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Reactivity of Radical Cations: Generation, Characterization, and Reactivity of 1,3-Diene Radical Cations[1]

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Conjugated diene radical cations have been generated by either photoionization of the parent diene or photosensitized electron transfer using triplet chloranil or 1,4-dicyanonaphthalene/biphenyl in acetonitrile and have been characterized by laser flash photolysis. The radical cations have a moderately strong absorption in the 340−400 nm region with a broader and weaker band at longer wavelength, in agreement with literature data for the same species in matrices. The radical cations react with anionic nucleophiles with rates that approach the diffusion-controlled limit and are insensitive to oxygen. Reaction of the diene radical cation with its precursor diene is the predominant decay pathway in the absence of added nucleophiles or alkenes and occurs with rate constants on the order of 10^8−10^9 M^{-1} s^{-1}. Product studies for 2,5-dimethyl-2,4-hexadiene indicate that this reaction does lead to dimer formation although the major dimeric product results from substantial rearrangement of the initial adduct. The complex chemistry is consistent with the observation of negative curvature at high diene concentrations in the quenching plots for reaction of the diene radical cations with their precursors. Rate constants for reaction of the diene radical cations with methanol range from 1.2×10^5 M^{-1} s^{-1} for 2,5-dimethyl-2,4-hexadiene to 1.8×10^8 M^{-1} s^{-1} for 2,4-hexadiene and demonstrate the effects of alkyl substitution on the radical cation reactivity. The reactivity of the diene radical cations toward a number of alkyl- and alkoxy-substituted ethylenes was also measured and provides some of the first kinetic data for cross-cycloaddition reactions for simple nonaryl-substituted radical cations.

There is considerable current interest in synthetic applications of radical cation chemistry. Alkene radical cations have been studied extensively from the point of view of both mechanistic studies and synthetic applications,[3−9] with notable examples including the anti-Markovnikov addition of nucleophiles,[10] the photo-NOCAS reaction,[11,12] and cycloaddition reactions to generate either cyclobutanes or Diels−Alder adducts.[13−18] The cycloaddition reactions provide useful alternatives to the conventional thermal Diels−Alder and cyclobutanation reactions. For example, the radical cation-mediated Diels−Alder reaction proceeds readily for electron-rich dienophiles for which thermal Diels−Alder reactions are inefficient.[14,15] In addition, radical cation cycloadditions can be carried out under relatively mild conditions and frequently result in product yields, stereoselectivity, and regioselectivity that equal or surpass their thermal counterparts. The utility of intramolecular radical cation cycloaddition reactions in designing radical cation probes has also recently been demonstrated.[19−21]

Much of the early mechanistic work on radical cation-mediated cycloadditions focused on the dimerization of arylalkenes with more recent examples dealing with diene dimerizations and cross-additions to other alkenes.[3,5,13−17] This work has provided detailed information on the scope of these reactions, the mechanistic pathways involved, and the effects of factors such as the solvent, the method of generation of the radical cation, and redox potentials on controlling the competition

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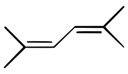
between competing reactions. However, despite this progress, the widespread use of radical cation cycloadditions is still hampered by a lack of kinetic data for the various radical ions. Such data are essential for the design of synthetic strategies that allow one to control the chemistry and maximize product yields and are particularly important in carrying out cross-additions of a radical cation to a different alkene.

There have been a number of recent kinetic and mechanistic studies of the reactions of arylalkene radical cations primarily using laser flash photolysis.[22-24] However, simple alkyl-substituted alkenes have not been extensively studied by time-resolved methods at room temperature under conditions comparable to those used for product studies and mechanistic work. This is despite the fact that a large number of substituted ethylene, conjugated diene, and polyene radical cations have been generated at low temperature in matrices and characterized using UV−visible spectroscopy, ESR, and resonance Raman techniques.[25-28] The only room temperature kinetic data are provided by a laser flash photolysis study of 1,3-dioxole radical cations in aqueous solution and several ESR and pulse radiolysis studies of alkene and diene radical cations, with the latter methods being poorly suited to detailed kinetic studies.[29-33] In particular, the pulse radiolysis results are frequently complicated by the presence of a number of reactive species derived from both the solvent and the alkene. It is thus evident that a routine method for generating alkene radical cations for detailed spectroscopic and kinetic characterization in solution at room temperature is required. We report herein our initial studies on the generation and characterization of radical cations of a number of conjugated dienes using laser flash photolysis. We also report rate constants for the reactions of four diene radical cations (**1**−**4**$^{\bullet+}$) with their precursor dienes and with different alkenes, thus providing some of the first absolute kinetic data for cycloaddition reactions of these important intermediates. The kinetic and mechanistic studies are supported by product studies of the radical cation-initiated dimerization of diene **1**.



