Radicals through Photoinduced Electron Transfer. Addition to Olefin and Addition to Olefin–Aromatic Substitution Reactions

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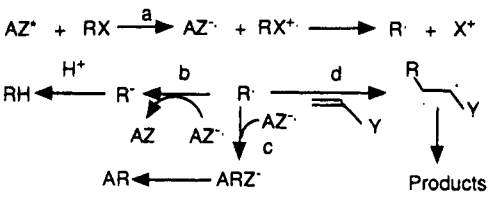
The radical cations of 2,2-dialkyl- and 2-alkyl-2-aryl-1,3-dioxolanes, when generated in solution by photoinduced electron transfer to 1,2,4,5-benzenetetracarbonitrile (TCB), fragment to yield alkyl radicals. These are trapped by electron-withdrawing substituted alkenes (acrylonitrile, methyl acrylate, methyl vinyl ketone, as well as dimethyl maleate and fumarate). The radicals thus formed are either reduced by the TCB radical anion or add to it. In the first process (observed only with the diesters) the end result is reductive alkylation of the olefin, while the latter process results in an addition to the olefin–aromatic substitution reaction. The selectivity of the process is explained on the basis of steric hindrance, since the radicals react when still in the cage with the aromatic radical anion.

Photoinduced electron transfer (PET) between organic molecules leads to a radical ion pair. In a suitably devised system, composed of a chemically stable radical anion and a radical cation bearing a good electrofugal group, chemical reaction will depend on the competition between back-electron transfer and fragmentation of the radical cation to yield a cation and a neutral radical.[1,3] Considerable evidence has been accumulated recently that shows that one-electron oxidation greatly weakens carbon–hydrogen,[4–11] carbon–carbon,[12–14] and carbon–heteroatom[11,13,15–20] σ bonds in a variety of substrates. Thus PET is a convenient method for the preparation of radicals and cations in solution (Scheme 1).

Scheme 1



The ensuing chemistry of these reactive intermediates depends primarily on the chemical nature of the substrates. The electrofugal group X^+ (e.g. H^+, R_3Si^+) is usually transferred to $A^{\bullet-}$ if the acceptor is a ketone,[9,11] while if the radical anion arises from an aromatic hydrocarbon or an aromatic nitrile, and thus is a poor nucleophile, direct addition is usually unimportant and the cation is instead trapped by other bases present, e.g. the solvent (often acetonitrile). As for the radicals, their interactions with aromatic radical anions involve either reduction when this is an exergonic process [i.e. when $E_{red}(R^\bullet) < E_{red}(AZ)$, path b in Scheme 1][12] or addition when the opposite is true (path c).[13] Since the efficiency of the initial electron transfer step (path a) depends on the excited-state reduction potential of the acceptor [$E_{red}(AZ^*) = E_{red}(AZ) + E_{exc}(AZ)$], while competition between paths b and c depends on its ground-state reduction potential, one can direct the process toward either result. As an example, benzylic radicals are reduced to the corresponding hydrocarbons in a PET process with 1,4-benzenedicarbonitrile as the acceptor,[12] while 1,4-naphthalenedicarbonitrile, which is much easier to reduce in the ground state, is benzylated under similar conditions.[13a]

The process depicted in Scheme 1 deserves further mechanistic investigation, since a detailed picture of each step has yet to be obtained. From the preparative point of view, several new reactions have emerged. The above mentioned alkylation of aromatics via PET-generated radicals is one and is a useful reaction in view of its regioselectivity (the attack involves only the position(s) with the highest spin density in the radical anion).[6,13c] As seen above, in this case the aromatic molecule has the double role of electron and radical acceptor.

However, it would be more interesting from the synthetic point of view to trap the radicals with an added

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substrate, e.g. an alkene (path d, Scheme 1). In such a case, the photoexcited acceptor would function as a nonconsumed photosensitizer, and the entire sequence would correspond to a new procedure for radical addition to olefins. This could be compared with other procedures for the generation of radicals, in particular with other known redox methods, such as metal-drawn and electrochemical oxidation, where the radical precursor is similarly oxidized, an electrofugal group is split off, and the radical formed adds to a substrate.[21] With respect to such alternatives, the PET method has some inherent advantages. Problems of solubility and inhomogeneity, often encountered when inorganic oxidants or anodic oxidation are used, are avoided and electron transfer occurs in an organic solvent under mild conditions. Furthermore, the exceptionally high reduction potential of the excited states allows for the oxidation of relatively poor electron donors and thus greatly increases the choice of possible substrates. Indeed, it has been shown that relatively weak donors, such as acetals or silanes, undergo photoinduced oxidation with the appropriate acceptors and, in this way, not only resonance-stabilized radicals (e.g. benzyl, allyl, α-amino) but also unstabilized (alkyl) radicals can be generated.[13b,c,15,17,18]

We recently reported that fragmentation of aliphatic acetals, induced by electron transfer to the singlet excited state of 1,2,4,5-benzenetetracarbonitrile (TCB), results in an efficient alkylation of the nitrile as shown in Scheme 1, path c.[13b] The reaction was clean, and these appeared to be convenient substrates for testing the feasibility of radical alkylation according to path d, with the aromatic nitrile functioning as the photosensitizer and a non-light-absorbing substrate functioning as the radical acceptor. Accordingly, we presently report the photochemical reaction of TCB in the presence of acetals and electron-withdrawing substituted alkenes.

Results

Preparative Irradiations. Previous work on various classes of acetals has shown that the PET-induced fragmentation of 2,2-dialkyl-1,3-dioxolanes occurs efficiently.[13b] Thus we chose for the present study some dioxolanes, namely compounds **1a–c** (Scheme 2).

We first tested the course of the aromatic alkylation and found that irradiation of TCB in the presence of these substrates in acetonitrile followed by chromatography gave the 5-alkyl-1,2,4-benzenetricarbonitriles (**2a–c**) in 90% yield, along with the β-hydroxyethyl esters **3a,c** (Scheme 2a, Table 1). In every case, a single pair of photoproducts was obtained, viz. alkylation resulted from the more substituted alkyl radical (*tert*-butyl or *n*-pentyl rather than methyl in **1a** and **1b**, methyl rather than phenyl in **1c**), with ≪5% of the products resulting from the alternative fragmentation [viz. $R'C_6H_2(CN)_3$ and $RCOOCH_2CH_2OH$].

The reactions were carried out in the presence of various alkenes (compounds **4–8**). Concentrations in the range 0.02–0.2 M were tested, and the results reported in Table 1 refer to the preparatively more convenient conditions. As indicated by the data reported, the reaction was strongly affected by these additives.

The irradiation of TCB in the presence of 0.05M **1a** and acrylonitrile (**4**) gave a 42% yield of another aromatic product along with **2a** (40%). As analytical and spectroscopic data clearly showed (see the Experimental Section), this was a different 5-alkyl-1,2,4-benzenetricarbonitrile, viz. compound **9a**, wherein acrylonitrile had inserted between the radical and the aromatic moiety (see Scheme 2a). Similarly, the reaction of TCB in the

