and 7.00–7.31 (m, aromatic, 8 H). Anal. Calcd for $C_{18}H_{23}NS_2$: C, 68.09; H, 7.30; N, 4.41. Found: C, 68.44; H, 7.18; N, 4.17.

N,N-Bis[(4-chlorophenyl)thio]-*tert*-butylamine (1e): colorless prisms (methanol); mp 78–79 °C; UV (hexane) λ_{max} 255 (ϵ 21 800) and 231 nm (sh, 16 000); NMR (CCl_4) δ 1.30 (s, *t*-Bu, 9 H) and 7.27 (s, aromatic, 8 H). Anal. Calcd for $C_{16}H_{17}Cl_2NS_2$: C, 53.63; H, 4.78; N, 3.91. Found: C, 53.33; H, 4.88; N, 3.97.

N,N-Bis[(4-chlorophenyl)thio]isopropylamine (1f): colorless needles (methanol); mp 80.5–81.5 °C; yield 47% UV (hexane) λ_{max} 252 nm (ϵ 21 800); NMR (CCl_4) δ 1.16 (d, *J* = 5.9 Hz, Me, 6 H), 3.65 (sept, *J* = 5.9 Hz, Me_2CH, 1 H), and 7.29 (s, aromatic, 8 H). Anal. Calcd for $C_{15}H_{15}Cl_2NS_2$: C, 52.32; H, 4.39; N, 4.07. Found: C, 51.93; H, 4.40; N, 3.95.

N,N-Bis[(4-chlorophenyl)thio]cyclohexylamine (1g): colorless needles (ethanol); mp 75–76 °C; yield 72%; UV (hexane) λ_{max} 252 nm (ϵ 22 000); NMR (CCl_4) δ 1.06–2.05 [br, $(CH_2)_5$, 10 H], 3.18 (br s, CHN, 1 H), and 7.36 (s, aromatic, 8 H). Anal. Calcd for $C_{18}H_{19}Cl_2NS_2$: C, 56.24; H, 4.98; N, 3.64. Found: C, 56.18; H, 5.04; N, 3.68.

N,N-Bis[(4-chlorophenyl)thio]-1-adamantanamine (1h): colorless needles (ethanol); mp 128–129 °C; yield 41%; UV (hexane) λ_{max} 256 (ϵ 23 800) and 233 nm (16 500); NMR (CCl_4) δ 1.56–2.08 (m, adamantyl, 15 H) and 7.27 (s, aromatic, 8 H). Anal. Calcd for $C_{22}H_{23}Cl_2NS_2$: C, 60.54; H, 5.31; N, 3.21. Found: C, 60.22; H, 5.35; N, 3.22.

N,N-Bis[(3-chlorophenyl)thio]-*tert*-butylamine (1i): viscous oil (not distilled, TLC almost one spot); yield 50%; NMR (CCl_4) δ 1.34 (s, *t*-Bu, 9 H) and 7.14–7.29 (m, aromatic, 8 H). The elemental analyses were unsatisfactory (C, 51.90; H, 4.74; N, 3.11).

N,N-Bis[(3-chlorophenyl)thio]-1-adamantanamine (1j): colorless prisms (methanol); mp 114–116 °C; yield 25%; UV (hexane) λ_{max} 253 (ϵ 22 700) and 229 nm (sh, 14 900); NMR (CCl_4) δ 1.59–2.10 (m, adamantyl, 15 H) and 7.11–7.25 (m, aromatic, 8 H). Anal. Calcd for $C_{22}H_{23}Cl_2NS_2$: C, 60.54; H, 5.31; N, 3.21. Found: C, 60.17; H, 5.19; N, 3.24.

N,N-Bis[(3,5-dichlorophenyl)thio]-*tert*-butylamine (1k): colorless prisms (ethanol); mp 117.5–118.5 °C; yield 6.2%; UV (hexane) λ_{max} 256 nm (ϵ 18 400); NMR (CCl_4) δ 1.37 (s, *t*-Bu, 9 H) and 7.15 (s, aromatic, 6 H). Anal. Calcd for $C_{16}H_{15}Cl_4NS_2$: C, 44.98; H, 3.54; N, 3.28. Found: C, 44.82; H, 3.52; N, 3.14.

N,N-Bis[(4-bromophenyl)thio]-*tert*-butylamine (1l): colorless prisms (ethanol); mp 123.5–125.5 °C; yield 66%; UV (hexane) λ_{max} 256 nm (ϵ 25 200); NMR (CCl_4) δ 1.29 (s, *t*-Bu, 9 H) and 7.21 and 7.44 (d, *J* = 9.0 Hz, aromatic, 8 H). Anal. Calcd for $C_{16}H_{17}Br_2NS_2$: C, 42.97; H, 3.83; N, 3.13. Found: C, 43.30; H, 3.78; N, 2.98.

N,N-Bis[(4-bromophenyl)thio]-1-adamantanamine (1m): colorless prisms (ethanol); mp 153–155 °C; yield 40%; UV (hexane) λ_{max} 257 nm (ϵ 25 600); NMR (CCl_4) δ 1.56–2.07 (m, adamantyl, 15 H) and 7.18 and 7.41 (d, *J* = 9.0 Hz, 8 H). Anal. Calcd for $C_{22}H_{23}Br_2NS_2$: C, 50.29; H, 4.41; N, 2.67. Found: C, 49.92; H, 4.31; N, 2.49.

