Photochemical Reaction of Arenecarbonitriles in the Presence of Alkylsilanes, Silyl Ethers and Silyl Amines

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The irradiation of benzene-1,2,4,5-tetracarbonitrile, and benzene-1,2,4- as well as benzene-1,3,5-tricarbonitrile in the presence of various tetraalkylsilanes, alkoxytrialkylsilanes, hexamethyldisiloxane or heptamethyldisilazane leads to alkylation of the aromatics. The more substituted alkyl group is selectively fragmented, and the attack takes place at the position(s) of highest spin density in the nitrile radical anion. The reaction involves electron transfer to the nitrile's singlet excited state, and the radical cation appears to cleave mainly in the initial radical ion pair.

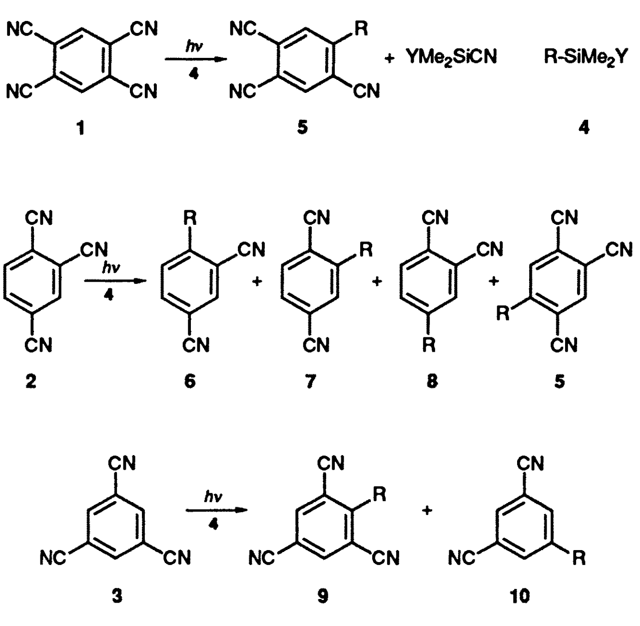
The recent literature has shown that aromatic and olefinic donors[1-9] can be oxidized to the corresponding radical cations through photoinduced electron transfer, and that such species easily undergo cleavage of a σ bond and generate a neutral radical and a cation [eqns. (1)–(3)].

$$A \rightarrow A^* \tag{1}$$

$$A^* + X\text{–}Y \rightarrow A^{\cdot -} + X\text{–}Y^{\cdot +} \tag{2}$$

$$X\text{–}Y^{\cdot +} \rightarrow X^{\cdot} + Y^{+} \tag{3}$$

In this way stabilized radicals (*e.g.* benzyl, allyl) have been prepared under unconventional conditions and have been found to react with the sensitizer (in most cases an aromatic molecule). Similarly α-aminoradicals have been obtained in this way.[10-12] It is of obvious interest to extend this method to the generation of non-stabilized (alkyl) radicals. This raises two problems, first to have a functionality in the molecule that could make it a sufficiently good donor, so that step (2) can occur, and second that a fragment of the molecule corresponds to a stable cation so that step (3) is feasible. We considered that both aims could be reached by using organosilicon derivatives and work on the project was underway when a communication[13] by Ohashi's group disclosed that alkylsilanes, germanes and stannanes do undergo such a cleavage when irradiated in the presence of benzenecarbonitriles. Alkylation of the aromatic takes place under these conditions. However, our investigation had taken a quite different line, with the exploration of various classes of organosilicon derivatives besides alkylsilanes, as well as of the effect of the acceptor structure, and with only marginal duplication of the above-mentioned results. We report here the photochemical reaction of some benzene-tri- and tetra-carbonitriles with silanes, silyl ether and silylamines.



$$Me_3SiOH \xleftarrow{H_2O} Me_3SiCN \xrightarrow{EtOH} Me_3SiOEt$$

4j **4l** **4e**

	R	Y
a	Me	Me
b	C_5H_{11}	Me
c	Pr^i	Me
d	Bu^t	Me
e	Me	OEt
f	Bu^t	OC_8H_{17}
g	Me	$OSiMe_3$
h	Me	$NMeSiMe_3$

