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A Molecular Orbital Approach to the SRN1 Mechanism of Aromatic Substitution[1]

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The perturbation molecular orbital approach applied to the reaction of an aromatic radical with an anionic nucleophile gives a good starting point to rationalize the SRN1 mechanism of aromatic substitution. It is shown that there is an attractive molecular orbital interaction between an aromatic radical and a carbanion nucleophile; the strongest interaction occurs at the nucleophile position with highest coefficient in the highest occupied molecular orbital (HOMO). Experimental results suggest that when the nucleophile has two or more equivalent positions (equal coefficients in the HOMO) the coupling occurs at the one which leads to the more stable radical anion as predicted by comparing the energy of the lowest unoccupied molecular orbital (LUMO) of the radical anion intermediate. When the nucleophile is of the type $^-CH_2Z$, where Z is an unsaturated moiety, the extra electron in the radical anion intermediate is probably mainly located in the lowest LUMO either in Ar or Z. The body of experimental data to date is in good agreement with the predictions made using this approach.

Chemical reactivity is usually discussed in terms of transition state theory, but in recent years the principles of orbital symmetry,[2] the perturbation molecular orbital, and frontier molecular approaches[3] have been particularly successful in delineating in a simple way those reactions which can occur and in predicting which reaction path is more favorable.

It is a known fact that aryl radicals (Ar·) react with some nucleophiles (Nu^-) at rates which can compete efficiently with the rate of the reaction with solvated electrons (eq 1) as indicated by the product ratio analysis.[4–6]

$$\mathrm{Ar}\cdot \begin{cases} \xrightarrow{e^-} \mathrm{Ar}^- \\ \xrightarrow{\mathrm{Nu}^-} (\mathrm{Ar{-}Nu})\cdot^- \end{cases} \tag{1}$$

As far as we know, there are no kinetic or thermodynamic data available for reactions of Ar· with Nu^-, although it is known that such reactions are quite fast.

It has been shown by the frontier molecular orbital approach that the strongest interaction between two reacting centers occurs through the frontier orbitals of similar energy,[3] so the single occupied molecular orbital (SOMO) of Ar· will interact with the highest occupied molecular orbital (HOMO) of the Nu^-. This interaction will give one two-electrons bonding orbital and only one electron in the antibonding orbital. Assuming that the energy of the SOMO of Ar· and the HOMO of the Nu^- are equal, the change in the π energy as calculated by the first-order perturbation is given by eq 2.[3a]

$$\Delta E\pi = c_{\mathrm{Ar}\cdot}{}^{\mathrm{SOMO}} c_{\mathrm{r,Nu}^-}{}^{\mathrm{HOMO}} \beta \tag{2}$$

Since $c_{\mathrm{Ar}\cdot}{}^{\mathrm{SOMO}} = 1$, eq 2 simplifies to eq 3.

$$\Delta E\pi = c_{\mathrm{r,Nu}^-}{}^{\mathrm{HOMO}} \beta \tag{3}$$

If the SOMO of Ar· and the HOMO of Nu^- are not degenerate, the first-order change in π energy is zero. In this case the change in π energy is given by the second-order perturbation for the interaction of atom r of the Nu^- with s of the electrophile which can be calculated by eq 4.[3a]

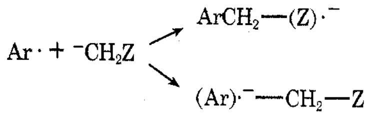
$$\Delta E\pi = 2\sum_j^{\mathrm{occ}} \sum_k^{\mathrm{unocc}} \frac{c_{rj}{}^2 c_{sk}{}^2 \beta_{rs}{}^2}{E_j - E_k} \tag{4}$$

In our particular case where the electrophile is Ar· we have only one orbital with energy close to α and $c_s = 1$; then for the interaction eq 4 simplifies to eq 5.

$$\Delta E\pi = \sum_j^{\mathrm{all}} \frac{c_{rj}{}^2 \beta_{rs}{}^2}{E_j} \tag{5}$$

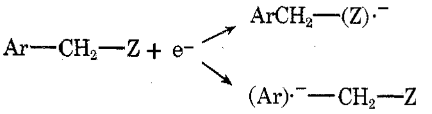
It follows from eq 5 that the coefficient c_{rj} will determine the position of the coupling. Provided that the predominant term in eq 5 is the one involving the coefficients of the HOMO, this coefficient will determine the most reactive position of the Nu^-.