N,N-Bis[(2,4,6-trimethylphenyl)thio]-*tert*-butylamine (1n): colorless prisms (methanol); mp 100–101.5 °C; yield 15%; UV (hexane) λ_{max} 249 (sh, ϵ 19 500) and 211 nm; NMR (CCl_4) δ 1.17 (s, *t*-Bu, 9 H), 2.19 (s, *p*-Me, 6 H), 2.42 (s, *o*-Me, 12 H), and 6.71 (s, aromatic, 4 H). Anal. Calcd for $C_{22}H_{31}NS_2$: C, 70.72; H, 8.36; N, 3.75. Found: C, 71.00; H, 8.67; N, 3.77.

ESR Measurements. *N,N*-Bis(arylthio)alkylamine (10–30 mg) and 0.20–0.40 mL of solvent were placed in an ESR cell, the mixture was degassed by three freeze–pump–thaw cycles, and the cell was sealed off from the vacuum system. The cell was then set in the cavity of an ESR spectrometer and irradiated with a high-pressure mercury lamp (JEOL JES-UV-1, 100 W). ESR spectra were recorded during the irradiation or after interruption of the irradiation with a JEOL JES-ME-3X spectrometer equipped with an X-band microwave unit and 100-kHz field modulation. Temperature control was performed with a JEOL JES-VT-3 apparatus. Hyperfine splitting constants and *g* values were determined by comparison with those for Fremy's salt in K_2CO_3 aqueous solution (a_N 13.09 G, *g* 2.0057).

Determination of the Enthalpies of Dissociation for Dimers 3. Samples were prepared as described above. The samples were placed in the cavity of an ESR spectrometer and the peak-to-peak line width (w) and peak-to-peak amplitude (h) of the ESR signal were measured at five different temperatures between 6 and 35 °C. In the cases of **2a**, **2c**, and **2d** the relative radical concentration was also estimated by the area (s) under the absorption curve of the integrated ESR spectrum. The integration was performed with a JEOL JES-ID-2 integrator. The enthalpies of dissociation of **3** were obtained from the least-squares slopes of plots of $\ln w^2hT$ (or $\ln sT$) vs. $1/T$.[13,14] The measurements were repeated at least four times for each radical and averaged. The errors reported in Table II refer to the maximum deviation from the average value.

Registry No. **1a**, 90584-40-0; **1b**, 90584-41-1; **1c**, 90584-42-2; **1d**, 90584-43-3; **1e**, 90584-44-4; **1f**, 90584-45-5; **1g**, 90584-46-6; **1h**, 90584-47-7; **1i**, 90584-48-8; **1j**, 90584-49-9; **1k**, 90584-50-2; **1l**, 90584-51-3; **1m**, 90584-52-4; **1n**, 90584-53-5; **2a**, 64178-06-9; **2b**, 90584-54-6; **2c**, 90584-55-7; **2d**, 90584-56-8; **2e**, 64178-07-0; **2f**, 90584-57-9; **2g**, 90584-58-0; **2h**, 90584-59-1; **2i**, 90584-60-4; **2j**, 90584-61-5; **2k**, 90584-62-6; **2l**, 64209-54-7; **2m**, 90584-63-7; **2n**, 90584-64-8.

Photochemical Aromatic Cyanomethylation: Aromatic Substitution by Way of Radical Cations

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Photolysis at 254 nm of chloroacetonitrile in the presence of aromatic hydrocarbons led to ring cyanomethylation. In addition radical coupling products were found, especially with toluene where 3-phenylpropionitrile, succinonitrile, and bibenzyl accompanied the tolylacetonitriles. These same byproducts were obtained from toluene and chloroacetonitrile upon thermolysis with peroxide initiators, but no nuclear cyanomethylation was observed. The mechanism for aromatic cyanomethylation involves initial excitation of the aromatic hydrocarbons, followed by an electron transfer (probably by way of an exiplex) to chloroacetonitrile, which was found to quench aromatic fluorescence at high rates. Direct spectral evidence for the resulting radical cation with *p*-dimethoxybenzene was obtained by using laser flash spectroscopy. Loss of a chloride ion from the resulting radical anion produces a cyanomethyl radical in close proximity to an aromatic radical cation. Coupling leads to the aromatic substitution product whereas radicals escaping from the cage account for the observed byproducts.

Aromatic photoalkylations have been accomplished upon photolysis of appropriate alkyl halides with aromatic hydrocarbons (eq 1). Most of these have been alkyl halides with electron-withdrawing substituents attached (eq 1, R

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

= $CH_2CO_2CH_3$,[2] $CH_2CO_2C_2H_5$,[3-6] CH_2CONH_2,[7] and CH_2CN[8]) though simple alkyl halides like methyl iodide[9] have also been used. The ethyl chloroacetate system has been looked at in some detail but much of this work focused on the role of metal halides in promoting the aromatic substitution.[4-6] The authors suggested mechanisms ranging from substitution by carbethoxymethyl radical in the absence of metal halides[3,4] to a photo-Friedel–Crafts process in the presence of zinc or aluminum chloride.[4-6]

Many of the organic chlorides that lead to aromatic photosubstitution have also been found to be effective fluorescence quenchers.[1,4,10] This factor has been incorporated into some of the proposed photosubstitution mechanisms in that the radicals are purported to form as a result of energy transfer from the aromatic singlet excited state (eq 2–4)[4,10] rather than by direct photolytic homolysis of the halide (eq 5).

$$\mathrm{ArH \xrightarrow{h\nu} ArH^{*1}} \qquad (2)$$

$$\mathrm{ArH^{*1} + RCl \rightarrow ArH + RCl^{*}} \qquad (3)$$

$$\mathrm{RCl^{*} \rightarrow R\cdot + Cl\cdot} \qquad (4)$$

$$\mathrm{RCl \xrightarrow{h\nu} R\cdot + Cl\cdot} \qquad (5)$$

We have been interested in aromatic substitutions by electron-deficient alkyl radicals,[11-13] and set out to photolyze chloroacetonitrile in hopes of determining the role, if any, of the cyanomethyl radical in this system.

