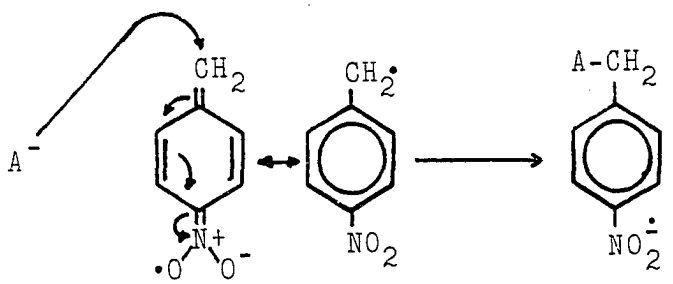
2. Theoretical Approaches

As has been pointed out, the coupling reaction of a radical and nucleophile ($R\cdot + N^-$) is the formal

reverse of the dissociation of a radical anion ($RX^{\cdot -}$). Hence, the theoretical foundation for these processes should be quite similar.

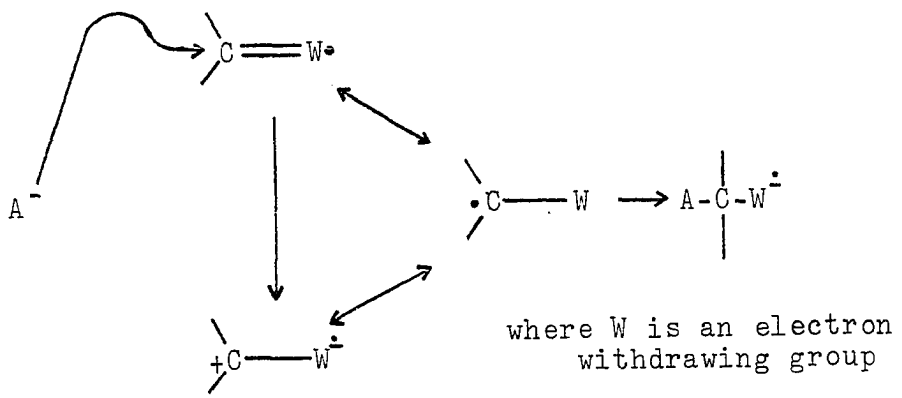
The coupling of anions with p-nitrobenzyl radical has been rationalized as analogous to a Michael addition, Scheme XVIII (19).

Scheme XVIII



It would seem reasonable to extend this concept to all substituted alkyl radicals listed in Table 1. In Scheme XIX, this extension is made.

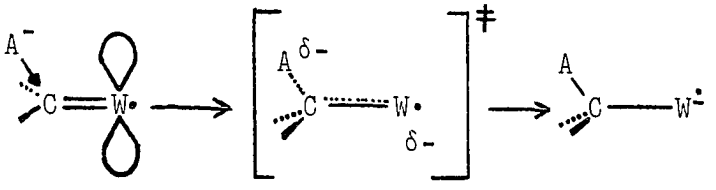
Scheme XIX



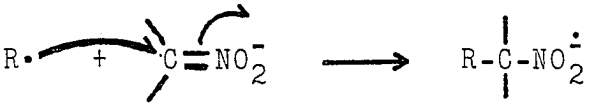
Since the departure of chloride from $ClCH_2NO_2^{\cdot-}$ was shown to be under stereoelectronic control (64) such that the fragmenting C-Cl bond overlaps favorably with the π-system of the nitro functionality, such stereoelectronic control is likely in the reverse direction.

Scheme XX depicts the likely trajectory and transition state for nucleophilic attack on a stabilized carbon radical.

Scheme XX



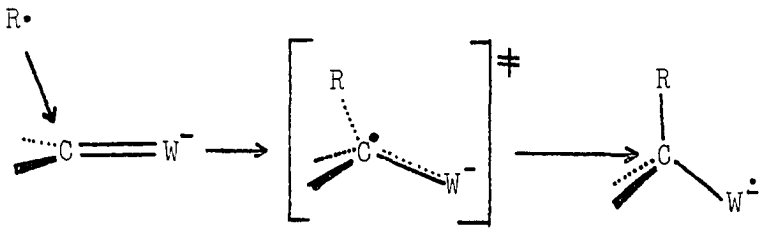
The coupling of unsubstituted alkyl radicals with nucleophiles has not been treated on a theoretical basis. It seems reasonable to speculate that since all the nucleophiles contain low energy π-systems and electron withdrawing groups capable of stabilizing the resultant radical anion, that the coupling can be viewed analogously to the addition of a free radical to a π-system (Eq. 44).



(44)

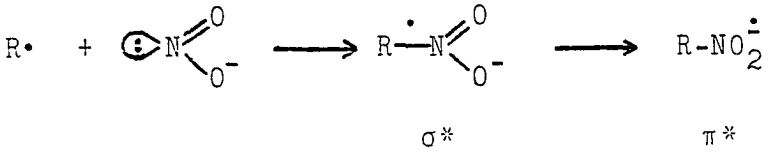
Scheme XXI suggests a possible trajectory, perpendicular to the plane of the molecule, and likely transition state.

Scheme XXI



Another possiblilty, particularly with anions such as NO_2^- which have lone pair electrons, would involve an in-line, in-plane attack of the radical on the orbital containing the non-bonding electrons (Scheme XXIII). The transition state would be σ^* in character, which presumably could rearrange to the more stable π^*-state.

Scheme XXII



σ^* π^*

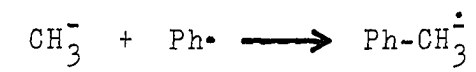
This latter process is exactly what is envisioned for the reaction of aryl radicals with several nucleophiles (89).

The interaction of a σ-aryl radical with a nucleophile involves 3 electrons. The interaction assumes the species approach each other along the axis of the new bond being formed (Eq. 45) (89).

(45)

Based on molecular orbital calculations, this situation can be treated in three different manners depending on the structure of the nucleophile and adduct ($ArNu^{\cdot -}$) (89).

Case I Consider the hypothetical reaction of methyl anion with phenyl radical (Eq. 46).



(46)

As CH_3^- approaches Ph·, the energy of the σ-orbital decreases and σ*-orbital increases (Figure 6) (89). At some point along the reaction coordinate, the energy of the occupied σ*-orbital equals the energy of the unoccupied π*-orbital. At this "crossing point," the electron transfers from the σ*-orbital to the π*-orbital. This argument is identical to that previously presented for the dissociation of $ArX^{\cdot -}$. It is assumed that this electron transfer, while formally

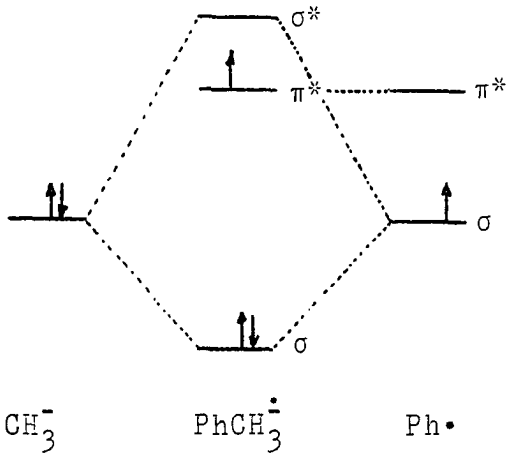


Figure 6. Molecular orbital correlation diagram for the coupling of methyl anion and phenyl radical

symmetry forbidden, is made feasible by coupling to a molecular vibration which momentarily destroys the symmetry (89).

Case II Consider the hypothetical reaction of phenyl radical with an anion $^-CH_2W$, where W is an electron withdrawing substituent (Eq. 47). Furthermore,

$$Ph\bullet + {}^-CH_2\text{-}W \longrightarrow (Ph\text{-}CH_2\text{-}W)^{\cdot-} \qquad (47)$$

52

suppose that the radical anion (52) is such that the π*-antibonding orbital corresponding to W is lower in

energy than the π*-antibonding orbital corresponding to the aryl functionality. These two π-systems are not in conjugation as they are separated by the saturated methylene (89).

As Ph· and $^{-}CH_2W$ approach each other and begin bond formation, the energy of the σ- and σ*-orbitals separate as in the case of Ph· and CH_3^-. At some point along the reaction coordinate, the energy of the σ*-orbital will equal the energy of π^*_W and the electron will "move" into this orbital as in Figure 7 (89). Thus, the structure of the resultant radical anion

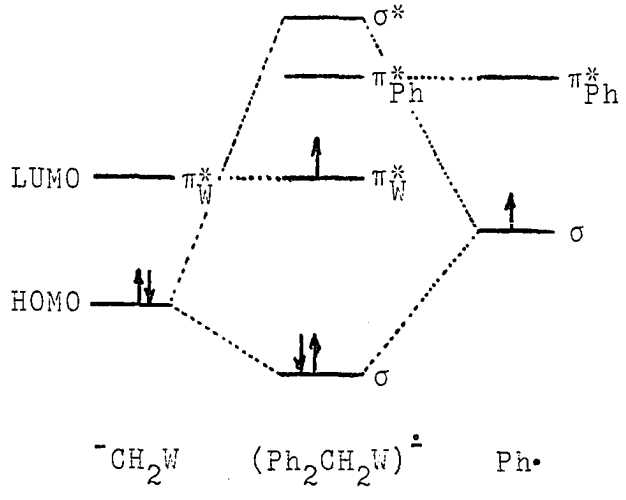
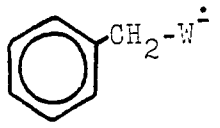
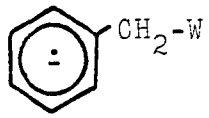


Figure 7. Molecular orbital correlation diagram for the coupling of stabilized anions with phenyl radical

more closely resembles (53) than (54).



53



54

Case III In the reaction of Cl^- with Ph•, it is assumed, based upon MO calculations, that the σ*-orbital of $PhCl^{\cdot-}$ is lower in energy than the π*-orbital. Thus, the electron never moves from the initial σ*-orbital (Figure 8) (89).

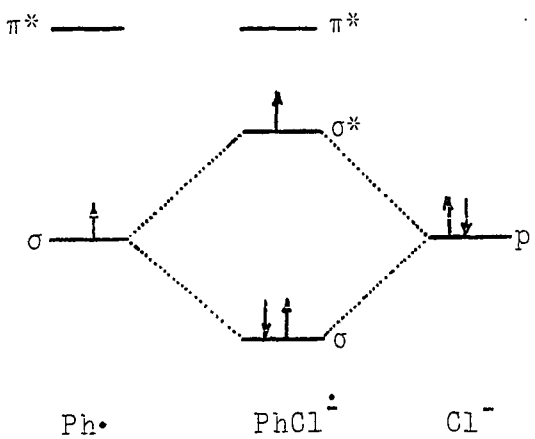


Figure 8. Molecular orbital correlation diagram for the coupling of chloride ion with phenyl radical

The resulting adduct ($PhCl^{\cdot -}$) is assumed to be a σ^*-radical anion (89). However, it is again necessary to point out that experiment and theory disagree on the structure of $PhCl^{\cdot -}$, experiment favoring the π^*-state (69, 70).

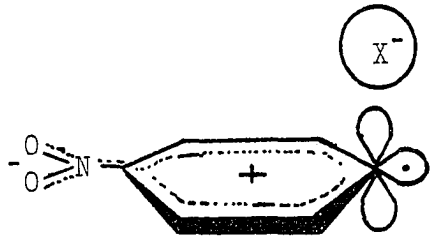
The underlying assumption in this MO approach to the formation or decomposition of radical anions has been that the entering or departing group does so in line with the sp^2 orbital of the phenyl radical, in the nodal plane of the π-system. Yet, it is readily recognized that for the presumed intramolecular electron transfer to take place, the translational motion must be coupled to some sort of vibrational or bending motion to avoid violating symmetry requirements (20, 42, 43, 45, 47, 48, 75, 84, 89).

The implication then is that the transition state is not planar after all, but somehow bent. A question now arises: If the transition state is bent, is it reasonable to assume that the lowest energy pathway for its formation involves a coplanar arrangement of atoms?

To calculate a potential energy surface for these reactions, it may be more reasonable to abandon this assumption.

A non-coplanar transition state (55) has been

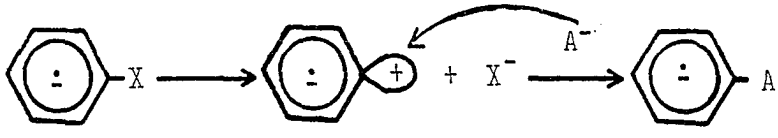
proposed for the interaction of p-nitrophenyl radical with halide (60).



55

Finally, if aryldiazonium salts, upon electron capture, decompose to an excited aryl radical, see Eq. 48 (77), then a similar event could be postulated for the decomposition of $ArX^{\cdot-}$. The coupling of an anion to such an aryl radical intermediate (Eq. 49) is intuitively appealing.

(48)



(49)

C. The Electron Transfer Step

The final propagation step of the $S_{RN}1$ reaction involves electron transfer from $RN^{\cdot}$ to RX. This is

vitally important as it simultaneously forms the product of the reaction, RN, and generates a reactive intermediate, $RX^{\cdot -}$, that can continue the chain. This section will develop in a qualitative manner a means of understanding the kinetics of this process based on Marcus theory (90).

The electron transfer reaction mechanism between donor molecule $D^{\cdot -}$ and acceptor molecule A can be visualized as in Scheme XXIII where k_d is the rate constant of diffusion of reactants and/or products into an encounter complex, k_{act} and k_{-act} are the rate constants for electron transfer within the encounter complex in the forward and reverse directions respectively, and k_{-d} is the rate constant for diffusion of species out of the encounter complex (90).

Scheme XXIII

$$D^{\cdot -} + A \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} (D^{\cdot -}\ A) \underset{k_{-act}}{\overset{k_{act}}{\rightleftharpoons}} (D\ A^{\cdot -}) \underset{k_d}{\overset{k_{-d}}{\rightleftharpoons}} D + A^{\cdot -}$$

In Scheme XXIII, $D^{\cdot -}$ and A diffuse towards each other forming an encounter complex $(D^{\cdot -}\ A)$. Within this encounter complex, electron transfer occurs yielding $(D\ A^{\cdot -})$, and these products then diffuse apart (90).

The overall reaction appears in Eq. 50.

$$D^{\cdot-} + A \xrightarrow{k_{obs}} D + A^{\cdot-} \qquad (50)$$

The observed rate constant for Eq. 50, k_{obs}, is a function of the microscopic rate constants k_d, k_{-d}, k_{act}, and k_{-act} according to Eq. 51 (90).

$$k_{obs} = \frac{k_d k_{act}}{k_{-d} + k_{act}} \qquad (51)$$

If the electron transfer were thermodynamically favorable, it might be expected that the electron transfer (k_{act}) step would have a low energy of activation. Assuming $k_{act} > k_{-d}$, Eq. 51 simplifies to Eq. 52 (90).

$$k_{obs} = k_d \qquad (52)$$

Hence, electron transfer in the thermodynamically favorable direction is expected to occur at a diffusion controlled rate--once the encounter complex is formed, electron transfer <u>always</u> takes place (51, 90, 91).

When the electron transfer is thermodynamically unfavorable, the activation energy for electron transfer is expected to come into play. Thus, each encounter of $D^{\cdot-}$ and A does not necessarily result in electron transfer since $k_{-d} \geq k_{act}$. Thus, k_{obs} is attenuated

from the diffusion controlled rate. This attenuation factor, f, is expressed by Eq. 53, where E_D and E_A are the respective standard reduction potentials of D and A, F is Faraday's constant, R is the ideal gas constant and T is the temperature (90).

$$f = 10^{(2.303F/RT)(E_A - E_D)} \qquad (53)$$

Eqs. 54 and 55 express $\log(k_{obs})$ as a function of standard reduction potentials of D and A under the two possible conditions, thus providing a useful model for predicting the rate of Eq. 50 (90).

$$\log(k_{obs}) = 10 \qquad E_D \leq E_A \qquad (54)$$

$$\log(k_{obs}) = 10 - (2.303F/RT)(E_D - E_A) \qquad (55)$$
$$E_D \geq E_A$$

A more recent approach to the kinetics of electron transfer has revolved around correlating the rates of electron transfer from 9-arylfluorenyl carbanions (9-ArFl^-) to suitable electron acceptors (RX) such as $PhSO_2CH_2Br$, $PhSO_2CH_2I$ and $R_2C(NO_2)_2$ with the basicity of the anion, see Eq. 56 (92).

$$9\text{-ArFl}^{\cdot} + RX \xrightarrow{k_2} 9\text{-ArFl} + RX^{\cdot} \qquad (56)$$

An excellent correlation between $\log(k_2)$ and the pKa of the parent hydrocarbon 9-ArFl-H was observed, the more basic anion donating an electron more readily (92). However, since the pKa also correlates well with the oxidation potential of the anions (92), and subsequently with the reduction potential of the radicals 9-ArFl·, the two approaches are similar--not too surprising since basicity and reduction potential are both empirical measurements of thermodynamic quantities somehow relating to the intrinsic nature or absolute free energy of 9-ArFl$^-$.

D. The Initiation/Termination Steps

This review of the $S_{RN}1$ reaction has treated the initiation and termination steps somewhat superficially, the primary reason being that it is the propagation steps that govern the net conversion of starting material to product. A secondary reason is that these steps are often poorly understood and easily ignored. Nonetheless, these steps are important as they do contribute to the rate of the reaction, and this section will discuss them in a general manner.

1. Initiation

Any process that can produce any reactive intermediate of the $S_{RN}1$ reaction ($RX^{\cdot-}$, R·, or $RN^{\cdot-}$) will

be an initiating event. The initiation can occur spontaneously, presumably involving electron transfer from the nucleophile to the substrate (Eq. 57) (6). Spontaneous initiation of the $S_{RN}1$ reaction is not a general phenomenon.

$$N^- + RX \longrightarrow N\cdot + RX^{\cdot-} \qquad (57)$$

Thus, reduction of starting material (RX) provides a means of entering the propagation sequence. Obvious reduction techniques include solvated electrons (alkali metal in NH_3) (20), direct (22) and indirect (93) electrochemical reduction of RX, and the addition of one-electron reducing agents (20).

The most popular means of initiating an $S_{RN}1$ reaction is photochemically. It is also the most mystical of methods. Possible mechanisms of photo-initiation are outlined in Scheme XXIV. All share the common feature of producing a reactive intermediate capable of entering the propagation cycle.

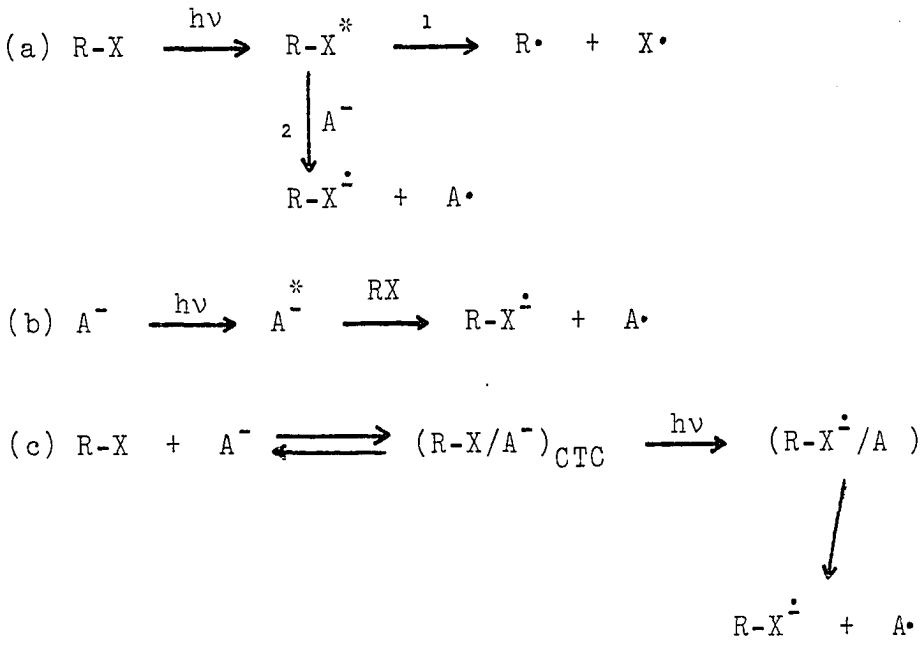
Entry (a) of Scheme XXIV involves the photochemical excitation of RX to RX^*. The excited species can fragment homolytically (path 1) to R· and X·, or react bimolecularly with A^- (path 2) resulting in a formal photo-induced electron transfer (40).

Entry (b) of Scheme XXIV assumes photochemical

excitation of the anion to a state A^{-*} that can readily transfer an electron to substrate RX (31).

Finally, entry (c) of Scheme XXIV assumes the light absorbing species is a charge transfer complex formed between the anion and starting RX. Excitation of the CT-complex results in an overall photo-induced electron transfer (40).

Scheme XXIV



2. Termination

Any event that destroys a reactive intermediate in the $S_{RN}1$ propagation cycle results in chain termination. Such steps can be elucidated since they often produce identifiable products of hydrogen abstraction, radical dimerization, etc.... Scheme XXV

highlights several possible termination events.

Scheme XXV

ELECTRON TRANSFER:

(a) $RX^{\cdot -} + R\cdot \longrightarrow R^- + RX$

$RN^{\cdot -} + R\cdot \longrightarrow R^- + RN$

(b) $R\cdot + A^- \longrightarrow R^- + A\cdot$

FRAGMENTATION:

(c) $RX^{\cdot -} \longrightarrow R^- + X\cdot$

(d) $Ar\cdot + {}^-CH_2CN \longrightarrow ArCH_2CN^{\cdot -} \longrightarrow ArCH_2\cdot + CN^-$

H-ATOM ABSTRACTION:

(e) $R\cdot + H\text{-}S \longrightarrow R\text{-}H + S\cdot$

(f) $R\cdot + AH^- \longrightarrow R\text{-}H + A^{\cdot -}$

DIMERIZATION/DISPROPORTIONATION:

(g) $R\cdot + R\cdot \longrightarrow R\text{-}R$

(h) $R\cdot + R\cdot \longrightarrow R\text{-}H + R(-H)$

Undesirable electron transfer between the propagating radical anions $RX^{\cdot -}$ or $RN^{\cdot -}$ and the free radical R·, entry (a), results in chain termination. Such a step has been discussed in the context of the aromatic $S_{RN}1$ reaction (91). The reduction potential of aryl radical is greater than product ArNu or reagent ArX, so the electron transfer is likely to be diffusion controlled (51, 91).

Entry (b) of Scheme XXV supposes an electron

transfer between R• and A^- occurring rather than coupling. So long as R^- is unreactive towards R• or A•, or A• unreactive towards A^- or R^-, the event is chain terminating. Examples where A• and A^- couple successfully and propagate a chain were discussed earlier (38).

Entry (c) proposes undesirable fragmentation of $RX^{\cdot-}$. Entry (d) assumes fragmentation of adduct $RNu^{\cdot-}$ into a free radical incapable of supporting the chain. The reaction of acetonitrile anion with halobenzenes provides a good example of this process (23).

Chain termination will result if R• is able to abstract a H-atom from the medium and the resultant radical S• is unreactive towards N^- (entry (e) of Scheme XXV) (91).

Entry (f) supposes H-atom abstraction from the anion itself, and that the resultant radical anion $A^{\cdot-}$ cannot propagate the chain. A mechanism very similar to the aromatic $S_{RN}1$ reaction has been studied kinetically, where the anion HA^- is an alchohloate ($R_2CH\text{-}O^-$). In this instance however, the radical anion ($R_2C{=}O^{\cdot-}$) <u>was</u> able to propagate a chain reaction (88).

Finally, destruction of the paramagnetic intermediates by dimerization or disproportionation (entries

(g) and (h) of Scheme XXV) will result in chain termination (91).

CHAPTER II. RESULTS AND DISCUSSION

I. STATEMENT OF THE RESEARCH PROBLEM

It has been pointed out that nucleophiles that work well in the aromatic $S_{RN}1$ reaction do not work well in the aliphatic $S_{RN}1$ reaction, and vice versa (17, 20). Table 4 reveals that while such a statement is not strictly true, aryl radicals tend more to resemble alkyl radicals substituted with electron withdrawing groups than simple alkyl radicals. This point is particularly obvious considering the high reactivity of aryl radicals toward highly localized anions such as diethyl phosphite anion, amide, etc.... It appears that the π-system plays a major role as an electron acceptor. However, given the σ-structure of aryl radicals, this seems difficult to reconcile assuming a direct approach of the nucleophile onto the sp^2 orbital in a plane orthogonal to the π-system.

This thesis will attempt to develop a rationale for understanding the factors involved in the coupling reactions of radicals with nucleophiles. Since the role of the π-system of aryl radicals in these reactions is a major point of confusion, the nature of the aryl radical intermediate in the aromatic $S_{RN}1$ reaction will be the major subject of this investigation.

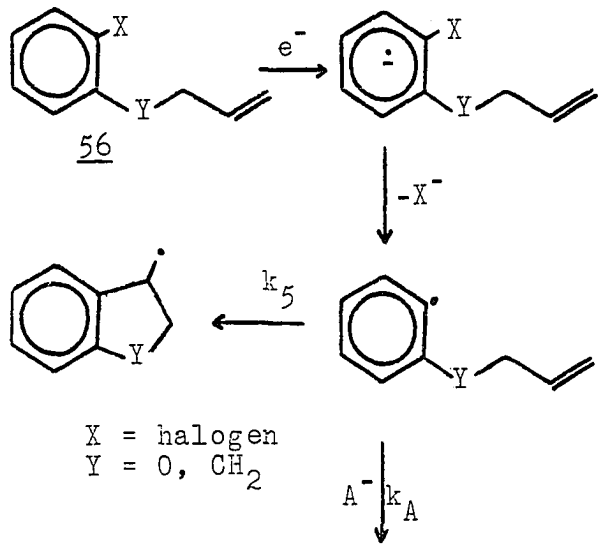
The problem will be approached from two perspectives:

Aryl radical, generated from an unambiguous source, will be compared to the aryl radical intermediate

in the aromatic $S_{RN}1$ reaction with respect to reactivity toward several reagents. Similar reactivity will further establish the intermediacy of free aryl radical in the $S_{RN}1$ reaction, whereas vastly different reactivity would require another mechanistic formulation.

Intramolecular rearrangements of radicals are especially useful for diagnosing radical intermediates in reactions. Furthermore, such rearrangements can be used as "clocks" for determining absolute rate constants, if the unimolecular rate constant for the rearrangement is known (94). A substrate such as (56) (95 - 98) in Scheme XXVI appears an ideal candidate for the application of such a rearrangement to the aromatic $S_{RN}1$ reaction.

Scheme XXVI



II. COMPARISON OF THE REACTIVITY OF THE ARYL RADICAL INTERMEDIATE IN THE AROMATIC $S_{RN}1$ REACTION TO THAT OF PHENYL RADICAL GENERATED FROM AN UNAMBIGUOUS SOURCE

If free aryl radical is truly an intermediate in the aromatic $S_{RN}1$ reaction, then the reactivity of this $S_{RN}1$ intermediate should parallel the reactivity of free aryl radical generated from any other source. The results discussed in this section will focus on the intermediate generated from the $S_{RN}1$ reactions of iodobenzene with several anions and comparison of its reactivity to that of phenyl radical generated from an unambiguous source.

A. Phenylazotriphenylmethane (PAT) as an Unambiguous Source of Phenyl Radical

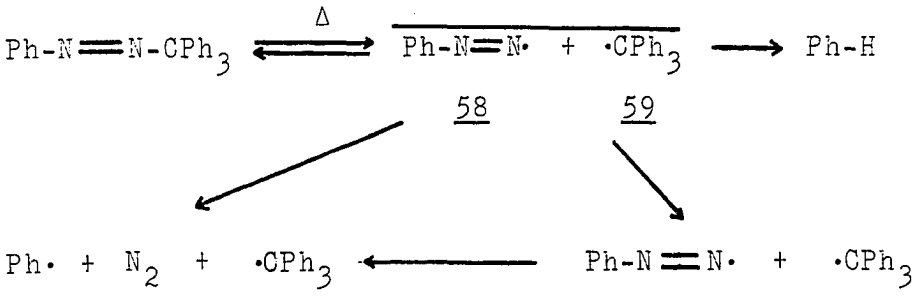
PAT, phenylazotriphenylmethane (57), is an excellent source of phenyl radical. The thermolysis of PAT (Eq. 58) generates phenyl radical in greater than 90% yield (99 - 101). Furthermore, the reactivity of phenyl radical generated from PAT has been extensively studied (99 - 101).

57

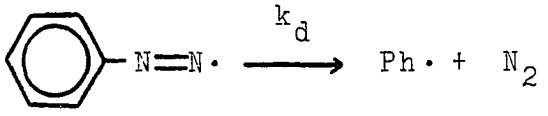
(58)

Scheme XXVII depicts the probable mechanism for the theromolysis of PAT (78, 99 - 103). The cleavage

Scheme XXVII



of the C(phenyl)-N and C(trityl)-N bonds are not synchronous. Upon thermolysis, diazenyl radical (58) and trityl radical (59) are produced within a solvent cage. This caged pair then diffuses apart, and phenyl radical is generated by the loss of nitrogen from the diazenyl radical (Eq. 59).



58 (59)

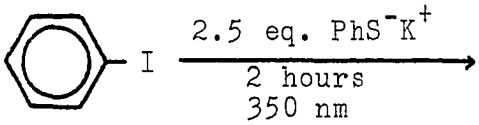
The rate constant (k_d) for loss of nitrogen from phenyldiazenyl radical is on the order of 1.6×10^5 s^{-1} (103). The intermediacy of diazenyl radical has been clearly established by ^{15}N CIDNP (chemically induced dynamic nuclear polarization) and trapping experiments (18, 102, 103).

It is reported that a small amount of benzene (5.4%) is formed in the decomposition of PAT, without the intervention of any H-atom donating species

(99 - 101). Apparently, H-abstraction occurs within the solvent cage (58/59). Thus in the following section, when a benzene yield is reported as "corrected," 5.4% was subtracted from the actual yield of benzene.

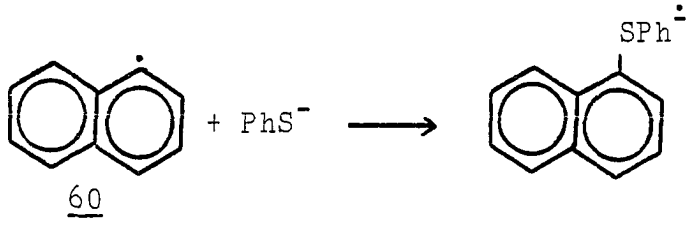
B. Evidence for a Free Phenyl Radical Intermediate in the $S_{RN}1$ Reaction of PhS^- with PhI

The photostimulated $S_{RN}1$ reaction of thiophenoxide ion and iodobenzene (in Me_2SO) has been reported (Eq. 60) (104). An anomaly in these results has been pointed



(60)

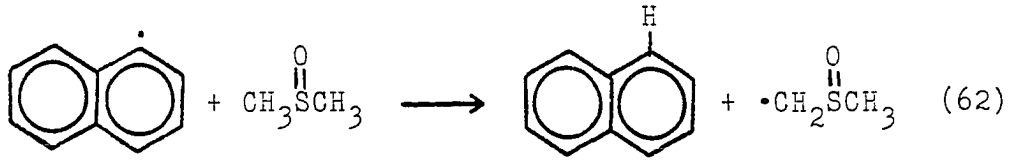
out (83). The absolute rate constant for reaction of 1-naphthyl radical (60) with PhS^- (Eq. 61) has been reported to be $1.7 \times 10^8\ M^{-1}s^{-1}$ (83). Furthermore,



60

(61)

the absolute rate constant for abstraction of hydrogen by 1-naphthyl radical from Me_2SO (Eq. 62) is reported to be $3 \times 10^5\ M^{-1}s^{-1}$ (83).



(62)

Thus it is argued, assuming similar rate constants for 1-naphthyl and phenyl radicals, that the yield of benzene in Eq. 60 is entirely too low (83). Based upon these rate constants: assuming 0.1 M PhS^- in 14 M Me_2SO, the production of 65% PhSPh should have been accompanied by a 15% yield of benzene.

Table 16 presents results for the reactions of PhS^- with PhI ($S_{RN}1$ reaction) and PAT in the presence of added reagents. Assuming a single phenyl radical intermediate in all these reactions (Scheme XXVIII), several relative rate constants can be derived from these results (Table 17).

