and of a simple formula for the metal-hydroperoxide complex has been adopted for simplicity. It is recognized that the metal exists in a more highly coordinated state. This paper does produce evidence, however, that the hydroperoxide complexes with the metal in a 1:1 ratio.
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$$RO_2\cdot + Co^{2+} \rightarrow RO_2^- + Co^{3+} \qquad (18)$$

which implies that only the addition of a proton is needed to result in the generation of a complex which can produce initiation through reaction 6. Evidence against the validity of this implication is the fact that the lower valence ions of Co[1,3,22] and Mn[11,23] are experimentally observed to produce true inhibition. To do so they must react to remove one of the radicals responsible for chain propagation by a reaction which cannot result in the initiation of another chain. Emanuel et al.[14] postulate the production of a ketone as a noninitiator product from reaction 18. Tkáč et al.[43] postulate the production of a very stable, long-lived radical complex which does not convert to a hydroperoxide. Ingold[44] cites evidence against this conclusion. In any case, as mentioned before, the experimental evidence for inhibition indicates that the radical scavenging action of Co^{2+} and Mn^{2+} ions does not regenerate a chain initiator.
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Radical Ions in Photochemistry. 5. Photosensitized (Electron Transfer) Cyanation of Olefins[1]

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Abstract: The ultraviolet irradiation of phenyl olefins (1,1-diphenylethylene (Ia), 2-phenylnorbornene (Ib), and 1-phenylcyclohexene (Ic)) and potassium cyanide in acetonitrile–2,2,2-trifluoroethanol solution, in the presence of 1-cyanonaphthalene (II) or methyl *p*-cyanobenzoate (III) photosensitizer (electron transfer), gives good yields of nitriles having the anti-Markownikoff orientation. The reaction is believed to involve electron transfer from the olefin (Ia–c) to the singlet excited state of the sensitizer (II or III) and subsequent reaction of the radical cation of the olefin. Fluorescence quenching studies (the olefins (Ia–c) quench the fluorescence emission of II) and thermodynamic considerations ($E_{1/2}^{\mathrm{ox}}$ of Ia–c, $E_{1/2}^{\mathrm{red}}$ of II and III, and singlet energies) are consistent with the proposed mechanism.

Introduction

We have shown, in previous parts of this series, that the photosensitized (electron transfer) addition of oxygen-centered nucleophiles to olefins can be a synthetically useful reaction for the preparation of alcohols, ethers, and esters having the anti-Markownikoff orientation.[3] The utility of this type of reaction has now been extended to include carbon–carbon bond formation; we have found conditions where cyanide ion can serve as the nucleophile.

There are many photochemically induced nucleophilic aromatic substitution reactions.[4] Several of these examples involve substitution with cyanide ion. However, the examples of photoaddition of nucleophiles to aromatic hydrocarbons[5] are rare and this report describes the first examples of the addition of cyanide ion to olefins.

We found that when 1,1-diphenylethylene (Ia), 2-phenylnorbornene (Ib), or 1-phenylcyclohexene (Ic), in acetonitrile–2,2,2-trifluoroethanol solution, was irradiated in the presence of 1-cyanonaphthalene (II) or methyl *p*-cyanobenzoate (III), (electron acceptor sensitizer), and potassium cyanide (reactions 1, 2, and 4), good yields (between 40 and 50%) of the nitriles having the anti-Markownikoff orientation (IV, VI, VIII, XII, and XIV) were obtained. Products having the Markownikoff orientation were not detected.

Ethers resulting from the anti-Markownikoff addition of the 2,2,2-trifluoroethanol, present as a nonnucleophilic proton source in the reaction mixture, were sometimes formed in small yield (<7%).

The mechanism we propose for the photosensitized (electron transfer) cyanation of olefins is similar to that invoked for the addition of oxygen-centered nucleophiles[3] and is summarized in Scheme I.

In this paper we report the characterization of the products from the photosensitized (electron transfer) addition of cyanide ion to olefins (Ia–c) in acetonitrile and 2,2,2-trifluoroethanol (or methanol-*O-d*) mixtures and the results of photophysical studies which support the proposed mechanism (Scheme I). We also report the oxidation potential of the olefins Ib and Ic

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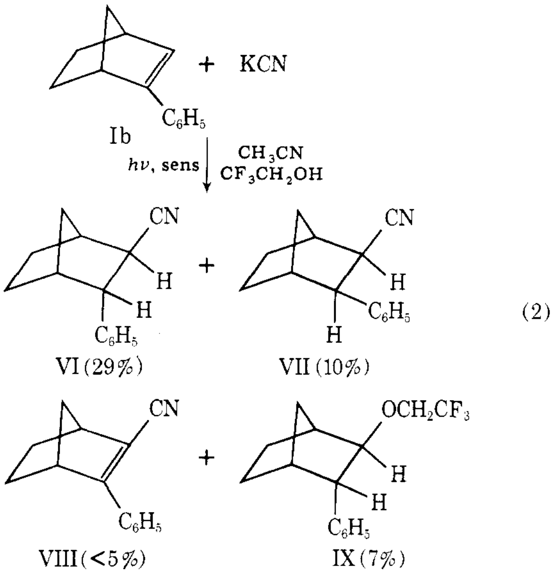
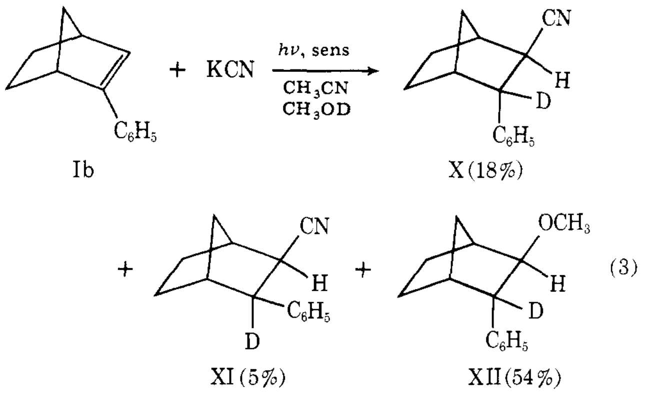
$$\underset{\text{Ia}}{(C_6H_5)_2C{=}CH_2} + \text{KCN} \xrightarrow[\substack{\text{18-crown-6 ether}\\ CH_3CN\\ CF_3CH_2OH}]{h\nu,\ \text{sens}} \underset{\text{IV}(48\%)}{(C_6H_5)_2CHCH_2CN} + \underset{\text{V}(18\%)}{(C_6H_5)_2CHCH_3} \quad (1)$$

