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Radical Ions in Photochemistry. 44. The Photo-NOCAS Reaction with Acetonitrile as the Nucleophile[†]

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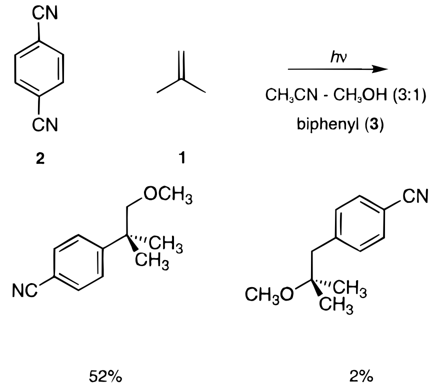
Studies on the photoinduced electron transfer (PET) reactions of isobutylene (2-methylpropene, **1**) in the absence of methanol have identified a new photochemical nucleophile−olefin combination, aromatic substitution (photo-NOCAS) reaction. Under these conditions acetonitrile was found to act as the nucleophile and to combine with the alkene radical cation. The resulting distonic radical cation then adds to the radical anion of 1,4-dicyanobenzene ($\mathbf{2}^{-\bullet}$). The final product (**6**) results from cyclization into the ortho postion of the phenyl group. This product formation is rationalized on the basis of the relatively high oxidation potential of the alkene (i.e., one-electron oxidation yields a reactive radical cation), the fact that addition of the nucleophile (acetonitrile) to the radical cation is relatively unhindered, and the relatively low acidity of the radical cation due to the low radical stability of the allylic radical formed upon deprotonation. High-level ab initio molecular orbital calculations were used to determine the structures and relative energies of the possible intermediate distonic and bridged radical cations. The scope and mechanism of this type of photo-NOCAS reaction are discussed.

Introduction

It has been well established that alkene radical cations undergo rapid nucelophilic addition when generated in the presence of a nucleophile.[1−3] A commonly used nucleophile in this reaction is an alcohol (e.g., methanol). Several examples are provided by the extensive studies on the photochemical nucleophile−olefin combination, aromatic substitution (photo-NOCAS) reactions of a wide variety of alkenes and dienes.[1] For example, irradiation of an acetonitrile−methanol (3:1) solution of isobutylene (2-methylpropene, **1**), 1,4-dicyanobenzene (**2**), and biphenyl (**3**), serving as a codonor, leads to the formation of the two 1:1:1 (nucleophile−alkene−aromatic) substitution products (reaction [1]).[1b] The yield of this reaction is relatively high, considering the measured (cyclic voltammetry, CV)[4] oxidation potential of **1** (2.65 V vs Ag/Ag^+; 2.99 V vs SCE),[5] which is near the upper limit for electron transfer to the first excited singlet state of 1,4-dicyanobenzene (**2**).



[1]

In the absence of a good nucleophile the radical cations of alkenes and dienes normally deprotonate and the resulting allylic radical then combines with the electron acceptor radical anion. Loss of cyanide anion from this adduct yields 1:1 (olefin−aromatic) substitution products. Examples of these reactions are also well-known.[1]

In a previous paper we reported the photochemical reactions of methylenecyclopropane (MCP), an alkene with a measured (CV) oxidation potential (OP, 2.41 V vs SCE, Pt electrodes) lower than that of isobutylene (**1**).[2c] Surprisingly this alkene did not give products resulting from electron transfer (ET); only cycloaddition products were found. On the basis of the Weller equation (eq 1),[6] ET from MCP to **2** was expected to proceed at the diffusion-controlled rate.

$$\Delta G_{\mathrm{ET}} = F[\mathrm{E}^{\mathrm{ox}}(\mathrm{D}) - E^{\mathrm{red}}(\mathrm{A}) - e/\epsilon\alpha] - E_{0,0}(\mathrm{A}) \quad (1)$$

Using the well-established correlation[7] between the IP and the OP of a number of alkenes, it became evident

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[†] See ref 1 for preceding parts in this series

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(4) (a) It must be noted that the oxidation potentials of the alkenes are irreversible, i.e., the number has no thermodynamic significance. However, it has been well established that in many cases reliable values for the OP can be obtained from the measured peak potentials.[4b,c] (b) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706. (c) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 178.

