



## Scope and Mechanism of the Electron Transfer Photoinduced Alkylation of an Aromatic Nitrile

Maurizio Fagnoni, Mariella Mella and Angelo Albini

Dipartimento di Chimica Organica, Università, v.Taramelli 10, 27100 Pavia, Italy

**Abstract.** The photoinduced alkylation of 1,2,4,5-tetracyanobenzene in the presence of tetralkylsilane or -stannane derivatives as well of 2,2-dialkyldioxolanes has been studied using substrates containing rearranging radicals (5-hexenyl and cyclopropylmethyl). The quantum yield of the rearranged and non rearranged alkyltricyanobenzenes has been determined in acetonitrile, ethyl acetate and in the presence of radical traps, protic and nucleophilic agents, a cosensitizer (biphenyl) and various salts. The results support unimolecular fragmentation of the donor radical cation followed by radical - radical anion combination for the case of stannane and silane derivatives, while with the dioxolanes a  $S_N2$ -like mechanism has an important role. This study allows some predictions about the use of photoinduced electron transfer for synthetic reactions via radicals.

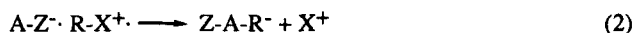
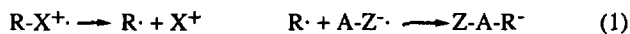
Photoinduced electron transfer from a donor R-X to an acceptor A-Z leads to a radical ion pair, and following fragmentation of the radical cations R-X<sup>+</sup> leads to radicals.<sup>1</sup> These couple with the anion radicals of the acceptor A-Z<sup>-</sup> (when these are stable species, e.g. when starting from aromatics or ketones). This is a new method for the formation of a C-C bond,<sup>2</sup> the potential of which in synthetic chemistry has been recently demonstrated in some nice examples. The key factor for the efficiency of the entire process is obviously the rate of fragmentation of the radical cation, since back electron transfer will cut down any relatively slow process.

However, direct evidence on the mechanism of this important step is almost entirely lacking. Thus, while forward and back electron transfer and radical ion separation have been extensively investigated,<sup>3</sup> these studies refer to examples where both radical ions do not undergo any chemical reaction. Direct measurements of the rate of radical cations fragmentation are scarce; it is known that the radical cations of *p*-methoxybicumenes fragment within some nanoseconds;<sup>4</sup> in the case of *p*-methoxybenzyltrimethylsilane the (pseudo)unimolecular rate of cleavage of the radical cation in acetonitrile is  $2.3 \times 10^6 \text{ s}^{-1}$ .<sup>5</sup>

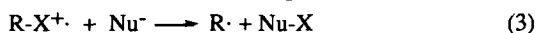
Failing direct evidence, estimates have been obtained based on the thermodynamics of radical cation fragmentation, as calculated through thermochemical cycles based on radical oxidation potentials, when available, or gas-phase appearance potential of the ions.<sup>2,5-8</sup>

Obvious experimental alternatives would be studies are based on rearranging radicals ("radical clocks")<sup>9</sup> or on medium effects. Both methods have been used in particular cases. For example, using 5-hexenylborates,<sup>10</sup> silanes, or stannanes<sup>11,12</sup> as the donors with some arenenitriles<sup>10,11</sup> and pyrilium salts<sup>12</sup> as the acceptor *both* hexenyl and cyclopropylmethyl alkylated derivatives are obtained. This fact has been

regarded by different authors either as an evidence that the reaction involves free alkyl radicals and an  $S_N1$ -like mechanism is operating (eq.1) or as an evidence that nucleophile assistance by the radical anion via a  $S_N2$ -like mechanism plays a role, as shown in equation 2. Obviously both conclusions are correct, at least under the experimental conditions employed.