Scheme 1

Results

Aromatic Alkylation.—Benzene-1,2,4,5-tetracarbonitrile **1**, benzene-1,2,4-tricarbonitrile **2** and benzene-1,3,5-tricarbonitrile **3** were chosen as the light absorbing electron-acceptors. Irradiation of acetonitrile solutions of such materials in the presence of various alkylsilanes caused alkylation of the aromatic ring with high chemical yield (Table 1). Thus, tetracarbonitrile **1** and tetramethylsilane **4a** gave 5-methylbenzene-1,2,4-tricarbonitrile **5a**. With pentyltrimethylsilane **4b** only the pentylbenzenetricarbonitrile **5b** and none of the methyl derivative **5a** were obtained. Likewise, with isopropyltrimethylsilane **4c** and *tert*-butyltrimethylsilane **4d** substitution of the more substituted alkyl for a cyano group on **1** was observed.

Different organosilicon derivatives were tested. Thus, ethoxytrimethylsilane **4e** and hexamethyldisiloxane **4g** gave tricarbonitrile **5a** and octyloxy-*tert*-butyldimethylsilane **4f** gave the *tert*-butyl analogue **5d**, in every case as the only aromatic products. Compound **5a** was again obtained from heptamethyldisilazane

Table 1 Alkylaromatics from the irradiation of cyanoaromatics in the presence of organosilicon derivatives in acetonitrile

Substrate	Silicon derivative	Product [(yield (%)][a]
1[b]	**4a**	**5a** (80)
	4b	**5b** (85)[c]
	4c	**5c** (85)
	4d	**5d** (88)
	4e	**5a** (85)
	4f	**5b** (90)
	4g	**5a** (90)
	4h[d]	**5a** (50)
2	**4a**	**5a** (23), **6a** (18), **7a** (35), **8a** (14)
	4e	**5a** (21), **6a** (17), **7a** (36), **8a** (15)
	4g	**5a** (24), **6a** (16), **7a** (32), **8a** (15)
	4h	**5a** (24), **6a** (15), **7a** (35), **8a** (11)
3	**4b**	**9b** (62), **10b** (18)
	4g	**9a** (52), **10a** (13)

[a] Calculated based on the reacted nitrile. Conversion is usually ~90%. [b] Traces of the three dialkyldicyanobenzenes formed by secondary photo-reaction of the monoalkyltricyanobenzenes[23] were present in the photolysate (total amount < 5%). [c] Traces of **5a** also present (⩽2%). [d] Some substrate **1** is consumed through an unrecognized path.

Table 2 Steady-state parameters for the reaction of cyanoaromatics in the presence of organosilicon derivatives

Substrate	Silicon derivative	Solvent	K_{sv}/dm^3 mol^{-1}	$\Delta G_{et}{}^a$/kcal dm^3 mol^{-1}	Φ^b	Φ^c
1	**4a**	MeCN	20	-5^e	0.11	0.035
	4a	AcOEt			0.02	
	4c	MeCN		-11^f	0.125	
	4f	MeCN			0.07	0.05[d]
	4g	MeCN	45	-9^g	0.08	0.035
	4g	AcOEt			0.02	
	4h	MeCN			0.02	
2	**4a**	MeCN			0.01	
	4e	MeCN			0.02	
	4g	MeCN	15		0.02	
3	**4b**	MeCN			0.01	
	4g	MeCN	5	-5^h	0.003	

[a] Free energy change for electron transfer to the singlet excited nitriles calculated by the Weller equation[24] and the E_i data from ref. 15. [b] Quantum yield of formation of the alkylated nitrile(s) with donor (0.1 mol dm^{-3}). [c] Quantum yield of formation of MeSiCN under the same conditions as *b*. [d] In the presence of MeOH (0.1 mol dm^{-3}), $C_8H_{17}OSiMe_2OMe$ is formed with a quantum yield of 0.04 and $C_8H_{17}OH$ with $\Phi = 0.08$. [e] E_i 9.80 eV,[14] E_{red}(**1**) −0.65 V *vs.* SCE,[25] E_{exc}(**1**) 3.83 eV. [f] E_i 9.50 eV.[15] [g] 9.59 eV.[15] [h] E_{red}(**3**) −1.02 V *vs.* SCE,[26] E_{exc}(**3**) 4.03 eV.