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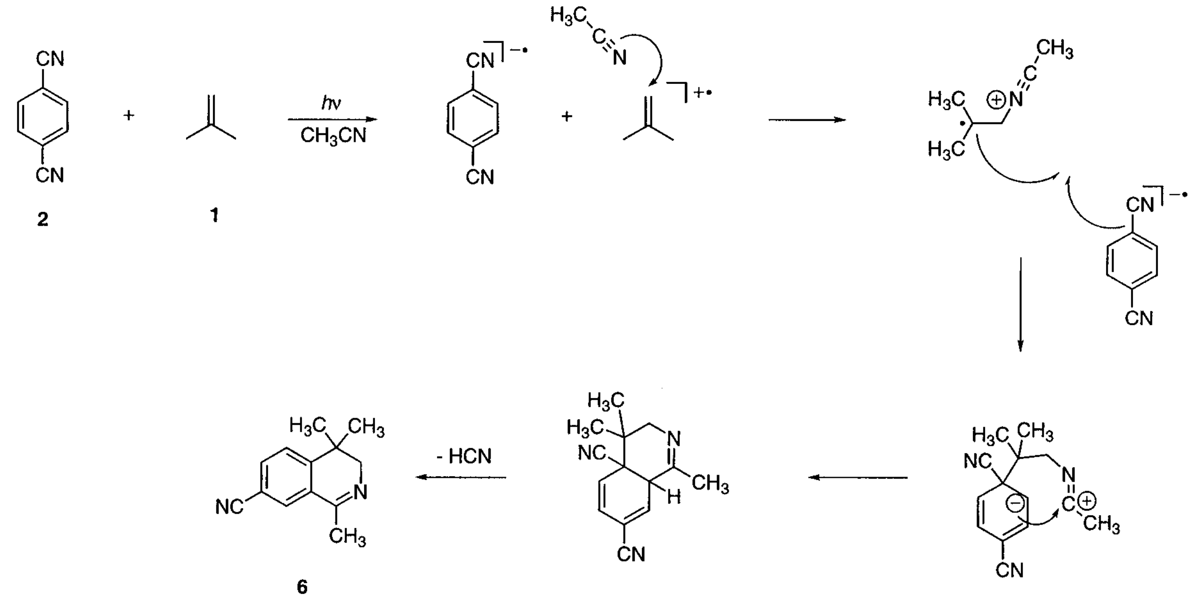
Scheme 1



that for PET reactions ET is controlled by the vertical ionization potential (IP) of the alkene, not the adiabatic ionization potential.[2c] In electrochemical (EC) experiments the OP reflects the adiabatic IP, a result of interaction between the alkene and the electrode (Pt) surface.[2c] Due to the obvious structural similarity of MCP and isobutylene (**1**), we have now focused on the reactivity of $\mathbf{1}^{+\bullet}$ in the absence of a nucleophile. The measured OP of **1** indicates that the free energy for electron transfer to the singlet excited state of **2** (ΔG_{ET}, eq 1) will be close to zero, i.e., products from both ET ($\Delta G < 0$) and from cycloaddition ($\Delta G > 0$) may be expected. To determine the reactivity of $\mathbf{1}^{+\bullet}$, the photoreaction of **1** with 1,4-dicyanobenzene (**2**) in acetonitrile (no methanol) was studied. Using these conditions a new photo-NOCAS reaction was discovered; in the absence of a better nucleophile, acetonitrile combines with $\mathbf{1}^{+\bullet}$. The resulting distonic radical cation then reacts with the electron acceptor radical anion. The final product (**6**) is formed after cyclization of this intermediate into the adjacent position of the aromatic ring, and rearomatization. The results of this study, complemented by ab initio calculations, are reported.

Results and Discussion

Irradiation of a solution of DCB (**2**, 0.1 M) and isobutylene (**1**, ca. 0.5 M) in acetonitrile resulted in the formation of one major product in good yield (**6**, 70%, reaction [2]).

[2]

Progress of the reaction was followed by capillary gas chromatography using a flame ionization (GC/FID) and a mass selective (gc/ms) detector. At short irradiation times, **6** was the only product observed. After prolonged irradiation small amounts of other products were formed. Addition of biphenyl (**3**) to the mixture decreased the efficiency of the reaction significantly.

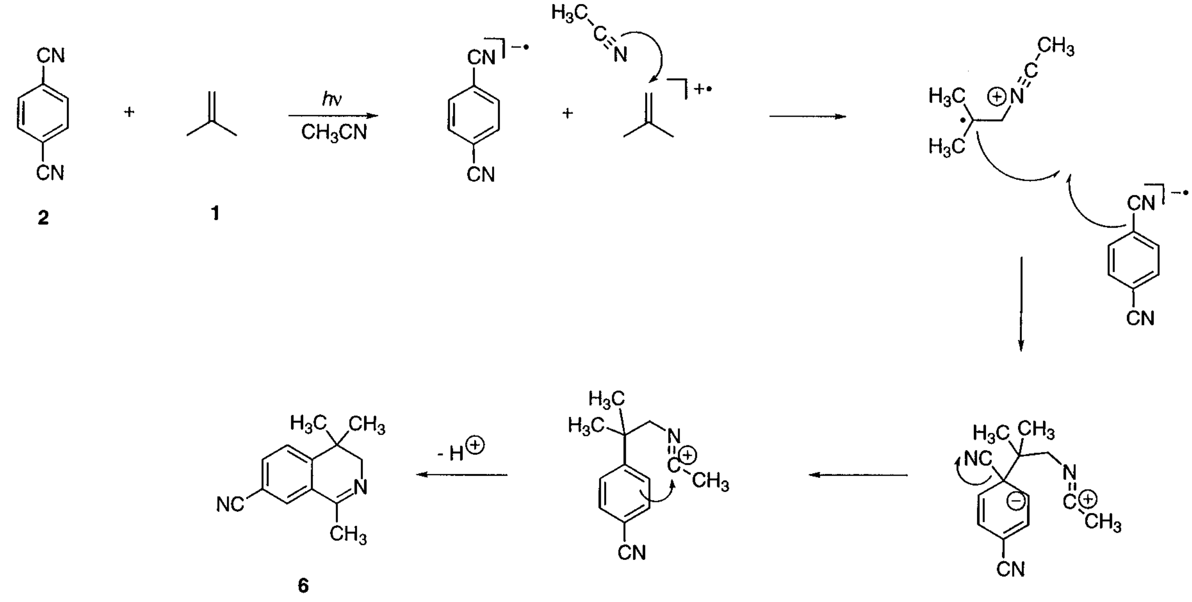
Identification of product **6** was aided by a detailed analysis of the NOESY (^{1}H nmr) spectrum which indicated that there is an interaction between the single methyl (2.45 ppm) and the single proton (7.77 ppm) on the phenyl ring. The two equivalent methyls (1.24 ppm) interact with the two adjacent protons (7.49 (strong) and 7.71 (weak) ppm) on the phenyl ring but not with the single proton (7.77 ppm). The methylene protons (3.58 ppm) do not show any interaction with any of the phenyl protons. These results were confirmed by the observed nuclear Overhauser effect (NOE): irradiation of the *gem*-dimethyl group (1.24 ppm) led to an enhancement of the signal (doublet) at 7.49 ppm; irradiation of the single methyl group (2.45 ppm) led to an enhancement of the signal (doublet) at 7.77 ppm. Irradiation of the methylene protons (3.58 ppm) did not result in enhancement of any of the signals of protons on the phenyl ring. These results firmly establish the structure of product **6**.