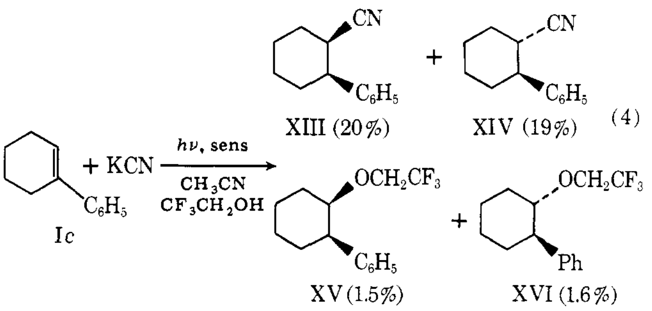
sens: 1-cyanonaphthalene (II), methyl *p*-cyanobenzoate (III)



sens: II



sens: II

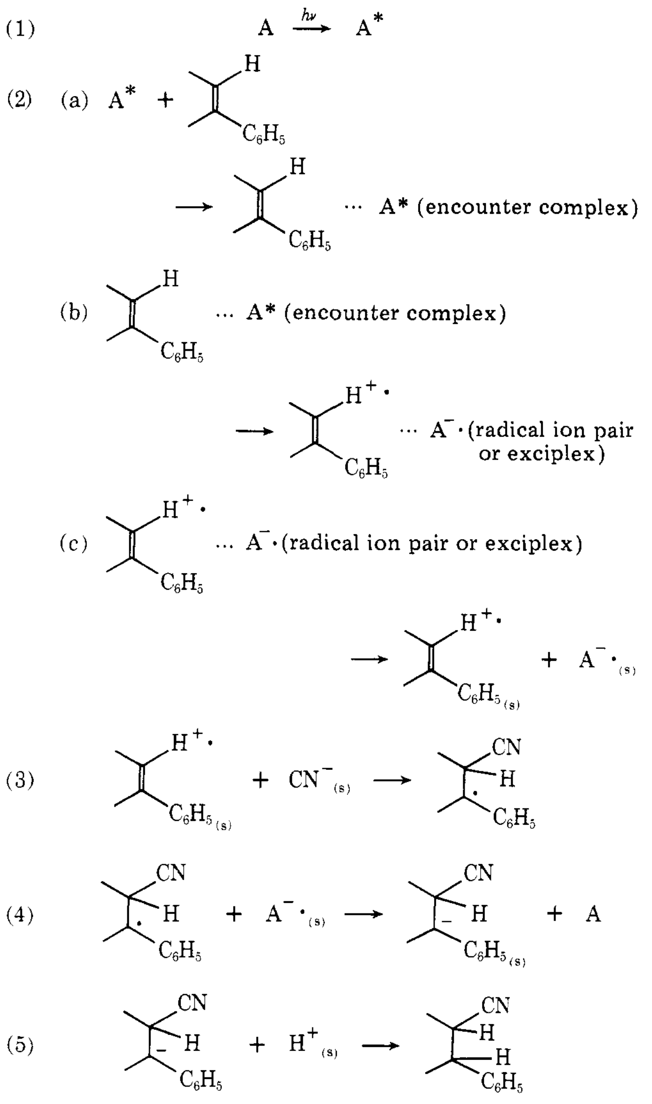


sens: II

in acetonitrile, and discuss the thermodynamics of the electron transfer process (step 2).

This reaction is related to, and in fact should complement, controlled potential anodic cyanation. In the electrolytic process the radical resulting from step 3 would be near the anode and would thus be oxidized to the corresponding carbonium ion, which subsequently should yield a dinitrile (ECE process).[6]

Scheme I

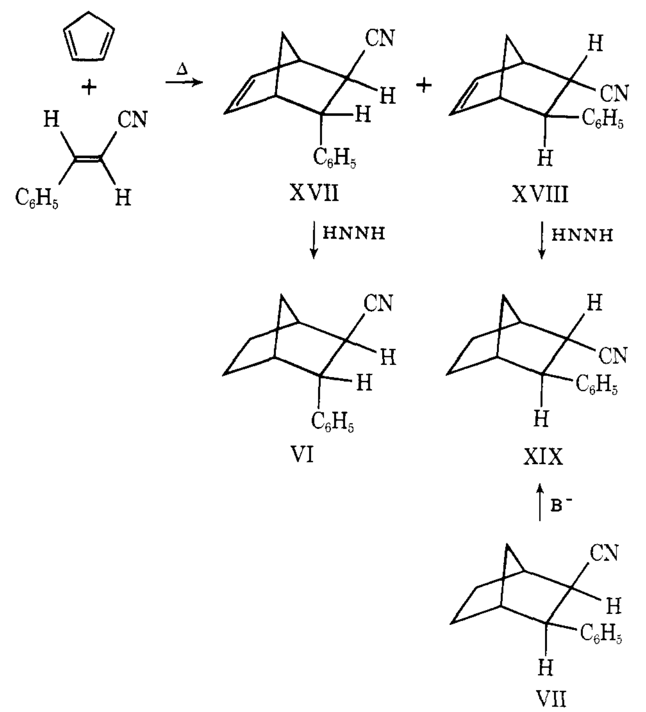


Results

Typical conditions for the photocyanations undertaken in this study involve irradiation of a solution of olefin (0.2 M), sensitizer (0.08 M), 2,2,2-trifluoroethanol (6.0 M), and potassium cyanide (0.4 M) in acetonitrile through a Pyrex filter which absorbs wavelengths shorter than 280 nm. Under these conditions light is absorbed only by the sensitizer. The necessity of the sensitizer was confirmed by separate control experiments; under identical conditions, but in the absence of a sensitizer, no reaction occurred upon prolonged irradiation. In the case of Ia the reaction was more efficient and the yield of nitrile (IV) higher, when the 18-crown-6-ether–potassium cyanide complex was used. The sensitizer was partially (>50%) recovered. The progress of the reaction was followed by nuclear magnetic resonance spectroscopy (NMR) and/or by vapor phase chromatography (VPC). The products were isolated from the reaction mixture by column chromatography and were further purified by preparative VPC. Details are given in the Experimental Section.

The structure of the products of reaction 1 rests on direct comparison of their infrared (IR) spectra with those of authentic samples. The structures and the stereochemistry assigned to the products from reaction 2 were based on an analysis of the NMR spectrum, in conjunction with the corresponding deuterated products from reaction 3, and were confirmed by independent synthesis as outlined in Scheme II.