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Scheme 2

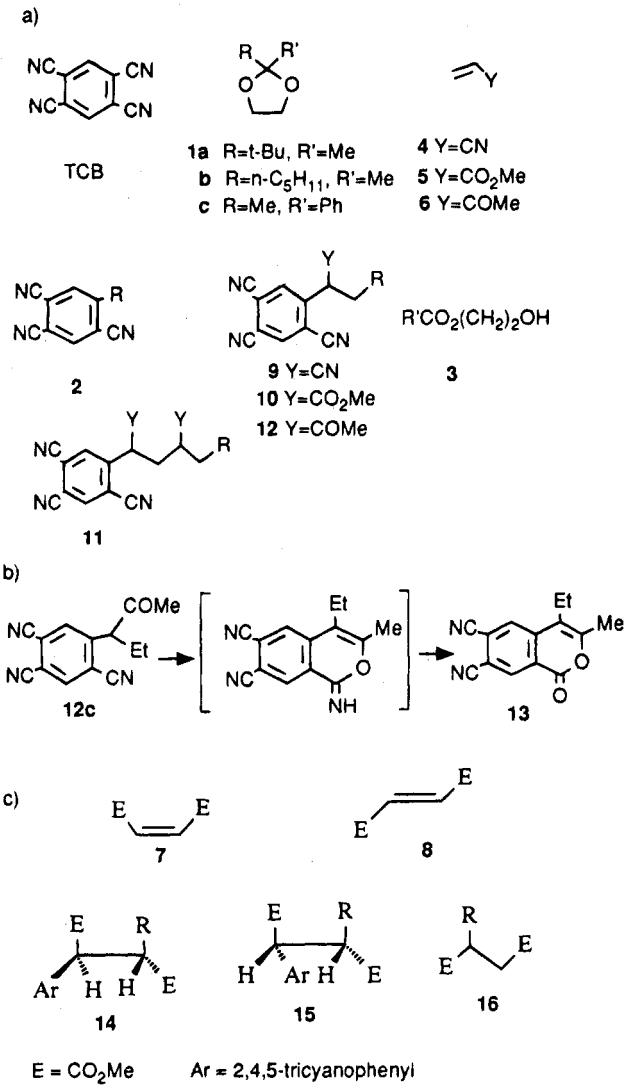

Table 1. Products Obtained from the Irradiation of TCB in the Presence of the Dioxolanes 1 and the Olefins 4–8

		product (% yield)		
dioxolane	additive	aromatic substition	ROCAS	addition to the olefin[a]
1a	none	**2a** (90)		
1b	none	**2b** (90)		
1c	none	**2c** (90)		
1a	**4**, 0.05 M	**2a** (40)	**9a** (42)	
1b	**4**, 0.1 M	**2b** (50)	**9b** (30)	
1c	**4**, 0.1 M	**2c** (5)	**9c** (80)	
1a	**5**, 0.1 M	**2a** (53)	**10a** (7.5), **11a** (14.6)	
1b	**5**, 0.1 M	**2b** (90)		
1c	**5**, 0.1 M	**2c** (5)	**10c** (40), **11c** (30)	
1a	**6**, 0.05 M	**2a** (40)	**12a** (30)	
1b	**6**, 0.15 M	**2b** (90)		
1c	**6**, 0.05 M	**2c** (5)	**13** (75)	
1a	**7**, 0.08 M	**2a** (30)	**14a+15a** (40)	**16a** (120)
1b	**7**, 0.1 M	**2b** (55)	**14b+15b** (20.5)	**16b** (16)
1c	**7**, 0.1 M	**2c** (10)	**14c+15c** (80)	**16c** (2)
1a	**8**, 0.08 M	**2a** (30)	**14a+15a** (40)	**16a** (120)

[a] Molar yield calculated on consumed TCB.

presence of **1b** and **4** gave the new nitrile **9b** along with **2b**, and when **1c** and **4** were used, compound **9c** was obtained, in this case in 80% yield, while the product of simple alkylation (**2c**) diminished to 5%. In no case did a significant polymerization of the alkene take place, and this was true in the experiments decribed below, also.

The irradiation in the presence of methyl acrylate (**5**) gave results in part similar to those obtained with acrylonitrile. Thus, in the case of **1a**, two new products were formed along with the alkyltricyanobenzene **2a**, viz. compounds **10a**, with a structure analogous to **9a**, and a further trapping product incorporating two molecules of acrylate, which was demonstrated to be the diester **11a** (mixture of two diastereoisomers). With **1b**, however, the yield of **2b** remained practically unchanged and the expected **10b** was not detected. In the case of **1c**, the reaction to give **2c** was almost completely prevented, just as when **4** was used, and two new products were formed, viz. **10c** and **11c** (the latter as a mixture of two diastereoisomers).

In the case of methyl vinyl ketone (**6**) there was some experimental complication since this additive absorbed the light competitively with TCB and underwent independent photodimerization. Apart from this, in the case of **1a**, both **2a** and the alkene trapping product **12a** were formed, while with **1b** only the product of simple alkylation (**2b**) was obtained. With **1c**, the formation of the termolecular adduct **12c** could be detected by examination of the raw photolysate, but during chromatography this material was converted to the lactone **13** (see Scheme 2b); **2b** was formed in traces.

The effect of unsaturated diesters was next considered. With the acetal **1a** and both dimethyl maleate (**7**) and dimethyl fumarate (**8**), practically the same product distribution was obtained (see Scheme 2c). This included the *tert*-butylbenzenetrinitrile (**2a**) as well as two termolecular adducts, the diastereoisomers **14a** and **15a**. (The stereochemistry was assigned on the basis of their spectroscopic properties; see the Experimental Section). The ratio of these two compounds was the same with **7** and with **8**. Some geometric isomerization, due to direct absorption of the light by the disters, takes place during preparative irradiations, but is limited to a few percent. Besides the above aromatic compounds, in both cases a major product was an aliphatic ester, the succinate **16a**.

The reaction in the presence of the diester **7** followed a similar course with **1b**, although in this case products **14b** and **15b** (not separated but characterized as the diastereoisomeric mixture in this case), and particularly the succinate **16b**, were obtained in lower yields. With **1c**, on the other hand, the diastereoisomeric termolecular adducts **14c** and **15c** were by far the predominant products, and the methyl succinate **16c** was formed only in traces.

Mechanistic Studies. The gross features of the reaction include formation of an alkyl radical from the dioxolane, followed by addition to the alkene and substitution on the aromatic ring to yield products **9**–**15** or reduction to the succinate **16**. Some experiments were carried out in order to obtain mechanistic information about these novel processes.

Thus, the competition between the different radical processes was evaluated by measuring the dependence on the alkene concentration of the quantum yield of formation of products **2a** and **9a** from **1a**, and, respectively, of **2b** and **9b** from **1b**, in the presence of acrylonitrile, as well as of **2a**, **14a**, **15a**, and **16a** from **1a** in the presence of dimethyl maleate, and similarly for **1c**. The results are shown in graphical form in Figures 1 and 2, and selected values are reported in Table 2. These include some experiments in ethyl acetate, aimed to give some indication about the effect of the medium polarity.

As for the reduction step leading to products **16**, the reaction of TCB and **1a** in the presence of the diesters **7** and **8** was repeated in acetonitrile containing 0.1% D_2O. This resulted in ca. 65% deuteration of the methylene group, with the same CHD diastereoisomeric distribution in both cases.

Discussion

Previous work has clarified the photoinitiation step of these reactions. Thus, the acetal quenches the singlet excited state of TCB, and the resulting radical cation cleaves to give an alkyl radical and the stabilized dialkoxy cation. Fragmentation occurs with high selectivity, as confirmed again here, e.g. in the case of **1b** where all the products obtained in a preparatively significant proportion arise from the pentyl radical, and the competitive formation of the methyl radical is quite limited. While previous studies were limited to aliphatic acetals,[13b] in this work, the aromatic ketal **1c** has also been considered. It has been found that, as one may expect, an α,α-dialkoxyphenyl carbocation behaves as a good electrofugal group, and thus the acetals of aryl alkyl ketones can be used as efficient sources of alkyl radicals with the present procedure.

In this work, the nucleophilic alkyl radicals have been generated in the presence of electron-poor olefins, and indeed it has been found that products incorporating the olefin are formed with the aromatic substitution products in fair to excellent overall yield, and, interestingly, this occurs with no attendant olefin polymerization.

Two different radical addition reactions have been discovered. Both of them involve addition of the radicals to the electron-withdrawing substituted alkene, occurring, as expected, at the β position in monosubstituted alkenes, as when they are generated by other methods.

