Oxidative Functionalization of Adamantane and Some of Its Derivatives in Solution

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1,2,4,5-Benzenetetracarbonitrile (TCB) is irradiated in the presence of adamantane (**1**) and some of its derivatives. The singlet excited state of TCB is a strong oxidant, and there is various evidence, including time-resolved spectroscopy, to prove that SET from the alkane to TCB[1]* takes place and yields the corresponding radical ions. The adamantane radical cation deprotonates from the bridgehead position, and the resulting radical couples with $TCB^{-\bullet}$. Deprotonation via the radical cation occurs with a number of substituted adamantanes and remains the exclusive or predominating reaction also with derivatives containing a potential electrofugal group, such as one of the following carbocations: *t*-Bu, CH_2OMe, CH_2OH (notable here is that C−H deprotonation is more efficient than O−H deprotonation). A carboxy group is lost more efficiently than a proton, however. In contrast, detaching of such cations is the main process when the radical cations of substituted adamantanes is produced anodically. This different behavior is explained on the basis of thermochemical calculation and of the different environments experienced by the radical cation in the two cases, viz reaction from the solvated radical cation in the first case and from the substrate adsorbed on the anode in the latter one. 1-Methoxyadamantane deprotonates from the methyl group, a reaction explained by the different structure of the radical cation. On the other hand, the radical $NO_3^{\bullet}$, conveniently produced by photolysis of cerium(IV) ammonium nitrate, reacts by hydrogen abstraction with selective attack at the bridgehead position and little interference by substituents and thus offers a useful way for the selective oxidative functionalization of adamantanes.

Due to their stability and their high symmetry, adamantane and its derivatives have enjoyed particular fortune in mechanistic studies of a variety of reactions. As an example, adamantane is often the model of choice in studies on the solution phase functionalization of alkanes, also because of its relatively low volatility, which allows a good material balance to be obtained. Introduction of a substituent is possible through different mechanisms, including electrophilic,[1] radical,[2] and photochemical[3] reactions, as well as various oxidative (mainly based on inorganic oxidants or metal-catalyzed)[4] methodologies. The last group includes also anodic oxidation,[5] where characteristically some carbon-centered substituents have been found to be split off during oxidation. This has been attributed to the fragmentation of an electrofugal group other than the proton, such as *tert*-butyl or adamantyl cation from the radical cation (ECE reaction, see Discussion).

The generation of radical ions through single electron transfer (SET)[6a] and the subsequent chemistry are presently the subject of active interest, particularity since mild methods for the unambiguous generation of such species in solutions are now available, e.g., photoinduced SET,[6] where the strong oxidizing properties of excited states are exploited. Adamantane has a delocalized σ_{C-C} bond as the HOMO[7] and is ideally suited for studying the chemistry of the radical cations of alkanes. In view of this fact, we tested the behavior of adamantane and some of its derivatives in the presence of photogenerated oxidants. Since it soon appeared that the results were at variance with what would be expected from the previously reported electrochemical results, we decided to systematically study the reaction of a range of substituted adamantanes under three different conditions, viz. (1) irradiation in the presence of 1,2,4,5-benzenetetracarbonitrile (TCB), the singlet excited state of which is a strong oxidant;[6d] (2) anodic oxidation; (3) reaction with the nitrate radical, a species conveniently generated by irradiation of cerium ammonium nitrate in solution[8] and known to have both oxidizing and hydrogen-abstracting properties. We report in the following the results ob-

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Scheme 1

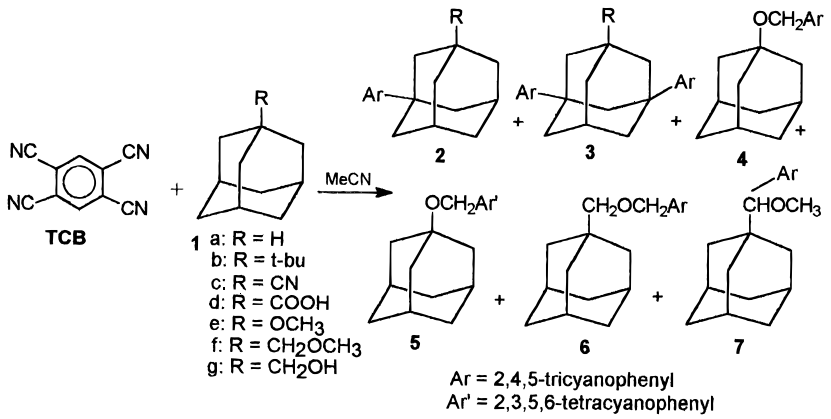

Table 1. Products Isolated from the Photochemical Reactions between TCB and the Adamantanes 1a−g

substrate	irradiation time (h)	converted TCB (%)	products (% yield)
1a	3	56	**2a** (80), **3a** (12)
1b	4	40	**2b** (76)
1c	2	57	**2c** (80), **3c** (6)
1d	2	70	**2a** (75), **2d** (20)
1e	10	30	**4** (62), **5** (23)
1f	6	28	**2a** (15), **2f** (68), **6** (3), **7** (5)
1g	8	30	**2a** (28), **2g** (64)

tained, which, we think, add to our understanding of the mechanism of alkanes oxidation.

Results

Photochemical Reaction in the Presence of TCB. Irradiation of acetonitrile solutions of TCB and adamantane (**1a**) led initially to the formation of a single product, 5-(1-adamantyl)-1,2,4-benzenetricarbonitrile (**2a**, Scheme 1, Table 1; prolonged irradiation until a high conversion was reached caused the formation of a small amount a 1,3-bis(2,4,5-tricyanophenyl)adamantane (**3a**), see Experimental Section). The examination was extended to a range of adamantanes substituted in position 1 and in most cases resulted in a clean reaction. Thus, 1-*tert*-butyladamantane (**1b**) gave the 3-*tert*-butyladamantyl trinitrile **2b** and 1-adamantanecarbonitrile (**1c**) the 3-cyanoadamantyl derivative **2c** (with a small amount of **3c**). On the other hand, the reaction between 1-adamantanecarboxylic acid (**1d**) and TCB mainly occurred with decarboxylation to give **2a**, accompanied by a minor amount of the product conserving the carboxy group, **2d**. 1-Methoxyadamantane (**1e**) reacted differently, with attack at the methyl group rather than at the adamantyl moiety, giving the two ethers **4** (the main product) and **5**. Finally, the reaction was extended to 1-adamantylmethyl methyl ether (**1f**) and 1-adamantylmethanol (**1g**). The ether reacted similarly to **1b**,**c**, yielding the 1-(3-substituted)adamantyl derivative **2f** as the main product, but substituent elimination to yield **2a** and attack at the side chain to yield compounds **6** and **7** also occurred to a minor extent. Likewise with the alcohol the reaction gave both the substituted (**2g**) and the unsubstituted (**2a**) adamantylbenzenecarbotrinitriles, with the former product predominating.

In order to find mechanistic evidence, we checked that the adamantanes **1a−g** quenched the fluorescence of TCB (the respective rate constants are reported in Table 2). Furthermore, flash photolysis experiments were carried out, with selective excitation of TCB. The formation of a transient absorbing in the range 410−490 nm with λ_{max} 448, 468 nm was apparent (Figure 1). This was similar to the absorption attributed to the TCB radical anion, previously obtained by ionization in matrix (λ_{max} 462 nm)[9a] and in solution by chemical reduction (λ_{max} 460 nm),[9b] except that the short-wavelength part was overestimated due to imperfect correction of the TCB fluorescence. It decayed with a second-order law, rate constant 4.78×10^3 M^{-1} s^{-1}. Study of the transient at very short times was precluded by the strong TCB emission. The same spectrum was observed with other adamantanes, e.g., **1c**, with smaller intensity (see Figure 1).

Photochemical Reaction in the Presence of CAN. The photoinduced reaction between cerium(IV) ammonium nitrate (CAN) and the adamantanes **1a** and **1b** has been previously reported by Baciocchi and co-workers.[8a] In accordance with their results, we found that irradiation of CAN and **1a** in acetonitrile led to reduction of the former to a Ce(III) salt and formation of *N*-(1-adamantyl)-acetamide (**8a**) as the main product. This was accompanied by a trace of the corresponding 2-adamantyl acetamide (**9**) as well as by 1-adamantanol nitrate (**10a**); the last compound was evidenced by NMR of the raw photolysate, but underwent hydrolysis to the alcohol (**11a**) during chromatography (Scheme 2, Table 3).

As will be shown in the following, the CAN-induced reaction on the adamantane ring mainly occurred at the bridgehead position. Products resulting from functionalization of a methylene group, such as **9** from **1a**, were present only in traces, and their characterization was not pursued. In the case of **1b** the 3-*tert*-butyladamantyl amide **8b** as well as 3-*tert*-butyladamantanol (**11b**) were obtained.

The reaction was extended to the other substrates. The nitrile **1c** gave the amide **8c** and the nitrate **10c**. The acid **1d** gave the amide **8d** and the nitrate **10d** as the main products, with loss of the carboxy group to yield the amide **8a** occurring as a minor path. The corresponding amide and nitrate, **8e** and **10e**, were the main products also from **1e**, along with traces of 1-adamantanol (**11a**). The ether **1f** gave a complex mixture of

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Table 2. Oxidation Potentials of the Adamantanes, Quenching Rate Constants, and Reaction Quantum Yields

substrate	E_p, V vs SCE	$\Delta G_{et}(TCB^{1*})$, eV	$k_q(TCB^{1*})$, M^{-1} s^{-1}	$\Delta G_{et}(NO_3^{\bullet})$, eV	$k_q(NO_3^{\bullet})$, M^{-1} s^{-1}	Φ_r(TCB)
1a	2.72	−0.72	1.1×10^{10}	0.72	5.6×10^7	0.055[a]
1b	2.64	−0.8	1	0.63	9.6	0.01[a]
1c	3.10	−0.38	0.26	1.1	0.8	0.11[b]
1d	2.90	−0.5	1.1	0.9	2.3	0.1[b]
1e	2.50	−0.94	0.7	0.5	9.5	0.007[a]
1f	2.59	−0.85	0.6	0.59	7.5	0.01[b]
1g	2.55	−0.89	1.2	0.55	6.8	0.01[b]

[a] Substrate 0.02 M. [b] Substrate 0.1 M.