In the coupling of an Ar· with a carbanionic nucleophile of $^-CH_2Z$ type, Ar and Z will not be conjugated in the product, since the two moieties are separated by an sp^3 carbon. Therefore the extra electron must be located in the lowest unoccupied molecular orbital (LUMO) of either Ar or Z (eq 6).[7]



$$\mathrm{Ar\cdot + {}^{-}CH_2Z} \rightarrow \mathrm{ArCH_2{-}(Z)\cdot^{-}} \text{ or } \mathrm{(Ar)\cdot^{-}{-}CH_2{-}Z} \quad (6)$$

We suggest that the radical anion (RA) formed will be that one where the electron is located in the LUMO of lowest energy, which in turn will be the same as the one formed when the neutral product takes an electron (eq 7).



$$\mathrm{Ar{-}CH_2{-}Z + e^{-}} \rightarrow \mathrm{ArCH_2{-}(Z)\cdot^{-}} \text{ or } \mathrm{(Ar)\cdot^{-}{-}CH_2{-}Z} \quad (7)$$

Note at this point that we do not mean to say that the RA with lowest energy LUMO is the one formed initially from the reaction of Ar· with $^{-}CH_2Z$. We are referring here to the RA intermediate that predominates in this type of reaction.

No matter which RA is initially formed, a fast equilibrium (eq 8) must be established, and this equilibrium will favor the more stable RA.

$$\mathrm{Ar{-}CH_2{-}(Z)\cdot^{-}} \rightleftharpoons \mathrm{(Ar)\cdot^{-}{-}CH_2{-}Z} \quad (8)$$

ESR studies have shown that this type of equilibrium indeed exists in compounds of type $Ar_1(CH_2)_n(Ar_2)\cdot^{-}$, with $Ar_1 = Ar_2$[8]. Although compounds where $Ar_1 \neq Ar_2$ have not been studied, it is expected that in such a case the equilibrium be shifted toward the more stable RA, considering that in intermolecular electron transfer reactions the equilibrium depicted in eq 9 favors the most stable RA.[9]

$$\mathrm{arene_1 + (arene_2)\cdot^{-}} \rightleftharpoons \mathrm{(arene_1)\cdot^{-} + arene_2} \quad (9)$$

In compounds somewhat related to ours, like triptycenes and benzotriptycenes, it has recently been found that the RA formed from electrochemical or alkali metal reduction has the unpaired electron localized in the aromatic ring with largest electron affinity (lowest energy LUMO) with no exchange at all.[10]

On the basis of the ideas outlined above, we will deal next with the experimental facts which give support to them.

Coupling of Phenyl Radical with Hydrocarbon Derived Carbanions. In these reactions phenyl radicals (Ph·) were formed by reaction of monosubstituted benzenes and solvated electrons in liquid ammonia, to give a RA which decomposes to Ph·[11] (eq 10). This radical then reacts with the anionic nucleophile to form a new RA (eq 11), which can transfer its extra electron (eq 12) or take another electron and be reduced (eq 13).[12]

$$\mathrm{PhX + e^{-} \longrightarrow (PhX)\cdot^{-} \longrightarrow Ph\cdot + X^{-}} \quad (10)$$

$$\mathrm{Ph\cdot + Nu^{-} \longrightarrow (PhNu)\cdot^{-}} \quad (11)$$

$$\mathrm{(PhNu)\cdot^{-} + PhX \longrightarrow PhNu + (PhX)\cdot^{-}} \quad (12)$$