Convincing evidence for incorporation of acetonitrile in the final product (**6**) was obtained by carrying out the experiment in acetonitrile-d_3. The mass spectrum of this product (**6**) clearly showed the $\mathrm{M}^{+\bullet}$ peak at *m*/*z* 201, consistent with a molecular formula $C_{13}H_{11}N_2D_3$.

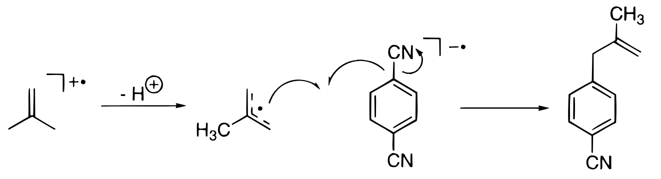
A possible mechanism for the formation of product **6** is shown in Scheme 1. The first step in this sequence involves an ET process leading to the formation of the radical cation ($\mathbf{1}^{+\bullet}$) and radical anion ($\mathbf{2}^{-\bullet}$). Addition of acetonitrile to $\mathbf{1}^{+\bullet}$ yields a distonic radical cation which combines with $\mathbf{2}^{-\bullet}$. The intermediate zwitterion will have excess negative charge on the *ortho* and *para* positions of the benzene ring; cyclization into the *ortho* position will be favorable. Loss of hydrogen cyanide (rearomatization) yields the final product (**6**) (Scheme 1).

Another possible mechanism (Scheme 2) is addition of the alkene radical cation to acetonitrile, followed by coupling with the radical anion. The final product (**6**) would be obtained after loss of cyanide anion, cyclization into the *ortho* position, and loss of a proton (i.e., a type of Friedel−Crafts alkylation). On the basis of these

Scheme 2



Scheme 3



results it is not possible to distinguish between these two processes.

These proposed mechanisms parallel that of the photo-NOCAS reaction with, in this case, acetonitrile acting as the nucleophile. It also shows similarities to that of the addition of cations to acetonitrile (as is observed in electrochemical experiments)[2b,8] except for the fact that no hydrolysis (to yield the acetamide) is observed. This type of reaction (photo-NOCAS reaction with acetonitrile as the nucleophile) is unprecedented. As shown before,[2b] in cases when the alkene does not undergo the photo-NOCAS reaction, the most common competing reaction involves deprotonation of the radical cation. The expected product(s) under these conditions are the 1:1 (alkene−aromatic) adducts which arise from deprotonation of the alkene radical cation followed by addition of the allylic radical to the radical anion and loss of cyanide anion (Scheme 3). The fact that this product is formed in only trace amounts indicates that the isobutylene radical cation ($\mathbf{1}^{+\bullet}$) is not acidic enough to protonate the base (acetonitrile). The resulting radical, although allylic, is not expected to be particularly stable since it is primary on both ambident ends; deprotonation will therefore be less favorable.

Addition reactions to the solvent (acetonitrile) have been observed for both radicals (addition to the carbon of the CN triple bond)[2b,9] and for cations (electrochemistry; addition to the nitrogen of the CN triple bond).[2b,8] While nucleophilic addition of acetonitrile to radical cations is not commonly observed, some related reactions have been reported and these are listed in Chart 1.[2b,10,11]

One of the products in the photoinduced electron-transfer reactions of 1,4-bis(methylene)cyclohexane in the presence of **2** in acetonitrile was the result of addition of the alkene radical cation to acetonitrile. The intermediate distonic radical cation in this case was trapped by cyanide anion rather than the 1,4-dicyanobenzene radical anion ($\mathbf{2}^{-\bullet}$), i.e., a tandem nucleophilic addition.[2b] Roth et al.[10b] found a similar product in their studies on the photoinduced electron-transfer reactions of (1*R*,5*R*)-(+)-sabinene.[10h]

A particularly interesting example is the nucleophile-assisted C−Si bond cleavage reaction of substituted benzylsilane radical cations.[10d] In this study acetonitrile and methanol were both used as the nucleophiles in non-hydrogen-bonding solvents. Under certain conditions, the reaction with acetonitrile was actually faster than the corresponding reaction with methanol. The rate constants for these bimolecular processes vary between 1.2×10^5 and 3.2×10^9 $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$, depending on the substituents. However, in dilute solution of methanol in acetonitrile, the rate constant for the reaction of the radical cation with methanol is 46 times that for the reaction with acetonitrile.

