Radical Addition to Alkenes via Electron Transfer Photosensitization

M. Fagnoni, M. Mella,* and A. Albini

Contribution from the Dipartimento di Chimica Organica, Universitá, via Taramelli 10, 27100 Pavia, Italy

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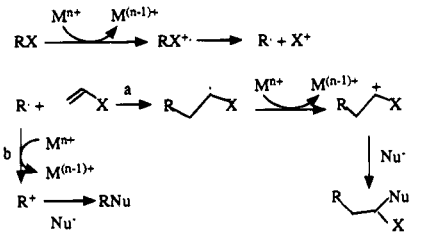
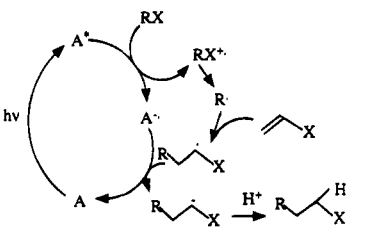
Abstract: A method for radical addition to alkenes is reported which is based on the photosensitized oxidation of a tetraalkylstannane by an excited acceptor (A*), fragmentation of the radical cation, and addition of the thus formed radical to an electron-withdrawing substituted alkene (acrylonitrile and dimethyl maleate). Aromatic nitriles and esters can be used as the electron acceptors, and they are chosen in such a way that their radical anion ($A^{\bullet -}$) reduces the adduct (and not the educt) radical. In this way the adduct radical is reduced and protonated to yield the end product, and the acceptor functions as a nonconsumed electron transfer sensitizer. In several cases the alkylation occurs more efficiently in the presence of a secondary donor (phenanthrene or biphenyl). However, when the acceptor is too easily reduced in the ground state (as with 1,2,4,5-benzenetetracarbonitrile), coupling of the adduct radical with $A^{\bullet -}$ competes with its reduction.

A key problem in organic synthesis via radicals is that the reactivity of the adduct radical has to be sufficiently different from that of the educt radical in order to obtain a clean process.[1] As an example, in chain reactions via hydrogen transfer abstraction by the adduct radical must be fast enough to preclude further addition (and the reverse has to be true for the educt radical). A similar situation is encountered in nonchain redox methods, where the adduct radical must be selectively oxidized. As shown in Scheme 1, in that case single electron (SET) oxidation is followed by radical cation fragmentation, addition, and a second oxidation step. This limits somewhat the method, since the nucleophile introduced in the final step may induce side reactions, and, furthermore, the strongly oxidizing medium may cause oxidation of the educt radical before addition (path b in Scheme 1). We wish to show here that suitably devised *photosensitized* SET[2] allows the generation of radicals via an *oxidative* path and, on the other hand, differentiates educt and adduct radicals via a selective *reduction*, thus offering a novel method for radical addition.

Scheme 1



Scheme 2



Results and Discussion

Strategy Chosen. In photoinduced SET reactions advantage is taken of the great change in the redox properties obtained upon electronic excitation of an organic molecule, thus allowing the formation in situ of a strong (and short-lived) oxidant. We thought that reductive alkylation of an alkene could be obtained according to the mechanism depicted in Scheme 2. In order that the reaction occurs satisfactorily, the following conditions must be satisfied: (1) The photosensitizer (A) should have a sufficiently high reduction potential in the excited state [$E_{red}(A^*) = E_{red}(A) + E_{exc}(A)$] in order to oxidize the substrate.[2] (2) The radical cation cleaves fast enough to compete with back electron transfer.[3,4] (3) The ground state reduction potential of A is such that its radical anion reduces the adduct radical and not the educt radical (see Scheme 2; oxidation of the radicals is in any case precluded since the only oxidant present is the extremely short-lived A*). (4) The radical anion $A^{\bullet -}$ does not trap either the educt or the adduct radical, so that A is not consumed and the sensitization cycle can continue.

tert-Butyltrimethylstannane (**1**) and tetrabutylstannane (**2**) were chosen for this investigation, since these are easily oxidized substrates, and therefore allow the exploration of the effect of a large number of acceptors, and, furthermore, it has been shown that organometallic donors of this type cleave efficiently upon photoinduced SET and yield selectively the more substituted radical.[5] The oxidants were chosen from among aromatic nitriles and esters and the substrates for alkylation from among electron-withdrawing substituted alkenes.