A potential complication arises in the PAT reactions. In Scheme XXVIII, it is assumed that the oxidation of $PhSPh^{\cdot -}$ is fast. Thus in Eq. 63, $k_{et}(A) > k_{-1}$, where (A) is the concentration of some electron accepting species.

$$Ph\cdot + PhS^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PhSPh^{\cdot -} \xrightarrow{k_{et}(A)} PhSPh + A^{\cdot -} \qquad (63)$$

For the $S_{RN}1$ reaction, A = PhI. With PAT however, iodobenzene is not present to accept the electron and

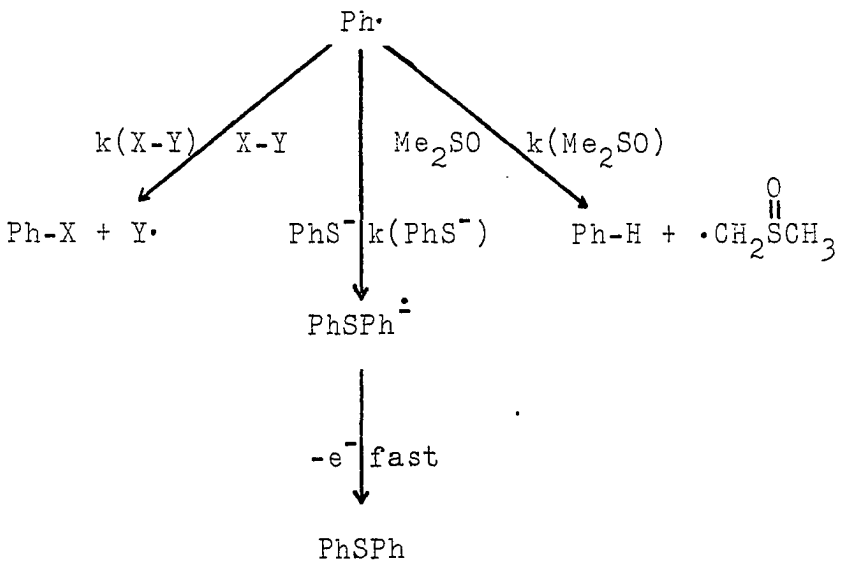
Table 16. Reactions of PhS^- with PAT and PhI under a variety of conditions in Me_2SO at 45 C

Initial Concentrations						Product yields (%)[a]			
PAT (M)	PhI (M)	PhS^- (M)	Counter-ion	Addend	Conditions	Ph-H	Ph-D	PhCl	Ph_2S
0.0	0.051	0.090	K^+	none	350 nm, 1.5 h	11.4	-	-	64.9
0.050	0.0	0.090	K^+	none	dark, 24 h	15.6[b]	-	-	69.3
0.050	0.050	0.099	K^+	none	dark, 24 h	9.3	-	-	59.2
0.052	0.0	0.087	K^+	1.29 M CCl_4	dark, 24 h	-	-	39.3	18.2
0.051	0.050	0.090	K^+	1.30 M CCl_4	dark, 24 h	-	-	18.4	9.5
0.0	0.050	0.091	K^+	PhSH	350 nm, 27 h	57.3	-	-	34.1
0.050	0.0	0.091	K^+	PhSH	dark, 24 h	66.8[b]	-	-	27.4
0.034	0.0	0.041	K^+ 18-crown-6	d_6-Me_2SO	dark, 24 h	7.99	6.23	-	63.3

[a]Total yield based upon all sources of Ph• (PhI and PAT).

[b]Corrected.

Scheme XXVIII



the assumption that $k_{et}(A) > k_{-1}$ may not be valid.

The fact that the PAT results in the presence of PhI (Table 17) are in agreement with those obtained with PAT alone verify the assumption that oxidation of $PhSPh^{\cdot-}$ is rapid. In the absence of PhI, the oxidizing agent is most likely trityl radical (59) (Eq. 64).

$$PhSPh^{\cdot-} + {\cdot}CPh_3 \underset{59}{\longrightarrow} PhSPh + {}^{-}CPh_3 \xrightarrow{H\text{-}S} Ph_3CH + S^{-} \qquad (64)$$

The results of Table 17 indicate the reactivity of phenyl radical (from PAT) parallels the reactivity of the intermediate of the $S_{RN}1$ reaction of iodobenzene and thiophenoxide ion. Thus, it appears quite likely

Table 17. Relative reactivity of several reagents towards phenyl radical generated from PAT or $PhI^{\cdot-}$

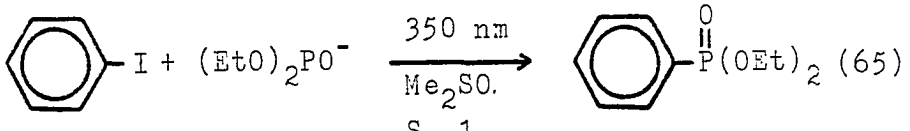
Reagents		Relative reactivity (k_A/k_B)		
		Source of phenyl		
A	B	PAT	PAT[a]	$PhI^{\cdot-}$
PhS^-K^+	Me_2SO	910	894	901
PhS^-K^+	PhSH	5.9	-	9.0
PhS^-K^+	CCl_4	7.4	8.7	-
PhS^-K^+/18-crown-6	d_6-Me_2SO	5029	-	-

[a]In the presence of PhI as an electron acceptor.

that this intermediate is phenyl radical.

C. Reactivity of $(EtO)_2PO^-$ Towards Phenyl Radical: Comparison to the $S_{RN}1$ Reaction of $(EtO)_2PO^-$ with PhI

The photo-stimulated $S_{RN}1$ reaction of diethyl phosphite anion and iodobenzene in Me_2SO has been reported (Eq. 65) (20, 40, 104).



(65)

61

Products and yields of this reaction were determined, with particular attention paid to the volatile by-product benzene, and are listed in Table 18. The production of significant amounts of benzene in this reaction is due to a thermal reaction between iodobenzene and diethyl phosphite anion. This thermal process however does not result in the formation of substitution product (40).

When PAT was decomposed in the presence of diethyl phosphite anion (Table 19), no diethyl phenylphosphonate (61) was observed. The possibility exists that in the PAT experiments, the $PhP(O)(OEt)_2^{\bullet}$ initially formed is not rapidly oxidized by trityl radical. However, when the thermolysis was carried out in the presence of diethyl phosphite and several suitable electron acceptors (m-dinitrobenzene, o-dicyanobenzene, azobenzene) the results remained unchanged--no phenylphosphonate was produced!

There are several possible explanations for these observations:

(a) Phenyl radical is not readily attacked by diethyl phosphite anion.

(b) Phenyl radical is attacked by diethyl phosphite, but the resulting radical anion is diverted to some unrecognized product.

Table 18. Products and yields in the photo-stimulated reaction of iodobenzene and diethyl phosphite anion under various conditions

Initial Concentration (M)				Yield (%)	
PhI	$(EtO)_2PO^-$	Counter-ion	Conditions[a]	Ph-H	$PhP(O)(OEt)_2$
0.056	0.126	K^+	350 nm, 5 h	15.3	44.1
0.056	0.126	K^+	dark, 5 h	9.6	2.9
0.056	0.127	K^+	350 nm, 7 h	18.1	36.7
0.056	0.127	K^+	350 nm, 8 h	16.7	38.6
0.056	0.121	K^{+b}	350 nm, 12 h	17.2	34.0
0.028	0.143	K^{+b}	350 nm. 11 h	32.8	33.1

[a]Solvent = Me_2SO, T = 45 C.

[b]In the presence of 18-crown-6.

in the presence of PAT

(c) PAT reacts with diethyl phosphite anion directly, destroying both the PAT and diethyl phosphite anion, but not resulting in phenylphosphonate.

Although the latter two possibilities hardly seem reasonable, they were nonetheless easily tested by running the <u>normal</u> $S_{RN}1$ reaction of PhI and $(EtO)_2PO^-$

Table 19. Products and yields of the thermolysis of PAT in the presence of diethyl phosphite anion at 45° C

Initial Concentration (M)[a]		Product yield (%)	
PAT	$(EtO)_2PO^-$	Ph-H	$PhP(O)(OEt)_2$
0.056	0.126	32	0[b]
0.056	0.126	19	0[b]

[a]PAT decomposed for 10 half-lives (24 -27 h).

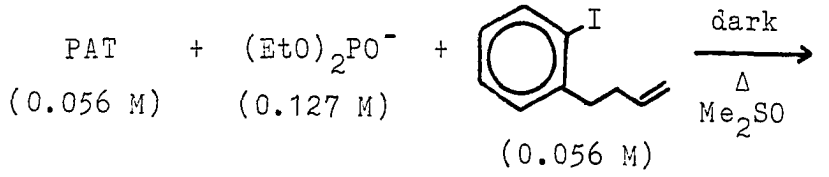
[b]In the presence of 0.058 M m-dinitrobenzene, o-dicyanobenzene or azobenzene the yield is unaffected.

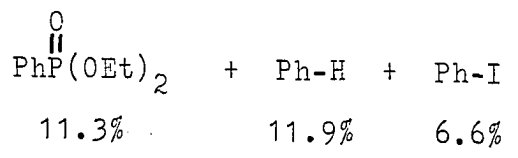
in the presence of PAT. The yield of phenylphosphonate was unaffected by the presence of PAT.

Finally, in an attempt to duplicate $S_{RN}1$ conditions as closely as possible, an aryl halide was chosen as an electron acceptor. The results are presented in Eq. 66.

Unfortunately, these results are somewhat ambiguous. The phenylphosphonate product is formed, but accompanied by a significant amount of hydrogen and iodine abstraction products.

If in fact phenylphosphonate is produced by trapping of phenyl radical by $(EtO)_2PO^-$, an unlikely





(66)

possibility given the results in the presence of other electron acceptors, the rate constant for that attack is not very large. Assuming $k(Me_2SO) = 3.0 \times 10^5\ M^{-1}s^{-1}$, see Table 25, a rough estimate of $k((EtO)_2PO^-)$ based upon these results would be approximately $3 \times 10^7\ M^{-1}s^{-1}$. Recall that the trapping of the aryl radical intermediate in the $S_{RN}1$ reaction was reported to be diffusion controlled, 10^9 - $10^{10}\ M^{-1}s^{-1}$ (41).

The presence of iodobenzene as a product is an interesting result. The process of iodine abstraction by phenyl radical from aryl halides involves the mechanism of Scheme XXIX (105). The iodine atom is not abstracted directly. Instead a 9-I-2 intermediate (62) is involved.

It may be possible that this 9-I-2 intermediate is also involved in the production of phenyl phosphonate in the reaction of PAT with $(EtO)_2PO^-$ in the presence of

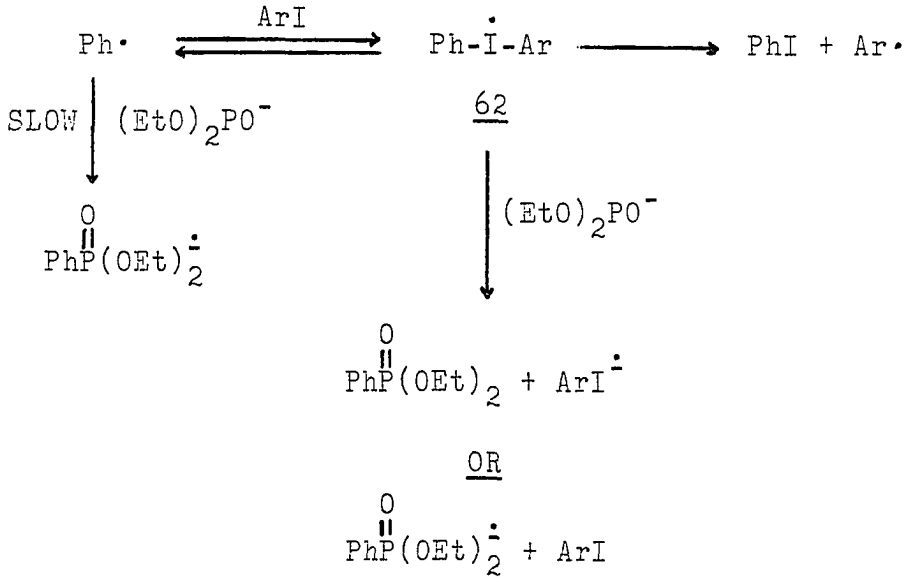
Scheme XXIX

$$Ph\cdot + I\text{-}Ar \rightleftharpoons Ph\text{-}\dot{I}\text{-}Ar \longrightarrow PhI + Ar\cdot$$

62

an aryl halide (Scheme XXX). Thus, a 9-I-2 intermediate (62) may be a potential intermediate in the $S_{RN}1$ reaction of iodobenzene and diethyl phosphite anion.

Scheme XXX



It is notable that the mass balance in the reaction of PAT with $(EtO)_2PO^-$ (30%) was lower than the decomposition of PAT in Me_2SO without $(EtO)_2PO^-$ present (70%). This observation may be the result of reaction between diethyl phosphite and the intermediate diazenyl

radical in the PAT decomposition (Eq. 67).

$$\begin{array}{ccccc} Ph\text{-}N{=}N\text{-}CPh_3 & \xrightarrow{\Delta} & Ph\text{-}N{=}N\cdot + \cdot CPh_3 & & \\ & & \Big\downarrow (EtO)_2PO^- & & (67) \\ Ph\text{-}N{=}NH & \longleftarrow & Ph\text{-}N{=}N^- + (EtO)_2PO\cdot & & \end{array}$$

D. Reactivity of Nitronate Anion Towards Phenyl Radical

It appears that nitronate anion can trap phenyl radical (Eq. 68) since the resultant radical anion (63) can be detected when benzenediazonium salts are reduced in the presence of nitronate (81). The

$$Ph\cdot + \rangle C{=}NO_2^- \longrightarrow Ph\text{—}\underset{|}{\overset{|}{C}}\text{—}NO_2^{\cdot} \qquad (68)$$

63

feasibility of this coupling reaction was further demonstrated by the decomposition of PAT in the presence of nitronate anion. These results are presented in Table 20. The formation of the various products is readily explained by the fragmentation of initially formed radical anion (63) according to Scheme XXXI.

It is interesting to note that 2-phenyl-2-nitropropane is only formed when Li^+ is the counter-ion. Apparently, ion-pairing stabilizes the radical anion

Table 20. The thermolysis of PAT in the presence of nitronate at 45 C

Initial Concentration (M)		Product yield (%)						
PAT	$Me_2C{=}NO_2^-$	$PhCHMe_2$	$PhC(CH_3){=}CH_2$	$Ph{-}NO_2$	$Ph{-}Ph$	$Ph{-}CPh_3$	Ph-H	Ph-D
0.028	0.105[a,b]	0.3	11.6	6.4	0.6	29.4	44.6	-
0.028	0.072[a,c]	0.64	12.4	0	5.2	25.3	24.3	-
0.021	0.072[c,d]	0.5	16.0	0	3.9	21.8	16.5[e]	1.1

[a] Solvent = Me_2SO.

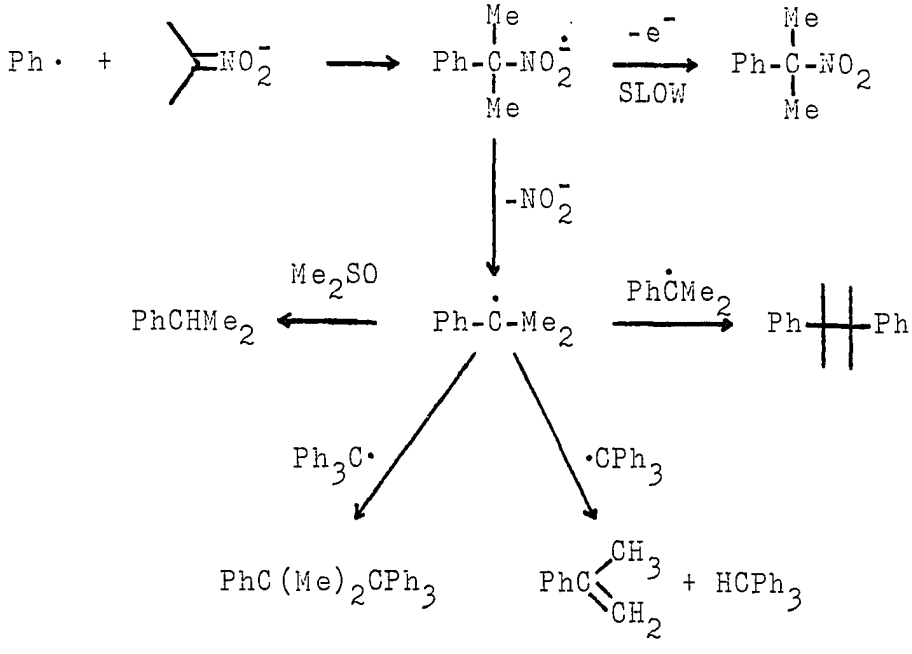
[b] Counter-ion is Li^+.

[c] Counter-ion is K^+/18-crown-6.

[d] Solvent = d_6-Me_2SO.

[e] Corrected.

Scheme XXXI



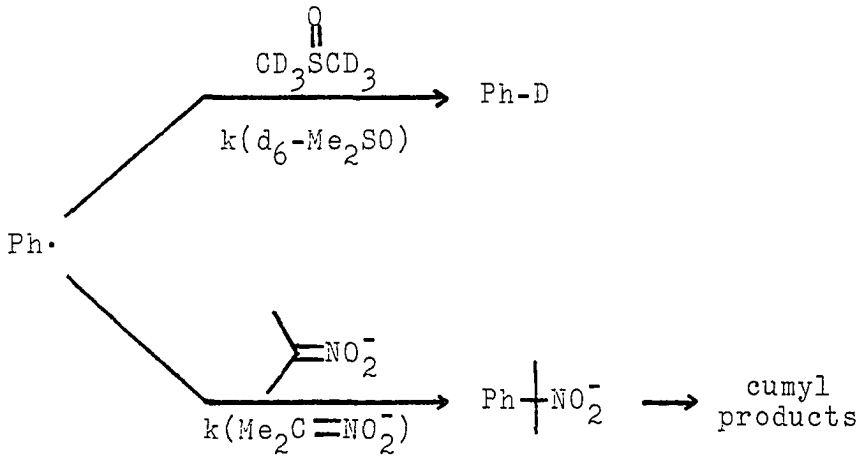
(63) against fragmentation into NO_2^- and cumyl radical.

From the results in d_6-Me_2SO, the relative reactivity of phenyl radical towards nitronate (addition) and d_6-Me_2SO (D-abstraction) can be calculated (Scheme XXXII and Eqs. 69 and 70).

It also appears that nitronate, in addition to reacting with phenyl radical in a coupling process, is susceptible to H-abstraction (Eq. 71). This point is borne out by the production of a significant amount of non-deuterated benzene in d_6-Me_2SO.

The only other species possessing abstractable

Scheme XXXII



$$\frac{k(Me_2C{=}NO_2^-)}{k(d_6\text{-}Me_2SO)} = \frac{\text{YIELD CUMYL PRODUCTS}}{\text{YIELD DEUTEROBENZENE}} \times \frac{(d_6\text{-}Me_2SO)}{(Me_2C{=}NO_2^-)} \qquad (69)$$

$$\frac{k(Me_2C{=}NO_2^-)}{k(d_6\text{-}Me_2SO)} = 8200 \qquad (70)$$

H-atoms is 18-crown-6, however the rate constant ratio for H-abstraction from 18-crown-6 relative to D-abstraction from d_6-Me_2SO is 887 (Table 25). Given the concentrations of 18-crown-6 and d_6-Me_2SO are 0.10 and 14 M respectively, it is estimated that the yield of non-deuterated benzene directly from 18-crown-6 should be about 7% when 1.1% Ph-D is produced. The other 9.5% that is formed must be due to H-abstraction from nitronate. Hence for nitronate, the ratio of coupling to H-abstraction is expressed by Eq. 72.

$$Ph\cdot + CH_3\text{-}\overset{\overset{NO_2^-}{\|}}{C}\text{-}CH_3 \longrightarrow Ph\text{-}H + \cdot CH_2\text{-}\overset{\overset{NO_2^-}{\|}}{C}\text{-}CH_3 \qquad (71)$$

$$\frac{k(Me_2C{=}NO_2^-)_{add'n}}{k(Me_2C{=}NO_2^-)_{H\text{-}abstr}} = 4.4 \qquad (72)$$

Although the aromatic $S_{RN}1$ reaction is reported to be unsuccessful with nitronate (20), it appeared worthwhile to attempt it nonetheless. The results are presented in Eq. 73.

$$PhI + \text{(nitronate)}Li^+ \xrightarrow[Me_2SO]{\substack{350\ nm \\ 30\ hours}} \underset{25\%}{Ph\text{-}H} + \underset{58\%}{Ph\text{-}I} + \qquad (73)$$

$$\underset{<1\%}{PhCHMe_2} + \underset{1\%}{PhC(CH_2)CH_3} + \underset{1.5\%}{Ph\text{-}NO_2} + \underset{3.4\%}{Ph\text{-}Ph}$$

Thus, there is an observable reaction between iodobenzene and nitronate, however it is very sluggish. Table 21 compares the rate of this reaction to the rate of photolysis of iodobenzene without nitronate present. The observation that the rate of the nitronate/iodobenzene run was only modestly faster than the rate of the simple photolysis of iodobenzene

implies that electron transfer is relatively unimportant in the former. Hence, an $S_{RN}1$ reaction is unlikely and the products undoubtedly arise from coupling of phenyl radical, produced by photolysis, with nitronate (Scheme XXXIII). The failure to observe an aromatic $S_{RN}1$ reaction with nitronate is apparently due to slow electron transfer from radical anion (63) to iodobenzene in addition to fragmentation of this radical anion into the unreactive cumyl radical.

Scheme XXXIII

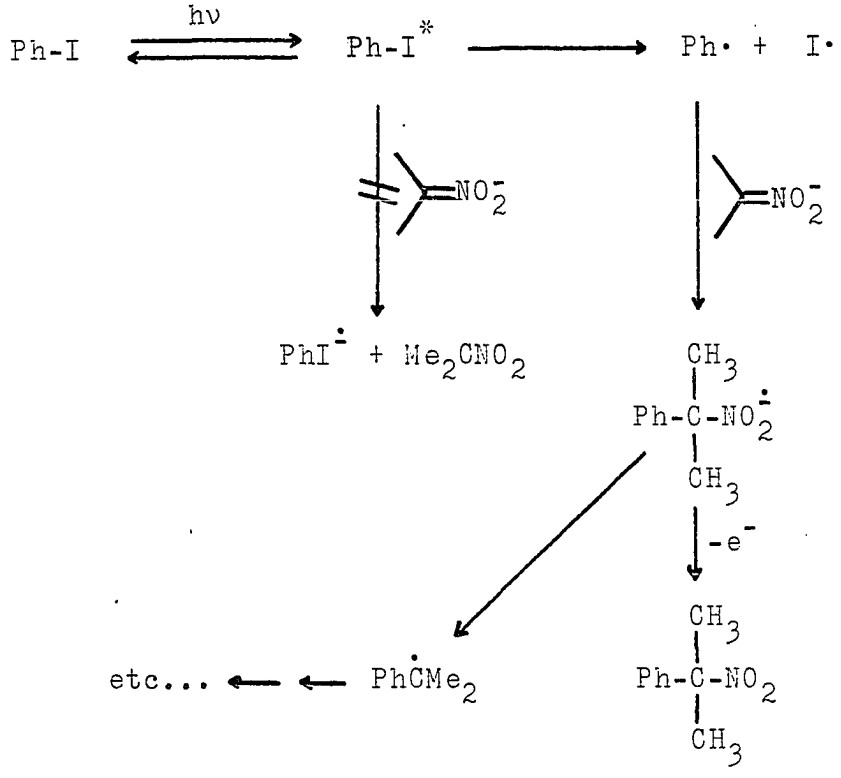


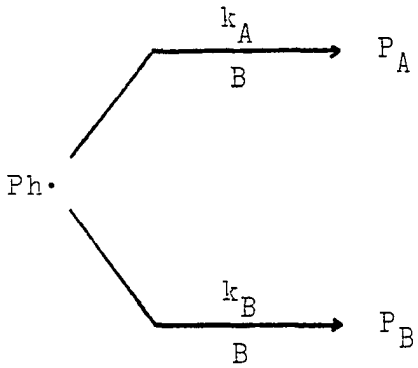
Table 21. Irradiation of iodobenzene in the presence and absence of nitronate anion at 350 nm in Me_2SO at 45 C

Initial Concentration (M)				
PhI	$Me_2C{=}NO_2^-$	Counter-ion	Time (h)	%-conversion
0.022	0.098	K^+/18-crown-6	21	58
0.022	0.000	-	21	37

E. Reactivity of Several Other Reagents Towards Phenyl Radical

The determination of the relative reactivities towards phenyl radical was based upon Scheme XXXIV where k_A and k_B are the respective absolute rate constants for reaction of species A and B with Ph•, and P_A and P_B are the products.

Scheme XXXIV



1. Benzenethiol

The rate constant for the reaction of phenyl radical with benzenethiol is reported to be at or near the diffusion controlled limit in CCl_4 (Eq. 74) (100, 101). The value k(PhSH) = 1.9×10^9 $M^{-1}s^{-1}$ was arrived at by determining the rate constant for phenyl radical abstracting a H-atom from PhSH relative to the rate constant for abstraction of chlorine atom from CCl_4 (101). Since $k(PhSH)/k(CCl_4)$ was found to be 518 (100) and $k(CCl_4) = 3.7 \times 10^6$ $M^{-1}s^{-1}$ (101). k(PhSH) is obtained by simple multiplication.

$$Ph\cdot + PhSH \longrightarrow Ph\text{-}H + PhS\cdot \qquad (74)$$

In an earlier section, competition experiments between thiophenoxide and benzenethiol were reported for phenyl radical (generated from PAT) and for the phenyl radical intermediate in the $S_{RN}1$ reaction. Due to the importance of those results, it became necessary to verify the literature data, and further

Table 22. Reactivity of benzenethiol (relative to CCl_4) towards phenyl radical generated from PAT at 45 C

moles CCl_4	moles PhSH	solvent	Yield (%) PhH[b]	Yield (%) PhCl	k(PhSH)/k(CCl_4)
0.100	1.95×10^{-3}	CCl_4[a]	83.3	8.38	53.1
0.0103	1.95×10^{-3}	Me_2SO[a]	77.0	6.3	65.1

[a]PAT concentration ≃ 0.05 M.

[b]Corrected.

extend it to Me_2SO solvent. Table 22 summarizes these findings.

The values k(PhSH)/k(CCl_4) obtained in CCl_4 was reasonably close to the reported literature value of 518 (100). A surprising result is obtained in Me_2SO however. The rate constant for H-abstraction (from PhSH) relative to Cl-abstraction (from CCl_4) decreases by a factor of 8 in Me_2SO. Since these are relative rate constants, the results do not reveal whether Cl-abstraction becomes faster in Me_2SO, or H-abstraction becomes slower, or if some combination of the two effects occur.

However, chemical intuition may provide some insight into this phenomenon. It has been shown that H-bonding of phenols to Me_2SO can have observable kinetic consequences in terms of decreased reactivity (106). A similar sort of H-bonding of thiophenol in Me_2SO may result in diminishing k(PhSH) and hence account for the lowered $k(PhSH)/k(CCl_4)$ ratio.

2. Diphenyl disulfide

The reaction of phenyl radical, generated either from PAT or benzenediazonium salts, with diphenyl disulfide has been reported (Eq. 75) (107, 108).

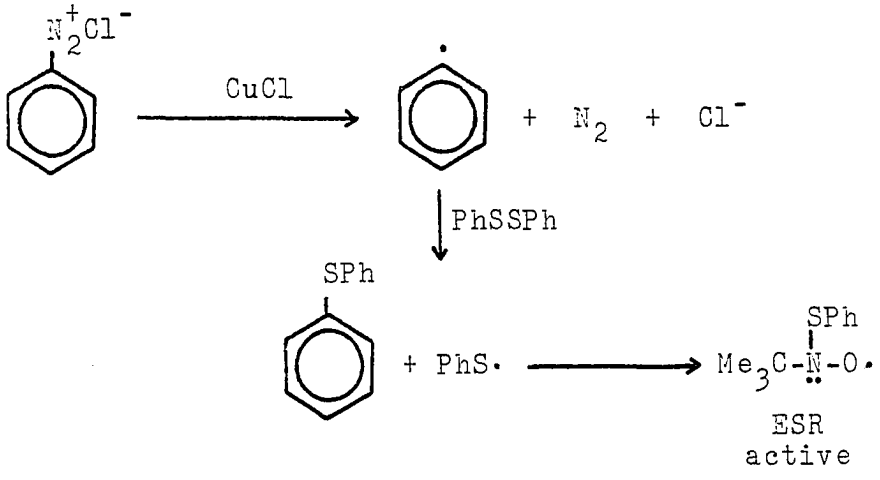
$$\begin{array}{ccccccc} Ph\cdot & + & PhSSPh & \longrightarrow & PhSPh & + & PhS\cdot \\ \uparrow & & & & & & \\ \text{from } PhN_2^+ & & & & & & \\ \text{or PAT} & & & & & & \end{array} \qquad (75)$$

When benzenediazonium salts are reduced in the presence of diphenyl disulfide and 2-methyl-2-nitroso-propane spin trap, the resultant thiyl radical (PhS•) can be detected by ESR spectroscopy (Scheme XXXV) (109).

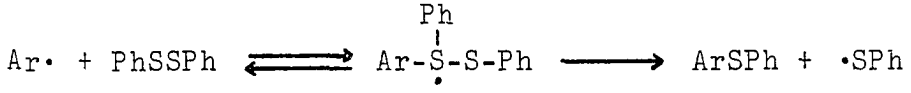
While Eq. 75 has the appearance of an S_H2 reaction at sulfur, the actual mechanism of the reaction more probably involves an addition/elimination sequence (Scheme XXXVI) (107).

The reactivity of phenyl radical (from PAT) towards diphenyl disulfide was determined via competition experiments with CCl_4. The results of these experiments

Scheme XXXV



Scheme XXXVI



are summarized in Table 23.

As with PhSH in Me_2SO, the rate constant for reaction of phenyl radical with PhSSPh in Me_2SO is diminished relative to Cl-abstraction from CCl_4, from the value observed in CCl_4. A reasonable accounting for these results would be increased solvation of PhSSPh in Me_2SO lowering its reactivity. PhSSPh can be an electrophilic species, so perhaps a dipolar interaction is present in Me_2SO, although not to so large an extent as that of PhSH in Me_2SO.

Table 23. Reactivity of diphenyl disulfide (relative to CCl_4) towards phenyl radical generated from PAT

moles CCl_4	moles PhSSPh	solvent	Yield (%) Ph-H[a]	PhCl	PhSPh	$\frac{k(PhSSPh)}{k(CCl_4)}$
0.154	0.0164	CCl_4[b]	-	16.7	68.6	38.61
0.0103	3.21×10^{-3}	Me_2SO[c]	6.1	12.7	68.2	17.2

[a]Corrected.

[b]PAT concentration ≃ 0.07 M.

[c]PAT concentration ≃ 0.05 M.

3. Hexadeuterodimethyl sulfoxide

The reactivities of two nucleophiles ($Me_2C{=}NO_2^-$, PhS^-) relative to D-abstraction from d_6-Me_2SO towards phenyl radical were determined. The rate constant for H-abstraction from Me_2SO by phenyl radical (relative to Cl-abstraction from CCl_4), $k(Me_2SO)/k(CCl_4)$, was found to be 0.039 (99). However, no data were reported for D-abstraction from d_6-Me_2SO. Table 24 summarizes the results obtained in the competition between d_6-Me_2SO amd CCl_4 for phenyl radical generated from PAT.

As expected, D-abstraction proceeds with a lower rate than H-abstraction. The kinetic isotope effect,

Table 24. Reactivity of d_6-Me_2SO (relative to CCl_4) towards phenyl radical generated from PAT at 45 C[a]

moles d_6-Me_2SO	moles CCl_4	Yield (%) Ph-H	Ph-D	PhCl	$\frac{k(d_6\text{-}Me_2SO)}{k(CCl_4)}$
2.81×10^{-2}	7.21×10^{-3}	3.71	1.22	56.9	0.0055

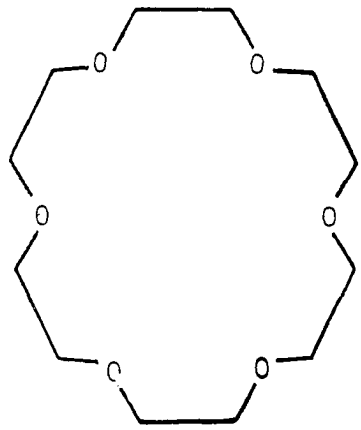
[a]PAT concentration ≈ 0.05 M.

k_H/k_D = 7.1, is a reasonable value for a primary isotope effect.

4. 18-Crown-6

Finally, in many of the competition experiments involving nucleophiles, 18-crown-6 was added to complex the potassium counter-ion and thereby eliminate ion-pairing effects. However, in 18-crown-6 (64), all the hydrogen atoms are likely to be abstractable by phenyl radical since all are α to an oxygen atom.

In a series of competition experiments, the rate constant for H-abstraction (relative to Cl-abstraction from CCl_4) was determined at 45 C. The result is expressed in Eq. 76.



64

$$\frac{k(18\text{-crown-6})}{k(CCl_4)} = 4.88 \qquad (76)$$

F. Summary

The absolute rate constant for the abstraction of chlorine atom from CCl_4 by phenyl radical (Eq. 77) has recently been determined by flash photolysis (110).

$$Ph\cdot + Cl\text{-}CCl_3 \longrightarrow Ph\text{-}Cl + \cdot CCl_3 \qquad (77)$$

$$k(CCl_4) = 7.8 \times 10^6\ M^{-1}s^{-1}\ (110)$$

Thus, given the results of the competition experiments reported in this section, it is possible to report absolute rate constants for the reactions of phenyl radical with several species. These values are compiled in Table 25.