As mentioned above, the measured (CV) OP of **1** is high enough to expect some cycloaddition products. There were indications (GC/MS) that some cycloaddition products were formed in this reaction, but the amounts were considered insignificant. When a solution of isobutylene (**1**) and 1,4-dicyanobenzene (**2**) in chloroform is irradiated,

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Chart 1

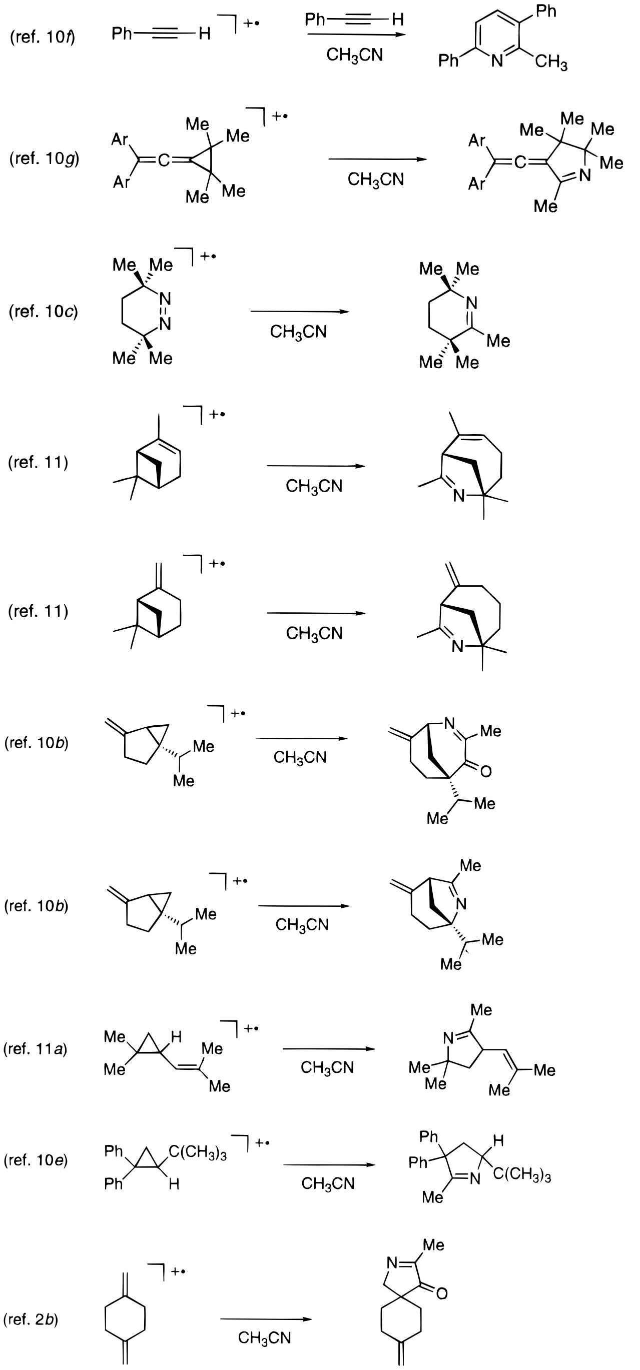


Chart 2

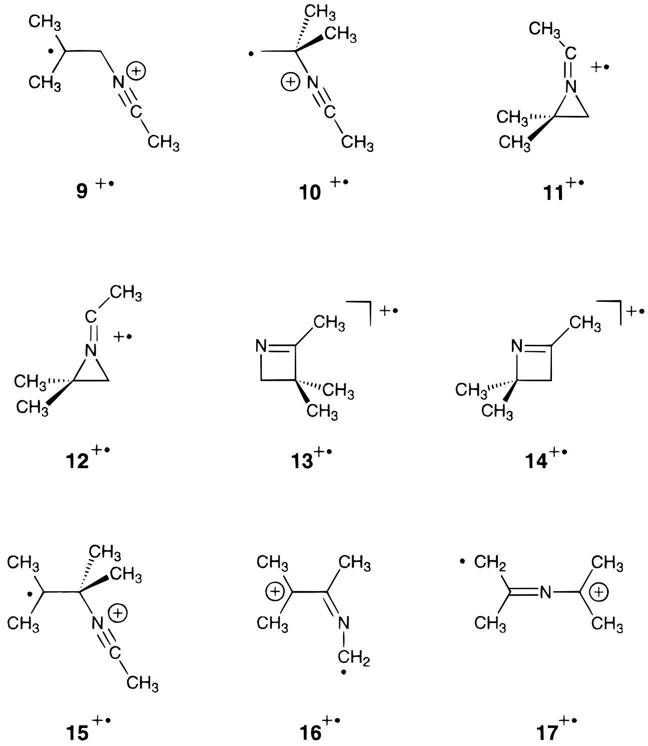


Table 1. Relative Total Energies (MP2/6-31G*//HF/6-31G*) for 2-Methylpropene (1) Intermediates

intermediate	energy (au)	relative energy (kcal/mol)
acetonitrile	−132.333 73	
$\mathbf{1}^{+\bullet}$	−156.302 59	
sum	−288.636 32	0.0
$\mathbf{9}^{+\bullet}$	−288.678 39	−26.4
$\mathbf{10}^{+\bullet}$	−288.680 35	−27.6
$\mathbf{11}^{+\bullet}$	−288.647 82	−7.2
$\mathbf{12}^{+\bullet}$	−288.648 08	−7.4
$\mathbf{13}^{+\bullet}$	−288.657 44	−13.3
$\mathbf{14}^{+\bullet}$	−288.661 66	−15.9
$\mathbf{16}^{+\bullet}$	−288.690 48	−34.0
$\mathbf{17}^{+\bullet}$	−288.703 20	−42.0