On the other hand, medium effects can also be important, e.g. added salts slow down back electron transfer,<sup>13-15</sup> therefore, processes occurring in cage are disfavoured and processes involving the free radical ions are enhanced. One expects that this leads either to an increase or to a decrease of the chemical quantum yield according to the mechanism involved. A related case is assistance of the radical cation cleavage by an added nucleophile (eq.3), which is expected to be important when the energetic barrier for unimolecular fragmentation is high. As an example, the rate of disappearance of the *p*-methoxybenzyltrimethylsilyl radical cation (see above) increases in the presence of alcohols (reaction rate with methanol,  $5.5 \times 10^{-6} M^{-1} s^{-1}$ ).<sup>5</sup>

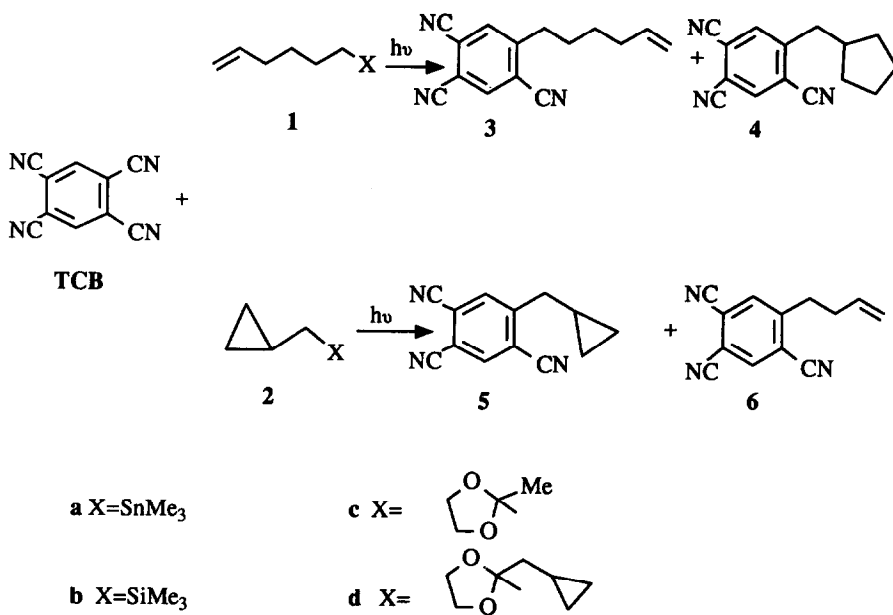


## RESULTS

We thought that a systematic exploration through both perspectives, i.e. using the radical clock method and medium effect, would be helpful. Since the investigation should involve a reasonable number of substrates, we chose a strong photochemical oxidant, 1,2,4,5-tetracyanobenzene (TCB), for which single electron transfer would be effective also with relatively weak donors. The investigation was extended to two radical clocks (5-hexenyl and cyclopropylmethyl radicals), known to rearrange at a largely different rate, with three different electrofugal groups (trialkylstannyl and -silyl cation, as well as dialkoxy carbocation), and the reaction was carried out in acetonitrile under a variety of conditions, viz in the presence of radical traps (acrylonitrile, oxygen), protic agents (trifluoroethanol), protic nucleophiles (methanol), electron donors (biphenyl), and finally in the presence of various salts as well as in a less polar solvent, ethyl acetate.

The substrates used (a stannane, two silanes and two acetals), containing either the 5-hexenyl chain (compounds **1a-c**) or the cyclopropylmethyl chain (compounds **2b,d**) as well the photoproducts obtained, viz the alkyltricyanobenzenes **3-6** are shown in Scheme 1. The quantum yields for the formation of each products under the conditions explored are reported in Tables 1 and 2. At the donor concentration used, the measured quantum yield is close to the limiting value. In every case, the relative yield (referred to neat acetonitrile) is also indicated in parentheses.

*Scope of the reaction.* Under the present condition, TCB is excited, and the substrates quench a substantial fraction of the excited singlet state (>80%). In every case, the chemical yield is high. In neat acetonitrile, the two possible alkylated trinitriles account for at least 90% of the consumed TCB. Thus, whatever the mechanism might be, the TCB radical anion functions as an efficient trap for the alkyl radicals, and Scheme 1 accounts for the observed chemistry. Some complications are possible. For example, at high TCB conversion dialkylation becomes important (compare ref.16), but the experiments in Tables 1 and 2 were limited at ca 10% TCB consumption. Furthermore, in the presence of some additives (this is the case with acrylonitrile) further aromatic derivatives are formed; the structure of these products will be further investigated, but also there the alkyltricyanobenzenes remain main products.