Results and Discussion

Aromatic cyanomethylation was observed upon photolysis at 254 nm of equimolar mixtures of chloroacetonitrile and an aromatic hydrocarbon in acetonitrile for 10–24 h (Table I). The general reaction stoichiometry is shown below (eq 6).

$$\mathrm{ArH + ClCH_2CN \xrightarrow{h\nu} ArCH_2CN + HCl} \qquad (6)$$

In addition to the aromatic substitution products, succinonitrile and a few minor (<0.5%) unidentified byproducts were formed in most of the chloroacetonitrile photolyses indicative of the involvement of the cyanomethyl radical. The photolyses of toluene with chloroacetonitrile had the extra byproducts 3-phenylpropionitrile and bibenzyl as well, implicating that benzyl radical was also involved in this case.

A number of experimental parameters were checked in the chloroacetonitrile reactions. The yield of phenylacetonitrile vs. the exposure time for the benzene reaction is shown in Table II. The maximum yield of product was obtained at approximately 10 h after which time its production essentially leveled off. After a 24-h photolysis was complete approximately half of the unreacted chloroacetonitrile remained in solution (Table I). It is likely that the reaction stopped because much of the incident light was blocked by a brown discoloration (gunking) on the inner walls of the quartz reaction tubes.

Table I. Cyanomethylation Products from Chloroacetonitrile Photolysis with Aromatics[a]

ArH	ArCH$_2$CN products: % yield[b]	o	m	p	(CH$_2$CN)$_2$, %[b]
C_6H_6	1.9				0.5
C_6H_5F	<1	36	43	21	<0.5
$C_6H_5CH_3$	2.6[c]	33	47	20	0.7[d]
$C_6H_5OCH_3$	11.0[e]	67	20	12	2.3
$C_{10}H_8$	4.8				
p-$C_6H_4(OCH_3)_2$	16.3				

[a] After exposure for 10–24 h to light at 254 nm, $ClCH_2CN$ and aromatic, both 0.5 M, in acetonitrile. [b] Based on $ClCH_2CN$ as limiting reagent; since half or more of this reagent was recovered after 24 h, the actual yields based on $ClCH_2CN$ consumed are higher. [c] Unreacted chloroacetonitrile, 81%, after 24 h. [d] Phenylpropionitrile, 6.4%, and bibenzyl, 2.1%, were also formed. [e] Unreacted chloroacetonitrile, 48%, after 24 h.

Table II. Phenylacetonitrile Yield vs. Time of Exposure to UV Light[a]

time, h	$C_6H_5CH_2CN$, %[b]
1	0.3
2	0.6
5	0.9
6	1.3
8	1.8
10	1.6
14	1.7
17	1.9

[a] Equimolar $ClCH_2CN$ and aromatic, 0.5 M, in acetonitrile solvent, 254 nm. [b] Based on $ClCH_2CN$ as limiting reagent; actual yields based on consumed $ClCH_2CN$ are higher.

Table III. Effect of Solvent on Photochemical Cyanomethylation with $ClCH_2CN$

ArH	ArCH$_2$CN, %[a]: CH_3CN[b]	excess $ClCH_2CN$[c]	excess ArH[b]
benzene	1.9	4.3	0.3
fluorobenzene	<1	2.4	
toluene	2.6	4.2	1.3
anisole	11.0	10.2	6.4

[a] Based on starting limiting reagent; actual yields based on reactants consumed are higher. [b] $ClCH_2CN$, 0.5 M, limiting reagent. [c] ArH, 0.5 M, limiting reagent.

Table IV. Photochemical Cyanomethylation of C_6H_5X

X	rel rate[a,b]	partial rate factors: o_f	m_f	p_f
F	1.3	1.4	1.6	1.6
CH_3	4.2	4.2	6.0	5.0
OCH_3	11.5	23.0	6.9	8.3

[a] Relative to benzene based on a 1:1:0.5 mixture of C_6H_5X:C_6H_6:$ClCH_2CN$ in acetonitrile, 254 nm, 22 h. [b] The relative substitution rates for naphthalene and 1,4-dimethoxybenzene were 87 and 107, respectively.

In addition to running reactions with acetonitrile as a solvent, a number of photolyses were run by using excess chloroacetonitrile or the aromatic as the solvent. Table III shows the effect of changing these reaction conditions on the product yield. In general the best yields were obtained when excess chloroacetonitrile served as the solvent and the poorest yields when excess aromatic was used as the solvent.

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Table V. Fluorescence Quenching by Chloroacetonitrile[a]

aromatic	ϵ_{254}	k_q, M^{-1} s^{-1} × 10^8	ΔG_{ET}, kcal/mol[b]
C_6H_6	121	0.1	−5.5
C_6H_5F	530	0.6	
$C_6H_5CH_3$	174	0.7	−11.8
$C_6H_5OCH_3$	426	35	−18.4
$C_{10}H_8$	2823	0.03	
p-$C_6H_4(OCH_3)_2$	115	96	−19.4

[a] In acetonitrile solvent. [b] Calculated using the Weller equation[14,16–18] with singlet energies from ref 20, aromatic oxidation potentials in acetonitrile from ref 21, and the chloroacetonitrile reduction potential from ref 14; larger values (−17 to −23 kcal/mol) were found with other reported aromatic oxidation potentials.