Preparative Alkylation. Typical experiments were carried by irradiating MeCN solution of the acceptor, the stannane, and the alkene (with the addition of a secondary donor when

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(1) (a) Giese, B. *Radicals in Organic Synthesis. Formation of Carbon−Carbon Bonds*; Pergamon: Oxford, 1986. (b) Curran, D. P. In *Comprehensive Organic Synthesis* Trost, B. M., Fleming I., Eds.; Pergamon, Oxford, 1991; pp 714, 779.

(2) (a) *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988. (b) Kavarnos, G. J. *Top. Curr. Chem.* **1991**, *156*, 21. (c) Mattay, J.; Vondenhof, M. *Top. Curr. Chem.* **1991**; *159*, 219.

(3) (a) Albini, A.; Mella, M.; Freccero, M. *Tetrahedron* **1994**, *50*, 575. (b) Albini, A.; Fasani, E.; d'Alessandro, N. *Coord. Chem. Rev.* **1993**, *125*, 269.

(4) (a) Saeva, F. D. *Top. Curr. Chem.* **1991**, *156*, 59. (b) Maslak, P. *Top. Curr. Chem.* **1993**, *168*, 143.

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Table 1. Olefin Alkylation with Stannanes through SET Photosensitization in Acetonitrile[a]

substrates[b]	products yield (%)[c]	sensitizer[d]
3 + **1**	**5a**(40)	1,4-$C_{10}H_6(CN)_2$-Biph
3 + **2**	**5b**(50)	1,4-$C_6H_4(CO_2Me)_2$-Phen
4 + **1**	**6a**(85)	1,4-$C_{10}H_6(CN)_2$-Biph
4 + **2**	**6b**(80)	1,2,4,5-$C_6H_2(CO_2Me)_4$
4 + **1**	**6a**(9), **7**(52),[e,f] **8**(36)[e]	1,2,4,5-$C_6H_2(CN)_4$
4 + **1**	**6a**(19), **7**(56),[e,f] **8**(16)[e]	1,2,4,5-$C_6H_2(CN)_4$-Biph

[a] Isolated yield by bulb-to-bulb distillation or column chromatography (see Experimental Section). Vpc calculated yields are always >85%. [b] Stannane (**1** or **2**), 0.05 M; dimethyl maleate (**4**) or acrylonitrile (**3**), 0.1 M. [c] Calculated on the stannane used. [d] Acceptor, 5×10^{-3} M; phenanthrene 0.05 M; biphenyl 0.1 M. [e] Calculated on the acceptor (benzenetetracarbonitrile) used. [f] Mixture of the diastereoisomers.

convenient, see below) after nitrogen purging. After irradiation the solvent was evaporated, and the alkylation products were separated by bulb-to-bulb distillation or chromatography. The method gave a satisfactory yield of the desired products with minor consumption of the acceptor and could be applied for the alkylation both with tertiary radicals (using **1** as the donor, see Scheme 3) and with primary radicals (using **2**), using both monosubstituted (acrylonitrile, **3**) and disubstituted alkenes (dimethyl maleate, **4**) as the substrates. The expected saturated nitriles **5** and esters **6** were formed in >85% yield, as evaluated by vpc, although the isolated yields of products **5** were moderate due to their volatility.