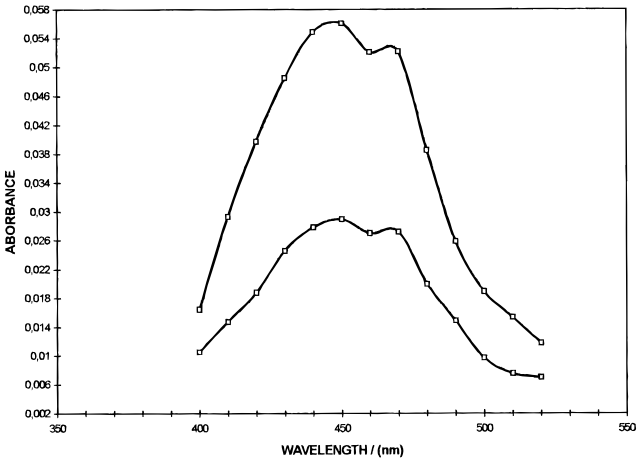


Figure 1. Absorption observed 1 ms after flashing (266 nm) a 0.1 mM TCB solution in MeCN, containing 15 mM **1a** (upper trace) or respectively 10 mM **1c** (lower trace).

Scheme 2

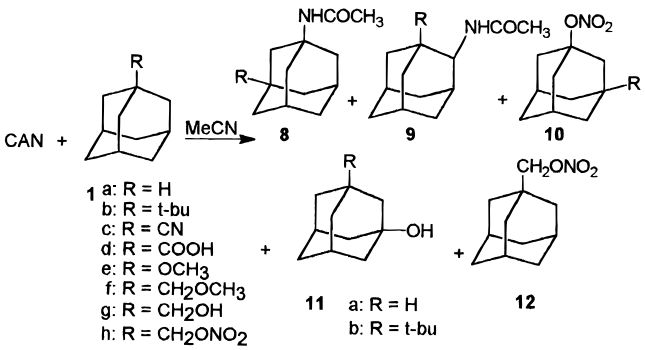


Table 3. Products Isolated from the Photoinduced Reaction between CAN and the Adamantanes

substrate	irradiation time (h)	converted substrate (%)	products (% yield)
1a	1.5	76	**8a** (53), **9** (4), **11a** (30)
1b	4	70	**8b** (54), **11b** (29)
1c	3	55	**8c** (28), **11c** (56)
1d	3	45	**8a** (10), **8d** (41), **10d** (47)
1e	2	34	**8e** (43), **10e** (30), **11a** (15)
1f	2	40	**8f** (35), **10f** (40), **8h**+**10h** (3.5), **1g** (4.5), **1d** (tr), **12** (10)
1g	2	42	**8a** (5), **8g** (43), **8h** (7), **10g** (33), **10h** (7), **1d** (tr)[a]

[a] Part of the alcohol **1g** is esterified during the reaction to give the nitrate **12**.

products, including the amide **8f** (with a small amount of the nitroxylated derivative **8h**) and the nitrate **10f** (with a small amount of the dinitrate **10h**), as well as smaller amounts of the alcohol **1g**, its nitrate **12**, and a trace of the acid **1d**. As for **1g**, the products were the amide **8g** (with a small amount of **8h**) and the nitrate **10g** (with a small amount of the dinitrate **8h**), as well as a small amount of the unsubstituted amide **8a**. In all these cases, parallel experiments in the dark showed no significant conversion of the reagents for the time considered, even in the presence of dilute nitric acid (except for the esterification of the alcohols, as in the case of **1g**, see Table 3).

Table 4. Products Formed in the Anodic Oxidation of the Adamantanes

substrate	converted substrate (%)	products (% yield)
1a	50	**8a** (80)
1b	75	**8a** (59), **8b** (12)
1c	30	**8c** (80)
1e	80	**8a** (20), **8e** (32), **11a** (30)
1f	60	**6a** (67), **6f** (13)
1g	90	**6a** (80)

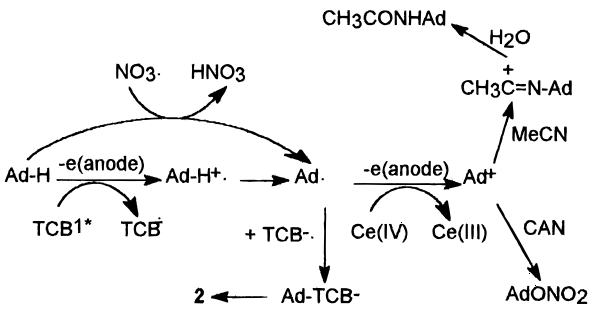
Since it is known that the photolysis of CAN produces the $NO_3^{\bullet}$ radical, and this can be monitored by its transient absorption in flash photolysis, appropriate experiments were carried out and the second-order rate constants for the quenching of the radical by the adamantanes **1a**−**g** were determined (see Table 2).

Electrochemical Studies. The oxidation potentials of the above adamantanes were voltammetrically measured in MeCN. In the case of **1a**, two irreversible waves were observed in the 2−3 V vs SCE region. The first wave showed a linear dependence of the diffusion current on the substrate concentration in the range (2×10^{-4})−(8×10^{-3}) M). The experiments were extended to the other adamantanes considered, and the values measured for the first wave are reported in Table 2. Comparison with a standard (ferrocene) showed that this was a two-electron wave, in accordance with previous findings.[5b] Furthermore, preparative anodic oxidations were carried out (see Table 4), in part repeating previously reported experiments.[5] The observed substrate oxidation required slightly more than 2 Faraday per mole, and the products obtained were as follows. The amide **8a** was formed from **1a**. Extensive conversion led to the gradual accumulation of a second product, reasonably resulting from the further oxidation of **8a**, which was not investigated (compare ref 5b). With **1b**, acetamidation occurred for the main part with loss of the *tert*-butyl group (to yield **8a**) and for the minor part conserving it (to yield **8b**). From the nitrile **1c** the corresponding amide **8c** was obtained while from the ether **1e** the substituted (**8e**) and the unsubstituted (**8a**) adamantyl amides were both obtained along with 1-adamantanol (**11a**). As for the ether **1f**, the main product was **8a** and the minor one **8f**, and from the alcohol **1g** only the unsubstituted amide **8a** was formed.

Discussion

In all of the reactions reported above the material balance is good. Furthermore, transient studies have delineated the initial steps. Thus, the product distribu-

Scheme 3



tion can be used in connection with spectroscopic evidence for a mechanistic discussion.

General Mechanism. The three set of reactions which have been carried are oxidative processes, but the conditions involved are quite different. Voltammetric measurement show a well-distinguished oxidation wave, also in the case of electron-withdrawing substituted adamantanes. When a preparative anodic oxidation is carried out, an overall two-electron process occurs, as found also in previous studies.[5] The mechanism shown in Scheme 3 had been postulated for this reaction.[3] This is an ECE process, where cleavage of the radical cation precedes a second electron transfer to the radical. The cation thus formed is trapped by the solvent, and addition of water finally yields the observed amides **8** (Scheme 3).

As for the photochemical reaction with TCB, this is a strong oxidant in the singlet excited state [$E_{red}(TCB^{1*}) = E_{red}(TCB) - E_{exc} = 3.44$ V vs SCE].[6d] Adamantane and its derivatives are moderate donors (see Table 2), and SET to TCB^{1*} is an exoergonic process, expected to occur at a diffusion-controlled rate. This is indeed the case, as shown in Table 2, where the observed rate constants are compared with ΔG_{et}. The rate constant level is close to the diffusion-controlled limit with all the substrates, except than with the cyano derivative **1c**, where it is somewhat lower. Thus, it can be safely assumed that the first step in the photoreaction between TCB and adamantane involves the singlet state of the former and leads to a radical ion pair, as shown by the detection of a transient attributable to the TCB radical anion in flash photolysis (Figure 1). The intensity of this transient is likewise proportional to the E_{ox} of the donor, e.g., with **1c** it is about a half that with **1a**. The adamantane radical cation transfers a proton to the solvent. The radical thus formed combines with $TCB^{-\bullet}$, and the resulting anion rearomatizes through cyanide loss to yield the benzotricarbonitriles **2** (Scheme 3), analogously to what is observed with other alkyl radicals.[10]

Finally, it has been demonstrated that irradiation of CAN generates the nitrate radical. The process is largely reversible in an "inert" solvent such as MeCN, unless $NO_3^{\bullet}$ reacts with a suitable substrate. A detailed examination by Baciocchi et al. has shown that this radical is a powerful oxidant, although not comparable with TCB (estimated $E_{red} = 2.0$ V vs SCE).[8b] In some cases, e.g., with sufficiently electron-rich aromatics, the reaction involves SET (rate up to the diffusion-controlled limit) followed by proton transfer, whereas with less oxidizable substrates, such as alkylbenzenes, the rate is comparable to that expected for hydrogen abstraction. In the present case, the observed quenching constants are much lower, varying over 1 order of magnitude around 10^7 M^{-1} s^{-1} (Table 2), and since hydrogen abstraction by the strongly electrophylic $NO_3^{\bullet}$ radical is expected to occur in this range of rates,[11] the latter mechanism is favored (see below for the evidence from substituted adamantanes). The adamantyl radical is formed in this way and is further oxidized to the cation by CAN, with following trapping either by the solvent to give the amides **8** or by CAN to give the nitrates **10** (Scheme 3).