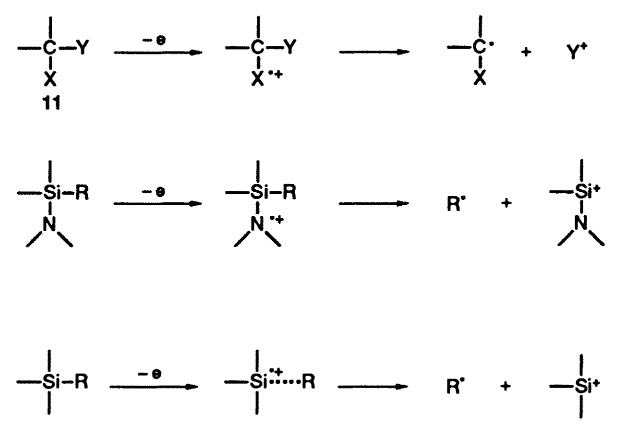
4h, though in this case some compound **1** was consumed through an unrecognized path. Furthermore, the reactivity of other acceptors was tested. Thus, the irradiation of tricarbonitrile **2** with **4a** in acetonitrile gave the methylbenzenetricarbonitrile **5a** as well as the three expected methylbenzenedicarbonitriles **6a**–**8a** (unambiguous identification of the isomers is possible on the basis of spectral data, particularly ^{13}C chemical shifts). Exactly the same product distribution resulted from the reaction with the silyl ether **4e**, the siloxane **4g** and the silazane **4h**. With tricarbonitrile **3** the reaction was slow, but again led to alkylation on the ring. Both with **4a** and with **4b** two products were obtained, the main one being 2-alkylbenzene-1,3,5-tricarbonitriles **9a** and **9b**, respectively and the minor one 5-alkylbenzene-1,3-dicarbonitriles **10a**, **b**. The mixture **9a**–**10a** was obtained in the same ratio also from the siloxane **4g**.

Silicon-containing Products.—No silicon-containing aromatic compound was obtained under these conditions. With **4a** and using rigorously dried acetonitrile, trimethylsilylcyanide **4i** was the only identified silicon-containing product, and its amount accounted for 40–50% of the silane consumed in the reaction with the nitrile. In the presence of traces of moisture some hexamethylsiloxane **4g** was found too. When acetonitrile containing 0.1% water was used, the silicon derivative obtained was trimethylsilanol **4j** accounting for 50–70% of the consumed **1a**, and with 0.1% ethanol both ethoxytrimethylsilane **4e** and some silanol were formed. Under this condition (water or methanol ⩽0.1%), the rate of the reaction was not affected, while this was the case with larger amounts of the additives. Thus, with 1% ethanol the product distribution did not change (the methylbenzenetricarbonitrile **5a** and ethoxytrimethylsilane were formed), but the rate of the conversion was somewhat diminished. With silicon containing substrates of higher molecular weight, it was easier to ascertain whether other processes involving the organosilicon derivatives could occur. With the octyloxytrialkylsilane **4f** in acetonitrile containing 0.1% H_2O, as an example, octyloxydimethylsilanol was formed in an amount corresponding to 75% of the aromatic alkylation occurring and was accompanied by some octanol (15% with respect to the alkylation occurring). Separate experiments showed that **4f** suffered virtually no dark hydrolysis under these conditions. In acetonitrile containing 0.1% MeOH, the reaction took a similar course yielding methoxyoctyloxydimethylsilane. No other products were formed in significant amounts in any other case.

Mechanistic Data.—Further experiments were carried out in order to obtain information about the scope and the mechanism of the reaction. It was observed that a very polar medium such as acetonitrile is not a prerequisite for the occurrence of the photochemical alkylation. Thus, the methylbenzenetricarbonitrile **5a** was obtained from the nitrile **1** and tetramethylsilane **4a**, the siloxane **4g** or the silazane **4h** also in ethyl acetate, although the reaction became slower. Unfortunately, the solubility of the present nitriles in less polar solvents was too low for preparative experiments. As for the excited state involved it was observed that all the silicon derivatives used quenched the fluorescence of the nitriles **1**–**3**. Representative Stern Volmer constants ($K_{sv} = k_q\tau$), are reported in Table 2 and show that the rate of quenching is below diffusion controlled [τ(**1**) = 10.8 ns]. Furthermore, the Table collects some data for the chemical quantum yield at a fixed concentration of the silanes. In the case of siloxane **4g**, a double reciprocal plot of quantum yield *vs.* donor concentration gave limiting $\Phi = 0.14$ and intercept: slope ratio $K' = 52$ dm^3 mol^{-1}.