Table 2. Relative Total Energies (MP2/6-31G*//HF/6-31G*) for 2,3-Dimethyl-2-butene (8) Intermediates

intermediate	energy (au)	relative energy (kcal/mol)
acetonitrile	−132.333 73	
$\mathbf{8}^{+\bullet}$	−234.670 82	
sum	−367.004 55	0.0
$\mathbf{15}^{+\bullet}$	−367.024 72	−12.7

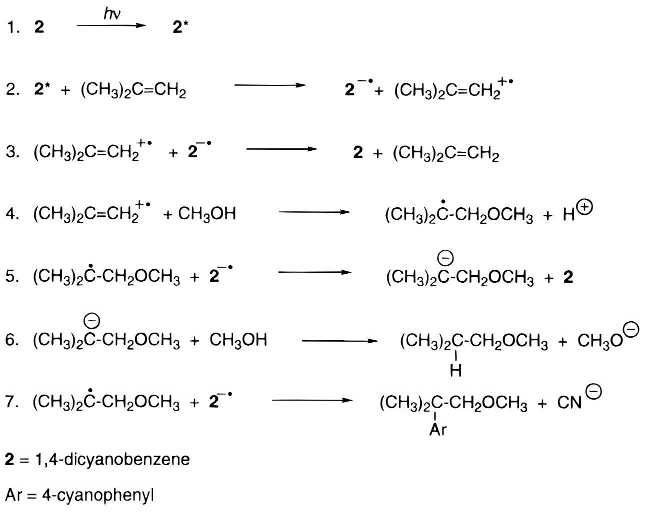
as expected, only cycloaddition products were observed. The tentative identification of these cycloaddition products is based on their mass spectra which show significant similarities to those observed in the reaction of MCP with **2**.[2c] Comparison of the final product mixtures (GC/FID and GC/MS) of the reactions carried out in acetonitrile and in chloroform confirms the initial observation; appreciable amounts of cycloaddition products are not formed in the polar solvent.

From the results described above it can be concluded that electron transfer from **1** to **2** does take place even though the oxidation potential of **1** is relatively high. This could mean that the measured value (CV, $E^{ox} = 2.65$ V vs Ag/Ag$^+$; 2.99 V vs SCE)[5] is incorrect. The expected value, based on the ionization potentials, is between 2.2 V (adiabatic IP, calculated) and 2.7 V (vertical IP, calculated).[2c] Using the experimentally determined vertical IP,[7d] a value of 2.58 V for the OP is predicted.[2c] A value close to the latter seems the most likely since small amounts of cycloaddition products were observed, consistent with the value for ΔG_{ET} (eq 1) close to zero.

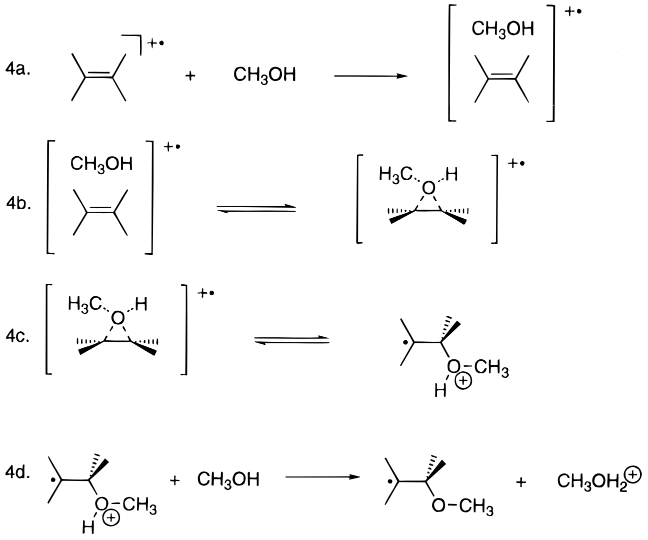
To account for these observations (addition of $\mathbf{1}^{+\bullet}$ to acetonitrile; no deprotonation), ab intio molecular orbital calculations (MP2/6-31G*//HF/6-31G*) were performed on the species shown in Chart 2. The results (energies) of these calculations are summarized in Tables 1 and 2. The reaction of isobutylene radical cation ($\mathbf{1}^{+\bullet}$) with acetonitrile can proceed in a number of ways. Considering the proposed mechanism for the photo-NOCAS reaction with methanol as the nucleophile (Scheme 4),[1d] the addition step (step 4) may involve a number of intermediates (Scheme 5): a dipole-induced radical-ion complex (a), a bridged radical cation (b), a distonic radical cation (c), and the β-alkoxyalkyl radical (d).[1d,f]

A similar mechanism seems likely for the reaction of

Scheme 4



Scheme 5



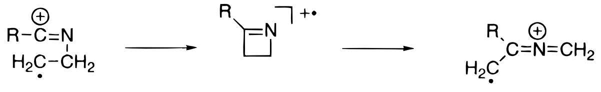
$1^{+\bullet}$ with acetonitrile. Possible intermediates considered are the distonic radical cations (**9**$^{+\bullet}$ and **10**$^{+\bullet}$), the bridged radical cations (**11**$^{+\bullet}$ and **12**$^{+\bullet}$), and the cyclic (four-membered ring) radical cations (**13**$^{+\bullet}$ and **14**$^{+\bullet}$) (Chart 2). Similar calculations were carried out for 2,3-dimethyl-2-butene (**8**) and its corresponding intermediate (distonic radical cation, **15**$^{+\bullet}$).

