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ON THE $S_{RN}1$-$S_{RN}2$ MECHANISTIC POSSIBILITIES

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Abstract- For the last years there has been an increasing interest in nucleophilic substitution reactions that occur through a chain process with radicals and radical anions as intermediates. The propagation reactions proposed have been, among others, the fragmentation of the radical anion intermediate of the substrate to give a radical which reacts with the nucleophile ($S_{RN}1$ mechanism), or the reaction of this radical anion with a nucleophile to give the substitution product ($S_{RN}2$ mechanism). We will discuss further these two mechanistic possibilities.

A report has recently been published discussing mainly the literature data about nucleophilic substitution of aromatic systems that occurs by electron transfer (ET) with radical anions as intermediates ($S_{RN}1$ mechanism). The existing results were considered from a different point of view, based mostly on the stability and reactivity of certain nitrobenzene halide radical anions, and it was concluded that all the known results can also be explained by the $S_{RN}2$ mechanism.[1]

The $S_{RN}1$ mechanism was proposed in 1966 by Kornblum[2] and Russell[3] for aliphatic systems with electron withdrawing groups (EWG), and in 1970 by Bunnett[4] for aromatic systems. This is a chain mechanism that has radical and radical anions as intermediates as sketched in Scheme I.[5]

Scheme I

$$(RX)^{\cdot -} \longrightarrow R^{\cdot} + X^{-} \qquad (1)$$

$$R^{\cdot} + Nu^{-} \longrightarrow (RNu)^{\cdot -} \qquad (2)$$

$$(RNu)^{\cdot -} + RX \longrightarrow RNu + (RX)^{\cdot -} \qquad (3)$$

In the propagation cycle of the $S_{RN}1$ mechanism the fragmentation of the radical anion of the substrate to give a radical and the anion of the nucleofugal group (eq. 1) is proposed. The radical thus formed couples with the nucleophile to give the radical anion of the substitution product (eq. 2), which afterward by an electron transfer (ET) to the substrate RX continues the chain process (eq. 3).

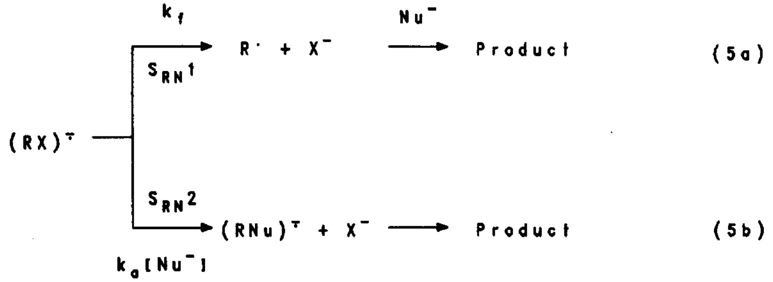
In the $S_{RN}2$ mechanism it has been proposed that the radical anion $(RX)^{\overline{\cdot}}$ does not fragment, instead it is able to react with the nucleophile to give the radical anion of the substitution product and the anion of the leaving group (eq. 4), followed by the ET to the substrate (eq. 3).[1]

$$(RX)^{\overline{\cdot}} + Nu^{-} \longrightarrow (RNu)^{\overline{\cdot}} + X^{-} \qquad (4)$$

Both mechanisms require the same initiation step, that is, the formation of the radical anion intermediate $(RX)^{\overline{\cdot}}$ (spontaneously;[5] by photostimulation;[5] by reaction with electrons from dissolution of alkali metals in liquid ammonia;[5] electrons from a cathode[6] or by sodium amalgam[7]); and both are also chain processes that give the same substitution product. In this paper we discuss some reported results taking into consideration both mechanisms.

Kinetic Considerations: Once the radical anion $(RX)^{\overline{\cdot}}$ is formed it may either fragment ($S_{RN}1$ mechanism) (eq. 5a) or react with the nucleophile ($S_{RN}2$ mechanism) (eq. 5b) as sketched in Scheme II.

Scheme II



The rate of formation of $R^\cdot$ radicals will depend on the concentration of the radical anion $(RX)^{\overline{\cdot}}$ as well as on its unimolecular rate constant of fragmentation (k_f). On the other hand, the rate of coupling of the nucleophile with the radical anion will depend on the bimolecular rate constant for the addition (k_a), on the concentration of the radical anion $(RX)^{\overline{\cdot}}$ as well as on the nucleophile.