It was desired that the method could have general applicability, and thus excitation with relatively long wavelength (>300 nm, in our case using the commonly available phosphor-coated lamps with the center of emission at 320 nm) was chosen in order to minimize light absorption by the unsaturated substrates. Typical preparative results are shown in Table 1. Different arrangements were possible: light could be absorbed by the acceptors, as when the sensitizing oxidants used were 1,4-naphthalenedicarbonitrile (best results obtained, as reported in Table 1, in the presence of biphenyl, Biph) and tetramethyl pyromellitate. However, the reaction was likewise successful using a light-absorbing donor (phenanthrene, Phen) and dimethyl terephthalate as the nonabsorbing acceptor (see below for the definition of the mechanistic role of all species). In all these cases a satisfactory alkylation of the substrate was obtained, and the acceptor was used in a small amount (10% of the stannane) and at least in part recoverd after the irradiation. On the contrary, the alkylation was unsatisfactory with 1,2,4,5-benzenetetracarbonitrile as the (light-absorbing) sensitizer, since this acceptor was rapidly consumed during the irradiation, even in the presence of Biph (see below).

That the reaction actually followed the course indicated in Scheme 2, with the adduct radical evolving to the final product through electron transfer from $A^{\bullet-}$ and protonation by water present in the solvent, rather than, e.g., by hydrogen abstraction, was indicated by the isolation of deuterated adducts when the reaction was carried out in the presence of D_2O (see Experimental Section).

Competing Paths. A part of the stannane consumed did not lead to the alkylation of the alkene. Thus, part of the alkyl radical produced was lost either by coupling or disproportionation reactions or by competitive trapping by the sensitizer. It is well-known that addition of alkyl radicals to the radical anion of aromatic nitriles leads to ipso-substitution of a cyano group.[5,6] Among the presently considered oxidants, the occurrence of aromatic substitution was apparent in the case of 1,2,4,5-benzenetetracarbonitrile, which reacted under this condition. Analysis of the products showed that in this case substitution of a cyano group by the *tert*-butyl radical (to give product **8**, Scheme 4) is accompanied by formation of a product incorporating both the *tert*-butyl radical and the alkene (compound **7**). The latter reaction had been previously characterized and indicated with the acronym ROCAS (radical olefin combination aromatic substitution).[7] Both these paths were somewhat diminished when Biph was used as a cosensitizer. In the other cases, alkylation of the aromatic acceptor in the presence of the electron poor olefin was minimal.[6]

Mechanistic Data. The choice of the appropriate conditions for the preparative experiments reported above was based on an extensive exploratory study, the most relevant results from which are reported in Table 2. This shows the yields obtained for the alkylation of **4** by either **1** or **2** after irradiation for a fixed time in the presence of various sensitizers as well as the turnover number, viz. the ratio between the moles of adduct (**6a** or **6b**, respectively) formed vs the moles of acceptor consumed.

Furthermore, in Table 2 the reduction potentials of the acceptors used are indicated as well as the species which we believe is actually involved in the oxidation of the stannane (see below), be it an excited state of the acceptor or an aromatic radical cation, as it is the case when a secondary donor is used, with the relevant reduction potential. In conjunction with the stannanes oxidation potential [E_{ox}(**1**) = 1.60 V vs SCE, E_{ox}(**2**) = 1.75 V], this allows the ascertaining of the feasibility of the SET step. Finally, in Table 3 the calculated (Weller equation)[2] free energy change for electron transfer from the stannanes **1** and **2** and some of the acceptors used in their excited state (singlet and triplet) is compared with Stern–Volmer constants for the quenching of the sensitizer fluorescence by the stannane **2**.

Discussion. The results obtained, and thus the efficiency of the proposed synthetic procedure, can be rationalized on the basis of Scheme 2 and of the relevant redox parameters which are reported in a monodimensional diagram in Figure1.