Scheme 1

*Effects observed.* Acrylonitrile, a known trap for alkyl radicals, quenches the formation of the products containing the rearranged alkyl chain (hereinafter indicated for short as "rearranged products"), and to a much lesser degree, that of the "unrearranged products", which actually somewhat increases in the case of **1a**. Oxygen has a similar, but stronger, effect. Trifluoroethanol has a limited effect, with either a small increase (e.g. with **1a**) or decrease (with **1b,c**) and little variation in the rearranged/unrearranged ratio. MeOH generally causes a large decrease in the quantum yield, though again with little effect on the product distribution. Biphenyl quenches the TCB singlet competitively with the substrate (ca 2:1). In all cases this leads to a corresponding decrease of the alkylation quantum yield except than with the stannane, where the yield increases. Addition of salts shifts the product ratio towards the rearranged products, with an overall increase of the quantum yield with the silanes and the stannane, much less so with the acetals. Finally, the reaction follows a similar course when carried out in ethyl acetate, although the quantum yield is lower and the proportion of the unrearranged product is higher.

## DISCUSSION

All of the reactions involves SET to singlet excited TCB, as indicated by fluorescence quenching (see the data for related donors in ref.16,17) and the favorable effect of the medium polarity. One should also take

Table 1. Effect of Radicals Traps, Protic and Nucleophilic Additives, Secondary Donors

Substrate	Bond Cleaved	Products	Neat	Quantum Yield ( $\times 10^2$ ) <sup>a</sup>						
				Acrylonitrile $10^{-2}$ M	Acrylonitrile $5 \times 10^{-2}$ M	O <sub>2</sub> (Saturated)	MeOH $5 \times 10^{-2}$ M	MeOH 0.5 M	CF <sub>3</sub> CH <sub>2</sub> OH 0.2 M	Biphenyl 0.1 M
<b>1a</b>	C-Sn	<b>3</b>	6.4	8.7 (1.36)	7.2 (1.13)	2.2 (0.34)	4.2 (0.66)	1.0 (0.16)	7.9 (1.23)	4.5 (0.70)
		<b>4</b>	12.2	3.5 (0.29)	0.4 (0.03)	0 (0.00)	10.3 (0.84)	1.4 (0.11)	12.5 (1.02)	17.8 (1.46)
<b>1b</b>	C-Si	<b>3</b>	3.2	2.4 (0.75)	1.5 (0.47)	0.6 (0.19)	1.1 (0.34)	0.3 (0.09)	2.2 (0.69)	0.7 (0.22)
		<b>4</b>	1.0	0.23 (0.23)	0.08 (0.08)	0 (0.00)	0.8 (0.80)	0.07 (0.07)	0.7 (0.70)	0.17 (0.17)
<b>1c</b>	C-C	<b>3</b>	6.3	4.7 (0.75)	3.9 (0.62)	3.3 (0.52)	2.0 (0.32)	1.4 (0.22)	4.8 (0.76)	1.9 (0.30)
		<b>4</b>	5.8	0.9 (0.16)	0 (0.00)	0 (0.00)	2.5 (0.43)	0.4 (0.07)	3.1 (0.53)	2.1 (0.36)
<b>2b</b>	C-Si	<b>5</b>	0.13	0.03 (0.23)	0.02 (0.15)	0 (0.00)	0.06 (0.46)	0.13 (1.00)	0.15 (1.15)	0.01 (0.08)
		<b>6</b>	3.0	0.25 (0.08)	0.04 (0.01)	0 (0.00)	2.3 (0.77)	1.1 (0.37)	2.3 (0.77)	0.7 (0.23)
<b>2d</b>	C-C	<b>5</b>	5.3	4.7 (0.89)	4.1 (0.77)	2.1 (0.40)	3.3 (0.62)	1.0 (0.19)	4.3 (0.81)	1.2 (0.23)
		<b>6</b>	4.9	1.6 (0.33)	0 (0.00)	0 (0.00)	2.6 (0.53)	0.4 (0.08)	6.0 (1.22)	0.9 (0.18)

a. In parentheses relative quantum yield with the respect to the value observed with the same donor in neat MeCN

