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The Photochemical Approach to the Functionalization of Open-Chain and Cyclic Alkanes: 1. Single Electron Transfer Oxidation.

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Abstract. Irradiation of 1,2,4,5-benzenetetracarbonitrile (TCB) in the presence of various open-chain, cyclic and polycyclic alkanes leads to single electron transfer (SET), k_{et} 10^8 to 10^{10} $M^{-1}s^{-1}$, as demonstrated by the detection of the TCB radical anion. This affords a way to evaluate the oxidation potential of such substrates, which are difficult to measure voltammetrically. The thus formed alkane radical cations undergo deprotonation, in accordandance with thermochemical predictions showing that these species are strong acids ($pK_a < -13$). The alkyl radical is trapped by $TCB^{-\cdot}$ to yield alkylbenzenetricarbonitriles. Deprotonation occurs from the contact ion pair. With open-chain derivatives, it takes place selectively from the more substituted position, while with cyclic and policyclic alkanes the position of deprotonation depends on the radical ion pair structure. Copyright © 1996 Elsevier Science Ltd

One of the most difficult challenge to chemists remains the fuctionalization of alkanes. Several methods have been evolved for the activation of a C-H bond, and can be classed in three main groups: electrophilic reactions,[1] radicalic reactions[2] and organometallic insertions,[3] or at any rate metal catalysed processes.[4] While the first two categories are the most important from the industrial point of view and require drastic treatment, the last group includes several recently evolved reactions occurring under remarkably mild conditions, well suited for laboratory syntheses and, possibly, of biomimetic significance, although their mechanisms are not necessarily unambiguously known. These are based on the use of various inorganic oxidants, and are presumed to occur through a complex mechanism, generally involving activation by the metal of the substrate through complexation.[4]

It would obviously be desirable to test the elementary steps of alkane functionalization by experiments carried out under mild and unambiguous conditions, but the problem here is due to the prohibitively high energy barrier encountered. Thus, the energy involved in homolytic hydrogen abstraction is in the range 92-105 kcal mol^{-1}, and requires very strong, and often poorly selective reagents.

$$R\text{-}H \rightarrow R\cdot + H\cdot \qquad (1)$$

On the other hand, obtaining the radical through a two-step path, electron and then proton abstraction, is also hindered by the extremely high oxidation potential of alkanes. There is some uncertainty about the potential at which anodic oxidation takes place (vide infra), but this certainly occurs above 2.7 V vs SCE (in the gas phase, IP>9.8 eV),[5] and thus the involvement of a direct redox step in a chemical oxidation is unlikely, since with all known inorganic oxidants a single electron transfer (SET) step would be too slow to contribute significantly.

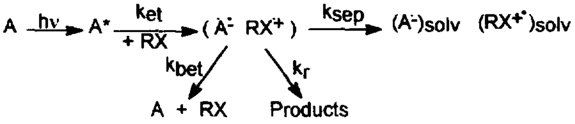
$$\text{R-H} \xrightarrow{-e} \text{R-H}^{+\cdot} \qquad (2)$$

$$\text{R-H}^{+\cdot} \rightarrow \text{R}^{\cdot} + \text{H}^{+} \qquad (3)$$

The SET mechanism remains appealing however, since this energetically demanding oxidation implies that the energy accumulated in the radical cation should make its chemical reaction easy, provided that there is a way to produce it.

The recent literature shows that the *excited states* of some *organic molecules*, are very strong one electron oxidants.[6,7] In particular, electron-withdrawing substituted arenes, e.g. nitriles, while unreactive in the ground state, are easily reduced in the excited state, reaching values much more positive than those of ground state inorganic oxidants [E_{red}(excited state)>3 V vs SCE],[6] and thus attain the limit required for alkanes oxidation, while allowing to work in common organic solvents under easily controlled conditions.

Scheme 1



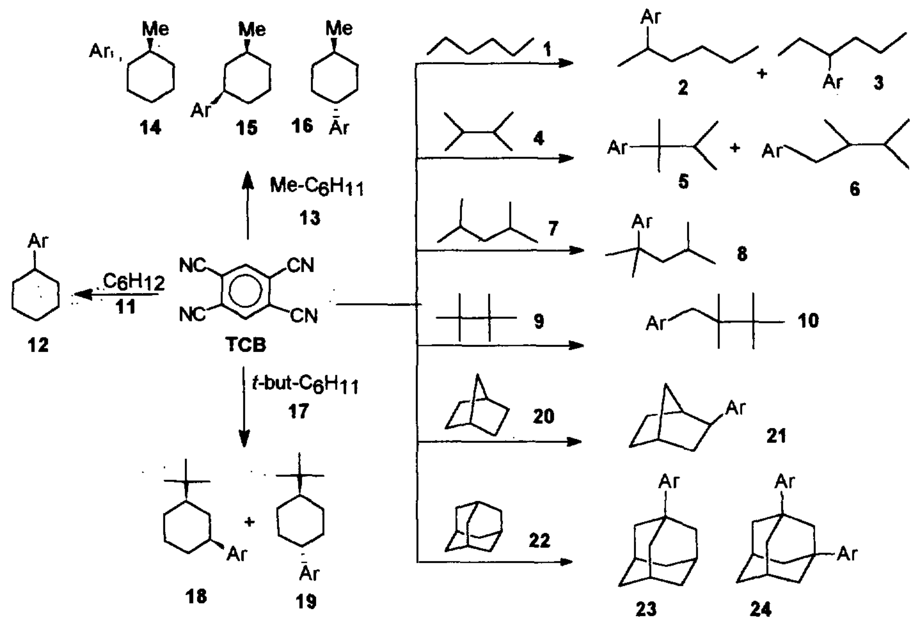
A process based on this principle must confront a double kinetic limitation, both because of the short lifetime of the oxidant, an excited state (A^* in Scheme 1) decaying in the ns to μs range (k_d), and because a radical cation paired with a strongly reducing (organic) radical anion, rather than with a stable (inorganic) anion, is generated, and thus back electron transfer ($k_{bet} \geq 10^8 s^{-1}$) cuts down any but the fastest radical cation reactions. Despite this fact, we show in the present report that the strong thermodynamic drive for the initial SET (rate constant k_{et} in Scheme 1) and for radical cation deprotonation (k_r) makes the direct generation of alkyl radicals from alkanes by photoinduced electron transfer a viable path, and that these reactions occur under unparalleled mild conditions and with a high selectivity, which in turn is related to the radical ion pair structure.[8] In an accompanying report,[9] we contrast the SET functionalization with hydrogen abstraction, likewise photoinduced, obtained with chloranil in order that the peculiarities of the two methods of functionalization are revealed.