All of the reactions considered are initiated by photoinduced SET. In the case of 1,2,4,5-benzenetetracarbonitrile as well as of the naphthalene- and anthracenenitriles, the singlet excited state of the acceptor is involved and directly oxidizes the stannanes, as shown by the negative calculated ΔG_{et} and measured fluorescence quenching (Table 3, notice that no ground state complex is formed, or at least none is revealed by UV spectroscopy). With the pyromellitate, the singlet of which is probably too short-lived to be quenched, as it is generally the case with aromatic esters,[13] the triplet is reasonably involved, and indeed its reduction by **2** is viable (see Table 3). In both these cases, the radical ion pair $A^{\bullet-}/R_4Sn^{\bullet+}$ is directly formed (see Scheme 5, path a). However, an indirect sensitization is also possible. Thus, in the experiments with Phen, the singlet excited state of the latter is reduced by the acceptor, and the radical cation $Phen^{\bullet+}$ is then reduced back to Phen by the stannane in a secondary SET step (this is thermoneutral or slightly endothermic, since E_{ox}(Phen) = 1.58V vs SCE; Scheme 5, path b). Thus, ultimately the same radical ions as before are formed. On the other hand, when a nonabsorbing secondary donor such as Biph is used, the acceptor absorbs the light and is competitively reduced both by the stannane and by Biph.

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(6) (a) In the absence of the alkene, alkylation of the nitrile is the exclusive reaction, compare ref 5 and unpublished results from this laboratory.

(7) Mella, M.; Fagnoni, M.; Albini, A. *J. Org. Chem.* **1994**, *59*, 5614.

Table 2. Olefin Alkylation with Stannanes through SET Photosensitization in Acetonitrile

Sensitizer (A, 5×10^{-3}M)	E_{red}(A) (V, vs SCE)	oxidizing species E_{red} (V, vs SCE)	yield[a] of alkylation of **4** with **1**	yield[a] of alkylation of **4** with **2**	turnover no.[b]
Phen-1,4-$C_6H_4(CN)_2$	−1.6[c]	$Phen^{\bullet+}$ (1.58)	48	23 (62)[h]	10
Phen-1,2-$C_6H_4(CN)_2$	−1.76[d]	$Phen^{\bullet+}$ (1.58)	46	9 (47)[h]	13
Phen-1,4-$C_6H_4(CO_2Me)_2$	−1.78[e]	$Phen^{\bullet+}$ (1.58)	31	17 (51)[h]	49
Phen-1,2-$C_6H_4(CO_2Me)_2$	−2.07[f]	$Phen^{\bullet+}$ (1.58)	29	9 (35)[h]	56
Phen-1,4-$C_6H_4(CN)(CO_2Me)$	−1.76[e]	$Phen^{\bullet+}$ (1.58)	27	35 (78)[h]	11
1,2,4,5-$C_6H_2(CO_2Me)_4$	−1.31[g]	A^{3}* (1.73)	33	23 (64)[h]	24
1,2,4,5-$C_6H_2(CN)_4$	−0.65[c]	A^{1}* (3.15)	9[i]		4
1,2,4,5-$C_6H_2(CN)_4$-Biph		A^{1}* + $Biph^{\bullet+}$ (1.8)	19[i]	52 (82)[h], 6	
1,4-$C_{10}H_6(CN)_2$	−1.28[c]	A^{1}* (2.19)	26		6
1,4-$C_{10}H_6(CN)_2$-Biph		A^{1}* + $Biph^{\bullet+}$ (1.8)	78	25 (36)[h]	29
9,10-$C_{14}H_8(CN)_2$-Biph	−0.89[c]	A^{1}* (1.97) + $Biph^{\bullet+}$	2[j]		3[j]

[a] Yield of the alkylation product (**6a** or **6b**) as evaluated by vpc after 5 h irradiation at 320 nm (see Experimental Section). [b] Moles of alkylation product formed (**6a**)/moles of sensitizer consumed for the irradiation with **1** for 5h. [c] Reference 10b. [d] Reference 11a. [e] Reference 11b. [f] Reference 11c. [g] Reference 11d, value in DMF. [h] Yield of **6b** after 15 h irradiation. [i] Yield of **6a** after 1 h irradiation; at this point the sensitizer (1,2,4,5-benzenetetracarbonitrile) was almost completely consumed; however, if the irradiation was prolonged for further 4 h, the yield of **6a** reached 43% (without Biph) and 46% (with Biph), since the alkylated benzenetricarbonitriles **7** and **8** sensitized the alkylation of dimethyl maleate similarly to the tetranitrile (see text). [j] After 4 min irradiation at 360 nm with the sensitizer 5×10^{-4}M; prolonging the irradiation for 15 h gave a 7% yield of alkylation and complete consumption of the sensitizer.