Reactions of Substituted Adamantanes. In the case of parent adamantane the 1-adamantyl radical is selectively formed (only in the reaction with CAN a small amount of the 2-isomer was detected), but this occurs according to two different mechanisms, electron and then proton transfer (in anodic oxidation and in the reaction with TCB) or homolytic hydrogen abstraction (in the case of CAN). The follow-up reactions of the adamantyl radical, as shown in Scheme 3, have precedent in other reactions of alkyl radicals and need not be further discussed here.

With substituted adamantanes, on the other hand, the chemistry observed is quite varied, with ring functionalization, ipso substitution, and, in the case of alcohols and ethers, attack at the side chain all occurring, in quite different proportions in the three types of experiment which were carried out (for convenience, the reactions occurring are summarized in Table 5 and classed as involving ring deprotonation, substituent loss, or attack at the side chain in the photochemical reactions with TCB (a) and CAN (b) or in anodic oxidation (c), respectively). While the different paths followed in case (b) may be assigned to a difference in the primary step (hydrogen rather than electron transfer, see above), Table 5 shows that different processes occur even when the same intermediates are invoked. As an example, with adamantanes containing a carbon-centered electrofugal group, such as **1b**, **1f**, and **1g**, C−C cleavage largely predominates over deprotonation in anodic oxidation (Scheme 4), but in the reaction with TCB, deprotonation is the exclusive process with **1b** and remains predominating also with **1f** and **1g**, with C−C cleavage occurring efficiently only with **1d**. These results should be reconciled with the above mechanism (Scheme 3), where fragmentation takes place at the radical cation stage in both reactions.

Reactions via Radical Cation. The free energy change for fragmentation of a radical cation, $\Delta G(Ad-R^{+\bullet})$, can be evaluated through a thermochemical cycle (eq 1)[12] when the appropriate parameters [relevant bond dissociation energy, ΔG(Ad-R), oxidation potential of the substrate, E_{ox}(Ad−R) and of the radical corresponding to the cation set free, $E_{ox}(R^{\bullet})$] are known. For most of the

$$\Delta G(Ad-R^{+\bullet}) = \Delta G(Ad-R) + E_{ox}(R^{\bullet}) - E_{ox}(Ad-R) \quad (1)$$

present adamantanes the required quantities in MeCN are known or can be approximated from related compounds (the presently determined peak potentials rather than half-wave potentials are used, but this does not

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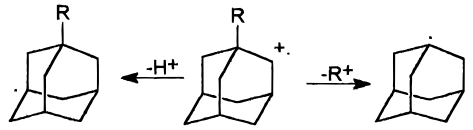
Table 5. Competitive Reactions of the Substituted Adamantanes. Fractions of the Observed Paths

	functionalization at the bridgehead CH			ipso substitution[a]			attack at the side chain		
substrate	TCB	CAN	anode	TCB	CAN	anode	TCB	CAN	anode
1b	1	1	0.15			0.85			
1c	1	1	1						
1d	0.79	0.90		0.21	0.10				
1e		0.83	0.39				1	0.17	0.61
1f	0.75	0.84	0.16	0.16		0.84	0.09	0.16	
1g	0.70	0.94		0.30	0.08	1		0.06	

[a] In the reaction with CAN, products of apparent ipso substitution such as **8a** from **1g** are considered as resulting from attack at the side chain, due to the radical nature of the reaction (see text).

Scheme 4



affect qualitatively the results), and application of eq 1 leads to the values reported in Table 6 for competitive deprotonation and carbocation loss (see Scheme 4).

One can see that deprotonation of the adamantane radical cation is a strongly exoergonic process (−17 kcal mol^{-1}, i.e., this species is an acid comparable with mineral acids (pK_a −12)). These values are practically the same as those evaluated for toluene:[12] the lower energy of the benzylic C−H bond in the latter substrate is compensated for by the larger amount of energy accumulated in the adamantane radical cation. A more powerful oxidant is required for an aliphatic than for an aromatic substrate (e.g., TCB for adamantane, while for toluene the less powerful 1,4-naphthalenedicarbonitrile is sufficient), but once that the SET step is accomplished the expected chemistry is the same, and indeed deprotonation occurs in both cases.[13]

In the adamantane radical cation, deprotonation at position 1 is preferred over reaction at position 2, since a difference in bond strength translates to a difference in acidity (see Table 6). Deprotonation remains by far the favored process also with the substituted adamantanes, where C−C cleavage is endoergonic.[14a] Although the precision of the evaluation in Table 6 is certainly no better than a few kcal mol^{-1}, it is apparent that the barrier confronted for C−C cleavage with *tert*-butyl- and (methoxymethyl)adamantane is quite high (around 10 kcal mol^{-1}). Thus, at least at room temperature, fragmentation of the *tert*-butyl cation does not compete with deprotonation, and loss of the methoxymethyl cation from **1f**$^{+\bullet}$ occurs only as a minor path.

Table 6. Evaluation of the Free Energy Change for the Fragmentation of the Radical Cation of Some Adamantanes in Acetonitrile

reaction	ΔG(Ad-R$^{+\bullet}$), kcal M^{-1} [a]
1a$^{+\bullet}$ → 1-Ad$^\bullet$ + H$^+$	−17.1
1a$^{+\bullet}$ → 2-Ad$^\bullet$ + H$^+$	−13.6
1b$^{+\bullet}$ → 1-(3-*t*-Bu)Ad$^\bullet$ + H$^+$	−15.3
1b$^{+\bullet}$ → 1-Ad$^\bullet$ + *t*-Bu$^+$	10.0
1c$^{+\bullet}$ → 1-(3-CN)Ad$^\bullet$ + H$^+$	−25.9
1e$^{+\bullet}$ → 1-(3-MeOCH$_2$)Ad$^\bullet$ + H$^+$	−14.1
1e$^{+\bullet}$ → 1-Ad$^\bullet$ + MeOCH$_2^+$	11.4

[a] Free energy change for the fragmentation of the radical cation, calculated through the appropriate thermochemical cycle (see text). Oxidation potential of the adamantanes, see Table 2. Further data used: **1a**, BDE(C−H$_t$) taken equal to that of *t*-Bu−H, 92 kcal mol^{-1}, ref 19. BDE(C−H$_s$) taken equal to that of the C−H bond in cyclohexane, 95.5 kcal mol^{-1}, ref 19, E_{ox}(H$^\bullet$) = 2.01 V vs SCE; the BDE(C−H) is presumed not to change appreciably in the derivatives considered; **1b**, BDE(C−C) taken equal to that of *t*-Bu−*t*-Bu, 68.8 kcal mol^{-1}, ref 19, E_{ox}(*t*-Bu$^\bullet$) = 0.09 V vs SCE, ref 20. **1e**, BDE(C−C) taken equal to that of *t*-BuCH$_2$OMe, 76.7 kcal mol^{-1}, ref 19, E_{ox}(MeOCH$_2^\bullet$) = −0.24 V vs SCE, ref 20.

In complete contrast, C−C bond cleavage is largely preferred in anodic oxidation. Since, as has been discussed above, both thermochemical arguments and the photochemical reaction with TCB support the view that the radical cation deprotonates, the substituent loss observed in anodic oxidation (e.g., in the case of **1b**) must be explained through a mechanism different from ECE. We believe that this is due to the fundamental difference of the two experiments, one involving generation of the radical cation at extremely low steady state concentration in solution, the other involving the molecules adsorbed on the anode. In electrochemistry the high local radical cation concentration on the anode surface may favor disproportionation (e.g., eq 2), or alternatively the metal atoms on the surface may stabilize the carbocation liberated through back-electron donation, thus substantially lowering the fragmentation barrier via a metal

(13) (a) The proton is transfered to the solvent; although MeCN is a poor base, it is well-known that it is protonated by mineral acids,[13c] to which the present radical cations can be compared. The TCB radical anion probably has no role in the process. Indeed, the radical anions of arene nitriles are known to be poor bases;[13c,d] for example, Robinson and Schulte-Frohlinde found that the basicity of the 1,4-benzenedicarbonitrile radical anion is lower than the detection limit of their experiment (pK_a < 0).[13e] As far as the benzylic derivatives are concerned, there is evidence that proton transfer involves the solvent, not the sensitizer,[13f] and there is no ground to think of a different path in the present case. The situation is certainly different when weaker acids, such as α-amino radical cations, and more nucleophilic radical anions, such as those of ketones, are involved.[13g,h] Furthermore, the chemical products obtained here follow the same pattern as many other alkylations of arene nitriles involving radical−radical anion addition, as shown in Scheme 3, and there is now abundant evidence that the same process is followed when the radical (whether a benzyl radical or an alkyl radical) arises from deprotonation of the radical cation or from the splitting of a different electrofugal cation,[6d,10] again supporting the view that the sensitizer radical anion is not involved in the deprotonation and all electrofugal groups are transferred to the solvent. (b) Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 1047. (c) Freccero, M.; Mella, M.; Albini, A. *Tetrahedron* **1994**, *50*, 2155. (d) Kellet, M. A.; Whitten, D. G.; Gould, I. R.; Bergmark, W. R. *J. Am. Chem. Soc.* **1991**, *113*, 358. (e) Robinson, E. A.; Schulte-Frohlinde, D. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 707. (f) Fasani, E.; d'Alessandro, N.; Mella, M.; Mariano, P. S. *J. Org. Chem.* **1994**, *59*, 1047. (g) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **1992**, *25*, 233. (h) Zhang, X.; Yeh, S.; Hong, S.; Freccero, M.; Albini, A.; Falvey, D. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1994**, *116*, 4211.