Table 2. Effect of Medium Polarity and of Added Salts

Substrate	Bond Cleaved	Products	Neat		In Ethyl acetate		Quantum Yield ( $\times 10^2$ ) <sup>a</sup>			
			MeCN	MeCN	0.1 M	0.2 M	Et <sub>4</sub> NClO <sub>4</sub>	Et <sub>4</sub> NClO <sub>4</sub>	Bu <sub>4</sub> NClO <sub>4</sub>	LiClO <sub>4</sub>
1a	C-Sn	3	6.4	2.9 (0.45)	8.4 (1.31)	7.5 (1.17)	7.3 (1.14)	11.1 (1.73)		
		4	12.2	6.2 (0.51)	25.1 (2.06)	22.1 (1.81)	14.1 (1.16)	24.3 (1.99)		
1b	C-Si	3	3.2	1.5 (0.47)	1.9 (0.59)	1.1 (0.34)	2.1 (0.66)	2.0 (0.63)		
		4	1.0	0.3 (0.30)	2.3 (2.30)	1.4 (1.40)	1.7 (1.70)	1.5 (1.50)		
1c	C-C	3	6.3	3.7 (0.59)	4.5 (0.71)	3.3 (0.52)	5.4 (0.86)	5.8 (0.92)		
		4	5.8	1.4 (0.24)	5.7 (0.98)	4.5 (0.78)	6.2 (1.07)	6.8 (1.17)		
2b	C-Si	5	0.13	0.5 (3.85)	0.13 (1.00)	0.10 (0.77)	0.09 (0.69)	0.19 (1.46)		
		6	3.0	0.8 (0.27)	7.8 (2.60)	7.9 (2.63)	6.2 (2.07)	4.5 (1.50)		
2d	C-C	5	5.3	5.4 (1.02)	3.1 (0.58)	3.2 (0.60)	3.5 (0.66)	4.2 (0.79)		
		6	4.9	2.2 (0.45)	5.7 (1.16)	10.5 (2.14)	6.0 (1.22)	6.0 (1.22)		

a. In parentheses relative quantum yield with the respect to the value observed with the same donor in neat MeCN

into account that, while the salts we used have virtually no effect on the TCB fluorescence, the other additives quench measurably TCB<sup>1\*</sup>, and thus some overall lowering of the yield is expected. As Tables 1 and 2 show, however, this effect is limited, while the differences in yield and rearranged/unrearranged ratio with the different substrates and the effects of the various additives are sufficiently large. Therefore, since, as mentioned before, changes in the medium do not greatly affect the initial electron transfer, and the material balance remains good throughout, the observed variations in the product quantum yields can be exploited for obtaining information about the mechanism of the radical cation cleavage and the subsequent radical reactions.

*General Mechanism.* The effects observed fully support the mechanism indicated in Scheme 2. The formation of the radical cations of silanes and stannanes and their fragmentation to yield alkyl radicals had been previously suggested.<sup>11,17</sup> In the present study, the intermediacy of radical ions and of radicals is indicated by the favorable effect of increasing polarity and adding salts and, respectively, by the quenching of alkylation in the presence of radical traps. The C-C bond is formed through the interaction of the alkyl radical and TCB radical anion. This is a persisting and non basic species, as and behaves similarly to the radical anions of other aromatic nitriles.<sup>18-20</sup> Indeed, trifluoroethanol causes a small effect, and in some cases an increase in the yield of alkylation, reasonably related to the increase of the medium polarity. Obviously, proticity has no effect in the case of methanol too. The observed yields decrease with this additive shows that no nucleophile assistance (eq.3) is involved in the alkylation, as indeed previously observed in related alkylations.<sup>5,21,22</sup> Since the drop of the yield is not accompanied by a change in the rearranged/unrearranged ratio, quenching of the intact radical cation is involved. Apparently, the interaction with methanol does not lead to alkyl radicals.