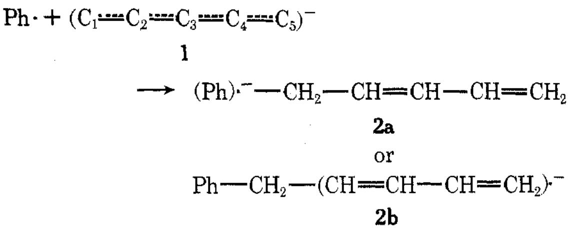
$$\mathrm{(PhNu)\cdot^{-} + e^{-} \xrightarrow{NH_3,\ H^{+}} PhNuH_2} \quad (13)$$

Pentadienide anion has an energy of α in its HOMO and the coefficients $c_1^H = -c_3^H = c_5^H$, with the charge density in the three carbons being the same.[13] Considering only the coefficients c^H, two products should have been formed, i.e., reaction at carbon 1 and carbon 3.

Pentadienide anion 1 reacts with Ph· giving phenylpentadienes and phenylpentenes,[12] all with the benzene ring attached to carbon 1 (eq 14).[15]

The reaction at carbon 3 would have given the RA **3a** and/or **3b**.

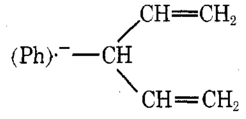
The energy of the LUMO of ethylene is equal to that of



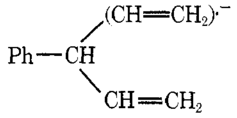
$$\mathrm{Ph\cdot + (C_1{\cdots}C_2{\cdots}C_3{\cdots}C_4{\cdots}C_5)^{-}} \longrightarrow \mathrm{(Ph)\cdot^{-}{-}CH_2{-}CH{=}CH{-}CH{=}CH_2} \text{ or } \mathrm{Ph{-}CH_2{-}(CH{=}CH{-}CH{=}CH_2)\cdot^{-}} \quad (14)$$

1 **2a** **2b**

benzene = -1.000β,[16] whereas the value of the LUMO of the butadiene moiety in the RA **2b** is lower (Table I). We know from the product distribution that the formation of the RA **3a** and **3b** does not compete with RA **2a** or **2b**, but we do not



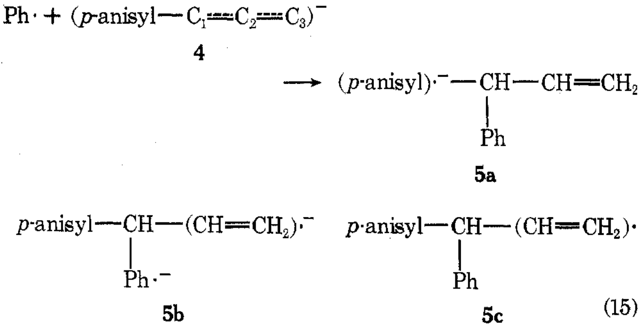
3a



3b

have any strong evidence as to which of them is formed, although the formation of phenylpentenes might suggest that RA **2b** was formed and reduced in the sense of eq 13. Product distribution has been used previously as a criterion to establish which RA is formed.[5,17]

p-Anisylpropenide anion 4 has c_1^H and $-c_3^H$ almost equal in the HOMO. However, attack of Ph· occurs three times more rapidly at carbon 3 than at carbon 1.[12] For the addition of Ph· at atom 1 of p-anisylpropenide, there are three unsaturated systems isolated which can accept the extra electron, forming RA **5a, 5b,** and **5c**; all of them have the same energy in their LUMO, -1.000β (eq 15).[15]



$$\mathrm{Ph\cdot + (\textit{p}\text{-anisyl}{-}C_1{\cdots}C_2{\cdots}C_3)^{-}} \longrightarrow \mathrm{(\textit{p}\text{-anisyl})\cdot^{-}{-}CH(Ph){-}CH{=}CH_2},\ \mathrm{\textit{p}\text{-anisyl}{-}CH(Ph\cdot^{-}){-}(CH{=}CH_2)\cdot^{-}},\ \mathrm{\textit{p}\text{-anisyl}{-}CH(Ph){-}(CH{=}CH_2)\cdot} \quad (15)$$