With regard to the intermediacy of phenyl radical in the aromatic $S_{RN}1$ reaction, the photo-stimulated

Table 25. Absolute rate constants for several reactions of phenyl radical at 45 C based upon $k(CCl_4) = 7.8 \times 10^6\ M^{-1}s^{-1}$ (110)

Substrate	Reaction type	Solvent	k ($M^{-1}s^{-1}$)	Source
Me_2SO	H-abstraction	Me_2SO	3.0×10^5	a
d_6-Me_2SO	D-abstraction	Me_2SO	4.3×10^4	b
$Me_2C{=}NO_2^-$ [c]	coupling	Me_2SO	1.2×10^9	d
$Me_2C{=}NO_2^-$ [c]	H-abstraction	Me_2SO	2.8×10^8	e
PhS^- [c]	coupling	Me_2SO	2.2×10^8	f
PhS^-K^+	coupling	Me_2SO	5.7×10^7	g
$(EtO)_2PO^-K^+$	coupling	Me_2SO	$\leq 3.0 \times 10^7$	h
$(EtO)_2PO^-$ [c]	coupling	Me_2SO	$\leq 2.6 \times 10^7$	i

[a] $k(Me_2SO)/k(CCl_4) = 0.039$ (99).

[b] $k(d_6\text{-}Me_2SO)/k(CCl_4) = 0.0055$ (this work).

[c] Counter-ion is K^+/18-crown-6.

[d] $k(Me_2C{=}NO_2^-)_{add'n}/k(PhS^-) = 5.5$ (next section).

[e] $k(Me_2C{=}NO_2^-)_{add'n}/k(Me_2C{=}NO_2^-)_{H\text{-}abstr} = 4.4$ (this work).

[f] $k(PhS^-)/k(d_6\text{-}Me_2SO) = 5029$ (this work).

[g] $k(PhS^-K^+)/k(CCl_4) = 7.4$ (this work).

[h] See text.

[i] See next section.

Table 25. (Continued)

Substrate	Reaction type	Solvent	$k(M^{-1}s^{-1})$	Source
PhSSPh	overall S_H2	Me_2SO	1.3×10^8	j
PhSSPh	overall S_H2	CCl_4	3.0×10^8	k
PhSH	H-abstraction	Me_2SO	5.1×10^8	l
PhSH	H-abstraction	CCl_4	4.1×10^9	m
18-crown-6	H-abstraction	CCl_4	3.8×10^7	n

[j] $k(PhSSPh)/k(CCl_4) = 17.2$ in Me_2SO (this work).

[k] $k(PhSSPh)/k(CCl_4) = 38.6$ in CCl_4 (this work).

[l] $k(PhSH)/k(CCl_4) = 65.1$ in Me_2SO (this work).

[m] $k(PhSH)/k(CCl_4) = 518$ (reference 100) and 531 (this work).

[n] $k(18\text{-crown-6})/k(CCl_4) = 4.88$ (this work).

reaction of thiophenoxide with iodobenzene suggests that a phenyl radical intermediate is likely since the reactivity of the $S_{RN}1$ intermediate parallels that of phenyl radical generated from PAT. For the reaction of diethyl phosphite anion with iodobenzene however, the results suggest just the opposite--phenyl radical is not an intermediate.

III. EVIDENCE FOR A KINETICALLY SIGNIFICANT INTERMEDIATE IN THE AROMATIC $S_{RN}1$ REACTION THAT PRECEDES FREE ARYL RADICAL

The results in the previous section demonstrate that phenyl radical is a likely intermediate in the $S_{RN}1$ reaction of iodobenzene and PhS^-. In addition, although it does not participate in an aromatic $S_{RN}1$ reaction per se, nitronate couples with phenyl radical quite rapidly. Finally, diethyl phosphite anion does not appear to couple with phenyl radical.

The conclusion regarding the coupling of diethyl phosphite anion with phenyl radical is in direct contradiction with the conclusions in the literature. The trapping of phenyl radical in the $S_{RN}1$ reaction by $(EtO)_2PO^-$ is believed to be diffusion controlled (41).

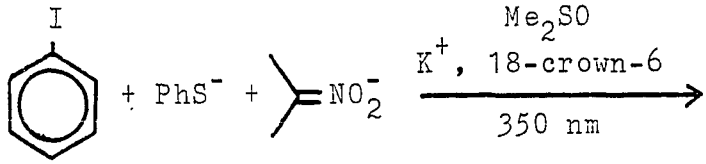
The evidence in the literature regarding the reaction of diethyl phosphite anion with aryl halides is indicative of the involvement of radical anions, particularly the results with dihalobenzenes (20), and a chain mechanism is established (20, 40). Since the reaction of diethyl phosphite anion with halobenzene is considered the prototypical $S_{RN}1$ reaction (20), it is of enormous importance to resolve this dilemma.

The coupling reaction of nitronate anion with phenyl radical (Scheme XXXI) produces a radical anion

(63) which decomposes by loss of NO_2^- forming cumyl radical, leading eventually to products of dimerization, H-abstraction, etc.... In solutions containing nitronate, the appearance of these "characteristic" products can be used to signal the presence of phenyl radical intermediates. Thus, nitronate anion can be utilized as a probe for phenyl radical in the aromatic $S_{RN}1$ reaction.

A. Competition Between Nitronate and Thiophenoxide Anions for Phenyl Radical in the $S_{RN}1$ Reaction

The utilization of competition experiments in the $S_{RN}1$ reaction was discussed earlier. In this section, the results of competition experiments between nitronate and thiophenoxide anions (Eq. 78) are reported for the photo-stimulated reactions involving iodobenzene.



(78)

$$PhCHMe_2 + PhC(=CH_2)CH_3 + Ph\text{-}NO_2 +$$

$$Ph\text{-}Ph + PhSPh$$

Table 26. Competition between nitronate and thiophenoxide anions for intermediates in the aromatic $S_{RN}1$ reaction

Initial Concentration[a] (M)		Yields (%)			$\frac{\text{Yield cumyl products}}{\text{Yield PhSPh}}$	$\frac{k(Me_2C{=}NO_2^-)}{k(PhS^-)}$
$Me_2C{=}NO_2^-$	PhS^-	$PhCHMe_2$	Ph‡Ph	PhSPh		
0.100	0.130	6.57	16.36	5.92	3.87	5.0
0.047	0.061	6.93	10.58	3.79	4.62	6.0
0.027	0.035	5.65	10.26	3.71	4.29	5.6
					Average:	5.5

[a]Solvent = Me_2SO, T = 45 C, counter-ion = K^+/18-crown-6 and reaction time = 3 h.

Table 26 summarizes the results of several experiments. The observed $k(Me_2C{=}NO_2^-)/k(PhSH)$ ratio is constant for all these experiments, and thus consistent with a phenyl radical intermediate.

B. Results of Competition Experiments Between Diethyl Phosphite and Nitronate Anions

Table 27 summarizes the results of competition experiments involving diethyl phosphite anion versus nitronate in reactions of PAT and PhI. The results with PAT, in the dark and in the presence or absence of iodobenzene as an electron acceptor, demonstrate that phenyl radical reacts <u>exclusively</u> with nitronate over diethyl phosphite anion, since no phenylphosphonate is formed at all! Furthermore, the appearance of cumyl type products clearly indicates that diethyl phosphite anion does not in any way impede the formation of phenyl radical from PAT.

Thus for attack of phenyl radical by these two anions, $k(Me_2C{=}NO_2^-) >> k((EtO)_2PO^-)$. If it is assumed that the yield of phenylphosphonate has a lower detection limit of 0.5%, then nitronate anion is at least 45 times more reactive towards phenyl radical than diethyl phosphite anion. Given the absolute rate constant for the nitronate reaction (1.2×10^9 $M^{-1}s^{-1}$), it appears that the rate constant for coupling of

Table 27. Results of competition experiments pitting diethyl phosphite anion against nitronate anion for phenyl radical (from PAT) and the intermediate(s) of the $S_{RN}1$ reaction of PhI

Experiment[a]	Product yields (%): Ph-H	Ph-I	$PhCHMe_2$	$PhC(CH_3)=CH_2$	$Ph-NO_2$	Ph-Ph	$Ph-CPh_3$	$PhP(O)(OEt)_2$
1[b]	18.0	--	0.94	7.5	0.0	5.1	9.2	0.0
2[c]	16.7	65.7	0.75	10.2	0.05	5.4	16.6	0.0
3[d]	20.1	9.2	0.14	1.2	2.1	5.4	--	9.74

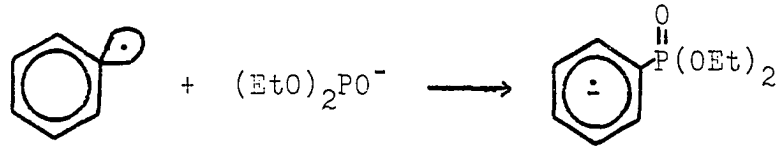
[a] Solvent = Me_2SO, counter-ion = K^+/18-crown-6.

[b] (PAT) = 0.028 M, $((EtO)_2PO^-)$ = 0.072 M and $(Me_2C{=}NO_2^-)$ = 0.072 M. Reaction carried out in the dark for 24 h. T = 45 C.

[c] (PhI) = 0.028 M, (PAT) = 0.028 M, $((EtO)_2PO^-)$ = 0.072 M, $(Me_2C{=}NO_2^-)$ = 0.072 M. Reaction carried out in the dark for 24 h. T = 45 C. All yields except PhI are based upon PAT.

[d] (PhI) = 0.028 M, $((EtO)_2PO^-)$ = 0.100 and $(Me_2C{=}NO_2^-)$ = 0.100 M. Reaction mixture irradiated at 350 nm for 12 h at 45 C.

phenyl radical with diethyl phosphite anion (Eq. 79) is less than or equal to 2.6×10^7 $M^{-1}s^{-1}$.



(79)

The results of the photo-stimulated $S_{RN}1$ reaction of iodobenzene with these anions paints an entirely different picture however. The yield of the phenylphosphonate product exceeds the sum of the yield of the cumyl products. The cumyl products indicate that phenyl radical was produced in this reaction, but it seems unlikely that the phenylphosphonate was produced from phenyl radical since diethyl phosphite anion reacts 45 times slower than nitronate anion.

The conclusion to draw from these observations is that although phenyl radical is produced, it is not the sole or primary intermediate in the reaction of diethyl phosphite with iodobenzene. The question to ask then is with what does diethyl phosphite anion react? A detailed discussion of this unknown intermediate will be withheld until the end of the results and discussion chapter.

To simplify the following discussion, the following abbreviations shall be adopted:

P = diethyl phenylphosphonate (61)

N = products arising from the reaction of

nitronate and phenyl radical: $PhCHMe_2$, $PhC(Me)=CH_2$, $PhC(Me)_2-C(Me)_2Ph$ and $PhC(Me)_2NO_2$

X = the unknown intermediate with which diethyl phosphite anion reacts

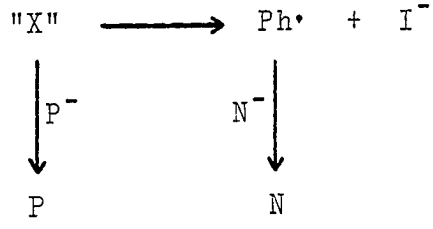
P^- = $(EtO)_2PO^-$

N^- = $Me_2C=NO_2^-$

Several questions regarding "X" will be addressed at this point:

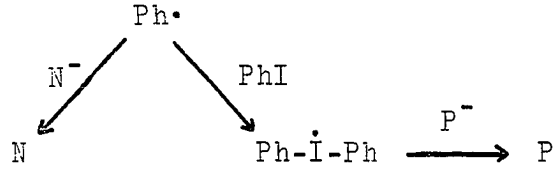
Is "X" a precursor to phenyl radical (Scheme XXXVII)?

Scheme XXXVII



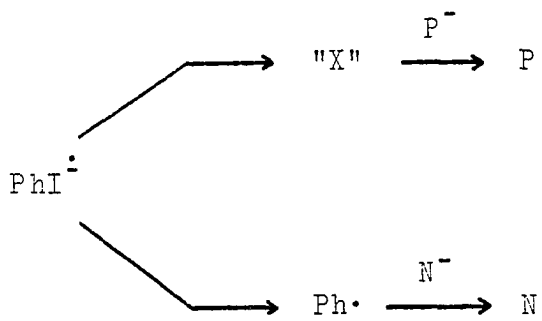
Is "X" a product of phenyl radical, perhaps a 9-I-2 intermediate (Scheme XXXVIII)?

Scheme XXXVIII



Are "X" and phenyl radical produced simultaneously (Scheme XXXIX)?

Scheme XXXIX



The scenarios of Schemes XXXVII - XXXIX represent the only reasonable possibilities that will be consistent with both the results reported in this section and data in the literature regarding the reaction of diethyl phosphite anion with iodobenzene. Fortunately, these schemes can be distinguished by varying the concentrations of diethyl phosphite and nitronate anions. Table 28 summarizes the effect of varying concentrations on the N/P ratio predicted for each scheme.

Table 29 summarizes the results obtained at various concentrations of the two anions. A plot of N/P versus the inverse of the diethyl phosphite anion concentration is presented in Figure 9. It is quite clear from these results that the N/P ratio is inversely related to (P^-) while independent of (N^-). Hence, the

Table 28. Effect of varying P^-, N^- concentrations on the N/P ratio predicted by Schemes XXVII - XXXIX

Scheme	Nature of X	$P^- \to \infty$, N^- constant	$N^- \to \infty$, P^- constant
XXVII	precursor to phenyl radical	$\frac{N}{P} \to 0$	$\frac{N}{P}$ constant
XXXVIII	product of phenyl radical	$\frac{N}{P}$ constant	$\frac{N}{P} \to \infty$
XXXIX	produced simultaneously with phenyl radical	$\frac{N}{P}$ constant	$\frac{N}{P}$ constant

intermediate "X" appears to be a precursor to phenyl radical.

Scheme XL is an elaboration of Scheme XXXVII. In addition to assigning rate constants to all the processes, the abstraction of hydrogen atoms, which will effect the N/P ratio, from various species in solution is taken into account. The following quantities need be defined in Scheme XL:

k_P = the absolute rate constant for attack of P^- on intermediate "X"

Table 29. Competition between diethyl phosphite and nitronate anions for intermediates in the $S_{RN}1$ reaction of PhI

$((EtO)_2PO^-)$, M[a]	$(Me_2C{=}NO_2^-)$, M	$\frac{1}{(P^-)}$, M^{-1}	$\frac{N}{P}$[b]	f[b]	$\frac{N}{P}$[c]
0.100	0.100	10.0	0.90	0.742	1.2
0.072	0.072	13.9	1.6	0.734	2.1
0.057	0.057	17.5	1.5	0.727	2.1
0.029	0.029	34.5	4.9	0.697	7.0
0.111	0.056	9.0	0.70	0.711	0.98
0.099	0.049	10.1	0.79	0.706	1.1
0.071	0.036	14.1	1.1	0.694	1.6
0.047	0.024	21.3	1.9	0.671	2.8

[a]Solvent = Me_2SO, counter-ion K^+/18-crown-6 and T = 45 C.

[b]See text for explanation.

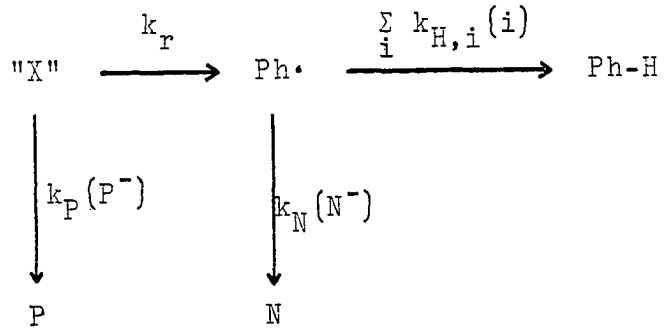
[c]Corrected (see Eq. 88 and text).

k_r = the unimolecular rate constant for the conversion of "X" into phenyl radical

k_N = the absolute rate constant for the coupling of nitronate with phenyl radical

$\sum_i k_{H,i}(i)$ = the combined rate of hydrogen abstraction from all relevant species in solution (solvent, 18-crown-6, N^-)

Scheme XL



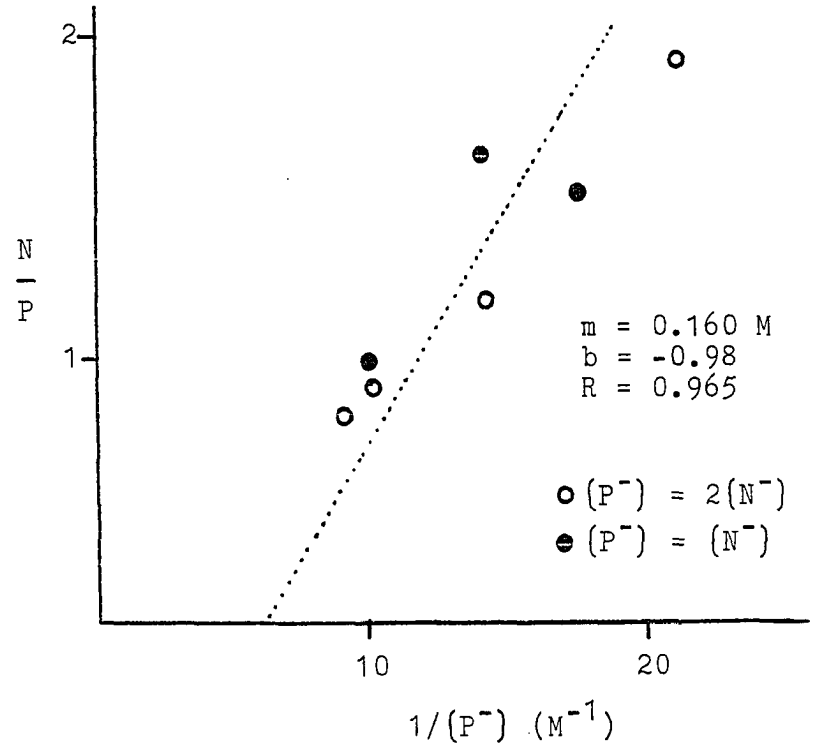


Figure 9. A plot of N/P versus $(P^-)^{-1}$

Using the steady state approximation for $Ph\cdot$, it is possible to derive an expression for the N/P ratio:

$$\frac{d(N)}{dt} = k_N(N^-)(Ph\cdot)_{ss} \tag{80}$$

$$\frac{d(P)}{dt} = k_P(P^-)(X) \tag{81}$$

$$k_r(X) = k_N(N^-)(Ph\cdot)_{ss} + \sum_i k_{H,i}(i)(Ph\cdot)_{ss} \tag{82}$$

$$(Ph\cdot)_{ss} = \frac{k_r(X)}{k_N(N^-) + \sum_i k_{H,i}(i)} \tag{83}$$

$$\frac{d(N)}{d(P)} = \frac{k_r k_N(N^-)}{k_P(P^-)\{k_N(N^-) + \sum_i k_{H,i}(i)\}} \tag{84}$$

$$= \frac{fk_r}{k_P(P^-)} \tag{85}$$

where:

$$f = \frac{k_N(N^-)}{k_N(N^-) + \sum_i k_{H,i}(i)} \tag{86}$$

In Eq. 85, "f" is the fraction of phenyl radical that is trapped by N^-. From Figure 9, if it is assumed that f = 1 (all phenyl is trapped by N^-) then the slope of this line is equal to k_r/k_P. Based upon this assumption, k_r/k_P = 0.16 M.

However, the assumption that f = 1 is not valid

since H-abstraction from N^- and 18-crown-6 is important. If in Scheme XL, the following assumptions are made (absolute rate constants are from Table 25):

$$(\text{18-crown-6}) = (N^-) + (P^-)$$

$$k(\text{18-crown-6}) = 3.8 \times 10^7\ M^{-1}s^{-1}$$

$$(Me_2SO) = 14\ M$$

$$k(Me_2SO) = 3.0 \times 10^5\ M^{-1}s^{-1}$$

$$k(Me_2C{=}NO_2^-)_{\text{H-abstr}} = 2.8 \times 10^8\ M^{-1}s^{-1}$$

$$k(Me_2C{=}NO_2^-)_{\text{add'n}} = 1.2 \times 10^9\ M^{-1}s^{-1}$$

then the values of f listed can be derived since:

$$f = \frac{k(Me_2C{=}NO_2^-)_{\text{add'n}}(N^-)}{\{k(Me_2C{=}NO_2^-)_{\text{add'n}} + k(Me_2C{=}NO_2^-)_{\text{H-abstr}}\}(N^-) + k(\text{18-crown-6})(\text{18-crown-6}) + k(Me_2SO)(Me_2SO)} \qquad (87)$$

and the values:

$$\left[\frac{N}{P}\right]_{\text{corrected}} = \frac{1}{f}\left[\frac{N}{P}\right]_{\text{observed}} \qquad (88)$$

When these "corrected" values are plotted versus the inverse of diethyl phosphite anion concentration (Figure 10), the correlation coefficent and slope of the least squares line do not change significantly. However, the intercept becomes much closer to zero, as required by Scheme XL.

Thus, it appears that the $S_{RN}1$ reaction of iodobenzene and diethyl phosphite anion proceeds through an intermediate "X" that is a precursor to phenyl

radical. The ratio k_r/k_p (Scheme XL) was determined to be 0.143 M. Furthermore, given the assumption that diethyl phosphite anion attacks this intermediate at a diffusion controlled rate ($k_p \sim 10^{10}$ $M^{-1}s^{-1}$) (41), then $k_r \sim 1.4 \times 10^9$ s^{-1}.

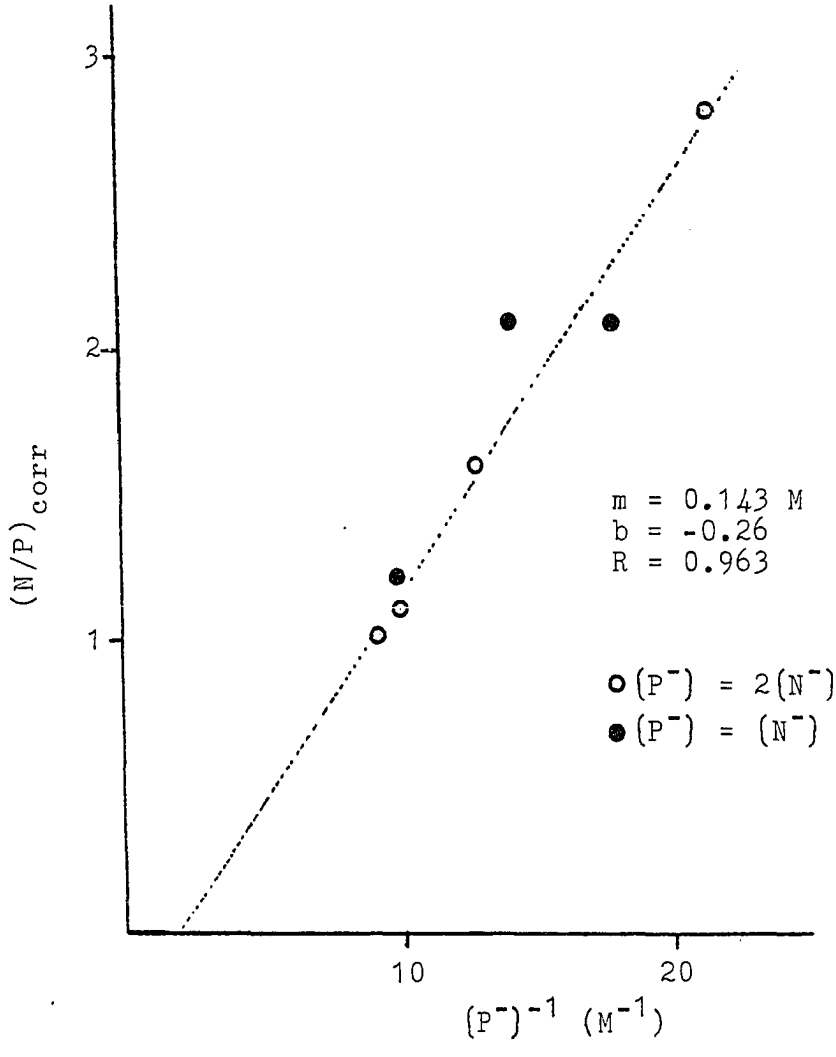


Figure 10. A plot of $(N/P)_{corr}$ versus $(P^-)^{-1}$

C. Results of Competition Experiments Between Diethyl Phosphite and Thiophenoxide Anions

Thiophenoxide anion was shown to react competitively with nitronate in the aromatic $S_{RN}1$ reaction. Hence, it was established that nitronate and thiophenoxide appear to trap the same intermediate, presumably a phenyl radical. It was also shown that the intermediate trapped by diethyl phosphite anion was not a phenyl radical, but some species "X" that is a precursor to the phenyl radical.

It thus appears reasonable to expect that competition experiments between $(EtO)_2PO^-$ and PhS^- should produce results similar to the competition experiments between $(EtO)_2PO^-$ and $Me_2C{=}NO_2^-$, since $(EtO)_2PO^-$ will trap "X" and PhS^- will trap phenyl radical. Table 30 presents results obtained in competition experiments pitting $(EtO)_2PO^-$ against PhS^- for phenyl radical (from PAT) and the intermediate(s) in the aromatic $S_{RN}1$ reaction.

The results appear consistent with the "dual-intermediate" hypothesis. It appears again as though $(EtO)_2PO^-$ traps "X" in the aromatic $S_{RN}1$ reaction, while PhS^- traps only the phenyl radical. Efforts to expand these results by competing PhS^- and $(EtO)_2PO^-$, at varying concentrations, for intermediates in the aromatic $S_{RN}1$ reaction were not fruitful primarily

Table 30. The photolysis of iodobenzene and thermolysis of PAT in the presence of diethyl phosphite and thiophenoxide anions in in Me_2SO at 45 C

Initial Concentrations (M):				Product Yield (%):		
PAT	PhI	PhS^-K^+	$(EtO)_2PO^-K^+$	Ph-H	$PhP(O)(OEt)_2$	PhSPh
-	0.056[a]	0.060	0.060	28.6	1.6	39.7
0.051[b]	-	0.060	0.060	27.3	0.0	29.8
-	0.056[a]	0.029	0.093	-[c]	16.2	37.5
0.056[b]	-	0.029	0.093	-[c]	0.0	28.1

[a]Irradiated at 350 nm for 5 h.

[b]PAT decomposed for 10 half-lives, approximately 24 -27 h.

[c]Not determined.

Table 31. Results of competition experiments pitting thiophenoxide against diethyl phosphite anion for intermediates in the aromatic $S_{RN}1$ reaction in Me_2SO at 45 C

Initial Concentrations (M)[a]:			Product Yields (%):	
$(EtO)_2PO^-$	PhS^-	PhI	$PhP(O)(OEt)_2$	PhSPh
0.15	0.15	0.006	24.4	3.7
0.11	0.11	0.006	19.4	2.3
0.07	0.07	0.006	6.3	1.9
0.04	0.04	0.006	6.8	0.8
0.121	0.249	0.112	0.0	57.0
0.121	0.095	0.112	1.8	40.5
0.121	0.0099	0.112	2.5	35.4

[a]In all cases the counter-ion is K^+/18-crown-6 and the solutions were irradiated at 350 nm for 1 - 3 h.

because of the irreproducibility of the results (Table 31).

The problems arise partly from the fact that one of the products (PhSPh) is unstable under the reaction conditions, being an $S_{RN}1$ substrate itself (20, 41). Thus in Me_2SO at 45 C, the reaction of Eq. 90 occurs at a comparable rate to that of Eq. 89 (23).

$$Ph\text{-}\overset{O}{\overset{\|}{P}}(OEt)_2^{\cdot-} + Ph\text{-}I \longrightarrow Ph\text{-}\overset{O}{\overset{\|}{P}}(OEt)_2 + Ph\text{-}I^{\cdot-} \qquad (89)$$

$$Ph\text{-}\overset{O}{\overset{\|}{P}}(OEt)_2^{\cdot-} + PhSPh \longrightarrow Ph\text{-}\overset{O}{\overset{\|}{P}}(OEt)_2 + PhSPh^{\cdot-} \qquad (90)$$

Another possible pathway for destruction of PhSPh is suggested in Eq. 91 where $(EtO)_2PO^-$ is the electron donor. The net result is that PhSPh is destroyed during the course of the reaction, making the results meaningless.

$$(EtO)_2PO^- + PhSPh \xrightarrow{h\nu} (EtO)_2PO\cdot + PhSPh^{\cdot-} \qquad (91)$$

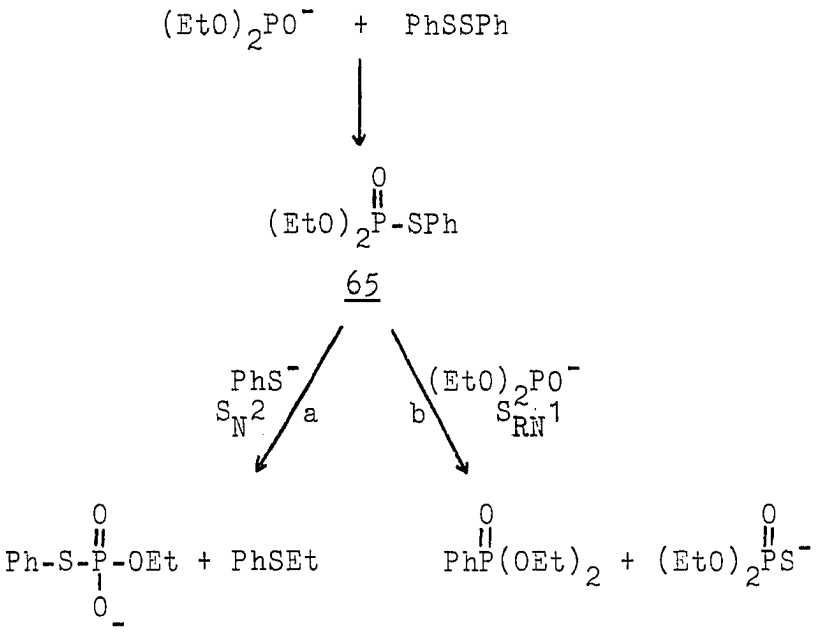
A way to circumvent these problems would be to add a large excess of PhI, to enhance the rate of Eq. 89, and run the reaction to only a low %-conversion. The problem with this approach is that $(EtO)_2PO^-$ and PhI form a charge transfer complex--hence there is no "free" $(EtO)_2PO^-$ around to react.

The possibility that PhS^- and $(EtO)_2PO^-$ react photochemically to generate products was tested. Solutions, 0.2 M of each anion in Me_2SO (K^+, 18-crown-6 counter-ion), were irradiated up to 18 hours at 350 nm without product formation, thereby negating this hypothesis. However, if in the same solution 0.068 M PhSSPh is present, products are observed as per Eq. 92. Scheme XLI provides a mechanism to account for these

observations.

$$PhS^- + (EtO)_2PO^- + PhSSPh \xrightarrow{h\nu} \underset{2.5\%}{Ph\text{-}\overset{O}{\overset{\|}{P}}(OEt)_2} + \underset{21.2\%}{PhSEt} \quad (92)$$

Scheme XLI



In Scheme XLI, nucleophilic attack of $(EtO)_2PO^-$ on PhSSPh produces intermediate compound (65). This species possesses a good leaving group for an S_N2 reaction (path a) or an $S_{RN}1$ reaction (path b) (20). The significance of this finding is that PhSSPh is a by-product of $S_{RN}1$ reactions involving PhS^-, presumably a product of photo-initiation (Eq. 93) (111).

Thus, the possible formation of PhSSPh in the

$$PhS^- + ArX \xrightarrow{h\nu} PhS\cdot + ArX^{\cdot-} \qquad (93)$$
$$\downarrow$$
$$PhSSPh$$

$PhS^-/(EtO)_2PO^-$ competition provides a pathway for destruction of $(EtO)_2PO^-$, generating an intermediate compound (65) which apparently undergoes $S_{RN}1$ chemistry producing $PhP(O)(OEt)_2$. Additionally, thiyl radical produced in Eq. 93 may react with $(EtO)_2PO^-$ directly (Eq. 94) in analogy to Eq. 95 where PhS^- and PhS· react with a reported rate constant of 4.9×10^9 $M^{-1}s^{-1}$ (112).

$$PhS\cdot + (EtO)_2PO^- \longrightarrow PhS\overset{O}{\overset{\|}{P}}(OEt)_2^{\cdot-} \qquad (94)$$

$$PhS\cdot + PhS^- \longrightarrow PhSSPh^{\cdot-} \qquad (95)$$

Thus, competition experiments involving $(EtO)_2PO^-$ and PhS^- serve more to cloud the issue with additional complications than to clarify it. When identical solutions are reacted with PAT and PhI, only the latter is found to produce products with diethyl phosphite anion. This result does seem to comfirm the hypothesis that while PhS^- reacts with phenyl radical, $(EtO)_2PO^-$ does not.

D. Summary

From the results presented in this section, it has been argued that the aromatic $S_{RN}1$ reaction involves a second intermediate "X" and that this intermediate decomposes to phenyl radical with a first order rate constant of approximately 1.4×10^9 s^{-1}. Diethyl phosphite anion appears to trap this intermediate, while having little or no reactivity towards phenyl radical. Thiophenoxide and nitronate ions on the other hand appear to trap only the phenyl radical, having little or no measurable reactivity towards "X".