It is well known that the rate of fragmentation of aromatic radical anions depends on the SOMO value of the π^* system and its spin distribution, as well as on the antibonding value of the aryl-leaving group bond (σ^* MO).[5b,8] For instance, in halobenzenes radical anions (chloro-, bromo- and iodo-), the rate of fragmentation is very high (ca. 10^{10} s^{-1}).[5b,8b,9] If we assume that the reaction of halobenzenes with nucleophiles takes place by the $S_{RN}2$ mechanism, at least with a ratio of $S_{RN}2/S_{RN}1$ products of 100:1, and with a concentration of the nucleophile of 10^{-2} M, as an average of the usually reported reactions, the estimated k_a must be of the order of 10^{14} s^{-1} M^{-1}.[10]

In eq. 5b the negatively charged nucleophile has to react with the radical anion on the carbon where the leaving group is attached. In these types of radical anions, such as halobenzenes, or halopyridines, etc., the carbon bonded to the leaving group has a relative large negative charge density,[11] while according to the above estimation a very large k_a

for two negatively charged reagents has to be postulated (see below).

It is therefore clear that in the case of simple halobenzenes, the $S_{RN}2$ mechanism can not compete with the $S_{RN}1$, and this also applies to haloarenes with lower fragmentation rates down to 10^5 s^{-1} (in this case the k_a must be diffusional).

Another piece of evidence is the relative reactivity of substrates toward pinacolone enolate ions.[12a] Bromobenzene has a relative reactivity of 1, with a k_f of 10^{10} s^{-1}.[12a] With substrates having the same leaving group, but lower LUMO, the rate of fragmentation decreases with an increasing relative reactivity toward pinacolone enolate anion. Further decrease of the fragmentation rate of the radical anion is accompanied by an overall decrease of the reactivity. For instance, 1-bromonaphthalene ($k_f = 10^8$ s^{-1}) reacts 198 times faster than bromobenzene. However, 4-bromobenzophenone with a $k_f = 6$ 10^2 s^{-1} reacts slower than bromobenzene.[12a] It is known that the coupling reaction of phenyl radicals with acetone enolate ions is 2.7 10^8 M^{-1} s^{-1} in liquid ammonia, whereas 1-naphthyl radical reacts with the same nucleophile at a rate constant of 4.2 10^{10} M^{-1} s^{-1}, similar to that of the 4-benzoylphenyl radical.[12b]

These results can clearly be explained considering that radicals are intermediates in this chain process. When the fragmentation rate of the radical anion intermediate is fairly slow, the overall reactivity decays.[12a]

The o-iodonitrobenzene, whose radical anion has a k_f of 8 10^4 s^{-1},[13] reacts with pinacolone enolate ions under irradiation, and it was suggested that it reacts by fragmentation of the radical anion of o-iodonitrobenzene and coupling of the radical with the nucleophile.[14] However, m-iodonitrobenzene (k_f of the radical anion equal to 0.31 s^{-1})[13] and p-iodonitrobenzene (k_f of the radical anion equal to 0.9 s^{-1})[13] did not react.

These experimental results suggest that even with long-living radical anion intermediates, the $S_{RN}2$ mechanism is not relevant because only the substrate, whose radical anion fragments fast to give radicals, reacts with the nucleophile.

On the other hand, if the o-iodonitrobenzene radical anion were the intermediate, the nucleophile would have to react with a rate of ca. 10^9 M^{-1} s^{-1} to observe substitution by the $S_{RN}2$ mechanism.

In aromatic nucleophilic substitution reactions ($S_{Ar}N$), the reaction of p-halonitrobenzenes with nucleophiles is rather slow. For instance, the rate constants for the reaction of 9-phenylfluorenide anion with p-fluoro, p-chloro and p-bromo nitrobenzenes are 4.88 10^{-2}, 8.07 10^{-3} and 1.88 10^{-2} M^{-1} s^{-1} respectively (DMSO, 25 ºC),[15a] and the rate constant of the reaction of potassium methoxide with p-chloronitrobenzene is 1.4 10^{-4} M^{-1} s^{-1} (MeOH, 18-crown-6 ether, 75 ºC).[15b] If the $S_{RN}2$ mechanism is applied, the radical anion of halonitrobenzenes, with a negative charge, is expected to react with the nucleophile, that also is negatively charged, at a rate constant several orders of magnitude higher than the neutral molecule; so this hypotesis seems unlikely.