In the first reaction, the new radical couples with the TCB radical anion and the resulting anion rearomatizes with cyanide loss. Thus, the overall process includes radical–olefin coupling and aromatic substitution (see Scheme 3a). The acronym ROCAS can be used for this process, also in view of its formal analogy with the nucleophile–olefin coupling aromatic substitution (NOCAS) process reported by Arnold (Scheme 3b).[22] Notice that both of these reactions take advantage of radical cation chemistry in obtaining an ordered termolecular addition, in the sense that in the NOCAS sequence, a nucleophile adds to the radical cation (which has to be a stable species, such as those obtained from electron-rich alkenes) and the resulting neutral radical adds to the acceptor radical anion, while in the present ROCAS reaction, an easily fragmentable radical cation generates an alkyl radical, this adds to an electron-poor olefin, and the adduct radical, in turn, couples with the acceptor radical anion.

The ROCAS process accounts for a large part of the output in all the cases explored, using a large variety of alkenes. The trapping efficiency is higher both when a more stable radical is generated and when a more stable

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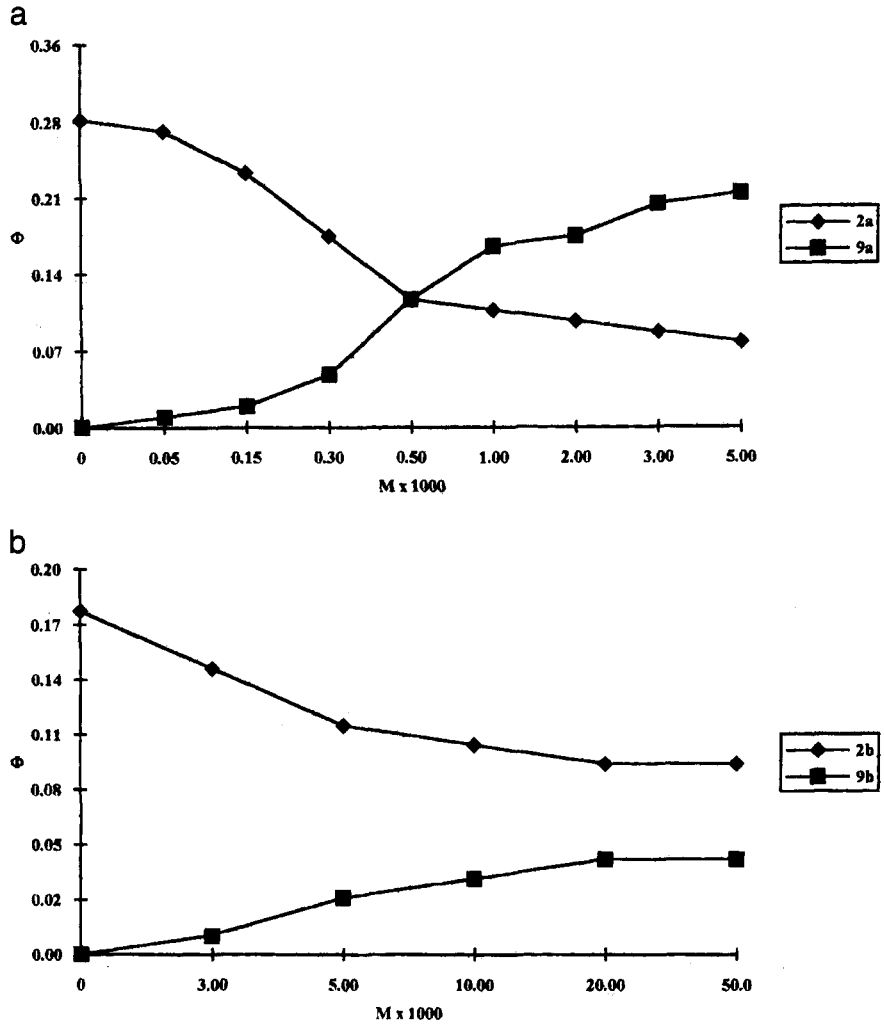


Figure 1. (a) Quantum yield for the formation of products **2a** and **9a** in the photochemical reaction between TCB and **1a** vs the concentration of the latter compound and (b) for products **2b** and **9b** in the reaction with **1b**.

cation is split off (i.e. the efficiency is higher with both **1a** and **1c** than with **1b**). With some combinations of the reagents, the yield exceeds 80% (e.g. **1c** + **4**, or **1c** + **7**). The reaction with methyl acrylate is complicated by the competitive addition of a second alkene unit to yield products **11**, occurring about as efficiently as the simple ROCAS process that gives **10**. The conversion of **12c** to the lactone **13** during chromatography is due to intramolecular attack of the enolized carbonyl onto the aromatic ring, catalyzed by the acidity of silica gel (Scheme 2b), and entails no change in the primary reaction sequence.

In the second process, which is limited to olefins substituted with two electron-withdrawing groups, radical addition is followed by reduction of the new radical. The D_2O experiments show that this step mainly occurs through electron transfer (from the radical anion) and protonation. This reaction is appealing from the synthetic point of view because the aromatic nitrile required as the photochemical oxidant in this method of radical generation functions as an unconsumed sensitizer and is not incorporated in the final product. Indeed, at least in some cases (**1a** + **7** and **1a** + **8**) the yield of the dimethyl succinates **16** is preparatively useful and exceeds the consumption of TCB (see Table 1). Therefore, it is important to distinguish the factors determining the competition between the three processes observed, viz. aromatic substitution, ROCAS reaction, and olefin addition. The products are grouped in this way in Tables 1 and 2.

However, the mechanism will be discussed with reference to the low-conversion experiments (Table 2), since in the preparative experiments the proportion of the succinates is higher because of two facts: (1) the alkylated trinitriles **2** are in part converted to dialkyldinitriles (see the Experimental Section),[13b] and (2) the primary products function as sensitizers for the addition of alkyl radicals to the alkene in the same way as TCB does. (This has been confirmed by separate experiments showing that **2a**, when irradiated in the presence of **1a** and **7**, sensitizes the addition of the *tert*-butyl radical to the maleate more efficiently (ϕ ca. 0.16) than it undergoes ring alkylation, as do the ROCAS adducts **14a** and **15a**.)

In order to rationalize the product distribution observed, one has to identify the factors determining the two divergence points in the mechanism, viz. (1) the partitioning of the educt radical between addition to the alkene and to the acceptor radical anion (path b vs path a in Scheme 4) and (2) the divergent fate of the adduct radical in its interaction with $TCB^{\bullet-}$ toward either addition or reduction (path c vs path d in Scheme 4; only the first is observed when the alkene is monosubstituted, while both compete with the diesters).