Table 3. Relevant Parameters for Electron Transfer from the Alkylstannanes to Some Photoexcited Aromatic Acceptors

acceptor	$\Delta G_{et}(S_1)$,[a] kcal M^{-1}	$\Delta G_{et}(T_1)$,[a] kcal M^{-1}	K_{sv},[b] M^{-1}
1,2,4,5-$C_6H_2(CN)_4$	−33		121
1,4-$C_6H_4(CN)_2$	−20	7[c]	80
1,2,4,5-$C_6H_2(CO_2Me)_4$	−22	1[d]	*e*
1,4-$C_{10}H_6(CN)_2$	−10	14[f]	86

[a] Calculated by means of the Weller equation for electron tansfer from **2** (E_{ox} 1.75 V vs SCE, converted from the IP value, see ref 12a). Similar results are obtained with **1** (E_{ox} 1.60 V). [b] Measured for fluorescence quenching by **2**. [c] Triplet energy 70.1 kcal M^{-1}, ref 12b. [d] Triplet energy 70−71 kcal M^{-1}, compare ref 12c. [e] Fluorescence too weak for unambigous determination, compare ref 13. [f] Triplet energy 55.5 kcal M^{-1}, ref 12b.

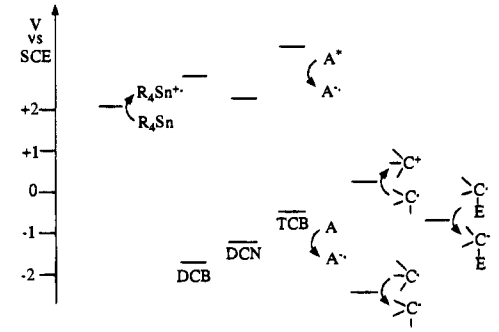
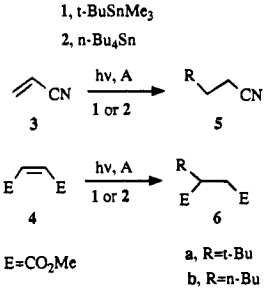


Figure 1. Relevant redox potentials for the sensitized radical addition. The ground and excited singlet excited state E_{red} of 1,4-benzenedicarbonitrile (DCB), 1,4-naphthalenedicarbonitrile (DCN), and 1,2,4,5-benzenetetracarbonitrile (TCB) used as acceptors (A) are shown. The singlet excited state of all of them will oxidize tetralkylstannanes (left). Fragmentation of the thus formed radical cation yields alkyl radicals (right). These are not reduced by the radical anion $A^{\bullet-}$, and add to electron-withdrawing substituted olefins to yield α-substituted adduct radicals (E = CN or CO_2Me). These are reduced by $DCB^{\bullet-}$ and $DCN^{\bullet-}$, while in the case of $TCB^{\bullet-}$ reduction and coupling compete since E_{red}(TCB) is higher.

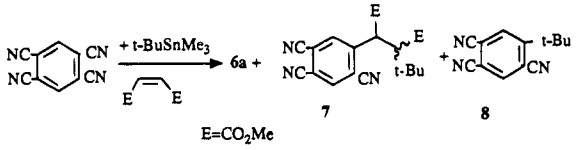
Secondary electron transfer between R_4Sn and $Biph^{\bullet+}$ then generates further molecules of the stannane radical cation (Scheme 5, in this case both path a and path c operate).