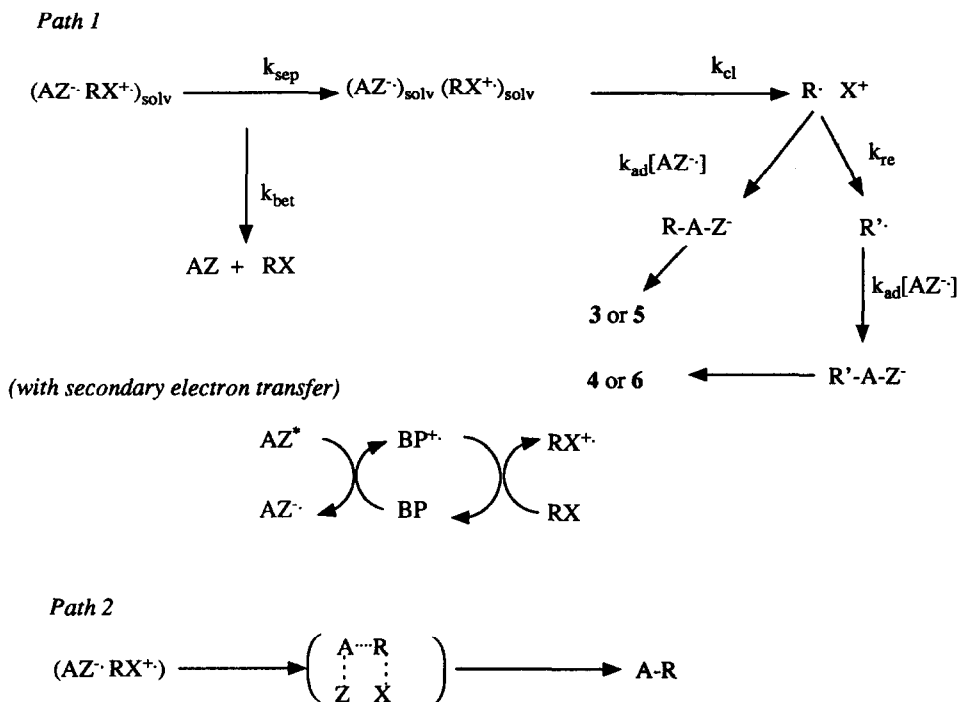
*Formation and reaction of the radicals.* The total alkylation yield depends on the electrofugal group. Since no other chemical paths have been detected, this yield is a measure of the competition between radical cation cleavage and back electron transfer. Thus,  $k_{cl}$  is ca 25% of  $k_{bet}$  for the stannane, 11% for the dioxolans, and 4% for the silanes. This is not due to a decrease of the rate for back electron transfer, since the energies of the radical ion pairs considered here are very high, and thus lie in the inverted Marcus region, where an increase of  $k_{bet}$  would be expected with decreasing oxidation potential of the donors (and thus decreasing ion pair energy). Thus, the rate of bond fragmentation grows in the series C-Si<C-C<C-Sn. Reported measurements for  $k_{bet}$  involve only aromatic donors, with the smallest values of ca  $5 \times 10^8 \text{ mol}^{-1} \text{ sec}^{-1}$  (for highly exothermic back electron transfer, e.g.  $\Delta G_{bet}$  2.8-2.9 V)<sup>3</sup> It seems unlikely that in the present case ( $\Delta G_{bet}$  ca 2.6-3.2 V) are lower than that. This put  $k_{cl}$  in the range  $10^7$ - $10^8 \text{ sec}^{-1}$ .

A calculation of the bond dissociation in the radical cations energy via thermochemical cycles is hampered by the fact that the required parameters are not all known. For example, oxidation potentials in solution for the relevant radicals have been reported only for dioxolanes (and there a BDE of 5 to 10 kcal mol<sup>-1</sup> can be calculated).<sup>16,23</sup> For silanes and stannanes one can refer to appearance potential of the ions in the gas phase, with the uncertainty that such a method gives for localized ions like the present ones. In this way, a value of 5 to 15 kcal mol<sup>-1</sup> for the silanes<sup>17,23</sup> and a negative value for the stannanes<sup>23</sup> result. Thus, the observed rates of fragmentation follow the same order as calculated BDE. It should also be noted that the cleavage occurs with remarkable efficiency also in ethyl acetate, and does not require assistance by a nucleophile different from the solvent (eq.4).

