2 + 2 + 2 Cycloaddition vs Radical Ion Chemistry in the Photoreactions of 1,2,4,5-Benzenetetracarbonitrile with Alkenes in Acetonitrile

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Abstract: Irradiation of 1,2,4,5-benzenetetracarbonitrile (TCB) in acetonitrile in the presence of 1-hexene leads to two isomeric tetrahydroisoquinolines through a 2 + 2 + 2 cycloaddition between TCB, the alkene, and MeCN. The process occurs with moderate quantum yield via a strongly polarized exciplex. With di- and polysubstituted alkenes no cycloaddition takes place, the only reaction observed being substitution of a cyano group by an allyl radical. This is a low quantum yield process occurring via deprotonation of the alkene radical cation and $TCB^{\bullet-}$–allyl radical coupling. The selectivity in the attack on the allyl radical depends on steric hindering. Alternatively, the alkene radical cation can be trapped by methanol, yielding a (β-methoxyethyl)benzenetricarbonitrile. In the presence of water, the corresponding alcohols are not isolated, since they rapidly fragment to yield alkylbenzenetricarbonitriles. The mechanism is discussed on the basis of the competition of chemical reactions and back electron transfer.

The photochemical reactions between aromatics and alkenes can be classed in two groups. The first is cycloaddition, one of the most useful photochemical reactions from the synthetic point of view.[1] An important characteristic of this group is that the mode of reaction (ortho, meta, or para cycloaddition) can be predicted on the basis of the reagent's redox potential.[2-4] Thus, a large body of experimental and theoretical observations show that the ortho process is greatly preferred for addend pairs which have a donor–acceptor relationship, e.g., in the irradiation of benzene and dienophiles.[5,6] The same type of reaction takes place when the alkene is the donor and the aromatic the acceptor, e.g., with electron-rich alkenes such as vinyl ethers in the presence of unactivated benzenes[7,8] or with electron-withdrawing substituted benzenes and simple alkenes.[9-12]

The second group includes electron transfer (SET)-promoted reactions, where the radical anion of an electron-withdrawing substituted arene (often a nitrile) and the radical cation of the alkene are formed.[13] The reactions observed include dimerization[14-18] and nucleophilic addition to the olefin,[17,18] as well as substitution on the aromatic ring by the radical formed from the olefin radical cation.[19-22]

Furthermore, other processes may compete, e.g., a reaction involving a substituent rather than the aromatic ring. As an example, in the reaction between benzonitrile and alkenes, the meta addition is observed only for largely positive ΔG_{et}, the ortho process for moderately positive ΔG_{et} (from the examples available, ca. 0.4–1.7 eV).[13b,23] However, for near-thermoneutral conditions (ΔG_{et} 0–0.4 eV), cycloadditition onto the cyano group is favored,[23a,24] and finally, when ΔG_{et} is negative, cycloaddition is no longer observed and is replaced by single electron transfer to give a radical ion pair.

Exergonic SET is a very fast process. Therefore, the exploration of the chemistry of very polar exciplexes is precluded, since charge separation (and eventual collapse to free solvated radical ions) is expected to predominate. For example, this is the case for the photochemical reaction between alkenes and benzenedicarbonitriles.[19]

We have been concerned for a long time with the differentiation between exciplex and radical ion chemistry,[25] and we presently report some recent results showing that irradiation of the good acceptor 1,2,4,5-benzenetetracarbonitrile (TCB) leads to some unexpected reactions, with strong dependence on the alkene structure. These chemical results suggest some addition to the currently accepted mechanistic schemes for the photoreactions of the arene/alkene systems.

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Scheme 1

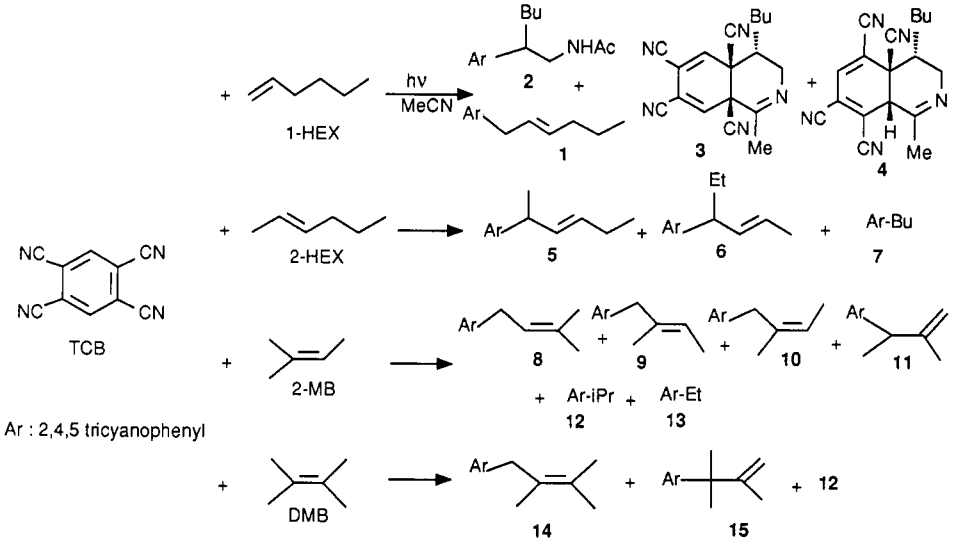


Table 1. Products From the Irradiation of Benzene-1,2,4,5-tetracarbonitrile in Acetonitrile in the Presence of Alkenes

alkene	products (yield, %)
1-HEX[a]	**1** (2), **2** (36), **3** (29), **4** (12)
2-HEX	**5** (3.5), **6** (1), **7** (3.5)
2-MB	**8** (14), **9** (6), **10** (5), **11** (3), **12** (4), **13** (1)
DMB	**12** (tr),[d] **14** (50), **15** (1)
DMB[b]	**12** (3), **14** (20), **15** (tr), **16** (25)
DMB[c]	**12** (40), **14** (15), **15** (tr), **17** (4)

[a] Irradiation at –40 °C. [b] In acetonitrile containing 3% methanol. [c] In acetonitrile containing 3% water. [d] Tr, trace.