RESULTS

Photochemical reactions were carried out in degassed acetonitrile 0.1 M in the alkane (or saturated when less soluble). The light-absorbing acceptor used was 1,2,4,5-benzenetetracarbonitrile (TCB). In order to explore for any selective functionalization, a reasonably large array of alkanes, both linear and cyclic were examined. Preparative irradiations were supplemented by physico chemical experiments.

Reactions with Linear Alkanes. With these compounds the photochemical reaction with TCB was sluggish, and when carried out to a high conversion of the acceptor, it gave a complex mixture of products arising from secondary photoreactions of the primary products (fragmentation of the side chain). Therefore in the following we report the results obtained at a limited TCB conversion (≤25%, see Scheme 2, Table 1). Irradiation of *n*-hexane 1 and TCB in acetonitrile followed by chromatographic separation gave an inseparable mixture of two isomeric aromatic compounds in about the same amount. The ^{1}H-NMR of this mixture identified them as 5-(2-hexyl)-benzene-1,2,4-tricarbonitrile (**2**) and 5-(3-hexyl)-benzene-1,2,4-tricarbonitrile (**3**). With 2,3-dimethylbutane (**4**) both possible alkylation products, 5-(2,3-dimethyl-2-butyl)-benzene-1,2,4-tricarbonitrile (**5**) and 5-(2,3-dimethyl-1-butyl)-benzene-1,2,4-tricarbonitrile (**6**), were formed with the reaction at the tertiary carbon by far predominating (**5** >> **6**). With 2,4-dimethylpentane (**7**) a selective reaction limited at the tertiary carbon was observed and the only product obtained was 5-(2,4-dimethyl-2-pentyl)-benzene-1,2,4-tricarbonitril (**8**). TCB alkylation occurred also with 2,2,3,3-tetramethylbutane (**9**), and gave 5-(2,2,3,3-tetramethylbutyl)-benzene-1,2,4-tricarbonitrile (**10**), although the photochemical reaction took place at a lower rate than in the previous cases.

Scheme 2



Ar = 2,4,5-tricyanophenyl

Reaction with Cyclic Alkanes. With these derivatives, the reaction was faster than with the previously considered hydrocarbons, and in most cases the reaction could be carried out to a higher TCB conversion. 5-Cyclohexyl-benzene-1,2,4-tricarbonitrile (**12**) was isolated in good yield from the irradiation of TCB and cyclohexane (**11**). With methylcyclohexane (**13**) a complex mixture of isomers was obtained. Although it proved impossibible to separate each individual compound by repeated silica gel chromatography, ^{1}H ,^{13}C and ^{1}H-^{13}C correlated NMR spectra of the mixture allowed unambiguous identification of the three main components as *trans*-5-(2-methylcyclohexyl)-benzene-1,2,4-tricarbonitrile (**14**), *cis*-5-(3-methylcyclohexyl)-benzene-1,2,4-tricarbonitrile (**15**) and *trans*-5-(4-methyl-cyclohexyl)-benzene-1,2,4-tricarbonitrile (**16**). These isomers (the 2-methylcyclohexyl derivative **14** was the most abundant one) were all characterised by having the two substituents in diequatorial conformation. Minor unidentified products were present, but an accurate scrutiny of all the chromatographic fractions showed that no appreciable amount of either (1-methylcyclohexyl) or of (cyclohexylmethyl) benzenetrinitriles, which would have been easily identified from the pattern of the methyl group, were formed.

With *tert*-butylcyclohexane (**17**) the reaction was rather selective and gave *cis*-5-(3-*tert*-butylcyclohexyl)-benzenetricarbonitrile (**18**) as the main product with a lesser amount of another isomer, the *trans*-(4-*tert*-butylcyclohexyl) derivatives **19**. Again, examination of the other chromatographic fractions gave no evidence for further isomers, in particular of the one resulting from reaction at the methine group.

With norbornane (**20**), a single alkylated benzenetrinitrile (**21**) was obtained. This resulted from reaction at the ethylene bridge, and ^{1}H-NOE experiments (see Experimental) allowed its identification as the *exo*-isomer. As it appears in Table 1, product **21** was obtained in satisfactory yield, but the TCB conversion had to be taken low also in this case, due to a relatively fast secondary photoreaction of the primary product.

The irradiation of adamantane (**22**) and TCB afforded a good chemical yield 5-(1-adamantyl)-benzene-1,2,4-tetracarbonitrile (**23**), with no detectable amount of the corresponding 2-adamantyl derivative. Despite the fact the product **23** was itself photolabile, a low amount of a diarylated adamantane (**24**, see Experimental for structure attribution) was also formed.

Table 1. Products obtained from the irradiation of TCB in the presence of alkanes in acetonitrile.

Substrate	Irradiation time (h)	Converted Acceptor (%)	Products (% Isolated Yield)[a]
1	2	20	**2**(42), **3**(32)
4	1	15	**5**(63), **6**(6.5)
7	2	25	**8**(70)
9	2	10	**10**(75)
11	4	75	**12**(80)
13	3	70	**14**(30), **15**(18), **16**(22)
17	2	50	**18**(58), **19**(7)
20	0.5	15	**21**(70)
22	3	55	**23**(80), **24**(12)

a. Yield calculated on the consumed acceptor.

Medium Effect and Mechanistic Studies. Some of the reactions were carried out also in ethyl acetate, where TCB is sufficiently soluble. In all the cases tested (**4**, **11**, **20**, **22**) the products formed were the same as in the acetonitrile experiments, although the reaction was much slower.

Some indications about the mechanism of the reaction were obtained through quantitative measurements. Thus, Stern-Volmer constants for the quenching of the TCB fluorescence and quantum yield values for TCB alkylation are reported in Table 2 (note the lower Φ values in ethyl acetate). Laser pulse excitation of a TCB solution saturated in adamantane (**22**) showed a transient in the region 410-490 nm (Fig.1). The signal was weak. Since complete quenching was not attained due to the limited solubility of these substrates, fluorescence from unquenched TCB caused considerable interference. As a result, the obtained spectrum is considerably overestimated at the low wavelength edge. However, the peak at 470 nm well corresponds to that attributed to the TCB radical anion, as previously obtained by different techniques in matrix and in solution.[10] It showed a second-order decay, k_{obs} $4.78 \times 10^3 M^{-1} s^{-1}$. Likewise in the presence of cyclohexane (**11**) the same transient was observed, although its intensity was lower even in a saturated solution (Fig. 1).

