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Experimental and Theoretical Investigations into the Addition of Cations, Radicals, and Radical Cations to Nitriles†

H. J. P. de Lijser and Donald R. Arnold*

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

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The additions of cations, radicals, and radical cations to nitriles, in particular acetonitrile, have been investigated. The literature reports examples of all of these reactions and on the basis of these reports as well as our own experimental and theoretical results, conclusions can be drawn concerning the preferred mode of addition to the nitrile moiety. There is a clear preference for cations to add to the nitrogen of the nitrile. Similar behavior is observed with radical cations. Radicals, on the other hand, prefer to add to the carbon of the nitrile. Examples of reactions that proceed via these preferred modes of addition, as well as some examples of reactions that do not follow these general trends, are discussed. The experimental results are compared to those of ab initio molecular orbital calculations.

Introduction

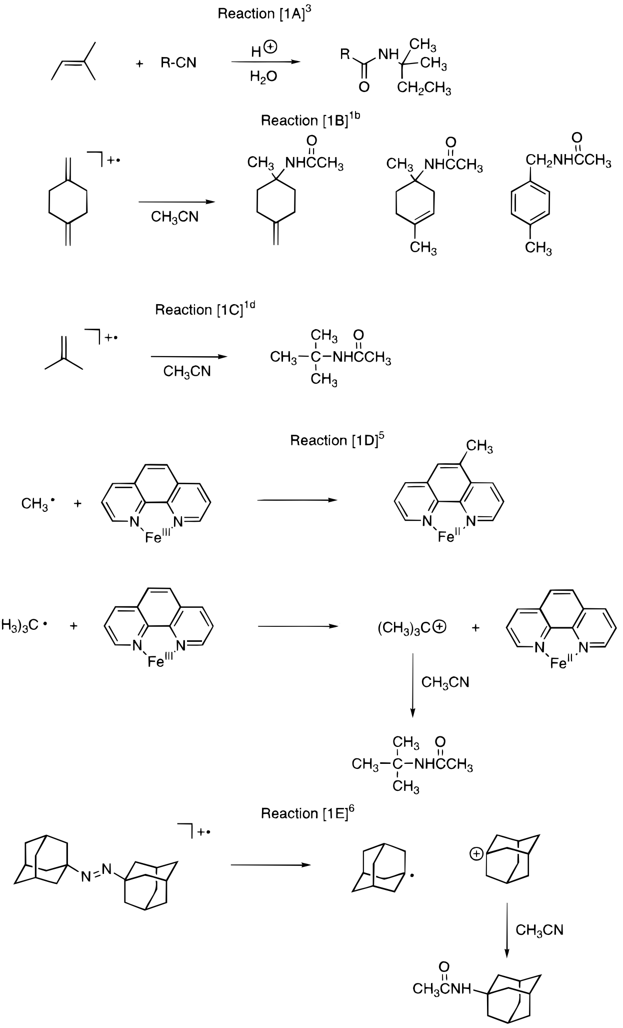
In our studies on the rearrangement and interconversion of radical cations,[1] we have observed a number of examples where the solvent (acetonitrile) plays an important role. From this work there are clear indications that radicals, cations, and radical cations can react with acetonitrile (and other nitriles). Examples of these reactions can be found in the literature; however, for a solvent so frequently used and normally considered to be inert, it is somewhat surprising that this reactivity has not been further explored and exploited. In addition, it must be noted that in some cases there seem to be different mechanistic explanations for these types of reactions, although all lead to the same products. In this paper we provide additional examples of these processes and recent results from ab initio molecular orbital calculations that help explain the observed reactivity.

Results and Discussion

Addition of Cations to Acetonitrile. There are many examples of cationic additions to acetonitrile and to other nitriles (Chart 1), the most common being the Ritter reaction.[3] Reaction of an alkene with nitriles in the presence of sulfuric acid yields amides (reaction 1A). The mechanism for this reaction involves protonation of the alkene followed by addition of the carbocation to the nitrogen of the nitrile. The intermediate iminium ion is then hydrolyzed to give the amide as the final product.

Similar reactions are often observed in electrochemical oxidations, when carried out in acetonitrile solution.[1b,c,4] For example, the anodic oxidation of 1,4-bis(methylene)cyclohexane in acetonitrile yields a number of products which incorporate the solvent (reaction 1B). The mechanism, shown in Scheme 1, involves the intermediate carbocation, and therefore these reactions are often referred to as Ritter-type reactions. Similarly, the electrochemical oxidation of methylenecyclopropane in acetonitrile yields as a final product *tert*-butylacetamide (reaction 1C). The proposed mechanism (Scheme 2) also closely resembles that of the Ritter reaction; the intermediate is believed to be isobutylene which is converted into the final product by an acid-catalyzed process.[1c]

CHART 1



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* To whom correspondence may be addressed. Phone: (902) 494-3714. Fax: (902) 494-1310. E-mail: arnold@chem1.chem.dal.ca.

† This is part 46 in the series Radical Ions in Photochemistry; see refs 1 and 2 for preceding parts of this series.