Recently[16a] it has been reported that the photolysis of 1-iodoanthraquinone radical anion gives the reduction product anthraquinone, but this reaction is quenched in the presence of iodide ions, and these results were explained by the capture of the photogenerated anthraquinolyl radicals by iodide ions in a process analogous to the $S_{RN}1$, and based on the kinetic results the possibility of an $S_{RN}2$ process is rejected.

Electrochemical Evidences: There are many examples of electrochemically induced radical nucleophilic substitution reactions,[6] and an interesting fact is that when the rate of fragmentation of the radical anion intermediate is high, the radical intermediate is formed close to the electrode, being reduced further to the aryl anion, which is protonated to give ultimately the reduced arene (eq. 6).

$$\mathrm{ArX} \xrightarrow{e^-} (\mathrm{ArX})^{\cdot -} \xrightarrow[\text{fast}]{-X^-} \mathrm{Ar}^{\cdot} \xrightarrow{e^-} \mathrm{Ar}^- \xrightarrow{\mathrm{SH}} \mathrm{ArH} \qquad (6)$$

On the other hand, when a redox mediator M is added, which has a more positive reduction potential than the haloarene, it forms the stable radical anion $M^{\cdot -}$, which diffuses to the bulk solution (eq. 7). By an ET from $M^{\cdot -}$ to the haloarene, the radical anion $(ArX)^{\cdot -}$ is formed far from the electrode (eq. 8). With this methodology are obtained high yields of the substitution products.

$$\mathrm{M} \xrightarrow{e^-} \mathrm{M}^{\cdot -} \overset{\text{difussion}}{\rightsquigarrow} \mathrm{M}^{\cdot -}\ (\text{bulk solution}) \qquad (7)$$

$$\mathrm{M}^{\cdot -} + \mathrm{ArX} \xrightarrow{\mathrm{ET}} \mathrm{M} + (\mathrm{ArX})^{\cdot -} \longrightarrow \mathrm{Ar}^{\cdot} + X^- \qquad (8)$$

The fact that haloarenes with high fragmention rate are able to react with nucleophiles when a mediator M is used suggests that aryl radicals are the intermediates leading to products, but not their radical anions. When the haloarene radical anion does not fragment fast, it can diffuse to the bulk solution, and in this case it is not neccesary the use of a redox mediator and good yields of substitution products were found.

Also there are many kinetic evidences using electrochemical methods that favor the $S_{RN}1$ mechanism and not the $S_{RN}2$ mechanism.[6,16b]

Reactivity of Nucleophiles: In order to determine the possibility of an $S_{RN}2$ mechanism, Galli and Bunnett studied the relative reactivity of five nucleophiles for a series of substrates with a common aryl group but with different leaving groups.[17] The relative reactivity of two nucleophiles of rather different electronic character and steric requirements should be constant for the $S_{RN}1$ mechanism but variable and dependent on the leaving group for the $S_{RN}2$ process.

The mean value for the reactivity of diethyl phosphite vs. pinacolone enolate ion for six substrates, PhI, PhBr, PhCl, PhF, Ph_2S and $PhNMe_3^+$ in liquid ammonia is 1.37 (±0.11), in agreement with 1.40 as determined by Savéant et al.[18] who measured the absolute rate constants for the coupling reaction of phenyl radicals with diethyl phosphite and with acetone enolate ions in an electrochemical system.

The same behaviour was observed for the photostimulated competition of Ph_2PO^-, Ph_2P^- and PhS^- *vs.* pinacolone enolate ion with PhI, PhBr, PhCl. All of them present the same reactivity with the nucleophiles independently of the leaving group.[17]

These results clearly suggest that the nucleophiles react with a common intermediate regardless of the type of substrate being used.