(14) (a) Here too the results can be compared with π-delocalized radical cations. Thus, in similar photoinduced SET reactions of bibenzyls it has been shown that C−C bond cleavage occurs at room temperature and indeed is preferred to the largely exoergonic deprotonation even when slightly (by ca. 5 kcal M^{-1}) exoergonic, and more easily (up to 13 kcal M^{-1}) at 80 °C,[10,14b] but above this limit only deprotonation takes place.[14c] The present results show that the results with σ radical cations can be similarly rationalized. (b) Popielartz, R.; Arnold, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 3068. (c) Sulpizio, A.; Albini, A.; d'Alessandro, N.; Fasani, E.; Pietra, S. *J. Am. Chem. Soc.* **1989**, *111*, 5773.

assisted process (eq 3). Attempts to carry out the anodic

$$\mathbf{1b}^{+\bullet} + \mathbf{1b}^{+\bullet} \rightarrow \mathbf{1b} + \mathbf{1b}^{2+} \rightarrow \text{1-Ad}^{+} + \text{tBu}^{+} \quad (2)$$

$$\mathbf{1b}^{+\bullet}\cdots\text{metal} \rightarrow \text{1-Ad}^{\bullet} + \text{tBu}^{+}\cdots\text{metal} \quad (3)$$

oxidation with a glass electrode, which should minimize surface effects, were frustrated since the anode is rapidly covered by a polymer and the electrolysis stops.

Thus at present we consider that the difference between the two experiment is a further example of the fragmentation mode of a radical cation being determined by the stabilization of the leaving cation; proton transfer to MeCN from the solvated radical cation (or the radical ion pair) is easy, while this is not the case when the radical cation is adsorbed (nor indeed in the gas phase, where a hydrogen atom, not a proton, is lost).

The carboxylic acid **1d** is the only exception, since here substituent loss predominates also in the TCB reaction. This reaction has been already reported for other aliphatic carboxylic acids.[15] Apparently, in this case deprotonation from the COOH group takes place competitively with that from a CH bond, and the carboxy radical then cleaves (eq 4).

$$\text{AdCOOH}^{+\bullet} \rightarrow \text{AdCOO}^{\bullet} \rightarrow \text{Ad}^{\bullet} + \text{CO}_2 \quad (4)$$

Indeed, the fact that even in the presence of a carboxy group, with the easily heterolytically broken O−H bond, C−H deprotonation from the ring takes place at a rate one-fifth of that from the substituent shows that alkane radical cations are strong C−H acids not only from the *thermodynamic* (see above) but also from the *kinetic* point of view. Furthermore it is notable that apparently only minimal O−H deprotonation takes place in the case of the alcohol **1g**, where in principle an analogous path (eq 5) may have been expected, as judged from the fact that ipso substitution is only 8% and attack to the ring is as efficient as with the corresponding ether **1f** (see Table 5). This selectivity can be rationalized on the basis of

$$\text{AdCH}_2\text{OH}^{+\bullet} \rightarrow \text{AdCH}_2\text{O}^{\bullet} \rightarrow \text{Ad}^{\bullet} + \text{CH}_2\text{O} \quad (5)$$

eq 1. Thus, when the electrofugal group is the same (in this case the proton), it is the bond energy which makes the difference, and thus the weakest bond is cleaved, resulting in preferential C−H vs O−H deprotonation, just as it happens in a homolytic process, although through a completely different mechanism.

A further evidence can be found in the reactions of the ethers **1e** and **1f**. These substrates undergo side-chain functionalization in addition to attack at the ring. The former reaction leads to the appropriate benzotrinitriles with TCB (**4** and **5**, and respectively **6** and **7**) and to dealkylation to give the corresponding alcohols in the electrochemical experiments (eq 6):

$$\text{ROMe}^{+\bullet} \rightarrow \text{ROCH}_2^{\bullet} \rightarrow \text{ROCH}_2^{+} \rightarrow \text{ROCH}_2\text{Nu} \rightarrow \text{ROH (R = Ad or AdCH}_2\text{)} \quad (6)$$

However, the proportion of the two paths is different with the two substrates; e.g., in the TCB reaction side-chain attack is the exclusive reaction with **1e**, while it is only a minor path with **1f**. This can be explained by the different charge localization in the radical cation. Indeed, the oxidation potential of aliphatic ethers and adamantane lies quite close to one another. The latter one is somewhat lower, and indeed the quenching constant of TCB fluorescence by **1a** is twice as much as that with aliphatic ethers.[16a] As a result, in the case of **1f** where the two moieties are separated by a CH_2 bridge, the radical cation is localized on the adamantane residue, and deprotonation takes place from that site. On the contrary, with **1e**, where the methoxy group is directly linked to the adamantane skeleton, the radical cation is delocalized also on the oxygen atom, and deprotonation takes place from the position α to the ether function. The side-chain vs ring attack is then somewhat different in the TCB reaction and anodic oxidation, due, as discussed above, to the different environment in which the radical cation reaction takes place, as well as to the fact that in the TCB case the reaction in part takes place from an exciplex, as shown by the formation of a small amount of the tetranitrile **5**.[16]

A final note is appropriate about the efficiency of the photochemical reaction. The quantum yield (essentially a measure of the competition between radical cation cleavage and back-electron transfer, since the initial SET is almost quantitative in all cases) is around 6% with adamantane. It is somewhat increased by electron-withdrawing substituents (e.g., it is twice as much with the nitrile **1c**), and this may result from the fact that here deprotonation is even more exoergonic (compare eq 1 and Table 6, the oxidation potential of the substrate, E_{ox}(Ad-R), is more positive in this case and hence ionization weakens the bond more than with the parent molecule). On the contrary, the reaction quantum yield decreases to ca. 1% in the presence of electron-donating groups, probably not so much because of a change in ΔG(Ad-$R^{+\bullet}$), since the difference is small and the value remains largely negative (see Table 6), but due to the fact that such derivatives contain a further donating moiety which may disfavor proton transfer to the solvent vs back-electron transfer to the radical anion, a competition which is reasonably related to the conformation of the initial radical ion pair.

Hydrogen Abstraction in the Reaction with CAN. As mentioned at the beginning of the Discussion, the quenching rate constant for the reaction with $NO_3^{\bullet}$ (10^7−10^8 M^{-1} s^{-1}) unambiguously indicated a hydrogen transfer mechanism (on the other hand, SET would be too endoergonic). Nethertheless, the quenching rate significantly depends on the oxidation potential of the adamantanes, and so does the overall rate of reaction, with the cyano and carboxy derivatives **1c** and **1d** requiring a longer irradiation for their conversion than more easily oxidized substrates. Noteworthy is the selectivity of the process. Recent investigations show that hydrogen abstraction from adamantane by most radicals is quite

(15) (a) Tsujimoto, K.; Nakao, N.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1992**, 366. (b) Fasani, E.; Peverali, D.; Albini, A. *Tetrahedron Lett.* **1994**, *49*, 9275.

(16) (a) Notice also that in the TCB reaction a small amount of the 6-alkylated benzenetetracarbonitrile (**5**), resulting from the alkylation at one of the unsubstituted positions, is formed besides the usual product of ipso substitution, viz. the 5-alkylated benzenetricarbonitrile (**4**), which, at any rate, remains the main one. A case of attack at the unsubstituted position of TCB has been previously observed, again as a minor path and again with an ether, 1,4-dioxane, ref 15b. We suggested that this products arises from an alternative mechanism, e.g., direct proton transfer within the contact radical ion pair (or exciplex) which has probably a different conformation when the donor contains an oxygen atom than when it is a hydrocarbon, ref 15b. At any rate this remains a minor path and has no bearing on the main mode of fragmentation of the radical cation. (b) Fasani, E.; Mella, M.; Albini, A. *J. Chem. Soc., Perkin Trans. 2* **1995**, 449.

unselective (secondary vs tertiary functionalization ratio ca. 1), except when there is a strong polar effect, e.g., with $Pr_2N^{+\bullet}$ radicals (sec/tert ratio 0.09). Clearly the $NO_3^\bullet$ radical pertains to the latter category (ratio 0.07). The adamantyl radicals thus formed are then oxidized by CAN (E_{red} 1.27 V vs SCE) and trapped by the solvent (see Scheme 3).

The useful characteristics of this reaction appear to be its efficiency and its tolerance of substituents. As for the first point, the quantum yield of the reaction with CAN is as large as that with TCB, the lower reaction rate being compensated for by the longer lifetime of the $NO_3^\bullet$ radical (ca. 0.13 ms in MeCN, unaffected by dissolved oxygen). As for the latter one, it is noticeable that ring functionalization always accounts for > ca. 85% of the reaction, as is shown in Table 5. Apparently the bridgehead C−H remains the weakest bond (or at least the most susceptible to attack by this type of radical), even in the presence of potentially competitive hydrogens α to alkoxy or hydroxy functions.