From the calculated energies listed in Table 1, it is clear that the addition reaction of acetonitrile with **1**$^{+\bullet}$ is exothermic in all cases. Formation of the open distonic radical cations (**9**$^{+\bullet}$ and **10**$^{+\bullet}$) is most favorable. As was observed before, the more heavily alkyl substituted radical is not necessarily the more stable radical![1d,f] The charge density in **9**$^{+\bullet}$ is delocalized on carbons 1, 2, and 4. In **10**$^{+\bullet}$ the charge is even more delocalized: carbons 3, 4, 5, 6, and 7 all bear a significant portion of the total charge (Figure 1). Greater delocalization of the positive charge contributes to a lower energy. The fact that the major product arises from the less stable intermediate (**9**$^{+\bullet}$) is indicative that the formation of this intermediate is kinetically rather than thermodynamically controlled. Steric hindrance causes the nucleophile (acetonitrile) to add to the least-substituted terminal end of this alkene radical cation. This reactivity can also be explained on the basis of the hard−soft acid−base theory.[1f]

9$^{+\bullet}$ **10**$^{+\bullet}$

Figure 1. Atom numbering for the two acetonitrile−isobutylene adduct radical cations **9**$^{+\bullet}$ and **10**$^{+\bullet}$ (see text).

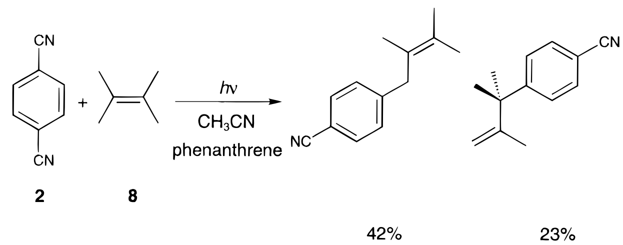
Scheme 6



The bridged radical cations (**11**$^{+\bullet}$ and **12**$^{+\bullet}$) are also stable relative to the summed total energies of the two individual reactants. Both bridged radical cations are symmetric (i.e., both C−N bonds in the three-membered ring are equal). This indicates that these species could be intermediates on the pathway to the more stable ring-opened distonic radical cations (**9**$^{+\bullet}$ and **10**$^{+\bullet}$). There does not seem to be an energetic preference for bonding on either side of the alkene radical cation. This is consistent with the fact that both distonic radical cations (**9**$^{+\bullet}$ and **10**$^{+\bullet}$) are close in energy ($\Delta = 1.2$ kcal/mol). These results are in good agreement with those obtained for methanol as the nucleophile.[1d] The intermediate distonic radical cations in the reaction of 2-methylpropene with methanol differed in energy by only 6.1 kJ/mol (1.5 kcal/mol).

There is no evidence for the involvement of the four-membered cyclic azetine radical cations **13**$^{+\bullet}$ or **14**$^{+\bullet}$. These species are less stable than the distonic (open) radical cations; involvement of these intermediates could result in different products than that observed. The spin density in **13**$^{+\bullet}$ and **14**$^{+\bullet}$ is localized on the nitrogen; reaction of these radical cations with the radical anion of the electron acceptor (**2**$^{-\bullet}$) could result in the formation of species with the nitrogen attached to the phenyl ring and the four-membered ring intact.

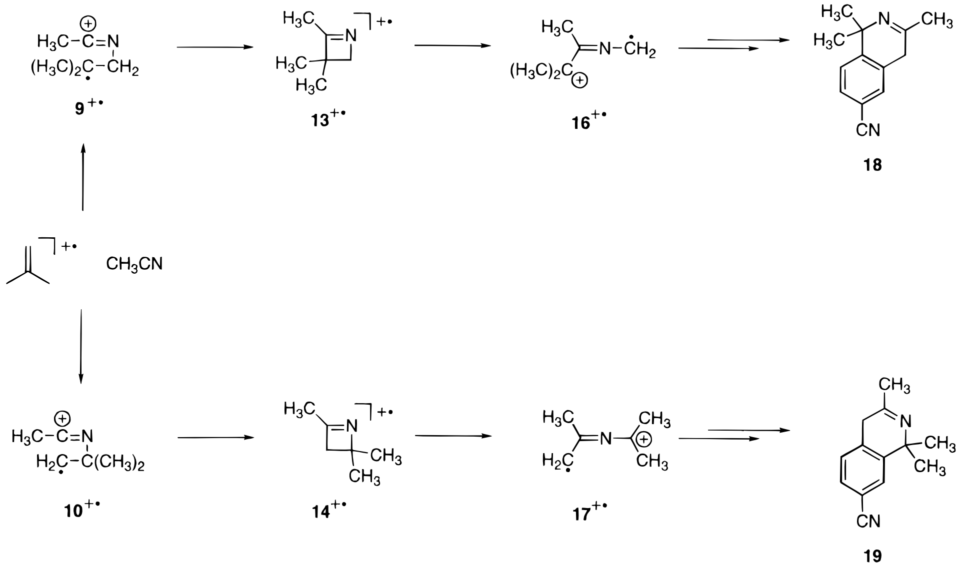
In the absence of a nucleophile, the radical cation of 2,3-dimethyl-2-butene undergoes the usual deprotonation. The resulting allylic radical combines with the radical anion of the electron acceptor at the *ipso* position. Loss of cyanide anion yields the two observed (1:1 substitution) products (reaction [3]).[1a]