The photochemical cyanomethylation of monosubstituted benzene derivatives led to a mixture of ortho, meta, and para isomers (Table I). The observed isomer distributions show that there was little isomeric selectivity for this reaction especially with fluorobenzene and toluene.

The relative rates of the photochemical cyanomethylations were determined by photolyzing excess amounts of an aromatic and benzene together, with a limiting amount of chloroacetonitrile. The data are summarized in Table IV. All of the aromatics used in this reaction were found to be more reactive than benzene. Naphthalene and 1,4-dimethoxybenzene showed much larger relative rates of substitution than any of the other aromatics.

By combining the relative rates and isomeric compositions of anisole, toluene, and fluorobenzene, partial rate factors for the cyanomethylation processes were determined (Table IV). Each position on these aromatics was found to be more reactive than a position on benzene, with the ortho position of anisole being particularly activated.

The observation of radical coupling products in chloroacetonitrile photolyses indicated the presence of cyanomethyl radicals in that system. More direct evidence of a radical was obtained by photolyzing a mixture of chloroacetonitrile and 1,4-dimethoxybenzene within the sample cavity of an ESR spectrometer and observing a faint signal indicative of the presence of radicals. There was no hyperfine splitting observed, and, therefore, it was not possible to identify this radical. However, no signal was seen when either chloroacetonitrile or 1,4-dimethoxybenzene was photolyzed alone.

There are a number of potential pathways for the formation of cyanomethyl radical from chloroacetonitrile photolyses. At the wavelength of irradiation chloroacetonitrile absorbs very weakly ($\epsilon_{254} < 1$) whereas all of the aromatics absorb appreciably (Table IV). Thus, it is plausible to suggest that cyanomethyl radical forms as a result of some sort of energy transfer from the excited state of the aromatic rather than by the direct photolytic homolysis of chloroacetonitrile.

The fact that chloroacetonitrile has been shown to be a good quencher of fluorescence from electron-rich aromatics[10,14] supports this energy-transfer concept. We determined the quenching rate constants (k_q) by a Stern–Volmer treatment of fluorescence intensities of the aromatic series in the presence of varying concentrations of chloroacetonitrile (Table V) by using known aromatic fluorescence lifetimes.[15] These values of k_q were found to span more than three orders of magnitude ranging from 10^6 to 10^9 M^{-1} s^{-1}. Although the rate constants vary over a wide range, they are all large enough to show that energy transfer from the singlet excited state of the aromatic to chloroacetonitrile is a favorable process. The quenching constant observed with p-dimethoxybenzene was very similar to that found in an earlier study.[2]

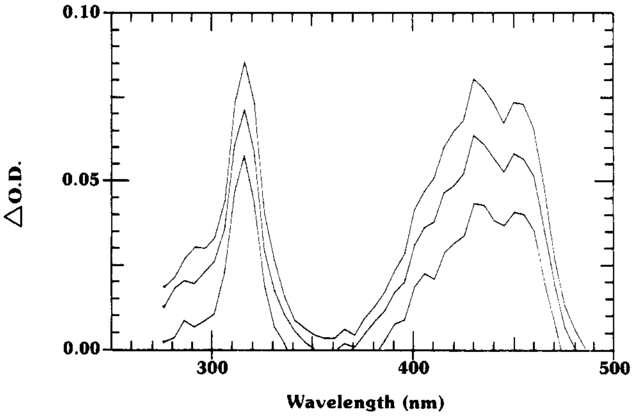

Figure 1. UV-visible spectrum of transient radical cation (PDMB$^{+\cdot}$) from p-$C_6H_4(OCH_3)_2$ + $ClCH_2CN$ photolysis. Conditions: $ClCH_2CN$, 1.26 M; p-dimethoxybenzene, 3.5 × 10^{-3} M in CH_3CN. Optical density measured every 5 nm. The three curves represent spectra obtained after 8 μs (top), 20 μs (middle), and 60 μs (bottom).

Although apriori there are a couple of mechanisms by which chloroacetonitrile could quench the fluorescence of the aromatics and subsequently generate a cyanomethyl radical, classical singlet energy transfer from the aromatic to the chloroacetonitrile (eq 7) is unlikely. Chloroacetonitrile has a higher singlet energy than the aromatics making the energy transfer (eq 7) an endergonic process.[10,14,16]

$$ArH^{*1} + ClCH_2CN \rightarrow ArH + ClCH_2CN^{*1} \quad (7)$$

A more energetically favorable mechanism for fluorescence quenching would be an electron-transfer mechanism[14,16–18] which would involve the transfer of an electron from the singlet excited state of the aromatic to chloroacetonitrile (eq 9) probably by way of an exiplex 1 (eq 8). The chloroacetonitrile radical–anion, **3**, could then lose a chloride ion to form the cyanomethyl radical (eq 10).[10,19]

$$ArH^{*1} + ClCH_2CN \rightarrow \underset{\mathbf{1}}{[ArH\text{-----}ClCH_2CN]^{*}} \quad (8)$$

$$\mathbf{1} \rightarrow \underset{\mathbf{2}}{ArH^{+\cdot}} + \underset{\mathbf{3}}{\cdot^{-}ClCH_2CN} \quad (9)$$

$$\mathbf{3} \rightarrow \cdot CH_2CN + Cl^{-} \quad (10)$$

The energetics of this electron-transfer process can be approximated by using the Weller equation.[14,16–18] Such calculations indicate that electron transfer is favorable for each aromatic substrate with chloroacetonitrile (Table V) where the calculated values range from 5 to 20 kcal/mol. It is interesting to note that the quenching rates qualitatively parallel the calculated ease of electron transfer (a plot of log k_q vs. ΔG_{ET} shows good linearity).