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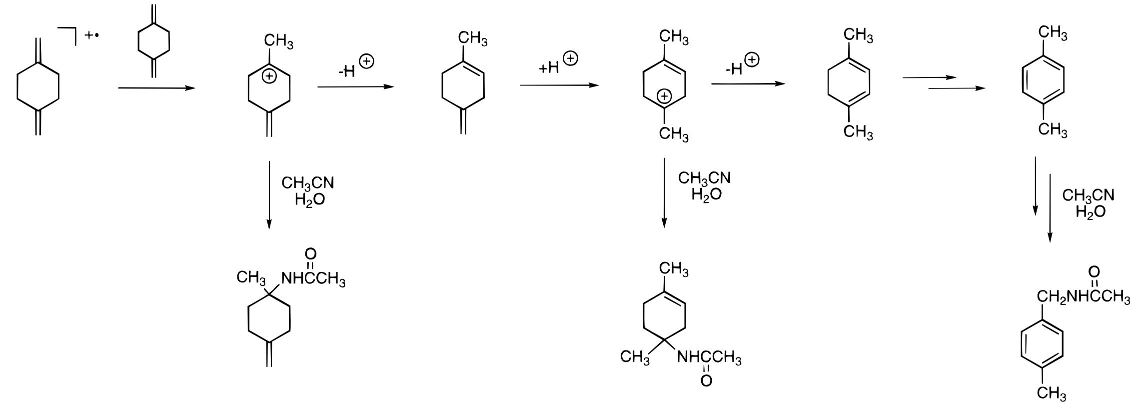
SCHEME 1



SCHEME 2

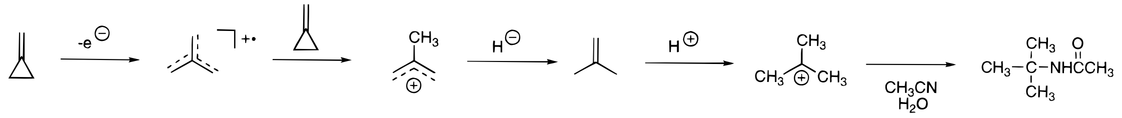


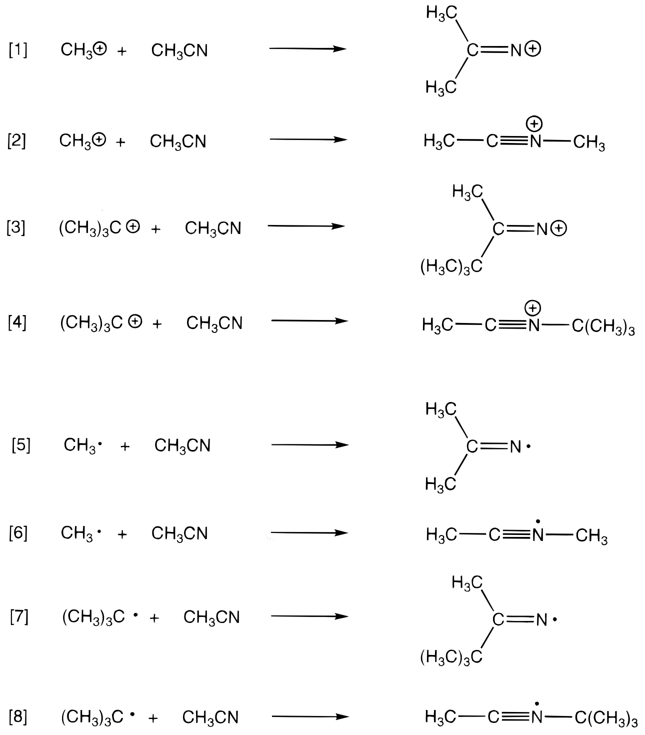
TABLE 1: Calculated Energies (MP2/6-31G*//HF/6-31G*) for the Addition Products of the Reactions $R^+ + CH_3CN$ ($R = CH_3, (CH_3)_3C$)

eq	R	energy (au)	E_{rel} (kcal/mol)
1	CH_3^+	−171.683 43	+85.9
2	CH_3^+	−171.820 35	0.0
3	$(CH_3)_3C^+$	−289.531 58	+87.5
4	$(CH_3)_3C^+$	−289.513 61	0.0

In their investigation on the inner-sphere and outer-sphere electron-transfer processes in the oxidation of alkyl radicals by iron(III), ruthenium(III), and osmium(III) complexes, Kochi and co-workers identified two oxidative processes.[5] An inner-sphere electron-transfer process leads to ligand substitution processes (reaction 1D) whereas an outer-sphere electron-transfer process leads to the formation of cations. The latter process results in the formation of alkenes and *N*-alkylacetamides by reaction of the cation with the solvent (acetonitrile) followed by hydrolysis. In the case of larger alkyl chains, rearrangements were observed for the outer-sphere electron-transfer process (indicative of the carbocation) whereas no rearrangements were observed for the inner-sphere electron-transfer process.