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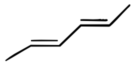

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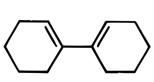

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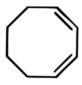

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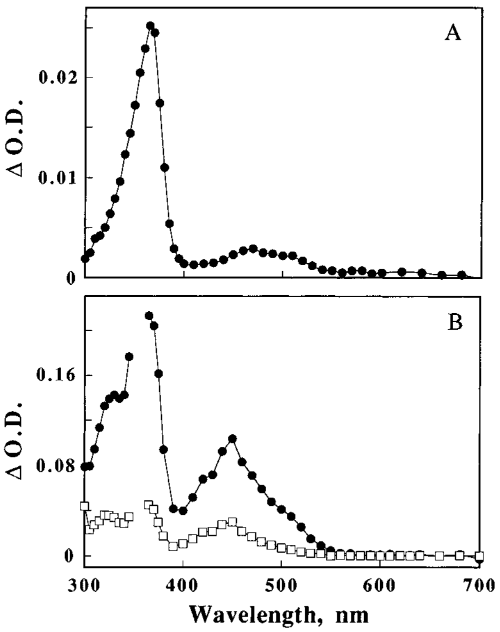
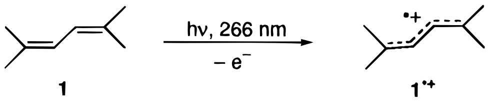


Figure 1. Transient absorption spectra generated by 266 nm laser photoionization of 7.5×10^{-4} M 2,5-dimethyl-2,4-hexadiene (**1**) in aerated acetonitrile (A) and by 355 nm irradiation of a solution of 3×10^{-4} M chloranil and 1×10^{-3} M 2,5-dimethyl-2,4-hexadiene in acetonitrile (B). The two spectra in B were recorded 0.1 (●) and 4.5 (☐) μs after the laser pulse.

Results

Generation and Characterization of 1,3-Diene Radical Cations. (a) Photoionization. Laser excitation of 0.75 mM 2,5-dimethyl-2,4-hexadiene, **1**, at 266 nm in aerated acetonitrile generates a transient absorption spectrum with an absorption maximum at 365 nm and a weaker broad band between 400 and 580 nm (Figure 1A). Decay kinetics for both bands are the same, indicating the presence of a single transient with a lifetime of ~5 μs. This species is assigned to the radical cation produced by photoionization of diene **1**, eq 1. This assignment is based on (1) the similarity of the spectrum in Figure 1A to the reported spectrum for **1**$^{\bullet+}$ generated by γ-irradiation in a freon matrix at low temperature,[26] (2) the fact that neither the yield nor lifetime of the observed transient is affected by oxygen, and (3) the efficient reaction of the transient with nucleophiles such as methanol or bromide ion. Plots of the yield of radical cation as a function of the laser intensity are linear, suggesting that it is formed in a one-photon process. Note that in acetonitrile the photoejected electron is trapped by solvent to give an acetonitrile dimer radical anion that absorbs only weakly below 750 nm and cannot be observed upon excitation of **1** in nitrogen-saturated solutions.[34]



(1)

Attempts to generate the radical cations of a variety of other conjugated dienes (including **2**−**4**) by photoionization using either 266 or 248 nm excitation were unsuccessful. However, a weakly absorbing transient with λ_{max} at 350 nm was observed upon 266 nm excitation

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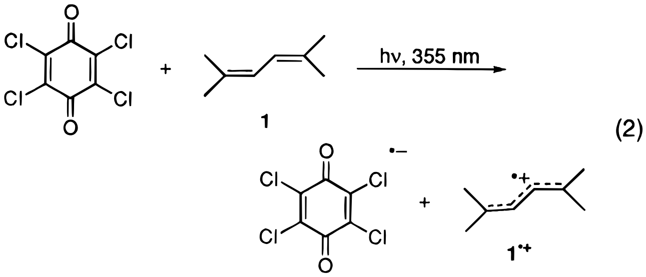
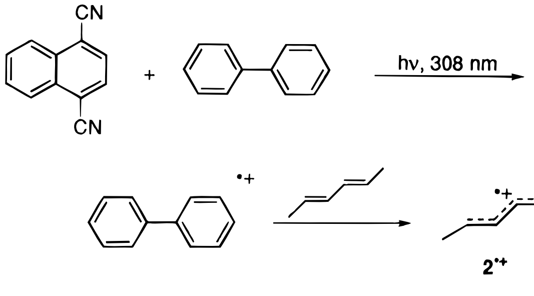
of 2-methyl-2,4-hexadiene in acetonitrile. This transient may reasonably be assigned to the diene radical cation, by analogy to the results described above. There are a number of potential explanations for our failure to observe radical cations upon direct excitation of the other dienes. As discussed below, the diene radical cation reacts relatively rapidly with the diene precursor; the short lifetime of the radical cation at the millimolar concentrations required for sufficient ground state absorption by some of the dienes at the laser wavelength may thus be a limitation. Furthermore, the lower oxidation potential of **1** relative to the other dienes that have been examined may contribute to its facile photoionization. Although it appears that $\mathbf{1}^{\bullet+}$ is formed in a one-photon process, there is ample precedent for the generation of radical cations via biphotonic photoionization.[22] The latter will be very sensitive to the relative extinction coefficients of the radical cation and starting material at the laser wavelength and to the lifetime of the excited state that absorbs the second photon. Variations in these parameters may be responsible for the fact that photoionization is not a suitable method for the generation of diene radical cations that can be readily generated by photosensitized electron transfer, as outlined below.