[3]

The fact that in the case of **8**$^{+\bullet}$ deprotonation rather than nucleophilic addition is observed can be explained in terms of the lower oxidation potential of **8** and the relatively stable allylic radical that results. The lower oxidation potential ($E_{ox^-} = 1.28$ V (vs Ag/Ag$^+$))[1a] indicates that the radical cation (**8**$^{+\bullet}$) is relatively stable (less reactive). Addition to acetonitrile will therefore be less exothermic than addition of a higher energy (less stable) radical cation such as **1**$^{+\bullet}$. This is confirmed by the ab intio calculations. Addition of **8**$^{+\bullet}$ to acetonitrile is

Scheme 7



exothermic by only 12.7 kcal/mol (Table 2), a value less than half that of the reaction of **1**$^{+\bullet}$ with acetonitrile (Table 1).

It was shown that, in the gas phase, alkyl radical cations can be transferred to nitriles. The initial addition is followed by a rearrangement yielding a distonic radical cation (Scheme 6).[12] In the case of **1** this would lead to the cyclic intermediates **13**$^{+\bullet}$ or **14**$^{+\bullet}$ and, eventually, distonic radical cations **16**$^{+\bullet}$ or **17**$^{+\bullet}$. It was shown above that formation of the cyclic intermediate (**13**$^{+\bullet}$ and **14**$^{+\bullet}$) is energetically favorable. Further calculations show that the distonic radical cations **16**$^{+\bullet}$ and **17**$^{+\bullet}$ are actually the global minima (ca. 7−15 kcal/mol lower in energy than the distonic radical cations **9**$^{+\bullet}$ and **10**$^{+\bullet}$; Table 1). However, formation of these distonic radical cations (**16**$^{+\bullet}$ or **17**$^{+\bullet}$) would lead to different products (**18** and **19**, Scheme 7) than the one observed (**6**), and this mechanism can therefore be ruled out.

So far, isobutylene (**1**) is the only alkene which has undergone this type of photo-NOCAS reaction. Another alkene that shows a somewhat similar behavior is 1,4-bis(methylene)cyclohexane.[2b] This compound also is a terminal alkene with a relatively high oxidation potential (2.49 V vs SCE). As described above, this alkene, upon irradiation in acetonitrile in the presence of an electron acceptor (**2**), was found to add to the acetonitrile to yield an addition product. However, the initially formed distonic radical cation did not combine with **2**$^{-\bullet}$ to give the photo-NOCAS product. In addition to this product, several other products were also formed. Two 1:1 substitution products were detected, indicating that deprotonation was also an important pathway.[2b] Taking these observations into account, we conclude that the photo-NOCAS reaction with acetonitrile as the nucleophile may occur if the oxidation potential of the alkene is relatively high, between 2.5 and 2.7 V (vs SCE) and if deprotonation of the radical cation is unfavorable. Below 2.5 V, deprotonation will be favored; above 2.7 V the initial electron transfer will be exergonic. Obviously, isobutylene (**1**) is well suited for this type of behavior. Other prospective alkenes are currently being studied.

Conclusions

The PET reaction of isobutylene in acetonitrile results in the formation of a photo-NOCAS product with acetonitrile acting as the nucleophile. The initially formed alkene radical cation adds to acetonitrile rather than undergoing a deprotonation. It is believed that deprotonation is relatively unfavorable in this case due to the fact that the resulting allylic radical is primary on both ambident ends. Furthermore, combination of the relatively unstable (reactive) radical cation with the nucleophile (acetonitrile) is favored due to its unhindered terminal alkene. Supporting evidence for this hypothesis was provided by ab initio calculations on the possible distonic radical cation intermediates of this reaction. This is the first example of this type of photo-NOCAS reaction. The addition of a radical cation to acetonitrile was observed in our previous work as well,[2b,11] and in fact, this work has now provided examples of radicals, cations, and radical cations adding to acetonitrile.[2b]

Experimental Section

General Information. The general information on procedures, materials, irradiations, and other experimental techniques has been reported.[1,2]

Irradiation of a Solution of 2-Methylpropene (Isobutylene, 1) and 1,4-Dicyanobenzene (2) in Acetonitrile—Analytical scale. 2-Methylpropene (**1**) was bubbled for 2 min through a solution of 25 mg (2.0×10^{-4} mol) of 1,4-dicyanobenzene (**2**) in 2 mL of acetonitrile. The solution was irradiated for 41 h with the 1-kW lamp. The reaction was followed by GC/FID and GC/MS. Analysis of the final product mixture revealed the presence of one major product (**6**; ca. 70% yield at 60% conversion of **2**).