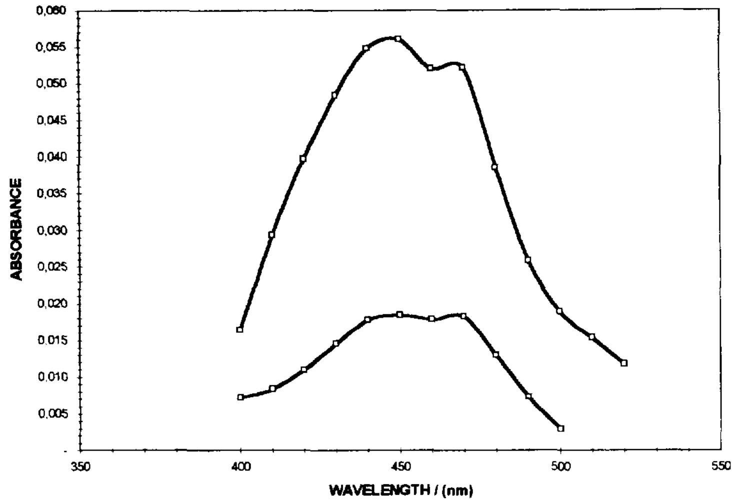


Figure 1: absorption observed 1 ms after flashing (266 nm) a 0.1 mM TCB solution in MeCN, containing 15 mM **22** (upper trace), or respectively 1 mM **11** (lower trace)

DISCUSSION

The SET Mechanism. As stated in the introduction, our aim was to ascertain the possibility of single electron oxidation of alkanes through the photochemical method, and to explore the chemistry of the thus generated radical cations. The rationalisation of the data is somewhat blurred by the fact that the oxidation potential of alkanes is not known with exactitude. With the more easily oxidised substrates, such as the bicyclic alkanes **20** and **22**, voltammetric measurements show a well defined, if irreversible, anodic wave.[5a,b,11] With open chain and monocyclic derivatives, on the other hand, the peaks are poorly resolved and quite near to the limit imposed by the conducing electrolyte and the solvent. The actually reported literature values are at variance, with differences of over one Volt unit for identic or similar compounds.[12-15] Thus, apart from the problem of establishing the thermodynamic values from irreversible waves, it is not obvious which values should be used. IP values follow a rather consistent pattern, with a regular decrease with substitution and cyclization.[5d] The existence of a linear correlation between E_{ox} and IPs has been recognized, but never tested with hard to oxidize substrates such as the present ones.[16]

Here the photochemical experiment is useful, since the quenching of singlet excited TCB has to involve electron transfer. The photochemistry of aromatic nitriles in the presence of a variety of substrates has been thouroughly studied and consistently shown to involve SET (or formation of an exciplex in suitable cases) and in no case hydrogen abstraction.[17] That this path is followed also in this case is supported by the detection of a transient absorption in the flash photolysis experiments (Fig. 1) which may be assigned to the TCB radical anion.[10] In the pioneering studies by Weller and in the following works, it has been demonstrated that quenching of fluorescence of aromatics occurs at the diffusion controlled rate for ΔG_{et} negative by some kcal M^{-1}, about an order of magnitude slower when thermoneutral and then rapidly decreases for positive ΔG_{et} values.[18]

Table 2. Quenching constants and quantum yield data.[a]

Substrate	$k_q(TCB^{1*})$ $M^{-1}s^{-1}$	$\Phi(TCB)^b$	$\Phi(TCB)^{b,c}$
1		0.005	
4	0.02×10^{10}	0.005	0.001
9	0.01	0.005	
11	0.06	0.06	0.002
20		0.06	0.002
22	1	0.06^d	0.003^d

a. In acetonitrile unless otherwise noted. b. Substrate concentration 0.1 M unless otherwise noted. c. In Ethyl acetate. d. 0.02 M.

Table 3. Selected oxidation potential and dissociation energy data.

Substrate	$\Delta G_{et}{}^a$ kcal/M	E_{ox} V, vs SCE	Fragmentation	$BDE(R\text{-}X)^b$	$BDE(R\text{-}X^{+\cdot})^c$
4	3	3.45^d	$Me_2CHCHMe_2{}^{+\cdot} \rightarrow Me_2CHCHMeCH_2{}^{\cdot} + H^+$	98	-27
			$Me_2CHCHMe_2{}^{+\cdot} \rightarrow Me_2CHC^{\cdot}Me_2 + H^+$	92	-33
			$Me_2CHCHMe_2{}^{+\cdot} \rightarrow Me_2CH^{\cdot} + Me_2CH^+$	78.2	7.5
11	1	3.35^d	$C_6H_{12}{}^{+\cdot} \rightarrow C_6H_{11}{}^{\cdot} + H^+$	95.5	-27.5
22	-16^e	2.72^f	Adamantane$^{+\cdot}$ $\rightarrow$ 1-Adamantyl$^{\cdot}$ + H^+	92	-17.1
			Adamantane$^{+\cdot}$ $\rightarrow$ 2-Adamantyl$^{\cdot}$ + H^+	95.5	-13.6

a. Calculated from the measured quenching of the TCB singlet state (see Table 2) and the Weller equation, ref.18. b. BDE from Egger, K.W.; Cocks, A.T. *Helv.Chem.Acta* **1973**, *56*, 1516. c. Calculated according to eq.5; $E_{ox}(H)$ -2.01 V vs SCE, Griller, D.; Simoes, J.A.M.; Mulder, P.; Sim, B.A.; Wayner, D.D.M. *J.Am.Chem.Soc.* **1989**, *111*, 7872. $E_{ox}(Me_2CH^{\cdot})$ taken 0.35 V vs SCE on the basis of the reported value for $E_{OX}(Me_3C^{\cdot})$=0.09 and on an average of the reported effect of methyl substitution, see ref.20b. d. Calculated from ΔG_{et}. e. Calculated from the measured E_{ox}. f. Measured, see ref.5a,b, 11

As it appears in Table 2, the observed quenching varies from diffusion controlled with adamantane to two orders of magnitude smaller with the open-chain derivative **4**. From the k_q the ΔG_{et} values are calculated, and hence the E_{ox} values for simple alkanes (see Table 3). In view of the above mentioned uncertainty of voltammetric measurement, this seems to be a reasonable alternative.