4 **5a** **5b** **5c**

On the other hand, in the reaction at carbon 3, there are two possible RA's: **6a** and **6b** (eq 16).

$$\mathrm{(\textit{p}\text{-anisyl}{-}CH{=}CH)\cdot^{-}{-}CH_2{-}Ph}$$

6a

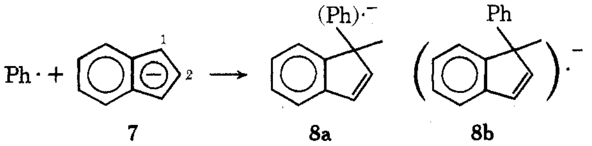
$$\mathrm{\textit{p}\text{-anisyl}{-}CH{=}CH{-}CH_2{-}(Ph)\cdot^{-}} \quad (16)$$

6b

RA **6a** has the extra electron in a LUMO with lower energy than RA **6b**; therefore, it will be preferentially formed.

It follows from the two examples mentioned above that when the coefficients c^H in the nucleophile have the same value, the reaction path followed is that which leads to the RA with the LUMO of lower energy. In other words, although the perturbation theory predicts that all positions in the nucleophile with equal c^H are equally reactive, the stability of the intermediate RA controls the reaction and the thermodynamically more stable product is formed preferentially.

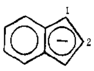
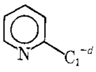
Indene anion 7, on the other hand, has $c_1^H > c_2^H$, so the attack occurs exclusively at carbon 1 (eq 17).[12]



(17)

7 **8a** **8b**

Table I. HMO Values of the Frontier Molecular Orbital of Nucleophiles and Products in Aromatic SRN1 Reactions[a]

Aromatic radical	Nucleophile	Registry no.	Coefficients (HOMO)[b]	Position in the coupling	RA formed	LUMO[c]	Ref
Phenyl	$(C_1\text{-}C_2\text{-}C_3\text{-}C_4\text{-}C_5)^{-d}$	56094-24-7	$c_1^H = c_3^H$	C_1	2b	0.618	12
Phenyl		12128-54-0	$c_1^H \gg c_2^H$	C_1	8b	0.662	12
Phenyl	$(p\text{-Anisyl-}C_1\text{-}C_2\text{-}C_3)^{-d}$	40719-29-7	$c_1^H = c_3^H$	$C_1 < C_3$ (on C_3) (on C_1)	6a 5[e,f]	0.698 1.000	12
Phenyl	$^-CH_2COCH_3$	24262-31-5	$c_C^H > c_O^H$	C_1	10	0.740	5
Mesityl	$^-C_1\text{-CO-}^-C_3\text{-COCH}_3{}^d$	54210-56-9	$c_1^H > c_3^H$	C_1	12[e]	0.683	22
Phenyl		18860-16-7	$c_1^H > c_N^H$	C_1	17a[e]	0.667	25
Phenyl	$^-CH_2\text{-CN}$	21438-99-3	$c_C^H > c_N^H$	C_1	19	0.820[g]	26
4-Biphenylyl	$^-CH_2\text{-CN}$		$c_C^H > c_N^H$	C_1	21a	0.705	27
p-Benzoylphenyl	$^-CH_2\text{-CN}$		$c_C^H > c_N^H$	C_1	21b	0.294	27
2-Quinolyl	$^-C_1\text{-CO-}^-C_3\text{-COPh}^d$	59922-52-0	$c_1^H > c_3^H$	C_1	14a[e] 14b[e]	0.438 0.460	23
2-Pyridyl	$^-CH_2\text{-CN}$		$c_C^H > c_N^H$	C_1	26	0.667	27
1-Naphthyl	$^-CH_2COCH_3$		$c_C^H > c_O^H$	C_1	15	0.618	17
1-Naphthyl	$^-CH_2\text{-CN}$		$c_C^H > c_N^H$	C_1	23	0.618	17
2-Naphthyl	$^-CH_2\text{-CN}$		$c_C^H > c_N^H$	C_1	24	0.618	27
9-Phenanthryl	$^-CH_2\text{-CN}$		$c_C^H > c_N^H$	C_1	25	0.605	27
1-Naphthyl	$^-CH_2COPh$	59922-53-1	$c_C^H > c_O^H$	C_1	16a	0.386	17