Scheme II



The triplet signal at δ 3.52 of VI indicated the presence of one exo proton. Irradiation of a solution of 2-phenylnorbornene (Ib) in methanol-*O-d* and acetonitrile, in the presence of II and potassium cyanide (reaction 3), afforded X, which is the corresponding monodeuterated nitrile of VI, and XI, which is the monodeuterated nitrile of VII. (In addition to these products, XII was obtained and identified by comparison with an authentic sample.[3b]) The NMR spectrum of X showed complete loss of the triplet at δ 3.52, which indicates that this triplet is due to H_3. Therefore, the structure of VI was assigned as 2-*exo*-cyano-3-*endo*-phenylnorbornane.

The NMR spectrum of VII displayed a typical ABX multiplet at δ 3.01. This multiplet collapsed to a doublet pair ($J_{2,3}$ = 9 Hz)[7] while H_{7a} was irradiated (δ around 1.53). This indicates that both H_2 and H_3 are coupled to H_{7a} through long-range interaction and is consistent with these two protons being in the endo position. The signal assignment for H_2 and H_3 was consistent with an analysis of the NMR spectrum of the deuterated nitrile XI, which showed a broad singlet at δ 3.0 attributable to H_2 coupled to H_{7a}. This indicates that H_2 is not significantly coupled to H_1 and therefore must be in the endo position. The structure assigned then to VII was 2-*exo*-cyano-3-*exo*-phenylnorbornane.

The presence of a double bond in the minor product VIII was verified by a weak absorption band in the IR spectrum at 1570 cm^{-1}.[8] The mass spectrum of VIII showed a peak assigned to the parent ion. The NMR spectrum showed no olefinic hydrogens. Therefore, the structure tentatively assigned for VIII was 2-cyano-3-phenylnorbornene-2. The structures assigned to VI and VII were confirmed by the alternative synthesis outlined in Scheme II. The spectra (mass, IR, NMR) of the intermediates XVII, XVIII, and XIX are consistent with the structural assignments and are summarized in detail in the Experimental Section.

IX was an expected minor product resulting from the competing addition of 2,2,2-trifluoroethoxide anion. The structure and stereochemistry were established by analysis of its NMR spectrum in a manner similar to that described for VI above.

Reaction 4 gave the epimeric nitriles XIII and XIV and also the epimeric ethers XV and XVI. Both nitriles gave the equilibrium mixture, upon treatment with base. In accord with conformational energy considerations the trans (XIV) was slightly favored (58:42) over the cis (XIII). Additional support for the assigned stereochemistry of the nitriles comes from their NMR spectra. The H α to the cyano group in cis (XIII), being equatorial, is coupled to a lesser extent, to the axial hydrogens in the 2 and 6 positions, than the corresponding axial hydrogen in XIV. Furthermore, the chromatographic behavior of this isomeric pair is as one would predict on the basis of the observed trend.[9] The nitrile XIII, having the dipolar cyano group axial, runs faster than nitrile XIV upon elution on a silica gel column.

Table I. Fluorescence Quenching of 1-Cyanonaphthalene (II) by 1,1-Diphenylethylene (Ia), 2-Phenylnorbornene (Ib), and 1-Phenylcyclohexene (Ic) in Acetonitrile Solution at 20 °C

		kq, M^{-1} s^{-1} [b]		
Fluorophor	τ, ns	Ia	Ib	Ic
1-Cyanonaphthalene	8.92[a]	1.26×10^{10}	4.80×10^{10} [c]	1.43×10^{10}

[a] Taken from ref 3c. [b] Exciting the fluorophor at 313 nm. [c] We consider this value an indication of the magnitude of kq rather than an accurate value, since rapid polymerization and colloid formation occurred after distillation of the purified sample (Ib).

Table II. Half-Wave Oxidation and Reduction Potentials Obtained by Cyclic Voltammetry[a]

Compd	$E_{1/2}{}^{\text{red}}$, V[b]	$E_{1/2}{}^{\text{ox}}$, V[b]
1-Cyanonaphthalene (II)	2.33[c]	*d*
Methyl *p*-cyanobenzoate (III)	2.10[c]	*d*
1,1-Diphenylethylene (Ia)	*e*	1.48[c,f]
2-Phenylnorbornene (Ib)	*e*	1.07[g]
1-Phenylcyclohexene (Ic)	*e*	1.26[f]

[a] Pt electrode, tetraethylammonium perchlorate (TEAP, 0.1 M) in acetonitrile solution, vs. Ag/0.1 M AgNO$_3$. [b] Taken as 0.028 V before the anodic peak potential and 0.029 V before the cathodic peak potential: R. S. Nicholson, *Anal. Chem.*, **38,** 1406 (1966). [c] From ref 3c. [d] In these cases the oxidation wave was not observed, i.e., >2.0 V. [e] In these cases the reduction wave was not observed, i.e., <2.2 V. [f] The oxidative process was not reversible; the half-wave potential was estimated using the 100 mV/s sweep rate. [g] As above (*f*), only the 200 mV/s sweep rate was used.

The identification and the assignment of the stereochemistry of the ethers XV and XVI was based on analogous reasoning and details will be reported elsewhere.

In order to identify the excited state responsible for the photocyanation reaction we have studied the fluorescence of II as a function of the olefin (Ia-c) concentration in acetonitrile solution. The quenching rate constants obtained from these Stern-Volmer plots and the measured fluorescence lifetimes in the absence of quencher (τ) are summarized in table I. The calculated diffusion limited rate constant for acetonitrile solution at 20 °C is kq (diffusion) = 1.82×10^{10} M^{-1} s^{-1}.[10] Therefore, the fluorescence quenching of II by all olefins studied is essentially diffusion controlled.

In order to obtain some indication about the energetics of the electron transfer step (step 2) we have considered the reduction potentials of the sensitizers and the oxidation potentials of the olefins. For this reason, we have studied the electrooxidation and/or reduction processes of these compounds using cyclic voltammetry. Half-wave oxidation and reduction potentials have been calculated from these data and are summarized in Table II.