The initial SET yields a radical ion pair. This mainly decays directly by back electron transfer or by chemical reaction (see below), with only a minor fraction escaping out of cage. Escaped $(TCB^{\cdot-})_{solv}$ is spectroscopically detected (see Fig.1, Scheme 1). This absorption is weak, and is somewhat more intense with better donors, e.g. with adamantane than with cyclohexane, reasonably due to the (sligthly) more efficient separation and solvation of the radical ions in the former case. The solvated TCB radical anion is persistent species, with a lifetime of several ms under the present conditions. The path involved in this decay has not been determined, it may be a disproportion, since it is second order. At any rate, the small part of $TCB^{-\cdot}$ escaping out of cage does not affect the radical cation fragmentation, and its long lifetime is in accordance with previous observation showing the chemical inertness of the radical anions of arenenitriles, in particular their non-nucleophilicity.[19]

Chemistry of the Alkane Radical Cations. The chemical reaction observed is TCB alkylation, and its quantum yield ranges from ca 0.5% for open-chain to ca 6% for cyclic alkanes. These products result form combination between alkyl radicals and $TCB^{\cdot-}$, as it has been demonstrated for related reactions[17] and will more fully discussed below. It follows that the radical cations of alkanes undergo fast deprotonation. To a first approximation the limiting quantum yield is equal to the ratio between the rate of radical cation deprotonation and the overall decay rate of this species, viz primarily back electron transfer ($\Phi_{lim} \approx k_r/k_{bet}$, see Scheme 1). Since k_{bet} is larger than 10^8 s^{-1}, $k_r >> 10^6$ s^{-1}.

In previous cases, a useful clue for the rationalisation of radical ions cleavage (eq.4) has been obtained through the use of a thermochemical cycles.[6,20-23] This leads to eq.5, showing that in the radical cation a bond is weakened by an amount corresponding to the substrate oxidation potential and (with changed sign) to the oxidation potential of the cation splitted off.

$$R\text{-}X^{+\cdot} \rightarrow R + X^{+} \qquad (4)$$

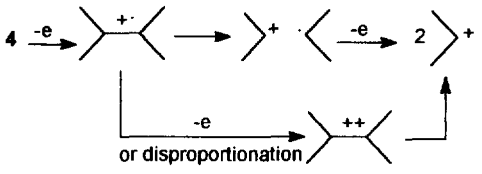
$$BDE(R\text{-}X^{+\cdot}) = BDE(R\text{-}X) - E_{ox}(R\text{-}X) + E_{ox}(X^{\cdot}) \qquad (5)$$

Application of this method to the present case shows that with all alkanes deprotonation is a strongly exothermic process (see Table 3), and such species are acids as strong as mineral acids (pK_a ca-13 for **22**$^{+\cdot}$ and more negative for the other radical cations), so that proton transfer even to a weak nucleophile such as acetonitrile is favoured. It may be interesting to note that on a similar reasoning it had been previously predicted and experimentally confirmed that the benzylic position of aromatic radical cations has a pK_a in this range.[20,23,24] Thus, the fact that the C-H bond is stronger in alkanes with respect to the activated benzylic bond of alkyl aromatics is overcome by the much larger bond weakening due to the more positive oxidation potential of such substrates (see eq.5). Obviously, oxidation of these poor donors requires as strong an oxidant as TCB, while alkyl aromatics are oxidised also under less stringent conditions.[23,25] However, once the radical cation is formed deprotonation (more precisely proton transfer to the solvent) is expected to be facile also in this case, and the observed results fully confirm this expectation, with the reaction quantum yield roughly proportional to the TCB singlet quenching efficiency. Notice also that in ethyl acetate the same reaction occurs, although with a lower efficiency. This solvent has a lower dielectric constant, and thus ΔG_{et} is more positive due to the coulombic term present in the Weller equation,[18] but hydrogen bonding accepting property equal to that of acetonitrile. Thus, the result shows that SET is slower, and again supports the acidic properties of the alkane radical cations.

Several points are worth notice with regard to the present radical cation cleavage. First, the process is chemoselective, in the sense that deprotonation is the only reaction observed. There is no competitive C-C bond fragmentation, since with these alkanes the BDE(C-C) in the radical cation is markedly positive (see the case of alkane **4** in Table 3; notice also that with **7** proton transfer form a primary position and no C-C bond cleavage takes place).

It is interesting to compare these results with anodic oxidation. With linear alkanes deprotonation takes place.[12] On the other hand it has been observed that some branched alkanes (e.g. **4**)[15] undergo carbon-carbon bond cleavage (see Scheme 3), at least when the electrolysis is carried out at -40°C (no products isolated at room temperature. It has been proposed that this reaction occurs via an ECE process, with cleavage of the radical cation as the key step. However, in the photochemical reaction the alkyl radicals formed are efficiently trapped by TCB$^{-\cdot}$,[6,17] and all the alkylated benzotrinititriles obtained contain the intact alkane skeleton. Furthermore, C-C cleavage is endothermic. Thus, we conclude that the radical cation reaction is deprotonation and not to C-C fragmentation, and that the electrochemical reaction probably occurs via a EEC mechanism (see Scheme 3), which is at any rate difficult to exclude with these hard to oxidise substrates. Notice also that the low temperature requirement does points to the role that absorption on the electrode and radical cations disproportionation may have on the overall process.

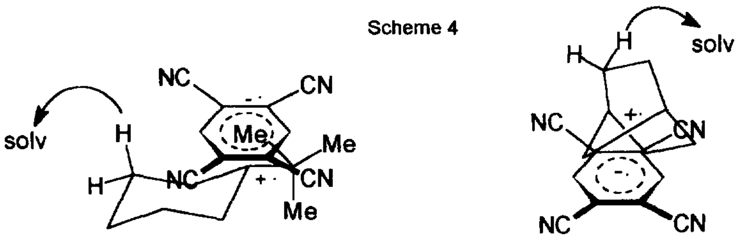
Scheme 3



Secondly, the deprotonation is highly regioselective. In several cases, the observed selectivity is rationalised on thermochemical grounds, viz a difference of some kcal mol^{-1} in the ground state BDE translate in an equal difference in the radical cation BDE (see Table 3), and this is sufficient to induce the observed effect. Open-chain alkanes well conform to this model. Thus, the (statistically corrected) ratios are: secondary vs primary >10 with alkane **1**, tertiary vs primary = 60 for **4**, and tertiary vs secondary > 10 for **7**. Kinetic acidities of benzylic radical cations have also been shown to depend on the substrate BDE.[26] Adamantane (**22**) is an interesting case. We observe a high selectivity for deprotonation at the tertiary (bridgehead) vs secondary (bridge) position (ratio ≈ 100). On the other hand, an estimation based on photoelectronic spectroscopy (and thus gas phase) measurements shows that the BDE for the bridgehead C-H is larger than that for an open chain tertiary C-H bond, and rather close to that of a secondary C-H.[27] In accordance with this, recent work shows that homolytic hydrogen abstraction occurs indisciminately from the 1 and 2 position of this substrate, except when there is a "polar effect"; thus, when the abstracting radical is $R_2N^{+\cdot}$ the ratio is ca 30, while with bromine or alkoxy radicals the ratio is ca 3.[28] Adamantane is therefore a sensitive mechanistic probe, since ionization leads to deprotonation from the tertiary position, and easily reduced radicals approach this selectivity, while homolytic hydrogen abstraction is unselective.