As for the first question, the following points are

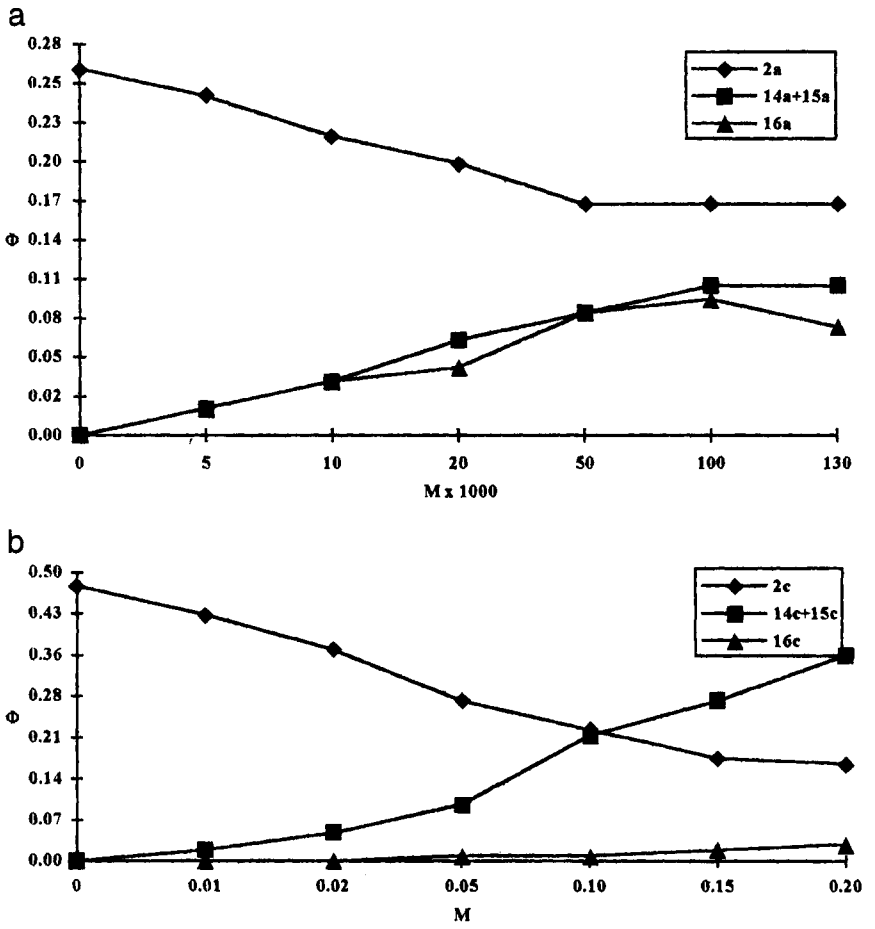


Figure 2. (a) Quantum yield for the formation of products **14a**, **15a** and **16a** in the photochemical reaction between TCB and **1a** vs the concentration of the latter compound and (b) for products **14c**, **15a**, and **16c** in the reaction with **1c**.

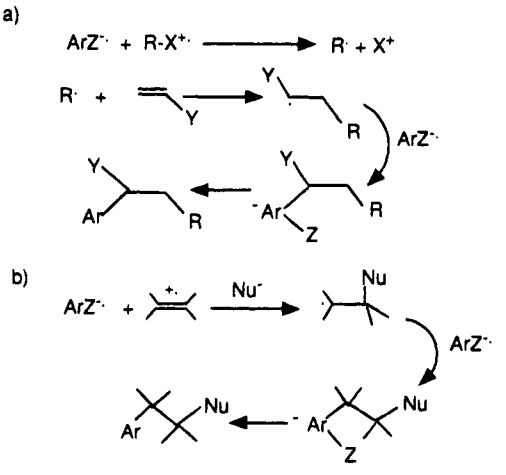
Table 2. Quantum Yield for the PET Reactions

dioxolane	solvent	additive	products (quantum yield) aromatic	ROCAS	addition
1a	MeCN	none	**2a** (0.27)		
1a	MeCN	**4**, 0.005 M	**2a** (0.08)	**9a** (0.22)	
1a	AcOEt	**4**, 0.02 M	**2a** (0.15)	**9a** (0.17)	
1a	MeCN	**7**, 0.05 M	**2a** (0.17)	**14a+15a** (0.09)	**16a** (0.09)
1a	AcOEt	**7**, 0.05 M	**2a** (0.13)	**14a+15a** (0.06)	**16a** (0.09)
1b	MeCN	none	**2b** (0.18)		
1b	MeCN	**4**, 0.02 M	**2b** (0.10)	**9b** (0.05)	
1c	MeCN	none	**2c** (0.48)		
1c	MeCN	**4**, 0.05 M	**2c** (0.12)	**9c** (0.34)	
1c	MeCN	**7**, 0.1 M	**2c** (0.23)	**14c+15c** (0.22)	**16c** (0.001)

relevant. The relatively high alkylation quantum yield (0.2−0.5, see Table 2) requires that fragmentation of the radical cation competes efficiently with back-electron transfer, which occurs at a rate of ca 10^8 s^{-1}. Therefore, the cleavage may take place (in part) within the initial contact ion pair, before separation and solvation of the radical ions, and thus the coupling between the alkyl radical and $TCB^{\bullet-}$ likewise occurs, in part, in the cage.

Figure 1 shows tat the trapping of the radical with acrylonitrile reaches a nearly maximum value at a relatively low alkene concentration (with **1a**, ROCAS vs aromatic substitution ca. 2:1 at 5×10^{-3} M; with **1b**, 1:2, and with **1c** 3:1 at 5×10^{-2} M). At a higher trap concentration, the proportion of the ROCAS process increases slightly (at concentrations of 0.1 M or higher, the overall quantum yield decreases, due to competitive quenching of TCB^{1*} by acrylonitrile, $K_{sv} = 6$ M^{-1}). This is compatible with the free-radical model, with competition between addition to acrylonitrile (occurring at a rate

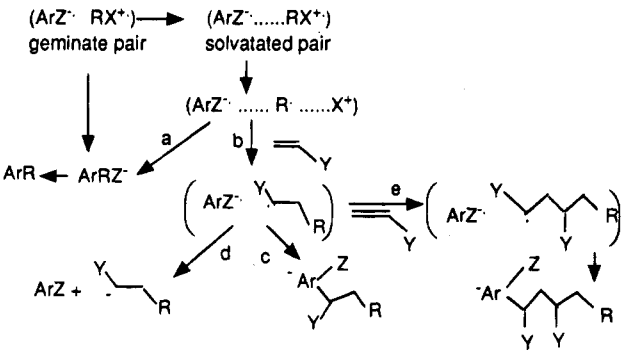
Scheme 3



of ca. 10^5 M^{-1} s^{-1}) and reencounter and coupling with $TCB^{\bullet-}$ (expected to occur at diffusion controlled rate).

Likewise, when using maleate as the trap, a maximum value of ca. 1:1 for the (ROCAS + alkene addition) vs aromatic substitution yield is reached (see Figure 2). However, this occurs at a higher concentration than in the previous case (0.1 M with **1a** and 0.2 M with **1c**). In free-radical reactions, addition to maleate occurs at a somewhat higher rate than to acrylonitrile, since the activation due to electronic factors is counterbalanced by the increased steric hindrance. That maleate is a poorer trap than acrylonitrile suggests that steric hindrance plays a larger role in the present reaction than with

Scheme 4



actual "free" radicals. Furthermore, the fact that aromatic substitution is not diminished below ca. 1/3 of the original value fits with the previous observation that even when very fast radical clocks are used (cyclopropylmethyl radical), ca. 40% of the alkylated trinitrile contains the unrearranged radical.[13b]

Thus, the model presented above, with fragmentation (and alkylation of $TCB^{\bullet-}$) occurring in part within the initial geminate pair and in part out of the cage or at least after solvation of the radical ion pair, can be extended, admitting that only the latter mechanism allows reaction with the alkene. The increased steric hindrance observed with respect to a typical free radical reaction is consistent with the idea that trapping occurs with the solvated radical ions. Again consistent with this model, the fraction intercepted grows for more stabilized radicals (*tert*-butyl > *n*-pentyl) and more stabilized leaving cations (e.g. **1c** > **1a,b**); both factors are expected to increase the "free-radical" character of the reaction.

As for the second point, one should first notice that the ratio between the ROCAS and the alkene addition processes does not change, while the sum of these reactions grows with respect to aromatic substitution with growing trap concentration (see Figure 2). Furthermore, the ratio of the two trapping processes is the same when using either maleate or fumarate, and the same holds for the ratio between the two diastereoisomers resulting from the ROCAS process. Therefore, a single intermediate is quenched and the adduct radical partitions between the two types of reactions after attaining the most stable conformation.

Reduction of alkyl radicals by the acceptor radical anion is fast when exothermic. This has been shown with benzyl radicals and the *p*-dicyanobenzene radical anion.[12] Upon direct comparison, $TCB^{\bullet-}$ is a poor reductant [E_{red}(TCB) = 0.7V, E_{red}(DCB) = −1.62V vs SCE).[23] The reduction potential of the α-cyano and α-alkoxycarbonyl radicals considered here is not known, but is probably rather low. The additional β substituent in the adduct radicals from maleate and fumarate is expected to affect its reactivity with respect to the adduct radicals from monosubstituted alkenes through a steric, rather than an electronic, effect. Thus, in the reaction with acrylonitrile, steric hindrance is small, and radical anion and radical remain in close contact. This results in bond formation as the only process. In contrast, with the more bulky diesters, the two radical centers are less proximate, and electron transfer from $TCB^{\bullet-}$, obviously less dependent on distance, becomes competitive. This rationalization is in accord with the steric effect on the rate of trapping by alkenes mentioned above. Furthermore, it is in accord with the fact that benzenetricarbonitriles carrying a bulky alkyl substituent, like **2a**, **14a** and **15a**, also sensitize the radical addition to **7** rather than undergoing further alkylation.