Discussion

The proposed mechanism for the photocyanation reaction (Scheme I) is similar to that proposed for the photosensitized

Table III. Calculated ΔG for the Electron Transfer Process (Step 2) using Equation 5

Sensitizer	Singlet and triplet energy, kcal mol^{-1}		Calcd ΔG,[a,b] kcal mol^{-1} singlet (triplet) Ia	Ib	Ic
II	89.4[c]	57.4[c]	−2.8 (+29.2)	−12.3 (+19.7)	−7.9 (+24.1)
III	95.3[c]	72.0[d]	−14.0 (+8.3)	−23.5 (−0.17)	−19.2 (+4.1)

[a] The energy required for the electron transfer process (step 2b), assuming the encounter distance to be 7 Å and the dielectric constant of acetonitrile (ϵ_{25} 36.7). [b] The singlet and the triplet energy of the sensitizer was used. From the absorption spectra of the olefins we estimated their singlet energies to be E_s(Ia) $\geqslant$ 97.9 kcal mol^{-1}, (Ib) $\geqslant$ 96.9 kcal mol^{-1}, (Ic) $\geqslant$ 98.6 kcal mol^{-1}. The triplet energies of the olefins (Ia–c), while not known, are certainly less (note experiment with acetonaphthone in text) than the triplet energies of II and III and therefore the electron transfer process cannot be more favorable than calculated here. [c] Taken from ref 3c. [d] D. R. Arnold, J. R. Bolton, G. E. Palmer, and K. V. Prabhu, in press.

(electron transfer) addition of oxygen nucleophiles to phenyl olefins.[3a,b] The first step involves excitation of the sensitizer (A). This can be achieved by irradiating through a Pyrex filter which absorbs radiation of wavelengths shorter than 280 nm. There was no evidence in the UV/vis absorption spectra of charge transfer complex formation between the ground-state molecules.

Step 2 is the electron transfer step which may involve the sequential formation of an encounter complex, an exciplex, a radical ion pair, and finally the solvent-separated radical ions. We have little evidence pertaining to the various stages involved. However, a reasonable correlation concerning the free-energy change (ΔG) associated with the electron transfer process can be made using fluorescence emission quenching, oxidation and reduction potentials, and singlet energy.[11-13] We have used eq 5, first proposed by Weller[11b] to correlate (experimental and calculated) electron transfer quenching rate constants, in order to obtain some indication about the energetics of step 2.

$$\Delta G\ (\text{kcal mol}^{-1}) = 23.06 \times \left[E(\mathrm{D/D^+})v - E(\mathrm{A/A^-})v - \frac{eo^2}{\epsilon\alpha} \right] - \Delta E_{0,0}(\text{kcal mol}^{-1}) \quad (5)$$

The term in brackets represents the energy required for the electron transfer and it is a function of the oxidation potential of the donor (E(D/D$^+$)) (in this case the olefin), the reduction potential of the acceptor (E(A/A$^-$)) (in this case the sensitizer), and the Coulombic attraction term. We have measured the peak potentials using cyclic voltammetry and from the values obtained gleaned the half-wave potentials.[14] When the electrooxidation or reduction processes are not reversible the half-wave potentials do not have thermodynamic significance. Nevertheless, since they were obtained under identical conditions they are internally consistent and have been shown to be useful.[3c,11b,13a] We believe that in this polar medium (acetonitrile, ϵ_{25} 36.7), the Coulombic attraction term is small (1.3 kcal mol^{-1}, assuming an encounter distance of ca. 7 Å) and the radical ions can dissociate before reaction.

The energy available for the electron transfer process is the lowest singlet or triplet energy of the donor or acceptor. In the case of the singlet, the sensitizers (acceptors) have the lowest energy, and in fact the fluorescence quenching studies summarized in Table I indicate that the singlet state of sensitizer II was involved in the reaction. In Table III are listed the singlet energies of the sensitizers, and the calculated ΔG values for the electron transfer process, derived from eq 5. It can be seen that in all cases the electron transfer process is spontaneous.

We have used the nomograph on p 267 of ref 11b to obtain calculated values for the fluorescence quenching process. With Ia and Ic the agreement is fairly good (within a factor of 2) while Ib shows a slightly higher than the calculated experimental value (agreement within a factor of 4). We believe that the observed quenching rate constant with Ib is anomalously high owing to partial polymerization and subsequent formation of polymer suspension in acetonitrile. We consider this agreement between the calculated and experimental quenching rate constants as evidence in favor of the electron transfer quenching mechanism. This is a reasonable conclusion in view of the large difference in the oxidation and reduction potentials of the fluorescer and quencher and the high polarity of the solvent.

During step 2 of the proposed mechanism (Scheme I) the reaction progresses from an excited-state reaction to a ground-state one. Whether or not this transition occurs via an excited-state complex (exciplex) is an interesting and difficult question. The best way to implicate the involvement of an exciplex is to observe emission from it. Exciplex emission, common in nonpolar solvents, is usually quenched by the addition of polar solvents due to the rapid dissociation of the exciplex to give the radical ions. Although weak exciplex emission has been observed in some cases even in acetonitrile solution,[11d,13b] we were unable to detect it from solutions of II quenched by high concentrations of the olefins (Ia–c).

As can be seen from the data in Table III electron transfer to the triplet of the sensitizers is in all cases but one a nonspontaneous process. Furthermore, it is well established[15] that triplet–triplet *energy transfer* would not lead to anti-Markownikoff products. The triplet of Ia will rapidly deactivate owing to the free-rotor effect, while the triplet of Ib and Ic would be expected to yield the Markownikoff addition products.[15a,16] Indeed, 1-phenylcyclohexene (Ic) irradiated in the presence of 1-acetonaphthone (XVII, E_T = 56.4 kcal mol^{-1} [17]) and 2,2,2-trifluoroethanol in acetonitrile gave a good yield of 1-phenyl-1-(2,2,2-trifluoroethoxy)cyclohexane (XVIII).[18]

Step 3 in the proposed mechanism involves reaction of the radical cation of the olefin (Ia–c) with the nucleophile (CN$^-$). The advantage of 2,2,2-trifluoroethanol as a solvent of low intrinsic nucleophilicity,[19] good ionizing ability,[20] and acceptably low acidity[21] (pK_a(H$_2$O) = 12.37), which can also serve as a proton source later on in the reaction, is evident upon comparing the yields of nitriles, VI (X) and VII (XI), vs. that of the ethers IX and XII. The lower acidity permits the dissociation of hydrogen cyanide (pK_a(H$_2$O) = 9.1) and also prevents possible protonation of the olefins to give the Markownikoff products via a ground-state reaction. We have tried to increase the concentration of cyanide ion in solution by the use of 18-crown-6 ether;[4b] this resulted in higher yields of nitriles for reaction 1, but lower yields and longer irradiation times for reactions 2 and 4. The inability to generally improve the reaction with 18-crown-6 ether probably results from the rapid development of colored side products which prevent the further efficient irradiation of the solution. It has been shown that the 18-crown-6 ether (and other polycyclic ethers) undergo transformations when irradiated without KCN in the presence of aromatic hydrocarbons.[4b] The approach of the nucleophile during this step is to the less hindered side and formation of the more stable radical requires the addition in the anti-Markownikoff orientation.