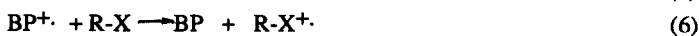


Since there is some important difference with the acetals, a more detailed discussion will be first referred only to the stannane and the silanes. With the last substrates, the ratio rearranged/unrearranged products drops by more than two orders of magnitude in going from the cyclopropylmethyl to the 5-hexenyl derivatives. Thus, it is reasonably responsive to the drop in the radical rearrangement rate ( $k_{re}$   $1.3 \times 10^8$  and  $1.0 \times 10^5 \text{ sec}^{-1}$  respectively),<sup>9</sup> supporting the intermediate formation of radicals, and their subsequent addition to the acceptor radical anion (presumably occurring at the diffusion controlled rate) according to Scheme 2.

This is also supported by the radical trapping experiments with acrylonitrile (expected to add primary radicals at a rate of  $2.5 \times 10^5 \text{ mol}^{-1} \text{ sec}^{-1}$ ) and oxygen (quenching radicals at the diffusion controlled rate, while having no effects on acceptor radical anion, since it is known that  $E_{red}(TCB) = -0.7 \text{ V}$ ). These experiments follow the expected trend when changing the trap concentration or the rearranging radical. The high rate of addition  $k_{ad}$  required by these data is compatible with two models, viz 1) separation of the radical ions, fragmentation and reencounter of the radical with  $TCB^{\cdot-}$ , expected to accumulate since  $R-X^{\cdot+}$  is substracted to back electron transfer by its fragmentation and 2) both processes, bond cleavage and bond formation occurring within solvent cage before ions separation. In the case of the stannane, where electron transfer to the biphenyl radical cation ( $BP^{\cdot+}$ ) is exothermic, the occurrence of path 1 is proved by the observed increase in both overall quantum yield and proportion of the rearranged product proportion with 0.1M BP, where >70% of the reaction proceeds through secondary electron transfer (eqs 5 and 6).



Scheme 2



This fact, together with the recent demonstration that radical anions of related nitriles reach a high steady state concentration (up to  $10^{-4}\text{M}$ ) under comparable conditions,<sup>20</sup> shows that path 1 is a viable mechanism for the reaction. However, path 2 may play a role, since  $k_{\text{cl}}$  is high enough to compete with ion separation (measured, for some aromatic radical ions, as  $k_{\text{sep}}=5 \times 10^8 \text{ sec}^{-1}$ ).<sup>3</sup> The mechanism discussed above is not applicable to the dioxolanes without some modification. Indeed, in this case the rearranged vs unrearranged ratio does not change in going from the 5-hexenyl to the cyclopropylmethyl derivatives, and both the quenching with radical traps and the yield enhancements with added salts are smaller, although qualitatively the same, than in the previous case. This fits well with the idea that although the radical cation cleavage - radical radical anion addition sequence is followed also in this case, the first step occurs in part unimolecularly as in the previous case (roughly a half, thus making the rate of cleavage of the C-C bond as fast as that of the C-Si bond in silanes), and for the remaining part through a reaction with the TCB radical anion through a  $\text{S}_{\text{N}}2$ -type mechanism as in eq.2.

*Conclusion.* The above photo-alkylation of TCB occurs with a quantum yield remarkably high for an electron transfer process, where usually back electron transfer severely cuts down the efficiency, and is well described as involving free radicals. Thus, photo-induced SET is a viable method for preparing radicals from unconventional substrates, such as tetralkylstannanes and silanes, under exceptionally mild conditions. The same holds for acetals, although in that case the mechanism is more complex.

The efficiency of the process suggests that this method should be applied to synthetic radical reactions in organic chemistry. Furthermore, the above data about the effect of the donor structure and of the medium on the alkylation efficiency should offer a guide for the choice of the best synthetic conditions. As an example, using stannanes in the presence of BP is probably a good way for obtaining a reaction of free radicals with no interference by the acceptor.