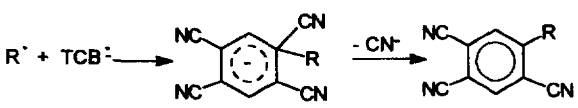
Furthermore, the selectivity observed with some of the other cyclic alkanes is not immediately explained by simple thermochemical data, as shown by the lack of deprotonation from the tertiary position both with **20** and with the cyclohexanes **13** and **17** (the last alkane, also shows a strong selectivity also in the ring methylenes deprotonation, see Table 1). We think that this selectivity is rationalized by taking into account that radical cation deprotonatation occurs from the radical ion pair. The alkane radical cation (σ delocalized) is not efficiently stabilized by solvation and only a minimal fraction diffuses apart (compare the weak signal for TCB$^{-\cdot}$). Thus, the chemical reaction takes place when the radical ion pair has not yet relaxed to the free solvated species and the radical anion hinders proton transfer to the solvent from the carbon atoms to which it is closest. The preferred conformation of the radical ion pair is such as to maximise charge pairing. With the substituted cyclohexanes **12** and **15** hence the acceptor remains as close as possible to the more substituted centre (the branching point, see Scheme 4) and this hinders proton transfer from the tertiary carbon. With the heavily substituted **15**, the methylene in position 2 is also hindered and reaction is fastest at position 3, i.e. close to the site where the charge density is larger, yet not hindered. Another reasoning which leads to the same conclusion is admitting that axial C-H bonds, in particular the tertiary C-Hs of both **12** and **15** are face to face to the acceptor in the complex, and thus are not accessible to transfer to the solvent, while this is easier for the equatoria ones. Likewise, the preferred arrangement of the pair in the case of norbornane (**20**) is as shown in Scheme 4, and again hindering by the acceptor of the methylene brige and of the methine groups explains the observed preference for reaction at the ethylene bridge. Obviously such effect is not shown by conformationally free open-chain alkanes.

Scheme 4



Formation of the Final Products. The following chemistry is completely consistent with what previously ascertained for related radicalic ipso substitutions of arene nitriles.[6,29-32] Thus, alkyl radicals combine with the persistent TCB radical anion and cyanide loss leads to the final products (see Scheme 5). When there are different possibilities, the stereochemistry of the final product is determined by thermodynamics, as usual in radical additions, and shown here by the formation of the *exo* norbornyl derivative **21**. The fair yield of alkylbenzenetricarbonitriles obtained in each case allows to obtain information about the radical cation cleavage mechanism from the product distribution, as we did above.

Scheme 5



Conclusion. In conclusion, the present work provides for the convenience of a photochemical method for the generation of bona-fide radical ions. The method can be applied even to extremely poor donors such as alkanes. This on one hand affords a way to estimate the oxidation potential of such subtrates, which are difficult to evaluate voltammetrically, and on the other one allows the study of SET chemistry under extremely mild conditions. In this way, the high chemo and regioselectivity of the cleavage of alkanes radical cations, which are strong (comparable to mineral) acids, has been demonstrated. It has also been shown that this holds also from the dynamic point of view, and deprotonation is fast enough to compete with back electron transfer, thus offering a way for generating alkyl radicals directly from alkanes. We are confident that this work may give useful suggestions both for new synthetic methods and for interpreting complex reaction mechanisms where homolytic or electron transfer paths are invoked.

EXPERIMENTAL

General ^{1}H, ^{13}C and ^{13}C-DEPT 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. TCB and alkanes **1**, **4**, 7, **9**, **11**, **13**, **17**, **20** and **22** were commercial products.

Photochemical reaction between TCB and n-hexane 1. A solution of TCB (71 mg, 0.4 mmol) and *n*-hexane **1** (4 mmol, 345 mg) in MeCN (40 mL, subdivided in two quartz tubes), was purged with argon and irradiated for 2h 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. In order to avoid secondary photoreactions with decomposition of the primary products, the reaction was stopped at a low TCB conversion (20%). Workup of the photolysate involved concentration in vacuo and chromatographic separation employing Merck 60 silica gel and a cyclohexane-ethyl acetate 8:2 mixture as eluant. 55 mg of TCB and a single fraction (14 mg, 74%, oil) containing two products were obtained. This mixture was inseparable but the spectroscopic data (^{1}H, ^{13}C and ^{1}H-^{13}C correlated spectra) identified the two component as isomeric 5-(2-hexyl)-benzene-1,2,4-tricarbonitrile (**2**)(42%) and 5-(3-hexyl)-benzene-1,2,4-tricarbonitrile (**3**)(32%).

2: ^{1}H NMR (in $CDCl_3$) δ 0.9 (*t*, J = 7 Hz, 3H), 1.35 (*d*, J = 7 Hz, 3H), 1.1-1.98 (*m*, 6H), 3.3 (*sext*, J = 7 Hz, 1H), 7.8 (*s*, 1H), 8.05 (*s*, 1H). ^{13}C NMR δ 13.75 (CH_3), 20.85 (CH_3), 22.37 (CH_2), 29.39 (CH_2), 37.04 (CH_2), 38.44 (CH), 113.5, 114.1, 114.2 (CN, 114.5 (CN), 117.4 (CN), 119.5, 132.11 (CH), 136.9 (CH), 157.7. **3**: ^{1}H NMR (in $CDCl_3$) δ 0.85 (*t*, J = 7 Hz, 3H), 0.92 (*t*, J = 7 Hz, 3H), 1.1-1.8 (*m*, 6H), 3.15 (*m*, 1H), 7.75 (*s*, 1H), 8.06 (*s*, 1H). ^{13}C NMR δ 11.67 (CH_3), 13.72 (CH_3), 20.42 (CH_2), 29.00 (CH_2), 37.76 (CH_2), 45.87 (CH), 113.5, 114.2, 114.6 (CN), 114.1 (CN), 117.4 (CN), 119.5, 132.48 (CH), 136.61 (CH), 156.59. Anal. Calcd. for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.45; H, 6.15; N, 17.5.