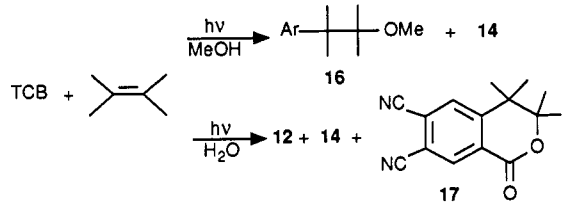
Results

Irradiation of TCB and 1-hexene (1-HEX) in acetonitrile led to a fast reaction. The best preparative results were obtained when the reaction was carried out at –40 °C. The products isolated from the chromatography (Scheme 1, Table 1) included a small amount of the alkylated trinitrile **1** and three main products. One of these, quite unexpectedly, turned out to be an open-chain amide (structure **2**, see a detailed discussion of the identification in the Experimental Section). As for the other compounds (**3**, **4**), elemental analysis and mass spectrometry showed that both of them were 1:1:1 TCB–alkene–MeCN adducts. The structure of 4-butyl-1-methyl-4a,6,7,8a-tetracyano-3,4,4a,8a-tetrahydroisoquinoline was assigned to compound **3** on the basis of the NMR data (including NOE experiments on the methyl group, see Experimental Section). On similar grounds, compound **4** was recognized as the 4a,5,7,8-tetracyano isomer of **3**; however, in this case some further signals in the NMR spectrum showed the presence of minor amounts of the 2,3,4,4a-tetrahydro tautomer **4'**, which, as judged from the IR spectrum, was the exclusive form in the crystalline state. NOE experiments established that in compound **4** the ring fusion is cis and the butyl group equatorial, and the same stereochemistry was suggested for isomer **3**. The isoquinoline **3** was converted into amide **2** by hydrolysis under mildly acidic conditions (see Experimental Section).

In contrast to the case of 1-hexene, the reaction between TCB and (*E*)-2-hexene (2-HEX) proceeded quite sluggishly under all the conditions used and gave a poor yield of characterized products. Two of these were identified as the isomeric hexenylbenzenetricarbonitriles **5** and **6** (the latter one in a small amount in a non completely separated fraction), and another one was 5-butylbenzene-1,2,4-tricarbonitrile (**7**).

The reaction with 2-methyl-2-butene (2-MB) was again slow, with a poor material balance. A mixture of four compounds was present in a fraction, and examination of the spectra showed that these were 5-alkyl-1,2,4-trinitriles containing isomeric unsatured five-carbon side chains (products **8-11**). From further fractions, the 5-isopropyl trinitrile **12** and a trace of the corresponding 5-ethyl derivative **13** were isolated.

Scheme 2



The irradiation of TCB with 2,3-dimethylbutene (DMB) gave a better material balance. By far the main product was the alkenyl derivative **14**, accompanied by a trace of its isomer **15** and a small amount of the isopropyl derivative **12**.

Alkylation is the main process of reaction with all the alkenes tested, except 1-hexene, but it occurs with low efficiency . Therefore, we explored whether the reaction was sensitive to a change in the medium. When the reaction of TCB and DMB was carried out in the presence of 2,6-lutidine, an increase in the rate of conversion was observed, with **14** again as the main product. On the other hand, when TCB and DMB were irradiated in acetonitrile containing 1–5% methanol, the increase in the rate was accompanied by a change in the product distribution, with the ether **16** now the main product (Scheme 2). Similar experiments were carried out in the presence of water, but the corresponding alcohol was not isolated; instead of this, a high yield of the isopropyl trinitrile **12** was obtained; some minor compounds were present, and among these the lactone **17** was isolated.

In view of these results with DMB, the irradiation in the presence of water was extended also to the other alkenes. With 2-HEX and 2-MB, a cleaner and faster reaction was obtained, with the butyltrinitrile **7** and the corresponding isopropyl derivative **12** as the main products. With 1-HEX, on the contrary, the change in the product distribution was minimal.

The above preparative studies were complemented by measurements of the quenching of TCB fluorescence by the alkenes and determination of the product quantum yield under representative conditions. These are gathered in Table 2.

Discussion

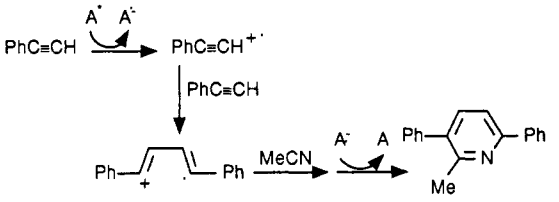
All the alkenes considered quench the TCB fluorescence (10.8 ns) at a rate near to diffusion controlled ($k_q > {}^1/_2 k_{diff}$). The free energy change for photoinduced electron transfer calculated

Table 2. Quenching Constants of the TCB Fluorescence in Acetonitrile and Calculated[a] pK_a Values of the Alkene Radical Cations

alkene	ΔG, eV	K_{SV}, M^{-1}	pK_a ($RH^{\bullet+}$)
1-HEX	−0.3	98	−18.4
2-HEX	−0.8	121	−9.9
2-MB	−1.4	181	+2.8
DMB	−1.6	196	+6.5

[a] According to the Nicholas–Arnold equation, see text.

Scheme 3



through the Weller equation[26] is moderately to strongly negative (Table 2). Thus, in all the cases considered, quenching of TCB^{1*} leads to a single type of intermediate, which may be described as a radical ion pair or a very polarized exciplex. Despite this fact, the course of the photoreaction between TCB and alkenes is highly dependent on substrate structure and experimental conditions.

Indeed, three different reactions have been observed, viz. (1) Termolecular TCB–alkene–MeCN cycloaddition, yielding the isoquinolines **3** and **4** in the case of 1-HEX; (2) aromatic substitution (an allyl for a cyano group), yielding products **1** from 1-HEX, **5** and **6** from 2-HEX, **8–11** from 2-MB, and **14** and **15** from DMB; and (3) nucleophile alkene addition–aromatic substitution, giving **16** from DMB in the presence of methanol. As it will be shown later, a subcase of the latter reaction is aromatic substitution by a fragment of the alkene, as in the case of the formation of the isopropyl tricarbonitrile **12** from TCB and DMB.