Irradiation of a Solution of 2-Methylpropene (Isobutylene, 1) and 1,4-Dicyanobenzene (2) in Acetonitrile-*d*$_3$. 2-Methylpropene (**1**) was bubbled for 2 min through a solution of 25 mg (2.0×10^{-4} mol) of 1,4-dicyanobenzene (**2**) in 2 mL of acetonitrile-*d*$_3$. The solution was irradiated for 14 h with the 1-kW lamp. The reaction was followed by GC/FID and GC/MS. Analysis of the final product mixture revealed the presence of only one major product. The mass spectrum (m/z ($M^{+\bullet}$) = 201) indicated that deuterium had been incorporated into the molecule (**6**-*d*$_3$).

Irradiation of a Solution of 2-Methylpropene (Isobutylene, 1) and 1,4-Dicyanobenzene (2) in Acetonitrile—Preparative scale. 2-Methylpropene (**1**) was added to a

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[12] Busch, K. L.; Nixon, W. B.; Bursey, M. M. *J. Am. Chem. Soc.* **1978**, *100*, 1621.

solution of 2.6 g (2.0×10^{-2} mol) of 1,4-dicyanobenzene (**2**) in 200 mL of acetonitrile by ebullition of the gas through the solution for 5 min. The mixture was irradiated with the 1-kW lamp for 8 days. The reaction was followed by GC/FID and GC/MS. Only one product (**6**) was detected. The solvent was evaporated by rotary evaporation, and the residue was chromatographed on silica gel (DCFC) using a hexanes−dichloromethane gradient. The isolated product was characterized by ^{1}H NMR, ^{13}C NMR, IR, and MS and was identified as 7-cyano-1,4,4-trimethyl-2-benzazine (**6**).

7-Cyano-1,4,4-trimethyl-2-benzazine (6): IR (Nicolet) ν 2966 (m), 2931 (m), 2902 (w), 2231 (m), 1637 (m), 1465 (w), 1438 (w), 1387 (w), 1374 (m), 1307 (w), 1295 (m), 912 (m), 732 (s); ^{1}H NMR (AC250, $CDCl_3$) δ 7.77 (d, 1.22 Hz, 1H), 7.71 (dd, 1.22 Hz, 7.93 Hz, 1H), 7.49 (d, 7.93 Hz, 1H), 3.58 (br. s, 2H), 2.45 (s, 3H), 1.24 (s, 6H); ^{13}C NMR (AC250, $CDCl_3$) δ 162.48 (s), 151.26 (s), 134.51 (d), 129.19 (d), 128.30 (s), 124.82 (d), 118.39 (s), 110.55 (s), 59.46 (t), 32.06 (s), 25.86 (q), 23.01 (q); MS *m/z* 198 ($M^{+\bullet}$, 52%), 197 (100), 183 (90), 168 (8), 154 (17), 140 (17), 127 (18), 116 (13), 101 (6), 89 (7), 77 (11), 63 (12), 51 (13); actual mass of ion $C_{13}H_{14}N_2$ 198.1157, measured 198.1166.

Irradiation of a Solution of 2-Methylpropene (Isobutylene, 1) and 1,4-Dicyanobenzene (2) in Chloroform. 2-Methylpropene (**1**) was bubbled for 2 min through a solution of 25 mg (2.0×10^{-4} mol) of 1,4-dicyanobenzene (**2**) in 2 mL of chloroform. The solution was irradiated for 41 h with the 1-kW lamp. The reaction was followed by GC/FID and GC/MS. Analysis of the final product mixture revealed the presence of several products in low yields. On the basis of their mass spectra, these compounds were tentatively identified as cycloaddition products.

Influence of Biphenyl on the Photoinduced Electron-Transfer Reaction of 2-Methylpropene (Isobutylene, 1) and 1,4-Dicyanobenzene (2) in Acetonitrile. 2-Methylpropene (**1**) was bubbled for 1 min through a solution of 25 mg (2.0×10^{-4} mol) of 1,4-dicyanobenzene (**2**) and 30 mg (1.9×10^{-4} mol) of biphenyl (**3**) in 2 mL of acetonitrile. A similar mixture without biphenyl (**3**) present was prepared as well. The solutions were irradiated for 8 h with the 1-kW lamp. The reactions were followed by GC/FID and GC/MS. The reaction was less efficient in the presence of biphenyl (**3**).

Calculations. Ab initio molecular orbital calculations were carried out using the GAUSSIAN 94 package of programs[13] to obtain fully optimized structures (HF/6-31G*) of the radical cations of the alkene−acetonitrile adducts $\mathbf{9}^{+\bullet}$−$\mathbf{17}^{+\bullet}$. A thorough search was made for possible intermediates involved upon reaction of acetonitrile with the alkene radical cations. The results of these calculations, optimized structures and spin and charge density distributions obtained from Mulliken population analysis, are available as Supporting Information. The total energies, corrected for spin contamination, were obtained from single-point calculations with Möller−Plesset perturbation theory (MP2) on the HF/6-31G* geometries and are listed in Tables 1 and 2.

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Supporting Information Available: Results from the ab initio molecular orbital calculations. Optimized geometries and spin and charge distributions of the radical cations $\mathbf{9}^{+\bullet}$−$\mathbf{17}^{+\bullet}$ (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, N.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. GAUSSIAN 94, Revision B.2, Gaussian, Inc., Pittsburgh, PA, 1995.