(b) Photosensitized Electron Transfer. Two different sensitizer systems were used to generate diene radical cations for spectroscopic and kinetic studies. The first method used triplet chloranil which has previously been shown to generate high yields of arylalkene radical cations.[22,35] The efficient formation of free radical ions results from the slower rate of back-electron-transfer for triplet as compared to singlet radical ion pairs. Excitation of 3×10^{-4} M chloranil in acetonitrile with 355 nm laser pulses generates triplet chloranil with absorption maxima at 370 and 530 nm. The triplet is quenched by dienes **1**−**4**, with rate constants of 1.1 and 0.94×10^{10} M^{-1} s^{-1} measured for **1** and **2**, respectively. In each case, triplet quenching is accompanied by the concomitant formation of the chloranil radical anion with λ_{max} at 450 and 320 nm[36] and additional signals attributed to the diene radical cation, eq 2. For example, Figure 1B shows the transient spectra obtained for diene **1**; the 360 nm band observed by photoionization of diene **1** is clearly visible in the spectrum recorded at early times, although the chloranil radical anion obscures the weaker visible band. The decay kinetics of the two species are similar, indicating that a substantial fraction of the radical ions decay by back-electron-transfer. Although the triplet chloranil sensitization method gives good yields of the radical ions, there is substantial overlap of the diene radical cation with the chloranil radical anion for all of dienes **1**−**4**, and bleaching of ground state chloranil also contributes to the spectra at wavelengths <360 nm. Furthermore, it is not possible to remove the radical anion by oxygen quenching, and in all cases the radical cation decays on a similar or faster time scale than the anion at the diene concentrations needed for efficient triplet quenching. Therefore, additional photosensitizers were examined in order to provide cleaner sources of the desired diene radical cations.



(2)

The second sensitization method for the generation of diene radical cations used 1,4-dicyanonaphthalene with biphenyl as a cosensitizer. The addition of a cosensitizer has been widely used to improve the yield of cage escape from singlet radical ion pairs generated by photosensitized electron transfer quenching of singlet states of cyanoaromatics.[22] Thus, efficient quenching of the short-lived singlet requires relatively high concentrations of biphenyl (0.1−0.2 M) and leads to high quantum yields of free radical ions as a result of the slow rate of back-electron-transfer for donors that fall in the Marcus inverted region.[37] The biphenyl radical cation then serves as the oxidizing agent to generate the radical cation of a more easily oxidized secondary donor (eq 3)



(3)

which is added at millimolar concentrations and does not compete with biphenyl for the cyanoaromatic excited state. Note that in addition to giving good yields of radical cations, the cosensitization method also has the advantage of requiring relatively modest concentrations of the secondary donor, an important point when the radical cation is expected to react with its precursor. In the present case 1,4-dicyanonaphthalene was chosen as the singlet sensitizer since, unlike the cyanoanthracenes, it reacts at close to the diffusion-controlled rate with biphenyl and does not absorb appreciably above 350 nm, allowing kinetic measurements of the diene radical cations in this region.[37,38]

Figure 2A shows the transient spectrum of the biphenyl radical cation obtained upon 308 nm excitation of 5×10^{-5} M 1,4-dicyanonaphthalene in oxygen-saturated acetonitrile in the presence of 0.15 M biphenyl. This concentration of biphenyl corresponds to ~95% quenching of the singlet sensitizer, based on a quenching rate constant of 1×10^{10} M^{-1} s^{-1}.[38] The 1,4-dicyanonaphthalene radical anion is efficiently scavenged by oxygen and is not observed in the transient spectrum shown in Figure 2A. Biphenyl radical cation reacts with dienes **1** and **2** with rate constants of 1.7×10^{10} and 1.4×10^{10} M^{-1} s^{-1}, respectively, whereas the reaction with **4** is slightly slower (5.3×10^{9} M^{-1} s^{-1}), eq 3. In each case the product diene radical cation is clearly visible. For example, Figure 2B shows the spectrum of the 2,4-hexadiene radical cation with λ_{max} at 340 nm obtained by quenching

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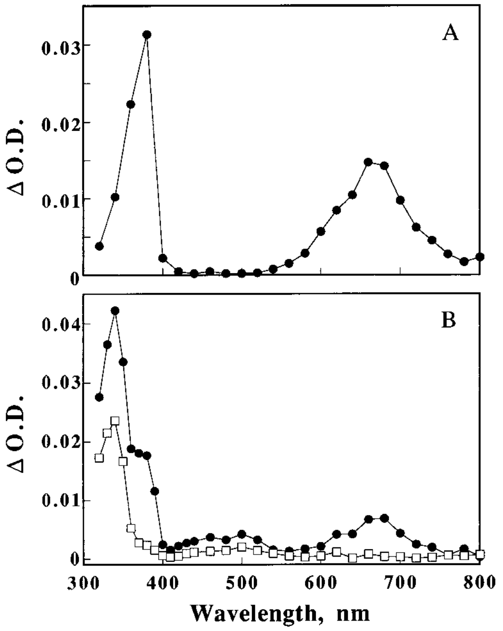

Figure 2. (A) Transient absorption spectrum of the biphenyl radical cation obtained by 308 nm irradiation of 5×10^{-5} M 1,4-dicyanonaphthalene and 0.15 M biphenyl in oxygenated acetonitrile. (B) Transient absorption spectra measured 0.1 (●) and 0.4 (□) μs after 308 nm irradiation of a solution of 5×10^{-5} M 1,4-dicyanonaphthalene, 0.15 M biphenyl, and 1×10^{-3} M 2,4-hexadiene (**2**) in oxygenated acetonitrile.