The present reaction with CAN seems to be a new and quite general way for the selective oxidative functionalization of adamantanes. Under the present conditions the reaction leads to a mixture of nitrate and acetamide, but under suitable conditions one could convert the radical into a single compound functionalized in position 1. Further radicalic traps may be used, as has already been shown with oxygen.[17a] Indeed, even in the TCB case we recently showed that, when carried out in the presence of oxygen, the irradiation of adamantane and TCB leads to 1-adamantanol.[17b]

Conclusion. The results presented here may be useful in two respects. First, the potentiality of photoinduced SET has been demonstrated, extending this method to the oxidation of alkanes,[18] after the several examples previously reported with n or π donors.[6d,10] The different product distribution between photoinduced SET and anodic oxidation is thought to be due to the adsorption of the substrate at the electrode in the latter case, in contrast with the suggestion of an ECE in previous literature. In general, the chemistry of radical cations is largely environment-dependent. Second, new selective functionalizations of adamantanes have been reported, both via a SET mechanism (with TCB) and via hydrogen abstraction (with CAN). The latter reaction offers a rather general, substituent-independent way for the oxidative functionalization of adamantanes at position 1.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer, and chemical shifts are reported in ppm downfield from TMS. Elemental analyses were made using a Carlo Erba Model 1106 instrument. 1,2,4,5-Benzenetetracarbonitrile (TCB), adamantane, 1-adamantanecarboxylic acid, 1-adamantanecarbonitrile, and 1-adamantylmethyl alcohol were commercial products. 1-adamantylmethyl alcohol and 1-adamantylmethyl methyl ether were prepared by standard treatment of the corresponding alcohol with NaH and CH_3I. 1-*tert*-Butyladamantane was prepared through a published method.[21] The yields of the photoreactions are calculated on consumed TCB or on the consumed adamantanes in the reaction with CAN.

Photochemical Reaction between TCB and Adamantane (1a). A solution of TCB (72 mg, 0.4 mmol, 0.01 M) and adamantane (**1a**) (0.02 M, 110 mg, 0.8 mmol) in MeCN (40 mL, subdivided in two quartz tubes) was purged with argon and irradiated for 3 h with a multilamp reactor fitted with six 15-W phosphor-coated lamps (maximum of emission, 320 nm). The reaction course was followed by TLC and GC. Workup of the photolysate involved concentration in vacuo and chromatographic separation employing Merck 60 silica gel and a 7:3 cyclohexane−ethyl acetate mixture as eluant. TCB (32 mg) was recovered, and 50 mg of 5-(1-adamantyl)benzene-1,2,4-tricarbonitrile (**2a**) (80%, mp 268−270 °C, EtOH) was obtained. Moreover a minor product was isolated which contained two aromatic rings for one molecule of adamantane; to this was attributed the structure of 1,3-bis(2,4,5-tricyanophenyl)adamantane (**3a**) (11 mg, 12%, dec >270 °C) in accordance with spectroscopic data and elemental analysis.

2a: ^1H NMR (in $CDCl_3$) δ 1.8 (bs, 6H), 2.1 (bs, 6H), 2.2 (bs, 3H), 7.9 and 8.08 (s, 2H); ^{13}C NMR δ 28.28 (3CH), 35.73 ($3CH_2$), 40.39 ($3CH_2$), 38.45, 113.54, 113.73, 114.41 (CN), 115.73 (CN), 116.57 (CN), 119.19, 132.12 (CH), 139.40 (CH), 159.45. Anal. Calcd for $C_{19}H_{17}N_3$: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.4; H, 5.97; N, 14.44.

3a: ^1H NMR (in $CDCl_3$) δ 1.9 (bs, 2H), 2.2−2.4 (m, 8H), 2.55 (bs, 4H), 7.91 (s, 2H), 8.1 (s, 2H); ^{13}C NMR δ 28.62 (2CH), 34.24 (CH_2), 39.05 ($4CH_2$), 39.31, 42.49 (CH_2), 113.22, 114.10, 114.98 (CN), 115.59 (CN), 116.38 (CN), 119.81, 131.99 (CH), 139.56 (CH), 156.80. Anal. Calcd for $C_{28}H_{18}N_6$: C, 76.69; H, 4.14; N, 19.17. Found: C, 76.27; H, 4.15; N, 19.25.

Photochemical Reaction between TCB and *tert*-Butyladamantane (1b). A solution containing TCB and *tert*-butyladamantane (**1b**) (0.02 M, 153 mg, 0.8 mmol) was irradiated as above for 4 h. After general workup and silica gel chromatography, 43 mg of TCB were recovered unreacted and 23 mg of [1-(3-*tert*-butyladamantyl)]benzene-1,2,4-tricarbonitrile (**2b**) (76%, mp 225−228 °C with decomposition, EtOH) was isolated.

2b: ^1H NMR (in $CDCl_3$) δ 0.9 (s, 9H), 1.65 (bs, 6H), 1.9−2.2 (m, 6H), 2.3 (bs, 2H), 7.9 and 8.05 (s, 2H); ^{13}C NMR δ 24.51 ($3CH_3$), 28.87 (2CH), 34.67 ($2CH_2$), 35.19, 35.49 (CH_2), 37.52, 39.45, 39.57 (CH_2), 40.22 ($2CH_2$), 113.55, 113.78, 114.43 (CN), 115.90 (CN), 116.63 (CN), 119.19, 132.11 (CH), 139.41 (CH), 159.84. Anal. Calcd for $C_{23}H_{25}N_3$: C, 80.43; H, 7.34; N, 12.24. Found: C, 79.95; H, 6.97; N, 12.44.

Photochemical Reaction between TCB and 1-Adamantanecarbonitrile (1c). Irradiation of a solution of TCB and 1-adamantanecarbonitrile (**1c**) (0.05 M, 320 mg, 2 mmol) for 2 h, followed by the general workup, gave, after silica gel chromatography (cyclohexane−EtOAc), 55 mg (80%, dec >270 °C, EtOH) of [1-(3-cyanoadamantyl)]benzene-1,2,4-tricarbonitrile (**2c**) as main product. A small amount of a product containing two aromatic rings for one molecule of adamantanecarbonitrile (**3c**) (6 mg, 6%), was isolated, although it was not sufficiently pure for a complete characterization.

2c: ^1H NMR (in $CDCl_3$) δ 1.8 (bs, 2H), 2.1 (bs, 4H), 2.15 (bs, 4H), 2.3 (bs, 2H), 2.4 (bs, 2H), 7.8 and 8.1 (s, 2H); ^{13}C NMR δ 27.26 (2CH), 30.90, 33.85 (CH_2), 37.84, 38.23 ($2CH_2$), 38.69 ($2CH_2$), 41.81 (CH_2), 113.10, 113.95, 114.64 (CN), 115.52 (CN), 116.02 (CN), 119.56, 123.30 (CN), 131.70 (CH), 139.42 (CH), 156.15. Anal. Calcd for $C_{20}H_{16}N_4$: C, 76.90; H, 5.16; N, 17.94. Found: C, 76.38; H, 5.01; N, 17.38.

3c: ^1H NMR (in $CDCl_3$) δ 2.1−2.4 (m, 6H), 2.45−2.7 (m, 7H), 7.85 and 8.15 (s, 4H); ^{13}C NMR δ 28.94 (CH), 34.0, 39.10, 39.46 (CH_2), 40.68 ($2CH_2$), 42.82 ($2CH_2$), 43.22 (CH_2), 113.81, 113.70, 114.65 (CN), 115.37 (CN), 116.58 (CN), 116.91, 121.12 (CN), 132.61 (CH), 140.58 (CH), 154.78.

Photochemical Reaction between TCB and 1-Adamantanecarboxylic Acid (1d). Irradiation of a solution of

(17) (a) Baciocchi, E.; Del Giacco, T.; Sebastiani, G. V. *Tetraedron Lett.* **1987**, *28*, 1941. (b) Mella, M.; Freccero, M.; Albini, A. *J. Chem. Soc., Chem. Commun.* **1995**, 41.

(18) (a) The extension of the method to different alkanes will be reported in a following paper concerning open-chain and cyclic alkanes. A related, but different, case is that of strained hydrocarbons, see ref 18b. (b) Gassman, P. G., in ref 6b, part C, p 70.

(19) Egger, K. W.; Cocks A. T. *Helv. Chim. Acta* **1973**, *56*, 1516.

(20) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

(21) Reetz, M. T.; Westermann, J.; Kyung, S. H. *Chem. Ber.* **1985**, *118*, 1050.

TCB and adamantanecarboxylic acid (**1d**) (0.05 M, 360 mg, 2 mmol) for 2 h, followed by general workup and silica gel chromatography (cyclohexane−EtOAc and then EtOAc−MeOH), gave 60 mg of 5-(1-adamantyl)benzene-1,2,4-tricarbonitrile (**2a**) (75%) and 20 mg of 3-(2,4,5-tricyanophenyl)-adamantanecarboxylic acid (**2d**) (20%, dec >270 °C, nitroethane).

2d: ^{1}H NMR (in CD_3OD) δ 1.7−2.0 (m, 8H), 2.2 (bs, 4H), 2.25 (bs, 2H), 7.93 and 8.1 (s, 2H); ^{13}C NMR δ 29.33 (2CH), 34.68 (CH_2), 37.75 ($2CH_2$), 38.87, 39.37 ($2CH_2$), 41.64, 41.82 (CH_2), 113.44, 113.72, 114.25 (CN), 115.53 (CN), 116.42 (CN), 119.12, 132.24 (CH), 139.44 (CH), 158.70, 183.17 (COOH). Anal. Calcd for $C_{20}H_{17}N_3O_2$: C, 72.49; H, 5.17; N, 12.68. Found: C, 72.08; H, 5.01; N, 12.28.

Photochemical Reaction between TCB and 1-Methoxyadamantane (1e). Irradiation of a solution of TCB and 1-methoxyadamantane (**1e**) (0.03 M, 200 mg, 1.2 mmol) for 10 h, followed by general workup, gave, after silica gel chromatography (cyclohexane−EtOAc), 20 mg of (2,4,5-tricyanophenyl)methyl adamantyl ether (**4**) (62%, oil) and 10 mg of (2,3,5,6-tetracyanophenyl)methyl adamantyl ether (**5**) (23%, oil).