[a] Simple Hückel MO method was used in the calculations. The parameters were taken from Streitwieser[14] unless otherwise stated. [b] Coefficients of the highest occupied MO in the nucleophile. [c] The lowest unoccupied MO of the product $ArCH_2Z$ is the single occupied MO in the radical anion. [d] Hydrogen atoms in the nucleophile are omitted for clarity. [e] There is no evidence which radical anion is formed. [f] Any one of the three possibilities (ethylene, benzene, and anisole) have the same LUMO value. [g] Parameters for CN were taken from ref 28.

RA **8b** has the extra electron in a LUMO with lower energy than RA **8a**; therefore, it will be preferentially formed, and the reduction to 1-phenylindan[12] might indicate the reduction of RA **8b** in the sense of eq 13.

Coupling of Aromatic Radicals with Ketone Enolate, Picolyl, and Cyanomethyl Anions as Nucleophiles. Allyl anion has a c_1^H equal to $-c_3^H$, but when carbon 3 is replaced by a heteroatom, the charge density in the heteroatom (oxygen or nitrogen) is higher than on carbon; however, in the HOMO, c_C^H is higher than c_O^H or c_N^H.

In the reaction of a radical with a bidentate nucleophile, the value of the coefficient of the frontier molecular orbital will determine the position of reaction. This conclusion is supported by the fact that ketone enolate, picolyl, and cyanomethyl anions react only through the carbon with higher c^H (Table I).

There is a precedent in aliphatic SRN1,[18] where it was pointed out that the reaction of an aliphatic radical with a bidentate nucleophile is an orbital-controlled reaction.[19]

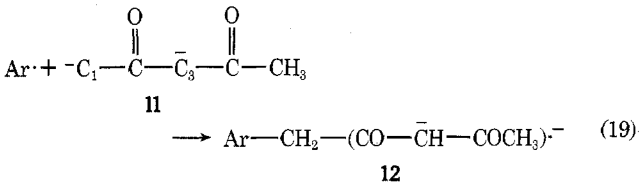
In the reaction of Ph· with acetonate anion **9** the substitution occurs only on carbon (eq 18).

$$\underset{\mathbf{9}}{Ph\cdot + {}^-CH_2COCH_3} \longrightarrow \underset{\mathbf{10}}{Ph\text{—}CH_2\text{—}(COCH_3)\cdot^-} \tag{18}$$

There are experimental indications that **10** is the RA formed,[5,20] in agreement with the LUMO values shown in Table I.[21]

Several cyclic and noncyclic ketone enolate ions have been arylated by this method under photostimulation in liquid ammonia; all of them reacted at the α carbon atom.[22]

Ph· do not react with monoenolate ions of β-dicarbonyl compounds, but 2-bromomesitylene reacted with the dipotassium salt of 2,4-pentadione **11** giving 1-mesityl-2,4-pentadione in 82% yield. The dianion **11** has two nucleophilic centers, carbon 1 and carbon 3, with $c_1^H > c_3^H$, and the only product obtained was that of reaction on carbon 1 (eq 19).[22]