The efficiency of the desired process depends on (1) the competition between chemical reaction of the radical ions and back electron transfer regenerating the ground state starting material (path d vs path e in Scheme 5) and (2) the competition of side reactions of the radical with the sensitized cyclic process depicted in Scheme 2. Of the two radical ions produced, the

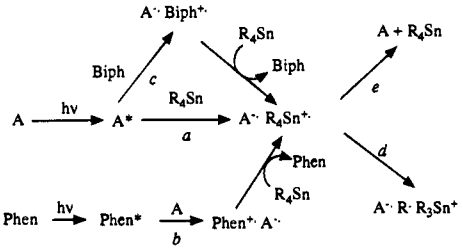
Scheme 3



Scheme 4



Scheme 5



acceptor radical anion is not expected to show any chemistry. In the case of aromatic nitriles, it has been shown that $A^{\bullet-}$ is a stabilized and persistent species;[8] this is confirmed in the present work by the large turnover numbers observed, and apparently the same holds for the aromatic esters. On the other hand, the stannane radical cation undergoes cleavage of a C−Sn bond to yield an alkyl radical and the stannyl cation (the bond dissociation energy for this process is calculated to be near to zero).[9] In the case of **1**, the cleavage is faster than with **2** and, as observed in previous cases, yields selectively the most stable (*tert*-butyl) radical.[5] Accordingly, the relative quantum yield

(8) Freccero, M.; Mella, M.; Albini, A. *Tetrahedron* **1994**, *50*, 2115.

(9) (a) Calculated through a thermochemical cycle; for analogies see refs 3 and 9b-d. (b) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132. (c) Popielartz, R.; Arnold, D. R. *J. Am.Chem.Soc.* **1990**, *112*, 3068. (d) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 7872.

of *tert*-butylation with **1** is higher than the yield of n-butylation with **2** (see Table 2), but prolonging the irradiation time leads to a satisfactory result also with **2**, since chemical yields are not worse in this case (see Table 2, values in parentheses). In most instances an irradiation of 24 h led to complete reaction of the stannane with alkylation of the alkene.

The observed quantum yield shows only a limited dependence on the sensitizer structure, with values ranging between 0.1 and 0.2 with **1** and somewhat lower values with **2**. Thus, a fraction between a few percent and almost 20% of the stannane radical cation fragments before back electron transfer. This is not very high, but one has to take into account the peculiar mildness of the method, and at any rate since the chemical process remains clean, a low quantum yield only means that one has to irradiate for a longer time. Notice inter alia that the large choice of sensitizers available minimizes the risk of causing a direct photochemical reaction of the substrate. Furthermore the efficiency of this step is enhanced when secondary electron transfer[10a,b] is operating: indeed the best results are obtained under those conditions (see Table 2). Such an effect has been previously observed[10c,d] and attributed to the fact that the chemically reacting radical cation is not generated as a geminate pair with $A^{\bullet-}$ (where back electron transfer is easier) but rather through electron transfer to a radical cation ($Biph^{\bullet+}$ or $Phen^{\bullet+}$).

The success of the following steps is based on radical reactions and their selectivity. A characteristic that all photosensitizers share with respect to oxidation by thermal or electrochemical methods is that, since the oxidant is an excited state present in a very low steady state concentration, overoxidation of the alkyl radical, itself a short-lived species, to the carbocation (which is a problem in thermal methods, see Scheme 1) is kinetically prohibited. On the other hand, the persistent acceptor radical anions $A^{\bullet-}$ do accumulate to appreciable concentrations,[8] and thus the radicals formed are exposed to a *reducing,* rather than to an oxidizing, medium. However, electron transfer from $A^{\bullet-}$ to a simple alkyl radical is largely endothermic (the known E_{red} of the *tert*-butyl radical[9b] is reported in Figure 1) and does not occur (while with more easily reduced, e.g., benzyl, radicals this is the main process under comparable circumstances).[9c] Thus, apart from homocoupling and disproportionation (more important for the *tert*-butyl than for the *n*-butyl radical), the remaining paths are coupling with the acceptor radical anion and addition to the alkene, and since the concentration of the latter species is obviously much larger, the balance shifts in that sense, provided that the alkene is activated by electron-withdrawing substitution.