4: ^{1}H NMR (in $CDCl_3$) δ 1.6−1.75 (m, 6H), 1.9 (bs, 6H), 2.25 (bs, 3H), 4.75 (s, 2H, H-1), 8.05 and 8.24 (s, 2H); ^{13}C NMR δ 30.4 (3CH), 36.06 ($3CH_2$), 41.27 ($3CH_2$), 59.06 (OCH_2), 74.55, 113.58, 113.66, 114.18 (CN), 114.87 (CN), 115.00 (CN), 119.36, 132.97 (CH), 136.17 (CH), 150.41. Anal. Calcd for $C_{20}H_{19}N_3O$: C, 75.68; H, 6.03; N, 13.24. Found: C, 76.05; H, 6.15; N, 13.05.

5: ^{1}H NMR (in $CDCl_3$) δ 1.6−1.75 (m, 6H), 1.9 (bs, 6H), 2.25 (bs, 3H), 4.85 (s, 2H, H-1), 8.12 (s, 1H); ^{13}C NMR δ 30.49 (3CH), 36.03 ($3CH_2$), 40.61 ($3CH_2$), 59.30 (OCH_2), 75.67, 111.67, 112.59, 120.67 (CN), 121.45 (CN), 135.66 (CH), 149.21. Anal. Calcd for $C_{21}H_{18}N_4O$: C, 73.66; H, 5.30; N, 16.36. Found: C, 73.95; H, 5.45; N, 16.15.

Photochemical Reaction between TCB and 1-Adamantylmethyl Methyl Ether (1f). Irradiation of a solution of TCB and ether **1f** (0.03 M, 216 mg, 1.2 mmol), for 6 h, gave, after general workup and silica gel chromatography (cyclohexane/EtOAc), 25 mg of [1-[3-(2,4,5-tricyanophenyl)adamantyl]]methyl methyl ether (**2f**) (68%, mp 188−190 °C, benzene−petroleum ether), 5 mg of 5-(1-adamantyl)benzene-1,2,4-tricarbonitrile (**2a**) (15%), and 3 mg of a two-product mixture arising from deprotonation from the methyl (**6**) (3%) and methylene groups (**7**) (5%) of the ether function. The small quantity of these two last compounds did not allowed a further purification but only a spectroscopic characterization. In the proton spectrum the aliphatic parts of **6** and **7** were superimposed while the corresponding ^{13}C signals were separated. The elemental analysis of this mixture was in accordance with the structures proposed.

2f: ^{1}H NMR (in $CDCl_3$) δ 1.5−1.65 (m, 4H), 1.65−1.85 (m, 2H), 1−9−2.2 (m, 4H), 2.2 - 2.4 (6H), 3.1 (s, 2H, OCH_2), 3.4 (s, 3H, OCH_3), 7.9 and 8.05 (s, 2H); ^{13}C NMR δ 28.42 (2CH), 35.13, 35.41 (CH), 36.11 ($2CH_2$), 39.08, 40.02 ($2CH_2$), 42.72 (CH_2), 59.42 (OCH_3), 82.91 (OCH_2), 113.6, 113.95, 114.46 (CN), 115.93 (CN), 116.65 (CN), 119.32, 132.26 (CH), 139.47 (CH), 159.16. Anal. Calcd for $C_{21}H_{21}N_3O$: C, 76.10; H, 6.39; N, 12.68. Found: C, 75.85; H, 6.50 ; N, 12.30.

6: ^{1}H NMR (in $CDCl_3$) δ 1.4−2.3 (m, aliphatic protons superimposed to those of **7**), 3.18 (s, 2H, OCH_2), 3.3 (s, 2H, OCH_2), 8.03 and 8.1 (s, 2H); ^{13}C NMR δ 27.93 (3CH), 36.92 ($3CH_2$), 38.76, 39.51 ($3CH_2$), 69.38 (OCH_2), 89.07 (OCH_2), 113.53, 113.78, 114.4 (CN), 115.21 (CN), 116.59 (CN), 119.47, 132.46 (CH), 136.43 (CH), 150.15. **7**: ^{1}H NMR (in $CDCl_3$) δ 1.4−2.3 (m, aliphatic protons superimposed to those of **6**), 3.2 (s, 3H, OCH_3), 4.75 (s, 1H), 7.95 and 8.05 (s, 2H); ^{13}C NMR δ 27.98 (3CH), 36.47 ($3CH_2$), 37.73 ($3CH_2$), 39.13, 58.51 (OCH_3), 89.07 (OCH), 113.5, 113.78, 114.21 (CN), 115.77 (CN), 116.57 (CN), 119.47, 134.02 (CH), 136.33 (CH), 157.5. Anal. Calcd for $C_{21}H_{21}N_3O$: C, 76.11; H, 6.39; N, 12.68. Found: C, 76.21; H, 6.25; N, 12.48.

Photochemical Reaction between TCB and 1-Adamantylmethanol (1g). From the irradiation of a solution of TCB and the alcohol **1g** (0.03 M, 200 mg, 1.2 mmol) for 8 h, and after general workup as above, were isolated 10 mg of 5-(1-adamantyl)-1,2,4-benzenetricarbonitrile (**2a**) (28%) and 23 mg of [1-[3-(2,4,5-tricyanophenyl)adamantyl]]methanol (**2g**) (64%, mp 220−222 °C, cyclohexane−benzene).

2g: ^{1}H NMR (in $CDCl_3$) δ 1.4 (exch; OH), 1.6 (bs, 4H), 1.8 (m, 2H), 1.95 (bs, 2H), 2.05−2.2 (m, 4H), 2.3 (bs, 2H), 3.35 (s, 2H), 7.9 and 8.05 (s, 2H); ^{13}C NMR 28.30 (2 CH), 35.31 (CH_2), 35.57 (2 CH_2), 38.98, 39.99 (2 CH_2), 42.08 (CH_2), 72.48 (OCH_2), 113.48, 113.94, 114.32 (CN), 115.80 (CN), 116.54 (CN), 119.29, 132.13 (CH), 139.39 (CH), 158.9. Anal. Calcd for $C_{20}H_{19}N_3O$: C, 75.68; H, 6.03; N, 13.24. Found: C, 75.18; H, 6.21; N, 13.18.

Photochemical Reaction in the Presence of CAN and Adamantane (1a). A solution containing 800 mg of cerium(IV) ammonium nitrate (CAN) (0.04 M, 1.6 mmol) and 108 mg (0.02 M, 0.8 mmol) of adamantane (**1a**) in 40 mL of MeCN subdivided in two quartz tubes was flushed with argon for 15 min and then irradiated with a multilamp reactor fitted with six 15-W phosphor-coated lamps (maximum of emission, 320 nm). After 2 h the orange color had disappeared and a white precipitate had formed. The solvent was evaporated and the residue treated with water and CH_2Cl_2. The organic layer was dried and concentrated. The conversion of adamantane was determined by GC analysis while the ^{1}H and ^{13}C NMR spectra of the organic residue were diagnostic for the identification of the type of products primarily formed during the irradiation (nitrates or alcohols or acetamides) and their relative ratios. In this case two main products were present in the crude mixture, both arising from the attack at the tertiary position: 1-adamantyl nitrate (characteristic was the quaternary carbon at 86.30 ppm) and 1-adamantylacetamide (characteristic were the quaternary carbons at 50.64 and 169.37 ppm and the methyl carbon at 24.56 ppm, compared with an authentic sample). The corresponding 2-adamantyl derivatives were present in smaller quantities (characteristic for 2-adamantylacetamide were the methyl carbon at 24.42 ppm and the methine carbon at 52.89 ppm and for 2-adamantyl nitrate the quaternary carbon at 86.23 ppm). The ratio between tertiary vs secondary position attack was 14:1 (as confirmed also by GC analysis). The mixture was then chromatographed on a silica gel column eluting with cyclohexane−EtOAc mixtures of increasing polarity, all containing 0.1% triethylamine to minimize the possible hydrolysis of nitrates owing to silica gel acidity. Despite this precaution, 1-adamantanol (**11a**) (30 mg) (30%) and *N*-(1-adamantyl)acetamide (**8a**) (60 mg, 53%) were isolated as main products (both identified by comparison). A spectroscopic characterization of 1-adamantyl nitrate (**10a**) was possible, since the carbon-13 signals were separated from those of adamantane and *N*-(1-adamantyl)acetamide, both reported in the literature.[22]

10a: ^{13}C NMR (in $CDCl_3$) δ 30.84 (3CH), 35.69 ($3CH_2$), 39.55 ($3CH_2$), 89.88 ($CONO_2$).

Photochemical Reaction in the Presence of CAN and *tert*-Butyladamantane (1b). A solution containing cerium(IV) ammonium nitrate (CAN) and 153 mg (0.02 M, 0.8 mmol) of *tert*-butyladamantane (**1b**) was irradiated for 4 h. After general workup as above, the raw photolysate was separated on a silica gel column (cyclohexane/EtOAc). Two main products were isolated in this case: *N*-[1-(3-*tert*-butyladamantyl)]-acetamide (**8b**) (108 mg, 54%, mp 138−140 °C, cyclohexane) and 3-*tert*-butyladamantanol (**11b**) (46 mg, 29%, mp 118−120 °C, cyclohexane), which was formed from the hydrolysis of the corresponding nitrate. The structures of these compounds were attributed on the basis of NMR and IR spectroscopic data.