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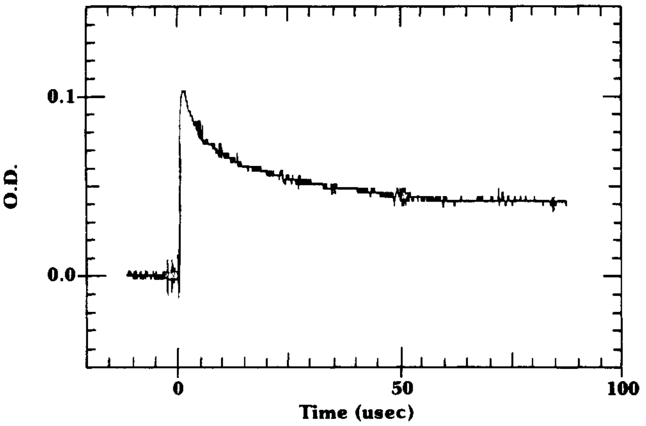

Figure 2. Decay of transient radical cation (PDMB$^{+}\cdot$) from photolysis of $C_6H_4(OCH_3)_2$ and $ClCH_2CN$ monitored at 465 nm.

Direct evidence that an aromatic radical cation could be produced in this type of photolysis was obtained. Laser flash photolysis of *p*-dimethoxybenzene and chloroacetonitrile in acetonitrile gave rise to a transient whose visible spectrum matched that reported for *p*-dimethoxybenzene[22] (Figure 1). Control flash photolysis of chloroacetonitrile alone showed no transients, whereas only fluorescence was observed when *p*-dimethoxybenzene alone was subjected to the same conditions. Previously radical cation intermediates had been detected upon methoxynaphthalene quenching by chloroacetonitrile.[10]

The decay of the resulting radical cation from chloroacetonitrile was monitored at 465 nm (Figure 2). Much of the radical cation was consumed rapidly, but some residual radical cation remained for up to 0.02 s. The initial decay did not give a good fit to first-order kinetics, but indicated a higher order.

Once the cyanomethyl radical is formed there are at least two different pathways it could take in forming the ultimate aromatic substitution products. Considering evidence for radical cations a likely mechanism for the actual substitution step with chloroacetonitrile involves the coupling of the aromatic radical cation, **2**, with the cyanomethyl radical (eq 11). This would be followed by deprotonation

$$2 + \cdot CH_2CN \rightarrow \underset{\mathbf{4}}{HAr^+CH_2CN} \qquad (11)$$

$$4 \xrightarrow{-H^+} ArCH_2CN \qquad (12)$$

to give the products (eq 12). The greater than first-order decay of a significant portion of the *p*-dimethoxybenzene radical cation (Figure 2) is consistent with the coupling process (eq 11).

It is likely that the electron transfer (eq 9) and subsequent radical pairing (eq 11) occur within a solvent cage. The photochemical cyanomethylation of toluene with chloroacetonitrile leads to the greatest amounts of side products (Table I) due to radical coupling reactions, consistent with the fact that the toluene radical cation is known to rapidly lose a proton to produce the benzyl radical (eq 13).[23] Radical pairing can account for the

$$(C_6H_5CH_3{}^+\text{-------}CH_2CN) \xrightarrow{-H^+} (C_6H_5CH_2\cdot + \cdot CH_2CN) \qquad (13)$$

aromatic cyanomethylated products including 3-phenylpropionitrile whereas only radicals escaping from the cage can lead to succinonitrile and bibenzyl. While all these products were produced in acetonitrile as a solvent (Table I), photolysis in cyclohexane led only to the isomeric tolylacetonitriles and 3-phenylpropionitrile. Radicals escaping from the cage in the latter solvent system apparently abstracted hydrogen from the solvent rather than coupling.[24]

Table VI. Products from $ClCH_2CN$–Toluene and Radical Initiators

system	products, %[a]				
	$CH_3C_6H_4CH_2CN$	$(CH_2CN)_2$	$C_6H_5CH_2CH_2CN$	$(C_6H_5CH_2)_2$	$C_6H_5CH_2X$
hν[b]	2.6	0.7	6.4	2.1	
$(ROCO_2)_2$[c]		0.2	3.4	1.0	
(RO_2CO_2R)[d,e]		1.2		3.6	5.7

[a] Toluene (0.5 M), $ClCH_2CN$ (0.5 M), peroxide (0.25 M); yields are based on initial XCH_2CN concentration. [b] Irradiated at 254 nm for 24 h, no peroxide. [c] 24 h, 60 °C. [d] 1 week, 80 °C. [e] Other minor unidentified products also present.

Though numerous reports of aromatic substitution by way of aromatic radical to anion coupling are known ($S_{RN}1$ mechanism),[25,26] this work represents one of the few cases of aromatic radical cation–radical coupling.[27]

A less likely pathway to account for the cyanomethylated products would be by a typical homolytic aromatic substitution reaction in which the cyanomethyl radical attacks the ground-state aromatic (eq 14 and 15).

$$ArH + \cdot CH_2CN \rightarrow \underset{\mathbf{5}}{HAr\cdot CH_2CN} \qquad (14)$$

$$5 \xrightarrow[{[O]}]{-H^+} ArCH_2CN \qquad (15)$$

If this mechanism were involved, a Hammett correlation should be possible for cyanomethylation since homolytic aromatic substitution is a process which has been known to show good Hammett correlations.[11,13,28] However, attempted Hammett plots of the log of the partial rate factors[29] from chloroacetonitrile (Table IV) photolysis vs. either σ or σ^+ substituent constants[30] gave a scattering of data points with no apparent correlation.