This leads to the adduct radical, which susbtitution makes more stable and more easily reduced (see Figure 1), and hence electron transfer from $A^{\bullet-}$ closes the sensitizing cycle (Scheme 2) generating an anion which is finally protonated by the moisture present in the solvent (as proved by the D_2O experiment). This holds provided that the *ground state* reduction potential of A is sufficiently negative. Table 2 shows that the turnover number is relatively high (considering the experiments in the presence of secondary donors) when $E_{red}(A) <$ ca. -1 V.

With the more easily reduced benzenetetracarbonitrile, on the contrary, electron transfer is less favored (see Figure 1), and combination of the adduct radical with the acceptor radical anion (to form product **8**) competes with reduction (the same factor is probably responsible of the low turnover number observed with anthracenedicarbonitrile).

The structure of the aromatic acceptor also affects these reactions. Thus, radical−radical anion combination, finally resulting in ipso-aromatic substitution is more important with nitriles (and particularly with the benzenetetracarbonitrile) than with esters. This holds both for the educt and for the adduct radical (in the case of the tetranitrile ipso-substitution by the adduct radical gives products **8** and **7** respectively) and is probably due to the larger spin localization on the ring atoms and less sterical hindering in the radical anion of the nitriles. Thus, when esters are used, a cleaner process results. At any rate, as far as the olefin alkylation is concerned, this side reaction is not very detrimental. Indeed, even with the tetranitrile, although the starting sensitizer is rapidly consumed, the resulting alkylated trinitriles sensitize the stannane cleavage just as well, and prolonging the irradiation time after all the starting tetranitrile has been consumed leads to an alkylation yield similar to that observed with more robust sensitizers (see Table 2, note h).

In conclusion, this work shows that radical addition to alkenes via photoinduced SET is a preparatively useful method, which is equivalent to and competitive with established procedures, such as reaction with tin or mercury hydrides. Generation of the key intermediate, an aliphatic radical cation, is obtained by photoinduced SET, using aromatic nitriles or esters as the acceptor (direct singlet or triplet state electron transfer or secondary electron transfer are all possible). In the present method, the key problem of differentiating educt and adduct radical is solved by exploiting their different reduction potentials rather than their different hydrogen abstraction rates.

Experimental Section

The aromatic compounds used as photosensitizers and the stannanes were either commercial samples or were synthesized according to conventional procedures (the nitriles by reaction of the corresponding bromides with CuCN, the esters from the acids, the stannane **1** from *t*-BuMgBr).[16]

Preparation of Heptanecarbonitrile (5b). A solution of tetrabutylstannane (**2**, 0.89 mL, 0.05M), acrylonitrile (0.71 mL, 0.2 M), dimethyl terephthalate (53 mg, 5×10^{-3} M), and phenanthrene (482 mg, 5×10^{-2} M) in acetonitrile (54 mL) was equally subdivided in three quartz tubes. These were deaerated by flushing with argon for 15 min and irradiated by means of six external 15 W phosphor coated lamps (center of emission 320 nm) for 15 h. The opaque solution was rotary evaporated under reduced pressure, and the residue bulb-to-bulb distilled at 25 Torr and 60 °C, to yield 100 mg (50%) of the title compound: p.eb 184 °C,[14] ^{1}H NMR ($CDCl_3$) 0.92 (t, $J = 7$ Hz, 3H), 1.3 (m, 4H), 1.45 (m, 2H), 1.65 (qui, $J = 7$ Hz, 2H), 2.32 (t, $J = 7$ Hz, 2H). Examination of the raw photolysate by vpc showed that the product was formed in 86% yield.