8b: ^{1}H NMR (in $CDCl_3$) δ 1.3 (s, 9H), 1.4−1.6 (m, 6H), 1.7 (bs, 2H), 1.8- 2.0 (m, 4H), 1.9 (s, 3H, $NCOCH_3$), 2.15 (bs, 2H), 5.15 (exch, NH); ^{13}C NMR δ 24.69 (CH_3), 29.51 (2CH), 34.68, 35.07 ($2CH_2$), 35.77 (CH_2), 38.85, 40.65 (CH_2), 41.00 ($2CH_2$), 52.94, 169.07 (NC=O); IR cm^{-1}1660, 3200. Anal. Calcd for $C_{16}H_{27}NO$: C, 77.06; H, 10.91; N, 5.62. Found: C, 76.85; H, 11.05; N, 5.45.

11b: ^{1}H NMR (in $CDCl_3$) δ 1.3 (s, 9H), 1.45−1.55 (m, 6H), 1.6−1.9 (m, 6H), 1.7 (exch, OH), 2.2 (bs, 2H); ^{13}C NMR δ 24.72

(22) Pouchert, C. J.; Behnke J. *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*; Aldrich, 1993.

(23) Mella, M.; d'Alessandro, N. ; Freccero, M.; Albini, A. *J. Chem. Soc., Perkin Trans. 2* **1993**, 515.

($3CH_3$), 30.67 (2CH), 34.57, 34.86 ($2CH_2$), 35.56 (CH_2), 40.49, 44.29 (CH_2), 44.77 ($2CH_2$), 69.42. Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.45; H, 11.75.

Photochemical Reaction between CAN and 1-Adamantanecarbonitrile (1c). A solution containing CAN and 128 mg of nitrile **1c** (0.02 M, 0.8 mmol) was irradiated for 3 h. The raw photolysate was treated as above. ^1H and ^{13}C NMR spectra of the organic residue showed the presence of two main products derived from **1c**: a nitrate (characteristic was the quaternary carbon at 86.30 ppm) and an acetamide (characterized by quaternary carbons at 50.64 and 169.37 ppm). After silica gel chromatography, the following products were isolated: 26 mg of *N*-[1-(3-cyanoadamantyl)]acetamide (**8c**) (28%, oil) and 54 mg of 3-cyanoadamantylnitrate (**10c**) (56%, mp 78−79 °C, cyclohexane).

8c: ^1H NMR (in $CDCl_3$) δ 1.7 (bs, 2H), 1.8−2.15 (m, 8H), 1.9 (s, 3H, $NCOCH_3$), 2.2 (bs, 2H), 2.35 (bs, 2H), 5.2 (exch, NH); ^{13}C NMR δ 24.36 (CH_3), 28.25 (2CH), 31.56, 34.54 (CH_2), 38.74 ($2CH_2$), 40.03 ($2CH_2$), 42.61 (CH_2), 50.64, 123.81 (CN), 169.37 (NC═O); IR cm^{-1} 1660, 2220, 3300. Anal. Calcd for $C_{13}H_{18}N_2O$: C, 71.52; H, 8.31; N, 12.83. Found: C, 71.70; H, 8.35; N, 12.65.

10c: ^1H NMR (in $CDCl_3$) δ 1.7 (bs, 2H), 2.0 (bs, 4H), 2.15 (bs, 4H), 2.5 (bs, 2H); ^{13}C NMR δ 29.52 (2CH), 32.99, 33.99 (CH_2), 38.17 ($2CH_2$), 38.47 ($2CH_2$), 41.38 (CH_2), 86.30, 122.75 (CN); IR cm^{-1} 1280, 1620, 2220. Anal. Calcd for $C_{11}H_{14}N_2O_3$: C, 59.45; H, 6.35; N, 12.60. Found: C, 59.95; H, 6.65; N, 12.35.

Photochemical Reaction between CAN and 1-Adamantanecarboxylic Acid (1d). Separate experiments with different workups were carried out in order to isolate products with or without the carboxy function. In the first experiment a solution of CAN with 144 mg (0.02 M, 0.8 mmol) of 1-adamantanecarboxylic acid (**1d**) was irradiated for 4 h. The solution was treated as above. In this case the adamantane acid and its derivatives containing the carboxylic group remained in the water phase while only decarboxylated products were extracted by dichloromethane. After concentration of the solvent, 4 mg of the organic extract was obtained. The main compound present in these few milligrams was *N*-(1-adamantyl)acetamide (**8a**) as shown by ^1H and ^{13}C NMR spectra. In the second experiment the irradiated solution was only filtered and concentrated. The residue was separated on a silica gel column eluting with $EtOAc/CH_3OH$. Two carboxylated derivatives were separated, viz. 3-acetamidoadamantanecarboxylic acid (**8d**) (34 mg, 41%, dec >250 °C) and 3-(nitrooxy)adamantanecarboxylic acid (**10d**) (40 mg, 47%, mp 130−132 °C, cyclohexane/benzene).

8d: ^1H NMR (in CD_3OD) δ 1.75 (bs, 2H), 1.9 (s, 3H, NCOCH3), 2−2.3 (m, 10H), 2.4 (bs, 2H); ^{13}C NMR δ 24.21 (CH_3), 30.65 (2CH), 36.65 (CH_2), 39.38 ($2CH_2$), 41.48 ($2CH_2$), 43.48 (CH_2), 53.42, 167.19 (NC═O), 173.6 (COOH); IR cm^{-1} 1660, 1700, 3100. Anal. Calcd for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; N, 5.90. Found: C, 66.00; H, 8.20; N, 5.60.

10d: ^1H NMR (in CD_3OD) δ 1.7 (bs, 2H), 1.9 (bs, 4H), 2.15 (bs, 4H), 2.3 (bs, 2H), 2.4 (bs, 2H); ^{13}C NMR δ 30.12 (2CH), 34.59 ($2CH_2$), 37.18 ($2CH_2$), 38.64 ($2CH_2$), 40.12 (CH_2), 44.12, 88.88 ($CONO_2$), 181.56 (COOH); IR cm^{-1} 1280, 1620, 1700, 3050. Anal. Calcd for $C_{11}H_{15}NO_5$: C, 54.76; H, 6.27; N, 5.81. Found: C, 54.50; H, 6.55; N, 5.45.

Photochemical Reaction between CAN and 1-Methoxyadamantane (1e). A solution containing 132 mg (0.02 M, 0.8 mmol) of 1-methoxyadamantane and CAN was irradiated for 2 h. After general workup, ^1H and ^{13}C NMR spectra of the raw photolysate showed the presence of two main products (the nitrate and the acetamide of methoxyadamantane as expected) admixed with minor amounts of two compounds characterized by the presence of a hydroxy group instead of the methoxy group. After silica gel chromatography, 26 mg of *N*-[1-(3-methoxyadamantyl)]acetamide (**8e**) (43%, oil) and 18 mg of 3-methoxyadamantyl nitrate (**10e**) (30%, oil) were isolated as main products. Moreover 6 mg of 1-adamantanol (**11a**) (15%) was also isolated. The raw fraction containing **8e** showed also signals compatible with the presence of another acetamide.

8e: ^1H NMR (in $CDCl_3$) δ 1.5−1.8 (m, 8H), 1.9 (s, 3H, $NCOCH_3$), 1.8−2.1 (m, 4H), 2.25 (bs, 2H), 3.25 (s, 3H, OCH_3), 5.2 (exch, NH); ^{13}C NMR δ 24.51 (CH_3), 30.21 (2CH), 35.10 (CH_2), 39.54 ($2CH_2$), 40.03 ($2CH_2$), 44.16 (CH_2), 45.88 (OCH_3), 54.17, 72.84, 169.26 (NC═O); IR 1660, 3300. Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48; N, 6.27. Found: C, 70.10; H, 9.45; N, 6.10.

10e: ^1H NMR (in $CDCl_3$) δ 1.5−1.8 (m, 6H), 2.0−2.1 (m, 6H), 2.45 (bs, 2H), 3.25 (s, OCH_3); ^{13}C NMR δ 30.79 (2CH), 34.65 (CH_2), 38.62 ($2CH_2$), 42.99 (CH_2), 48.39 (OCH_3), 74.09, 90.42 ($CONO_2$); IR 1280, 16620. Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.13; H, 7.54; N, 6.16. Found: C, 58.35; H, 7.60; N, 5.95.

Photochemical Reaction between CAN and 1-Adamantylmethyl Methyl Ether (1f). A MeCN solution of CAN and adamantylmethyl methyl ether (**1f**) (144 mg, 0.8 mmol, 0.02 M) was irradiated for 2 h. After general workup as above, ^1H and ^{13}C NMR spectra of the raw photolysate showed that 40% of ether **1f** had been converted into a complex mixture of products. The main ones were the expected nitrate and acetamide, arising from the attack onto the adamantane ring; moreover, also present was adamantylmethyl alcohol (**1g**) and some of its derivatives. This mixture was then separated on a silica gel column and the following compounds were obtained: 24 mg (35%, oil) of *N*-[1-(3-methoxymethyl)adamantyl]-acetamide (**8f**); 28 mg (40%, oil) of 3-(methoxymethyl)-adamantyl nitrate (**10f**); 4 mg (4.5%) of 1-adamantylmethyl alcohol (**1g**) with 6 mg (10%, oil) of the corresponding 1-adamantylmethyl nitrate (**12**); 3 mg (3.3%) of a mixture containing the nitrate and the acetamide of the above 1-adamantylmethyl nitrate, viz. compounds **8h** and **10h** (see the photochemical reaction with **1g** for their characterization). Traces of adamantanecarboxylic acid (**1d**) were detected in a more polar fraction. In order to check for the possible formation of the alcohol **1g** by a nonphotochemical path, HNO_3 was added to a MeCN solution of ether **1f** and the solution was kept at room temperature in the dark for 1 day. After this time no traces of alcohol were detected by GC analysis; thus acid hydrolysis of the ether had to be excluded as the source of the alcohol.