Independent evidence for toluene byproduct formation was obtained by carrying out a number of thermal reactions of toluene and chloroacetonitrile in the presence of the peroxide initiators, *OO-tert*-butyl isopropyl peroxycarbonate and di-*n*-propyl peroxydicarbonate. Although byproducts similar to those obtained in the toluene–chloroacetonitrile photolyses resulted (Table VI) there were no tolylacetonitriles. In the peroxide-initiated reactions alkoxy radicals formed upon homolysis (eq 16) can

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[22] O'Neill, P.; Steeken, S.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1975**, *79*, 2773.

[23] The rate constant for this process in acetonitrile is on the order of 10^3 s^{-1}; Parker, V. D. *Adv. Phys. Org. Chem.* **1983**, *19*, 131. C. Walling, unpublished work.

[24] Russell, G. In "Free Radicals"; Kochi, J., Ed.; Wiley-Interscience: New York, 1973; Vol. I, Chapter 7.

[25] Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

[26] Rossi, R. A. *Acc. Chem. Res.* **1982**, *15*, 164.

[27] For other examples see: Perrin, C. L. *J. Am. Chem. Soc.* **1977**, *99*, 5516. Schmitt, R. J.; Buttrill, S. E., Jr.; Ross, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 926 and ref. 21.

[28] Pryor, W. A.; Davis, W. H.; Gleaton, J. H. *J. Org. Chem.* **1975**, *40*, 2099.

[29] These relative rates would be accurate if cyanomethylation occurred on aromatic ground states. For a substitution scheme such as eq 8–12 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 V), different lifetimes, and quenching constants as well as the possibility of energy transfer from one aromatic excited singlet to the ground state of another.

[30] Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; p 131.

$$(ROCO_2)_2 \text{ or } ROOCO_2R \xrightarrow{\Delta} 2RO\cdot + CO_2 \tag{16}$$

$$RO\cdot + C_6H_5CH_3 \rightarrow ROH + C_6H_5CH_2\cdot \tag{17}$$

$$C_6H_5CH_2\cdot + XCH_2CN \rightarrow C_6H_5CH_2X + \cdot CH_2CN \tag{18}$$

readily abstract benzylic hydrogens from toluene (eq 17), providing an alternate source (to eq 13) for the benzyl radical. Once formed, interaction with haloacetonitrile provides cyanomethyl radicals and the observed benzyl halide products (eq 18).

Regular radical coupling processes can account for the succinonitrile, phenylpropionitrile, and bibenzyl observed. However, tolylacetonitriles can only be formed if cyanomethyl radical attacks ground-state aromatics (eq 14) and can be oxidatively rearomatized (eq 15), a process which apparently does not occur under these circumstances.

Summary

Photolysis of chloroacetonitrile in the presence of aromatic hydrocarbons leads to nuclear cyanomethylation. The evidence indicates aromatic excitation, quenching by electron transfer to chloroacetonitrile followed by coupling between an aromatic radical cation and cyanomethyl radical (eq 8–12).

Experimental Section

Qualitative and quantitative gas chromatographic analyses were performed on Hewlett Packard 5840 gas chromatographs equipped with flame-ionization detectors, capillary inlets (split mode), and the following capillary columns: (1) 30 m × 0.22 mm glass coated with SP-2100; (2) 15 m × 0.25 mm fused silica coated with Carbowax 20 m; (3) 15 m × 0.25 mm fused silica coated with OV-17. A Varian Model 90-P gas chromatograph equipped with thermal conductivity detector and a 10 ft × 0.25 in. stainless steel column packed with 15% SE-30 on chrom W (60–80 mesh) AW-DMCS was utilized for product isolation.

Routine infrared spectra were recorded as thin films or solutions in CCl_4 or $CDCl_3$ on a Perkin-Elmer Model 710-B spectrometer while a Perkin-Elmer Model 621 spectrometer was utilized for detailed isomer analyses. ^1H NMR spectra were recorded ($CDCl_3$ solutions containing 5% TMS) on a Perkin-Elmer Model R-24B 60-MHz NMR spectrometer. Beckman Model 35 and Perkin-Elmer Model 330 UV–vis spectrometers were used to obtain UV spectra (acetonitrile solvent).

Fluorescence measurements were made by using a Perkin-Elmer Model MPF-4 fluorescence spectrometer. This instrument was equipped with both excitation and emission monochrometers. All measurements were made in acetonitrile solvent by using 1.0-cm quartz sample cells. The concentrations of the aromatics used were on the order of 10^{-4}–10^{-5} M. No effort was made to degas the sample solutions. A fluorescence spectrum was taken of each aromatic by setting the excitation monochrometer on the absorption λ_{max} and scanning the emission spectrum. The fluorescence quenching measurements were made with both monochrometers at their respective λ_{max} settings. The concentration of chloroacetonitrile was adjusted in order to quench between 10% and 50% of the initial fluorescence. The relative fluorescence intensities were measured for at least four different quencher concentrations.