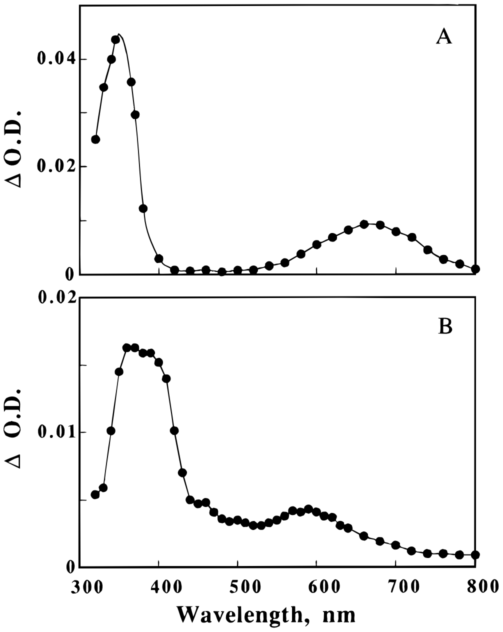

Figure 3. Transient absorption spectra for $3^{\bullet+}$ (A) and $4^{\bullet+}$ (B) generated by 308 nm irradiation of solutions of 5×10^{-5} M 1,4-dicyanonaphthalene, 0.15 M biphenyl, and 1.5×10^{-3} M 1,1-bicyclohexene (**3**; A) or 1×10^{-3} M 1,3-cyclooctadiene (**4**; B) in oxygenated acetonitrile.

the biphenyl radical cation with 1 mM (**2**). Note that some biphenyl radical cation is still visible at 0.1 μs delay, whereas only $2^{\bullet+}$ is observed at longer times. The spectra for $3^{\bullet+}$ and $4^{\bullet+}$ obtained using the same method are shown in Figure 3.

Table 1. Absorption Maxima for 1,3-Diene Radical Cations Generated by Laser Flash Photolysis in Acetonitrile and Rate Constants (k_{diene}) for Their Reaction with the Precursor Diene

diene	$E_{1/2}^{\text{ox}}$, V[a]	$\lambda_{\max}$, nm	k_{diene}, M^{-1} s^{-1} [b]
2,5-dimethyl-2,4-hexadiene, **1**	1.3	365, 470[c] (363, 455, 500)[d]	5.6×10^8
2,4-hexadiene, **2**	1.8	340, 500[c]	6.5×10^8
1,1′-bicyclohexene, **3**	1.7	365, 660	1×10^9
1,3-cyclooctadiene, **4**	1.9	370, 600 (363, 600)[d]	1.8×10^8
2-methyl-2,4-hexadiene		350	
2-methyl-1,3-pentadiene		340, 400−500[c]	
1,3,5,5-tetramethyl-1,3-cyclohexadiene		400, 480−580[c]	

[a] vs SCE in acetonitrile. [b] Estimated as the slope at zero diene concentration by polynomial fitting of the plot of k_{obs} vs [diene]. [c] Visible absorption bands are broad and weak. [d] Radical cation produced by γ-irradiation in a freon matrix.[26]

Data for the electronic absorption spectra for the radical cations of **1**−**4**, 2-methyl-2,4-hexadiene, 2-methyl-1,3-pentadiene, and 1,3,5,5-tetramethyl-1,3-cyclohexadiene in acetonitrile are summarized in Table 1.[39] Most of the radical cations were generated by several routes. Each has $\lambda_{\max}$ in the 340 −400 nm region with a substantially broader and weaker absorption in the visible. An estimate of 11 700 M^{-1} cm^{-1} for the extinction coefficient of $1^{\bullet+}$ at 365 nm was obtained from a comparison of the relative signal intensities for the biphenyl and diene radical cations at their respective maxima of 365 and 670 nm. The relative signal intensities were measured in a set of matched experiments for a sample of 1,4-dicyanonaphthalene and biphenyl alone and an identical sample containing 1 mM diene. It was assumed that quenching of the biphenyl radical cation leads quantitatively to the diene radical cation, and a value of 14 500 M^{-1} cm^{-1} was used for the extinction coefficient of the biphenyl radical cation.[37]

Oxidation potentials for dienes **1**−**4** were estimated by cyclic voltammetry in acetonitrile, and the data are reported as half-wave potentials in Table 1. In all cases the oxidation was irreversible under our experimental conditions. The data demonstrate that the more highly alkyl-substituted dienes are more easily oxidized. 1,3-Cyclooctadiene (**4**) is slightly more difficult to oxidize than 2,4-hexadiene (**2**), in agreement with the fact that **2** reacts with biphenyl radical cation with a rate constant that is approximately 2 times that observed for **4**. This suggests that the relative ordering of the half-wave potentials is reliable despite the fact that all the dienes give irreversible oxidation waves.