Invoking such an intermediate as "X" may provide a reasonable explanation for some literature results. For competition experiments conducted in liquid ammonia, it was reported that the reactivity of most aromatic $S_{RN}1$ anions ($Me_3CC(O^-)=CH_2$, $(EtO)_2PO^-$, etc....) fall within a factor of 10, attacking the intermediate at a diffusion controlled rate (41). The exception was PhS^-, which was substantially slower (41).

It is reasonably expected that k_r will be lower in magnitude at -40 C (NH_3) than at 45 C, hence the apparent low reactivity of PhS^- may be due to a lower steady state concentration of phenyl radical at this temperature.

IV. APPLICATION OF INTRAMOLECULAR FREE RADICAL REARRANGEMENTS TO THE AROMATIC $S_{RN}1$ REACTION

This section will deal with the application of intramolecular radical rearrangements to the aromatic $S_{RN}1$ reaction. The concept can be developed as follows. Suppose a radical ($R_1\cdot$) is known to rearrange intramolecularly to a new radical ($R_2\cdot$). This rearrangement can then be considered characteristic of the radical ($R_1\cdot$) and utilized to diagnose its intermediacy in chemical reactions. Thus in Eq. 96, the formation of rearranged product (R_2-H) implies the intermediacy of $R_1\cdot$ in the tri-n-butyltin hydride reduction of R_1-Cl.

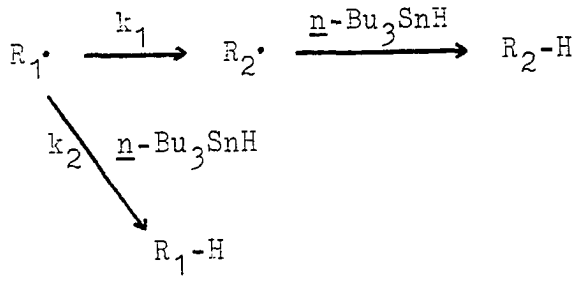
$$R_1\text{-Cl} \xrightarrow{n\text{-}Bu_3SnH} R_2\text{-H} \qquad (96)$$

Furthermore, if one is so fortunate as to know the absolute rate constant for the rearrangement, k_1 in Scheme XLII, then the absolute rate constants for bimolecular reactions of $R_1\cdot$ can be determined (94).

Thus according to Scheme XLII, the ratio of products R_2-H/R_1-H will depend on k_1, k_2 and the concentration of n-Bu_3Sn-H. Knowledge of k_1 and n-Bu_3Sn-H concentration allows k_2 to be determined by a simple product analysis.

Such radical rearrangements occurring with known

Scheme XLII

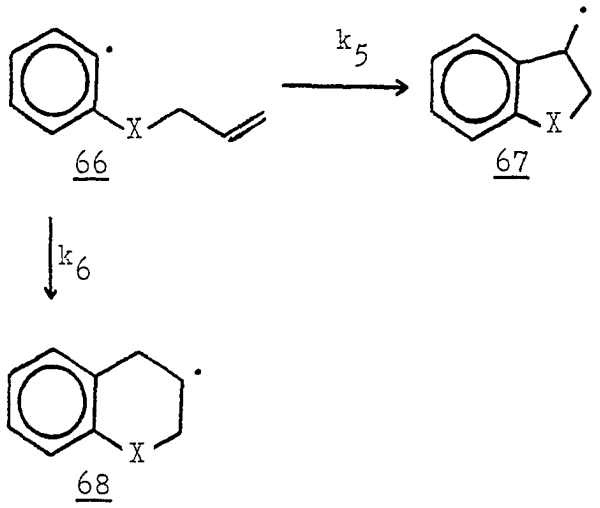


rate constants are termed "free radical clocks" and this topic has been recently reviewed (94). The classic Δ^5-hexenyl rearrangement has been applied to the aliphatic $S_{RN}1$ reaction both to diagnose the intermediacy of a free alkyl radical (17) and to determine the absolute rate constant for attack of nitronate anion on a primary alkyl radical (82).

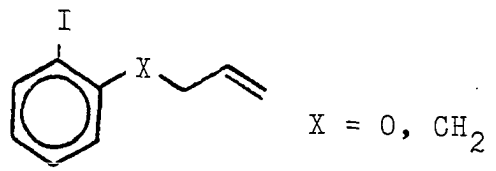
The cyclization of aryl radicals such as (66) according to Scheme XLIII has been reported and characterized for X = CH_2, NMe and O (95 - 98).

Cyclization of radical (66) is in principle capable of forming either five- or six-membered ring radicals (67) and (68) respectively. Cyclization to the five-membered ring predominates, the ratio k_5/k_6 reportedly being greater than 100 (95 - 97). The rate constant for rearrangement, k_5 in Scheme XLIII has been estimated to be approximately 10^6 s^{-1} for X = CH_2 (95, 97). For X = O, k_5 is apparently > 10^8 s^{-1} (95, 97).

Scheme XLIII



Clearly, substrates such as (69) afford the opportunity to test for the intermediacy of aryl radical in the aromatic $S_{RN}1$ reaction.



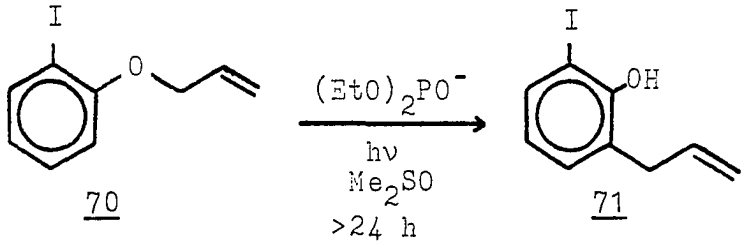
69

A. Reactions of o-Iodophenyl Allyl Ether with Various Anions

1. Diethyl phosphite anion

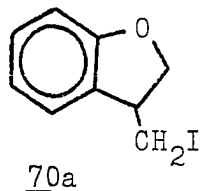
Irradiation of 0.1 M o-iodophenyl allyl ether (70) in the presence of 0.2 M $(EtO)_2PO^-K^+$ for three hours (350 nm) resulted in no reaction and greater than 95% recovery of starting material. Upon extended

irradiation (>24 h), (71) was produced, presumably arising from a Claisen rearrangement of (70) (Eq. 97). No products of $S_{RN}1$ chemistry between (70) and $(EtO)_2PO^-$ could be detected.



70 71 (97)

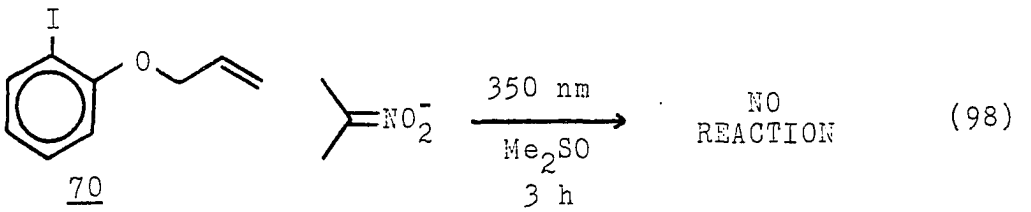
A plausible explanation for the lack of reaction, in light of the fact that the analogous reaction with PhI is quite rapid, might be that the normal $S_{RN}1$ chain reaction is in effect terminated by cyclization of the intermediate aryl radical, since $(EtO)_2PO^-$ is a poor trap for alkyl radicals (Scheme XLIV). The observations also argue against a free radical chain cyclization of (70) to (70a).



70a

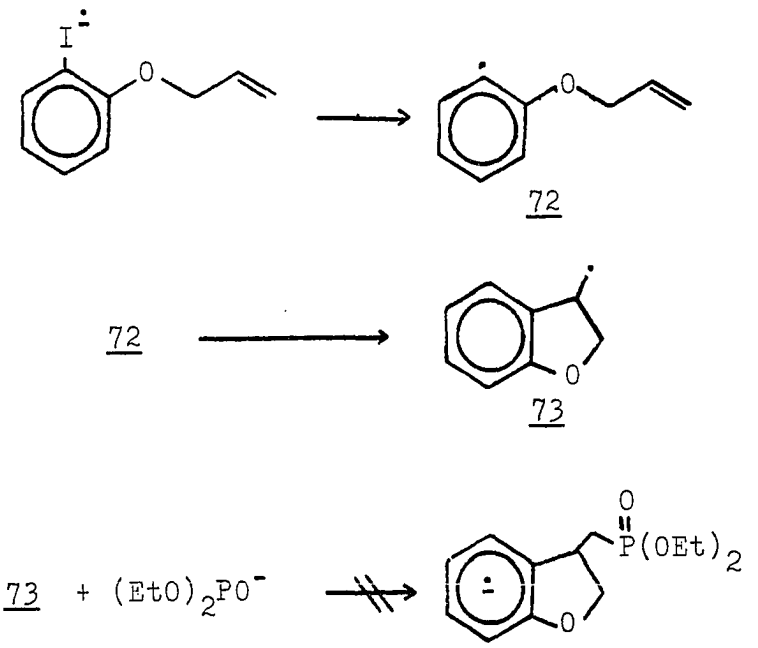
2. Nitronate anion

Nitronate anion was also found to be ineffective in persuading (70) to participate in $S_{RN}1$ chemistry (Eq. 98).



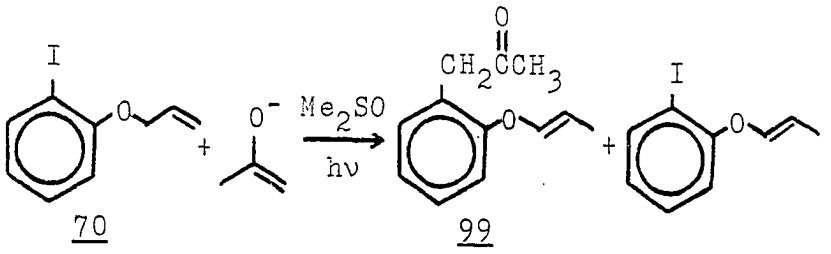
(98)

Scheme XLIV



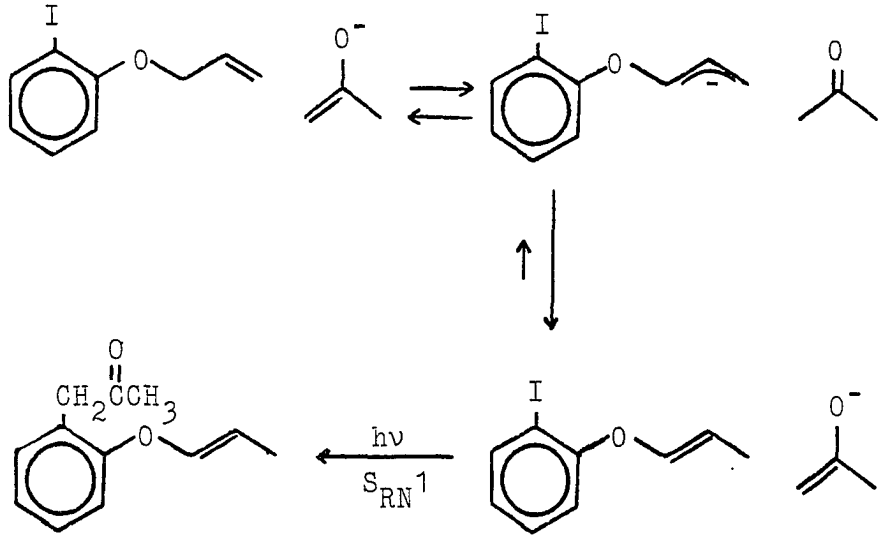
3. Acetone enolate

Irradiation of (70) in the presence of acetone enolate did result in an apparent $S_{RN}1$ reaction (Eq. 99), but apparently the $S_{RN}1$ reaction was preceded by a base catalyzed isomerization of starting material (Scheme XLV).



(99)

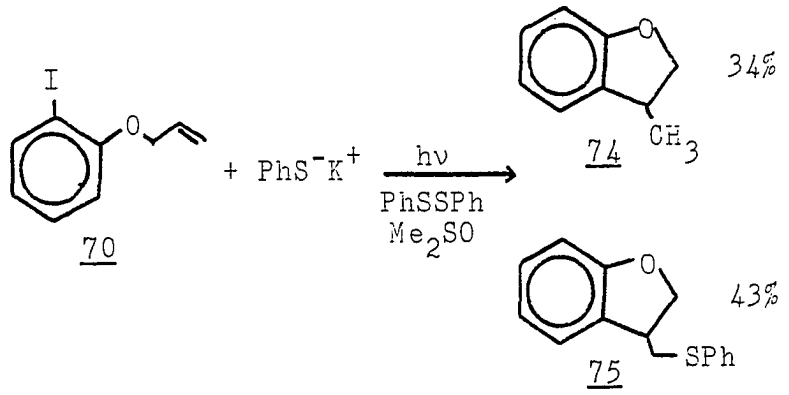
Scheme XLV



4. Thiophenoxide ion

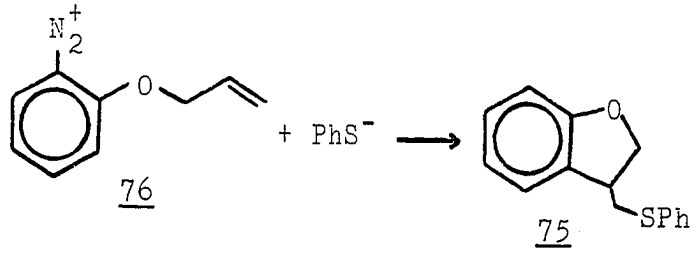
Irradiation of (70) in the presence of 0.21 M PhS^-K^+ (contaminated with PhSSPh, which was later shown to play a vital role in the reaction) resulted in an "apparent" $S_{RN}1$ reaction (Eq. 100). The formation of dihydrobenzofurans (74) and (75) clearly established the intermediacy of aryl radicals in this reaction.

A similar result has been reported in the literature.



(100)

Thus, reduction of diazonium salt (76) in the presence of PhS^- (Eq. 101) was reported to produce (75) (96).



(101)

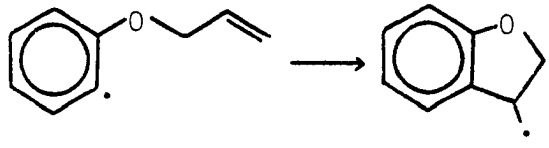
The proposed chain mechanism is outlined in Scheme XLVI (96). This mechanism requires that k_1 be favorable and $k_{et}(A) > k_{-1}$ (Eq. 102). While it may be tempting to propose such a mechanism for the reaction of (70) with PhS^-, it is probably unreasonable because PhS^- is a poor trap of alkyl radicals (k_1 is unfavorable). Additionally, the reverse reaction appears quite favorable, as evidenced by the fragmentation observed in the $S_{RN}1$ reaction of ethanethiolate (Scheme XLVII) (113).

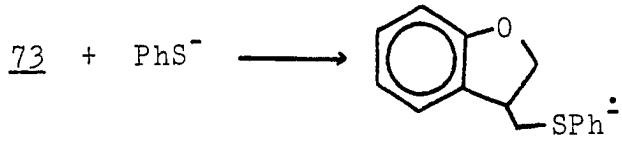
A potential source of (75) is by trapping of the intermediate alkyl radical (73) by PhSSPh (107),

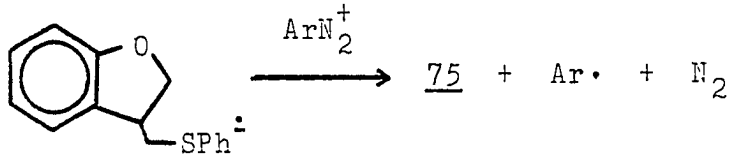
Scheme XLVI

INITIATION: $ArN_2^+ + e^- \longrightarrow Ar\cdot + N_2$

PROPAGATION:





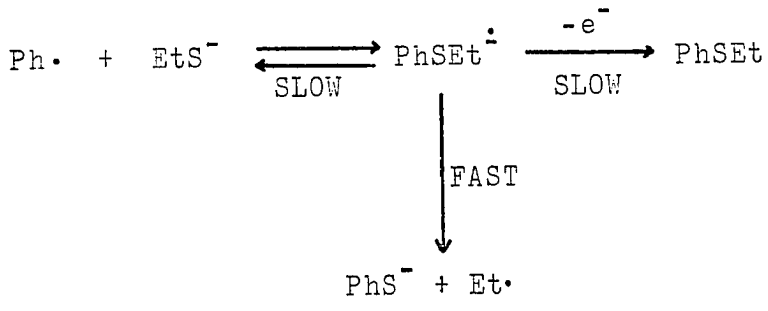


$$ArS^- + R\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar\text{-}S\text{-}R^{\cdot-} \xrightarrow[A]{k_{et}} Ar\text{-}S\text{-}R \qquad (102)$$

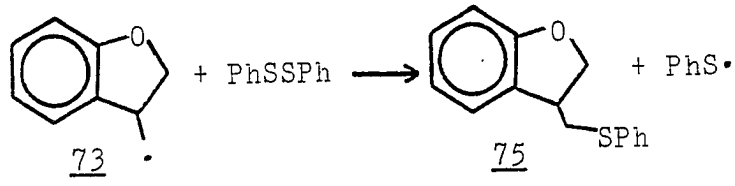
R = alkyl

A = electron acceptor (ArI or ArN_2^+)

Scheme XLVII

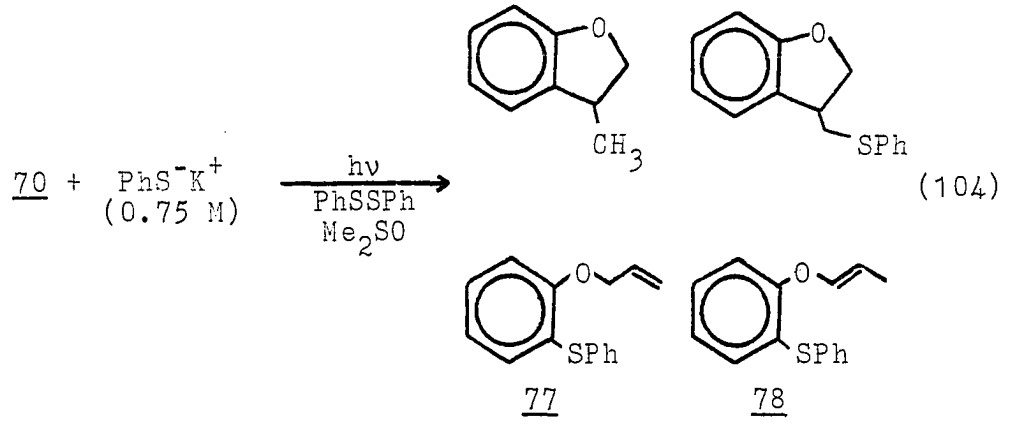


a common contaminant present in PhSH (Eq. 103).



73 75 (103)

It was hoped that it might be possible to intercept the intermediate aryl radical before cyclization by running the reaction of (70) in a more concentrated PhS^- solution. The results indicate that under these highly basic conditions, product indicative of trapping before cyclization (77) may be formed, but is accompanied by products of base catalyzed isomerization (Eq. 104).

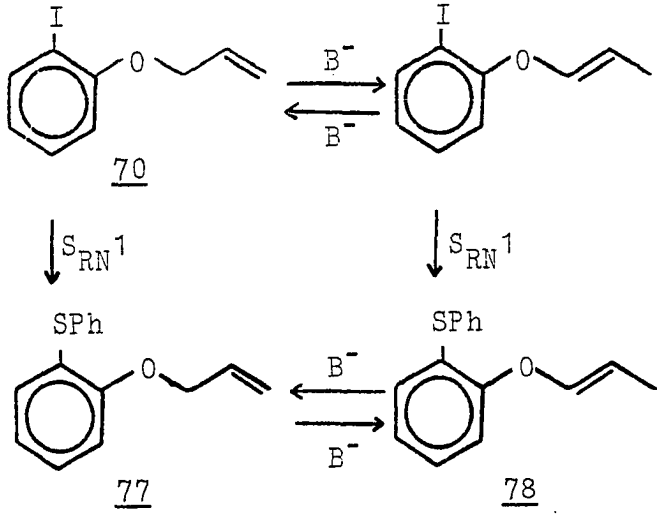


(104)

It is unclear how much trapping before cyclization actually occurred since (78) can be produced from two sources (Scheme XLVIII).

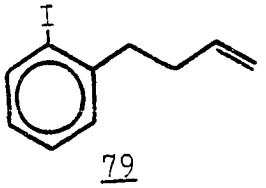
In conclusion, although the results from reactions of o-iodophenyl allyl ether with PhS^- point to the intermediacy of free aryl radical, two problems persist. The exact nature of the reaction mechanism has not been established, and the rearrangement appears to be sufficiently rapid so as to preclude trapping before cyclization. Attempts to overcome this obstacle by going to high PhS^- concentrations are thwarted by

Scheme XLVIII



a competing base-catalyzed isomerization of the double bond.

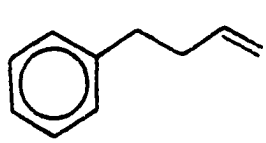
B. Reaction of 4-o-Iodophenylbut-1-ene (79) with Thiophenoxide--Initial Results



79

A detailed study of the mechanism of the reaction of 4-o-iodophenylbut-1-ene (79) with PhS^- was undertaken. Compound (79) was considered vastly superior to (70) as a substrate because the butene side chain should be less susceptible to base catalyzed isomerization, thereby allowing more concentrated solutions of anions

to be employed. Additionally, the radical generated from (79) cyclizes at a rate approximately 1/100th that of the radical generated from (70) (95, 97). This slower rate of cyclization should enable trapping of the intermediate aryl radical before cyclization. Table 32 summarizes the products and yields resulting from the irradiation of (79) in solutions containing PhS^-.



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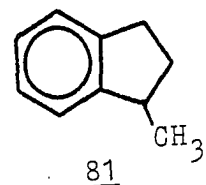

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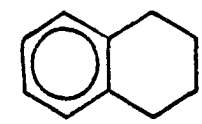

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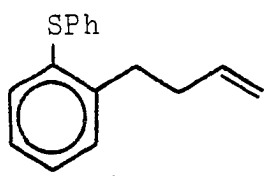

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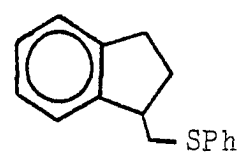

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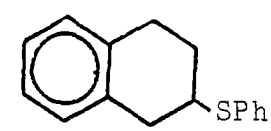

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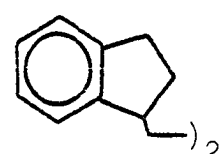
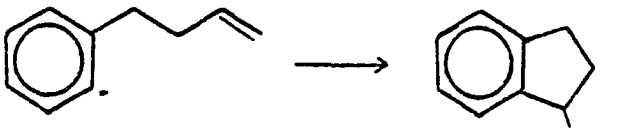


86

Several features of Table 32 are noteworthy. The most striking is the effect of added PhSSPh. In the absence of PhSSPh, the mass balance is poor (48.2%) compared to 77.5% in the presence of PhSSPh. Apparently,

the presence of PhSSPh facilitates the trapping of intermediate alkyl radical (88) as product (84), at the expense of the formation of dimer (86). As expected,



87 88

the lower rate of cyclization of the aryl radical (87) permits substantial bimolecular trapping before cyclization as evidenced by product (80) arising from H-abstraction, and (83) arising from coupling to $PhS^{\cdot}$.

An unexpected feature of these results is the large amount of six-membered ring compounds that are isolated. It was reported that the ratio of rate constants for cyclization to the five- and six-membered ring radicals, k_5/k_6, was 100 (95, 97). These results indicate a lower degree of selectivity, k_5/k_6 being in the range 8 - 11.

At this point, several questions need be answered. The observed k_5/k_6 ratio is vastly different from that reported in the literature. Is the literature value correct? If so, then the variation in k_5/k_6 indicates a source of cyclized product other than aryl radical, since k_5/k_6 should be constant for the same intermediate. Can the rate constant for cyclization

Table 32. Products and yields resulting from the irradiation of 4-o-iodophenylbut-1-ene in the presence of thiophenoxide at 45 C in Me_2SO

Initial concentrations[a] (M)		Product Yields (%)						
PhS^-K^+	PhSSPh	80	81	82	83	84	85	86
0.15	0.000	1.2	19.3	1.6	7.6	10.8	1.0	6.7
0.13	0.006	0.21	14.8	4.5	10.2	41.7	3.2	2.9

[a]Irradiated at 350 nm for 70 min.

of the aryl radical to the five-membered ring (k_5) be determined? If so, product analysis would permit the absolute rate constant for attack of PhS^- on aryl radical to be determined.

C. Characterization of the Kinetic Parameters for the Cyclization of o-Butenylphenyl Radical (87)

1. The ratio of rate constants for five- and six-membered ring formation (k_5/k_6)

The mechanism of the n-Bu_3SnH reduction of aryl halides is depicted in Scheme XLIX (114). The reaction is a free radical chain mechanism and can be initiated

Scheme XLIX

PROPAGATION:

$$ArX + \cdot SnR_3 \longrightarrow Ar\cdot + X\text{-}SnR_3$$

$$Ar\cdot + H\text{-}SnR_3 \longrightarrow Ar\text{-}H + \cdot SnR_3$$

OVERALL:

$$Ar\text{-}X + H\text{-}SnR_3 \longrightarrow Ar\text{-}H + X\text{-}SnR_3$$

either thermally (with a free radical initiator) or photochemically, according to Scheme L (114).

Scheme L

$$PAT \xrightarrow{\Delta} Ph\cdot + N_2 + \cdot CPh_3$$

$$Ph\cdot \xrightarrow{R_3SnH} Ph\text{-}H + R_3Sn\cdot$$

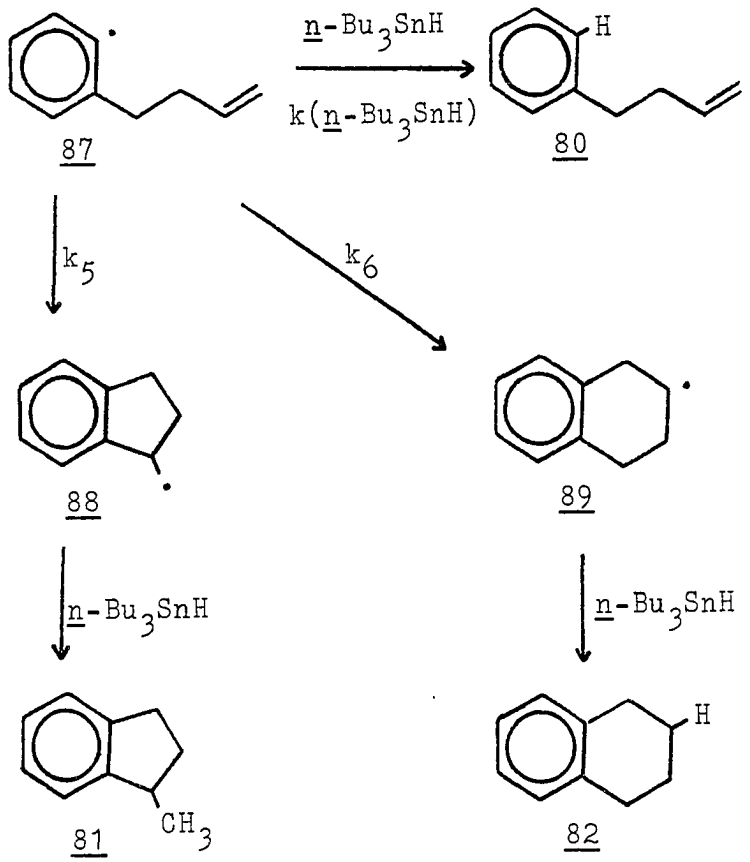
$$R_3Sn\text{-}H \xrightarrow{h\nu} R_3Sn\cdot + H\cdot$$

The complete mechanism for the formation of all products in the n-Bu_3SnH reduction of (79) is outlined in Scheme LI (95, 97). The ratio k_5/k_6 can be related to the product ratio (81)/(82) as follows:

$$\frac{d(81)}{d(82)} = \frac{k_5(87)}{k_6(87)} = \frac{k_5}{k_6} \qquad (105)$$

Integrating from $t = 0 \rightarrow t = \infty$, Eq. 106 is obtained:

Scheme LI



$$\frac{k_5}{k_6} = \frac{(\underline{81})}{(\underline{82})} \qquad (106)$$

Similarly, an expression relating $k(\underline{n}\text{-}Bu_3SnH)/k_5$ to the ratio of products $(\underline{80})/(\underline{81})$ can be derived:

$$\frac{d(\underline{80})}{d(\underline{81})} = \frac{k(\underline{n}\text{-}Bu_3SnH)(\underline{n}\text{-}Bu_3SnH)(\underline{87})}{k_5(\underline{87})} \qquad (107)$$

Assuming $(\underline{n}\text{-}Bu_3SnH)_i > (ArI)_i$ and again integrating from $t = 0 \rightarrow t = \infty$, Eq. 108 is obtained:

$$\frac{(80)}{(81)\,(n\text{-}Bu_3SnH)} = \frac{k(n\text{-}Bu_3SnH)}{k_5} \qquad (108)$$

Table 33 compiles results obtained for the n-Bu_3SnH reduction of (79) under a variety of conditions.

Although the ratio k_5/k_6 was not found to be quite as high as in the literature (> 100) (95 - 97), it nonetheless was higher than the reaction of (79) with PhS^- (k_5/k_6 < 10). The results also indicate that the ratio observed in the reaction with PhS^- is not the result of k_5/k_6 being unusually low in Me_2SO, nor is it some artifact of photochemistry.

The observed ratio $k(n\text{-}Bu_3SnH)/k_5$ (1.0 - 1.6) was found to be lower than the reported literature value of 1.9 (95, 97), the variation undoubtedly due to the fact that the reactions reported here were performed at ambient pressure at 45 C, while the literature values were obtained under sealed tube conditions at 130 C (95, 97).

The key point to be made however is that the low ratio k_5/k_6 observed in the reaction of PhS^- with (79) is not indicative of aryl radical (87) produced in the n-Bu_3SnH reduction, clearly indicating the existence of a second species capable of undergoing the cyclization reaction.

Table 33. Results of the tri-n-butyltin hydride reduction of 4-o-iodophenylbut-1-ene under a variety of conditions

Solvent	Method of initiation[a, b]	Product Yield (%) 80	81	82	k_5/k_6	$\frac{k(n\text{-}Bu_3SnH)}{k_5}$
PhH[c]	PAT, Δ, 1 h	35.5	68.3	2.3	29.7	1.0
Me_2SO[d]	PAT, Δ, 1 h	62.6	20.4	~0.5	40.8	-
PhH[c]	350 nm, 3 h	33.1	66.0	2.2	30.0	0.96
PhH[c]	350 nm, 3 h	41.1	50.7	1.7	29.8	1.6
Me_2SO[d]	350 nm, 3 h	43.2	21.7	0.61	35.6	-

[a] Temperature = 45 C.

[b] (ArI) = 0.08 M

[c] (n-Bu_3SnH) = 0.52 M

[d] (n-Bu_3SnH) = excess (n-Bu_3SnH not completely soluble in Me_2SO).

2. The absolute rate constant for five-membered ring formation (k_5)

If the absolute rate constant for abstraction of hydrogen from n-Bu_3SnH by phenyl radical were known, then given the value $k(n\text{-}Bu_3SnH)/k_5$ reported in the previous section, k_5 could be calculated assuming $k(n\text{-}Bu_3SnH)$ for (87) is the same as for phenyl radical. Unfortunately, this information is not available.

Absolute rate constants for H-abstraction by phenyl radical from a large number of substrates have been reported (99 - 101). The absence of n-Bu_3SnH from this list is because many of these results are derived from competition experiments with CCl_4, whose absolute rate constant for Cl-abstraction by phenyl radical is known. CCl_4 can not however be competed with n-Bu_3SnH, as the net result would be the reduction of CCl_4 by a free radical chain process (Eq. 109) (114).