Several reaction mixtures were photolyzed in the sample cavity of an ESR spectrometer. The instrument used was a Varian Model E4, X-band spectrometer. The ultraviolet light source used was a Hanovia 450-watt high-pressure mercury vapor lamp. The lamp was placed in a water jacketed quartz sleeve. The quartz sleeve was sealed in aluminum foil except for a 2 cm × 13 cm tube which allowed light to be directed to the ESR sample cavity. Sample solutions were placed in a quartz ESR flat cell. After allowing approximately 5 min for the lamp to reach full output the ESR spectrum was scanned from 3300 to 3500 gauss. This would correspond to an organic radical with a g value of 2.0.

Laser flash photolysis was performed on a system consisting of a frequency quadrupled Molectron Model MY-32 Nd-YAG laser (266 nm) which was focused onto a 1 × 1 cm quartz fluorescence cell. The probe beam, generated by a SLM Instruments LH-450 xenon arc lamp (450 watts), was passed through the cell perpendicular to the laser beam. The probe beam was then passed through a Jarrell Ash Model 82-410 monochromator to a Hamamatsu R928 photomultiplier tube. The signal from the photomultiplier was monitored by a Biomation 8100 waveform recorder which was interfaced to an LSI-11 computer. Solutions were degassed by bubbling nitrogen for 5 min prior to flash photolysis. In Figure 1 optical density readings were taken every 5 nm.

Reagents. Chloroacetonitrile (Aldrich, 98+%) was found to be greater than 99% pure by GC analysis and was used directly. Di-*n*-propyl peroxydicarbonate and *OO-tert*-butyl isopropyl peroxycarbonate were shown to be >99% by iodometry and were used directly. The aromatic hydrocarbons and acetonitrile and cyclohexane solvents were all high purity chemicals used without further purification.

With the exception of (*m*-fluorophenyl)acetonitrile all authentic compounds were available from Aldrich Chemical Company. (*m*-Fluorophenyl)acetonitrile (95% purity) was synthesized (80% yield) by the reaction of *m*-fluorobenzyl bromide with sodium cyanide using a modification of the procedure described by Adams.[31]

Photolysis General Procedure. All photochemical reactions were carried out in a Rayonet Model 100 photochemical reactor equipped with 16 low-pressure mercury-vapor ultraviolet lamps (>90% emission at 254 nm) and a merry-go-round apparatus. Solutions of the reaction mixtures were placed in 130 nm × 15 nm quartz test tubes. These tubes were sealed with a rubber septum and degassed to remove dissolved oxygen by bubbling nitrogen in each test tube for 5 min. The solutions were irradiated in the reactor for a period of time ranging from 10 to 24 h except in cases where the product yield was being measured as a function of the exposure time.

Solutions containing the reactants were mixed in the following proportions: (1) a limiting amount of chloroacetonitrile with the aromatic serving as the solvent; (2) a limiting amount of aromatic with chloroacetonitrile solvent; (3) dilute equimolar amounts of aromatic and chloroacetonitrile in acetonitrile solvent.

Upon completion, most reaction mixtures were passed through a column packed with activated alumina by using chloroform as an eluant in order to remove any black tarry material. After concentrating, the products from photolyses of chloroacetonitrile with benzene, toluene, anisole, and fluorobenzene were collected by preparative GC (repetitive 30-μL injections) and subjected to IR and NMR analysis and matched to the spectra of the corresponding authentic materials. In the naphthalene and *p*-dimethoxybenzene reactions the unreacted aromatic was separated from the products by using a silica column and hexane/chloroform as the eluants. It was possible to obtain 99% plus purity of the products. These products were identified by IR, NMR, and GC. (2,5-Dimethoxyphenyl)acetonitrile, so isolated, was 100% pure by GC: ^1H NMR ($CDCl_3$) 3.3–3.7 (m, 8 H), 7.0–6.8 (m, 3 H); IR (CCl_4) 2280 cm^{-1} ($C\equiv N$). Anal. Calcd for $C_{10}H_{11}NO_2$: C, 68.16; H, 6.29; N, 7.95. Found: C, 67.29; H, 6.29; N, 7.83.

Qualitative GC analysis was done by comparing the retention time of the unknown with authentic products on two dissimilar capillary columns (1 and 2) and by observing product peak enhancement upon coinjecting with authentics.

For quantitative determinations, phenylacetonitrile was chosen as an internal standard. The detector response factor (DRF) was determined by analyzing three mixtures containing known amounts of the products and internal standard in different ratios. The product mixture was worked up in the usual fashion after adding a known amount of phenylacetonitrile. Product yields were determined by comparing the relative areas for the products to that of the added internal standard and by using the DRF. Direct GC analysis using an internal standard was used to determine unreacted haloacetonitrile.

Competition Reactions. In each competition reaction, 10 mmol of either toluene, fluorobenzene, anisole, dimethoxybenzene, or naphthalene were combined with benzene (10 mmol) and chloroacetonitrile (5 mmol) and diluted with acetonitrile. The mixtures were then degassed and photolyzed according to the

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[31] Adams, R.; Thal, A. F. "Organic Syntheses"; Gilman, H., Ed.; Wiley: New York, 1941; Collect. Vol. 1, p 107.

earlier procedure. With the more reactive aromatics, *p*-dimethoxybenzene and naphthalene, additional competitions employing 2:1 or 5:1 molar ratios of benzene to *p*-dimethoxybenzene or naphthalene were also run.