Generation of the radical cation of 1,1′-azoadamantane leads to the formation of the adamantane radical and the adamantane cation.[6] Both species react with the solvent; however, only the reaction of the adamantane cation leads to the amide (reaction 1E). The reaction of the adamantyl radical with acetonitrile will be discussed below.

All of these examples indicate clearly that cations react with acetonitrile in only one way: addition occurs at the nitrogen of the nitrile. The intermediate iminium ion is frequently hydrolyzed to yield the amide. This preferred mode of addition, cation adding to nitrogen, is confirmed by ab initio molecular orbital calculations. A simple model was chosen to test the preferred mode of addition of cations, radicals, and radical cations to acetonitrile. The addition of the methyl cation (eqs 1 and 2), *tert*-butyl cation (eqs 3 and 4), methyl radical (eqs 5 and 6), and *tert*-butyl radical (eqs 7 and 8) to acetonitrile was investigated by performing calculations (MP2/6-31G*//HF/6-31G*) on the intermediates arising from addition to the nitrogen and to the carbon of the CN moiety. The results of the calculations involving the cations are summarized in Table 1.



It is clear from these results that addition will only occur at nitrogen. In fact, for these calculations, initial addition of the carbocation to the carbon of the nitrile and optimizing the structure lead to a rearrangement, ultimately yielding the alternative nitrogen adduct. The difference in energy between these two modes of addition was 85.9 kcal/mol for the methyl cation and 87.5 kcal/mol for the *tert*-butyl cation. These results support the experimental observation: cations add to nitriles at the nitrogen. Comparing the two intermediate cationic species, it is easy to understand why addition to the nitrogen of the nitrile is preferred over addition to the carbon: addition of a carbocation to the nitrogen leads to an iminium ion where the positive charge can be delocalized over both the carbon and the nitrogen. A similar delocalization of the positive charge is not possible upon addition of the carbocation to the carbon of the nitrile (Figure 1).

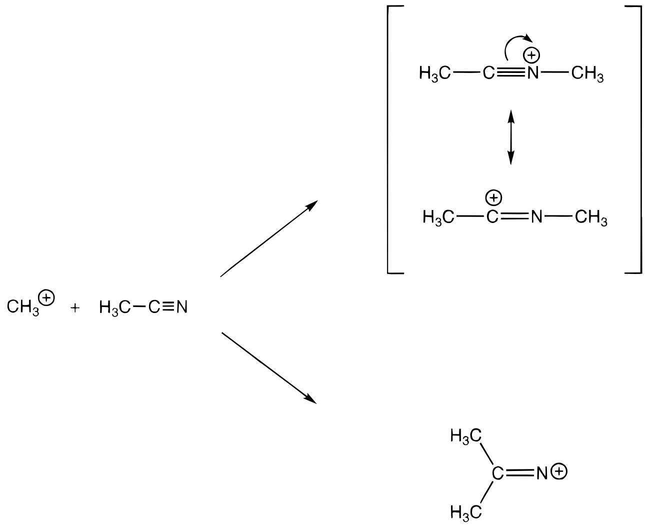
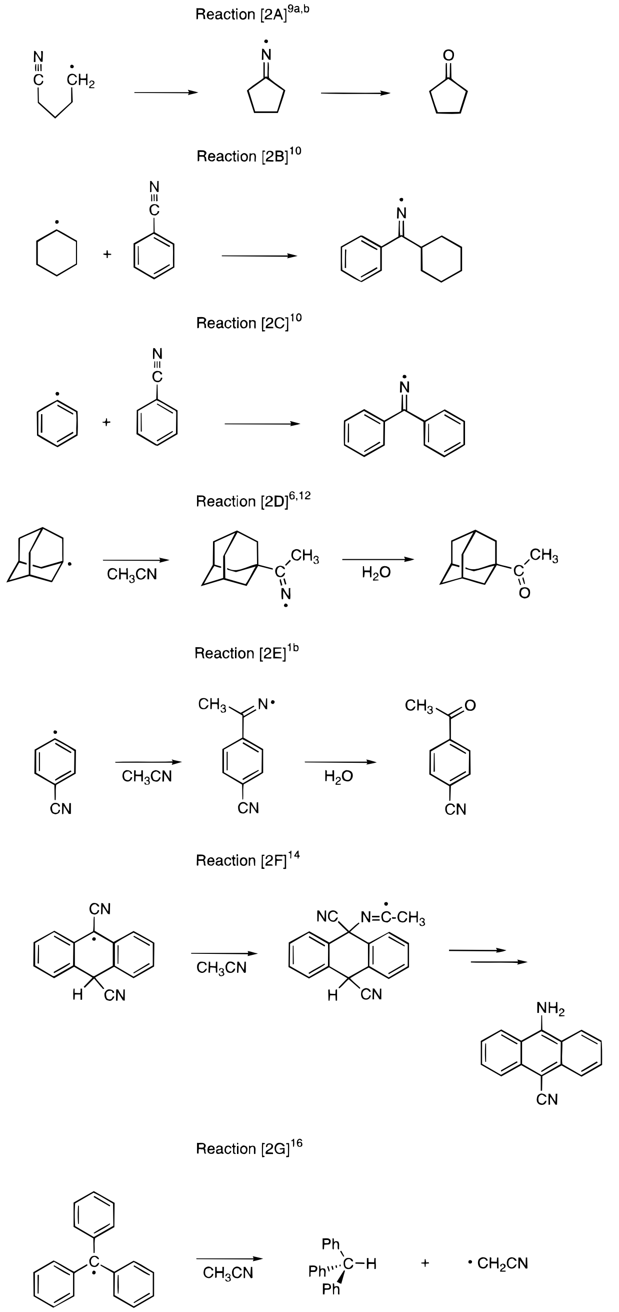
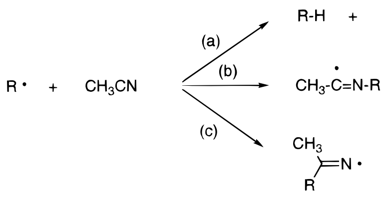