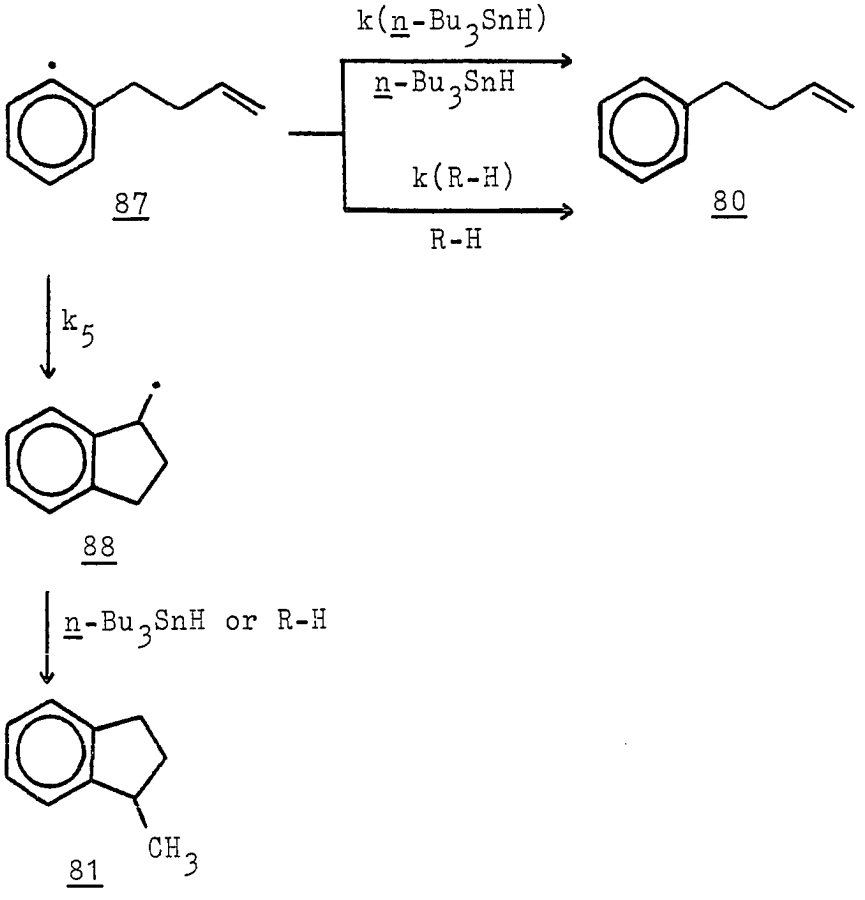
$$CCl_4 + n\text{-}Bu_3SnH \xrightarrow[\Delta]{PAT} n\text{-}Bu_3SnCl + CHCl_3 + CH_2Cl_2 + CH_3Cl + CH_4 \qquad (109)$$

The alternative to competition studies is direct observation. Indeed, absolute rate constants for the reactions of phenyl radical with a large variety of substrates have been determined by flash photolysis (105). Regretfully, n-Bu_3SnH was not one of the

substrates. This section summarizes attempts to determine k_5 by an "indirect" approach.

In the n-Bu_3SnH reduction of (79), suppose another H-atom donor (R-H) were present (Scheme LII). According

Scheme LII



to Scheme LII, the following equations can be derived:

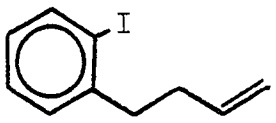
$$\frac{d(\underline{80})}{d(\underline{81})} = \frac{k(\underline{n}\text{-}Bu_3SnH)(\underline{n}\text{-}Bu_3SnH) + k(R\text{-}H)(R\text{-}H)}{k_5} \qquad (110)$$

Assuming $(\underline{n}\text{-}Bu_3SnH)_i$, $(R\text{-}H)_i > (ArI)_i$:

$$\frac{(\underline{80})}{(\underline{81})} = \frac{k(\underline{n}\text{-}Bu_3SnH)}{k_5}(\underline{n}\text{-}Bu_3SnH) + \frac{k(R\text{-}H)}{k_5}(R\text{-}H) \qquad (111)$$

Thus under conditions where $\underline{n}$-Bu_3SnH concentration is held constant, a plot of the product ratio $(\underline{80})/(\underline{81})$ versus R-H concentration yields a straight line of slope $k(R\text{-}H)/k_5$. Now the trick: If R-H is judiciously chosen such that its absolute rate constant for reaction with phenyl radical is known, k_5 can be estimated. Such was exactly the approach taken for R-H = Me_2SO, $CH_3C_6H_5$, and $CH_2(C_6H_5)_2$, whose absolute rate constants for reaction with phenyl radical are known.

Table 34 summarizes the results obtained for the reaction of Eq. 112 as a function of Me_2SO concentration.



$$+ \underline{n}\text{-}Bu_3SnH + Me_2SO \xrightarrow[Ph\text{-}H]{h\nu} \qquad (112)$$

(0.006 M) (0.562 M)

In Figure 11, the ratio $(\underline{80})/(\underline{81})$ is plotted against (Me_2SO), and data obtained from a linear least squares analysis of the data given. According to Eq. 111, the slope of this line equals $k(Me_2SO)/k_5$ and intercept $k(\underline{n}\text{-}Bu_3SnH)\ \underline{n}\text{-}Bu_3SnH\ /k_5$. The quantities $k(Me_2SO)/k_5$ and $k(\underline{n}\text{-}Bu_3SnH)/k_5$ appear in Eqs. 113 and 114 respectively. The estimate of k_5 based upon these results

Table 34. Tri-n-butyltin hydride reduction of 4-o-iodophenylbut-1-ene in the presence of varying concentrations of Me_2SO in benzene at 45 C

	Product Ratio				
(Me_2SO), M[a]	80	81	82	80/81	k_5/k_6
0.000	38.7	59.5	1.9	0.650	31
0.986	39.5	58.6	1.9	0.674	31
1.971	39.9	58.1	2.0	0.687	29
2.816	40.6	57.5	1.9	0.706	30
3.942	42.5	55.6	1.1	0.764	50

[a] $(n\text{-}Bu_3SnH)$ = 0.562 M and (ArI) = 0.066 M.

appears in Table 37.

$$\frac{k(Me_2SO)}{k_5} = 0.027\ M^{-1} \qquad (113)$$

$$\frac{k(n\text{-}Bu_3SnH)}{k_5} = 1.15\ M^{-1} \qquad (114)$$

The results obtained for the $n\text{-}Bu_3SnH$ reduction of (79) in the presence of varying concentrations of toluene (Eq. 115) are presented in Table 35. As before, the ratio (80)/(81) was plotted versus $(PhCH_3)$ (Figure 12), and the results of a linear least squares

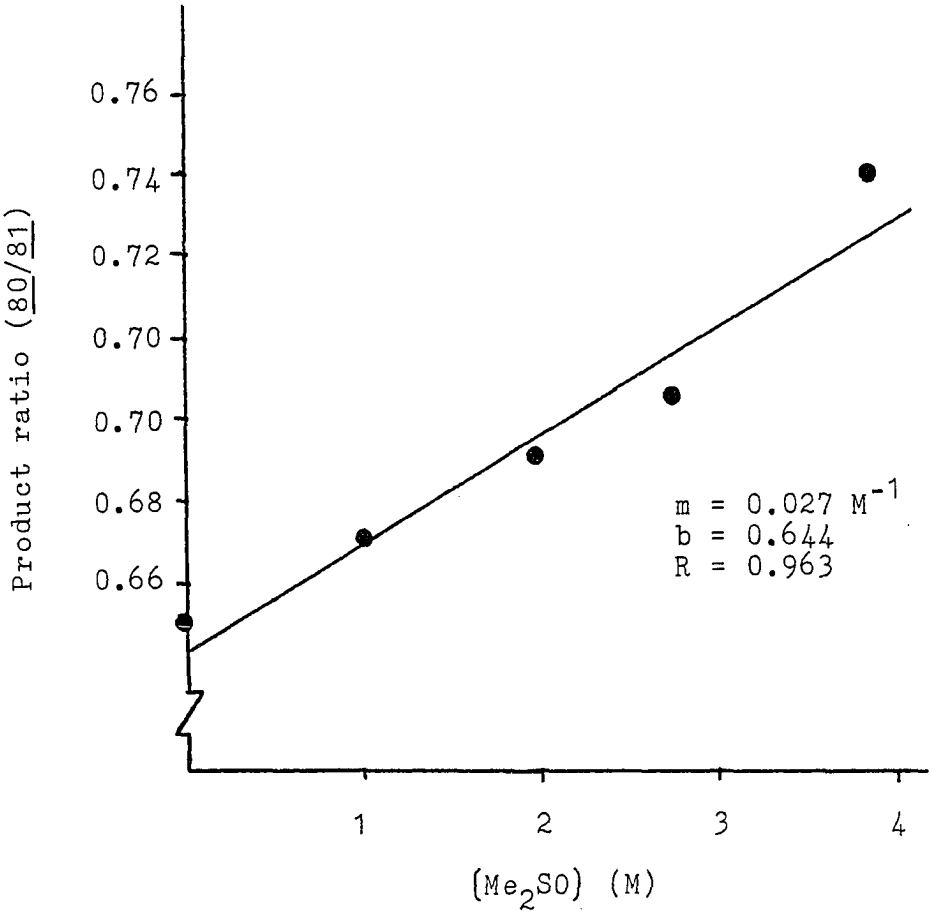


Figure 11. Plot of the product ratio (80/81) versus dimethyl sulfoxide concentration in the tri-n-butyltin hydride reduction of 4-o-iodophenylbut-1-ene (79)

analysis of the data given. Based upon this data, $k(PhCH_3)/k_5$ and $k(n\text{-}Bu_3SnH)/k_5$ were determined and are expressed by Eqs. 116 and 117. The estimation of k_5 from this data appears in Table 37.

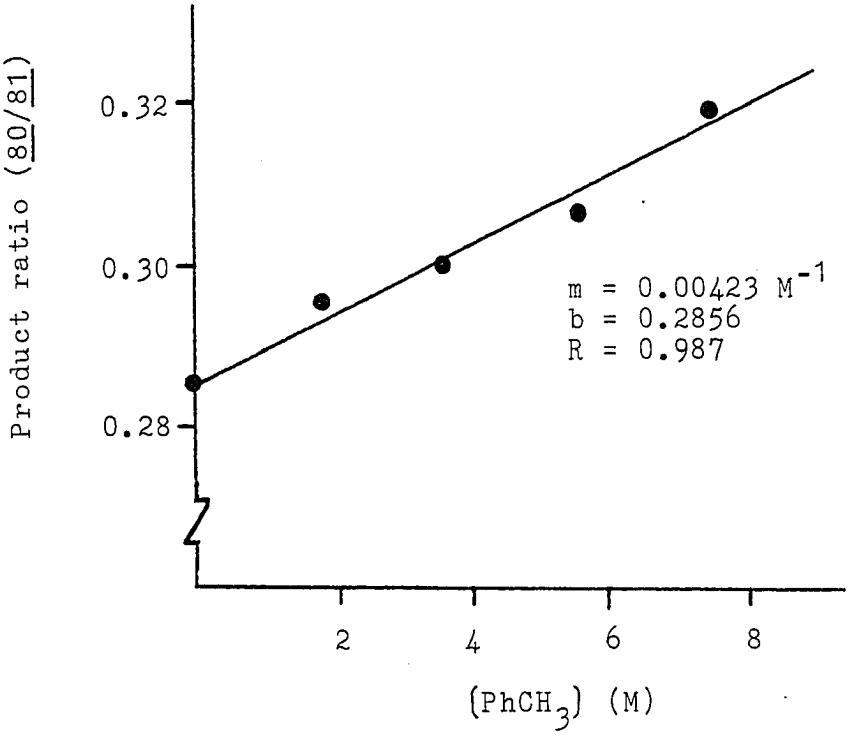
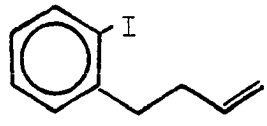


Figure 12. Plot of the product ratio (80/81) versus toluene concentration in the tri-n-butyltin hydride reduction of 4-o-iodophenylbut-1-ene



(0.0228 M) + n-Bu$_3$SnH (0.255 M) + PhCH$_3$ $\xrightarrow[\text{Ph-H}]{h\nu}$ (115)

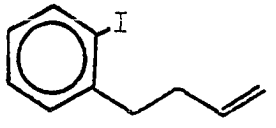
$$\frac{k(PhCH_3)}{k_5} = 0.00423\ M^{-1} \qquad (116)$$

$$\frac{k(n\text{-}Bu_3SnH)}{k_5} = 1.12\ M^{-1} \qquad (117)$$

Table 35. The product ratio 80/81 obtained in the tri-n-butyltin hydride reduction of 4-o-iodophenylbut-1-ene at varying toluene concentrations at 45 C

Toluene concentration (M)[a]	Product ratio 80/81
0.000	0.2857
1.856	0.2952
3.712	0.2998
5.568	0.3067
7.424	0.3192

[a]Solvent = benzene, $(n\text{-}Bu_3SnH)$ = 0.2547 M and (ArI) = 0.0228 M.



$$+ n\text{-}Bu_3SnH + Ph_2CH_2 \xrightarrow[Ph\text{-}H]{h\nu} \qquad (118)$$

(0.0228 M) (0.255 M)

Finally, the data obtained for the reaction of Eq. 118 appear in Table 36 and the product ratio (80)/(81) as a function of $(CH_2(C_6H_5)_2)$ plotted in Figure 13. From the linear least squares analysis of the data, $k(Ph_2CH_2)/k_5$ and $k(n\text{-}Bu_3SnH)/k_5$ can be determined and appear in Eqs. 119 and 120. The estimate

Table 36. The product ratio 80/81 obtained in the tri-n-butyltin hydride reduction of 4-o-iodophenylbut-1-ene at varying diphenylmethane concentrations at 45 C in benzene

Ph_2CH_2 concentration (M)[a]	Product ratio 80/81
0.00	0.2892
1.67	0.2968
3.33	0.3369

[a] (n-Bu_3SnH) = 0.2547 M and (ArI) = 0.0228 M.

of k_5 based upon these results appears in Table 37.

$$\frac{k(Ph_2CH_2)}{k_5} = 0.0148\ M^{-1} \qquad (119)$$

$$\frac{k(n\text{-}Bu_3SnH)}{k_5} = 1.12\ M^{-1} \qquad (120)$$

The key assumption in all these experiments is that phenyl radical and (87) have nearly the same absolute rate constant for H-abstraction from R-H. For phenyl, the reactivity order is: Ph_2CH_2 (36) > $PhCH_3$ (5.7) > Me_2SO (1) (99). However, based upon the results obtained here for aryl radical (87), the

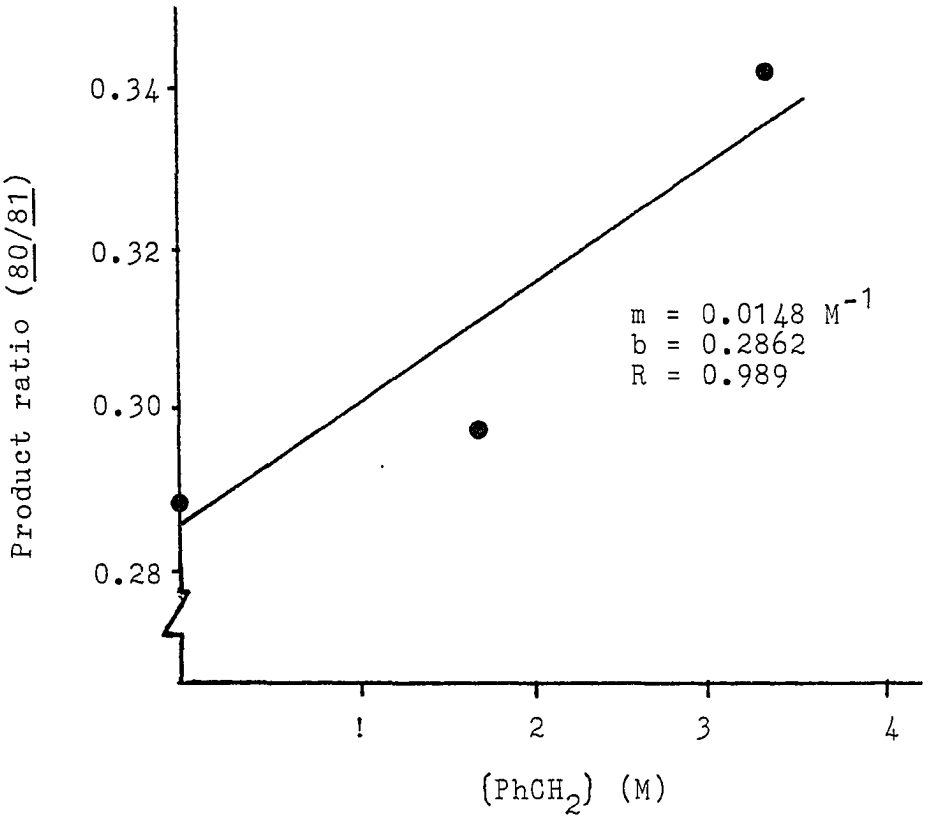


Figure 13. Plot of the product ratio (80/81) versus diphenyl methane concentration in the tri-n-butyltin hydride reduction of 4-o-iodophenylbut-1-ene (79)

following reactivity order is revealed: Me_2SO (6.4) > Ph_2CH_2 (3.6) > $PhCH_3$ (1).

Several factors need be considered. The first is whether the values $k(R\text{-}H)/k_5$ obtained by the methods described in this section are valid. An alternate possibility is that the slope observed in the plots of (80)/(81) versus R-H represent a "solvent" effect on the reactivity of n-Bu_3SnH towards aryl radical.

Table 37. Estimates of the rate constant for cyclization (k_5) for o-butenylphenyl radical (88) based upon competition experiments

Species (R-H)	Absolute rate constant for H-abstraction by phenyl from R-H ($M^{-1}s^{-1}$)	$\frac{k(R-H)}{k_5}$ (M^{-1})	k_5 (s^{-1})
Me_2SO	3.0×10^5[a]	0.027	1.1×10^7
$PhCH_3$	1.7×10^6[b]	0.0042	4.0×10^8
Ph_2CH_2	1.1×10^7[c]	0.015	7.3×10^8

[a] Table 25.

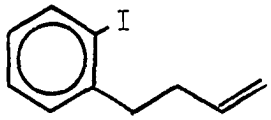
[b] Measured directly, see reference 112.

[c] Based upon competition experiments with CCl_4 where $k(Ph_2CH_2)/k(CCl_4) = 1.4$ (reference 99) and $k(CCl_4) = 7.8 \times 10^6\ M^{-1}s^{-1}$ (reference 110).

Presumably the solvent effects of Ph_2CH_2, $PhCH_3$ and PhH will not be substantially different, but perhaps the apparent high reactivity of Me_2SO towards aryl radical (87) really represents an enhanced reactivity of n-Bu_3SnH as a function of increasing Me_2SO

concentration, rather than H-abstraction from Me_2SO.

To test this possibility, the reaction was carried out in the absence of n-Bu_3SnH according to Eq. 121, using distannane (90) to generate aryl radicals.



$$\xrightarrow[\text{Ph-H}]{h\nu} \underset{2.5\%}{\underline{80}} + \underset{28.0\%}{\underline{81}} \quad (121)$$

(0.057 M) (0.059 M)

The ratio $k(Me_2SO)/k_5$ calculated from these results and Eq. 111 is on the same order of magnitude as the value obtained in the presence of n-Bu_3SnH. Thus, Me_2SO appears more potent an H-atom donor to aryl radical (87) than would be expected form the results with phenyl radical.

The discrepancy may arise from the assumption that phenyl radical and aryl radical (87) have similar absolute rate constants. The potential steric effect of an ortho substituent on the bimolecular rate constants of (87) would become more important for bulkier reagents (Figure 14).

Thus, a tentative estimate of k_5 based upon these results places it in the range 10^7 - 10^9 s^{-1} (Table 37), in contrast to the literature estimate of 10^6 s^{-1} (95, 97). The shortcomings of this estimate have been pointed out. The establishment of a more reliable

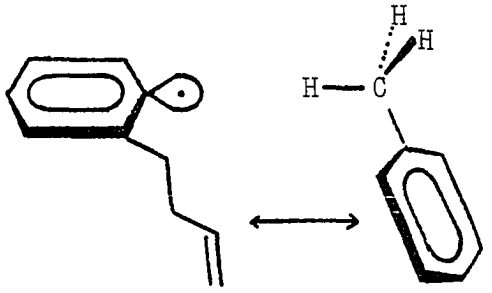


Figure 14. Potential steric effect in reactions of o-butenyl phenyl radical (87)

value of k_5 awaits either the reporting of the absolute rate constant for the abstraction of H from n-Bu_3SnH by the phenyl radical or experiments designed to directly measure k_5.

D. Mechanism of the Reaction Between Thiophenoxide and 4-o-Iodophenylbut-1-ene

It has now been established that the title reaction produces both rearranged and unrearranged products, suggesting successful trapping of an aryl radical before cyclization. Several unexpected features of this reaction were also revealed. The observed k_5/k_6 ratio was much lower than expected for aryl radical (87) of Scheme LI. The results of Table 31 suggest that PhSSPh plays some role in the trapping of alkyl radicals produced by rearrangement of aryl radical (87). Before any of these results can be successfully related to the aromatic $S_{RN}1$ reaction, it is clear that more

information regarding the mechanism of this reaction is required.

1. Role of diphenyl disulfide in the reaction

In order to ascertain what role PhSSPh might play in the reaction mechanism, product formation was monitored with respect to time in the absence and presence of diphenyl disulfide. The results of these studies appear in Tables 38 and 39.

Again, these results indicate that the observed k_5/k_6 ratio (6.3 - 6.4) is much lower than expected. Furthermore, the yield of hydrogen abstraction product (80) also appears lower than expected. From Table 37, assuming a Me_2SO concentration of 14.1 M, based upon Scheme LII and Eq. 111, $k(Me_2SO)/k_5$ is calculated to be on the order of 0.00043 M^{-1}--much lower than the the value of 0.027 M^{-1} determined in the previous section.

When the yields of products obtained in the absence and presence of PhSSPh are plotted against %-conversion, the function of PhSSPh in the reaction becomes clearer. Figure 15 graphically illustrates that in the absence of PhSSPh, the formation of alkyl sulfide (84) does not occur until sometime afer 50% conversion. Furthermore, after 50% conversion when

Table 38. Products and yields of the reaction between 4-o-iodophenylbut-1-ene (79) with thiophenoxide ion as a function of time

Time (min)	Product Yields (%)[a]: 80	81	82	79	83	84	85	86
7	0.44	3.9	0.29	64.9	2.4	0.0	0.0	1.1
15	0.45	6.6	0.73	48.2	4.4	0.0	0.0	2.6
30	--	12.1	2.1	21.4	6.9	1.1	0.0	3.9
52	--	14.8	2.4	0.6	7.7	3.7	0.07	4.0
74	0.70	15.4	3.7	0.0	7.0	3.7	0.0	4.4

[a] (PhS^-) = 0.13 M, (ArI) = 0.013 M, solvent = Me_2SO and temperature = 45 C. Counter-ion: K^+/18-crown-6. Solutions were irradiated at 350 nm.

this sulfide is forming, it does so apparently at the expense of dimer (86). A reasonable explanation for this phenomenon is that something formed during the course of the reaction facilitates the trapping of alkyl radical (88) as sulfide (84). Since the $S_{RN}1$ reaction of aryl halides with thiophenoxide are known to produce PhSSPh as a by-product (111), it seems likely that PhSSPh is the species responsible for the observed phenomenon.

Table 39. Product yields of the reaction between 4-o-iodophenylbut-1-ene (79) with thiophenoxide anion in the presence of PhSSPh as a function of time

Time (min)	Product yields (%)[a]: 80	81	82	79	83	84	85	86
7	--	1.6	0.84	83.6	1.4	3.9	0.13	0.1
15	--	2.4	1.1	68.7	3.2	10.9	0.92	0.7
32	--	4.4	1.1	62.4	4.4	15.8	0.99	1.3
45	--	6.5	3.1	35.8	7.1	25.1	1.9	2.0
65	0.29	9.8	5.5	13.5	8.9	35.4	2.1	2.4

[a] (PhS^-) = 0.130 M, (ArI) = 0.013 M, (PhSSPh) = 0.006 M, solvent = Me_2SO and temperature = 45 C. Solutions were irradiated at 350 nm.

Figure 16 confirms this hypothesis. In the presence of PhSSPh, formation of sulfide (84) is linear with respect to %-conversion and its yield is greatly enhanced at the expense of dimer (86) and hydrogen abstraction product (81).

What is not evident from these results is how PhSSPh permits alkyl radicals to be trapped. Two mechanisms can be suggested. Alkyl radicals are trapped

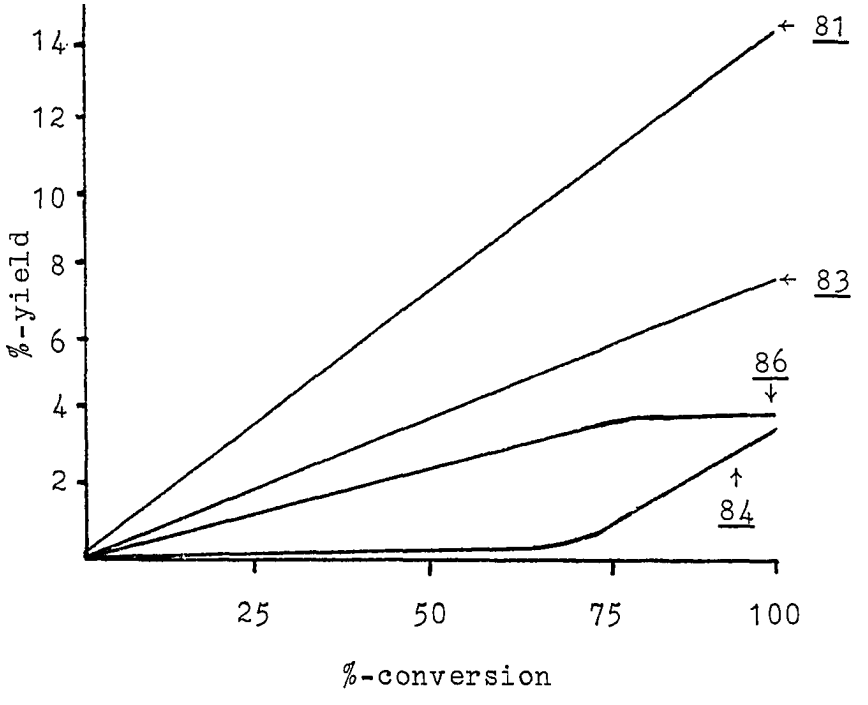
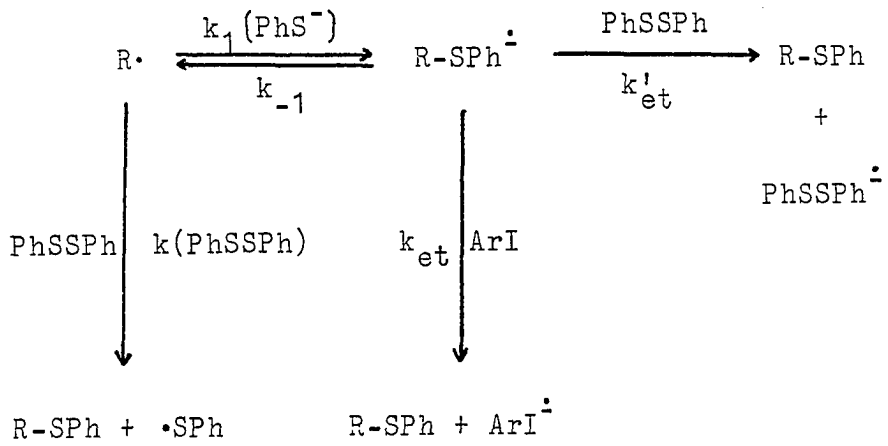


Figure 15. Product yields in the reaction of PhS^- with 4-o-iodophenylbut-1-ene as a function of %-conversion

by an overall S_H2 process at the sulfur of PhSSPh (107) more efficiently than by coupling with PhS^- $k(PhSSPh)(PhSSPh) >> k_1(PhS^-)$, or alkyl radicals are trapped by PhS^- in a reversible manner but electron transfer to starting ArI is inefficient $k_{et}(ArI) << k_{-1}$ (Scheme LIII). However, electron transfer to PhSSPh may be much faster (115), $k_{et}(PhSSPh) >> k_{-1}$, thereby allowing more efficient trapping of alkyl radical.

In either case, PhS^- must be either an inefficient

Scheme LIII



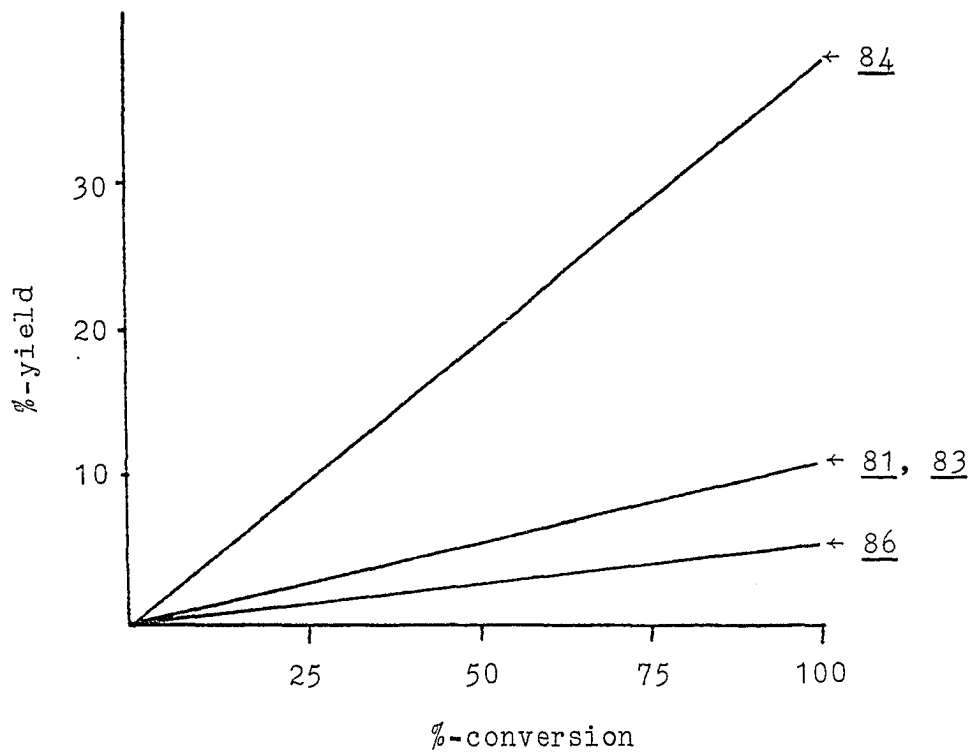


Figure 16. Product yields in the reaction of PhS^- with 4-o-iodophenylbut-1-ene in the presence of PhSSPh as a function of %-conversion

trap for alkyl radicals or the trapping is reversible and the subsequent electron transfer to ArI is inefficent. For the purpose of this discussion, it will not be necessary to distinguish between these two possibilities. However, each of these mechanisms imply that the reaction is a non-chain process.

Thus, the reactions of PhS^- with 4-o-iodophenylbut-1-ene (79) and o-iodophenyl allyl ether (70) are not $S_{RN}1$ reactions in the formal sense since they are not chain processes. However, electron transfer pathways are responsible for product formation since the reaction of PhS^- with either of these compounds goes to completion in little more than one hour, while simple photolysis of either compound in the absence of PhS^- results in complete recovery of starting material. Furthermore, the formation and intermediacy of aryl radical intermediates is confirmed by the formation of rearranged products. It seems reasonable then that the results generated from these reactions can be applied to the $S_{RN}1$ reaction since they are the result of electron transfer, aryl radical intermediates and coupling of said intermediates to PhS^-. The difference is the absence of electron transfer from products to starting materials propagating a chain reaction.

2. Nature of initiation

Since direct photolysis of these iodo compounds is slow, relative to the rate when PhS^- is present, and these are not chain reactions, aryl radical is likely not produced by direct photolysis and heterolysis of the C-I bond in ArI (Eq. 122). Electron transfer from

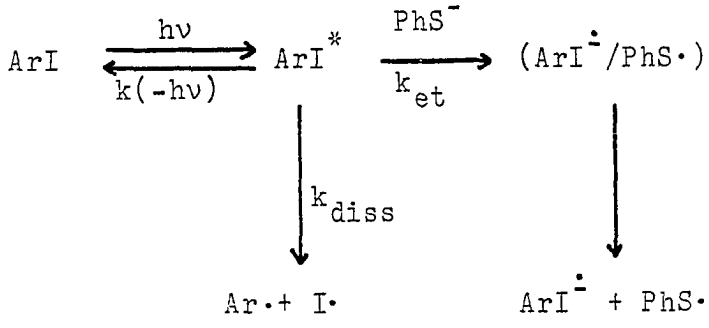
$$Ar\text{-}I \xrightarrow[\text{slow}]{h\nu} Ar\cdot + I\cdot \qquad (122)$$

PhS^- is clearly involved, and Schemes LIV and LV suggest two mechanisms by which this electron transfer might occur. Scheme LIV suggests formation of a charge transfer complex between ArI and PhS^-, and photolysis of this CT complex resulting in electron transfer. Scheme LV assumes photo-excitation of ArI to ArI^*. The dissociation of this species by heterolysis of the C-I bond is slower than electron transfer from PhS^-, $k_{et}(PhS^-) > k_{diss}$.

Scheme LIV

$$ArI + PhS^- \rightleftharpoons (ArI/PhS^-)_{CT} \xrightarrow{h\nu} (ArI^{\cdot-}/PhS\cdot) \longrightarrow ArI^{\cdot-} + PhS\cdot$$

Scheme LV



The mechanism of Scheme LV seems more probable based upon the following observations: Solutions of PhS^- and PhI are not highly colored suggesting charge transfer complex formation is unimportant. The photolysis of ArI in the presence of PhS^- follows pseudo-first order kinetics, Eq. 123, where k is a function of several variables including the intensity of the light, wavelength, reaction vessel, etc.... However, in experiments where all these variables are held constant, k is found to be independent of PhS^- concentration: $k = 0.060\ s^{-1}$ in 0.35 M PhS^- and $k = 0.068\ s^{-1}$ in 0.14 M PhS^-. This result is consistent with Scheme LV assuming $k(-h\nu) >> k(PhS^-) >> k_{diss}$. Based upon visual observations, solutions of ArI/PhS^- irradiated at 350 nm seem to fluoresce, also consistent with this interpretation.

$$\frac{-d(ArI)}{dt} = k(ArI) \qquad (123)$$

E. Reaction of 4-o-Iodophenylbut-1-ene in the Presence of Varying Amounts of Thiophenoxide--Use of a Free Radical Clock Reaction to Detect the Existence of a Second Intermediate in the Aromatic $S_{RN}1$ Reaction

The effect of varying PhS^- concentration on the products of its reaction with 4-o-iodophenylbut-1-ene (79) has been studied with 0.11 M PhSSPh added to ensure complete trapping of alkyl radicals. 18-Crown-6 was present to eliminate complications potentially introduced by ion-pairing phenomena. The results of these experiments appear in Table 40.