An alternative mechanism can be considered for this step. This would involve an electron transfer from the cyanide ion to the singlet of the sensitizer with the concomitant formation of cyano radical. Subsequent addition of the cyano radical to the olefin would similarly lead to the formation of the more stable radical. However, fluorescence quenching studies indicated that the fluorescence of II is not quenched by cyanide ion ([KCN] = 10^{-2} M), under conditions similar to those employed for the synthetic work.

In step 4 of the proposed reaction sequence the radical resulting from the addition of cyanide ion is reduced by the radical anion of the sensitizer to give the corresponding anion. While this type of electron transfer has received some attention, particularly in the reduction of alkyl halides upon treatment with alkali naphthalenes,[22] it is difficult to predict the energy associated with it. Nevertheless, considering the lack of any products resulting from coupling of the radicals, and the fact that the sensitizer is largely recovered, the electron transfer involved in step 4 (Scheme I) seems reasonable. As a consequence of this step the photochemical (electron transfer) addition of cyanide ion (and other potential nucleophiles) takes a completely different course than that of the anodic addition processes commonly occurring[6] by an ECE mechanism and resulting in the oxidative addition of two nucleophilic groups. A further oxidation of the intermediate radical to give a carbonium ion is inconceivable here since the radical is not subjected to the oxidative environment of the anode, and protonation following back electron transfer results in the formation of monoaddition products.

The final step in the reaction sequence (step 5) deserves some attention. It has been observed with the oxygen nucleophiles[3b] that the proton source approaches the norbornyl anion from the less hindered side yielding exclusively the endo-phenyl exo-substituted norbornanes, while the ratio of isomers from 1-phenylcyclohexene (Ic) indicates comparable rates of protonation from either side of the carbanion intermediate. We were intrigued by the fact that among the products of reaction 2, a considerable amount (10%) of 2-*exo*-cyano-3-*exo*-phenylnorbornane (VII) was present implying that some endo protonation (i.e., trans addition) took place. Control experiments indicated that VI did not isomerize to VII under the basic conditions of the irradiation and VII was therefore a primary product. In order to determine the factors responsible for the unexpected formation of this product (VII) we studied reaction 4. The observed product ratio (cis:trans, 20:19) indicates no preference for trans addition.

Finally, we wish to emphasize the fact that these results greatly enhance the synthetic utility of this type of reaction which previously was demonstrated only with oxygen-centered nucleophiles (water, alcohols, and carboxylic acids). Products VI–XVI are new compounds. Attempts to further extend the reaction to other nucleophiles are now in progress.

Experimental Section

General. Acetonitrile (Aldrich Gold Label) was refluxed over calcium hydride under dry nitrogen atmosphere and fractionated. 2,2,2-Trifluoroethanol (Aldrich Gold Label) was used after distillation. Methanol-*O-d* (Aldrich, 99.5+) was used without further purification. *tert*-Butyl alcohol was distilled over calcium hydride. Pyridine (Eastman Spectro) was distilled over barium oxide. 1-Cyanonaphthalene was sublimed under vacuum, once for the study of the photoreactions and three times for the quenching experiments. Methyl *p*-cyanobenzoate was prepared by acid-catalyzed esterification of *p*-cyanobenzoic acid and purified by recrystallization from ethanol (four times). 1,1-Diphenylethylene (Eastman Kodak Co.), 2-phenylnorbornene (Aldrich), and 1-phenylcyclohexene (Aldrich) were purified by distillation under vacuum; further purification for the quenching experiments and for the measurement of their oxidation potentials was carried out by preparative VPC (10% DEGS, Chromosorb W, NAW, 60/80 mesh) and subsequent bulb-to-bulb distillation prior to their use. 2,2-Diphenylpropanonitrile (IV) was prepared as described by Grebenyuk and Tsukervanik.[23] 1,1-Diphenylethane (V) was obtained by catalytic hydrogenation (Pt on C) of 1,1-diphenylethylene. 18-Crown-6 ether was prepared and purified as described by Gokel and Cram.[24] The dipotassium salt of azodicarboxylic acid (PADA) was prepared and purified as described by Trost.[25] Tetraethylammonium perchlorate (Eastman Kodak Co.) was recrystallized from water four times and dried under vacuum at 65 °C. All irradiations were carried out using a General Electric Co. 1-kW medium-pressure mercury vapor lamp through a Pyrex filter, at 10 °C. The progress of the reaction was followed by NMR and/or VPC. NMR spectra were obtained in deuteriochloroform solution with tetramethylsilane as internal standard, using a Varian HA-100 spectrometer. IR spectra were recorded on a Beckman IR-5A and/or Beckman IR-20A spectrometer and mass spectra on a Varian M-66 or MAT 311A mass spectrometer. Calibration of the IR spectra was done using the 1601.8-cm^{-1} absorption band of polystyrene. The combustion analyses were performed by Chemalytics, Inc., Tempe, Ariz. All reported yields are based on isolated products.

Quenching Experiments. Stern–Volmer plots were obtained using a conventional 90° two-monochromator spectrofluorimeter at room temperature, from the intensity of the spectra at the maximum. The samples were degassed on a mercury-free vacuum line using three freeze–pump–thaw cycles.

Oxidation and Reduction Potential Measurements. Cyclic voltammetric data were obtained using a three-electrode cell with a Princeton Applied Research Electrochemistry System Model 170. The working electrode was a platinum sphere sealed into glass and the counter electrode was a platinum wire. A Ag/Ag^+ (0.1 M) electrode was used as a reference electrode and 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

Irradiation of 1,1-Diphenylethylene (Ia), Potassium Cyanide, and 18-Crown-6 Ether in Acetonitrile–2,2,2-Trifluoroethanol Solution with 1-Cyanonaphthalene (II) (Electron Transfer Photosensitizer). Reaction 1. A solution of 1,1-diphenylethylene (Ia, 450 mg, 2.5 mmol), potassium cyanide (650 mg, 10 mmol), 18-crown-6 ether (2.64 g, 10 mmol), and 1-cyanonaphthalene (II, 382 mg, 2.5 mmol) in 2,2,2-trifluoroethanol (1.5 mL)–acetonitrile (20.0 mL) was irradiated for 90 h. After irradiation the mixture was poured into water and the organic part extracted with diethyl ether. Column chromatography of the ethereal extracts on silica gel (60–200 mesh) using solvents of varying polarity gave the products 2,2-diphenylpropanonitrile (IV, 48%) and 1,1-diphenylethane (V, 18%). The structure proof for these compounds rests upon direct comparison (IR, NMR) with authentic samples prepared by established procedures.