Figure 1.

CHART 2



SCHEME 3



Addition of Radicals to Acetonitrile. In contrast to the vast literature on carbocationic additions to nitriles, there are few reported examples of carbon-centered radicals adding to nitriles (Chart 2).[7] There are, however, several examples of intramolecular carbon radical cyclizations into the nitrile bond.[9] For example, Ogibin et al. found that cyclopentanone was formed ultimately as the major product upon generating the 4-cyanobutyl radical in aqueous media (reaction 2A) (i.e., the radical adds to the carbon of the nitrile).[9a,b] Ingold and co-workers[9e] measured a temperature dependence of the rate constant for this cyclization:

$$\log k\,(\mathrm{s}^{-1}) = (9.9 \pm 1.0) - (8.6 \pm 1.0)/2.3RT$$

Roberts and Winter[9f] measured a rate constant for the same process of $4.5 \times 10^2\ \mathrm{s}^{-1}$ at 259 K, in good agreement with the value obtained from Ingold's equation at the same temperature. This 1,5-exo cyclization is somewhat slower than the corresponding cyclizations of the 5-hexenyl and 5-hexynyl radicals.

Shelton and Uzelmeier have observed some of the few reported additions of carbon-centered radicals to a nitrile. Both cyclohexyl radicals (reaction 2B) and phenyl radicals (reaction 2C) add to benzonitrile.[10] Interestingly, phenyl radicals do not add to pivalonitrile (*tert*-butyl nitrile).[11]

Only three examples of the addition of radicals to acetonitrile are known. The case mentioned above, fragmentation of the radical cation of 1,1′-azoadamantane leads to the formation of adamantyl radicals.[6] These radicals were found to undergo three types of reactions with acetonitrile:[12] (a) hydrogen-atom abstraction, (b) addition to the nitrogen of the cyano group, and (c) addition to the carbon of the cyano group (Scheme 3). Under these conditions, the rate at which the adamantyl radical abstracted a hydrogen from acetonitrile was 4 times the rate of addition to the carbon of the cyano group of acetonitrile. Addition to the nitrogen of the cyano group would lead to the amide (as in the reactions of carbocations with acetonitrile; see above) but this product was present in very small amounts and this pathway is therefore of little significance. Radical addition to the carbon of the cyano group leads to an iminyl radical which ultimately yields a ketone (reaction 2D).[13]

The photoinduced electron-transfer reactions of 1,4-bis(methylene)cyclohexane in acetonitrile with 1,4-dicyanobenzene as the electron acceptor leads to a variety of products.[1b] One of the isolated products was *p*-cyanoacetophenone, which was thought to be a result of addition of the *p*-cyanophenyl radical to acetonitrile, followed by hydrolysis to give the ketone (reaction 2E). Additional evidence for this pathway was obtained by refluxing dibenzoylperoxide in acetonitrile. Analysis of the product mixture revealed the presence of small amounts of acetophenone.

Albini and co-workers have studied the photochemical reactions of 9,10-dicyanoanthracene in acetonitrile−methanol and acetonitrile−water mixtures, containing hydroxide or methoxide anions.[14] One of the products was 10-amino-9-cyanoan-

TABLE 2: Calculated Energies (MP2/6-31G*//HF/6-31G*) for the Addition Products of the Reactions R$^\bullet$ + CH$_3$CN (R = CH$_3$, (CH$_3$)$_3$C)

eq	R	energy (au)	E_{rel} (kcal/mol)
5	CH$_3^\bullet$	−172.030 00	0.0
6	CH$_3^\bullet$	−172.002 17	+17.5
7	(CH$_3$)$_3$C$^\bullet$	−289.531 58	0.0
8	(CH$_3$)$_3$C$^\bullet$	−289.513 61	+11.3

thracene. It was shown by Ohashi et al.[15] that the amino nitrogen originates from the solvent, acetonitrile. The mechanism proposed by Albini et al. involves addition of a carbon-centered radical (a result of protonation of the 9,10-dicyanoanthracene radical anion) to the *nitrogen* of acetonitrile. A hydrogen-atom abstraction (or reduction and protonation) followed by rearomatization (loss of HCN) leads to the imine which, in turn, is converted to the amine (reaction 2F).