For the purpose of this discussion, let P_U be defined as the yield of unrearranged sulfide (83), P_5 the sum of the yields of all five-membered ring rearranged products ((81), (84) and (86)) and P_H the yield of unrearranged H-abstraction product (80).

In Figure 17, P_U/P_5 is plotted against PhS^- concentration. It is clear that as the concentration of PhS^- goes to zero, the ratio P_U/P_5 does not. Thus, there is some source of sulfide (83) other than by trapping of aryl radical (87) by PhS^-. Since this is not a chain mechanism, this additional source may be the result of the photo-induced electron transfer (Scheme LVI).

Table 40. Ratio of trapped to cyclized products as a function of thiophenoxide concentration for the reaction of thiophenoxide anion with 4-o-iodophenylbut-1-ene

(PhS^-) (M)	$(P_U/P_5)^{a,b}$ actual	$(P_U/P_5)^{a,b}$ corrected[c]	$(P_H/P_5)^b$	$\left[\frac{P_U}{P_5}_{corr} \times \frac{P_5}{P_H}\right]^b$
0.399	0.2525	0.1194	0.026	4.6
0.300	0.2522	0.1191	0.026	4.6
0.200	0.2292	0.0961	0.023	4.2
0.100	0.2072	0.0741	0.022	3.4
0.074	0.2012	0.0681	0.011	6.2
0.048	0.1894	0.0563	0.005	10.0
0.026	0.1709	0.0378	-	-
				average = 5.5

[a](ArI) = 0.0102, (PhSSPh) = 0.011 M, solvent = Me_2SO, and temperature = 45 C. Solutions were irradiated at 350 nm for 1 h. Counter-ion: K^+/18-crown-6.

[b]See text for explanation.

[c]Corrected value = actual value - 0.1331 (see text).

Thus according to Scheme LVI, after electron transfer, $ArI^{\cdot-}$ and PhS• combine in the solvent cage forming $(ArISPh)^-$, which yields ArSPh after loss of

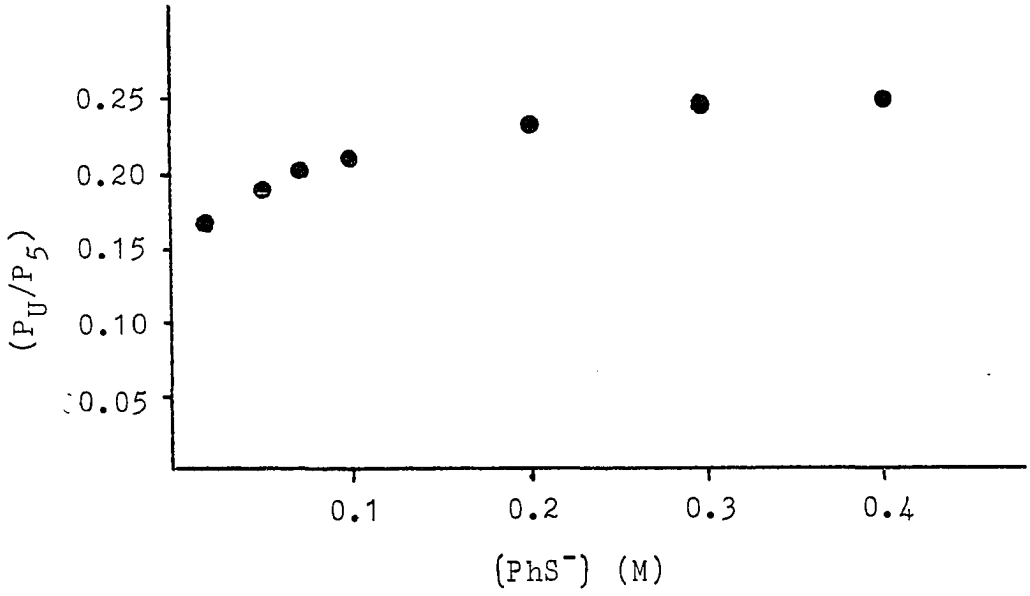
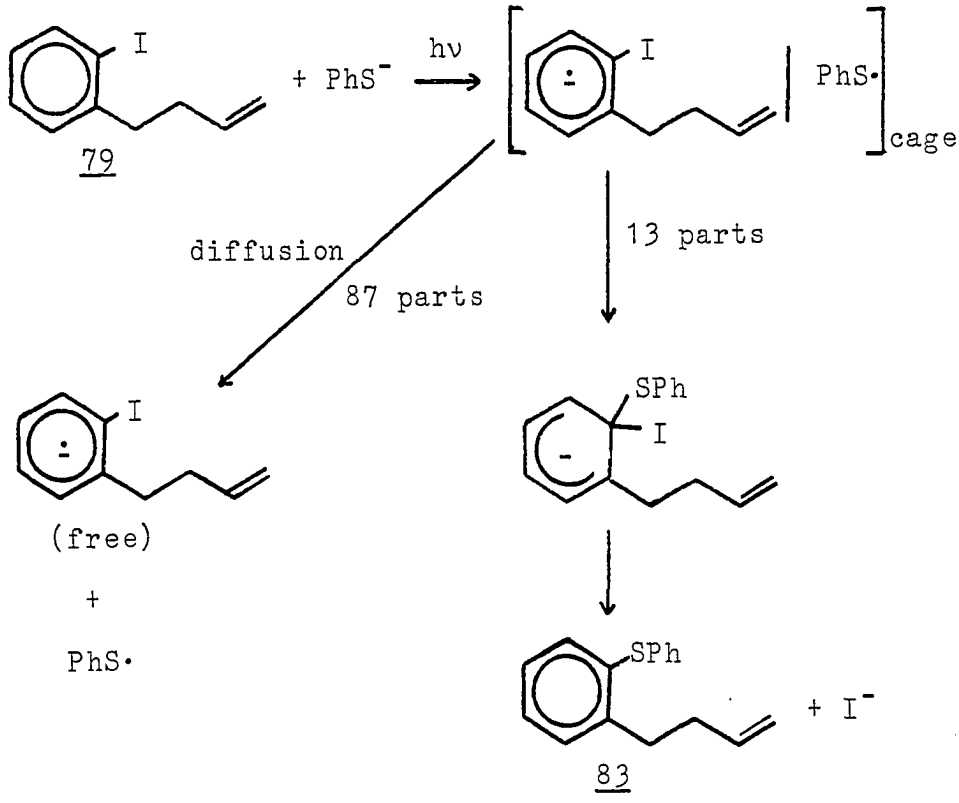


Figure 17. Plot of the ratio (P_U/P_5) versus PhS^- concentration for the reaction of PhS^- with 4-o-iodophenylbut-1-ene

I^-. The ratio P_U/P_5 extrapolated to zero PhS^- concentration is 0.1331, indicating that approximately 13% of the $(ArI^{\cdot-}/PhS\cdot)$ caged pair combines. The P_U/P_5 "corrected" values take this cage process into account by subtracting 0.1331 from the observed value.

Figure 18 plots the P_U/P_5 corrected values as well as the ratio P_H/P_5 as a function of PhS^- concentration. It is evident that trapping of aryl radical (87) by PhS^- and by H-abstraction from 18-crown-6 is competitive with cyclization at low PhS^- concentration. Additionally, the values of $(P_U/P_5)_{corr} \times (P_H/P_5)^{-1}$ are on the

Scheme LVI



order of 4 - 6. Since the concentrations of PhS^- and 18-crown-6 are approximately equal, this ratio is approximately the ratio of rate constants for attack of PhS^- and 18-crown-6 on the aryl radical. The ratio $k(PhS^-)/k(18\text{-crown-6}) = 5.8$, predicted from Table 25, is in good agreement with these results. Thus at low concentrations, the mechanism depicted in Scheme LVII appears to be operative.

There are some blatant problems with this interpretation however. The ratios P_U/P_5 and P_H/P_5

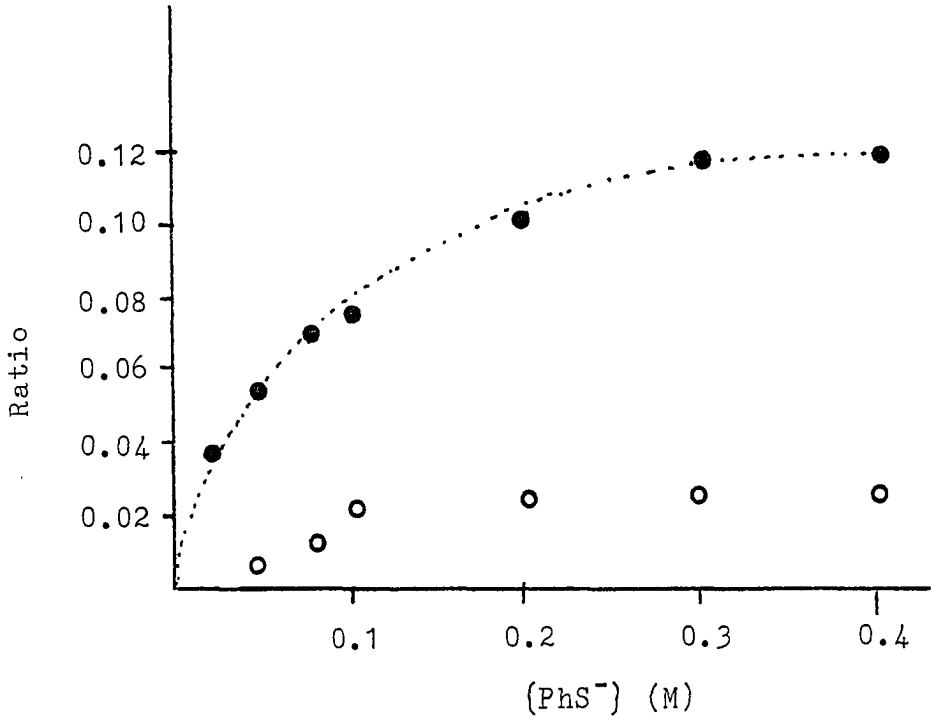


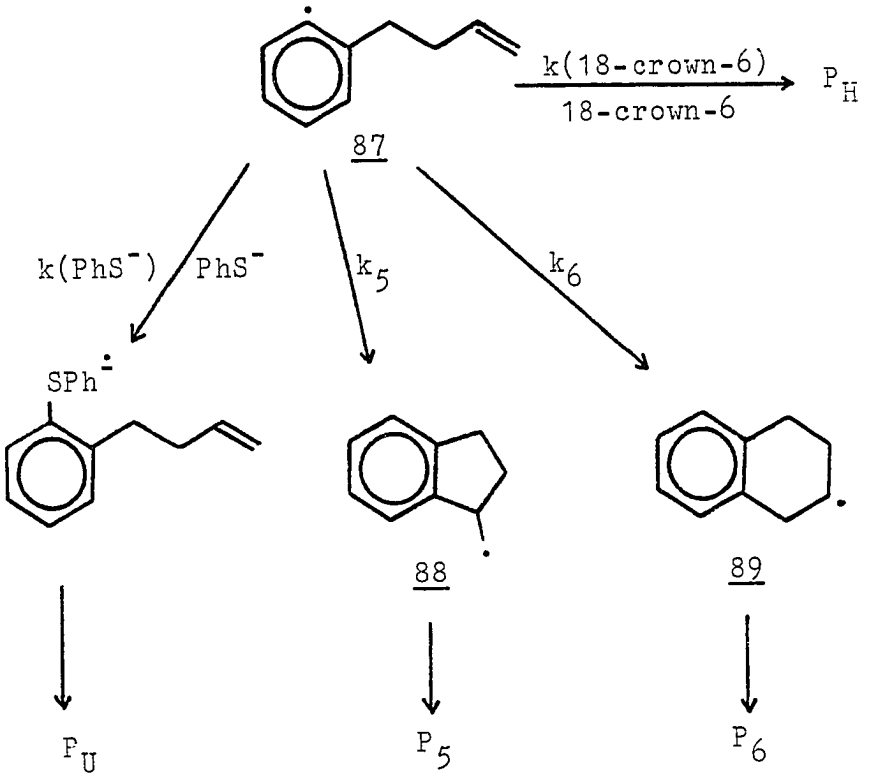
Figure 18. Plot of the ratio $(P_U/P_5)_{corr}$ (●) and (P_H/P_5) (○) versus thiophenoxide concentration for the reaction of PhS^- with 4-o-iodophenylbut-1-ene

appear to be quite a bit lower than expected. Using the data for phenyl radical (Table 25), and the estimated value of k_5 (10^8 s^{-1}), P_U/P_5 and P_H/P_5 can be estimated according to Eqs. 124 and 125, assuming the mechanism of Scheme LVII. These predicted values appear in Table 41.

$$\left[\frac{P_U}{P_5}\right]_{corr} = \frac{k(PhS^-)(PhS^-)}{k_5} \qquad (124)$$

$$\frac{P_H}{P_5} = \frac{k(18\text{-crown-6})(18\text{-crown-6}) + k(Me_2SO)(Me_2SO)}{k_5} \quad (125)$$

Scheme LVII



Furthermore, at high PhS^-/18-crown-6 concentrations, trapping of aryl radical in a bimolecular fashion by either of these reagents is not competitive with cyclization. These results, as well as the unusually low value of k_5/k_6 clearly indicate that the mechanism of Scheme LVII is inadequate. An alternative mechanism is required.

A mechanism which satisfactorily explains all these results is presented in Scheme LVIII. A

Table 41. Predicted values of $(P_U/P_5)_{corr}$ and (P_H/P_5) based upon Scheme LVII

(PhS^-) = (18-crown-6) (M)	$(P_U/P_5)_{corr}$	(P_H/P_5)
0.399	0.88	0.19
0.300	0.66	0.16
0.200	0.44	0.11
0.100	0.22	0.08
0.074	0.16	0.07
0.048	0.11	0.06
0.026	0.057	0.05

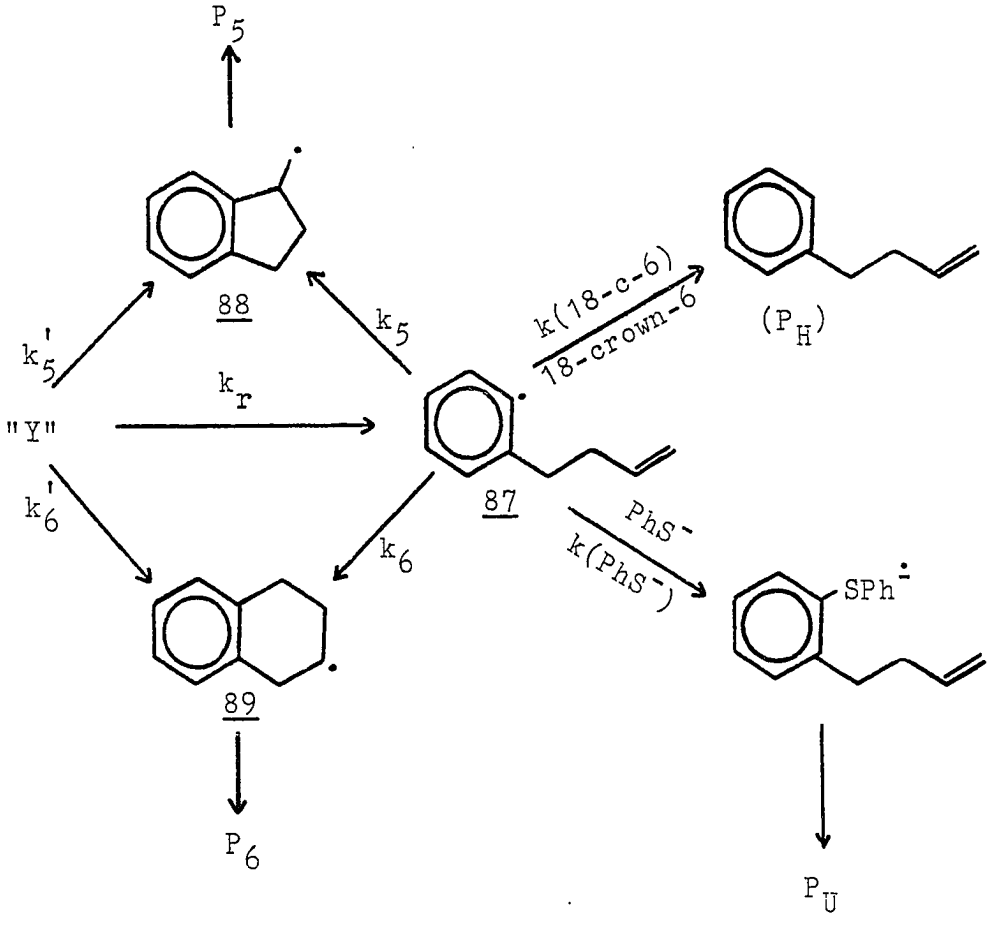
paramagnetic species "Y", capable of rearranging to five- and six-membered ring alkyl radicals (88) and (89) with $k_5'/k_6' < 10$ is proposed. This species "Y" can relax (k_r) to aryl radical (87).

Assuming a steady state concentration of (87), neglecting k_6 and k(18-crown-6), Eq. 130 can be derived as follows:

$$0 = \frac{d(87)}{dt} = k_r(Y) - k_5(87) - k(PhS^-)(PhS^-)(87) \quad (126)$$

$$(87) = \frac{k_r}{k_5 + k(PhS^-)(PhS^-)(87)}(Y) \quad (127)$$

Scheme LVIII



$$\frac{d(P_5)}{d(P_U)} = \frac{k_5'(Y) + k_5(\underline{87})}{k(PhS^-)(PhS^-)(\underline{87})} \qquad (128)$$

$$= \frac{k_5' + k_5\left[\dfrac{k_r}{k_5 + k(PhS^-)(PhS^-)}\right]}{k(PhS^-)(PhS^-)\left[\dfrac{k_r}{k_5 + k(PhS^-)(PhS^-)}\right]} \qquad (129)$$

$$\frac{d(P_5)}{d(P_U)} = \frac{k_5'k_5 + k_5'k(PhS^-)(PhS^-) + k_5k_r}{k_rk(PhS^-)(PhS^-)} \quad (130)$$

$$\frac{d(P_5)}{d(P_U)}(PhS^-) = \frac{k_5}{k(PhS^-)}\left[\frac{k_5'}{k_r} + 1\right] + \frac{k_5'}{k_r}(PhS^-) \quad (131)$$

$$m = k_5'/k_r \quad (132)$$

$$b = \frac{k_5}{k(PhS^-)}\left[\frac{k_5'}{k_r} + 1\right] \quad (133)$$

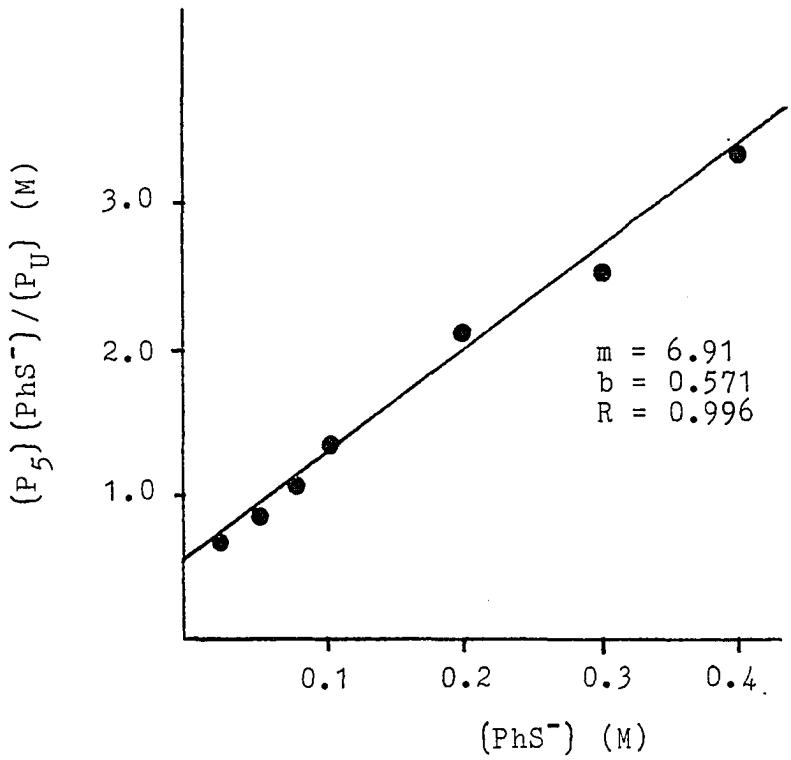
Thus, Eq. 131 predicts that a plot of $(P_5/P_U)_{corr}(PhS^-)$ versus PhS^- concentration will yield a straight line whose slope and intercept are defined by Eqs. 132 and 133 respectively. Such a plot, derived from the data in Table 40 appears in Figure 19. Using the values of m and b obtained from the linear least squares analysis of the data, Eqs. 132 and 133 can be solved. Thus from the results reported in this section, and assuming the mechanism of Scheme LVIII, the following quantities are derived:

$$k_5'/k_r = 6.91 \quad (134)$$

$$k(PhS^-)/k_5 = 13.84\ M^{-1} \quad (135)$$

$$k(18\text{-crown-}6)/k_5 = 2.52\ M^{-1} \quad (136)$$

The value of k_5 based upon these results and $k(PhS^-) = 2.2 \times 10^8\ M^{-1}s^{-1}$ (Table 25) is $1.6 \times 10^7\ s^{-1}$ and within the range expected for aryl radical (87).



$\frac{(P_5)}{(P_U)}(PhS^-)$ (M)	(PhS^-) (M)
3.342	0.399
2.519	0.300
2.081	0.200
1.350	0.100
1.087	0.074
0.853	0.048
0.688	0.026

Figure 19. Plot of $(P_5)(PhS^-)/(P_U)$ versus (PhS^-) according to Scheme LVIII and Eq. 131

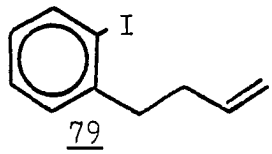
F. Reaction of 4-o-Iodophenylbut-1-ene in the Presence of Varying Amounts of Diethyl Phosphite Anion

The results obtained earlier indicate that $(EtO)_2PO^-$ has little or no reactivity towards phenyl radical, while PhS^- and $Me_2C{=}NO_2^-$ are quite reactive. Competition studies pitting $(EtO)_2PO^-$ against $Me_2C{=}NO_2^-$ for intermediates in the aromatic $S_{RN}1$ reaction revealed the former anion to be reactive towards an intermediate "X" which was apparently a precursor to free phenyl radical.

Similarly, using 4-o-iodophenylbut-1-ene, reactivity of PhS^- was measured against an intramolecular radical rearrangement indicating the existence of another intermediate, designated "Y", which was believed to be a precursor to free aryl radical. PhS^- had no measurable reactivity towards "Y".

An obvious question arises: Does "X" = "Y"? Since $(EtO)_2PO^-$ has high reactivity towards "X", it seems reasonable that if this anion is demonstrated to have the same reactivity towards "Y", then "X" and "Y" are probably the same type of species.

The reaction of $(EtO)_2PO^-K^+$ with (79) (Eq. 137) did not proceed in any reasonable length of time. However, the analogous reaction of PhS^- with (79) is over in about 1 hour. It has already been argued

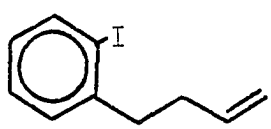


79

$$+ (EtO)_2PO^- \xrightarrow[Me_2SO]{350\ nm} \underset{24\ h}{\text{NO REACTION}} \qquad (137)$$

that this reaction is not a chain process. Thus, the problem in the reaction of (79) with $(EtO)_2PO^-$ must be that the photo-stimulated electron transfer between these substrates is slow. Since the analogous photo-stimulated electron transfer between (79) and PhS^- is rapid, it seemed reasonable to conduct the reaction of $(EtO)_2PO^-$ with (79) in the presence of PhS^-, the latter reagent serving to reduce the starting aryl iodide. This procedure is called "entrainment" and has been often used to stimulate $S_{RN}1$ reactions that would otherwise be sluggish (7).

The products and yields of the reaction of (79) with $(EtO)_2PO^-$ in the presence of PhS^- (Eq. 138) are listed in Table 42. Apparently, sulfides (83) and (84) are somewhat unstable under the reaction conditions, disappearing after all the ArI is consumed.



(0.0114 M)

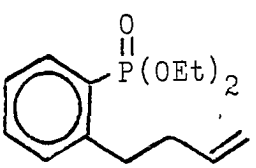
$$+ PhS^-K^+ + (EtO)_2PO^-K^+ \xrightarrow[Me_2SO]{h\nu} \qquad (138)$$

(0.0973 M) (0.202 M) 18-c-6

Table 42. Products and yields of the reaction between 4-o-iodophenylbut-1-ene and diethyl phosphite anion (initiated by thiophenoxide) as a function of time

	Product yields (%)[a]:							
Time (min)	79	81	82	91	83	92	84	86
5	72.2	6.1	1.8	1.6	1.0	0.9	0.40	0.90
10	54.1	11.9	1.5	3.8	2.4	2.7	0.74	0.64
25	22.7	21.2	2.6	6.9	3.3	7.4	0.97	1.30
38	1.1	22.5	1.6	8.8	2.5	11.4	0.88	1.80
56	0.0	29.4	1.3	8.4	0.0	12.3	0	2.20

[a](ArI) = 0.0114 M, (PhS^-) = 0.973 M, $((EtO)_2PO^-)$ = 0.202 M, solvent = Me_2SO and temperature = 45 C. Counter-ion: K^+/18-crown-6.



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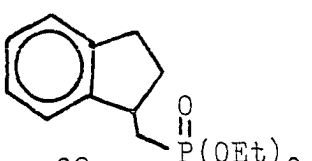

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The reaction of PhS^- with (79) in the presence of varying concentrations of $(EtO)_2PO^-$ produced the results which appear in Table 43, where P = the yield of trapping product (91) and P_5 is the sum of the

Table 43. The ratio (P/P_5) as a function of diethyl phosphite anion concentration in the reaction of 4-o-iodophenylbut-1-ene with diethyl phosphite anion

$((EtO)_2PO^-)$ (M)[a]	(P/P_5)
0.00	0.00
0.10	0.028
0.20	0.097
0.30	0.21
0.40	0.25

[a](ArI) = 0.010 M, (PhS^-) = 0.0936 M. Counter-ion: K^+/18-crown-6. Solvent: Me_2SO. Temperature: 45 C. Solutions were irradiated at 350 nm for 1 h.

yields of all five-membered ring products. It appears that attack of $(EtO)_2PO^-$ is competitive with cyclization. Apparently, intermediate "Y" can be trapped by $(EtO)_2PO^-$. A plot of the ratio P/P_5 versus $(EtO)_2PO^-$ concentration is presented in Figure 20. Assuming the mechanism of Scheme LIX, the following equations can be derived:

$$\frac{d(\underline{87})}{dt} = 0 = k_r(Y) - k_5(\underline{87}) \qquad (139)$$

$$(\underline{87}) = \frac{k_r}{k_5}(Y) \qquad (140)$$

$$\frac{d(P)}{d(P_5)} = \frac{k_p(P^-)(Y)}{k_5'(Y) + k_5(\underline{87})} \qquad (141)$$

$$\frac{d(P)}{d(P_5)} = \frac{k_p(P^-)}{k_5' + k_r} \qquad (142)$$

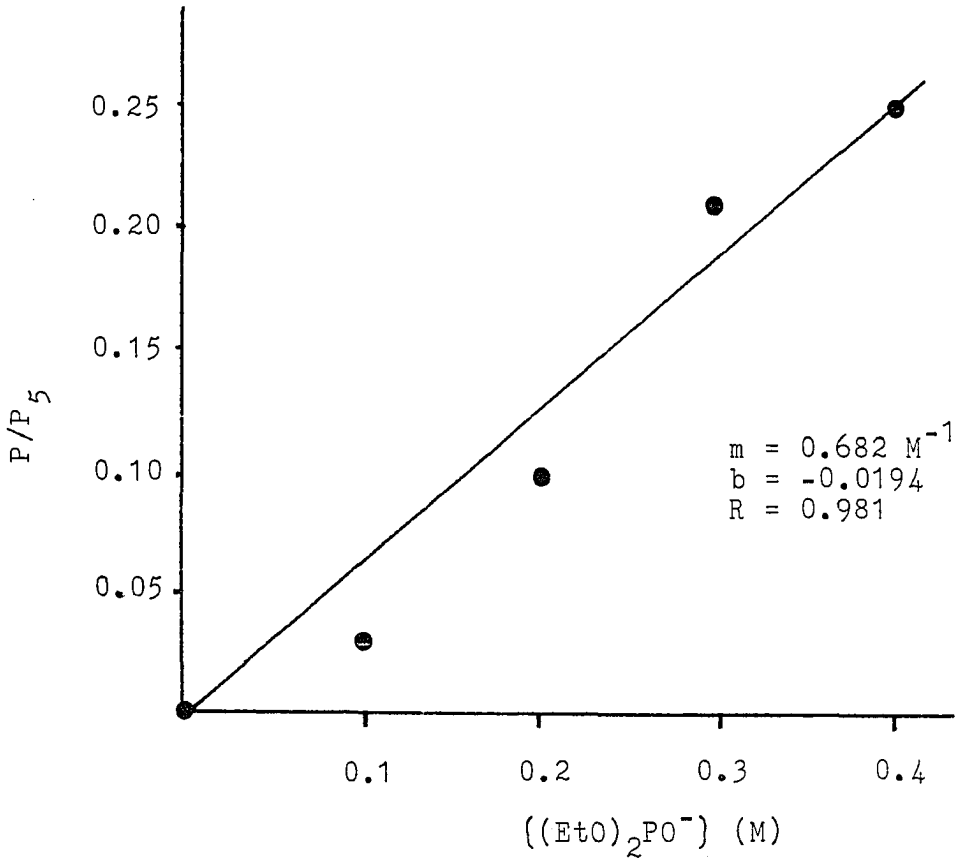
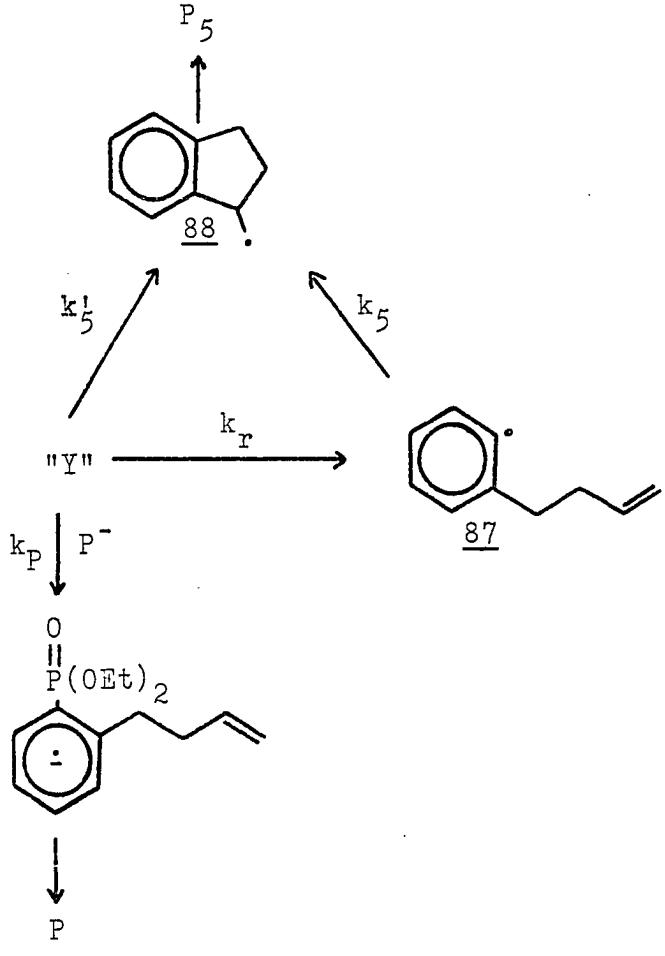


Figure 20. A plot of the ratio P/P_5 as a function of $(EtO)_2PO^-$ concentration

Scheme LIX



The plot of P/P_5 versus $(EtO)_2PO^-$ concentration yields a straight line (Figure 20) whose slope m, according to Eq. 142, is defined as:

$$m = \frac{k_P}{k_5' + k_r} = 0.682\ M^{-1} \qquad (143)$$

Given Eq. 134, k_r/k_P can be solved:

$$k_r/k_P = 0.19\ M \qquad (144)$$

The value of k_r/k_P = 0.19 M, derived from these results and assumptions, is nearly identical to the quantity k_r/k_P = 0.14 M derived from the results of competition experiments involving $(EtO)_2PO^-$ and $Me_2C{=}NO_2^-$ for the aryl radical intermediates produced from the $S_{RN}1$ reaction of iodobenzene. Thus, it appears quite likely that "X" and "Y" <u>are</u> the same type of species. Indeed, it seems quite meaningless to presume they are not.