Irradiation of 2-Phenylnorbornene (Ib) and Potassium Cyanide in Acetonitrile–2,2,2-Trifluoroethanol Solution with 1-Cyanonaphthalene (II) (Electron Transfer Photosensitizer). Reaction 2. A solution of 2-phenylnorbornene (Ib, 680 mg, 4 mmol), potassium cyanide (650 mg, 10 mmol), and 1-cyanonaphthalene (II, 308 mg, 2 mmol) in 2,2,2-trifluoroethanol (16 mL)–acetonitrile (20 mL) was irradiated. After 2.5 h of irradiation the solvent was evaporated and the residue was extracted with a benzene–pentane mixture. The mixture obtained, upon chromatography on a silica gel (60–200 mesh) column using solvents of varying polarity, gave the following products: 2-*exo*-cyano-3-*endo*-phenylnorbornane (VI, 29%), 2-*exo*-cyano-3-*exo*-phenylnorbornane (VII, 10%), 2-*exo*-(2,2,2-trifluoroethoxy)-3-*endo*-phenylnorbornane (IX, 7%), and a small amount (<5%) of an impure product which we believe is 2-cyano-3-phenylnorbornene (VIII). Further purification of the products VI, VII, and IX by VPC (10% DEGS, Chromosorb W, NAW, 60/80 mesh) and/or column chromatography was carried out in order to obtain samples for analysis and spectra.

2-*exo*-Cyano-3-*endo*-phenylnorbornane (VI): IR (neat) ν 2980, 2890, 2250, 1620, 1510, 1465, 745, 710 cm^{-1}; ^{1}H NMR $\delta_{\text{Me}_4\text{Si}}(\text{CDCl}_3)$ 7.67–7.25 (m, ArH), 3.52 (triplet, exo H_3), 2.84–2.52 (m, H_1, H_2, H_4), 1.96 (broad doublet, H_{7s}), 1.74–1.14 (m, H_5, H_6, H_{7a}); mass spectrum (70 eV) *m/e* (rel intensity) 197 (100, M^+), 131 (71), 91 (95).

Anal. Calcd for VI ($C_{14}H_{15}N$): C, 85.23; H, 7.66; N, 7.10. Found: C, 85.31; H, 7.40; N, 7.35.

2-*exo*-Cyano-3-*exo*-phenylnorbornane (VII): IR (neat) ν 2930, 2900, 2260, 1508, 1468, 1312, 740, 710 cm^{-1}; ^{1}H NMR $\delta_{\text{Me}_4\text{Si}}(\text{CDCl}_3)$ 7.33–7.08 (m, ArH), 3.10–2.84 (m, H_2, H_3, $J_{2,3} = 9$,

$J_{2,7a}$ = 1.8, $J_{3,7a}$ = 2.0 Hz), 2.75–2.59 (m, H_1, H_4), 2.08 (multiplet center, H_{7s}), 1.77–1.18 (m, H_5, H_6, H_{7a}); mass spectrum (70 eV) *m/e* (rel intensity) 197 (100, M^+), 131 (52), 91 (62).

Anal. Calcd for VII ($C_{14}H_{15}N$): C, 85.23; H, 7.66; N, 7.10. Found: C, 85.14; H, 7.62; N, 7.26.

2-*exo*-(2,2,2-Trifluoroethoxy)-3-*endo*-phenylnorbornane (IX): IR (neat) ν 2980, 1295, 1175, 1130, 980, 750, 710 cm^{-1}; ^{1}H NMR δ_{Me_4Si}(CDCl$_3$) 7.66–7.2 (m, ArH), 3.19 (triplet, H_3, $J_{2,3}$ = 3.5, $J_{3,4}$ = 4.0 Hz), 3.86 (q, methylene, J_F = 8.5 Hz), 3.5 (m, H_2, $J_{2,7a}$ = 1.5 Hz), 2.46–2.41 (m, H_1, H_4), 1.91 (broad doublet, H_{7s}), 1.7–0.93 (m, H_5, H_6, H_{7a}); mass spectrum (70 eV) *m/e* (rel intensity) 270 (100, M^+), 139 (45), 117 (65).

Anal. Calcd for IX ($C_{15}H_{17}F_3O$): C, 66.66; H, 6.34. Found: C, 66.77; H, 6.18.

Irradiation of 2-Phenylnorbornene (Ib) and Potassium Cyanide in Acetonitrile–Methanol-*O-d* Solution with 1-Cyanonaphthalene (Electron Transfer Photosensitizer). Reaction 3. A solution of 2-phenylnorbornene (Ib, 255 mg, 1.5 mmol), potassium cyanide (243 mg, 3.75 mmol), and 1-cyanonaphthalene (II, 115 mg, 0.75 mmol) in methanol-*O-d* (10 mL)–acetonitrile (13 mL) was irradiated for 2 h. After irradiation, the solvent was evaporated and the residue extracted with diethyl ether. Column chromatography of the ethereal extract, using silica gel (60–200 mesh) and solvents of varying polarity, gave the following products: 2-*exo*-cyano-3-*exo*-deuterio-3-*endo*-phenylnorbornane (X, 18%), 2-*exo*-cyano-3-*endo*-deuterio-3-*exo*-phenylnorbornane (XI, 5%), and 2-*exo*-methoxy-3-*exo*-deuterio-3-*endo*-phenylnorbornane (XII, 54%). Further purification of samples for spectral characterization was carried out using VPC (10% DEGS, Chromosorb W, NAW, 60/80 mesh).

2-*exo*-Cyano-3-*exo*-deuterio-3-*endo*-phenylnorbornane (X): IR (neat) ν 2998, 2910, 2262, 1515, 1465, 750, 712 cm^{-1}; ^{1}H NMR δ_{Me_4Si}(CDCl$_3$) 7.66–7.26 (m, ArH), 2.84–2.58 (m, H_1, H_2, H_4), 1.97 (multiplet center, H_{7s}), 1.75–1.10 (m, H_5, H_6, H_{7a}); mass spectrum (70 eV) *m/e* (rel intensity) 198 (100, M^+), 132 (90), 92 (99).