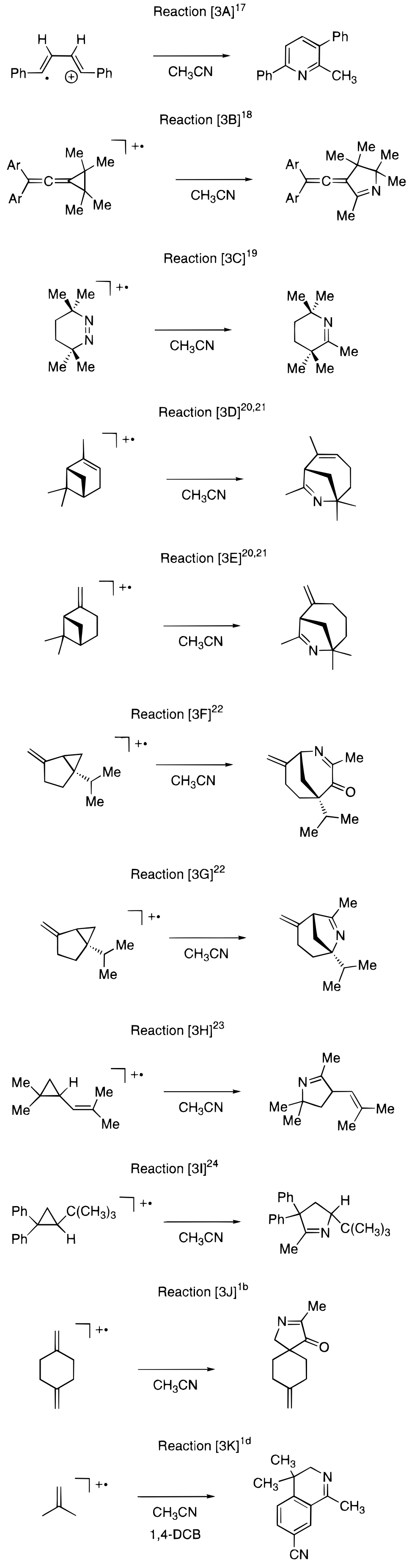
Triphenylmethyl radicals do not add to acetonitrile; only hydrogen-atom abstraction was observed (reaction 2G).[16] This reaction could be influenced by steric effects and spin delocalization; however, the trityl radical does recombine with other radicals (phenyl radical and ·CH$_2$CN).

From the examples discussed above it seems clear that carbon-centered radicals prefer to add to the carbon of the nitrile in acetonitrile and other nitriles. The only exception is the mechanism proposed by Albini for the formation of 10-amino-9-cyanoanthracene.[14] There is no evidence for the proposed intermediate (the carbon-centered imino radical; reaction 2F), and on the basis of Engel's observations[12] this intermediate is more likely to yield the amide, rather than the amine.

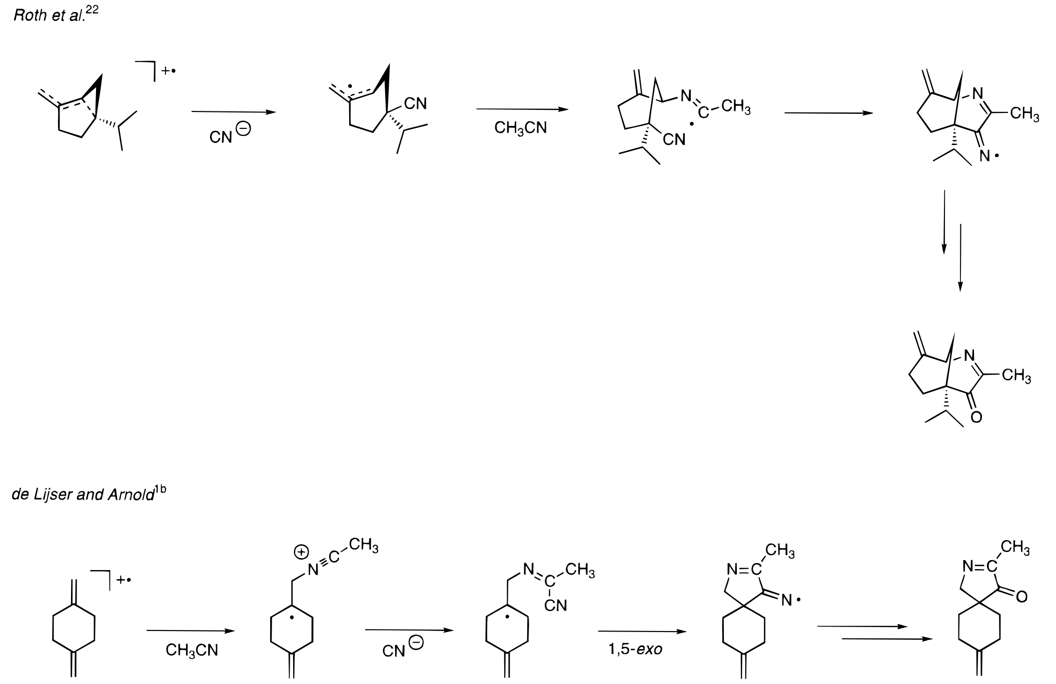
Ab initio molecular orbital calculations support the observations that carbon-centered radicals prefer to add to the carbon of the nitrile (Table 2). The calculations show that addition of the methyl radical to the carbon is more favorable than addition to the nitrogen of the nitrile by 17.5 kcal/mol. Steric effects are important; the addition of the *tert*-butyl radical to the carbon is only 11.3 kcal/mol more favorable than addition to the nitrogen. These results indicate that addition to the carbon is favored over addition to the nitrogen of a nitrile *when the reaction is thermodynamically controlled.* Kinetically controlled reactions (early transition states) could influence this reaction. It cannot be ruled out that this is indeed the case in Albini's reaction.[1d]