## EXPERIMENTAL

1,2,4,5-tetracyanobenzene (TCB) and the ketals **1c** and **2d** were prepared and purified as previously reported.<sup>16</sup> The hexenylstannane **1a** was prepared from 5-hexenylmagnesium bromide and  $\text{Me}_3\text{SnCl}$  in ether (compare ref.31): b.p.49-50°C at 0.1 torr, nmr  $\delta$  ( $\text{CDCl}_3$ ) 0.05 (s, 9H), 0.8 (t, 2H, J 7 Hz), 1.45 (m, 4H), 2.05 (m, 2H), 5.0 (m, 2H), 5.8 (m, 1H), IR 2925, 1640, 909, 765  $\text{cm}^{-1}$ . The silane **1b**<sup>32</sup> was obtained from the same bromide by reaction first with silicon tetrachloride and then with methylmagnesium iodide. The cyclopropylmethylsilane **2b**<sup>33</sup> was obtained from allyltrimethylsilane through a modified Simmons-Smith procedure.

The preparative photoreaction of TCB with the ketals **1c** and **2d** and the isolation and characterization of the alkylbenzenetricarbonitriles **3-6** has been previously reported.<sup>16</sup> Similar experiments in the presence of the stannane **1a** and the silanes **1b** and **2b** likewise gave a >80% yield of products **3-6**.

Relative quantum yield measurements were carried out on 3 mL aliquots of solutions of TCB ( $5 \times 10^{-3}\text{M}$ ) and the donor ( $5 \times 10^{-2}$ ) in acetonitrile in quartz tubes capped with a rubber septum. The solutions were purged with argon and irradiated by means of a multilamp apparatus fitted with six 15 W phosphor-coated lamps (center of emission 320 nm) while rotating in a merry-go-round apparatus. Conversion was generally



limited to ca 10%. Absolute quantum yield measurements were effected on similar solution in quartz cuvettes illuminated by a high pressure mercury arc, focalized and monochromatized by means of an interference filter. The formation of the products was monitored by glc (methylsilicone column, 50mx0.2mmx0.3µm). Dodecane was used as an internal standard.

**Acknowledgment.** Financial support of this work by Consiglio Nazionale delle Ricerche, Rome, is gratefully acknowledged.

## REFERENCES AND NOTES

1. Saeva, F.D. *Top.Curr.Chem.*, **1991**, *156*, 59
2. Albini, A.; Mella, M.; Freccero, M. *Tetrahedron*, **1994**, *50*, 595
3. Gould, I.R.; Ege, D.; Moser, J.E.; Farid, S. *J.Am.Chem.Soc.*, **1990**, *112*, 4290
4. Maslak, P.; Chapman, W.H. *J.Org.Chem.*, **1990**, *55*, 6334
5. Dinnocenzo, J.P.; Farid, S.; Goodman, J.L.; Todd, W.P.; Mattes, S.L. *J.Am.Chem.Soc.*, **1989**, *111*, 8973
6. Wayner, D.D.M.; Dannenberg, J.J.; Griller, D. *Chem.Phys.Lett.*, **1986**, *131*, 189; Wayner, D.D.M.; McPhee, D.J.; Griller, D. *J.Am.Chem.Soc.*, **1988**, *110*, 132
7. Popielartz, R.; Arnold, D.R. *J.Am.Chem.Soc.*, **1990**, *112*, 3068
8. Albini, A.; Fasani, E.; d'Alessandro, N. *Coord.Chem.Rev.*, **1993**, *125*, 269
9. Griller, D.; Ingold, K.U. *Acc.Chem.Res.*, **1980**, *13*, 317
10. Lan, J.Y.; Schuster, G.B. *Tetrahedron Lett.* **1985**, *26*, 5819
11. Kyushin, S.; Masuda, Y.; Matsushita, K.; Nadaira, Y.; Ohashi, M. *Tetrahedron Lett.*, **1990**, *31*, 6395
12. Kyushin, S.; Nadaira, Y.; Ohashi, M. *Chem.Lett.*, **1990**, 2191
13. Goodson, B.; Schuster, G.B. *Tetrahedron Lett.*, **1986**, *27*, 3123
14. Simon, J.D.; Peters, K.S. *J.Am.Chem.Soc.*, **1983**, *105*, 4875
15. Santamaria, J. in Fox, M.A., Chanon, M., Eds. *Photoinduced Electron Transfer*, Elsevier, Amsterdam, **1988**, vol.B, p.483
16. Mella, M.; Fasani, E.; Albini, A. *J.Org.Chem.*, **1992**, *57*, 3051
17. Mella, M.; d'Alessandro, N.; Freccero, M.; Albini, A. *J.Chem.Soc., Perkin Trans.2*, **1993**, 515
18. Kellet, M.A.; Whitten, D.G.; Gould, I.R.; Bergmark, W.R. *J.Am.Chem.Soc.*, **1991**, *113*, 358
19. Freccero, M.; Mella, M.; Albini, A. *Tetrahedron*, **1994**, *50*, in press
20. Robinson, E.A.; Shulte-Frohlinde, D.J. *J.Chem.Soc., Faraday Trans 1*, **1973**, *69*, 707
21. Ohga, K.; Yoon, U.C.; Mariano, P.S. *J.Org.Chem.*, **1984**, *49*, 213
22. Fasani, E.; d'Alessandro, N.; Albini, A.; Mariano, P.S. *J.Org.Chem.*, **1994**, *59*, 2115
23. The Bond Dissociation Energy for radical cations is calculated through a thermochemical cycle (see ref. 2,6,8) as :