(c) Kinetics of Radical Cation Decay in the Absence of Quenchers. The decays of all the diene radical cations can be adequately fit to first-order kinetics under most of the conditions described above, and in all cases the observed rate constants increase with increasing diene concentration. This results in radical cation lifetimes of ≤1 μs for most of the photosensitization experiments. Typical plots of the apparent first-order decay rate constant for $1^{\bullet+}$ and $3^{\bullet+}$ as a function of the precursor diene concentration are shown in Figure 4. In both cases the rate constant increases linearly with diene concentration and then reaches a plateau at concentrations above 1−2 mM. The limiting rate constants in the plateau region for $1^{\bullet+}$ and $3^{\bullet+}$ are 3.5×10^5 and 1.4×10^6 s^{-1}, respectively. Apparent rate constants for reaction of $1^{\bullet+}$ and $3^{\bullet+}$ with precursor diene (k_{diene}) of 5.6 ×

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[39] We were unable to detect radical cations from several other methyl- and methoxy-substituted 1,4-butadienes and several cyclic conjugated dienes (including 1,3-cyclohexadiene).

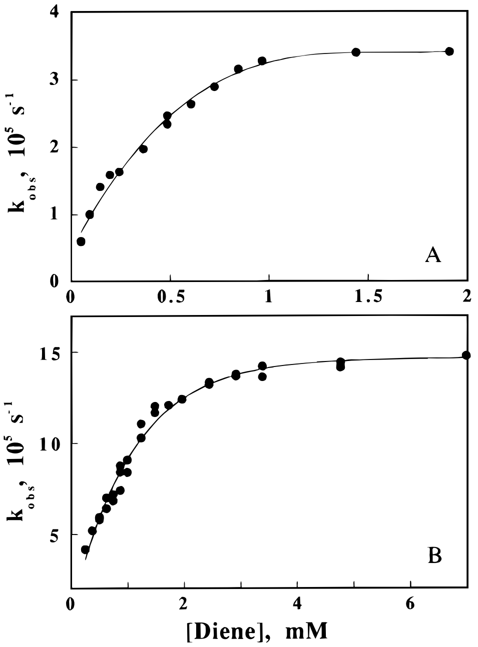

Figure 4. Plots of the observed rate constants for the decay of $\mathbf{1}^{\bullet+}$ (A) and $\mathbf{3}^{\bullet+}$ (B) as a function of the precursor diene concentration.

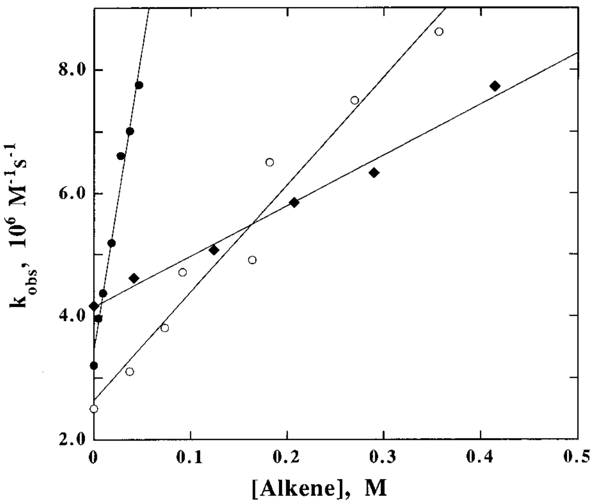

Figure 5. Plots of the observed rate constants for decay of $\mathbf{2}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ as a function of alkene concentration: (●) $\mathbf{2}^{\bullet+}$ with 2-methyl-1-butene, (◆) $\mathbf{2}^{\bullet+}$ with 3-methyl-2-pentene, and (○) $\mathbf{4}^{\bullet+}$ with 2-methyl-1-butene.

10^8 and 1×10^9 M^{-1} s^{-1}, respectively, are obtained as the slopes at zero diene concentrations of the curves obtained by polynomial fitting of the data shown in Figure 4. Similar results were obtained for reaction of $\mathbf{2}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ with their precursor dienes (Table 1). Limiting rate constants of 1.5−2 × 10^6 s^{-1} were reached at ~5 mM diene, with k_{diene} values of ~10^8 M^{-1} s^{-1}. Transient absorption spectra measured at 2 mM **1** showed no evidence for the production of products with absorption in the 330−700 nm region as a result of the reaction of the radical cation with its precursor.

The effect of added lithium perchlorate on the lifetimes of the diene radical cations was examined. Added salts have been shown to substantially increase the lifetimes of radical cation/anion pairs, an effect that is attributed to interactions between the radical anion and the cation of the salt.[9,40,41] In general, the lifetimes of the diene radical cations were substantially longer in the presence of lithium perchlorate. For example, the lifetime for $\mathbf{1}^{\bullet+}$ generated by photoionization increased from 5 μs in acetonitrile alone to 38 and 50 μs in the presence of 0.02 and 0.2 M lithium perchlorate, respectively, although the radical cation yield was the same within experimental error. Similar effects were observed in the photosensitized experiments. The measured lifetime for $\mathbf{1}^{\bullet+}$ generated by the DCN/biphenyl route increased by approximately 1 order of magnitude in the presence of 0.02 M salt. Since the longer radical cation lifetimes were not particularly advantageous for the kinetic experiments, the effects of added salt were not pursued any further.