Photochemical reaction between TCB and 2,3-dimethylbutane 4. A solution of TCB and 2,3-dimethylbutane **4** (4 mmol, 345 mg) was irradiated for 1h as above. The reaction was stopped after about 15 % of TCB conversion to avoid secondary reactions. After general work-up and silica gel chromatography (Cyclohexane-EtOAc), 9 mg (70%, oil) of a single fraction containing two alkylated products was obtained. The spectroscopic data identified these as two isomers in different proportion, viz 5-(2,3-dimethyl-2-butyl)-benzene-1,2,4-tricarbonitrile (**5**), the main one, and 5-(2,3-dimethyl-1-butyl)-benzene-1,2,4-tricarbonitrile (**6**).

The two isomers were in a 10 to 1 ratio (calculated from the integrals in the ^{1}H-NMR spectrum).

5: ^{1}H NMR (in CDCl$_3$) δ 0.8 (*d*, J = 7 Hz, 6H), 1.45 (*s*, 6H), 2.65 (*sett*, J = 7 Hz, 1H), 7.9 (*s*, 1H), 8.1 (*s*, 1H). ^{13}C NMR δ 17.71 (2CH$_3$), 23.42 (2CH$_3$), 35.16 (CH), 43.26, 113.44, 113.87, 114.37 (CN), 115.84 (CN), 116.70 (CN), 118.77, 133.00 (CH), 139.5 (CH), 160.37. **6**: ^{1}H-NMR (in CDCl$_3$) δ 0.95 (*d*, J = 7 Hz, 6H), 0.98 (*d*, J = 7 Hz, 3H), 1.4-1.6 (*m*, 2H, H-2 and H-3), 2.65 (*dd*, ^{2}J = 13 Hz, ^{2}J = 10 Hz, 1H, H-1), 3.05 (*dd*, ^{2}J = 13 Hz, ^{3}J = 5 Hz, 1H, H-1), 7.9 (*s*, 1H), 8.1 (*s*, 1H). Anal.Calcd for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.7; H, 6.4; N, 17.6.

Photochemical reaction between TCB and 2,4-dimethylpentane 7. The irradiation of a TCB and 2,4-dimethylpentane **7** (400 mg, 4 mmol) solution for 2h, gave, after general work-up and silica gel chromatography (Cyclohexane-EtOAc), 18 mg of 5-(2,4-dimethyl-2-pentyl)-benzene-1,2,4-tricarbonitrile (**8**) (70 %, mp 105-110°C, EtOH). Traces (< 4%) of the other two possible isomers, 5-(2.4-dimethyl-3-pentyl)-benzene-1,2,4-tricarbonitrile and 5-(2,4-dimethyl-1-pentyl)-benzene-1,2,4-tricarbonitrile were recognized in the ^{1}H-NMR spectrum of further fraction in mixture with **8**. Also in this case the irradiation was stopped after a low conversion of TCB (25 %) to avoid the formation of secondary products.

8: ^{1}H NMR (in CDCl$_3$) δ 0.75 (*d*, J = 7 Hz, 3H, Me), 0.9 (*m*, 1H, H-4), 1.55 (*s*, 6H, 2Me), 2.0 (*d*, J = 7 HZ, 2H, H-3), 7.9 (*s*, 1H), 8.05 (*s*, 1H). ^{13}C NMR δ 24.20 (CH$_3$), 25.24 (CH), 28.76 (CH$_3$), 40.21, 49.69 (CH$_2$), 113.44, 113.97, 114.33 (CN), 114.59 (CN), 116.41 (CN), 118.99, 132.77 (CH), 139.11 (CH), 159.36. Anal. Calc. for $C_{16}H_{17}N_3$: C, 76.46; H, 6.82; N, 16.72. Found: C, 76.3; H, 6.8; N, 16.5

Photochemical reaction between TCB and 2,2.3.3-tetramethylbutane 9. A solution of TCB and 2,2,3,3-tetramethylbutane **9** (450 mg, 4 mmol) was irradiated for 2h. The reaction was slower than in the previous case (10% conversion of TCB after the same irradiation time). After general work-up and silica gel chromatography (cyclohexane-EtOAc), only one alkylation product was obtained and identified as 5-(2,2,3,3-tetramethylbutyl)-benzene-1,2,4-tricarbonitrile (**10**) (8 mg, 75 %, mp 117-20°C).

10: ^{1}H NMR (in CDCl$_3$) δ 0.8 (*s*, 6H, 2Me), 1.0 (*s*, 9H, 3Me), 2.95 (*s*, 2H, H-1), 7.75 (*s*,1H), 8.03 (*s*, 1H). ^{13}C NMR δ 21.25 (CH$_3$), 25.46 (CH$_3$), 29.55, 36.34, 41.22 (CH$_2$), 113.44, 113.89, 114.43 (CN), 115.12 (CN), 117,23 (CN), 119.12, 136.53 (CH), 136.66 (CH), 151. Anal. Calc. for $C_{17}H_{19}N_3$: C, 76.94; H,7.22; N, 15.84. Found: C, 76.8; H, 7.3; N, 15.8.

Photochemical reaction between TCB and cyclohexane 11. A solution of TCB and cyclohexane **11** (336 mg, 4 mmol) was irradiated for 4h. After the general work-up and silica gel chromatography (cyclohexane-EtOAc), 57 mg of 5-cyclohexyl-benzene-1,2,4-tricarbonitrile (**12**) (80 %, mp 125-126 °C, EtOH). Anal. Calcd for and 20 mg of unreacted TCB were isolated.