V. SUMMARY:

THE DUAL INTERMEDIATE HYPOTHESIS

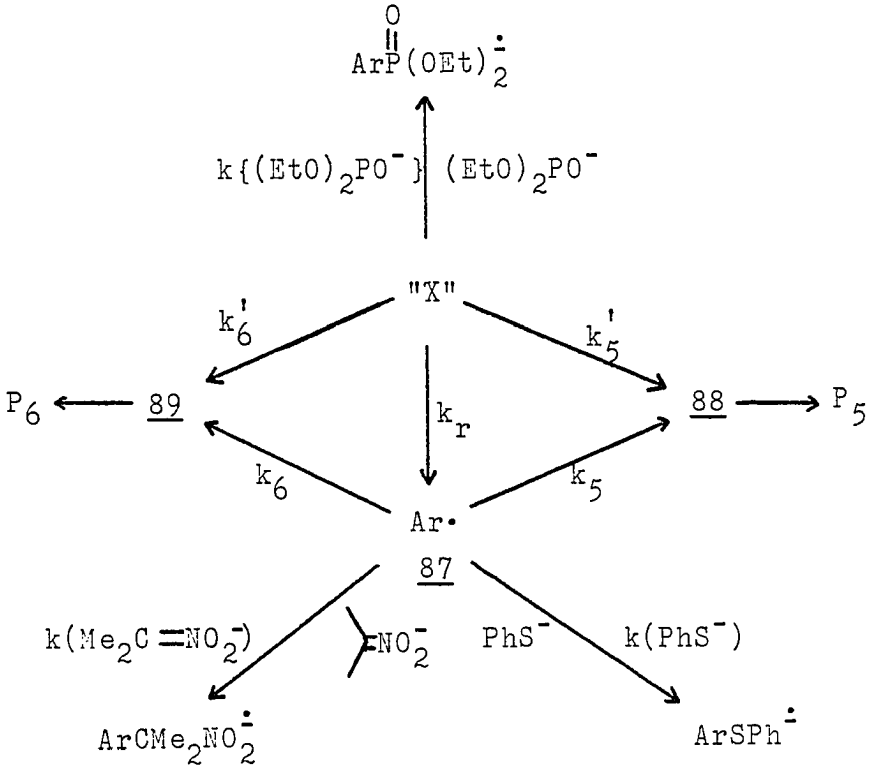
As stated at the beginning of this chapter, the aim of this thesis was to consider in a broad sense the coupling of radicals and anions. Specifically, the intermediacy of aryl radical in the aromatic $S_{RN}1$ reaction was tested. While the results certainly confirm aryl radical intermediacy, it is by no means the sole intermediate in the reaction with which nucleophiles can react. Evidence has suggested the existence of a second kinetically significant intermediate superficially referred to as "X", which is a precursor to free aryl radical. Scheme LX summarizes the key features of this hypothesis.

Assuming k_p be diffusion controlled (10^{10} $M^{-1}s^{-1}$) (41) from Eqs. 143 and 144, k_5' and k_r can be calculated:

$$k_5' = 1.3 \times 10^{10}\ s^{-1} \qquad (145)$$

$$k_r = 1.9 \times 10^{9}\ s^{-1} \qquad (146)$$

Scheme LX



$k_5/k_6 = 30$

$k'_5/k'_6 < 10$

VI. THE NATURE OF "X"

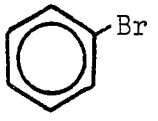
Thus far, this discussion has intentionally avoided any description of the identity of "X". The evidence establishes the existence of "X", indicating that it must be a species that decomposes or relaxes to aryl radical. This section will be directed, admittedly in a highly speculative manner, toward gaining some understanding or inclination of the nature and identity of "X".

A. Radical Anion ($ArX^{\cdot -}$)

Certainly a species that meets all criteria for "X", specifically that it be both paramagnetic and a precursor to aryl radical, is the haloarene radical anion. However, it is quite unlikely that $ArX^{\cdot -}$ is "X". The relative reactivities of diethyl phosphite anion and pinacolone enolate have been shown to be independent of the leaving group (41). Thus, if "X" is $ArX^{\cdot -}$, then one is forced to reach the unlikely conclusion that pinacolone enolate and diethyl phosphite anion have approximately the same reactivity towards it, irrespective of the leaving group.

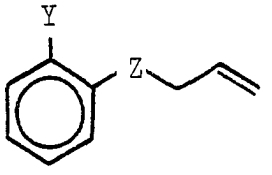
The rates of dissociation of aryl halide radical anions are completely dependent on the nature of the leaving group, see Table 8. Thus, the ratio $k_r/k(EtO)_2PO^-$ (Scheme LX) should be dependent on the

leaving group if $ArX^{\cdot -}$ is "X". An attempt was made to repeat these experiments using Ph-Br instead of Ph-I in competition experiments pitting nitronate anion against diethyl phosphite anion. Unfortunately, the inhibitory effect of nitronate anion coupled with the reduced $S_{RN}1$ reactivity of Ph-Br (20) proved too large an obstacle to overcome (Eq. 147). In a similar



$$+ \; Me_2C{=}NO_2^- + (EtO)_2PO^- \xrightarrow[Me_2SO]{h\nu} \underset{\text{REACTION}}{\overset{\text{NO}}{}} \quad (147)$$

fashion, the reaction of PhS^- with (93) proved entirely too slow to produce any meaningful results.



Y = Cl, Br
Z = O, CH_2

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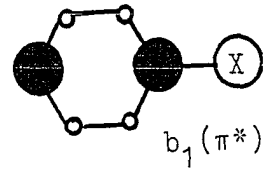
Thus, the techniques utilized to detect the existence of "X" in $S_{RN}1$ reactions of iodoarenes completely failed in attempts to resolve what "X" might actually be.

B. Excited State Aryl Radical

As pointed out in Chapter I, the excess electron in $ArX^{\cdot -}$ resides in a π^* molecular orbital. The suggestion has been made that the dissociation of

$ArX^{\cdot-}$ proceeds from the A^2B_1 state (94) since the $b_1(\pi^*)$ orbital is antibonding between the halogen and the ring (69).



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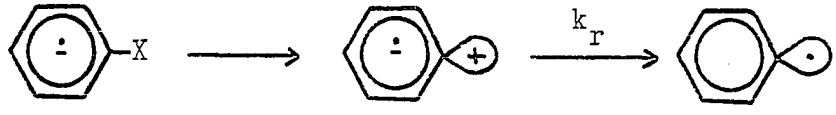
Thus, instead of proposing intramolecular electron transfer from a π^* to σ^* antibonding orbitals to account for the dissociation of $ArX^{\cdot-}$, perhaps the dissociation occurs in a symmetry allowed manner yielding an excited state aryl radical (95) which undergoes relaxation to the ground state σ-aryl radical (Eq. 148). Electronically, (95) is a seven π-electron system. An analogous process was proposed for the dissociation of $(ArN_2^+)^{\cdot-}$ (77).

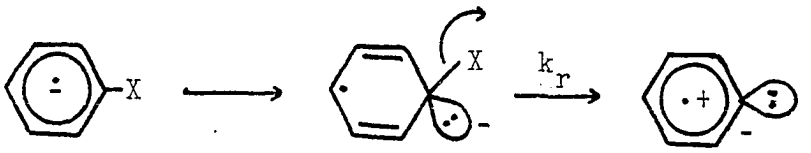


(148)

95

Eq. 148 assumes that dissociation occurs through stretching of the C-X bond. The process of intramolecular electron transfer, which so often has been applied to the dissociation of $ArX^{\cdot-}$ (see Chapter I), assumes the stretching to be coupled with a bending or vibration.

Perhaps then, another reaction coordinate is possible (Eq. 149):



(149)

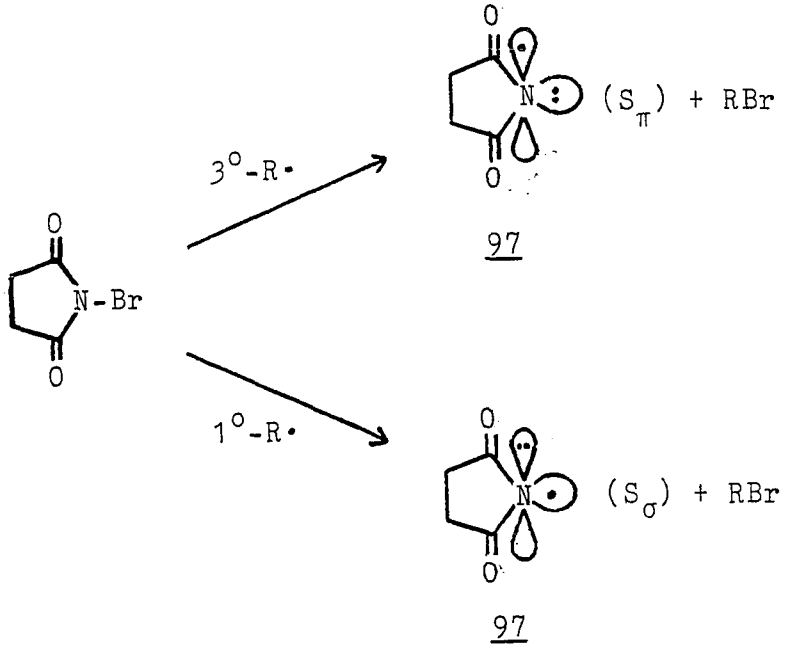
96

Again an excited π-aryl radical (96) is produced, although this species is formally a five π-electron system. Interestingly enough, such an excited species, involving a transition of one electron from the HOMO of the π-system to the sp^2 orbital of carbon, has been proposed to "contaminate" the ground state σ-phenyl radical. Using Huckel Molecular Orbital theory, a correlation was reported between the relative reactivity of a series of substituted phenyl radicals and the energy difference between the HOMO (π) and sp^2 orbital of carbon (116).

The relationship between structures (95), (96) and the ground state σ-phenyl radical has been referred to as "orbital isomerism" (117). The possible existence of excited state radicals, and their intermediacy in reactions, is receiving vast attention in the current literature. Succinimidyl radical (97), formed by bromine abstraction from N-bromosuccinimide by alkyl radicals, is reported to exist as each of two possible orbital isomers, depending on the energetics of the abstraction

process (Scheme LXI) (118).

Scheme LXI



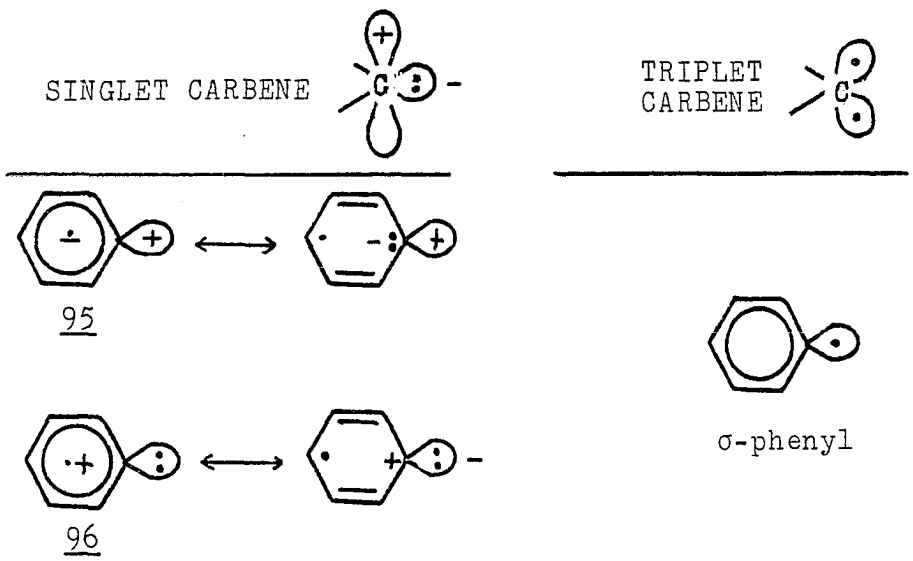
97

97

The advantage to zwitterionic species such as (95) and (96), is that the high reactivity of nucleophiles such as NH_2^- and $(EtO)_2PO^-$ is explained in an intuitively satisfying manner (Scheme LXII). Perhaps the relationship between structures (95) or (96) to the σ-phenyl radical can be viewed as analogous to the relationship between singlet and triplet carbenes (Scheme LXIII). Thus, the electrophilic nature of (95) or (96), as well as its apparent low affinity towards H-abstraction relative to σ-phenyl radical, can be rationalized. Furthermore, the unusual k_5/k_6 ratio for the intramolecular cyclization of "X" might be rationalized by

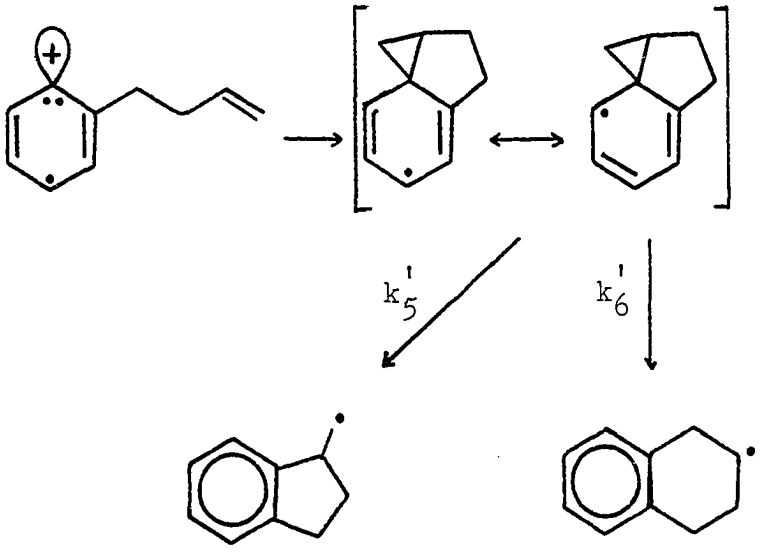
Scheme LXII

Scheme LXIII



a typical singlet carbene reaction, addition to a double bond forming a cyclopropane ring, followed by ring opening of the resultant cyclopropyl carbinyl radical (Scheme LXIV).

Scheme LXIV



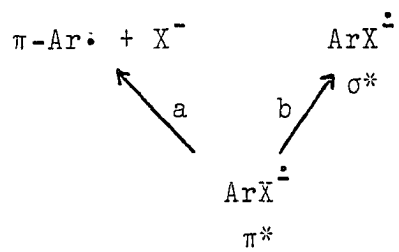
But alas, when surrounded by a silver lining, one is inevitably in a dark cloud. Theoretical results indicate that (96) is 2.45 eV (56 kcal/mol) higher in energy than σ-phenyl radical (65), (95) being even higher in energy. The proposal of such high energy species as reactive intermediates causes a certain amount of apprehension.

The decomposition of $PhI^{\cdot-}$ (gas phase) is essentially thermo-neutral, ΔE being about 1.6 kcal/mol (119). Clearly solvation of I^- will further facilitate this process. Solvation of zwitterionic species such as

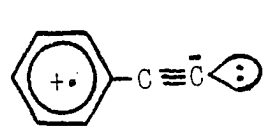
(95) or (96) may also lower the energies of these species relative to σ-phenyl radical.

It may be unwise to compare the energy of (95) or (96) to ground state aryl radical. Perhaps it is better to compare the energy of either π-phenyl radical to the energy of a σ*-$ArX^{\cdot -}$ (Scheme LXV), the real question being whether path (a) or path (b) provides a lower energy of activation. Furthermore, bending as well as stretching of the C-X bond, should be taken into account to properly construct a potential energy diagram. These considerations are all but ignored in theoretical studies of $ArX^{\cdot -}$ dissociation (see Chapter I).

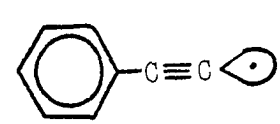
Scheme LXV



Interesting precedent worth mentioning centers on phenylethynyl radical, Ph-C≡C·, which has been shown to be a π-radical (98) instead of a σ-radical by ESR spectroscopy (120):



98



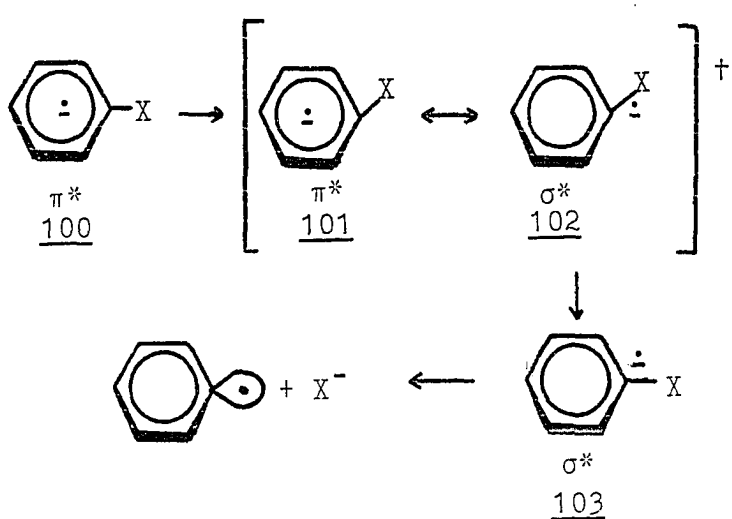
99

The extension of the π-system serves to lower its energy with respect to the sp orbital of carbon. Such a crossing of σ- and π-levels was predicted to occur in the series of radicals: phenyl, 1- and 2-naphthyl, 1- and 9-anthracyl and 1-pyrenyl (65). The fact that the crossing appears to have come much earlier suggests that the energies of the π-excited states may be overstated.

C. Aryl Radical/Halide Complex

The discussion of the dissociation of $ArX^{\cdot-}$ invoking "intramolecular electron transfer" (see Chapter I) presupposes bond bending (Scheme LXVI).

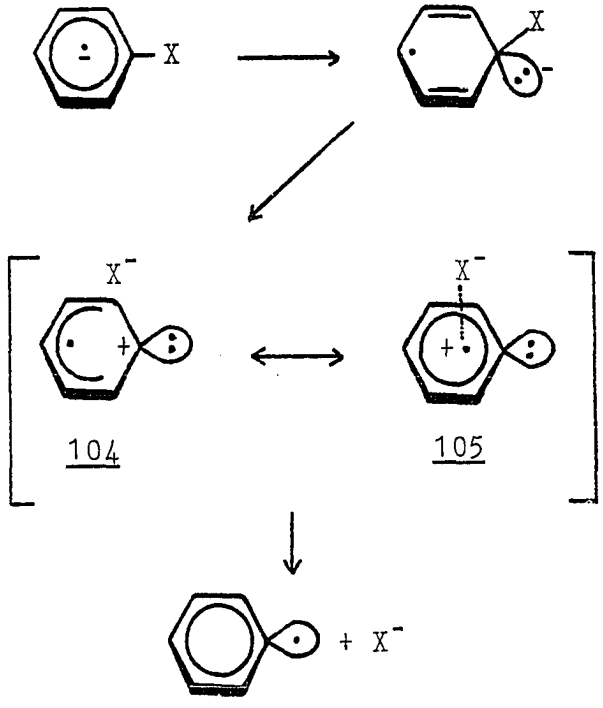
Scheme LXVI



Hence, structures (101)/(102) would be the transition state of this reaction. Suppose now, that such bond bending is important in the dissociation of $ArX^{\cdot-}$. Given a non-coplanar transition state (101)/(102), is it necessary that the conversion (102) → (103) occur for the halide to depart? In other words, if the transition state is non-planar, is it reasonable to assume that the lowest energy pathway for its formation or destruction is through a planar arrangement of atoms? The alternative has been presented already (Eq. 149) for the formation of the π^5-excited phenyl radical.

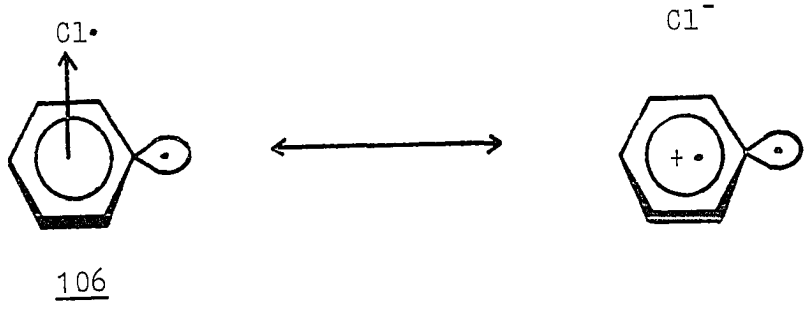
Scheme LXVII supposes that the halide interacts (complexes) with the formally positively charged π-system before it completely departs enroute to the σ-phenyl radical. The key feature of (104)/(105) is that an excited state π^5-phenyl radical is complexed with halide, presumably resulting in greater stability. Such a proposal provides a way around the fact that the π-phenyl radical is so high in energy. The absence of a leaving group effect in the pinacolone/diethyl phosphite competitions (41) may then be due to the fact that the C-X bond is almost entirely broken in (104)/(105). Hence, this proposal suggests that the aromatic $S_{RN}1$ reaction is neither strictly $S_{RN}1$ since there is some residual bonding to the leaving group, nor

Scheme LXVII



true $S_{RN}2$ since the C-X bond is almost completely broken.

This proposal is not without precedent. The photolysis of chlorobenzene has been reported to produce π-chlorobenzene (106). This species was suggested on the basis of reactivity patterns resembling neither a free chlorine nor phenyl radical (121).



Furthermore, the dissociation of $PhX^{\cdot -}$ was proposed to proceed through a charge transfer complex (CTC) of halide with the benzene ring, which was directly observed, and which had a reported lifetime of approximately 1 μs at 100 K (see Eq. 150 and Chapter I) (70).

$$Ph\text{-}X^{\cdot -} \longrightarrow \underset{\underline{107}}{(Ph\cdot/X^{-})_{CTC}} \xrightarrow{EtOH} Ph\text{-}H + X^{-} \qquad (150)$$

The lifetime of the proposed intermediate "X" at 45 C (k_r^{-1}) is about 5.3×10^{-10} s. Since it is reasonable to expect the lifetime of (107) to be decreased at higher temperatures, it may be that "X", (104)/(105) and (107) are all the same species.

In Chapter I, it was pointed out that for the rate of decomposition of radical anions studied by cyclic voltammetry and pulse radiolysis, the two techniques seldom agreed on the rate constant when the same system was studied by both techniques. To be more specific, the rate constants derived from cyclic voltammetry results for the dissociation of haloarene radical anions are always 100 - 1000 times greater than the same rate constant derived from pulse radiolytic results (see Table 8). A possible interpretation based upon the theory presented in this section follows.

Suppose the dissociation of $ArX^{\cdot-}$ does proceed through a second kinetically distinguishable intermediate, "X". If the UV absorption of "X" happened to be similar to $ArX^{\cdot-}$, then since pulse radiolysis relies on UV detection, the formation of "X" might go undetected. However, "X" would most likely be distinguishable from $ArX^{\cdot-}$ electrochemically.

Thus, pulse radiolysis may be measuring the rate constant for Eq. 151 while cyclic voltammetry measures the rate constant for Eq. 152, the latter process being faster by a factor of 100 or so.

$$X \longrightarrow Ar\cdot \qquad (151)$$

$$Ar\text{-}X^{\cdot-} \longrightarrow X \qquad (152)$$

Since pulse radiolysis indicates a variation in rate constant with the leaving group, based upon this interpretation, "X" would have to be some sort of aryl radical/halide pair rather than an excited aryl radical.

Thus, it may be that the $S_{RN}1$ and $S_{RN}2$ reactions derive more than their acronyms from the S_N1 and S_N2 reactions. They may also have an analogous "middle ground", a region between a pure $S_{RN}1$ and pure $S_{RN}2$ mechanism, with contributing elements of each.

VII. THE COUPLING OF RADICALS WITH NUCLEOPHILES

Having re-interpreted the intermediates in the aromatic $S_{RN}1$ reaction, it is now possible to propose simple guidelines for the coupling of radicals and nucleophiles. A large part of this discussion was begun in Chapter I, this section will now formalize these concepts into an overall theory.

It appears that the feasibility of a radical and anion undergoing a coupling reaction is determined by the nature of the anion, specifically whether it is localized or delocalized.

A. Localized Anions

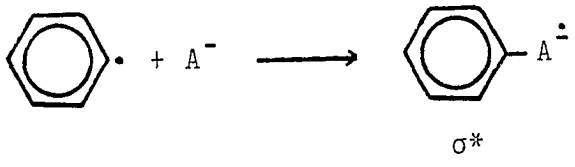
If an anion is localized, possessing a high charge density at the atom where the coupling occurs, then it is unlikely that this anion will react with a localized radical. Consider the coupling of simple alkyl radicals with A^-, a highly localized anion (Eq 153).

$$R\cdot + A^- \longrightarrow \underset{\sigma^*}{R\text{-}A^{\cdot -}} \qquad (153)$$

The coupling process, involving a 3-electron interaction, requires one of these electrons to occupy a σ^*-anti-bonding orbital. Since this will require a large amount of energy, the coupling is predicted not to

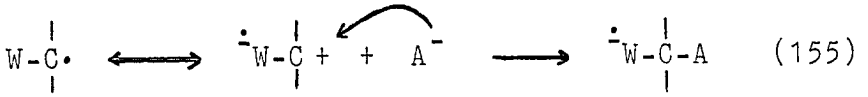
occur, or to occur slowly. Hence, it is observed that none of the anions with which simple alkyl radicals will couple (Table 4) are localized.

For the same reaction with σ-phenyl radical (Eq. 154), again the coupling is predicted not to occur for exactly the same reason. Hence, the low reactivity of $(EtO)_2PO^-$ towards σ-phenyl radical is explained.

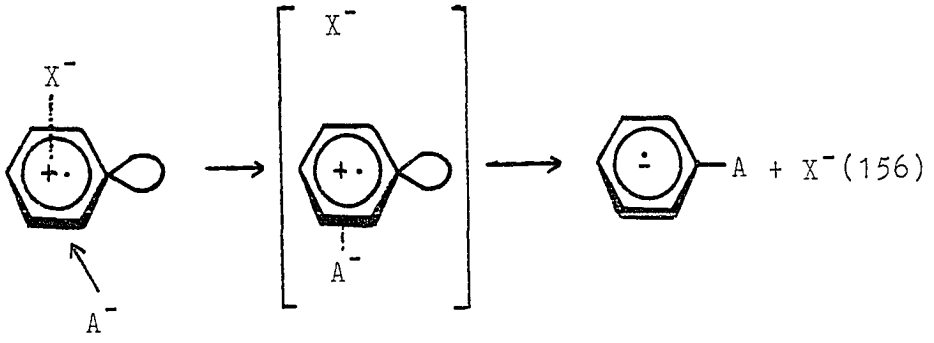


(154)

In coupling reactions involving alkyl radicals substituted with an electron withdrawing group, coupling with a localized anion (Eq. 155) is facile. Similarly, invoking an intermediate "X" in the aromatic $S_{RN}1$ reaction allows the coupling to a localized anion to be rationalized (Eq. 156).



(155)

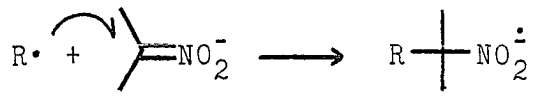


(156)

It seems reasonable to expect the reactivity of A^- now to parallel basicity--the more basic anions being more reactive. Thus, the contention in Chapter I regarding Table 4 that the intermediate in the aromatic $S_{RN}1$ reaction tended more to resemble stabilized rather than simple-alkyl radicals in terms of reactivity towards nucleophiles is supported by this theory.

B. Delocalized Anions

If an anion is delocalized, having its negative charge spread over several atoms and removed from the site of coupling, then such an anion is likely to couple with a localized radical. Such a process is best viewed as the addition of a radical to a π-system. Consider the coupling reaction of a simple alkyl radical with nitronate (Eq. 157):



(157)

Delocalization of the negative charge into the nitro group minimizes the 3-electron interaction in the approach of R· to nitronate. In Table 4 (Chapter I), it is apparent that <u>all</u> anions that have been shown to trap simple alkyl radicals are delocalized. A similar rationale explains the high reactivity of σ-phenyl radical towards nitronate (Eq. 158).

(158)

In terms of the reactivity of delocalized anions towards the intermediate "X" in the aromatic $S_{RN}1$ reaction, it is theorized that nitronate and thiophenoxide anions do not trap this intermediate because they are substantially less basic than $(EtO)_2PO^-$. Thus, delocalized anions are predicted to have low reactivity towards "X" because of lowered basicity.

C. Conclusion

The criterion for predicting whether a given radical and nucleophile will couple reduces to a very simple concept. The coupling is favorable when a 3-electron interaction between the radical ($R\cdot$) and nucleophile ($N:^-$) can be minimized.

CHAPTER III. EXPERIMENTAL

I. GENERAL CONSIDERATIONS

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Analytical gas chromatography (GLC) was performed on a Varian 3700 equipped with a Hewlett-Packard 3390A integrator. Preparative GLC was performed on an Aerograph model A-90-P gas chromatograph. High resolution mass spectra (HRMS) were recorded on an AEI MS 902 mass spectrometer. GC mass spectra (GCMS) were recorded on a Finnegan 4000 instrument. ^{1}H NMR (60 MHz) were recorded on a Varian A-60, Varian EM-360 or a Hitachi-Perkin Elmer R-20B instrument. ^{1}H NMR (300 MHz) were recorded on a Bruker WM-300. Infrared spectra (IR) were recorded on a Beckman 4250 spectrophotometer.

Diethyl phosphite, 2-nitropropane, potassium tert-butoxide, 18-crown-6, diphenyl sulfide and α-methyl styrene were purchased from Aldrich Chemical Co. Iodobenzene and benzenethiol were products of Eastman Organic. Tetralin was obtained from Matheson, Coleman and Bell. Cumene was a product of Phillips 66.

The preparations of 4-phenyl-1-butene (122), 1-methylindane (123), 4-(o-iodophenyl)but-1-ene (97), 2-chlorotetrahydronaphthalene (124), 2,3-dimethyl-2,3-diphenylbutane (125), o-iodophenyl allyl ether (97), diethyl phenylphosphonate (126), and PAT (99) were

as described in the literature.

Solvents were obtained from Fischer or Baker. Me_2SO was distilled from CaH_2 and stored over 4 A molecular sieves (under N_2). THF was distilled immediately before use from $LiAlH_4$.

Hydrogenations were carried out in a Vortex low pressure hydrogenator. Irradiations were carried out in a Rayonet (RPR-100) photochemical reactor equipped with 10 - 15 350 nm bulbs. PAT thermolyses were carried out in an Ultra Kryomat TK-30D constant temperature circulating bath at 45 C.

For reactions in Me_2SO, a general workup procedure was followed. The reaction mixture was poured onto 100 - 200 ml 10% NaCl (aq.), dried over $MgSO_4$, and evaporated on a rotary evaporator (bath at ambient temperature).

Benzene and chlorobenzene were analyzed by GLC utilizing a column composed of 7% Bentone 34 and 7% diisodecyl phthalate on Chromosorb W. Using a temperature program (50° - 125° at 5°/min.) the retention times of benzene and chlorobenzene were 3.8 and 5.3 min. respectively. For reactions in d_6-Me_2SO where deuterobenzene (Ph-D) was a product, the sample was further analyzed by GCMS at 20 eV. The ratio of the m/e peaks 79/78, after correcting for the M+1 of Ph-H, were assumed equal to the ratio Ph-D/Ph-H.

The GLC conditions, columns and retention times for non-volatile products of reactions involving PhI or PAT and 4-(o-iodophenyl)but-1-ene are presented in Tables 44 and 45 respectively.

Table 44. Retention times for products of reactions involving PhI or PAT

Compound	Retention time (min.)[a]
cumene	1.61
α-methylstyrene	2.01
iodobenzene	3.10
2-nitrocumene	4.91
diethyl phenylphosphonate	6.49
2,3-dimethyl-2,3-diphenylbutane	9.01
α-(triphenylmethyl)cumene	16.60
diphenyl sulfide	7.28

[a]Column: 7% OV-3 (1/8" × 5'). Temperature: 100 - 310° (15°/min.). He flow: 20 cc/min.

Table 45. Retention times for products of reactions involving 4-(o-iodophenyl)but-1-ene

Compound	Retention time (min.)[a]
4-phenylbut-1-ene	5.24
1-methylindane	5.97
tetralin	6.16
4-(o-iodophenyl)but-1-ene	10.59
4-(o-(phenylthio)phenyl)but-1-ene	16.59
4-(o-(diethoxyphosphinyl)phenyl)-but-1-ene	14.77
1-(phenylthiomethyl)indane	18.75
1-((diethoxyphosphinyl)methyl)indane	16.88
2-(phenylthio)tetrahydronaphthalene	19.06
1,2-di(1-indanyl)ethane	20.26

[a]Column: 15% OV-3 (1/8" × 10'). Temperature: 100 - 300°(hold) at 10°/min. He flow: 20 cc/min.