Peroxide-Initiated Reactions. Chloroacetonitrile, (5 mmol), toluene (10 mmol), and the peroxide (5 mmol) were dissolved in acetonitrile (100 mL), degassed with nitrogen, and heated. The *OO-tert*-butyl isopropyl peroxycarbonate reactions were refluxed (80 °C) for one week whereas the di-*n*-propyl peroxydicarbonate reactions were placed in a constant temperature bath at 60 °C for 6 h. In both cases iodometric analysis indicated that unreacted peroxide was negligible at the end of the reaction. Product analysis was carried out directly or after partial evaporation of the solvent and reactants.

Determination of Isomer Distributions. The meta and para isomers of (methylphenyl)acetonitrile and (fluorophenyl)acetonitrile could not be separated by capillary column GC. The isomer distributions could be determined however by using GC, IR, and NMR methods.

In the case of (fluorophenyl)acetonitrile the GC could separate the ortho isomer, but the meta and para isomers gave a single peak. Examination of the infrared spectra of the authentic compounds showed that a peak at 1140 cm^{-1} could be assigned to the meta isomer while a peak at 1160 cm^{-1} was unique to the para isomer. Absorbances were determined from a series of four standards containing different ratios of (*m*- and (*p*-fluorophenyl)acetonitrile and a calibration curve for absorbance to concentration ratios constructed. The meta:para ratio for the (fluorophenyl)acetonitrile produced by the photochemical reaction of fluorobenzene and chloroacetonitrile was determined from the calibration curve by running the IR spectrum of the preparative GC sample.

NMR was used to determine the isomer distribution of the products from the toluene photolyses. GC analysis of the products gave the (*m*- and (*p*-methylphenyl)acetonitrile products together in one peak, and (*o*-methylphenyl)acetonitrile along with phenylpropionitrile together in another peak. These products were collected together in a single preparative GC sample and analyzed by NMR. The methylene protons from the ortho isomer were resolved from those of the combined meta and para isomers as well as from phenylpropionitriles and could be integrated to find the fraction of ortho isomer. The meta to para isomer ratio was determined by preparing standard solutions of the pure isomers. These solutions were mixed in varying ratios until one was obtained which gave an NMR spectrum matching that of the signal from the reaction mixture. Alternately separation of the tolylacetonitriles could be accomplished on two different columns. Column 1 separated the meta isomer from the combined ortho and para isomers, whereas column 2 separated the ortho isomer from the other two. Once the meta and ortho isomers were determined, the para isomer was calculated by subtracting the ortho isomer determined by column 2 from the ortho + para isomers of column 1 and also by subtracting the meta isomer determined by column 1 from the meta and para isomers of column 2.

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Registry No. C_6H_6, 71-43-2; C_6H_5F, 462-06-6; $C_6H_5CH_3$, 108-88-3; $C_6H_5OCH_3$, 100-66-3; $C_{10}H_8$, 91-20-3; *p*-$C_6H_4(OCH_3)_2$, 150-78-7; $ClCH_2CN$, 107-14-2.

Product Studies of the Photocycloaddition Reactions of 5-Chloro- and 5-Fluorouracil Derivatives and Olefins. An Interesting and Useful Effect of Fluorine on Regioselectivity

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The acetone-sensitized photochemical cycloadditions of 1,3-dimethyl-5-chlorouracil (**1a**), 5-chlorouracil (**1b**), 1,3-dimethyl-5-fluorouracil (**4**), and 5-fluorouracil (**7**) have been studied. The 5-chlorouracil systems **1a** and **1b** gave complex, acidic product mixtures on attempted photocycloaddition to enol acetates. Only tetramethylethylene underwent clean photocycloaddition with **1a** and **1b**, affording a mixture of cycloadduct and 1,3-dimethyl-5-(1,1,2-trimethyl-2-propenyl)-2,4(1*H*,3*H*)-pyrimidinedione (**3**). By contrast, 5-fluorouracil derivatives **4** and **7** underwent clean photochemical cycloaddition to isopropenyl acetate, cyclopentenyl acetate, and cyclohexenyl acetate to form endo,exo mixtures of the head-to-tail photoadducts. In its photocycloaddition to simple olefins, 5-fluorouracil showed a much higher preference for formation of the head-to-tail photoadduct than do other simple uracil derivatives or cyclohexenone. The reaction of 5-fluorouracil with isobutylene, methylenecyclopentane, methylenecyclohexane, and methylenecycloheptane gave nearly exclusively the head-to-tail regioisomer. The ratio of head-to-tail to head-to-head isomers for the reaction of 5-fluorouracil with 1-methylcyclopentene, 2-methyl-2-butene, and propene was 89:11, 85:15, and 76:24, respectively. Extensive ^{19}F NMR data are reported for the photocycloadducts.

The initial impetus for investigating the photocycloaddition chemistry of 5-chloro- and 5-fluorouracil was to employ the adducts as intermediates in the synthesis of 5-functionalized uracils and uridines as noted in the accompanying paper.[1] A prelude to applying the above strategy to uracil functionalization was a study of the photochemical cycloaddition of the 5-halouracils with enol acetates; these results are reported herein.[2a] More interestingly, the photochemical cycloaddition of 5-fluorouracil with simple olefins showed an unexpectedly high

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[1] Kaminski, V. V.; Wexler, A. J.; Balchunis, R. J.; Swenton, J. S. *J. Org. Chem.*, following paper in this issue.

[2] Some of this material has been reported in preliminary form: (a) Wexler, A. J.; Balchunis, R. J.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1975**, 601. (b) Wexler, A. J.; Swenton, J. S. *J. Am. Chem. Soc.* **1976**, *98*, 1602.

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