Cycloaddition. The reaction with 1-HEX has the typical characteristics of a cycloaddition via exciplex. Thus, it occurs with a high chemical and quantum yield and is insensitive to protic and nucleophilic additives. A similar aromatic–alkene–nitrile 2 + 2 + 2 photocycloaddition has not been reported, but it is known that acetonitrile undergoes electrophilic attack by a 1,4-distonic radical cation in the SET-promoted formation of pyridines from arylalkynes (Scheme 3).[27] Therefore, one may envisage that the strongly polarized TCB–1-HEX exciplex evolves through single bond formation and the zwitterion is trapped by acetonitrile; formation of the second bond in the two possible ways would leads to the two observed termolecular adducts (Scheme 4, path a).

However, in both products the carbon–nitrogen bond is formed at the nonsubstituted alkene end; it is not expected that formation of the zwitterion involves bonding at the more hindered alkene end, giving the less stabilized cation. Thus, it is more appropriate to regard this reaction as a concerted process (Scheme 4, path b); a termolecular addition would be expected to show stringent steric requirements, and indeed sufficient superimposition of the short C≡N moiety with both the aromatic ring and the alkene π orbitals would be significant only when the unsubstituted alkene end is involved; hence the observed regiochemistry.

A concerted course with no discrete charged intermediate explains also the above-mentioned insensitivity to nucleophiles. The quantum yield does not change between 20 and −30 °C, but the isolated yields are much higher when the reaction is carried out at a lower temperature, due to the limited stability of the isoquinolines **3** and **4**. In particular, hydrolysis is facile; in the case of product **3**, this involves ring opening to yield the amide **2**, as shown in Scheme 5.

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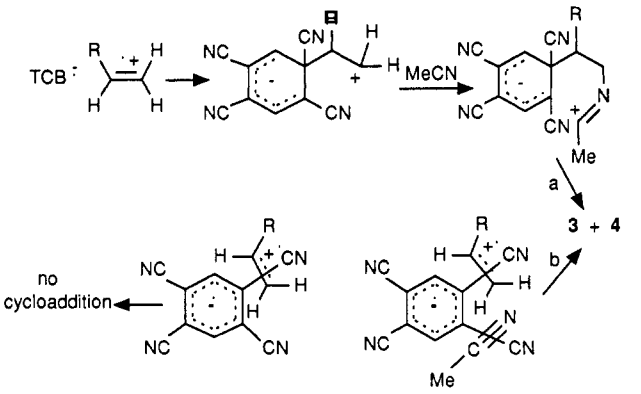
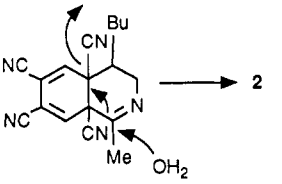
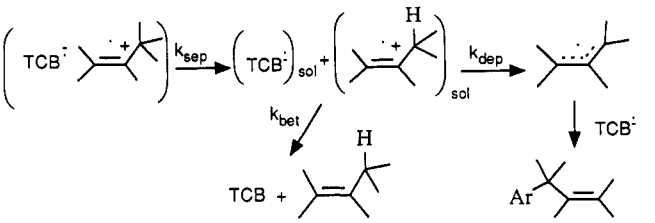
Scheme 4



Scheme 5



Scheme 6



Aromatic Substitution. For the reasons discussed above, cycloaddition is not possible for di- and polysubstituted alkenes. In this case, no reaction occurs via the initial complex, and the only pathway leading to chemical reaction involves collapse of the complex to yield the separated (and solvated) radical ions. Deprotonation of the radical cation yields an allyl radical, and this couples with the TCB radical anion (Scheme 6). Two points are worth considering in this reaction, viz. its selectivity and its efficiency.

First, deprotonation occurs from the allylic position(s), with preference for the weaker bond, judging from the case of 2-HEX, where it involves position 4 rather than position 1. Furthermore, in the ensuing coupling with $TCB^{\bullet-}$, the least hindered site of the allyl radical is preferred and thus yields mainly the more substituted arylalkene(s) (e.g., **8-10** rather than **11**, and **14** rather than **15**). This contrasts with what was observed by Arnold with the benzenedicarbonitriles, where the reaction is not selective, e.g., with DMB, both alkenes **18** and **19** are formed.[19] A rationalization that has been considered in that case is that the reaction occurs in part through an alternative mechanism, in which C–C bonding precedes elimination of H^+ and CN^-, possibly via an intermediate cyclohexadiene, and this explains the formation of **18** (Scheme 7).

Second, as for efficiency, one may notice that previously reported reactions via the SET–deprotonation sequence occurred uniformly with a low quantum yield ($\Phi \ll 0.1$),[13] and the same is true for the present one. A rationalization for this can be looked for in a slow deprotonation step, which competes unfavorably with back electron transfer. Calculation of the thermodynamic acidity by means of the Nicholas–Arnold equation[28]

$$pK_a(R\text{–}H^+) = -16.91E^\circ(R\text{–}H) - 27.55 + BDE(R\text{–}H)$$

shows that allyl radical cations are moderate ($DMB^{\bullet+}$) to very

(28) Nicholas, A. M. P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.

