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Photochemical Aromatic Cyanomethylation

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Summary Cyanomethylation is accomplished by the photolysis of chloroacetonitrile in the presence of aromatics by way of electron transfer followed by radical coupling.

ONLY a few aromatic photoalkylation reactions have been reported, most involving alkyl halides with appropriate electron-withdrawing substituents as precursors [equation (1), R = CH_2CO_2Me,[1] CH_2CO_2Et,[2] CH_2CONH_2,[3] and CH_2CN[4]]. A number of reaction pathways have been proposed, but

$$\mathrm{ArH} + \mathrm{RCl} \xrightarrow{h\nu} \mathrm{ArR} + \mathrm{HCl} \qquad (1)$$

for the most part, mechanistic studies have been sketchy. In light of our interest in aromatic substitutions by electron-deficient alkyl radicals[5] we set out to study aromatic cyanomethylations in hopes of determining the role, if any, of the cyanomethyl radical in this reaction.

TABLE 1. Product yields[a] for the photochemical cyanomethylation of aromatics.

Aromatic	Substitution products %	Succinonitrile %
Benzene	1·9	0·5
Fluorobenzene	<1	<0·5
Toluene	2·6	0·7[b]
Anisole	11·0	2·3
Naphthalene	4·8	—
1,4-Dimethoxybenzene	16·3	—

[a] After exposure for 22 h in a Rayonet model RPR-100 photochemical reactor. Yields are based on the initial amount of chloroacetonitrile as limiting reagent; since most of this reagent was recovered after 22 h, the actual yields based on chloroacetonitrile consumed are much higher. [b] 3-Phenylpropionitrile, 6·4%, and bibenzyl, 2·1%, were also formed.

Deoxygenated solutions of chloroacetonitrile (5 mmol) and various aromatic hydrocarbons (10 mmol) in acetonitrile were irradiated using low-pressure mercury lamps (> 99% emission at 254 nm). Cyanomethylated aromatics were produced along with a number of side products, particularly succinonitrile, indicative of the cyanomethyl radical (Table 1).

It is unlikely that the cyanomethyl radical is produced by direct photolytic homolysis since chloroacetonitrile absorbs so weakly ($\epsilon_{254} < 1$) in comparison with the aromatic compounds (Table 2). Instead, initial excitation to the excited aromatic singlet state [equation (2)] followed by energy transfer to chloroacetonitrile seems probable. The rate constants for this quenching process were actually determined by a Stern–Volmer treatment of fluorescence intensities of the various aromatic hydrocarbons in the presence of varying concentrations of chloroacetonitrile (Table 2).[6,7] Classical energy transfer is unlikely, being endergenic; instead this process probably occurs by way of an electron-transfer from the aromatic excited state to chloroacetonitrile.[8–10]† This electron-transfer [perhaps involving the exciplex (**1**)] would produce a radical·cation–

TABLE 2. Fluorescence quenching by chloroacetonitrile.[a]

Aromatic	ϵ_{254}	k_q/dm^3 mol^{-1} s^{-1}
Benzene	121	$1{\cdot}0 \times 10^7$
Fluorobenzene	530	$5{\cdot}9 \times 10^7$
Toluene	174	$6{\cdot}6 \times 10^7$
Anisole	426	$3{\cdot}5 \times 10^9$
Naphthalene	2823	$2{\cdot}5 \times 10^6$
1,4-Dimethoxybenzene	115	$9{\cdot}6 \times 10^9$

[a] In acetonitrile solvent.