It has been determined that aliphatic substrates like halobridgehead compounds,[19,20] neopenthyl halides,[21] and cycloalkyl halides[22] react with nucleophiles under photostimulation with Ph_2P^-, Ph_2As^-, PhS^-, $PhSe^-$, ketone enolate ions, etc.[23]

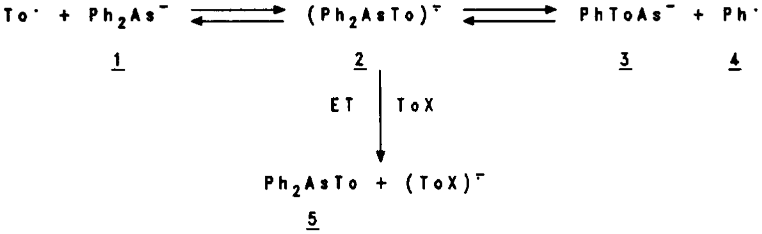
These reactions are inhibited by radical traps or lack of irradiation and they were explained as $S_{RN}1$ reactions, besides the indirect evidences for a radical process.[22b] These reactions present characteristics quite similar to the aromatic system.

It was found that the relative reactivity of carbanions toward 1-iodoadamantane was nitromethane ion > acetophenone enolate ion > acetone enolate ion, respectively.[24] The same order of reactivity was found with iodobenzene where the anthrone anion was more reactive than nitromethane and acetophenone enolate ion > acetone enolate ion >> monoanion of ß-dicarbonyl compounds, respectively.[25]

The same trend of relative reactivity in aromatic and aliphatic systems suggests that both have a similar mechanism, with the same type of intermediate. It has to be pointed out that for alkyl halides it is impossible to postulate a long-living radical anion able to suffer a bimolecular reaction with the nucleophile, as it is required for an $S_{RN}2$ mechanism.

In the aromatic system, the named scrambling reaction occurs with different nucleophiles and substrates.[5b,26] Thus, the photostimulated reaction of Ph_2As^- ions (1) with p-iodotoluene (ITo) gave four substitution products: Ph_3As, Ph_2ToAs, $PhTo_2As$ and To_3As. This behaviour was interpreted as a consequence of the unimolecular fragmentation of the arsine radical anion intermediate, as depicted in Scheme III.[27]

Scheme III



The coupling reaction of p-tolyl radical (To˙) with 1 gave the radical anion intermediate 2, which undergoes three competitive reactions: reversion to starting 1 and To˙, fragmentation to p-tolylphenylarsenide ion 3 and phenyl radical 4, and ET to the substrate to give the product p-tolyldiphenylarsine 5. In these reactions two new intermediates, 3 and 4, were formed. The arsenide ion 3 competes with 1 as nucleophile for the To˙ radical and the phenyl radical can react with 1. These reactions gave new arsine radical anions, which by the process of coupling and fragmentation gave ultimately the four arsines found.[26,27]

Also in the reactions of $PhTe^-$[28], $PhSe^-$[28,29] ions with haloarenes, scrambling products were found, and in all cases, including Ph_2As^- ions, the mixed products were not formed when these nucleophiles reacted with haloarenes with a relative low lying LUMO such as 4-bromobenzophenone or 2-chloroquinoline.[26-29]

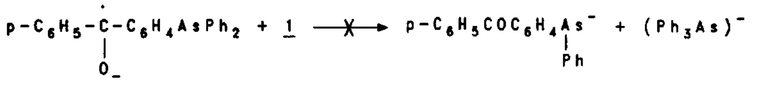
These results were re-interpreted by the $S_{RN}2$ mechanism, suggesting that radical anion 2 reacts with the nucleophile 1 (eq. 9).[1]

$$\underset{\underline{2}}{(Ph_2AsTo)^{-\cdot}} + \underset{\underline{1}}{Ph_2As^-} \longrightarrow (Ph_3As)^{-\cdot} + \underset{\underline{3}}{PhToAs^-} \qquad (9)$$

In the photostimulated reaction of 4-chlorobenzophenone 6 with 1, only the straightforward substitution product 7 was found as product (eq. 10).

$$\underset{6}{p\text{-}C_6H_5COC_6H_4Cl} + 1 \xrightarrow{h\nu} \underset{7}{p\text{-}C_6H_5COC_6H_4AsPh_2} + Cl^- \qquad (10)$$

The radical anion 7$^{\cdot-}$ is an intermediate in this reaction and according to the $S_{RN}2$ mechanism, the nucleophile 1 should react with 7$^{\cdot-}$ to give 8 to observe scrambling products (eq. 11).[1] However, in this reaction only the straightforward substitution product 7 was formed.