Scheme 7

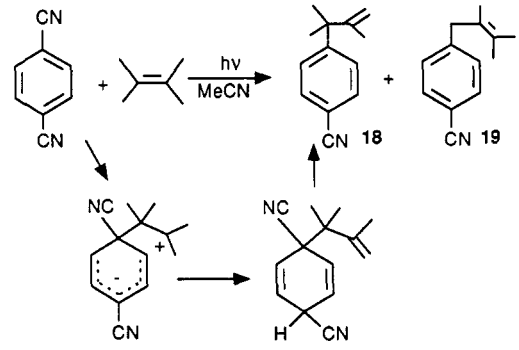


Table 3. Quantum Yields for the Photochemical Reactions

alkene	Φ_{-TCB}	product, $\Phi_{products}$	
1-HEX[a]	0.22		
2-HEX	<0.001		
DMB	0.008	**14**, 0.005	
DMB[b]	0.017	**14**, 0.015	
DMB[c]	0.08	**14**, 0.01	**16**, 0.04
DMB[d]	0.06	**14**, 0.01	**12**, 0.03

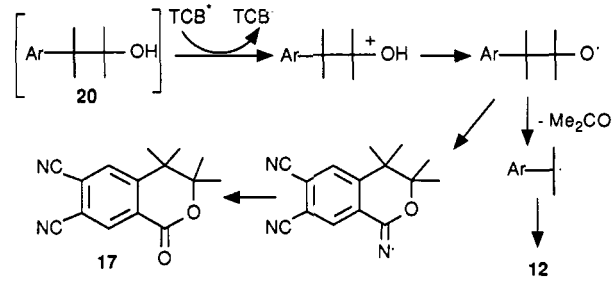
[a] No significant change of the quantum yield between 20 and −30 °C. [b] In the presence of 0.2 M 2,6-lutidine. [c] In acetonitrile containing 3% methanol. [d] In acetonitrile containing 3% water.

strong (1-HEX$^{\cdot+}$, 2-HEX$^{\cdot+}$) acids (Table 3). Since the involved bond dissociation energy changes only slightly along the series, the difference in oxidation potential translates directly in a difference in the pK_a, and thus the hardest to oxidize alkenes are much stronger allylic acids (intuitively, as long as the cation split-off remains the same, the larger the energy of the radical cation, the easier will be its cleavage). Correlation of the pK_a with quantum efficiency is very indirect, since the latter quantity depends also on the rate of separation (k_{sep}) of the radical ions and the rate of back electron transfer (k_{bet}). Due to the high energy of the radical ion pair, k_{bet} is expected to decrease with increasing alkene oxidation potential ("inverted" Marcus region).[29] Thus, evaluation of both k_{dep} (rate of deprotonation, based on a thermodynamic cycle) and k_{bet} predicts a more efficient deprotonation of the less substituted alkenes, whereas, at least judging from the efficiency of TCB alkylation, deprotonation of the alkenes is slow in all cases and somewhat faster in the case of DMB. This confirms the previous generalization that, even though it is calculated to be strongly favored from the thermodynamic point of view, C–H deprotonation of radical cations is inefficient, except when proton transfer within the original radical ion pair is involved.[30]

In the present case, the key factor is probably the separation efficiency. Indeed, the highest quantum yield is observed with DMB, yielding the most stabilized (and hindered) donor, which is expected to escape out of cage more efficiently. In that case, the observed quantum yield of 0.008 fits with the mechanism proposed in Scheme 6. The fact that $k_{bet} \geq 100k_{dep}$ is not surprising in view of expected values of $k_{bet} = 10^9$–10^{10} M^{-1} sec^{-1} [29] and the observation that base catalysis supports that deprotonation is the key step and fits with the idea of DMB$^{\cdot+}$ as a moderate acid. The lower quantum yield with less substituted alkenes is at least in part due to a less efficient diffusion out of cage of their less stabilized (and less hindered) radical cations.

Furthermore, in contrast to what is observed with 2-HEX and 2-MB, the reaction with DMB occurs with a satisfactory chemical yield in the alkylated trinitrile. This is reasonable, because in the sluggish reaction with the first two alkenes, some competitive path consumes the radical cations or the allyl radicals (a small amount of alkene oligomers is indeed present), and as a consequence some TCB$^{\cdot-}$, not reoxidized by back electron transfer, undergoes an irreversible decomposition rather than alkylation.

Scheme 8



Summing up the previous observations, in particular the effect of bases on deprotonation and the regioselective alkylation of TCB determined by steric factors, as appropriate for a radical reaction, we conclude that the allylation of TCB is well described as involving separation of the ions, out-of-cage deprotonation, and radical–radical anion coupling, whereas it is possible that with the dinitriles the occurrence of the reaction in part in cage or with a different sequence of the steps complicates the mechanism.

NOCAS Reaction. The formation of the ether **16** from the irradiation of TCB and DMB in the presence of methanol is a further example of the nucleophile olefin–addition aromatic substitution (NOCAS) process previously discovered by Arnold with the benzenedinitriles.[21,22] Methanol has two effects, viz. it both catalyzes deprotonation of the radical cation (increase in the quantum yield of **14**, see Table 3) and introduces a competing path, nucleophile addition. The neutral radical formed in the latter case adds to TCB$^{\cdot-}$ to give product **16**. Notice that the behavior of alkylalkenes contrasts with that previously observed with arylalkenes (anti-Markovnikov nucleophile addition);[13d,17] in that case, the benzyl radical ($E_{red} > -1.5$ V vs SCE)[31] formed from the nucleophile addition is reduced by the sensitizer radical anion, a process not feasible with the present radicals ($E_{red} < -2$ V).

In the presence of water, the NOCAS product **20** (Scheme 2) would be expected. We were unable to isolate this compound in reactions carried out at different degrees of conversion of TCB. However, the isolation of the isopropyl trinitrile **12** and the isocoumarin **17** from DMB is rationalized by admitting that **20** undergoes intermolecular (by TCB) or intramolecular photoinduced SET and deprotonation, followed by competing α-oxy radical fragmentation and cyclization to yield, after hydrogen abstraction, the observed products (Scheme 8). A related electron transfer-induced fragmentation of 2,2-diphenylethyl alkyl ethers has been reported.[32]

The alkylation by a fragment of the alkene observed with the other donors in the presence of water is rationalized in the same way. With asymmetric alkenes, nucleophile addition leading to the more stabilized radical is, as expected, preferred, and this leads, via fragmentation of the alcohols analogous to **20**, to the alkyl trinitriles containing the more substituted alkene fragment (**7** from 2-HEX, **12** from 2-MB). Since the allylation with 2-HEX and 2-MB is very slow, with those alkenes this reaction is observed also in "dry" acetonitrile, the moisture present being obviously enough to make addition to the radical cation competitive with deprotonation.