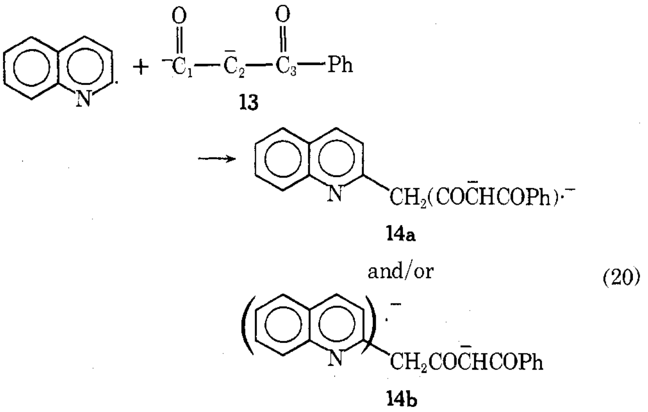


$$Ar\cdot + \underset{\mathbf{11}}{{}^-C_1\text{—}\overset{\overset{O}{\|}}{C}\text{—}\bar{C}_3\text{—}\overset{\overset{O}{\|}}{C}\text{—}CH_3} \longrightarrow \underset{\mathbf{12}}{Ar\text{—}CH_2\text{—}(CO\text{—}\bar{C}H\text{—}COCH_3)\cdot^-} \tag{19}$$

Ar = mesityl

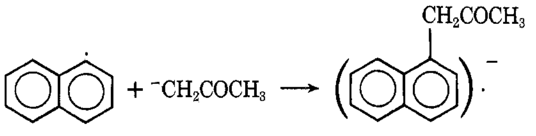
There are few examples of heteroaromatic radicals in reaction with Nu⁻ by the SRN1 mechanism of aromatic substitution.[23,24] 2-Chloroquinoline reacted with ketonate anions giving substitution products much as phenyl radical does, both stimulated by light or solvated electrons in liquid ammonia.[23]

One example involving benzoylacetone dianion **13** has been reported. This Nu⁻ has two nucleophilic centers on carbon 1 and on carbon 3, having c_1^H higher than c_3^H. Accordingly only one substitution product is obtained, namely the one attached to carbon 1 (eq 20).



RA **14a** has a similar value of the energy in the LUMO to **14b**, and there is no evidence as to which RA is formed.

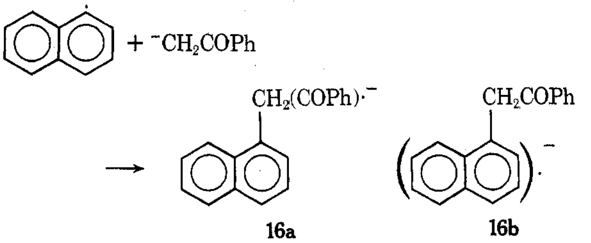
1-Naphthyl radicals react with acetonate anion to give substitution products on carbon as Ph· does, but the extra electron is located on the aromatic moiety and not in the nucleophile, owing to the lower energy LUMO of the naphthalene than the carbonyl group[21] (eq 21).



15 (21)

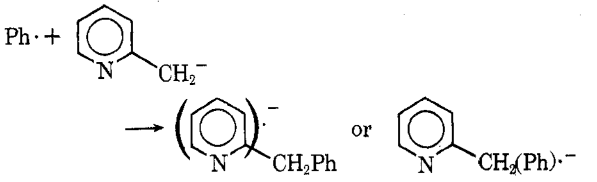
There is experimental evidence for the formation of RA **15** and not the ketyllike RA **10** as in the reaction with Ph·.[17]

Acetophenone anion is another nucleophile of the type $^{-}CH_2Z$, but where Z = COPh has a lower energy LUMO than naphthalene moiety. As expected in the reaction with 1-naphthyl radical, the RA formed was **16a** instead of **16b** (eq 22).[17]



16a 16b (22)

With 2- and 4-picolyl anions as nucleophiles, Ph· couples with carbon 1 (higher c^{H}) (eq 23).[25]



17a 17b (23)

There are no indications which RA is formed, but RA **17a** has the lowest energy LUMO, which lead us to suggest on the base of the above arguments that RA **17a** and not **17b** is the one formed.