12: ^{1}H NMR (in CDCl$_3$) δ 1.2-1.6 (*m*, 5H), 1.8-2.0 (*m*, 5H), 3.08 (*tt*, J = 12 and 3.5 Hz, 1H, H-1), 7.85 (*s*, 1H), 8.05 (*s*, 1H). ^{13}C NMR δ 25.28 (CH$_2$), 26.00 (CH$_2$), 33.04 (CH$_2$), 43.07 (CH$_2$), 113.62, 113.99, 114.23 (CN), 114.49 (CN), 117.07 (CN), 119.44, 132.06 (CH), 136.98 (CH), 157.17.Anal. Calc. for $C_{15}H_{13}N_3$: C, 76.57; H,5.57; N, 17.86. Found: C, 76.3; H, 5.8; N, 17.5

Photochemical reaction between TCB and methylcyclohexane 13. The irradiation of a solution of TCB and methylcyclohexane **13** (392 mg, 4 mmol) for 3h gave, after silica gel chromatography (cyclohexane-

EtOAc), 47 mg of a mixture of three disubstituted cyclohexyl derivatives obtained as a single fraction (70 %, mp 77-78 °C, EtOH). The ^{1}H, ^{13}C and ^{1}H-^{13}C correlated spectra identified them as *trans*-5-(2-methylcyclohexyl)-benzene-1,2-4-tricarbonitrile (**14**) (the main one, 30 % calculated by the integrals in the proton spectrum), *cis*-5-(3-methylcyclohexyl)-benzene-1,2,4-tricarbonitrile (**15**) (18%) and *trans*-5-(4-methylcyclohexyl)-benzene-1,2,4-tricarbonitrile (**16**) (22 %). The 1,2-disubstituted isomer (**14**) showed in the proton spectrum at 25°C, a broad signal at 2.78 ppm for H-1, due to hindered rotation. Upon heating at 50°C, the signal appeared as a double-triplet with two axial-axial (12 Hz) and one axial-equatorial (3 Hz) couplings, in accordance with *trans* arrangement. Likewise, the signal for H-1 in the 1,3-disubstituted isomer (**15**) was slightly broaden, but two axial-axial couplings were evident (data confirmed by DQF-COSY). The 1,4-disubstituted isomer (**16**) suffered no steric hindrance and the signal of H-1 appeared as a triple triplet at room temperature. Some of methylenic protons laid between 1 and 2 ppm, thus a correct attribution for each isomer was impossible. With DQF-COSY and ^{1}H-^{13}C correlated spectra the methyls and the methynes of the different isomers were unambiguously attributed. Minor unidentified products were present, but none of them arised from deprotonation at the primary or tertiary position, as shown by the absence of a arylated symmetric CH$_2$CH and a singlet methyl singals, respectively.

14: ^{1}H NMR (in CDCl$_3$) δ 0.75 (*d*, J = 7 Hz, 3H, Me), 1.68 (*m*, 1H, H-2 axial), 1.2 (*m*, 1H, H-3 axial), 1.8 (*m*, 1H, H-3 equatorial), 1.4 (*m*, 1H, H-6 axial), 1.9 (*m*, 1H, H-6 equatorial), 1.05-1.9 (H-4 and H-5), 2.78 (*'dt'*, J = 2 Hz, J = 3 Hz, 1H, H-1 axial), 7.81 and 8.03 (*s*, 2H, aromatic protons). ^{13}C NMR (in CDCl$_3$) δ 20.01 (CH$_3$), 32.60 (CH$_2$), 25.80 (CH$_2$), 34.71 (CH$_2$), 41.29 (CH$_2$), 37.29 (CH-2), 50.24 (CH-1), 113.59, 113.88, 114.24 (CN), 114.67 (CN), 117.08 (CN), 119.39, 132.04 (CH), 136.96 (CH), 157.30. **15**: ^{1}H NMR δ 1.05 (*d*, J = 7 Hz, 3H, Me), 1.63 (*m*, 1H, H-3), 1.45 (*m*, H-2 axial), 1.8 (*m*, H-2 equatorial), 1.65 (*m*, H-6 axial), 1.9 (*m*, H-6 equatorial), H-4 and H-5 were superimposed and not well identified, 7.82 and 8.03 (*s*, 2H, aromatic protons). ^{13}C NMR (only the signals unambigously attributed to this isomer are reported) δ 22.31 (CH$_3$), 27.51 (CH-3), 37:04 (CH-1), 132.10 (CH), 136.89 (CH), 156.97. **16**: ^{1}H NMR δ 1.15 (*d*, J = 7 Hz, 3H, Me), 1.1 (*m*, 1H, H-6 axial), 1.85 (*m*, 1H, H-6 equatorial), 1.35 (*m*, 1H, H-2 axial), 1.9 (*m*, 1H, H-2 equatorial), 2.1 (*m*, 1H, H-4 axial), 3.3 (*tt*, J = 12 Hz, J =3 Hz, 1H, H-1 axial), H-3 and H-5 were superimposed to the other, 7.85 and 8.02 (*s*, 2H, aromatic protons). ^{13}C NMR δ 17.52 (CH$_3$), 25.94 (2CH$_2$), 25.75 (2CH$_2$), 32.39 (CH-4), 42.78 (CH-1), 132.84 (CH), 136.93 (CH), 157.30. Anal.Calcd.for C$_{16}$H$_{15}$N$_3$: C, 77.08; H,6.06; N, 16.86. Found: C, 77.15; H, 6.0; N, 16.7.

Photochemical reaction between TCB and t-butylcyclohexane 17. A MeCN solution of TCB and *tert*-butylcyclohexane **17** (4 mmol, 560 mg) was irradiated for 2 h. After general work-up and silica gel chromatography (cyclohexane-EtOAc) about 35 mg of TCB was recovered unreacted and 34 mg of pure 5-(3-*tert*-butylcyclohexil)-benzene-1,2,4-tricarbonitrile (**18**) (58%) (mp 145-146 °C, EtOH) were obtained. The coupling constants in the proton spectrum identified **18** as a 1,3 diequatorial substituted cyclohexane: H-1 was axial (J = 12 Hz) to H-2 which had no hydrogens in an equatorial position (the signal at 1.95 ppm showed two axial couplings). Moreover in a second chromatographic (6 mg) fraction, **18** was present in mixture with a further isomer: spectroscopic analysis allowed to identified this as 5-(4-*tert*-butylcyclohexyl)-benzene-1,2,4-tricarbonitrile (**19**)(7%). Despite the partial superimposition of the signals in the proton spectrum, it was evident that H-1 was in axial position and H-2 had axial-equatorial couplings (data obtained from DQF-COSY); in the ^{13}C spectrum it was possible to recognise unambiguously the signals of a 1,4 disubstituted cyclohexyl derivative.