The reaction in the presence of nucleophiles is more efficient than the above discussed allylation of TCB in anhydrous acetonitrile (total quantum yield 0.08 with DMB and MeOH vs 0.008 in neat MeCN). At the nucleophile concentration used,

(29) (a) Gould, I. R.; Moody, R.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 7242. (b) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290..

(30) Albini, A.; Mella, M.; Freccero, M. *Tetrahedron* **1994**, *50*, 575. Exceptions are observed for proton exchange within the radical ion pair or when the radical anion is a good nucleophile.

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

(32) Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931.

trapping of the radical cation is complete. The fact that under all conditions the quantum yield remains below 0.1 with DMB and is much lower with less substituted alkenes shows the limits imposed by in-cage back electron transfer to a reaction via free radical ions. Notice further that in the case of 1-HEX, where the lifetime of the radical ion pair is further cut down by cycloaddition, nucleophiles do not divert the reaction from the path followed in neat MeCN.

Competition between the Reactions. From the discussion above, it is concluded that the competition between the 2 + 2 + 2 cycloaddition and the aromatic substitution depends on the efficiency of the radical ions separation. We have no direct measurement for this. However, we notice that for all reactions via the alkene radical cation (i.e., deprotonation, nucleophile trapping, and olefin dimerization, the last one not studied in detail but likewise inefficient), the quantum yield remains well below 0.1, much less than that observed for the cycloaddition with 1-HEX. Thus, the limiting factor is inefficient separation, and >90% of the chemical and physical decay takes place before collapse of the initial complex.

It is instructive to compare these results with what was observed with arylalkenes and aromatics as donors. In that case, the excited acceptor–donor interaction leads to a solvated ion pair, k_{sep} is assumed to be 5×10^8 s^{-1}, and the quantum yield for the formation of the free ions depends on k_{bet} (and is correlated with ΔG_{bet}).[29] It is likely that such a situation is typical of extensively delocalized radical ions, which are probably better stabilized by the solvent. When simple olefins are used, the localized radical cation is less easily stabilized, and on the other hand the higher coefficients of the frontier MO make the electronic coupling term more important. As a result, the initial interaction leads rather to a contact pair (or exciplex) than to solvent separated ions. No bimolecular benzene–alkene cycloaddition takes place, possibly because the atomic coefficients in the relevant TCB orbitals are not sufficiently large for 2 + 2 addition.

However, the 2 + 2 + 2 TCB–1-HEX–MeCN cycloaddition has the characteristics of the generally accepted mechanism for the arene–alkene addition (particularly high quantum yield and absence of medium effects) and probably reflects a situation of "incipient" cycloaddition with some charge localization, which in the favorable conformation (minimal steric hindering) leads to the termolecular addition, as depicted in Scheme 4, and otherwise undergoes internal conversion to the ground state.

On the other hand, when the strict steric requirements for this unusual cycloaddition are not met, the reaction via the free radical ions remains the only path available. The slow deprotonation of the alkene radical cation has been previously noticed. It may be that conformational factors play a role (the C–H bond is not aligned with the π bond in the preferred conformations).[33] Thermodynamic acidities calculated through thermochemical cycles are of little significance and the observed (kinetic) acidity depends on the competition between the rates of deprotonation and back electron transfer.

As for the following step, one may notice that since the TCB radical anion is endowed with peculiar stability, the coupling is more regioselective than that observed with less easily reduced acceptors. Thus, these reactions may be regarded as prototypical of the free radical cation–free radical path (Scheme 6), while in other cases competitive paths may play a role. The two unfavorable partitions (radical ions separation and radical cation deprotonation) cause the intrinsic inefficiency; nucleophile trapping overcomes the latter problem but not the first one.

Conclusion. The observed photochemistry of TCB in the presence of alkenes confirms the generalization that cycloaddition does not occur when the excited complex has a marked donor–acceptor character. However, a 2 + 2 + 2 cycloaddition with acetonitrile has been found which reflects an "incipient" cycloaddition path. With more hindered (and better donating) alkenes, reactions occur only via the small fraction of free radical ions.

(33) Perrot, A. L.; Arnold, D. R. *Can. J. Chem.* **1992**, *70*, 272.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC300 spectrometer, 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. The yields of the photoreactions are based on consumed TCB.

Photochemical Reaction between TCB and 1-HEX. A solution of TCB (100 mg, 0.56 mmol) and 1-HEX (672 mg, 8 mmol) in acetonitrile (80 mL) was purged with argon and irradiated in an immersion well apparatus by means of high-pressure mercury arc through Pyrex at –40 °C. After 1 h of irradiation, the solution was evaporated, and the residue was chromatographed using Merck 60 silica gel with cyclohexane–ethyl acetate 7:3 mixture as the eluant. The following products were isolated: TCB (5 mg); (*E*)-5-(2-hexenyl)benzene-1,2,4-tricarbonitrile (**1**) (2.5 mg, 2% on converted TCB, oil); *N*-[2-(2,4,5-tricyanophenyl)hexyl]acetamide (**2**) (60 mg , 36%, mp 79–81 °C from toluene); 4-butyl-1-methyl-3,4,-4a,8a-tetrahydroisoquinoline-4a,6,7,8a-tetracarbonitrile (**3**) (47 mg, 29%, oil); and 4-butyl-1-methyl-3,4,4a,8a-tetrahydroisoquinoline-4a,5,7,8-tetracarbonitrile (**4**) (19 mg, 12%, mp 220 °C, from acetone). A small amount of the (*Z*) isomer of compound **1** was present in a further chromatographic fraction (1 mg) as a mixture with (*E*)-**1**. The amide **2** was not a primary product but was derived from compound **3** by hydrolysis under mildly acidic conditions (see below). The structures of these compounds were attributed on the basis of ^{1}H–^{1}H COSY, ^{1}H–^{13}C HETCOR, and ^{1}H–^{13}C long-range HETCOR NMR experiments.