Discussion

General Mechanistic Scheme.—The present reaction is initiated by electron transfer to the singlet excited state of the cyanoaromatic, as indicated by quenching of the nitriles fluorescence, efficient reaction in polar media and negative calculated free energy change for electron transfer (Table 2). The organometallic radical cation then undergoes cleavage of the carbon–silicon bond yielding the alkyl radical which then adds to the radical anion of the nitrile; finally, cyanide loss leads to rearomatization. Thus, the question formulated in the introduction is answered in the positive. It is possible to generate unstabilized (alkyl) radicals *via* cleavage of a radical cation provided that an oxidant strong enough to accept an electron from relatively poor donors, such as those considered here is used. Suitable substrates include, besides silanes (as



Scheme 2

Table 3 Bond dissociation energy

Reaction	E_{bd}[a]/kcal mol^{-1}
$Me_4Si^{\bullet+} \rightarrow Me_3Si^+ + Me^\bullet$	15 (5.3)[b]
$Me_3SiBu^{t\bullet+} \rightarrow Me_3Si^+ + Bu^{t\bullet}$	27.4
$Me_3SiOMe^{\bullet+} \rightarrow MeOSiMe_2^+ + Me^\bullet$	10.6
$\rightarrow Me_3Si^+ + MeO^\bullet$	60.8
$Me_3SiOSiMe_3^{\bullet+} \rightarrow Me_3SiOSiMe_2^+ + Me^\bullet$	14.0
$\rightarrow Me_3SiO^\bullet + Me_3Si^+$	132.9
$Me_3SiNEt_2^{\bullet+} \rightarrow Me_3Si^+ + Et_2N^\bullet$	104.8

[a] Calculated from the appearance potential of the cation, from ref. 15, unless otherwise stated. [b] From refs. 14, 16.

already reported by Ohashi),[13] other easily accessible compounds such as silyl ethers, siloxanes and silylamines. However, the detailed description of the mechanism requires some further discussion. Desilylation of photochemically generated radical cations is largely precedented,[6] but it is important to realize that the present reaction differs in two respects, *viz.* the orbital involved in the initial electron donation, and the type of radical formed. As for the first point, donors of structure **11** (*e.g.* X = Ph, NR_2) have been considered in the previous cases, with the donation there involving an aryl π or a nitrogen n orbital. This mechanism likewise holds for the silazane **4h** (donating from the n_N orbital). This may be considered for the alkoxysilanes, since silanes and ethers have very similar ionization potentials (E_i), but obviously not for the silanes **4a–d**, where the HOMO is a σ silicon–carbon bond. As for the second point, the radical formed always carried a stabilizing substituent (often, but not necessarily, the same group involved in the initial donation), while here the unstabilized alkyl radicals are obtained.

Fragmentation of the Radical Cation.—This is the key step of the reaction. We tried to evaluate the thermodynamics of the process from the available data. The fragmentation of the radical cations of silicon derivatives has been studied in the gas phase. The bond dissociation energy (E_{bd}) of the radical cation, that is the excess energy necessary to induce fragmentation after generation of the molecular ion,[14–16] is

$$E_{bd}(X\text{–}Y^{\bullet+}) = E_{ap}(X^+) - E_i(X\text{–}Y)$$

where E_{ap} is the appearance potential of the given ion. This is equivalent to using the thermochemical cycle in Fig. 1 (as other authors have)[17] to give

$$E_{bd}(X\text{–}Y^{\bullet+}) = E_{bd}(X\text{–}Y) + E_i(X^\bullet) - E_i(X\text{–}Y)$$

where however $E_i(X^\bullet)$ is in turn calculated from the experimental $E_{ap}(X^+)$. Table 3 collects available E_{bd} data for compounds relevant to this work. The reported data (obtained in some cases by a different technique)[14–16] led to some uncertainty. Thus, the barrier to the cleavage of tetramethylsilane radical cation to yield the methyl radical and the trimethylsilyl cation ranges from low (5 kcal mol^{-1}) to moderate (15 kcal mol^{-1}).* Using the consistent set of data by Hess *et al.*,[16] one can see that branching of the chain in the silanes lowers the ionization potential of the molecule more than it does the energy of the carbon–silicon bond, and thus $E_{bd}(X\text{–}Y^{\bullet+})$ increases somewhat. In alkoxy and aminosilanes the barrier to cleavage of the silicon–heteroatom bond is prohibitively high, while that for the carbon–silicon bond is similar to that observed with the silanes. Translation of such data to a solution is problematic, however, since here the more complete expression results