18: ^{1}H NMR δ (in $CDCl_3$) 0.9 (*s*, 9H), 1.05 (*dq*, J = 12 Hz, J = 3 Hz, H-4 axial), 1.15 ('*q*', J = 12 Hz, H-2 axial), 1.3 ('*tt*', J = 12 Hz, J = 3 Hz, H-3 axial), 1.38 ('*dt*', J = 12 Hz, J = 3 Hz, H-6 axial), 1.5 ('*tq*', J = 12, J = 3 Hz, H-5 axial), 1.9 (*dq*, J = 12 Hz, J = 3 Hz, H-4 equatorial); 1.9 (*dq*, J = 12, J = 3, H-6 equatorial), 1.95 (*dt*, J = 12 Hz, J = 3 Hz, H-2 equatorial), 2.01 (*dq*, J = 12 Hz, J = 3 Hz, H-5 equatorial), 3.05 ('*tt*', J = 12, J=3, H-1 axial), 7.8 and 8.05 (s, 2H, aromatic protons). ^{13}C NMR δ 26.19 (CH_2-5), 26.33 (CH_2-6), 27.35 ($3CH_3$), 32.55, 32.88 (CH_2-4), 34.35 (CH_2-2), 43.45 (CH-1), 47.82 (CH-3), 113.62, 113.97, 114.23 (CN), 114.50 (CN), 117.11 (CN), 119.44, 132.10 (CH), 136.96 (CH), 157.29. Anal. Calcd for $C_{19}H_{21}N_3$: C, 78.31; H, 7.26; N, 14.42. Found: C, 78.0; H, 7.3; N, 14.3

19: ^{1}H NMR δ (in $CDCl_3$) 0.88 (*s*, 9H), 3.0 (*tt*, J = 12 Hz, J = 3, H-1 axial) other protons not distinguished. ^{13}C NMR δ 26.97 ($2CH_2$), 27.36 ($3CH_3$), 33.45 ($2CH_2$), 43.25 (CH), 46.82 (CH), 133.10 (CH), 137.12 (CH).

*Photochemical reaction between TCB and norbornane **20**.* A solution of TCB and norbornane **20** (384 mg, 4 mmol), was irradiated for a short time (30 min) since preliminary eperiments had shown that the primary product underwent fast secondary photoreactions leading to a mixture of alkenylbenzenetricarbonitriles. After general work-up and silica gel chromatography, a single isomer (10 mg, 70%) was isolated. The structure of the *exo*-2-norbornyl-benzene-1,2,4-tricarbonitrile (**21**) (mp 103-104 °C, Cy/Bz) was attributed on the basis of ^{1}H and ^{13}C NMR spectra. In particular in the proton spectrum recorded in CD_3COCD_3 as the solvent, the signal for one of the H-7 protons (1.34 ppm) was well separated from the others; a long range coupling (1.5 Hz) was apparent with H-2. This coupling required that the bonds linking the coupled nuclei were in strerically fixed "W" configuration, as it was the case with H-2 endo. Moreover the irradiation of H-2 gave 5% NOE enhancement on the signal at 1.5 ppm (H-6 endo) and 2% NOE enhancement on the signal at 1.38 ppm (H-5 endo).

21: ^{1}H NMR δ (in CD_3COCD_3) 1.34 (*ddq*, ^{2}J = 10 Hz, ^{3}J = 1.5 Hz, ^{4}J con H-2 = 1.5 Hz, ^{4}J con H-3 = 2 Hz, H-7), 1.38 (*m*, 1H, H-5 endo), 1.52 (*m*, H-6 endo), 1.63 (*m*, 1H, H-7), 1.65-1.75 (*m*, 2H, H-5 and H-6 exo), 1.75 (*m*, 1H, H-3 exo), 2.03 (*ddd*, ^{2}J = 11 Hz, ^{3}J = 9 Hz, ^{4}J = 2 Hz, 1H, H-3 endo), 2.45 (*m*, 1H, H-4), 2.55 (*m*, 1H, H-1), 3.25 (ddt, ^{3}J = 9 Hz, ^{3}J = 5.5 Hz, ^{3}J = 1.5 Hz, ^{4}J con H-7 = 1.5 Hz, 1H, H-2 endo), 8.23 and 8.5 (*s*, 2H, aromatic protons). ^{13}C NMR (in $CDCl_3$) δ 28.13 (CH_2-6), 30.04 (CH_2-5), 36.45 (CH_2-7), 36.89 (CH-4), 38.72 (CH_2-3), 42.05 (CH-1), 45.89 (CH-2), 113.58, 113.61, 114.32 (CN), 114.78 (CN), 117.74 (CN), 119.18, 131.14 (CH), 136.96 (CH), 157.37. Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.7; H, 5.3; N, 16.9

*Photochemical reaction between TCB and adamantane **22**.* A solution of TCB and adamantane **22** (110 mg, 0.8 mmol) was irradiated for 3h. After general workup and silica gel chromatography, 32 mg of TCB and 50 mg of 5-(1-adamantyl)-benzene-1,2,4-tricarbonitrile (**23**) (80%, mp 268-270 °C, EtOH) were obtained. Moreover a minor product was isolated which contained two aromatic rings for every molecule of adamantane. The structure of 1,3-bis-(2,4,5-tricyanophenyl)adamantane (**24**) (11 mg, 12%, dec >270°C) was attributed to this compound in accordance with spectroscopic data and elemental analysis.

23: ^{1}H NMR (in $CDCl_3$) δ 1.8 (*bs*, 6H, methylene protons), 2.1 (*bs*, 6H, methylene protons), 2.2 (*bs*, 3H, methine protons), 7.9 and 8.08 (*s*, 2H, aromatic protons); ^{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.

24: ^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.

Quantum Yield Determination. Quantum yields for TCB reactions were measured on 3 mL of a MeCN (or EtOAc) solutions of the acceptor (0.005 M) and the donor in quartz tubes. These were deaerated by argon purging, septum capped and irradiated as above in a rotating merry-go-round; the consumption of TCB was determined through the UV absorption at 313 nm. A benzophenone-benzhydrol solution was used as the actinometer.

Fluorescence Measurements. Fluorescence spectra and emission intensities were measured by means of an Aminco-Bowman MPF spectrofluorimeter on solutions contained in a 1 cm optical path couvettes after degassing. 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 in MeCN, 10.8 ns.[31]

Flash Photolysis Measurements. The laser flash photolysis studies were carried out by using the fourth (266 nm) harmonic of a Q-switched Nd-YAG laser (Model HY 200 Laser Ltd Lumonics). The duration of the pulse was approximately 8 ns and its energy 20 mJ. The detection system consisted of a Laser kinetic spectrometer (Model K347 Applied Photophysics) and an oscilloscope(Tektronix Model 2467).

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