The molecular mass of compound **2** was established as 294, corresponding to a molecular formula of $C_{17}H_{18}N_4O$. The IR spectrum showed absorption bands for an amidic carbonyl (1654 cm^{-1}) and N–H stretching (3263 cm^{-1}). In the ^{1}H NMR spectrum, the diastereotopic protons absorbing at 3.65 (1H, m) and 3.5 ppm (1H, m), corresponding to a ^{13}C NMR signal at 43.9 ppm, could be assigned to the H-1 protons which are coupled to the methine proton at 3.45 ppm (1H, m, H-2). In the ^{1}H–^{13}C long-range HETCOR spectrum, the carbonyl group (δ 170.3) was correlated with the methyl group at 1.75 ppm and with the methylene group at 3.65 and 3.5 ppm. The compounds **3** and **4** had the same molecular mass (*m/z* 320), corresponding to a molecular formula of $C_{18}H_{17}N_5$. In neither of them was there an aromatic ring, as evidenced by absorptions attributable to olefinic rather than aromatic protons in the ^{1}H NMR spectra. The ^{13}C and ^{13}C-DEPT NMR spectra of compound **3** proved the presence of two quaternary unsaturated carbons (C-6 and C-7) and two unsatured methines (C-5 and C-8). Moreover, two aliphatic quaternary carbons (43.2 and 46.6 ppm) were present. In the ^{1}H NMR spectrum, two diastereotopic protons absorbing at 4.25 and 3.4 ppm and corresponding to a ^{13}C NMR signal at 51.7 ppm could be assigned to the H-3 protons. This methylene group also showed a "long-range" coupling with the methyl group at 2.19 ppm. The presence of a carbon–nitrogen double bond was in accordance with IR (1675 cm^{-1}) and ^{13}C NMR (152.1 ppm) spectral data. The bicyclic structure of a tetrahydroisoquinoline proposed for compound **3** was also confirmed by NOE difference spectroscopy: saturation of the signal at 7.75 ppm (H-8) gave a 5% enhancement of the 2.19 ppm resonance. The conversion of this isoquinoline **3** into the amide **1** was followed conveniently by ^{1}H NMR: the mild acidity of a $CDCl_3$ solution was enough to obtain a complete conversion after 2 days.

The structure of compound **4** has been attributed in the same way. The ^{13}C and ^{13}C-DEPT NMR spectra proved the presence of three unsaturated quaternary carbons (C-5, C-7, and C-8) and one unsaturated methine (C-6). In addition, one aliphatic quaternary carbon (74.3 ppm) and two methines (41.8 and 43.7 ppm) were present. In the ^{1}H NMR spectrum, the diastereotopic protons absorbing at 3.75 and 3.48 ppm corresponded to a ^{13}C NMR signal at 47.9 ppm and could be assigned to H-3 protons. The methine proton at 4.6 ppm was correlated with the ^{13}C NMR signal at 41.8 ppm, while in the ^{1}H–^{13}C long-range HETCOR spectrum, it was correlated to the quaternary carbons at 121.5 and at 161.5 ppm (C=N). The cis ring fusion of this compound was also confirmed by NOE difference spectroscopy: saturation of the signal at 4.7 ppm (H-8a) gave a 9% enhancement of the 3.75 ppm resonance (H-3) and a 4.7% enhancement of the 3.04 ppm resonance (H-4). However some spectral data showed the presence of a minor amount of the tautomeric 2,3,4,4a-tetrahydro form **4'**. In detail, the presence of a N–H group was proved by IR

spectroscopy (band at 3350 cm^{-1}) and by ^1H NMR spectroscopy (signal at 7.1 ppm which exchanged with D_2O after one day); the IR spectrum recorded in KBr showed also an absorption band at 1580 cm^{-1}, which is characteristic for a carbon–carbon double bond and not for a carbon–nitrogen double bond, while in the ^{13}C NMR spectrum, the quaternary carbon at 161.5 ppm was attributable to a C=N group. The protons absorbing at 7.1 (NH) and 4.6 ppm (H-8a) were involved in a tautomeric equilibrium since the integral of each one was less than one proton. As shown by the IR spectrum (in KBr) the tautomeric form **4'** was the exclusive form in the crystalline state, while in solution the form **4** was favored.

1. ^1H NMR: δ (in $CDCl_3$) 0.95 (t, ^3J = 7 Hz, 3H, H-6); 1.4 (m, 2H, H-5), 2.1 (q, J = 7 Hz, 2H, H-4); 3.65 (d, ^3J = 7 Hz, 2H, H-1); 5.45 (dt, ^2J = 15 Hz, ^3J = 7 Hz, 1H, H-2); 5.68 (dt, ^2J = 15 Hz, ^3J = 7 Hz, 1H, H-3); 7.8 (s, 1H); 8.05 (s, 1H). In the following chromatographic fraction (1 mg), product **1** was accompanied by the corresponding (*Z*) isomer, with only the signal at 3.5 ppm (d, H-1) separated from the other absorptions of isomer (*E*). Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.44; H, 5.85; N, 17.56.

2. ^1H NMR: δ (in CD_3COCD_3) 0.9 (t, ^3J = 7 Hz, 3H); 1.35 (m, 4H); 1.8 (m, 2H); 3.45 (m, 1H, H-2); 3.5 and 3.65 (AB part of ABX system, 2H, H-1); 7.2 (exch, NH); 8.38 (s, 1H); 8.55 (s, 1H). ^{13}C NMR: δ (in CD_3COCD_3) 13.7 (CH_3); 22.4 (CH_2); 22.9 (CH_3); 32.5 (CH_2); 43.9 (CH_2); 45.2 (CH); 114.6 (CN); 114.8 (CN); 114.3 (CN); 113.7, 118.4; 119.8; 133.2 (CH); 136.7 (CH); 153.6; 170.3 (CONH). IR: ν 3263; 2242; 1654. Anal. Calcd for $C_{17}H_{18}N_4O$: C, 69.37; H, 6.16; N, 19.04. Found: C, 69.10; H, 6.05; N, 19.08.