A complex interplay of steric and thermodynamic factors determines the fate of the radical−radical anion pair, as evidenced by the formation of adducts containing two olefin units in the TCB and **1**−**5** reaction (path e in Scheme 4) but not (or at least not to a significant extent under the conditions explored) in the other cases. We note again that no alkene polymerization is induced under these conditions.

For the sake of completeness, we considered alternative explanations for the observed difference between mono- and disubstituted alkenes. One is that the diesters (E_{red} = −1.15 V vs SCE[24] for the fumarate) are reduced by $TCB^{\bullet-}$ (an endothermic process, that is less endothermic than that of acrylonitrile, E_{red} < −2.25 V)[25] and thus scavenge the aromatic radical anion. The ROCAS process would then be impossible and the radical would add directly to the diester radical anion (eqs 1 and 2). As a consequence, the product distribution would depend on trap concentration, which is not observed. Likewise, other rationalizations not based on the specific reactivity of a single radical anion−radical complex would display such a dependent. Therefore, the rationalization presented above seems sufficient.

$$TCB^{\bullet-} + \mathbf{7} \rightarrow TCB + \mathbf{7}^{\bullet-} \quad (1)$$

$$\mathbf{7}^{\bullet-} + R^{\bullet} \rightarrow \mathbf{16} \quad (2)$$

Conclusion

This work shows that radicals produced by the photoinduced electron transfer−radical cation fragmentation route are susceptible to the most classical of radical reactions, the addition to alkenes. Two new reactions have been revealed, the addition to alkenes (preparatively equivalent to radical addition by the metal hydride method) and the radical olefin coupling−aromatic substitution process. From the synthetic point of view, the first one is of more straightforward application to synthesis, but the latter one is potentially valuable in view of the possible transformation of the substituted aromatic ring that becomes incorporated in the product, a simple example being the spontaneous formation of the isocoumarin **13** during attempted isolation of **12c**.

Some limitations of this method for the generation of radicals are apparent in the present study. When aromatic nitriles are used as acceptors and aliphatic ketals as donors, part of the reaction is inaccessible to quenching by alkenes, since the fragmentation occurs in part via nucleophilic assistance by the radical anion. This shortcoming, however, is almost eliminated by using arylalkyl ketals such as **1c**. Furthermore, the reaction with alkenes shows a steric effect larger than that expected for free radicals. (This characteristic, however, is in common with radical generation by oxidation with metal salts.) We do not know at the moment whether these limitations could be overcome by choosing other donor−acceptor combinations where such radical cation

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fragmentation has been observed. At any rate the demonstration that this is a viable method for reaction via radicals, not limited to the alkylation of the acceptor but extended to addition to olefins, and the fact that in this way radicals are generated under extremely mild conditions from unconventional precursors, will prompt further research aimed not only at clarifying the detailed mechanism of this multistep reaction, but also at exploring its synthetic utility.

Experimental Section

General. ^{1}H, ^{13}C, and ^{13}C-DEPT NMR spectra were recorded on a Bruker AC300 spectrometer in $CDCl_3$ solutions, and chemical shifts are reported in ppm downfield from TMS. Elemental analyses were made using a Carlo Erba Model 1106 instrument. Fluorescence intensities were measured by means of an Aminco-Bowman MPF spectrofluorimeter. TCB was prepared and purified according to a previously reported method.[13b] The acetals **1a–c** were prepared from the corresponding carbonyl derivatives by azeotropic water elimination from the benzene–ethylene glycol solution in the presence of *p*-toluenesulfonic acid (TSA) and redistillation (or recrystallization for **1c**). Anhydrous acetonitrile for the D_2O experiments was obtained by refluxing and fractional distillation from P_2O_5.

All photochemical reactions were performed by using N_2-purged MeCN solution (80 mL, subdivided in four quartz tubes) of TCB (100 mg, 0.56 mmol) containing the amount of ketal required for making the solution ca. 0.05 M and a multilamp reactor fitted with six 15-W phosphor-coated lamps (maximum of emission, 320 nm) for the irradiation. The reaction course was followed by TLC and GC. Workup of the photolysates involved concentration in vacuo and chromatographic separation employing Merck 60 silica gel. The yields of the photoreactions are based on consumed TCB. With regard to the photochemical reaction in the presence of alkenes **4–8**, explorative tests were performed using 3 mL of a MeCN degassed solution 0.005 M in TCB and 0.05 M in the ketal. The concentration of the alkene was changed from 0.02 to 0.2 M in order to establish the best conditions for the preparative reactions.

Photochemical Reaction between TCB and Ketal 1a. A solution of TCB and ketal **1a** (600 mg, 4 mmol) was irradiated for 40 min. The formation of a small amount of 2-hydroxyethyl acetate (**3a**) was confirmed by GC analysis of the photolyzed solution and comparison with an authentic sample.[26] The solvent was evaporated and the residue was separated with flash chromatography eluting with cyclohexane–EtOAc mixtures of increasing polarity. 5-*tert*-butyl-1,2,4-benzenetricarbonitrile (**2a**)[13b] (75 mg, 90%) was isolated.

Photochemical Reaction between TCB and Ketal 1a in the Presence of Acrylonitrile 4. Irradiation of a solution of TCB, ketal **1a** (600 mg, 4 mmol), and acrylonitrile **4** (0.05M, 212 mg, 4 mmol) for 1 h, followed by the general workup, gave, after silica gel chromatography (cyclohexane–EtOAc), 40 mg of 5-*tert*-butyl-1,2,4-benzenetricarbonitrile (**2a**) (40%) and 50 mg of 2-(2,4,5-tricyanophenyl)-4,4-dimethylpentanenitrile (**9a**) (42%, mp 129–130 °C, cyclohexane/benzene).

9a: ^{1}H NMR δ 1.15 (s, 9H), 1.6 (dd, J = 14 Hz, J = 3 Hz, 1H, H-3), 2.05 (dd, J = 14 Hz, J = 11 Hz, 1H, H-3′); 4.3 (dd, J = 3 Hz, J = 11 Hz, 1H, H-2); 8.05 (s, 1H), 8.1 (s, 1H); ^{13}C NMR δ 29.2 (CH_3), 31.6, 32.5 (CH_2), 49.5 (CH), 112.9, 113.3, 113.4 (CN), 116.3 (CN), 116.6 (CN), 118.4, 120.5 (CN), 133.3 (CH), 137.5 (CH), 146.6. Anal. Calcd for $C_{16}H_{14}N_4$: C, 73.26; H, 5.38; N, 21.36. Found: C, 73.16; H, 5.43; N, 21.14.

Photochemical Reaction between TCB and Ketal 1a in the Presence of Methyl Acrylate 5. Irradiation of a solution of TCB and ketal **1a** (600 mg, 4 mmol) and methyl acrylate **5** (0.1 M, 800 mg, 8 mmol) for 1 h, followed by the general workup, gave, after silica gel chromatography (cyclohexane–EtOAc), 50 mg of 5-*tert*-butyl-1,2,4-benzenetricarbonitrile (**2a**) (53%), 10 mg of methyl 2-(2,4,5-tricyanophenyl)-4,4-dimethylpentanoate (**10a**) (7.5%, mp 116–118 °C, cyclohexane/benzene), and 25 mg of 2-(2,4,5-tricyanophenyl)-4-(2,2-dimethylpropyl)-1,5-pentanedicarboxylic acid dimethyl ester (**11a**) (14.6%, oil) as a mixture of two diastereoisomers in the ratio 55:45.