Addition of Radical Cations to Acetonitrile. There are also few reports of additions of radical cation additions to acetonitrile (Chart 3).[1b,d,17−24] The majority of these reactions indicate that there is a preference for adding to the nitrogen of the nitrile (i.e., the radical cation behaves as a cation rather than a radical). However, the mechanisms proposed for these reactions do not always reflect this preference. For example, the photoinduced electron-transfer reaction of 1,4-bis(methylene)cyclohexane in acetonitrile with 1,4-dicyanobenzene as the electron acceptor yields a spiroketone as one of the products (reaction 3J).[1b] A similar product was observed by Roth et al. (reaction 3F),[22] however the proposed mechanisms are different (Scheme 4). The authors claimed that identification of the structure was based upon the two-dimensional NOESY NMR spectrum. However, it can be seen from Scheme 5 that a different mechanism (in line with the other observations of radical cation additions to acetonitrile) could account for a product similar to the one proposed. On the basis of a NOESY spectrum only, it would not be possible to distinguish between these two products. The originally proposed mechanism also involves an addition of a carbon-centered radical to the nitrogen of acetonitrile. It was shown above that this type of reaction is unlikely. In addition,

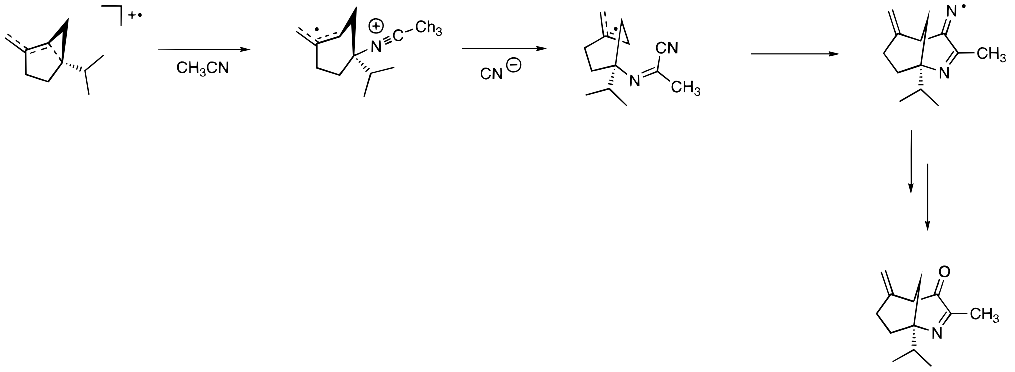
CHART 3



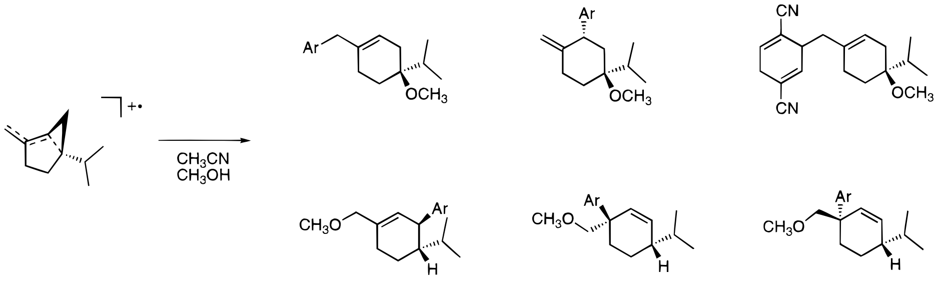
SCHEME 4



SCHEME 5



SCHEME 6



the second product from the same reaction (reaction 3G) shows clearly that acetonitrile has added to the more highly substituted carbon, yielding the expected imine. Furthermore, it must be noted that under different conditions (acetonitrile−methanol as the solvent) none of the observed products arise from nucleophilic attack on the less-substituted carbon (Scheme 6).[25] There is no reason to assume a priori that the nucleophilic preference of acetonitrile is different than that of methanol.

More recently, we investigated the behavior of the isobutylene radical cation in acetonitrile.[1d] It was shown that, under the conditions used, a new type of photo-NOCAS[2] product was formed (reaction 3K). The results were consistent with those obtained from ab initio molecular orbital calculations.[1d] Under similar conditions, but with small amounts of the cyanide anion added to the reaction mixture, the major product is the cyclic ketone shown in Scheme 7.[26] The mechanism for the formation of this product is consistent with the data presented above and argues against Roth's proposed mechanism.