$$\text{BDE (R-X}^{\cdot+}) = \text{BDE (R-X)} - [\text{E}_{\text{Ox}}(\text{R-X}) + \text{E}_{\text{Ox}}(\text{X}^{\cdot})]$$

Application to the detachment of a methyl radical from the radical cations of 2,2-dimethyldioxolane, tetramethylsilane and tetramethylstannane gives +5.7, +5.2 and -18.9 kcal M<sup>-1</sup> respectively, based on the following data: for the dioxolane BDE 82 kcal M<sup>-1</sup> (approximated to that of an ether, ref.24), IP(R-X) 9.71 eV (ref.25) and IP(X<sup>·</sup>) 6.40 eV (calculated from the measured oxidation potential in solution and the solvation energy of the ion, ref.6,26); for the silane BDE 78.8 kcal M<sup>-1</sup> (ref.27), IP 9.80 eV, IP(X<sup>·</sup>) 6.61 eV

(ref.28); for the stannane BDE 57 kcal M<sup>-1</sup> (ref. 29), IP 9.8 eV (ref. 30), IP(X·) 6.4 eV (estimated from that of the silane). IP values are used in the place of the generally unavailable oxidation potentials (see text).

24. Egger, K.W.; Cocks, A.T. *Helv.chim.Acta*, **1973**, *56*, 1516

25. Sweigart, D.A.; Turner, D.W. *J.Am.Chem.Soc.*, **1972**, *94*, 5599

26. Sim, M.A.; Milne, P.H.; Griller, D.; Wayner, D.D.M. *J.Am.Chem.Soc.*, **1990**, *112*, 6635

27. Helm, D.F.; Mark, E. *J.Am.Chem.Soc.*, **1937**, *59*, 60

28. Murphy, M.K.; Beauchamp, J.L. *J.Am.Chem.Soc.*, **1977**, *99*, 2085

29. Price, S.J.; Daly, M. *Can.J.Chem.*, **1976**, *54*, 1814

30. Eaton, D.F. *J.Am.Chem.Soc.*, **1981**, *103*, 7235

31. Ingham, R.K.; Rosenberg, S.D.; Gilman, H. *Chem.Rev.*, **1960**, *60*, 459

32. Jarvie, A.W.P.; Rowley, R.J. *J.Chem.Soc. (B)*, **1971**, 2439. Mironov, V.F.; Pogonkina, N.A. *Izv.Akad.Nauk S.S.S.R., Otdel khim.Nauk*, **1955**, 182

33. Grignon-Dubois, M.; Dunogues, J.; Calas, R. *Can.J.Chem.*, **1981**, *59*, 802

(Received in UK 24 January 1994; revised 21 March 1994; accepted 25 March 1994)