10a: ^{1}H NMR δ 0.9 (s, 9H), 1.55 (dd, J = 14 Hz, J = 4 Hz, 1H, H-3), 2.3 (dd, J = 14 Hz, J = 9 Hz, 1H, H-3′), 3.7 (s, 3H, OCH_3); 4.18 (dd, J = 9 Hz, J = 4 Hz, 1H, H-2), 7.72 (s, 1H); 7.89 (s, 1H). Anal. Calcd for $C_{17}H_{17}N_3O_2$: C, 69.14; H, 5.80; N, 14.13. Found: C, 69.23; H, 5.98; N, 14.10.

11a: (the chemical shifts attributable to the less abundant isomer are enclosed in brackets when distinguished from those of the major isomer) ^{1}H NMR δ 0.9 (0.8) (s, 9H), 1.28 (1.25) (dd, J = 14 Hz, J = 5 Hz, 1H), 1.85 (1.87) (t, J = 14 Hz, 1H), 2.0 (m, 1H, H-3), 2.32 (2.52) (ddd, J = 15 Hz, J = 10 Hz, J = 5 Hz, 1H, H-3′), 2.3 (2.5) (m, 1H, H-2), 3.65 (3.7) (s, 3H, OCH_3), 3.76 (3.74) (s, 3H, OCH_3), 4.15 (m, 1H, H-2), 7.95 (7.98) (s, 1H), 8.07 (8.1) (s, 1H); ^{13}C NMR δ 29.1 (29.03) (CH_3), 30.6 (30.7), 37.9 (37.2) (CH_2), 40.3 (39.2) (CH), 46.4 (46.2) (CH_2), 47.3 (47.1) (CH), 51.9 (52.1) (OCH_3), 53.2 (OCH_3), 113, 24 (113, 22), 113, 7, 113.8 (114) (CN), 115.7 (115.6) (CN), 118.6 (117.9) (CN), 119.6 (119.5), 133.3 (CH), 136.9 (137.1) (CH), 147.8 (147.2), 170.4 (170.3) (COOR), 175.7 (175.5) (COOR). Anal. Calcd for $C_{21}H_{22}N_3O_4$: C, 66.29; H, 5.83; N, 11.05. Found: C, 66.55; H, 5.63; N, 11.57.

Photochemical Reaction between TCB and Ketal 1a in the Presence of Methyl Vinyl Ketone 6. Irradiation of a solution of TCB, ketal **1a** (600 mg, 4 mmol) and methyl vinyl ketone **6** (0.05M, 280 mg, 4 mmol) for 1 h, followed by general workup, gave, after silica gel chromatography (cyclohexane–EtOAc), 23 mg of 5-*tert*-butyl-1,2,4-benzenetricarbonitrile (**2a**) (40%) and 28 mg of 5,5-dimethyl-3-(2,4,5-tricyanophenyl)-2-hexanone (**12a**) (30%, mp 103–104 °C, EtOH). A small amount of a dimer of methyl vinyl ketone was detected by GC–mass analysis (*m/z* 140).

12a: ^{1}H NMR δ 0.95 (s, 9H), 1.6 (dd, J = 14 Hz, J = 6 Hz, 1H, H-4), 2.35 (dd, J = 14 Hz, J = 6 Hz, 1H, H-4′), 2.37 (s, 3H), 4.5 (t, J = 6Hz, 1H, H-3), 7.95 (s, 1H), 8.1 (s, 1H); ^{13}C NMR δ 29.5 (CH_3), 30.4, 47.0 (CH_2), 53.2 (CH), 113.4, 113.9, 114.6 (CN), 115.1 (CN), 117.5 (CN), 119.5, 134.3 (CH), 136.8 (CH), 149.6, 204.1 (COR). Anal. Calcd for $C_{17}H_{17}N_3O$: C, 73.10; H, 6.13; N, 15.04. Found: C, 73.72; H, 5.96; N, 15.51.

Photochemical Reaction between TCB and Ketal 1a in the Presence of Dimethyl Maleate 7. A solution of TCB, ketal **1a** (600 mg, 4 mmol), and dimethyl maleate **7** (0.08 M, 900 mg, 6.4 mmol) was irradiated until complete conversion of TCB. After the general workup and silica gel chromatography (cyclohexane–EtOAc), 10 mg of dialkylated dinitriles identical to those found in previous work,[13b] 30 mg of 5-*tert*-butyl-1,2,4-benzenetricarbonitrile (**2a**) (30%), 120 mg of 2-*tert*-butyl-1,4-butandicarboxylic acid dimethyl ester (**16a**) (oil), and 60 mg of a mixture of two compounds were isolated. On the basis of the integral of protonic NMR this mixture was attributed as follows: 19 mg (13%) of (3*R*,4*R*)/(3*S*,4*S*)-2-(2,4,5-tricyanophenyl)-3-*tert*-butyl-1,4-butanedicarboxylic acid dimethyl ester (**14a**) and 41 mg (27%) of (3*R*,4*S*)/(3*S*,4*R*)-2-(2,4,5-tricyanophenyl)-3-*tert*-butyl-1,4-butanedicarboxylic acid dimethyl ester (**15a**). The mixture of the two diastereoisomers was separated by silica gel chromatography (cyclohexane–EtOAc). In this way 10 mg of pure **14a** (mp 143 °C, cyclohexane/benzene) and 15 mg of pure **15a** (mp 158 °C, cyclohexane/benzene) were obtained. The structure of the stereoisomers were attributed on the basis of the following properties. In the ^{1}H NMR spectra both **14a** and **15a** were each present as a single conformer with H-2 anti to H-3 (as deduced from the high value of the coupling constant). In the case of **14a** the two methoxy groups showed nearly the same chemical shift while with **15a** one of them was sizeably shielded, in accord with the fact that it was gauche to the aromatic ring.

The reaction was repeated using acetonitrile containing 0.1% of D_2O. The same product distribution was obtained. Some deuterium was retained in the product **16a** [42% on the proton at 2.45 δ (H-3) and 21% on the proton at 2.7 δ (H-3′)].

14a: ^{1}H NMR δ 0.8 (s, 9H), 3.1 (d, J = 11 Hz, 1H, H-2), 3.65 (s, OCH_3), 3.75 (s, OCH_3), 4.7 (d, J = 11 Hz, 1H, H-3), 8.08 (s, 1H), 8.11 (s, 1H); ^{13}C NMR δ 28.4 (CH_3), 33.9, 49.3 (CH), 51.7 (OCH_3), 53.2 (OCH_3), 58.5 (CH), 113.1, 113.6, 114.1

(CN), 115.8 (CN), 118.3 (CN), 119.5, 133.7 (CH), 137.7 (CH), 170.9 (COOR), 172.2 (COOR). Anal. Calcd for $C_{19}H_{19}N_3O_4$: C, 64.58; H, 5.42; N, 11.89. Found: C, 64.65; H, 5.53; N, 11.69.

15a: ^{1}H NMR δ 1.1 (s, 9H), 3.4 (d, J = 11 Hz, 1H, H-2), 3.37 (s, OCH_3), 3.73 (s, OCH_3), 4.55 (d, J = 11 Hz, 1H, H-3), 8.02 (s, 1H), 8.1 (s, 1H); ^{13}C NMR δ 27.8 (CH_3), 34.1, 47.8 (CH), 51.2 (OCH_3), 53.3 (OCH_3), 58.9 (CH), 113.2, 113.8, 114.1 (CN), 115.6 (CN), 118.3 (CN), 119.5, 133.05 (CH), 136.5 (CH), 147.05, 170.7 (COOR), 171.4 (COOR). Anal. Calcd for $C_{19}H_{19}N_3O_4$: C, 64.58; H, 5.42; N, 11.89. Found: C, 64.45; H, 5.56; N, 11.75.