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† The energetics of this electron-transfer can be approximated from the singlet energy and oxidation potential of the aromatic along with the reduction potential of the quencher (refs. 8 and 10). Calculations indicate that such energy transfer is favourable with chloroacetonitrile (*e.g.*, ΔG_{ET} = *ca.* −23 kcal/mol with benzene; 1 kcal = 4·18 kJ).

radical anion pair (**2**), [equation (3)].[11] Radical cation intermediates have been detected from methoxynaphthalene *quenching* by chloroacetonitrile.[10] Loss of a chloride ion from (**2**), a very rapid process,[10] produces the cyanomethyl radical [equation (4)], presumably still within a solvent cage.

$$\mathrm{ArH} \xrightarrow{h\nu} \mathrm{ArH}^{*} \qquad (2)$$

$$\mathrm{ArH}^{*} + \mathrm{ClCH_2CN} \rightarrow \underset{\mathbf{(1)}}{(\mathrm{ArH{-}{-}{-}ClCH_2CN})^{*}}$$

$$\rightarrow \underset{\mathbf{(2)}}{(\mathrm{ArH^{+\bullet}{-}{-}{-}{}^{\bullet-}ClCH_2CN})} \qquad (3)$$

$$\mathbf{(2)} \xrightarrow{-\mathrm{Cl}^-} \underset{\mathbf{(3)}}{(\mathrm{ArH^{+\bullet}{-}{-}{-}{}^{\bullet}CH_2CN})} \qquad (4)$$

$$\mathbf{(3)} \rightarrow \mathrm{HAr^{+}CH_2CN} \xrightarrow{-\mathrm{H}^+} \mathrm{ArCH_2CN} \qquad (5)$$

Table 3. Photochemical cyanomethylation of PhX.

X	Relative rate[a,b]	Isomer distribution *o*:*m*:*p*	Partial rate factors m_f	p_f
F	1·3	36:43:21	1·7	1·6
Me	4·2	33:47:20	5·9	5·4
OMe	11·5	67:20:12	6·9	8·3

[a] Relative to benzene based on a 1:1:0·5 mixture of aromatic: benzene: chloroacetonitrile in acetonitrile, 254 nm, 22 h. [b] The relative substitution rates for naphthalene and 1,4-dimethoxybenzene were 87 and 107, respectively.

The ultimate aromatic substitution product-forming step appears to involve radical coupling between the cyanomethyl radical and aromatic radical cation while still within a cage [equation (5)]. Two experimental observations support this scheme. (i) Pairs of aromatic compounds were photolysed with chloroacetonitrile and partial rate factors determined on the basis of apparent relative rates of substitution‡ and the isomeric composition (Table 3). Attempted Hammett treatments with the log of these partial rate factors *vs.* either σ or σ^+ values failed to give any sort of correlation. This indicated that aromatic substitution did not result from attack by cyanomethyl radicals of the ground state aromatic, since this type of homolytic aromatic substitution would be expected to give a good Hammett plot.[5,12] (ii) The photochemical cyanomethylation of toluene leads to the greatest amounts of side products due to radical coupling reactions, consistent with the fact that the toluene radical cation is known rapidly to lose a proton to produce the benzyl radical [equation (6)].[13] Radical pairing can account for the

$$(\mathrm{PhCH_3^{+\bullet}{-}{-}{-}{}^{\bullet}CH_2CN}) \xrightarrow{-\mathrm{H}^+} (\mathrm{PhCH_2^{\bullet}} + {}^{\bullet}\mathrm{CH_2CN}) \qquad \mathbf{(6)}$$

aromatic cyanomethylated products including 3-phenylpropionitrile whereas only radicals escaping from the cage can lead to succinonitrile and bibenzyl. While all of these products were produced in acetonitrile as a solvent (Table 1), photolysis in cyclohexane led only to the isomeric tolyl acetonitriles and 3-phenylpropionitrile. Radicals escaping from the cage in the latter solvent system apparently abstracted hydrogen from the solvent rather than coupling.[14]

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‡ These relative rates would be accurate if cyanomethylation occurred on aromatic ground states. For a substitution scheme such as equations (3)—(5) these relative rates are at best only approximate owing to uncertainties in determining relative excited aromatic singlet concentrations. Part of the complexity lies in their differing amounts of excitation (ϵ_{254}, Table 2), different lifetimes, and quenching constants as well as the possibility of energy transfer from one aromatic excited singlet to the ground state of another. The authors thank Dr. Gary Shuster for helpful discussions.

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