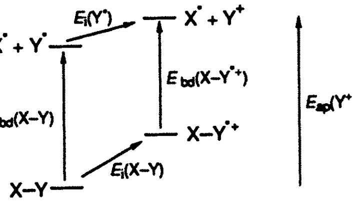


Fig. 1

$$E_{bd}(X\text{–}Y^{\bullet+}) = E_{bd}(X\text{–}Y) + E_i(X^\bullet) - E_i(X\text{–}Y) + \Delta H_{sol}(X^\bullet) + \Delta H_{sol}(Y^+) - \Delta H_{sol}(X\text{–}Y^{\bullet+})$$

where the last two solvation terms are expected to be large and may overturn the result in the gas phase. It may be that with largely delocalized cations and cation radicals the two terms are similar and compensation results, but this is certainly not the case with the present compounds. Nor, in our opinion, is it with benzyl- and allyl-silanes where charge localization in the starting π radical cation, and in the resulting trialkylsilyl cation, is obviously different (although other authors expressed a different view).[17] On the other hand, the relevant redox parameters in solution for our compounds are not available (except for the evaluation of the oxidation potential of tetraalkylsilanes from kinetic studies).[18]

The following observations can be made about this part of the problem. First, the energy barrier associated with the cleavage (in the gas phase) is much lower for the presently considered alkyl derivatives than with benzyl- or alkyl-silanes [$E_{bd}(X\text{–}Y^{\bullet+})$ = 35 and 40 kcal mol^{-1} respectively]. However, the quantum yield for alkylation is not that different (*e.g.* 0.11 for **1** and tetramethylsilane and 0.07 for **1** and allyltrimethylsilane in acetonitrile). Second, the more branched alkyl is exclusively involved in the reaction, even if E_{ap} values of different alkyls are close to one another in the gas phase.[16] Apparently the fragmentation in solution is governed by the stability of the radical formed. At least in the series of compounds we examined there is no steric effect (compare *e.g.* the quantum yield for **4a** and **4d** or **4f** and **4g**). Third, high energy processes, *e.g.* a fragmentation in the contrary way, to yield an alkyl cation [with a much higher $E_i(X^\bullet)$] and a silyl radical, remain unattainable in solution, and thus only alkylation and no silylation is observed.

Nucleophile Assistance in the Fragmentation.—Dinnocenzo and co-workers found that the lifetime of the solvated *p*-methoxyphenyltrimethylsilane radical cation drops with increasing concentration of alcohols (while the quantum yield

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* 1 kcal mol^{-1} = 4.184 kJ mol^{-1}.

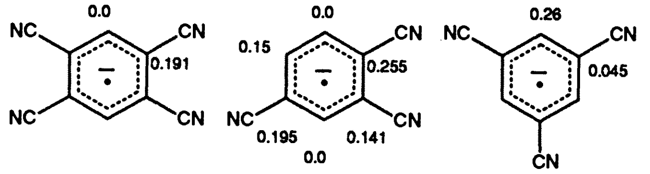
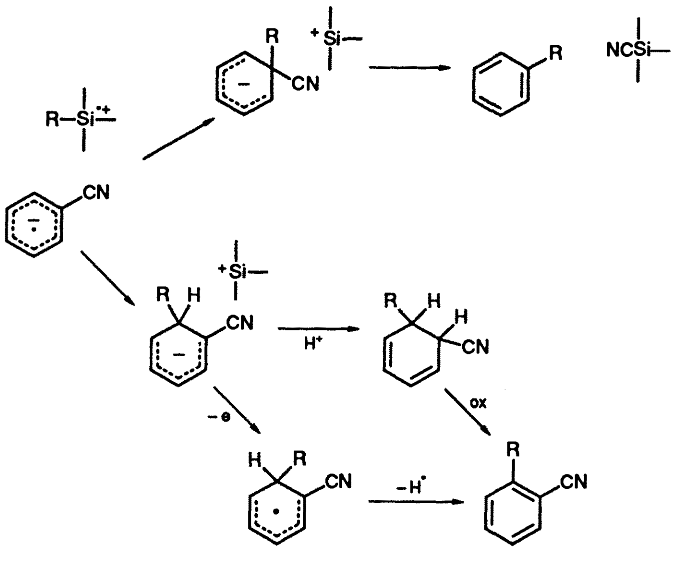