16a: ^{1}H NMR δ 0.95 (s, 9H); 2.45 and 2.78 (AB part of ABX system, 2H, H-3 and H-3′), 2.63 (X part of ABX system, 1H, H-2), 3.6 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3); ^{13}C NMR δ 27.7 (CH_3), 32.5 (CH_2), 32.5, 51.1 (CH), 51.3 (OCH_3), 51.7 (OCH_3), 173.1 (COOR), 174.7 (COOR). Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.85; H, 9.02.

Photochemical Reaction between TCB and Ketal 1a in the Presence of Dimethyl Fumarate 8. Irradiation of a solution of TCB and ketal **1a** (600 mg, 4 mmol) and dimethyl fumarate **8** (0.08 M, 900 mg, 6.4 mmol) for 1 h, followed by the general workup, gave the same product distribution as with dimethyl maleate. The reaction was also repeated using acetonitrile containing 0.1% of D_2O. Some deuterium was retained in the product **16a** (44% at H-3 and 19% at H-3′).

Photochemical Reaction between TCB and Ketal 1b. A solution of TCB and ketal **1b** (630 mg, 4 mmol) was irradiated for 1 h. The formation of a small amount of 2-hydroxyethyl acetate (**3a**) was confirmed by GC analysis by comparison with an authentic sample.[26] After general workup and silica gel chromatography (cyclohexane–EtOAc) 60 mg of 5-*n*-pentyl-1,2,4-benzenetricarbonitrile (**2b**) (90%)[13c] were obtained.

Photochemical Reaction between TCB and Ketal 1b in the Presence of Acrylonitrile 4. Irradiation of a solution of TCB and ketal **1b** (630 mg, 4 mmol) and acrylonitrile **4** (0.1 M, 430 mg, 8 mmol) for 1 h, followed by the general workup, gave, after silica gel chromatography (cyclohexane–EtOAc), 30 mg of 5-*n*-pentyl-1,2,4-benzenetricarbonitrile (**2b**) (50%) and 28 mg of 2-(2,4,5-tricyanophenyl)octanenitrile (**9b**) (30%).

9b: ^{1}H NMR δ 0.9 (t, J = 7 Hz, 3H), 1.4 (m, 6H), 1.6 (m, 2H), 2.0 (m, 2H, H-3), 4.2 (t, J = 7 Hz, 1H, H-2), 8.15 (s,2H). Anal. Calcd for $C_{17}H_{16}N_4$: C, 73.89; H, 5.84; N, 20.27. Found: C, 73.95; H, 5.89; N, 19.98.

Photochemical Reaction between TCB and Ketal 1b in the Presence of Methyl Acrylate 5. Irradiation of a solution of TCB and ketal **1b** (630 mg, 4 mmol) and methyl acrylate **5** (0.1 M, 1.2 g, 12 mmol) for 1 h, followed by the general workup, gave, after silica gel chromatography (cyclohexane–EtOAc), the 5-*n*-pentyl-1,2,4-benzenetricarbonitrile (**2b**) (40 mg, 90%) as the only isolated product. No other compounds were detected by GC and TLC.

Photochemical Reaction between TCB and Ketal 1b in the Presence of Methyl Vinyl Ketone 6. Irradiation of a solution of TCB and ketal **1b** (630 mg, 4 mmol) and methyl vinyl ketone **6** (0.15 M, 840 mg, 12 mmol) for 1 h, followed by the general workup, gave, after silica gel chromatography (cyclohexane–EtOAc), the 5-*n*-pentyl-2,3,5-benzenetricarbonitrile (**2b**) (35 mg, 90%) as the only isolated product. A small amount of a product formed by dimerization of methyl vinyl ketone was detected by VPC and confirmed by GC–mass analysis (*m/z* 140).

Photochemical Reaction between TCB and Ketal 1b in the Presence of Dimethyl Maleate 7. Irradiation of a solution of TCB and ketal **1b** (630 mg, 4 mmol) and dimethyl maleate **7** (0.1 M, 1.15 g, 8 mmol) for 1 h, followed by the general workup, gave, after silica gel chromatography (cyclohexane–EtOAc), 55 mg of 5-*n*-pentyl-1,2,4-benzenetricarbonitrile (**2b**) (55%) and 50 mg of a mixture which on the basis of ^{1}H NMR spectrum was attributed as follows: 16 mg of 2-*n*-pentyl-1,4-butanedicarboxylic acid dimethyl ester (**16b**), 10 mg (6%) of (3*R*,4*R*)/(3*S*,4*S*)-2-(2,4,5-tricyanophenyl)-3-*n*-pentyl-1,4-butanedicarboxylic acid dimethyl ester (**14b**), and 24 mg (14.5%) of (3*R*,4*S*)/(3*S*,4*R*)-2-(2,4,5-tricyanophenyl)-3-*n*-pentyl-1,4-butanedicarboxylic acid dimethyl ester (**15b**). The pattern of ^{1}H NMR spectra was similar to that observed for compounds **16a**, **14a**, and **15a**. The stereochemistry of the two last compounds was attributed by comparison with the spectra reported above.

16b: ^{1}H NMR δ 0.8 (t, J = 7 Hz, 3H), 1.2–1.4 (m, 8H), 2.45 (dd, J = 15 Hz, J = 4 Hz, 1H, H-3), 2.7 (dd, J = 15 Hz, J = 10 Hz, 1H, H-3′), 2.85 (m, 1H, H-2), 3.64 (s, OCH_3), 3.7 (s, OCH_3).

14b: ^{1}H NMR δ 0.8 (t, J = 7 Hz, 3H), 1.1–1.4 (m, 8H), 3.12 (m, 1H, H-3), 3.65 (s, OCH_3), 3.71 (s, OCH_3), 4.45 (d, J = 11 Hz, 1H, H-2), 7.9 (s, 1H), 8.05 (s, 1H).

15b: ^{1}H NMR δ 0.8 (t, J = 7 Hz, 3H), 1.1–1.2 (m, 8H), 3.2 (m, 1H, H-3), 3.48 (s, OCH_3), 3.69 (s, OCH_3), 4.37 (d, J = 11 Hz, 1H, H-2), 7.95 (s, 1H), 8.05 (s, 1H).

Photochemical Reaction between TCB and Ketal 1c. A solution of TCB and ketal **1c** (650 mg, 4 mmol) was irradiated for 40 min. After general workup and silica gel chromatography (cyclohexane–EtOAc) 48 mg of 5-methyl-1,2,4-benzenetricarbonitrile (**2c**) (90%)[13b] and 20 mg of 2-hydroxyethyl benzoate (**3c**) (oil) were obtained.

3c: ^{1}H NMR δ 2.1 (s, exch, 1H, OH), 4.0 and 4.5 (AA′BB′ system, 4H), 7.5 (m, 4H), 8.05 (dd, J = 7 Hz, J = 2.5 Hz, 2H). Anal. Calcd for $C_9H_{10}O_3$: C, 65.04; H, 6.07. Found: C, 65.43; H, 6.28.

Photochemical Reaction between TCB and Ketal 1c in the Presence of Acrylonitrile 4. Irradiation of a solution of TCB and ketal **1c** (650 mg, 4 mmol) and acrylonitrile **4** (0.1 M, 420 mg, 8 mmol) for 1 h, followed by the general workup, gave, after silica gel chromatography (cyclohexane–EtOAc), 3 mg of 5-methyl-1,2,4-benzenetricarbonitrile (**2c**) (5%),[13b] 25 mg of 2-hydroxyethyl benzoate (**3c**), and 80 mg of 2-(2,4,5-tricyanophenyl)butanenitrile (**9c**) (80%, oil).

9c: ^{1}H NMR δ 1.2 (t, J = 7 Hz, 3H), 2.05 (m, 2H), 4.3 (dd, J = 8 Hz, J = 6 Hz, 1H, H-1), 8.18 (s, 1H), 8.2 (s, 1H). Anal. Calcd for $C_{13}H_8N_4$: C, 70.90; H, 3.66; N, 25.44. Found: C, 70.98; H, 3.75; N, 25.56.