Reactions with Nucleophiles. The diene radical cations reacted efficiently with a variety of anionic nucleophiles and alcohols. Rate constants (k_{Nu}) for these reactions were obtained as the slopes of plots of the observed rate constant (k_{obs}) for decay of the radical cation as a function of the concentration of added nucleophile, according to eq 4, where k_0 is the observed rate constant

$$k_{\mathrm{obs}} = k_0 + k_{\mathrm{Nu}}[\mathrm{Nu}] \tag{4}$$

for decay of the radical cation in the absence of nucleophile. The data are summarized in Table 2. The results for $\mathbf{1}^{\bullet+}$ were obtained by generating the radical cation by photoionization, while those for the other radical cations were obtained using chloranil photosensitization. Note that the rate constants for decay of $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ were measured at 660 and 600 nm, respectively, to eliminate complications due to the overlap of the radical cation absorption with the chloranil radical anion. This was not possible for $\mathbf{2}^{\bullet+}$, and in this case the radical cation decay was measured at 340 nm where there was also a longer-lived residual absorption due to the chloranil radical anion.

The measured rate constants for reaction of $\mathbf{1}^{\bullet+}$ with chloride, bromide, acetate, and cyanide as well as those for reaction of $\mathbf{1}$−$\mathbf{4}^{\bullet+}$ with nitrate are summarized in Table 2. Reactions of $\mathbf{2}$−$\mathbf{4}^{\bullet+}$ with anions other than nitrate were not studied due to potential problems with quenching of the sensitizer by the anionic quencher. The rate constants for quenching of the diene radical cations are all at or close to the diffusion limit and are typical of the results observed for a variety of arylalkene radical cations.[35,43] Transient spectra measured in the presence of 5 mM Br$^-$ showed no evidence for the formation of $\mathrm{Br_2}^{\bullet-}$ as a product of the reaction of Br$^-$ with $\mathbf{1}^{\bullet+}$. Under these conditions any Br$^\bullet$ generated by electron transfer would be trapped by excess Br$^-$ to give the dimer radical anion with a strong absorption at 360 nm.[44] By contrast to the results for anionic nucleophiles, the rate constants for reaction of $\mathbf{1}^{\bullet+}$−$\mathbf{4}^{\bullet+}$ with methanol cover approximately 3 orders of magnitude with the more highly substituted radical cation ($\mathbf{1}^{\bullet+}$) being the least reactive. The plot of k_{obs} vs methanol concentration for $\mathbf{1}^{\bullet+}$ showed pronounced upward curvature, as has frequently been observed for reactions of other reactive intermediates with alcohols.[45]

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Table 2. Rate Constants for Reaction of Conjugated Diene Radical Cations with Nucleophiles in Acetonitrile

	k_{Nu}, M^{-1} s^{-1}			
nucleophile (E_{ox}, V)[a]	$1^{\bullet+}$	$2^{\bullet+}$	$3^{\bullet+}$	$4^{\bullet+}$
methanol	1.2×10^5 [b]	$(1.8 \pm 0.2) \times 10^8$	$(4.8 \pm 0.2) \times 10^6$	$(4.3 \pm 0.5) \times 10^7$
CN^- (1.3)	$(4.0 \pm 0.2) \times 10^{10}$			
Br^- (1.4)	$(4.1 \pm 0.5) \times 10^{10}$			
$CH_3CO_2^-$ (1.5)	$(3.8 \pm 0.4) \times 10^9$		$(2.6 \pm 0.2) \times 10^{10}$	
Cl^- (1.8)	$(3.8 \pm 0.2) \times 10^{10}$			
NO_3^- (1.8)	$(8.2 \pm 0.7) \times 10^9$	$(4.0 \pm 0.3) \times 10^{10}$	$(2.3 \pm 0.2) \times 10^{10}$	$(2.2 \pm 0.5) \times 10^{10}$

[a] vs SCE in acetonitrile.[42] [b] Curved plot; k_{Nu} estimated as the slope at zero methanol concentration by polynomial fitting of the plot of k_{obs} vs [methanol].

Table 3. Rate Constants for Reaction of Conjugated Diene Radical Cations with Alkenes in Acetonitrile

	k_{alkene}, M^{-1} s^{-1}			
alkene ($E_{1/2}$, V)[a]	$1^{\bullet+}$	$2^{\bullet+}$	$3^{\bullet+}$	$4^{\bullet+}$
1-hexene (2.9)		$<3 \times 10^6$	$<1 \times 10^6$	$\leq 4 \times 10^6$
2-methyl-1-butene (2.6)		$(9.8 \pm 0.6) \times 10^7$	$<1 \times 10^6$	$(1.7 \pm 0.3) \times 10^7$
3-methyl-2-pentene (1.98)		$(8.3 \pm 0.8) \times 10^6$	$<1 \times 10^6$	$<5 \times 10^6$
tetramethylethylene (1.6)			$<1 \times 10^6$	$(5.1 \pm 0.6) \times 10^9$
ethyl vinyl ether (2.0)	$(9.1 \pm 0.5) \times 10^5$	$(3.2 \pm 0.3) \times 10^9$	$(4.5 \pm 0.4) \times 10^8$ [b]	$(2.1 \pm 0.4) \times 10^9$
2-methoxy-1-propene (1.7)	$(3.2 \pm 0.2) \times 10^6$	$(6.5 \pm 0.4) \times 10^9$	$(3.5 \pm 0.2) \times 10^8$ [c]	$(4.0 \pm 0.7) \times 10^9$ [c]
1-ethoxy-1-propene (1.6)	$(8.7 \pm 0.8) \times 10^5$	$(7.1 \pm 0.6) \times 10^9$	$(9.5 \pm 0.6) \times 10^7$ [c]	$(5.6 \pm 0.8) \times 10^9$