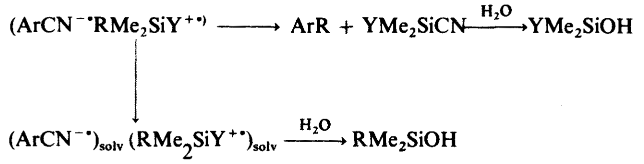
Fig. 2 Spin density in the radical anions of the carbonitriles **1–3** calculated according to ref. 27 with the parametrization suggested in ref. 28

for alkylation of the sensitizer is unchanged under these conditions), and concluded that cleavage of the radical cation is a nucleophile-assisted process.[17] As mentioned above, the $E_{bd}(X–Y^{\bullet +})$ for the gas phase is lower for the present alkylsilanes than for benzylsilanes. Predictions of the fragmentation based on such data are, as seen before, doubtful but at any rate our data clearly show that nucleophile assistance is not required in the observed alkylation. Thus, water and methanol have a minimal effect in the reaction, except at high concentration (*e.g.* 0.3 mol dm^{-3} methanol reduces the efficiency by 30%) showing that interaction of the radical cation with a nucleophile is normally unimportant (the effect at high concentration is probably due to protonation of the radical anion). Furthermore there is no steric effect (see above) and no effect of the leaving cation Y^+: the product distribution from nitriles **2** and **3** does not change with greatly differing silicon-containing electrofugal groups. This shows that the radical cation is already cleaved where the new carbon–carbon bond is formed. More precisely, the attack of the radical takes place at the position(s) of highest spin density in the nitrile radical anion, independent of whether there is a substituent at that position. The mechanisms leading to *ipso* substitution of the cyano group and to alkylation at an unsubstituted position must differ at some later stage. In the first case cyanide loss from the anion regenerates aromaticity, while in the latter case one can envisage either oxidation of the anion and hydrogen transfer or protonation and rearomatization during work up but these subsequent transformations have no effect on the initial carbon–carbon bond formation. Thus, the spin-controlled regioselectivity is in accordance with a reaction of the alkyl radical with the radical anion of the acceptor, as proposed for several other alkylations[19] (indeed, also the regioselectivity observed in the electron transfer nitration, which involves a radical–radical cation addition has been rationalized on the basis of the spin density).[20]

In-cage vs. *Out-of-cage Fragmentation*.—Several pieces of evidence militate for the fragmentation occurring within the original radical ion pair rather than from the free, solvated radical ion. Thus, quantum yields are reasonably high, despite the fact that back electron transfer between the radical ions is expected to be fast.[21] Alkanes arising from radical–radical coupling are not found. The efficiency is not changed in the presence of electron donors such as 1,4-dimethoxybenzene (10^{-2} mol dm^{-3}) which would reduce the silane radical cation, except for the amount due to competitive quenching of the sensitizer. No other products derived from the silanes or the alkyl radicals are detected except for the solvolysis of silyl ethers, the efficiency of which is however very low. Ohashi's experiments with 5-hexenyltrimethylsilane show that 2/3 of the radicals react with the nitrile within μs; it would be difficult to envisage an efficient process involving methyl and other alkyl radicals if a bimolecular reaction with such low concentration of the trapping agent (the radical anion) were required. Therefore, the alkylation of the aromatic occurs at least predominantly in-cage (see Schemes 3, 4). A polar solvent favours fragmentation, but this is linked with increased charge separation in the initial complex



Scheme 3



$$\begin{tikzcd} (ArCN^{-\bullet}RMe_2SiY^{+\bullet}) \arrow[r] \arrow[d] & ArR + YMe_2SiCN \arrow[r, "H_2O"] & YMe_2SiOH \\ (ArCN^{-\bullet})_{solv}(RMe_2SiY^{+\bullet})_{solv} \arrow[r, "H_2O"] & RMe_2SiOH \end{tikzcd}$$

Scheme 4

(or better ability for accepting the electrofugal group Y^+) rather than with a faster escape of the radical ions from the cage. Furthermore there are indications for competitive diffusion of the radical ions, *e.g.* on this basis can the solvolysis of $\mathbf{4f}^{\bullet +}$ be explained. Notice that the in-cage and out-of-cage processes are chemically different with silylethers such as **4f**: a Si–C bond is fragmented in-cage, while a Si–O bond undergoes nucleophile assisted cleavage out-of-cage. At any rate, the out-of-cage path may become more important for more stabilized radical cations, *e.g.* the methoxybenzyltrialkylsilanes studied by Dinnocenzo.[17]