8f: ^1H NMR (in $CDCl_3$) δ 1.55 (bs, 2H), 1.55−1.7 (m, 4H), 1.8 (bs, 2H), 1.9 (s, 3H, $NCOCH_3$), 1.9−2.0 (m, 4H), 2.1 (bs, 2H), 2.9 (s, 2H, CH_2O), 3.35 (s, 3H, OCH_3), 5.2 (exch, NH); ^{13}C NMR δ 24.53 (CH_3), 29.11 (2CH), 35.74 (CH_2), 36.01, 38.34 ($2CH_2$), 41.01 ($2CH_2$), 43.38 (CH_2), 59.19, 59.24 (OCH_3), 82.89 (CH_2O), 169.21 (NC═O); IR cm^{-1} 1660, 3250. Anal. Calcd for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.65; H, 10.10; N, 5.80.

10f: ^1H NMR (in $CDCl_3$) δ 1.55 (bs, 2H), 1.55−1.8 (m, 4H), 1.9−2.1 (m, 6H), 2.3 (bs, 2H), 3.0 (s, 2H, OCH_2), 3.35 (s, 3H, OCH_3); ^{13}C NMR δ 30.48 (2CH), 35.35 (CH_2), 37.98 ($2CH_2$), 38.28, 39.19 ($2CH_2$), 41.47 (CH_2), 59.29 (OCH_3), 82.19 (CH_2O), 90.45 ($CONO_2$); IR cm^{-1} 1280, 1620. Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.94; N, 5.81. Found: C, 59.50; H, 8.05; N, 5.60.

12: ^1H NMR (in $CDCl_3$) δ 1.55 (bs, 6H), 1.6−1.8 (m, 6H), 2.0 (bs, 3H), 4.05 (s, 3H); ^{13}C NMR δ 27.73 (3CH), 36.46, 36.56 ($3CH_2$), 38.94 ($3CH_2$), 82.28 ($CONO_2$); IR cm^{-1} 1280, 1620. Anal. Calcd for $C_{11}H_{17}NO_3$: C, 62.54; H, 8.11; N, 6.63. Found: C, 62.85; H, 8.24; N, 6.55.

Photochemical Reaction between CAN and 1-Adamantylmethanol (1g). A solution of CAN and alcohol **1g** (132 mg, 0.8 mmol, 0.02 M) was irradiated for 2 h. The MeCN solution was acidic owing to the HNO_3 formed by the irradiation of CAN; under these conditions part of the alcohol was transformed into the corresponding 1-adamantylmethyl nitrate (**12**) (in a separate experiment, it was shown that esterification was obtained by treating a MeCN solution of **1g** with HNO_3 at room temperature; after 24 h the alcohol was completely transformed into the corresponding nitrate **12**). After the general workup, ^1H and ^{13}C NMR spectra of the raw photolysate showed the presence of two kinds of products: the first one with the introduction of an amide or a nitrate function onto the adamantane ring of the alcohol **1g** and the second one arising from the nitrate **10**. In fact after silica gel chromatography (using cyclohexane−ethyl acetate mixtures of increasing polarity and then EtOAc only), the following products were isolated: 40 mg of 1-adamantylmethyl nitrate (**12**), 31 mg (43%) (oil) of *N*-[1-[3-(hydroxymethyl)]adamantyl]-acetamide (**8g**) and 6 mg (7%) (oil) of the corresponding methyl

nitrate (**8h**); 23 mg (33%) (oil) of 3-(hydroxymethyl)adamantyl nitrate (**10g**) and 6 mg (7%) of the corresponding methyl nitrate (**10h**) (mp 50 °C, cyclohexane), 3 mg (5%) of *N*-(1-adamantyl)acetamide (**8a**). Traces of 1-adamantanecarboxylic acid (**1d**) were also detected in the last fraction.

8g: ^{1}H NMR (in $CDCl_3$) δ 1.5−1.8 (m, 6H), 1.95 (s, 3H, $NCOCH_3$), 1.9−2.1 (m, 6H), 2.2 (bs, 2H), 3.3 (s, 2H, CH_2O), 5.2 (exch, NH); ^{13}C NMR δ 24.26 (CH_3), 27.53 (2CH), 36.36 (CH_2), 36.88 ($2CH_2$), 38.74 ($2CH_2$), 40.85 (CH_2), 51.16, 71.85 (CH_2OH), 169.70 (NC═O); IR cm^{-1} 1660, 3200. Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48; N, 6.27. Found: C, 70.05; H, 9.55; N, 6.25.

8h: ^{1}H NMR (in $CDCl_3$) δ 1.6−1.8 (m, 6H), 1.9 (s, 3H, $NCOCH_3$), 1.9−2.1 (m, 6H), 2.2 (bs, 2H), 4.15 (s, CH_2ONO_2), 5.15 (exch, NH); ^{13}C NMR δ 24.40 (CH_3), 28.67 (2CH), 35.26 (CH_2), 36.12, 37.70 ($2CH_2$), 40.66 ($2CH_2$), 42.34 (CH_2), 51.66, 80.99 (CH_2ONO_2), 169.22 (NC═O); IR cm^{-1} 1280, 1620, 1660, 3200.

10g: ^{1}H NMR (in $CDCl_3$) δ 1.5−1.8 (m, 6H), 1.95 (bs, 2H), 2.1 (bs, 4H), 2.4 (bs, 2H), 3.55 (s, 2H, CH_2OH); ^{13}C NMR δ 30.43 (2CH), 35.32 (CH_2), 37.44 ($2CH_2$), 39.92, 39.20 ($2CH_2$), 40.99 (CH_2), 72.06 (CH_2O), 90.36 ($CONO_2$); IR cm^{-1} 1280, 1620. Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.13; H, 7.54; N, 6.16. Found: C, 58.30; H, 7.55; N, 6.05.

10h: ^{1}H NMR (in $CDCl_3$) δ 1.55−1.8 (m, 6H), 2.01 (bs, 2H), 2.1 (bs, 4H), 2.4 (bs, 2H), 4.2 (s, CH_2ONO_2); ^{13}C NMR δ 30.05 ($2CH_2$), 34.66 (CH_2), 37.27, 37.52 ($2CH_2$), 38.82 ($2CH_2$), 41.01 (CH_2), 80.19 (CH_2ONO_2), 88.89 ($CONO_2$).

Quantum Yield Determination. Quantum yields were determined on 3 mL of a MeCN solution of the acceptor (0.005 M) and the donor in quartz tube, irradiating with a multilamp reactor fitted with six 15-W phosphor-coated lamps (maximum of emission, 320 nm). The TCB consumption was determined by monitoring the UV absorption at 315 nm.

Fluorescence Measurements. Fluorescence spectra and emission intensities were measured by means of an Aminco Bowman MPF spectrofluorimeter on a solution contained in a 1 cm optical path cuvette after deaeration. Stern−Volmer plots were linear. The singlet quenching rate constants reported in Table 2 are calculated from the Stern−Volmer constants and the previously measured TCB fluorescence lifetime, 10.8 ns.[23]

Flash Photolysis Measurements. The laser flash photolysis studies were carried out by using the third (355 nm, in the case of CAN) and the fourth (266 nm, in the case of TCB) harmonics of a Q-switched Nd-YAG laser (Model HY 200 JK Laser Ltd. Lumonics). The duration of the pulse was approximately 8 ns, and its energy ca. 30 mJ in the first and 20 mJ in the latter case. The detection system consisted of a laser kinetic spectrometer (Model K 347 Applied Photophysics) and an oscilloscope (Tektronix Model 2467).

Voltammetric Measurements. The measurements were carried out by means of a AMEL 514 polarograph on solutions of the substrates **1** in freshly purified MeCN containing 0.1 M tetrabutylammonium fluoborate as the supporting electrolyte, using a 0.2 diameter platinum disc hanging at a Teflon rod as the working electrode and a Ag/1 × 10^{-2} M $AgNO_3$ solution with a Pt counterelectrode as the reference. Between 2 and 3.2 V two irreversible, diffusion-controlled waves were registered for solutions up to 10^{-2} M. The DPV technique showed a linear diffusion/concentration dependence in the range (2 × 10^{-4})−(8 × 10^{-3}) M for the first wave, with a shift toward more positive values at higher concentrations. As for the second wave, the high background due to the supporting electrolyte around 3 V, and thus near to this wave, prevented quantitative determinations. The values in Table 2 are referred to the peak potential in DPV (scan 30 mV s^{-1}, pulse amplitude 50 mV, pulse width 40 ms) and are reported in Table 2 with reference to SCE.

Anodic Oxidation. Preparative electrolysis was carried out on MeCN solutions 0.1 M in NBu_4BF_4 containing the substrates **1** by means of an AMEL potentiostat set at a potential 0.1−0.2 V higher than the peak potential of the first oxidation wave. The electrodes were as follows: working electrode, a Pt gauze (10 cm^2); counterelectrode, a Pt plate (2 cm^2) immersed in a solution containing the same supporting electrolyte as the test solution and separated by a porous set; reference electrode, a Ag/1 × 10^{-2} M $AgNO_3$ solution in 0.1 M NBu_4BF_4 in MeCN.

Substrate conversion and product formation were determined by GC by comparison with authentic specimens, and using dodecane standard. The high background caused by the supporting electrolyte (0.3−0.4 mA) prevented a precise determination of the end of the oxidation and thus of the coulombs required for it. However, GC determination of the substrate converted and comparison with the coulombs flowed (after subtraction of the background) gave values slightly over 2 Faraday in all cases.

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