II. REACTIONS INVOLVING PAT OR PhI

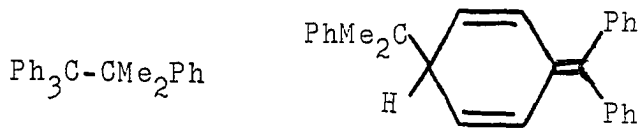
A. Preparation of Materials: 2-Nitrocumene and α-(Triphenylmethyl)cumene

PAT (2.0 g, 5.7 mmol) was added to a solution of the lithium salt of 2-nitropropane (0.9 g, 9.5 mmol) in 50 mL Me_2SO, and heated at 45 C for two days. After workup, the resulting residue was column chromatographed (alumina, hexane) to give α-nitrocumene and two isomers of a 1:1 adduct of $(C_6H_5)_3C$ and $C_6H_5CMe_2$.

α-Nitrocumene had bp 127 C/31 torr, lit. 103 C/9 torr (127, 128); ^{1}H NMR ($CDCl_3$) δ 7.4 (5 H, s), 2.0 (6 H, s); GCMS m/e (relative intensity) 120 (9.8), 119 (M^+ - NO_2, 100), 103 (12.2), 91 (89.2), 77 (19.7), 65 (5.8).

The two isomers of the 1:1 adduct of Ph_3C and $PhCMe_2$ presumably had the structures (108) and (109), separable only by capillary GLC. The mixture gave a ^{1}H NMR spectrum consistent with a 3.5/1 ratio of (108)/(109). The mixture gave ^{1}H NMR ($CDCl_3$) δ 7.0 - 7.5 (24.5 H, m), 5.5 (1.1 H, s), 2.1 (0.2 H, s), 1.6 (6.8 H, s); IR (KBr) 3059 (m), 3024 (m), 2968 (m), 1599 (m), 1508 (m), 1495 (m), 1448 (s), 1074 (m), 1030 (m), 1020 (m), 764 (m), 754 (m), 700 (s),

609 (m) cm^{-1}; GCMS of major isomer m/e (relative intensity) 363 (3.4), 362 (M^+, 12.6), 285 (3.1), 253 (2.8), 228 (2.4), 215 (2.6), 191 (6.2), 178 (13.2), 174 (26.3), 167 (100), 165 (86.9), 152 (37.9), 91 (60.1); GCMS of minor isomer m/e (relative intensity) 363 (3.98), 362 (M^+, 13.6), 285 (3.3), 253 (3.0), 228 (2.3), 215 (2.5), 191 (6.1), 178 (13.2), 174 (20.8), 167 (100), 165 (85.8), 152 (38.2), 91 (60.5); HRMS of mixture of isomers, m/e calculated for $C_{28}H_{26}$ 362.20358, found 362.20328, error -0.8 ppm.



108 109

B. Reactions of Anions (A^-)
with PAT or PhI
Under a Variety of Conditions
(A^- = PhS^-, $(EtO)_2PO^-$, or $Me_2C{=}NO_2^-$)

1. Preparation of standard anion solutions

a. K^+ or K^+/18-crown-6 counter-ion Potassium tert-butoxide, and in some instances 18-crown-6, were placed in a 25 - 50 mL volumetric flask, sealed with a septum and flushed with dry nitrogen. Dry, de-oxygenated Me_2SO was added to bring the volume to about 80% of

capacity, and the solution agitated until all the base was dissolved. The appropriate quantity of A-H (A-H = PhSH, $(EtO)_2P(O)H$, or 2-nitropropane) was injected via syringe, followed by Me_2SO.

b. Li^+ salt of 2-nitropropane The lithium salt of 2-nitropropane was placed in a volumetric flask, sealed with a septum and flushed with dry nitrogen. Dry, de-oxygenated Me_2SO was added to bring the solution to the appropriate volume.

2. Reactions of anions (A^-) with PhI

An appropriate quantity of PhI was placed in a glass ampule, flushed with nitrogen and sealed with a septum. Any additional reagents (PhSH in some cases where $A^- = PhS^-$) were added at this point. The appropriate quantities of standard A^- solution and Me_2SO were added so as to reach the desired overall concentration (volumes were assumed to be additive).

The solution was de-oxygenated (three freeze-pump-thaw cycles) and the ampule sealed with a torch. The solutions were irradiated at 350 nm for the appropriate period of time. Afterward, the solutions were frozen and the ampules opened.

For the analysis of benzene, the appropriate quantity of internal standard was added and the mixture

analyzed directly by GLC. For experiments in the presence of CCl_4, chlorobenzene was analyzed in an analogous manner. In experiments carried out in d_6-Me_2SO, the procedure was identical except the mixture was further analyzed by GCMS (see General Considerations).

For the analysis of non-volatile products (everything except PhH, PhD or PhCl), the solution was worked up in the usual manner (see General Considerations), the appropriate quantity of internal standard added and the resulting residue analyzed by GLC.

3. Thermolysis of PAT in the presence of anions (A^-)

The procedure followed for the PAT reactions was identical to the PhI experiments except PAT was substituted for PhI.

In experiments where additional reagents (o-dicyanobenzene, m-dinitrobenzene, azobenzene and 4-(o-iodophenyl)but-1-ene in the diethyl phosphite experiments; PhSH and CCl_4 in some of the PhS^- experiments), were employed, the reagents were introduced with the PAT.

C. Reactivity of Several Reagents Towards Phenyl Radical Generated from PAT

An appropriate quantity of PAT and the desired reagent (PhSH, PhSSPh, d_6-Me_2SO, PhI or 18-crown-6)

was introduced into a glass ampule and dissolved in an accurately known volume of CCl_4. The resulting solutions were de-oxygenated (three freeze-pump-thaw cycles) and the ampule sealed with a torch. PAT was decomposed for ten half-lives (24 - 27 h) at 45 C. Afterward, the solutions were frozen and the ampules opened. The appropriate quantity of internal standard was added and the reaction mixture analyzed directly by GLC. In the d_6-Me_2SO experiment, the reaction mixture was subjected to further GCMS analysis.

D. Competition Experiments Between Two Anions (A^-, B^-) For Intermediates in the $S_{RN}1$ Reaction of PhI or for Phenyl Radical from PAT

1. Preparation of standard A^-, B^- solutions

a. $A^- = PhS^-$, $B^- = Me_2C{=}NO_2^-$ Potassium tert-butoxide and 18-crown-6 were placed in a volumetric flask (25 - 50 mL), sealed with a septum and flushed with dry nitrogen. Dry, deoxygenated Me_2SO was added to bring the volume to about 80% of capacity, and the flask agitated until the complete dissolution of the base. An appropriate quantity of benzenethiol was injected, and the flask agitated. Shortly afterward, 2-nitropropane was added followed by the remaining Me_2SO.

b. $\underline{A^-}$ = $\underline{Me_2C{=}NO_2^-}$, $\underline{B^-}$ = $\underline{(EtO)_2PO^-}$ The procedure for the preparation of the standard nitronate/diethyl phosphite anion solutions was identical to the preparation of the nitronate/thiophenoxide solutions. In all cases, 2-nitropropane was added to the $Me_2SO/\underline{t}\text{-}BuO^-$ solution before diethyl phosphite.

c. $\underline{A^-}$ = $\underline{PhS^-}$, $\underline{B^-}$ = $\underline{(EtO)_2PO^-}$ The procedure for the preparation of standard $PhS^-/(EtO)_2PO^-$ was identical to that for $PhS^-/Me_2C{=}NO_2^-$. In all cases, thiophenol was added to the $\underline{t}\text{-}BuO^-/Me_2SO$ solution before $(EtO)_2PO^-$.

2. Reactions with iodobenzene

An appropriate quantity of PhI was placed in a glass ampule, flushed with dry nitrogen and sealed with a septum. The appropriate quantities of A^-/B^- standard solution and Me_2SO were injected so as to achieve the desired concentration (volumes again were assumed additive).

The solutions were de-oxygenated (three freeze-pump-thaw cycles) and the ampule sealed with a torch. The solutions were irradiated at 350 nm for the appropriate time period. Afterward the solution was frozen and the ampules opened. The analysis of benzene was accomplished by directly injecting the reaction mixture onto the GC, after the addition of internal standard. The non-volatiles (Ph-A, Ph-B) were analyzed after

workup and the addition of internal standard, by GLC. In all cases, the results were further checked by GCMS analysis of the reaction mixture to further ensure the assignments of product peaks in the GC trace.

3. Reaction with PAT

The procedure for the PAT experiments was identical to that for the PhI experiments except:

(a) PAT was substituted for PhI.

(b) Solutions were heated at 45 C in the dark for ten half-lives of PAT (24 - 27 h).

4. Reaction with PAT (in the presence of PhI)

These procedures were analogous to PhI alone, except that PAT was added along with PhI and heated at 45 C in the dark for 24 - 27 h.

III. REACTIONS INVOLVING o-IODOPHENYL ALLYL ETHER

A. Attempted Reaction of o-Iodophenyl Allyl Ether with the Anion of Diethyl Phosphite

o-Iodophenyl allyl ether (1.0 g, 3.9 mmol) was added to a solution of potassium tert-butoxide (0.95 g, 7.8 mmol) and diethyl phosphite (1.1 g, 7.8 mmol) in 40 mL dry Me_2SO under nitrogen. The reaction mixture was irradiated at 350 nm for 25 h. Workup afforded a complex mixture containing what appeared to be 1-iodo-2-hydroxyl-3-(2'-propenyl)benzene (71) as the major product judging from a crude ^1H NMR absorbance at 12.2 ($CDCl_3$, δ); GCMS m/e (relative intensity) 261 (5.5), 260 (M^+, 55.0), 220 (14.6), 191 (20.2), 133 (42.4), 127 (9.4), 119 (19.1), 105 (94.0), 92 (87.9), 77 (34.1), 63 (100).

No attempt was made to isolate or characterize this product further.

B. Attempted Reaction of o-Iodophenyl Allyl Ether with the Anion of 2-Nitropropane

o-Iodophenyl allyl ether (1.0 g, 3.9 mmol) was added to a solution of the lithium salt of 2-nitropropane (0.56 g, 5.9 mmol) in 40 mL dry Me_2SO. Irradiation of

the reaction mixture for 3 h at 350 nm resulted in no reaction as judged by ^{1}H NMR and GLC.

C. Reaction of o-Iodophenyl Allyl Ether with Acetone Enolate

o-Iodophenyl allyl ether (1.0 g, 3.9 mmol) was added to a solution of potassium tert-butoxide (1.0 g, 8.9 mmol) and acetone (0.47 g, 8.1 mmol) in 40 mL dry Me_2SO. The reaction mixture was irradiated at 350 nm for 3 h.

Workup and column chromatography (Baker 1-3404 silica gel, benzene) afforded two compounds, o-iodophenyl 1-propenyl ether and o-acetonylphenyl 1-propenyl ether.

o-Iodophenyl 1-propenyl ether had ^{1}H NMR ($CDCl_3$) δ 6.75 - 8.0 (4 H, m), 6.30 - 6.55 (1 H, m), 4.75 - 5.25 (1 H, m), 1.8 (3 H, dd, J = 7 Hz, J = 1.7 Hz); IR (NaCl plates) 3050 (m), 2920 (m), 1670 (m), 1585 (m), 1472 (s), 1445 (m), 1395 (m), 1260 (m), 1025 (m), 735 (s), 710 (w) cm^{-1}; GCMS m/e (relative intensity) 261 (7.9), 260 (M^+, 81.0), 231 (4.3), 220 (59.0), 203 (5.6), 191 (7.2), 131 (16.1), 105 (100), 92 (38.2).

o-Acetonylphenyl 1-propenyl ether had ^{1}H NMR ($CDCl_3$) δ 6.95 = 7.5 (4 H, m), 6.3 - 6.6 (1 H, m), 4.25 - 4.75 (1 H, m), 2.2 (3 H, s), 1.8 (3 H, dd, J = 7 Hz, J = 1.7 Hz); IR (NaCl plates) 3030 (w), 2910 (w), 2870(w), 1735 (s), 1680 (m), 1600 (m), 1500 (m), 1262 (s), 1130 (m), 1028 (m), 760 (s) cm^{-1}; GCMS m/e

(relative intensity) 191 (3.3), 190 (M^+, 24.9), 147 (16.4), 91 (100), 77 (25.2).

D. Reaction of o-Iodophenyl Allyl Ether with 0.21 M Thiophenoxide Ion

o-Iodophenyl allyl ether (2.0 g, 7.7 mmol) was added to a solution of potassium tert-butoxide (2.2 g, 20 mmol) and thiophenol (2.1 g, 19 mmol) in 90 mL dry Me_2SO under nitrogen. Irradiation of the reaction mixture for 19 h followed by workup and column chromatography (Baker 1-3404 silica gel, hexane) afforded 3-methyl-2,3-dihydrobenzofuran and 3-(thiophenylmethyl)-2,3-dihydrobenzofuran in yields of 34 and 43% respectively.

3-Methyl-2,3-dihydrobenzofuran gave ^1H NMR ($CDCl_3$) δ 6.4 - 7.1 (4 H, m), 4.45 (1 H, m), 3.85 (1 H, m), 2.95 - 3.65 (1 H, m), 1.18 (3 H, d); IR (NaCl plates) 3050 (m), 3030 (m), 2960 (s), 2930 (s), 2890 (s), 1600 (s), 1483 (s), 1415 (s), 1401 (s), 1379 (m), 1330 (m), 1220 (s), 1100 (m), 1018 (s), 960 (m), 835 (m), 748 (s) cm^{-1}; HRMS m/e calculated for $C_9H_{10}O$ 134.07317, found 134.07331, error +1.1 ppm; bp 90 - 93 C/16 torr. ^1H NMR and bp data match that of the literature (123) for 3-methyl-2,3-dihydrobenzofuran.

3-(Thiophenyl)-2,3-dihydrobenzofuran gave

bp 203 - 205/10 torr; ^{1}H NMR ($CDCl_3$) δ 6.4 - 7.3 (4 H, m), 3.95 - 4.55 (2 H, m), 3.1 - 3.6 (1 H, m), 2.45 - 3.15 (2 H, m); IR (NaCl plates) 3050 (m), 2950 (m), 2915 (m), 2885 (m), 1600 (s), 1480 (s), 1440 (m), 1228 (s), 1085 (m), 962 (m), 790(s), 690 (s) cm^{-1}; HRMS m/e calculated for $C_{15}H_{14}OS$ 242.07654, found 242.07609, error -1.9 ppm. This compound has been reported in the literature, but no spectral data or physical constants were given (96).

E. Attempted Reaction of o-Iodophenyl Allyl Ether with 0.75 M Thiophenoxide Ion

o-Iodophenyl allyl ether (3.2 g, 0.012 mol) was added to a solution of potassium tert-butoxide (13.8 g, 0.12 mol) and benzenethiol (13.2 g, 0.12 mol) in 160 mL dry Me_2SO under nitrogen. After irradiation at 350 nm for 13 h and workup, a crude ^{1}H NMR of the reaction mixture revealed an doublet of doublets at δ 1.8 ($CDCl_3$, J = 7 Hz, J = 1.7 Hz) characteristic of the rearranged allyl ether ($OCH{=}CHCH_3$).

In addition to the main products, 3-methyl-2,3-dihydrobenzofuran, 3-thiophenyl-2,3-dihydrobenzofuran and o-iodophenyl 1-propenyl ether, two additional minor products were tentatively assigned : o-(phenylthio)-phenyl allyl ether and o-(phenylthio)phenyl allyl ether.

o-(Phenylthio)phenyl allyl ether was assigned based upon GCMS m/e (relative intensity) 243 (7.5), 242 (M^+, 57.6), 201 (100), 183 (32.5), 171 (28.0), 129 (57.3). Similarly, o-(phenylthio)phenyl 1-propenyl ether was assigned based upon GCMS m/e (relative intensity) 243 (4.5), 242 (M^+, 34.6), 227 (3.3), 201 (100), 184 (48.1), 137 (94.4), 129 (43.4), 105 (66.1), 96 (98.8). No attempts were made to confirm these assignments.

IV. REACTIONS INVOLVING 4-(o-IODOPHENYL)BUT-1-ENE

A. Preparation of Materials

1. Preparative scale reaction of 4-(o-iodophenyl)-but-1-ene and thiophenoxide

4-(o-Iodophenyl)but-1-ene (4.2 g, 0.016 mol) was added to a solution of potassium tert-butoxide (5.1 g, 0.045 mol) and benzenethiol (4.4 g, 0.040 mol) in 100 mL dry Me_2SO. After overnight irradiation at 350 nm, workup and preparative GLC (1/4" × 20', 20% OV-3, 250 C) analytical samples of 4-[o-(phenylthio)phenyl]but-1-ene and 1-(phenylthiomethyl)indane were obtained.

4-[o-(Phenylthio)phenyl]but-1-ene had ^1H NMR ($CDCl_3$) δ 7.0 - 7.4 (9 H, m), 5.4 - 6.2 (1 H, m), 4.7 - 5.2 (2 H, m), 2.6 - 3.1 (2 H, m), 2.0 - 2.5 (2 H, m); IR (NaCl plates) 3040 (m), 2990 (m), 2960 (m), 2910 (m), 2900 (m), 1644 (m), 1583 (m), 1476 (m), 1441 (m), 1022 (m), 900 (m), 731 (s), 682 (m) cm^{-1}; GCMS m/e (relative intensity) 242 (1.46), 241 (5.78), 240 (M^+, 34.4), 211 (22.2), 197 (100), 165 (17.8); HRMS m/e calculated for $C_{16}H_{16}S$ 240.09728, found 240.09738, error +0.4 ppm.

1-(Phenylthiomethyl)indane had ^1H NMR (60 MHz, $CDCl_3$) δ 7.0 - 7.5 (9 H, m), 2.7 - 3.5 (4 H, m), 1.6 - 2.5

(3 H, m); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.83 (1 H, tt, 15.2 Hz, 7.7 Hz); IR (NaCl plates) 3175 (m), 3120 (m), 2945 (m), 2850 (m), 1578 (m), 1470 (s), 1430 (m), 1080 (m), 1015 (m), 728 (s), 682 (m) cm^{-1}; GCMS m/e (relative intensity) 242 (0.28), 241 (1.15), 240 (M^+, 6.97), 131 (10.9), 124 (12.5), 117 (100); HRMS m/e calculated for $C_{16}H_{16}S$ 240.09728, found 240.09738, error +0.4 ppm.

2. Synthesis of 1-(thiomethyl)indane by an alternate route

a. Preparation of 1-(hydroxylmethyl)indane Indene (13.9 g, 0.120 mol) was added to a solution containing n-BuLi (0.14 mol) in 150 mL THF at -78 C under nitrogen. The solution was warmed to -23 C, and an excess of formaldehyde, generated from the heating of para-formaldehyde (5.0 g, 0.17 mol CH_2O), was bubbled through the solution. The reaction mixture was quenched with saturated NH_4Cl (aq.), the organic layer washed with 10% NaCl (aq.), dried ($MgSO_4$) and evaporated. Overnight hydrogenation of the resultant residue (∿5.9 g) with 0.6 g 10% Pd/C in 170 mL ethanol at 50 psi, removal of the catalyst by filtration through Celite, evaporation of solvent and distillation (88 - 91 C/0.6 torr) afforded 7.0 g 1-(hydroxymethyl)indane): ^{1}H NMR ($CDCl_3$) δ 7.1 (4 H, s), 3.6 (2 H, d, J = 6 Hz), 1.7 - 3.45 (5 H, m);

IR (NaCl plates) 3300 (br), 3060 (m), 3010 (m), 2920 (m), 2840 (m), 1450 (m), 1015 (s), 735 (s) cm^{-1}.

b. Preparation of 1-(bromomethyl)indane To a solution of 1-(hydroxylmethyl)indane (5.4 g, 0.036 mol) in 40 mL ether at 0 C was added PBr_3 (4.3 g, 0.016 mol). The solution was allowed to warm to room temperature and stirred for 4 h. The reaction mixture was poured onto ice and extracted twice with 50 mL ether. The combined ether extracts were washed with 10% NaCl (aq.), dried over $MgSO_4$, and evaporated. The crude liquid was distilled (58 - 62 C/0.01 torr) yielding 3.0 g of the alkyl bromide ^1H NMR ($CDCl_3$) δ 7.1 (4 H, s), 3.8 (2 H, d, J = 6 Hz), 1.75 - 3.5 (5 H, m).

c. Preparation of 1-(phenylthiomethyl)indane 1-(Bromomethyl)indane (0.88 g, 4.2 mmol) was added to a solution containing potassium tert-butoxide (1.1 g, 9.8 mmol) and thiophenol (1.1 g, 9.4 mmol) in 25 mL dry Me_2SO. After 2 h, the reaction mixture was worked up in the usual manner. Column chromatography (Baker 1-3404 silica gel, hexane) yielded 0.65 g of the desired sulfide: ^1H NMR ($CDCl_3$) δ 6.95 - 7.5 (9 H, m), 2.7 - 3.45 (4 H, m), 1.6 - 2.5 (3 H, m); GCMS m/e (relative intensity) 242 (0.3), 241 (1.2), 240 (M^+, 6.9), 131 (10.9), 124 (12.7), 117 (100). It should be noted that the product of this reaction was identical in all

respects to 1-(phenylthiomethyl)indane produced in the reaction of PhS^- with 4-(o-iodophenyl)but-1-ene.

3. Preparation of 2-(phenylthio)tetrahydronapthalene

2-Chlorotetrahydronaphthalene (1.4 g, 8.4 mmol) was added to a solution containing potassium tert-butoxide (2.2 g, 0.021 mol) in 50 mL dry Me_2SO. After stirring overnight at ambient temperature, the reaction mixture was worked up in the usual manner. Column chromatography (Baker 1-3404 silica gel, hexane) afforded the desired sulfide: ^1H NMR ($CDCl_3$) δ 6.9 - 7.8 (9 H, m), 3.1 - 3.75 (1 H, m), 2.55 - 3.0 (4 H, m), 1.4 - 2.4 (2 H, m); IR (NaCl plates) 3055 (m), 3010 (m), 2920 (m), 2838 (m), 1575 (m) 1490 (m), 1470 (m), 1445 (m), 1430 (m), 1330 (w), 1285 (w), 1260 (w), 1220 (w), 1100 (w), 1080 (m), 1060 (w), 1015 (m), 940 (w), 910 (w), 810 (w), 725 (s), 680 (s) cm^{-1}; GCMS m/e (relative intensity) 242 (0.73), 241 (2.39), 240 (M^+, 13.3), 131 (100), 115 (21.0), 91 (32.5); HRMS m/e calculated for $C_{16}H_{16}S$ 240.09728, found 240.09744, error +0.7 ppm.

4. Preparation of 1,2-(di-1-indenyl)ethane

Freshly distilled indene (2.0 g, 17 mmol) was added to a solution of n-BuLi (0.017 mol) in 30 mL dry THF at -78 C under nitrogen. After 1 h, ethylene dibromide (1.5 g, 7.7 mmol) was added. The solution

was allowed to warm to room temperature whereupon it was quenched with saturated NH_4Cl (aq.). Ether (50 mL) was added and the organic layer separated, washed with 10% NaCl (aq.), dried ($MgSO_4$) and evaporated. After two recrystallizations of the crude solid from ethanol, 0.5 g (25%) of a pale yellow solid (mp 119.5 - 120 C) was obtained: ^{1}H NMR ($CDCl_3$) δ 6.9 - 7.5 (8 H, m), 6.2 (2 H, br s), 2.85 (8 H, br s); GCMS m/e (relative intensity) 259 (2.31), 258 (M^+, 11.40), 130 (67.4), 129 (53.3), 128 (100).

5. Preparation of 1,2-(di-1-indanyl)ethane

A solution of diindenylethane (0.33 g, 1.3 mmol) and 0.1 g 10% Pd/C in 20 mL ethyl acetate was hydrogenated overnight at 50 psi. The catalyst was removed by filtration through Celite. After evaporation of solvent and kugelrohr distillation of the resultant oil (174 - 180 C/0.4 torr), 0.30 g (88%) of a colorless oil, which crystallized on standing, was obtained: ^{1}H NMR ($CDCl_3$) δ 7.1 (8 H, s), 1.0 - 2.9 (14 H, m); IR ($CHCl_3$) 3060 (m), 3020 (m), 2920 (m), 2860 (m), 1600 (m), 1500 (m), 780 (s); GCMS m/e (relative intensity) 263 (0.74), 262 (M^+, 6.04), 157 (3.99), 130 (9.42), 117 (100), 91 (18.80).

6. Preparation of 4-[o-(diethoxyphosphinyl)phenyl]but-1-ene and 1-[(diethoxyphosphinyl)methyl]indane

4-(o-Iodophenyl)but-1-ene (1.47 g, 5.7 mmol) was added to a solution of potassium tert-butoxide (1.8 g, 0.016 mol), benzenethiol (0.62 g, 5.7 mmol) and diethyl phosphite (1.2 g, 8.5 mmol) in dry Me_2SO (50 mL) under nitrogen. After 18 h of irradiation at 350 nm, usual workup and flash chromatography (Woelm silica gel, 3:1 ethyl acetate/hexane) an oil containing a mixture of the title compounds was obtained. Flash chromatography (Woelm silica gel, hexane) of this oil yielded as pure compounds:

4-[o-(diethoxyphosphinyl)phenyl]but-1-ene: ^1H NMR ($CDCl_3$) δ 7.0 - 7.4 (4 H, m), 5.4 - 6.5 (1 H, m), 4,8 - 5.2 (2 H, m), 4.3 (4 H, m), 1.5 - 3.1 (4 H, m), 1.3 (6 H, t); IR (NaCl plates) 3070 (m), 2980 (m), 2960 (m), 2860 (m), 1630 (m), 1585 (m), 1460 (m), 1430 (m), 1235 (s), 1010 (s), 780 (s), 740 (s) cm^{-1}; GCMS m/e (relative intensity) 268 (M^+, 21.7), 211 (42.1), 171 (85.6), 153 (73.9), 139 (55.2), 130 (100), 91 (34.1); HRMS m/e calculated for $C_{14}H_{21}PO_3$ 268.12293, found 268.12331, error +1.4 ppm.

1-[(diethoxyphosphinyl)methyl]indane: ^1H NMR ($CDCl_3$) δ 7.1 (4 H, br s), 4.1 (4 H, m), 1.5 - 3.2 (7 H, m), 1.3 (6 H, t); IR (NaCl plates) 3080 (m), 3050 (m), 3030 (m), 2990 (m), 2940 (m), 2900 (m),

2860 (m), 1470 (m), 1450 (m), 1240 (m), 1160 (m), 1020 (s), 800 (s), 750 (s) cm^{-1}; GCMS m/e (relative intensity) 269 (0.69), 268 (M^+, 10.7), 239 (10.0), 211 (12.2), 131 (48.9), 130 (100), 115 (30.7); HRMS m/e calculated for $C_{14}H_{12}PO_3$ 268.12293, found 268.12331, error +1.4 ppm.

B. Reactions Involving the Generation of o-Butenyl Phenyl Radical from Organotin Reagents

1. Tri-n-butyltin hydride reduction of 4-(o-iodophenyl)-but-1-ene

a. Initiated by PAT In a typical procedure, 4-(o-iodophenyl)but-1-ene (0.30 g, 0.66 mmol) was added to a solution of PAT (0.010 g, 0.03 mmol) in 8.9 mL of solvent (PhH or Me_2SO) under nitrogen. Tri-n-butyltin hydride (1.4 g, 4.9 mmol) was added and the solution heated at 45 - 55 C for 1 h. An appropriate quantity of internal standard was added, and the reaction mixture analyzed directly by GLC.

b. Photoinitiated The procedure for the photoinitiated reactions was identical to that described above except PAT was absent and the solutions were irradiated at 350 nm for 3 h.

2. Tri-n-butyltin hydride reduction of 4-(o-iodophenyl)but-1-ene in the presence of added H-atom donors (R-H)

a. Typical procedure (R-H = $PhCH_3$) To a 25 mL volumetric flask containing n-Bu_3SnH (1.85 g, 6.37 mmol) was added a measured volume of toluene and enough benzene to bring the solution to volume. 4-(o-Iodophenyl)but-1-ene (0.15 g, 0.57 mmol) was added and the resulting solution irradiated at 350 nm for 3 h. An appropriate quantity of internal standard was added and the reaction mixture analyzed directly by GLC.

3. Reaction of 4-(o-iodophenyl)but-1-ene with $(n\text{-}Bu_3Sn)_2$

4-(o-Iodophenyl)but-1-ene (0.15 g, 0.57 mmol) was added to a solution containing $(n\text{-}Bu_3Sn)_2$ (0.34 g, 0.59 mmol) and Me_2SO (4.4 g, 0.056 mol) in 6 mL PhH. After irradiation at 350 nm for 28 h, the reaction mixture was poured onto 100 mL 10% NaCl (aq.), extracted twice with 50 mL ether, dried ($MgSO_4$) and evaporated. The resultant residue was analyzed by GLC.

C. Irradiation of 4-(o-Iodophenyl)but-1-ene in the Presence of Thiophenoxide: General Procedures

A standard solution of PhS^-K^+ or PhS^-K^+/18-crown-6 in Me_2SO was prepared in the manner described previously.

1. Product formation with respect to time--typical procedure

To a large test-tube that was flushed with nitrogen and sealed with a septum was added 100 mL of standard thiophenoxide/Me_2SO solution. 4-(o-Iodophenyl)but-1-ene (0.34 g, 1.3 mmol) was added and the resulting solution irradiated at 350 nm. Irradiation was interupted at various times during the reaction, and a 15 mL aliquot of the reaction mixture was removed via syringe. After workup in the usual manner and addition of an internal standard, the aliquot was analyzed by GLC.

2. Product yields as a function of PhS^- concentration--typical procedure

A 50 mL round bottomed flask containing diphenyl disulfide (0.060 g, 2.8 mmol) was flushed with dry nitrogen and sealed with a septum. The appropriate volumes of 0.40 M PhS^-K^+/18-crown-6 in Me_2SO and Me_2SO were injected so as to reach the desired PhS^- concentration and a total volume of 25 mL. 4-(o-Iodophenyl)but-1-ene (0.066 g, 0.26 mmol) was injected and the solution irradiated at 350 nm for 1 h. After workup and the addition of an appropriate internal standard, products were analyzed by GLC.

D. Kinetics of Photolysis of 4-(o-Iodophenyl)but-1-ene in the Presence of PhS^-

4-(o-Iodophenyl)but-1-ene (0.34 g, 1.3 mmol) was added to 100 mL of a standard solution of PhS^-K^+ in Me_2SO (0.14 M or 0.35 M) and irradiated at 350 nm. At various times, exactly 10.0 μL of the solution was removed and analyzed directly by GLC and the absolute area of the peak due to starting material recorded as a function of time. Plots of ln(Area) versus time yielded a straight line, the negative of the slope of which was taken to be equivalent to the pseudo-first order rate constant for the decomposition of ArI. First order kinetics were observed for 4 - 5 half-lives.

E. Irradiation of 4-(o-Iodophenyl)but-1-ene: Products as a Function of Varying $(EtO)_2PO^-$ Concentration (in the Presence of PhS^-)

4-(o-Iodophenyl)but-1-ene (0.068 g, 0.26 mmol) was added to a standard solution of 0.973 M PhS^-K^+/18-crown-6 and $(EtO)_2PO^-K^+$/18-crown-6 (variable concentration) and irradiated at 350 nm for 1 h. After usual workup, an internal standard was added and the mixture analyzed by GLC.

APPENDIX

The aromatic $S_{RN}1$ reaction is noteworthy in that it allows the use of aromatic substrates that are non-activated for direct nucleophilic attack, and nucleophiles that are not basic enough for an aryne mechanism. Other nucleophilic aromatic substitution reactions sharing these features usually require either a catalytic or stoichiometric quantity of a transition metal.

Migita et al. report a Pd^{o} catalyzed substitution involving ArI and PhS^{-} (129). It seemed interesting to probe for the intermediacy of aryl radical in this reaction. o-Iodophenyl allyl ether (0.52 g, 2.0 mmol) was refluxed ir a solution of potassium tert-butoxide (0.40 g, 3.6 mmol), benzenethiol (0.33 g, 2.9 mmol) and $Pd(PPh_3)_4$ (0.10 g, 0.09 mmol) in ethanol (20 mL) for 4 h. After evaporation of the solvent, ether was added and the organic extract was washed with satd. $NaHCO_3$ (aq.), 10% NaCl (aq.), dried over $MgSO_4$, and evaporated. ^1H NMR and GCMS of the resulting residue indicated the products were o-iodophenol and phenyl allyl sulfide. Thus, no conclusions could be reached regarding the intermediacy of aryl radical in this reaction.

Suzuki, Abe, and Osuka report that aryl halides

undergo facile nucleophilic attack by arenethiolate in the presence of Cu(I) (130). Following their procedure, this reaction was attempted with a radical probe. Thus, 4-(o-iodophenyl)but-1-ene (0.92g, 3.6 mmol) was added to a solution of potassium tert-butoxide (0.48 g, 4.3 mmol) and benzenethiol (0.47 g, 4.3 mmol) in 6 mL dry HMPA, and heated at 100 C for 1.5 h. Afterward, the reaction mixture was poured on 100 mL 10% NaCl (aq.) and extracted with 50 mL ether. The organic layer was washed with water, dried ($MgSO_4$) and evaporated. Analysis of the resulting residue by GLC indicated the only product formed was 4-[o-(phenylthio)phenyl]-but-1-ene (76.9%), accompanied by 19.5% recovered starting material. Since $k(PhS^-)/k_5$ for o-(3-butenyl)phenyl radical was determined earlier to be 13.8 M^{-1}, it is evident that this aromatic substitution does not involve an intermediate aryl radical.

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