Conclusions

Although these mechanistic conclusions cannot be regarded as definitive since they are based only on product studies, this work clarifies the scope of this class of reactions. Thus, benzene-tri- and tetra-carbonitriles are very strong photochemical oxidants and this allows mild generation of the radical cations of alkylsilanes. The subsequent chemistry involves the radical ion pair, rather than the free ions. Thus, the radical cations fragment efficiently, in good part directly from the initially formed ion pair, with the new carbon–carbon bond being formed immediately after the cleavage of the one-electron sigma bond. The fragmentation of the radical cation is very selective (only the more substituted alkyl radical is liberated, and neither Si–O nor Si–N bonds are cleaved in silyl ethers and amines). Alkylation of the arenenitriles is preparatively convenient, and the regiochemistry is predictable, since attack takes place at the position(s) of higher spin density in the radical anion, whether substituted or unsubstituted. Thus, a useful addition to the radical chemistry of aromatics has been found, while some limits to the generation of free radical ions by photoinduced electron transfer have been evidenced.

Experimental

The nitriles **1–3** were prepared by dehydration of the corresponding amides according to the literature.[22] The donors **4** either were commercial samples or were obtained by standard methods. Acetonitrile, when required dry was refluxed first over CaH_2 and then distilled from P_2O_5.

Preparative Irradiation.—A solution of compound **1** (100 mg, 0.55 mmol) in acetonitrile (40 cm^3) was equally divided into two septum-capped quartz tubes, and purged with argon. Tetramethylsilane (0.1 mol dm^{-3}; 0.35 g) was added and after a further purging, the tubes were irradiated for 2 h in a multilamp apparatus fitted with six 15 W phosphor-coated lamps, with a centre of emission at 320 nm. Evaporation of the solvent and chromatography of the residue on silica gel (eluting with cyclohexane–ethyl acetate, 9:1 mixture) gave unreacted **1** (5 mg) and 5-methylbenzene-1,2,4-tricarbonitrile **5a** (71 mg, 80% yield from **1**).[23]

The other preparative reactions were similarly carried out, as detailed in Table 1. (Isolated yield after chromatographic separation.) The following products were obtained.

5-*Pentylbenzene*-1,2,4-*tricarbonitrile* **5b**. Oil (Found: C, 75.4; H, 6.0; N, 18.5. Calc. for $C_{14}H_{13}N_3$: C, 75.31; H, 5.87; N, 18.82%); $\delta_H(CDCl_3)$ 0.9 (t, 3 H), 1.3 (m, 4 H), 1.6 (m, 2 H), 3.0 (t, 3 H), 7.85 (s, 1 H) and 8.1 (s, 1 H); ν/cm^{-1} 2220.

5-*Isopropylbenzene*-1,2,4-*tricarbonitrile* **5c**. M.p. 116–117 °C (EtOH) (Found: C, 73.6; H, 4.5; N, 21.2. Calc. for $C_{12}H_9N_3$: C, 73.83; H, 4.65; N, 21.53%); $\delta_H(CDCl_3)$ 1.25 (d, 6 H), 3.5 (m, 1 H), 7.85 (s, 1 H) and 8.05 (s, 1 H); ν/cm^{-1} 2220.

5-tert-*Butylbenzene*-1,2,4-*tricarbonitrile* **5d**. See ref. 23.

4-*Methylbenzene*-1,2-*dicarbonitrile* **8a**. M.p. 117–118 °C (EtOH) (Found: C, 76.3; H, 4.4; N, 19.5. Calc. for $C_9H_6N_2$: C, 76.04; H, 4.25; N, 19.71%); $\delta_H(CDCl_3)$ 2.5 (s, 3 H), 7.56 (dd, $J_{5,6}$ 8, $J_{3,5}$ 1, 5-H), 7.63 (d, $J_{3,5}$ 1, 3-H) and 7.73 (d, $J_{5,6}$ 8, 6-H); δ_C 21.6 (Me), 112.9 (C-1), 115.4, 115.5 (C≡N), 115.8 (C-2), 133.4 (C-6), 133.8 (C-3), 134.1 (C-5) and 144.6 (C-4); ν/cm^{-1} 2220.