The results from the *ab initio* calculations again confirm the general trends observed in the experimental work. Earlier we have reported results of the calculations concerning the addition of the isobutylene radical cation to acetonitrile.[14] A number of intermediates were considered; however, all were based on the initial assumption that addition takes place at the nitrogen of the nitrile. We have now also considered the products resulting from addition of the isobutylene radical cation to the carbon of

SCHEME 7

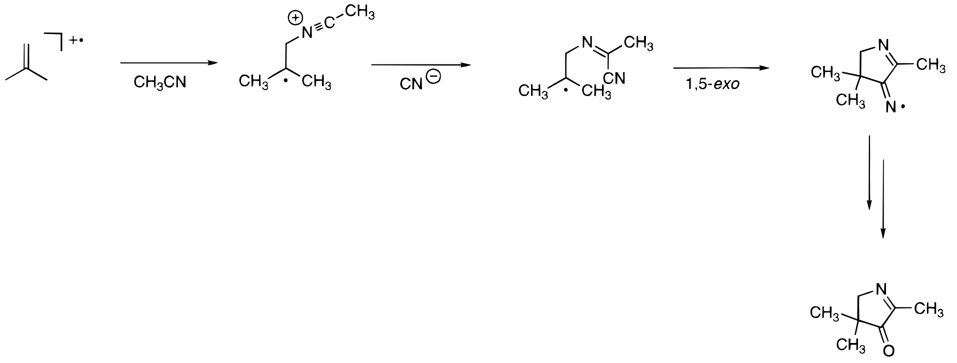


CHART 4

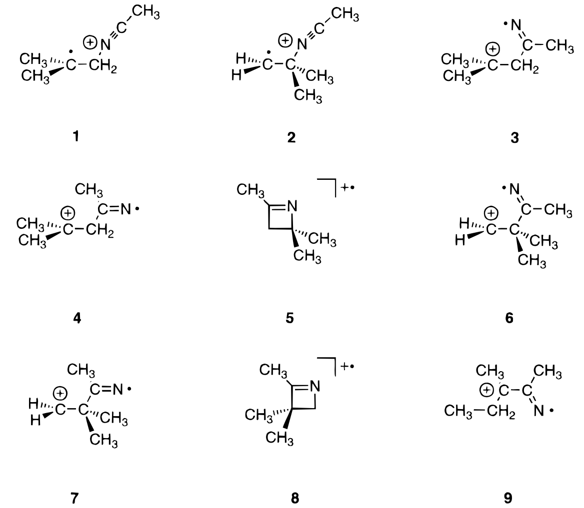
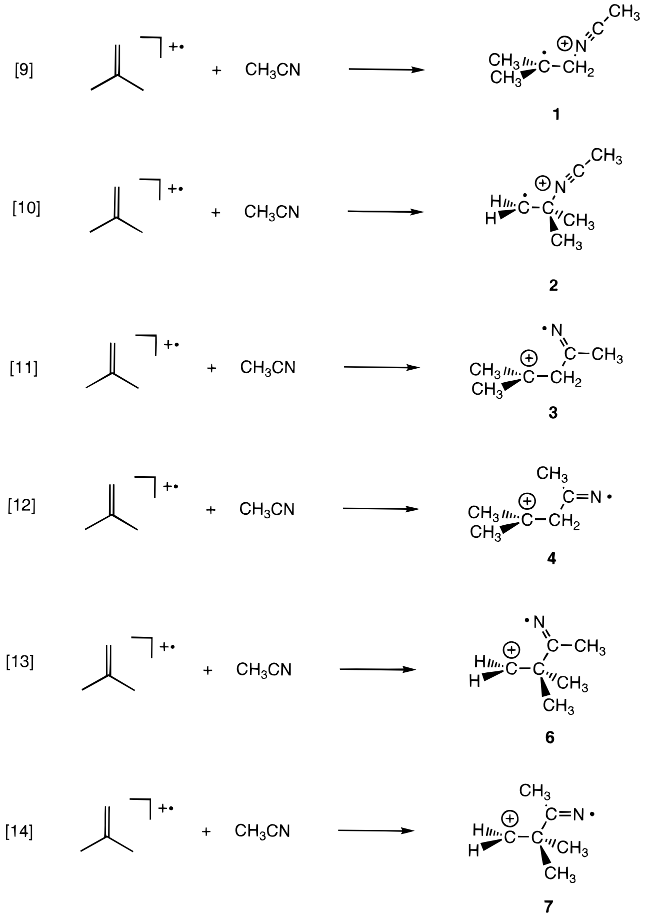