3. ^1H NMR: δ (in CD_3COCD_3) 0.95 (t, ^3J = 7 Hz, 3H); 1.4–1.6 (m, 4H); 1.85 (m, 2H); 2.19 (dd, ^5J = 1.5 Hz, ^5J = 2 Hz, 3H); 2.38 (m,1H, H-4); 3.4 (ddq, ^2J = 19 Hz, ^3J = 10 Hz, ^5J = 2 Hz, 1H, H-3); 4.25 (ddq, ^2J = 19 Hz, ^3J = 4.5 Hz, ^5J = 1.5 Hz, 1H, H-3'); 7.3 (*s*, 1H, H-5); 7.75 (*s*, 1H, H-8). ^{13}C NMR: δ (in CD_3COCD_3): 13.8 (CH_3); 23.1 (CH_2); 23.8 (CH_3); 28.2 CH_2); 29.2 (CH_2); 51.7 (CH_2); 34.7 (CH); 43.2; 46.6; 114.8 (CN); 114.9 (CN); 113.75 (CN); 115.6 (CN); 111.6, 113.7; 152.0; 137.5 (CH); 138.8 (CH); 152.1 (C=N). IR: ν 1675; 2240. Anal. Calcd for $C_{18}H_{17}N_5$: C, 71.27; H, 5.65; N, 23.09. Found: C, 71.35; H, 5.71; N, 23.19.

4. ^1H NMR: δ (in CD_3COCD_3) 0.95 (t, ^3J = 7 Hz, 3H); 1.3–1.4 (m, 4H); 1.6 and 1.8 (m, 2H); 2.2 (s, 3H); 3.04 (m, 1H, H-4); 3.48 and 3.75 (AB part of ABX system, 2H, H-3); 4.6 (s, H-8a); 7.2 (s, 1H, H-6); 7.1 (exch, NH). ^{13}C NMR: δ (in CD_3COCD_3) 14.0 (CH_3); 22.3 (CH_3); 23.2 (CH_2); 29.8 (CH_2); 31.9 (CH_2); 43.7 (CH); 47.9 (CH_2); 41.8 (CH); 74.3 (C-4a); 114.8 (CN); 115.1 (CN); 116.1 (CN); 122 (CN); 121.5; 127.0; 131.9; 137.3 (CH); 161.5 (C=N). IR: ν 1580; 2190; 3350. Anal. Calcd for $C_{18}H_{17}N_5$: C, 71.27; H, 5.65; N, 23.09. Found: C, 70.95; H, 5.61; N, 22.43.

Photochemical Reaction between TCB and 2-HEX. Irradiation for 13 h of a solution containing TCB (100 mg) and 2-HEX (672 mg, 8 mmol) followed by workup as above gave the following fractions: TCB (15 mg); (*E*)-5-(1-methyl-2-pentenyl)benzene-1,2,4-tricarbonitrile (**5**) (3.5 mg, 3.5%, oil); a following fraction containing some **5** and (*E*)-5-(1-ethyl-2-butenyl)benzene-1,2,4-tricarbonitrile (**6**) (ca. 1 mg, 1%); and 5-butylbenzene-1,2,4-tricarbonitrile (**7**) (3.5 mg, 3.5%).

5. ^1H NMR: δ (in $CDCl_3$) 0.95 (t, ^3J = 7 Hz, 3H); 1.45 (d, ^3J = Hz, 3H); 2.05 (qui, ^3J = 7 Hz, 2H); 4.05 (qui, ^3J = 7 Hz, 1H, H-1); 5.45 (ddt, ^2J = 15 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1H, H-2); 5.7 (ddt, ^2J = 5 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1H, H-3); 7.78 (s, 1H); 8.03 (s, 1H).

6. ^1H NMR: δ (in $CDCl_3$) 1.05 (t, ^3J = 7 Hz, 3H); 1.4 (d, ^3J = 7 Hz, 3H, H-4); 1.7 (m, 2H); 3.7 (q, ^3J = 7 Hz, 1H, H-1); 5.4 (ddq, ^3J = 6 Hz, ^3J = 15 Hz, ^4J = 1.5 Hz, 1H, H-2); 5.75 (ddq, ^3J = 15 Hz, ^3J = 7 Hz, ^4J = 1.5 Hz, 1H, H-3); 7.75 (s, 1H), 8.05 (s, 1H).

7. ^1H NMR: δ (in $CDCl_3$) 0.92 (t, ^3J = 7 Hz, 3H); 1.43 (sec, ^3J = 7 Hz, 2H); 1.72 (qui, ^3J = 7 Hz, 2H); 2.98 (t, ^3J = 7 Hz, 2H); 7.8 (s, 1H); 8.03 (s, 1H).

Photochemical Reaction between TCB and 2-MB. Irradiation for 30 h of a solution containing TCB (100 mg) and 2-MB (560 mg, 8 mmol) followed by workup as above gave the following fractions: TCB (25 mg); an oily fraction (26 mg) containing (the individual amounts were attributed by ^1H NMR) 5-(3-methyl-2-butenyl)benzene-1,2,4-tricarbonitrile (**8**) (10 mg, 14%), (*E*)-5-(2-methyl-2-butenyl)benzene-1,2,4-tricarbonitrile (**9**) (4 mg, 6%), the (*Z*) isomer of **9** (**10**) (3 mg, 5%), and 5-(1,2-dimethyl-2-propenyl)benzene-1,2,4-tricarbonitrile (**11**) (2 mg, 3%); and small amounts of 5-isopropylbenzene-1,2,4-tricarbonitrile (**12**)[34] (2.5 mg, 4%) and 5-ethylbenzene-1,2,4-tricarbonitrile (**13**)[34] (1 mg, 1%) isolated from further fractions. The compounds **8-11** were distinguished in the ^1H NMR spectrum on the basis of the multiplicity of the olefinic protons. Comparison with the spectrum of compound **1** allowed the attribution of the configuration to product **9**: the olefinic proton (H-2) of the first one was deshielded with respect to its (*Z*) isomer (**10**) since it was cis to the aromatic ring.