$$\underset{7^{\cdot-}}{p\text{-}C_6H_5\text{-}\overset{\cdot}{\underset{O^-}{C}}\text{-}C_6H_4AsPh_2} + 1 \xrightarrow{\quad\times\quad} \underset{8}{p\text{-}C_6H_5COC_6H_4\underset{Ph}{As^-}} + (Ph_3As)^- \qquad (11)$$

The $S_{RN}2$ mechanism does not explain the lack of scrambled products in this system, especially considering that 7$^{\cdot-}$ is more stable than 2$^{\cdot-}$, and reaction 11 did not occur; however, these results can be explained in terms of the $S_{RN}1$ mechanism. The stability of radical anion 7$^{\cdot-}$ with a low lying SOMO avoids its fragmentation because the ET to the σ^* MO of the C-As bond is a slow process.

Benzenethiolate ions did not give scrambled products in the reaction with haloarenes,[30] however, in the reaction of halobenzenes with alkanethiolate ions there is a fragmentation of the radical anion intermediate formed by the coupling of phenyl radical and RS^- ions, giving benzenethiolate ions as product (eq. 12).[31]

$$Ph^{\cdot} + {}^-S\text{-}R \longrightarrow (Ph\text{-}S\text{-}R)^{\cdot-} \longrightarrow Ph\text{-}S^- + R^{\cdot} \qquad (12)$$

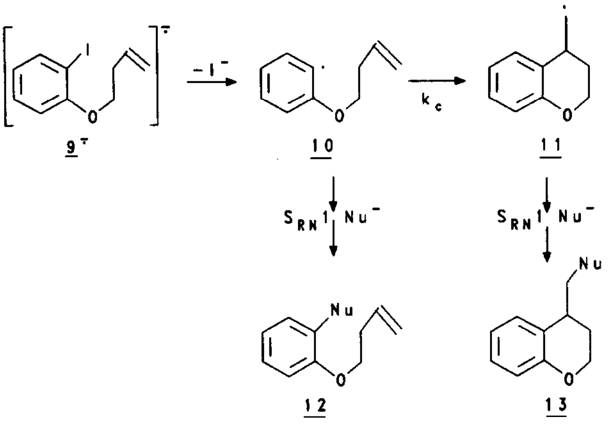
In the reaction of RS^- ions with haloarenes having low lying LUMO, fragmentation of the radical anion intermediate was not observed and good yields of substitution product were obtained.[31]

In the case of alkyl halides, scrambled products were observed in the reaction of 1-iodoadamantane with $PhSe^-$ and $PhTe^-$ ions. Nevertheless only the straightforward substitution product is observed when the nucleophile was 1-naphthalene selenate ion. As in this case the substrate is aliphatic, the low lying LUMO was provided by the naphthyl moiety of the nucleophile.[32]

Radical Probe Evidences: An experimental test for the $S_{RN}1$ mechanism was performed using o-(but-3-enyloxy)iodobenzene 9 as substrate (Scheme IV).[33]

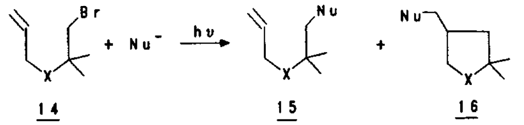
If the reaction follows an $S_{RN}1$ mechanism, the o-(but-3-enyloxy) iodobenzene radical anion 9$^{\cdot-}$ fragments to give the o-(but-3-enyloxy)phenyl radical intermediate 10, and it is well established that 10 undergoes a fast ring closure reaction to give 11 with a rate constant k_c of 7.9 10^9 s^{-1} (25 ºC).[34] When 9 was treated with Ph_2P^-, PhS^- and $(EtO)_2PO^-$ ions as nucleophiles in liquid ammonia, the straightforward substitution products 12 and the cyclized substitution products 13 were found.