With cyanomethyl anion also the substitution occurs at carbon 1 (higher c^{H}) and the RA **19** formed is the one with the lowest energy LUMO[28] (eq 24).

$$\mathrm{Ph}\cdot + \underset{\mathbf{18}}{^{-}CH_2{-}CN} \longrightarrow \underset{\mathbf{19}}{Ph{-}CH_2{-}(CN)^{\cdot -}} \qquad (24)$$

There is experimental evidence that RA **19** is the intermediate formed predominantly because it decomposes to benzyl radical and cyanide ions (eq 25).[26]

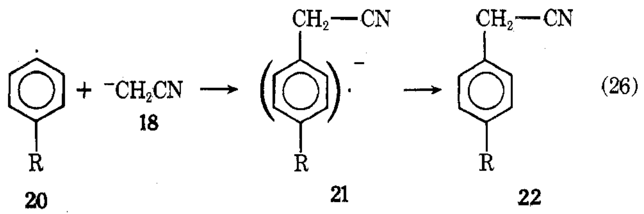
$$\mathbf{19} \longrightarrow Ph{-}CH_2\cdot + CN^{-} \qquad (25)$$

However, when a Ph· has a substituent which decreases the value of the LUMO of the aromatic moiety, such as **20**, the CN moiety has now higher LUMO than the aromatic moiety, and the RA formed predominantly is **21**, which does *not* suffer C–CN bond breaking. Consequently only the acetonitrile derivatives **22** are formed (eq 26).[27]

It is remarkable that the presence of a substituent R in the phenyl ring which lowers the value of the LUMO of the aromatic moiety can change so dramatically the product distribution.

1-Naphthyl, 2-naphthyl, and 9-phenanthryl radicals also reacted with cyanomethyl anion to give acetonitrile derivatives without C–CN bond rupture (Table I), which means that RA's **23, 24,** and **25** are the intermediates in these reactions.[27]

2-Chloropyridine reacts with cyanomethyl anion stimulated



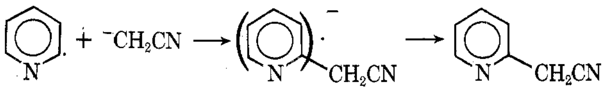
(26)

20a, Ph
b, COPh

$$\underset{\mathbf{23}}{(1\text{-naphthyl})^{\cdot -}{-}CH_2{-}CN} \qquad \underset{\mathbf{24}}{(2\text{-naphthyl})^{\cdot -}{-}CH_2{-}CN}$$

$$\underset{\mathbf{25}}{(9\text{-phenanthryl})^{\cdot -}CH_2{-}CN}$$

by light to give 2-pyridylacetonitrile, and no C–CN bond cleavage was observed.[27] Pyridine has a LUMO value lower than the CN moiety, and again the product distribution depends on which is the lowest LUMO in both moieties (eq 27).



26 27 (27)

The PMO method applied to the SRN1 mechanism allows one to predict the products to be expected in the reaction of aromatic radicals with ambidentate nucleophiles by simply calculating the coefficients of the HOMO of the reactive atoms of the nucleophile.[29] Moreover when there are several possible radical anion intermediates, consideration of the LUMO's of the groups involved allows one to predict which will be the intermediate that will predominate in the reaction and consequently the products.

We are aware that there are other possible approaches and other factors (solvation, ion pairs, etc.) besides molecular orbital considerations to be taken into account to deal with the problem in a more general way, but the method presented here seems very appropriate to explain the body of experimental data existent in the literature.

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Registry No.—Phenyl, 2396-01-2; mesityl, 19121-63-2; 4-biphenylyl, 2510-50-1; *p*-benzoylphenyl, 59922-54-2; 2-quinolyl, 54978-39-1; 2-pyridyl, 15905-71-2; 1-naphthyl, 2510-51-2; 2-naphthyl, 10237-50-0; 9-phenanthryl, 20199-82-0.

References and Notes

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$$Ph\cdot + {}^{-}CH_2{-}Z \longrightarrow (Ph)^{\cdot -}{-}CH_2{-}Z \text{ or } Ph{-}CH_2{-}(Z)^{\cdot -}$$

we calculated the LUMO of benzene and Z only.

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(29) As the use of HMO method when dealing with charged systems is questionable,[3a,14] other methods have been used. However, the fact that no exceptions were found led us to use the simple HMO.