8. ^1H NMR: δ (in $CDCl_3$) 1.75 (d, ^4J = 1.5 Hz, 3H); 1,82 (d, ^4J = 1.5 Hz, 3H); 3.65 (d, ^3J = 7 Hz, 2H, H-1); 5.23 (t, ^3J = 7 Hz, ^4J = 1.5 Hz, 1H, H-2); 7.78 (s, 1H); 8.05 (s, 1H).

9. ^1H NMR: δ (in $CDCl_3$) 1.65 (m, 3H); 1.7 (d, ^3J = 7 Hz, 3H, H-4); 3.7 (s, 2H, H-1); 5.65 (q, ^3J = 7 Hz, 1H, H-3); 7.78 (s, 1H); 8.05 (s, 1H).

10. ^1H NMR: δ (in $CDCl_3$) 1.6 (m, 3H); 1.68 (d, ^3J = 7 Hz, 3H, H-4); 3.6 (s, 2H, H-1); 5.35 (q, ^3J = 7 Hz, 1H, H-3); 7.7 (s, 1H); 8.04 (s, 1H).

11. ^1H NMR: δ (in $CDCl_3$) 1.47 (d, ^3J = 7 Hz, 3H); 1.6 (s, 3H); 3.9 (q, ^3J = 7 Hz, 1H, H-1); 4.95(s, 1H, H-3); 5.13 (s, 1H, H-3); 7.8 (s, 1H); 8.05 (s, 1H).

Photochemical Reaction between TCB and DMB. Irradiation for 9 h of a solution containing TCB (100 mg) and DMB (672 mg, 8 mmol) followed by workup as above gave the following fractions: TCB (10 mg); 5-(2,3-dimethyl-2-butenyl)benzene-1,2,4-tricarbonitrile (**14**) (59 mg, 50%, mp 135 °C from ethanol); 5-(2,2,3-trimethyl-2-propenyl)benzene-1,2,4-tricarbonitrile (**15**) (1 mg, 1%, oil); and 5-isopropylbenzene-1,2,4-tricarbonitrile (**12**) (trace).

14. ^1H NMR: δ (in $CDCl_3$) 1.6 (s, 3H); 1.8 (s, 3H); 1.82 (s, 3H); 3.75 (s, 2H, H-1); 7.70 (s, 1H); 8.05 (s, 1H). Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.45; H, 5.54; N, 17.25.

15. ^1H NMR: δ (in $CDCl_3$) 1.25 (s, 6H); 2.2 (s, 3H); 5.45 (s, 1H, H-3); 5.65 (s, 1H, H-3); 7.75 (s, 1H); 8.03 (s, 1H).

Photochemical Reaction between TCB and DMB in the Presence of Methanol. Some explorative tests were performed using 3 mL of a MeCN degassed solution 0.005 M in TCB and 0.1 M in DMB. The concentration of methanol was changed from 1% to 5% while the products distribution was checked by TLC and GC. For the preparative reaction, a solution of TCB (100 mg, 0.56 mmol) and DMB (672 mg, 8 mmol) in acetonitrile containing 3% methanol was irradiated for 1 h. After the general workup as above, the following fractions were obtained: TCB (10 mg); 5-isopropylbenzene-1,2,4-tricarbonitrile (**12**) (5 mg, 3%); 5-(2,3-dimethyl-2-butenyl)benzene-1,2,4-tricarbonitrile (**14**) (24 mg, 20%); and traces of 5-(2,2,3-trimethyl-2-propenyl)benzene-1,2,4-tricarbonitrile (**15**) and 2-(2,4,5-tricyanophenyl)-1,1,2,2-tetramethylethyl methyl ether (**16**) (34 mg, 25%, mp 150–151 °C from ethanol).

16. ^1H NMR: δ (in $CDCl_3$) 1.1 (s, 6H); 1.62 (s, 6H); 3.12 (s, 3H, OCH3); 7.78 (s, 1H); 8.02 (s, 1H). Anal. Calcd for $C_{16}H_{17}N_3O_2$: C, 71.88; H, 6.41; N, 15.72. Found: C, 71.95; H, 6.53; N, 15.63.

Photochemical Reaction between TCB and DMB in the Presence of Water. Similar explorative tests as above were performed using water as the nucleophile. For the preparative reaction, a solution of TCB (100 mg, 0.56 mmol) and DMB (672 mg, 8 mmol) in acetonitrile containig 3% water was irradiated for 1 h. After the general workup, the following fractions were obtained: TCB (10 mg); 5-isopropylbenzene-1,2,4-tricarbonitrile (**12**) (39 mg, 40%); 5-(2,3-dimethyl-2-butenyl)benzene-1,2,4-tricarbonitrile (**14**) (18 mg, 15%); and traces of 5-(2,2,3-trimethyl-2-propenyl)benzene-1,2,4-tricarbonitrile (**15**). Some minor compounds were present, and among these, 5 mg of 1*H*-3,4-dihydro-3,3,4,4-tetramethyl-6,7-dicyanobenzo[*c*]pyran-1-one (**17**) (4%) was isolated.

17. ^1H NMR: δ (in CD_3COCD_3) 1.4 (s, 6H); 1.45 (s, 6H); 8.32 (s,1H); 8.52 (s, 1H). ^{13}C NMR: δ (in CD_3COCD_3) 24.1 (CH_3); 29.4 (CH_3); 42.4; 87.7; 115.4 (CN); 116.1 (CN); 116.4; 129.9; 132.8 (CH); 135.4 (CH); 155.1; 162.2 (COOR). Anal. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.51; H, 5.76; N, 11.53.

Quantum Yield Determination. Absolute quantum yields were determined on 3 mL of a MeCN solution of the acceptor (0.005 M) and the donor 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. For actinometry, a potassium trioxalatoferrate(III) solution was used. The product formation and TCB consumption were determined by GC using dodecane as the internal standard.

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