2-*exo*-Cyano-3-*endo*-deuterio-3-*exo*-phenylnorbornane (XI): IR (neat) ν 2970, 2880, 2240, 1500, 1460, 700 cm^{-1}; ^{1}H NMR δ_{Me_4Si}(CDCl$_3$) 7.60–7.22 (m, ArH), 3.00 (broad singlet, H_2), 2.80–2.66 (m, H_1, H_4), 2.11 (multiplet center, H_{7s}), 1.8–0.79 (m, H_5, H_6, H_{7a}).

2-*exo*-Methoxy-3-*exo*-deuterio-3-*endo*-phenylnorbornane (XII): IR (neat) ν 2960, 2880, 1500, 1455, 1126, 1105, 740, 700 cm^{-1}; ^{1}H NMR δ_{Me_4Si}(CDCl$_3$) 7.60–7.30 (m, ArH), 3.5 (sharp doublet, H_2, $J_{2,7a}$ = 1.5 Hz), 3.36 (singlet, methoxy H), 2.54–2.36 (m, H_1, H_4), 1.82 (broad doublet, H_{7s}), 1.7–0.9 (m, H_5, H_6, H_{7a}); mass spectrum (70 eV) *m/e* (rel intensity) 203 (100, M^+), 171 (58), 118 (43), 92 (69), 71 (97).

Preparation of 2-*exo*-Cyano-3-*endo*-phenylnorbornene (XVII) and 2-*endo*-Cyano-3-*exo*-phenylnorbornene (XVIII) (Diels–Alder Reaction). A solution of *trans*-cinnamonitrile (1.3 g, 0.01 mol) and freshly distilled cyclopentadiene (0.66 g, 0.01 mol) in 5 mL of toluene was heated in a sealed glass tube at 154 °C for 64 h. The resultant mixture contained unreacted starting materials and a 1:1 ratio of the products XVII and XVIII (conversion 50%). Repeated chromatography on silica gel (60–200 mesh) using solvent of varying polarity gave 2-*exo*-cyano-3-*endo*-phenylnorbornene (XVII) and 2-*endo*-cyano-3-*exo*-phenylnorbornene (XVIII). Further purification of the adducts was carried out using VPC (10% DEGS, Chromosorb W, NAW, 60/80 mesh) in order to obtain their spectra.

2-*exo*-Cyano-3-*endo*-phenylnorbornene (XVII): IR (neat) ν 3062, 3030, 2980, 2944, 2875, 2232, 2200, 1600, 1620, 1495, 1450, 1336, 1196, 1080, 1030, 905, 868, 745, 720, 698 cm^{-1}; ^{1}H NMR δ_{Me_4Si}(CDCl$_3$) 7.40–7.00 (m, ArH), 6.24, 6.01 (multiplet center, olefinic H, $J_{5,6}$ = 6.0 Hz), 3.68 (doublet pair, H_3, $J_{2,3}$ = 5.0, $J_{3,4}$ = 3.2 Hz), 3.28 (broad singlet, H_1, H_4), 2.40 (doublet pair, H_2, $J_{2,7a}$ = 2 Hz), 1.96–1.56 (m, H_{7a}, H_{7s}); mass spectrum (70 eV) *m/e* (rel intensity) 195 (7, M^+), 130 (60), 67 (21), 66 (100). Exact mass calcd for ($C_{14}H_{13}N$), 195.1048; found (MS), 195.1044.

2-*endo*-Cyano-3-*exo*-phenylnorbornene (XVIII): IR (neat) ν 3065, 3030, 2980, 2880, 2238, 2200, 1500, 1450, 1340, 1160, 1035, 850, 792, 750, 728, 700 cm^{-1}; ^{1}H NMR δ_{Me_4Si}(CDCl$_3$) 7.58–7.04 (m, ArH), 6.56, 6.36 (multiplet center, olefinic H, $J_{5,6}$ = 6/0 Hz), 3.31 (broad singlet, H_1), 3.15 (broad singlet, H_4), 3.03 (broad doublet, coupled to 7a, H_3, $J_{2,3}$ = 5.0 Hz), 2.85 (doublet pair, H_2), 1.6 (multiplet center, H_{7a}, H_{7s}); mass spectrum (70 eV) *m/e* (rel intensity) 195 (3, M^+), 130 (19), 129 (22), 66 (100). Exact mass calcd for ($C_{14}H_{13}N$), 195.1048; found (MS), 195.1045.

Preparation of 2-*exo*-Cyano-3-*endo*-phenylnorbornane (VI) (Diimide Reduction of XVII). The dipotassium salt of azodicarboxylic acid (PADA) (25 mg, 0.13 mmol) and 10 mg (0.05 mmol) of 2-*exo*-cyano-3-*endo*-phenylnorbornene (XVII) were stirred in 0.4 mL of pyridine under nitrogen atmosphere. Glacial acetic acid (0.1 g, 0.1 mL) in 0.2 mL of pyridine was added dropwise over a period of 30 min. The mixture was stirred at room temperature for 6 h. This mixture was poured into water and extracted with ether. The ether layers were washed with dilute aqueous hydrochloric acid and then saturated aqueous sodium bicarbonate. After drying, evaporation gave 10 mg (100% yield) of a colorless liquid with IR and NMR spectra identical with those obtained for the photoproduct VI.

Preparation of 2-*endo*-Cyano-3-*exo*-phenylnorbornane (XIX) (Diimide Reduction of XVIII). The procedure outlined above was used also for the reduction of XVIII to XIX. The product was further purified using column chromatography on silica gel (60–200 mesh) in order to obtain its spectra.

2-*endo*-Cyano-3-*exo*-phenylnorbane (XIX): IR (neat) ν 3060, 3030, 2963, 2882, 2238, 1600, 1493, 1478, 1450, 1300, 1181, 1080, 1032, 752, 730, 700 cm^{-1}; ^{1}H NMR δ_{Me_4Si}(CDCl$_3$) 7.26 (singlet, ArH), 2.96 (broad doublet, H_3), 2.80–2.47 (m, H_1, H_2, H_4), 1.90–1.34 (m, H_5, H_6, H_7); mass spectrum (70 eV) *m/e* (rel intensity) 197 (31, M^+), 131 (53), 115 (34), 91 (100). Exact mass calcd for ($C_{14}H_{15}N$), 197.1204; found (MS), 197.1202.