Scheme IV



These results were interpreted considering that the reaction proceeds with the radicals **10** and **11** as intermediates. The radical probe **9** was used also to determine the rate constant of the reaction between aryl radical and nucleophiles, the rate constants values (10^8 - 10^9 M^{-1} s^{-1})[33] being in agrement with those previously determined by electrochemical methods.[35]

Also, the uncyclized and cyclized substitution products were determined in the reaction of the aliphatic radical probe **14**, a neopentyl-like substrate, with PhS⁻ and Ph_2P^- ions as nucleophiles, giving the substitution products **15** and the cyclized substitution products **16** (eq. 13).[33]



(13)

X= CH_2, O

This is another example of the similar behaviour between the aromatic (Scheme IV) and aliphatic systems (eq. 13), suggesting radicals as intermediates of these reactions.

Aryl Diazonium Ions Evidences: It is well established that arenediazonium salts react with nucleophiles to give substitution products, N_2 being the leaving group. Thus, it was found that these substrates react with arenethiolate ions,[36,37] nitroalkyl anions,[38] phenoxide ions,[39] cyanide ions,[37] etc. Aryl radicals have been proposed as intermediates in these reactions. In the coupling reaction of the aryl radicals with the nucleophiles a radical anion is generated, which by an ET reaction to the diazonium ion, gives N_2 and the aryl radical that propagates the cycle of the $S_{RN}1$ reaction. The $S_{RN}2$ postulation for these reactions is not possible because no radical anion of the substrate is formed.

In 1979 Russell et al. demonstrated by ESR the presence of the radical anion <u>17</u> in the reaction of ArN_2^+ with nitroalkyl anion and sodium dithionite, according to eqs. 14-16, which shows clearly that aryl radicals are able to react fast with this type of nucleophiles.[38]

$$S_2O_4^{-2} \rightleftharpoons 2\ SO_2^{\bar{\cdot}} \qquad (14)$$

$$ArN_2^+ + SO_2^{\bar{\cdot}} \xrightarrow[-SO_2]{ET} ArN_2^{\cdot} \longrightarrow Ar^{\cdot} + N2 \qquad (15)$$

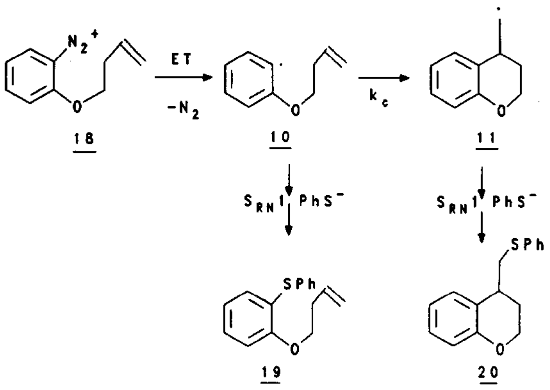
$$Ar^{\cdot} + \gt C{-}NO_2^- \longrightarrow Ar{-}\overset{|}{\underset{|}{C}}{-}NO_2^{\bar{\cdot}} \qquad (16)$$

<u>17</u>

$Ar = Ph,\ p\text{-}HO_2CC_6H_4,\ p\text{-}MeOC_6H_4$

The reaction of arenediazonium salts with benzenethiolate ions was studied in DMSO, using the radical probe <u>18</u> as substrate; the substitution product <u>19</u> and the cyclized product <u>20</u> were formed (Scheme V).[39]

<u>Scheme V</u>



The rate constant determined for the coupling of radical <u>10</u> and benzenethiolate ions (k_{PhS^-} = 0.8 10^8 M^{-1} s^{-1}) is in satisfactory agreement with that determined using radical probe <u>9</u> (k_{PhS^-} = 2 10^8 $M^{-}1$ s^{-1}) (see Scheme IV), thus suggesting a common intermediate in both systems.

<u>Conclusions:</u> Although some experimental facts known up to now still remain to be discussed, we conclude that in most of the examples published in the literature with halobenzenes, and more in general with haloarenes featuring a rate of fragmentation of their radical anions in the order of 10^4 s^{-1} or higher, the reaction of the radical anions with

nucleophiles postulated in the $S_{RN}2$ mechanism can not compete with the $S_{RN}1$ mechanism, based on kinetic grounds. When radical anions have a relative slow rate of fragmentation, the $S_{RN}2$ might perhaps operate.

The similar behaviour of some aliphatic halides that react by the $S_{RN}1$ mechanism and aromatic substrates with leaving groups as different as N_2 and halides ions does suggest the formation of a common intermediate where the leaving group is not present when it reacts with the nucleophile. This intermediate must be then a radical.

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