2-*Methylbenzene*-1,3-*dicarbonitrile* **6a**. M.p. 150–151 °C (EtOH) (Found; C, 75.8; H, 4.3; N, 19.4%); $\delta_H(CDCl_3)$ 2.65 (s, 3 H), 7.5 (d, $J_{5,6}$ 8, 5-H), 7.78 (dd, $J_{5,6}$ 8, $J_{2,5}$ 1.5, 6-H) and 7.92 (d, $J_{2,5}$ 1.5, 2-H); ν/cm^{-1} 2220.

2-*Methylbenzene*-1,4-*dicarbonitrile* **7a**. M.p. 141–142 °C (EtOH) (Found: C, 75.8; H, 4.2; N, 19.6%); $\delta_H(CDCl_3)$ 2.6 (s, 3 H), 7.64 (s, 3-H), 7.58 (d, $J_{5,6}$ 8, 5-H) and 7.64 (d, $J_{5,6}$ 8, 6-H); δ_C 20.4 (Me), 116.3, 116.4 (C-1), 117.17, 117.18 (C≡N), 129.7 (C-5), 133.0 (C-6), 133.5 (C-3) and 143.2 (C-2); ν/cm^{-1} 2220.

2-*Methylbenzene*-1,3,5-*tricarbonitrile* **9a** *and* 5-*methylbenzene*-1,3-*dicarbonitrile* **10a**. Unseparated mixture; **9a** $\delta_H(CDCl_3)$ 2.9 (s, 3 H) and 8.1 (s, 2 H, 2-H and 6-H); **10a** δ_H 2.5 (s, 3 H), 7.7 (d, *J* 1, 2 H, 4-H and 6-H) and 7.8 (d, *J* 1, 2-H).

2-*Pentylbenzene*-1,3,5-*tricarbonitrile* **9b**. M.p. 76–77 °C (EtOH) (Found: C, 75.6; H, 5.9; N, 18.6. Calc. for $C_{14}H_{13}N_3$; C, 75.31; H, 5.87; N, 18.82%); $\delta_H(CDCl_3)$ 0.9 (t, 3 H), 1.4 (m, 4 H), 1.7 (m, 2 H), 3.1 (t, 2 H) and 8.1 (s, 2 H, 2-H and 6-H); ν/cm^{-1} 2220.

5-*Pentylbenzene*-1,3-*dicarbonitrile* **10b**. Oil (Found: C, 78.5; H, 7.0; N, 13.9. Calc. for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13%); $\delta_H(CDCl_3)$ 0.9 (t, 3 H), 1.3 (m, 4 H), 1.6 (m, 2 H); 2.7 (t, 2 H), 7.7 (d, *J* 1, 2 H, 4-H and 6-H) and 7.8 (d, *J* 1, 1 H, 2-H); ν/cm^{-1} 2220.

The silicon derivatives and octanol were recognized by comparison of their GC–MS pattern with that of authentic samples. Methoxyoctyloxydimethylsilane was separated by bulb-to-bulb distillation (80 °C/20 mmHg); $\delta_H(CDCl_3)$ 0.05 (s, 9 H), 0.9 (t, 3 H), 1.3 (m, 10 H), 1.6 (m, 2 H), 3.6 (m, 2 H) and 3.5 (s, 3 H); *m/z* 203 ($M^+ - 15$). Octyloxydimethylsilanol was hydrolysed to octanol when a similar purification was attempted, but the GC–MS spectrum was in accordance with the formula.

Quantum Yield Measurements.—Relative quantum yields were measured on solutions of acceptor (0.01 mol dm^{-3}) and donor (0.1 mol dm^{-3}) as aliquots (5 cm^3) in septum-capped quartz tubes. These were deaerated and irradiated as above in a rotating merry-go-round; substrate conversion was $<25\%$; product formation was determined by VPC.

Absolute quantum yields were determined on similar solutions in spectrophotometric cuvettes irradiated with a focussed superhigh pressure 150 W mercury arc, whose output was controlled by an interference filter (λ_{max}/nm 313). Light flux was measured by ferrioxalate actinometry and found to be *ca.* 5×10^{-6} Einstein min^{-1} cm^{-2}.

The lifetime of the fluorescence of **1** in deaerated acetonitrile was measured by Professor G. G. Aloisi (Perugia) through the single photon counting technique.

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