[a] vs SCE in acetonitrile.[46] [b] $(4.8 \pm 0.2) \times 10^8$ M^{-1} s^{-1} in acetonitrile + 0.02 M $LiClO_4$. [c] Plots show negative curvature at high alkene concentrations.

Reactions with Alkenes. The reactivity of conjugated diene radical cations toward a variety of alkyl- and alkoxy-substituted ethylenes was examined. The method of generation of the radical cation is very important in these experiments since in many cases both the diene and the substituted ethylene used as quencher can react with the excited state sensitizer. This complication can be easily avoided for $\mathbf{1}^{\bullet+}$ which can be generated by photoionization, and it is straightforward to examine the reactivity of this radical cation with substrates that do not absorb at 266 nm. However, appreciable yields of radical cations $\mathbf{2}-\mathbf{4}^{\bullet+}$ can only be generated by photosensitization. Triplet chloranil has been shown to react with a variety of alkenes such as methylenecyclohexene, methylcyclohexene, and 1-methoxy-1-propene with rate constants in the range of $2-5 \times 10^9$ M^{-1} s^{-1} in acetonitrile.[46] The excited state energy and reduction potential of chloranil indicate that triplet chloranil should oxidize donors with oxidation potentials lower than 2.25 V (vs SCE) at the diffusion-controlled limit, and donors with higher oxidation potentials may still react via exciplex mechanisms.[42,47] Furthermore, the use of high diene concentrations to ensure that most of the chloranil triplet reacts with the diene rather than the quencher alkene results in relatively short radical cation lifetimes as a result of reaction with the diene precursor (see Table 1 and Figure 3). The 1,4-dicyanonaphthalene/biphenyl sensitizer system provides some advantages over triplet chloranil for kinetic measurements for the following reasons: (1) high concentrations of alkenes can be used without competing with 0.2 M biphenyl for the dicyanonaphthalene singlet and (2) efficient oxidation of the alkene quencher will only be a problem for alkenes with oxidation potentials below that of biphenyl (1.96 V vs SCE).[37] Ideally one should choose the cosensitizer with the lowest oxidation potential that will still generate the diene radical cation with a diffusion-controlled rate constant in order to maximize the range of alkene quenchers that can be employed without competitive reaction of the quencher with the biphenyl radical cation. Biphenyl is close to the optimum for dienes **2**−**4**, since its oxidation potential is only very slightly higher than those of the dienes (Table 1).

The above considerations led to the use of the 1,4-dicyanonaphthalene/biphenyl sensitizer system for most of the measurements of the reactivity of diene radical cations with substituted alkenes. These experiments were generally carried out at ≥4 mM diene in order to generate the diene radical cation via eq 3 within 10−20 ns and to minimize the reaction of the alkene quencher with the biphenyl radical cation. At these concentrations the lifetime of the radical cation is in the plateau region where it no longer changes substantially with increasing diene concentration; this was found to be the best compromise in terms of giving a reasonable time window for kinetic measurements. The radical cation decays were monitored at 340, 600, and 370 nm for $\mathbf{2}^{\bullet+}$, $\mathbf{3}^{\bullet+}$, and $\mathbf{4}^{\bullet+}$, respectively, and aerated or oxygenated samples were used to minimize interference from the 1,4-dicyanonaphthalene radical anion. Some measurements were also done using chloranil sensitization, although this was considerably less satisfactory, as outlined above.

Rate constants for reaction of $\mathbf{1}-\mathbf{4}^{\bullet+}$ with alkyl- and alkoxy-substituted ethylenes are summarized in Table 3. The rate constant for decay of $\mathbf{1}^{\bullet+}$ was unaffected by any of the alkyl-substituted ethylenes shown in Table 3; in most cases the concentration of alkene used leads to an estimated upper limit for the quenching rate constant of $\leq 5 \times 10^6$ M^{-1} s^{-1}. The data in Table 3 demonstrate that the reactions of all four diene radical cations are too slow to measure with terminal alkenes such as 1-hexene. However, the more electron-rich substrates such as 2-methyl-1-butene, 3-methyl-2-pentene, and the vinyl ethers are more reactive, with rate constants in the 10^7-10^9 M^{-1} s^{-1} range for $\mathbf{2}-\mathbf{4}^{\bullet+}$. For $\mathbf{1}^{\bullet+}$ rate constants could only be measured for the three vinyl ethers. For none of the alkenes studied was there any evidence for formation of either adduct or alkene radical cations as a result of

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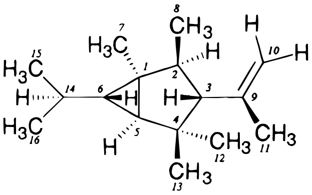
the reaction with the diene radical cation. Reaction of **3**$^{\bullet+}$ with ethyl vinyl ether was also examined in the presence of 0.02 M lithium perchlorate; the rate constant (Table 3) under these conditions was the same within experimental error as that measured in acetonitrile alone.