TABLE 3: Calculated Energies (MP2/6-31G*) for the Addition Products of the Isobutylene Radical Cation to Acetonitrile

eq	initial geometry	energy (au)	E_{rel} (kcal/mol)
9	**1**[a]	−288.678 39	+1.2
10	**2**[a]	−288.680 35	0.0
11	**3**[a]	−288.637 11	+27.1
12	**4**[a]	−288.637 12	+27.1
	5[a]	−288.637 11	+27.1
13	**6**[b]	−288.578 64	+63.8
14	**7**[b]	−288.573 67	+66.9
	8[b]	−288.577 91	+64.3

[a] HF/6-31G* optimized geometries. [b] AM1 optimized geometries.



the nitrile. The species that were considered are shown in Chart 4. The results of these calculations (eqs 9−14) are listed in Table 3. It is clear that addition to the nitrogen of the nitrile (eqs 9−10) is favored over addition to the carbon of the nitrile (eqs 11−14). It was pointed out that addition to the more heavily substituted carbon is thermodynamically favored due to a larger charge delocalization.[1d] Under the experimental conditions used, only the kinetically controlled product was observed.

Addition of the terminal methylene of the isobutylene radical cation to the carbon of the nitrile (eqs 11−12) leads to a species (**3**) with an energy that is 27 kcal/mol higher compared to that of the species resulting from addition to the nitrogen of the nitrile (**1**, **2**) (Table 3). A similar species was obtained when starting with the azetine radical cation $\mathbf{5}^{\bullet+}$ as the initial structure and breaking the N−C(CH$_3$)$_2$ bond. Addition of acetonitrile to the more heavily substituted carbon of the isobutylene radical cation (eqs 13−14) is predicted to lead to unstable intermediates; these intermediates gave a rearrangement (1,2-methyl shift to give **9**) upon optimization at the Hatree−Fock level of theory with the 3-21G* basis set. No rearrangement was predicted when the geometries were optimized using AM1. Similar results were obtained when starting with the azetine radical cation $\mathbf{8}^{\bullet+}$ and breaking the N−CH$_2$ bond. Single-point calculations (HF/6-31G* and MP2/6-31G*) were performed on the AM1 optimized geometries in order to obtain an indication of the energies of the unrearranged species. The energies, listed in Table 3, clearly indicate that these species are of much higher energy (ca. 60 kcal/mol) than those resulting from addition to the nitrogen of the nitrile. Together with the fact that a rearrangement occurs spontaneously, this is a clear indication that addition of radical cations to nitriles will occur at the nitrogen rather than the carbon of the nitrile. All the observed products shown in Chart 3 can be rationalized in this way. Comparing once again the intermediates that are formed in these reactions, the preference

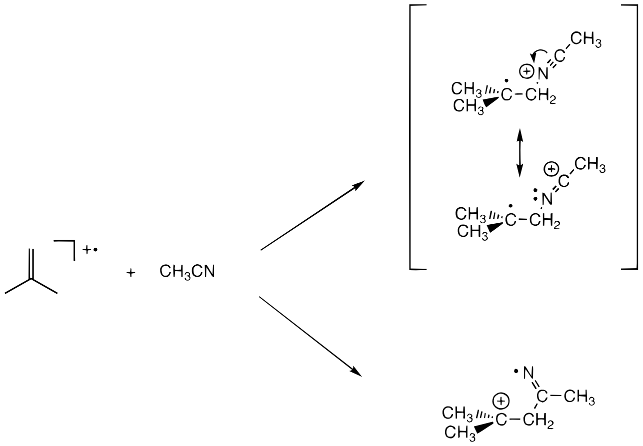


Figure 2.

for addition of the radical cations to the nitrogen of the nitrile becomes clear. Delocalization of the positive charge is possible in the intermediate that is formed upon addition of the radical cation to the nitrogen; no such delocalization is possible for the intermediate formed upon addition to the carbon of the nitrile (Figure 2).

Conclusions

The regiochemistry of the addition of cations, radicals, and radical cations to nitriles, acetonitrile in particular, has been examined and reviewed. From examples available in the literature as well as from our own experiments in combination with newly performed ab initio molecular orbital calculations, it can be concluded that cations react with acetonitrile via the Ritter reaction (i.e., the final products are alkenes (deprotonation) or amides (addition to the nitrogen of the nitrile followed by hydrolysis)). Carbon-centered radicals prefer to add to the carbon of the nitrile, eventually yielding ketones (after hydrolysis of the imine). Intermediates resulting from a carbon-centered radical addition to the nitrogen of the nitrile have been proposed; however, the ab initio calculations do not support this type of reaction. Radical cations were shown to behave as cations and add to the nitrogen of the nitrile. The intermediate distonic radical cations can then undergo a variety of follow-up reactions.

Experimental Section

General Information. The general information on procedures, materials, irradiations, and other experimental techniques can be found in the previous parts of this series.[1,2]

Calculations. Calculations were performed using the Gaussian 94 package of programs[27] and the MacSpartan program.[28] Geometry optimizations were performed at the AM1 and the Hartee−Fock level of theory with the 3-21G* and 6-31G* basis sets. The total energies were obtained from single-point calculations with Møller−Plesset perturbation theory (MP2) on the HF/6-31G* geometries. In some cases the AM1 geometries were used (see text for details).

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