Photostimulated Arylation of Cyanomethyl Anion by the SRN1 Mechanism of Aromatic Substitution[1]

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The photostimulated reaction of 1- or 2-chloronaphthalenes, 4-chlorobiphenyl, 4-bromobenzophenone, and 2-chloropyridine with cyanomethyl anion in liquid ammonia leads to the formation of α-aryl or hetaryl acetonitrile derivatives in excellent yields, probably by the SRN1 mechanism of aromatic substitution. The photostimulated reaction of bromobenzene with the same nucleophile gives a mixture of phenylacetonitrile, 1,2-diphenylethane, and toluene. The difference in behavior of this latter substrate compared to those reported in this study is postulated to be due to differences in the predominant intermediates formed when an aromatic radical couples with the cyanomethyl anion. These reactions have potential value in synthesis to obtain α-aryl or α-hetaryl acetonitrile derivatives.

The photostimulated reaction of bromobenzene and cyanomethyl anion in liquid ammonia afforded phenylacetonitrile (8%) and 1,2-diphenylethane (18%), together with small amounts of toluene, benzene, and 1,1-diphenylethane.[2] This reaction occurred by the SRN1 mechanism of aromatic substitution,[3] as depicted in Scheme I.

Scheme I

$$\underset{1}{\mathrm{ArX}} + {}^{-}\mathrm{CH_2CN} \xrightarrow{h\nu} \underset{2}{(\mathrm{ArX})\cdot^{-}} + \text{residue} \qquad (1)$$

$$2 \longrightarrow \underset{3}{\mathrm{Ar}\cdot} + \mathrm{X}^{-} \qquad (2)$$

$$3 + {}^{-}\mathrm{CH_2CN} \longrightarrow \underset{4}{(\mathrm{ArCH_2CN})\cdot^{-}} \qquad (3)$$

$$4 + 1 \longrightarrow \underset{5}{\mathrm{ArCH_2CN}} + 2 \qquad (4)$$

$$\text{termination steps} \qquad (5)$$

When Ar = Ph, other steps are involved, such as 6–8.[2]

$$4 \longrightarrow \underset{6}{\mathrm{PhCH_2}\cdot} + \mathrm{CN}^{-} \qquad (6)$$

$$6 \longrightarrow \mathrm{Ph{-}CH_2{-}CH_2{-}Ph} \qquad (7)$$

$$6 \longrightarrow \mathrm{PhCH_3} \qquad (8)$$

However, when the same reaction was carried out with 1-chloronaphthalene, the only product observed was the acetonitrile derivative **5.** No products from the decomposition of the radical anion 4 as in steps 6–8 were found.[4]

The difference in behavior found between the phenyl and naphthyl system was attributed to differences in the predominant intermediate formed in these reactions. The argument as reported previously[5] can be summarized as follows: when an aromatic radical couples with cyanomethyl anion or other carbanionic nucleophiles of the type $^{-}CH_2Z$ with Z being an unsaturated moiety, the extra electron in the intermediate can be located either in Z or Ar, forming intermediates **4a** and **4b,** depending on which moiety has lower value of the lowest unoccupied molecular orbital (LUMO) (eq 9).

$$\underset{\mathbf{4a}}{\mathrm{Ar{-}CH_2{-}(Z)\cdot^{-}}} \qquad \underset{\mathbf{4b}}{\mathrm{(Ar)\cdot^{-}{-}CH_2{-}Z}} \qquad (9)$$

For instance, when Ar = Ph and Z = CN, the predominant radical anion intermediate resembles structure **4a,** and this intermediate can transfer its extra electron as in step 4 to give ultimately phenylacetonitrile, or can decompose as in step 6 to give benzyl radical **6.** When Ar = 1-naphthyl, the aromatic moiety has a lower LUMO value than the CN moiety, and the structure of the predominant radical anion intermediate is **4b,** which only can transfer its extra electron as in step 4 to give the acetonitrile derivative **5.**

We now report a further study of arylation reactions of