Base-Catalyzed Isomerization of 2-*exo*-cyano-3-*exo*-phenylnorbornane (VII) to 2-*endo*-Cyano-3-*exo*-phenylnorbornane (XIX). 2-*exo*-Cyano-3-*exo*-phenylnorbornane (VII, 6 mg) was dissolved in 1 mL of *tert*-butyl alcohol under nitrogen atmosphere and a trace of potassium metal was added. After 3 h of stirring at room temperature, the reaction mixture was poured into water and extracted with ether. After drying, evaporation gave 4 mg of product whose IR spectrum was identical with that of XIX.

Irradiation of 1-Phenylcyclohexene (Ic) and Potassium Cyanide in Acetonitrile–2,2,2-Trifluoroethanol Solution with 1-Cyanonaphthalene (Electron Transfer Photosensitizer). Reaction 4. A solution of 1-phenylcyclohexene (Ic, 790 mg, 5 mmol), potassium cyanide (650 mg, 10 mmol), and 1-cyanonaphthalene (II, 308 mg, 2 mmol) in 2,2,2-trifluoroethanol (16 mL)–acetonitrile (20 mL) was irradiated. After 80 h of irradiation the solution was poured into water and the organic part extracted with diethyl ether. Column chromatography of the ethereal extract, using silica gel (60–200 mesh) and solvents of varying polarity, gave the following products: *cis*-1-cyano-2-phenylcyclohexane (XIII, 20%), *trans*-1-cyano-2-phenylcyclohexane (XIV, 19%), *cis*-2-phenyl-1-(2,2,2-trifluoroethoxy)cyclohexane (XV, 1.5%), and *trans*-2-phenyl-1-(2,2,2-trifluoroethoxy)cyclohexane (XVI, 1.6%). Further purification of the above products was carried out using VPC (10% DEGS, Chromosorb W, NAW, 60/80 mesh) and/or column chromatography, in order to obtain analytical samples and spectra.

cis-1-Cyano-2-phenylcyclohexane (XIII): IR (neat) ν 2949, 2874, 2237, 1497, 1449, 893, 855, 772, 745, 697 cm^{-1}; ^{1}H NMR δ_{Me_4Si}(CDCl$_3$) 7.32 (singlet, ArH), 3.08 (broad singlet, H α to CN group), 2.9–2.6 (m, benzylic H), 2.3–1.2 (m, methylene H); mass spectrum (70 eV) *m/e* (rel intensity) 185 (48, M^+), 117 (100), 91 (97).

Anal. Calcd for XIII ($C_{13}H_{15}N$): C, 84.28; H, 8.16; N, 7.56. Found: C, 84.32; H, 7.93; N, 7.74.

trans-1-Cyano-2-phenylcyclohexane (XIV): IR (neat) ν 2920, 2850, 2230, 1486, 1440, 1062, 1013, 750, 692 cm^{-1}; ^{1}H NMR δ_{Me_4Si}(CDCl$_3$) 7.46–7.1 (m, ArH), 2.82–1.1 (m, aliphatic H); mass spectrum (70 eV) *m/e* (rel intensity) 185 (47, M^+), 117 (100), 91 (98).

Anal. Calcd for XIV ($C_{13}H_{15}N$): C, 84.28; H, 8.16, N, 7.56. Found: C, 84.57; H, 8.11; N, 7.48.

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The Loss of C_2H_2O and of C_3H_4O from the Molecular Ions of 3-Phenylpropanal as Studied by Field Ionization Kinetics. Isomerization of the Molecular Ions of 3-Phenyl-2-propen-1-ol

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Abstract: As a result of carrying out field ionization kinetic studies upon the decompositions of labeled analogues of the molecular ions of 3-phenylpropanal we are able to show that the expulsion from these ions both of C_2H_2O and of C_3H_4O proceeds almost exclusively through a mechanism analogous to the McLafferty rearrangement. As the reaction time increases from $10^{-10.2}$ to $10^{-9.6}$ s it is found that some interchange begins to occur between the hydrogen atoms in the aldehydic, benzylic, and ortho positions of the benzene ring. The detailed field ionization kinetic data suggest that this interchange results from the occurrence of two distinct hydrogen exchange mechanisms: (1) interchange between the aldehydic and benzylic hydrogens, and (2) interchange between the aldehydic and ring ortho hydrogens. Similarities between the field ionization mass spectra of 3-phenylpropanal and spectra from its isomer 3-phenyl-2-propen-1-ol suggest that at least some of the molecular ions of the latter isomerize very rapidly to the structure of the molecular ions of the former. Further evidence to support this hypothesis is derived from electron impact ionization studies in which the kinetic energy released in the expulsion of C_2H_2O from the molecular ions of the two compounds has been measured.

Introduction

Until recently it has only been possible to investigate the mechanistic details of gas-phase ionic fragmentation reactions by studying the information contained in the conventional electron impact (EI) mass spectra of specifically labeled precursor neutral molecules. However, such spectral information provides only a time-integrated view of all the decompositions occurring in the first 10^{-6} s after ionization. Unfortunately it is frequently observed that extensive interchanges take place between the hydrogen and/or carbon atoms prior to decomposition. These interchanges can be specific, nonspecific, or incomplete at the time of observation so that it is often difficult to interpret the data obtained from the EI spectra of the labeled compounds. It is frequently difficult to separate the mechanism(s) of decomposition(s) from the interchange process(es), since the rates of interchange are generally comparable with the rates of decomposition.

Field ionization (FI) mass spectrometry and field ionization kinetics (FIK) provide methods whereby even processes which occur extremely rapidly may be studied. In the FIK method decompositions of molecular ions occurring in the first 10^{-11} to 10^{-9} s after ionization can be studied. The technique involves measuring the abundance of fragment ions as a function of field emitter potential while maintaining the electric sector voltage and magnetic field constant. The detection system of the instrument thus remains focused upon ions of some specific m/e value formed at a point in space close to the emitter where they acquire some specific energy (8.45 keV in our experiments). Increasing the emitter potential thus allows one to see decompositions of molecular ions occurring at ever-increasing distances from the emitter, which of course correspond to longer lived molecular ions.[1] The power of FIK has already been demonstrated in numerous cases (see ref 2), and this has prompted us to reexamine the decompositions of the molecular

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