Photochemical Reaction between TCB and Ketal 1c in the Presence of Methyl Acrylate 5. Irradiation of a solution of TCB and ketal **1c** (650 mg, 4 mmol) and methyl acrylate **5** (0.1 M, 800 mg, 8 mmol) for 1 h, followed by the general workup, gave, after silica gel chromatography (cyclohexane–EtOAc), 3 mg of 5-methyl-1,2,4-benzenetricarbonitrile (**2c**) (5%),[13b] 25 mg of 2-hydroxyethyl benzoate (**3c**), 45 mg of 2-(2,4,5-tricyanophenyl)butanecarboxylic acid methyl ester (**10c**) (40%, mp 105 °C, cyclohexane–benzene), and 45 mg of 2-(2,4,5-tricyanophenyl)-4-ethyl-1,5-pentanedicarboxylic acid dimethyl ester (**11c**) (30%, oil) as a mixture of two diastereoisomers in the ratio of 55:45.

10c: ^{1}H NMR δ 1.0 (t, J = 7 Hz, 3H), 2.0 (m, 1H, H-3), 2.25 (m, 1H, H-3′), 3.75 (s, 3H, OCH_3), 4.09 (t, J = 7 Hz, 1H, H-2), 8.03 (s, 1H), 8.05 (s, 1H); IR (ν, cm^{-1}) 1736, 2240. Anal. Calcd for $C_{14}H_{11}N_3O_2$: C, 66.40; H, 4.38; N, 16.59. Found: C, 66.56; H, 4.50; N, 16.45.

11c (the chemical shifts of the minor isomer are reported in brackets when distinguished from those of the major isomer): ^{1}H NMR δ 0.9 (0.5) (t, J = 7 Hz, CH_3), 1.65 (m, 2H), 2.0–2.65 (m, 3H), 4.2 (m, 1H, H-2), 8.0 (8.01) (s, 1H), 8.08 (8.1) (s, 1H); ^{13}C NMR δ 11.2 (11.24) (CH_3), 25.6 (25.7) (CH_2), 34.6 (35.2) (CH_2), 44.0 (45.1) (CH), 47.2 (47.5) (CH), 51.9 (51.8) (OCH_3), 53.1 (OCH_3), 113.2, 113.7 (113.8), 115.5 (115.8) (CN), 116.4 (CN), 117.8 (CN), 119.5, 133.5 (CH), 137.0 (136.9) (CH), 147.5 (148), 170.4 (170.6) (COOR), 174.4 (174.6) (COOR); IR (ν, cm^{-1}) 1734, 2240. Anal. Calcd for $C_{18}H_{17}N_3O_4$: C, 63.71; H, 5.05; N, 12.38. Found: C, 63.52; H, 5.28; N, 12.15.

Photochemical Reaction between TCB and Ketal 1c in the Presence of Methyl Vinyl Ketone 6. Irradiation of a solution of TCB and ketal **1b** (650 mg, 4 mmol) and methyl vinyl ketone **6** (0.05M, 280 mg, 4 mmol) for 1 h, followed by the general workup, gave, after silica gel chromatography (cyclohexane–EtOAc), 3 mg of 5-methyl-1,2,4-benzenetricarbonitrile (**2c**) (5%),[13b] 25 mg of 2-hydroxyethyl benzoate (**3c**), and 58 mg of 3,3-dihydro-4-ethyl-3-methyl-2-benzopyran-1-one (**13**) (75%, mp 222–223 °C, toluene). The last compound was a secondary product arising from 3-(2,4,5-tricyanophenyl)-2-pentanone (**12c**) through a cyclization during the chromatographic separation induced by the silica gel acidity. In fact

(26) Davis, W.; Ross, W. C. J. *J. Chem. Soc.* **1950**, 3056.

the ^1H NMR spectrum of the raw photolysate showed the presence of the ABX system characteristic of compound **12c**, while the signals of **13** were absent. Also in this case a small amount of a product formed by dimerization of methyl vinyl ketone was detected by GC and confirmed by GC–mass analysis (*m/z* 140).

12c: ^1H NMR (of the raw photolysate) δ 0.9 (t, J = 7 Hz, 3H, CH_3), 1.8 (ddd, J = 7 Hz, J = 14 Hz, J = 6 Hz, 1H, H-4), 2.23 (ddd, J = 7 Hz, J = 14 Hz, J = 9 Hz, 1H, H-4'), 2.3 (s, 3H, CH_3), 4.27 (dd, X part of ABX system, J = 9 Hz, J = 6 Hz, 1H, H-3).

13: ^1H NMR δ 1.2 (t, J = 7 Hz, 3H), 2.4 (s, 3H, CH_3), 2.65 (q, J = 7 Hz, 2H, CH_2), 7.95 (s, 1H), 8.7 (s, 1H); ^{13}C NMR, δ 13.3 (CH_3), 17.5 (CH_3), 19.5 (CH_2), 128.3 (CH), 135.6 (CH), 114.4 (CN), 114.6 (CN), 112.6, 112.7, 120.3, 123.2, 141.1, 156.3, 159.1 (COOR); IR (ν, cm^{-1}) 1730, 2240. Anal. Calcd for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23; N, 11.76. Found: C, 69.7; H, 4.17; N, 11.54.

Photochemical Reaction between TCB and Ketal 1c in the Presence of Dimethyl Maleate 7. Irradiation of a solution of TCB and ketal **1c** (650 mg, 4 mmol) and dimethyl maleate **7** (0.1M, 1.15 g, 8 mmol) for 1 h, followed by the general workup, gave, after silica gel chromatography (cyclohexane–EtOAc), 5 mg of 5-methyl-1,2,4-benzenetricarbonitrile (**2c**) (10%),[13b] 20 mg of 2-hydroxyethyl benzoate (**3c**), and 80 mg (80%) of a mixture which on the basis of ^1H NMR spectrum was attributed as follows: 30 mg of (3*R*,4*R*)/(3*S*,4*S*)-2-(2,4,5-tricyanophenyl)-3-methyl-1,4-butanedicarboxylic acid dimethyl ester (**14c**) and 50 mg of (3*R*,4*S*)/(3*S*,4*R*)-2-(2,4,5-tricyanophenyl)-3-methyl-1,4-butanedicarboxylic acid dimethyl ester (**15c**). The presence of a very small amount (2 mg) of 2-methyl-1,4-butanedicarboxylic acid dimethyl ester (**16c**) was revealed by GC and confirmed by comparison with an authentic sample prepared from 2-methylsuccinic acid.

14c: ^1H NMR δ 1.05 (d, J = 7 Hz, 3H), 3.24 (dq, J = 7 Hz, J = 10 Hz, 1H, H-3), 3.73 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 4.5 (d, J = 10 Hz, 1H, H-2), 7.98 (s, 1H), 8.15 (s, 1H).

15c: ^1H NMR δ 1.4 (t, J = 7 Hz, 3H), 3.35 (dq, J = 7 Hz, J = 10 Hz, 1H, H-3), 3.59 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 4.12 (d, J = 10 Hz, 1H, H-2), 8.05 (s, 1H), 8.1 (s, 1H). Anal. (of the mixture). Calcd for $C_{16}H_{13}N_3O_4$: C, 61.73; H, 4.21; N, 13.50. Found: C, 61.89; H, 4.52; N, 13.28.

Quantum Yield Determination. Relative quantum yields were measured on 3 mL of a MeCN (or EtOAc) solution of acceptor (0.005 M) and donor in septum capped quartz tubes. They were deaerated and irradiated as above in a rotating merry-go-round; substratum conversion was <25%; product formation was determined by GC. Absolute quantum yields were determined on similar solutions in spectrophotometric cuvettes irradiated by means of a focalized Osram 150-W high-pressure mercury arc fitted with an interference filter centered at 313 nm. A potassium trioxalatoferrate(III) solution was used, as an actinometric substance.