Preparation of 4,4-Dimethylpentanecarbonitrile (5a). A solution of the stannane **1** (0.6 mL, 0.05M), acrylonitrile (0.8 mL, 0.2M), 1,4-naphthalenedicarbonitrile (53 mg, 5.4 × 10−3M), and Biph (0.92 g,

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0.1M) in acetonitrile (54 mL) was treated as above (irradiation, 5 h). Column chromatography on a silica gel column (Merck 60 HR) eluting with a cyclohexane−ethyl acetate (95:5) mixture gave 120 mg (40%) of the title compound, distilled at 68−70 °C at 15 Torr:[15] ^{1}H NMR ($CDCl_3$) 0.92 (s, 9H), 1.6 (t, J = 7 Hz, 2H), 2.25 (t, J = 7 Hz, 2H); ^{13}C NMR (CDCl3) 14.4 (CH2), 30.3 (Me), 32.0, 40.9 (CH2), 119 (CN).

Preparation of Dimethyl 2-Butylbutanedicarboxylate (5b). A solution of the stannane **2** (1.245 mL, 0.07M), dimethyl maleate (0.338 mL, 0.05 M), and tetramethyl pyromellitate (84 mg, 5 × 10^{-3} M) in acetonitrile (54 mL) was treated (irradiation 15 h) and chromatographed as above to yield the title compound (415 mg, 76%), distilled at 105−107 °C at 15 Torr: ^{1}H NMR ($CDCl_3$) 0.9 (t, J = 7 Hz, 3H), 1.3 (m, 4H), 1.6 (m, 2H), 2.45 (dd, J_{gem} = 16 Hz, J = vic 5 Hz, 1H), 2.72 (dd, J_{gem} = 16 Hz, J_{vic} = 10 Hz, 1H), 2.85 (m, 1H), 3.67 (s, 3H), 3.70 (s, 3H).

Preparation of Dimethyl 2-(2,2-Dimethylpropyl)butanedicarboxylate (6a). A solution of the stannane **1** (0.596 mL, 0.05M), dimethyl maleate (0.336 mL, 0.05 M), 1,4-naphthalenedicarbonitrile (48 mg, 5 × 10^{-3} M), and Biph (734 mg, 0.1 M) in acetonitrile (54 mL) was treated (irradiation 5 h) and chromatographed as above to yield the title product admixed with some of the sensitizer, from which it was freed by washing with pentane. Filtration gave 434 mg (85%).[7] When the reaction was carried out using MeCN freshly distilled from calcium hydride and added with 0.1% D_2O, product **6a** was deuterated for a 60% (the diastereotopic methylene showed a 45% deuteration at the proton absorbing at 2.7 and 15% at the proton absorbing at 2.45; for a further example of deuteration of **6a** in the presence of D_2O and using a different fragmentable donor, see ref 7.

Attempted Alkylation with 1,2,4,5-Benzenetetracarbonitrile as the Photosensitizer. A solution of the stannane **1** (0.6 mL, 0.05 M), dimethyl maleate (0.336 mL, 0.1 M), and 1,2,4,5-benzenetetracarbonitrile (48 mg, 5 × 10^{-3} M) in acetonitrile (54 mL) was treated (irradiation 40 min) and chromatographed as above to yield **6a** (35 mg, 6.5%), **7** (25 mg, 44% referred to the initial amount of the acceptor) (mixture of two diastereoisomers), and **8** (28 mg, 29%). The characterization of products **7** and **8** has been previously reported.[7] A similar experiment carried out in the presence of biphenyl (0.1 M) gave the results reported in Table 1.

Small-Scale Experiments. These were similarly carried out using 3 mL portions of MeCN solutions containing the stannane (**1** or **2**, 0.05 M), dimethyl maleate (0.1 M), the acceptor (5 × 10^{-3}M, except in the case of 9,10-anthracenedicarbonitrile, which was 5 × 10^{-4} M due to the solubility limit) and when appropriate a cosensitizer (either Phen 0.05 M or Biph 0.1 M). The product distribution was determined by vpc using dodecane as the internal standard. Irradiation times and alkylation yields are reported in Table 2.

Fluorescence Measurements. These were carried out on deaerated solutions of the acceptors in optical cells by means of a Perkin Elmer spectrofluorimeter. Linear Stern−Volmer plots were obtained in all the cases reported in Table 3.

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