The reactivity of **1**$^{\bullet+}$ toward diene **4** was also examined. It is not possible to generate **1**$^{\bullet+}$ selectively by 266 nm excitation in the presence of **4**; however, **1**$^{\bullet+}$ could be produced by reduction of the β-methyl-4-methoxystyrene radical cation generated by 308 nm photoionization of the parent styrene, as previously reported.[46] The β-methyl-4-methoxystyrene radical cation reacts with a variety of 1,4-dialkyl-substituted dienes with rate constants of $\leq 5 \times 10^6$ M^{-1} s^{-1} so that concentrations of **4** as high as 0.4 M could be used.[46] However, the decay of **1**$^{\bullet+}$ was the same within experimental error in the presence and absence of 0.4 M **4**, leading to an estimated lower limit of $\leq 10^6$ M^{-1} s^{-1} for the rate constant.

Radical Cation-Mediated Dimerization of 1. Product studies were undertaken to establish the products responsible for the observed reaction of **1**$^{\bullet+}$ with its precursor. Irradiation of a sample containing 5 mM 1,4-dicyanonaphthalene, 0.2 M biphenyl, and 0.01 M **1** at 300 nm resulted in the disappearance of **1**, but GC/MS of the irradiated solution did not indicate the formation of either dimeric products or diene-sensitizer adducts. However, the dimerization of **1** was observed in dichloromethane using a stable radical cation salt, tris(4-bromophenyl)aminium hexachloroantimonate, as the electron transfer catalyst. GC and GC/MS analyses of the reaction mixture at low conversion indicated the formation of four dimeric products, with one of these accounting for ~80% of the dimer mixture, in addition to a number of other unidentified materials. The relative yields of the four dimeric products did not change appreciably with longer reaction time, although the number and amount of additional products increased at higher conversions. The product yield (based on the remaining unreacted diene) could not be increased beyond ~35% by longer reaction time or additional catalyst. The main component, dimer **5**, was isolated and purified as outlined in the Experimental Section. The molecular formula of $C_{16}H_{28}$ was established by HRMS. The structure of dimer **5** was assigned on the basis of detailed ^{1}H and ^{13}C NMR experiments (Table 4), as summarized below.



5

^{1}H and ^{13}C (^{1}H-decoupled and coupled; DEPT) NMR spectra indicated the presence of seven methyl groups, four methine protons, two olefinic protons, two aliphatic quaternary carbons, and two olefinic carbons. The coupling relationship of the proton resonances was determined from ^{1}H$-$^{1}H COSY (correlation spectroscopy). The coupling constants were determined by a J-resolved 2D-NMR experiment. ^{1}H$-$^{13}C HMQC (heteronuclear multiple quantum correlation spectroscopy) then led to the assignment of the carbon resonances (Table 4).

Table 4. 500 MHz NMR Data for 1,2,4,4-Tetramethyl-3-(propen-2-yl)-6-isopropylbicyclo-[3.1.0]hexane (5) in $CDCl_3$ at 298 K

carbon atom	^{13}C, δ	^{1}H, δ (attached proton)	multiplicity	J, Hz
1	30.66			
2	42.49	1.982	dq	6.4, 1
3	59.46	1.342	d	11
4	41.22			
5	42.42	0.437	d	3.5
6	29.60	0.302	dd	3.5, 10
7	15.76	1.164	s	
8	13.98	0.798	d	6.4
9	143.85			
10	112.49	4.589 (H10a)	s	*a*
		4.861 (H10b)	s	*a*
11	23.65	1.677	s	
12	25.02	0.792	s	*a*
13	26.01	0.961	s	*a*
14	28.51	1.065	m	
15	22.69	0.912	d	6.4
16	22.93	0.971	d	6.4

[a] Cross-peaks between H10a and H10b as well as between H12 and H13 in the COSY spectrum indicate the presence of long range couplings. Coupling constants J(H10a,H10b) and J(H12,H13) cannot be measured since they are less than the line width of the signals (1$-$2 Hz).

The ^{1}H$-$^{1}H COSY spectrum indicated two coupled cyclopropyl methine protons, H6 (δ 0.302) and H5 (δ 0.437), with H6 further coupled to a methine proton, H14 (δ 1.065), that is also coupled to two methyl doublets, H15 (δ 0.912) and H16 (δ 0.971). These data unequivocally establish the presence of an isopropyl group attached to a cyclopropyl ring. The ^{1}H$-$^{13}C HETCO showed that the two olefinic protons H10a (δ 4.589) and H10b (δ 4.861) are attached to the same carbon C10 (δ 112.49), indicative of a *gemi*-configured double band. The coupling constants between the two olefinic protons cannot be measured since they are less then the line width of the signals (1$-$2 Hz). ^{1}H$-$^{13}C HMBC (heteronuclear multiple bond correlation spectroscopy) showed that the methyl singlet H11 (δ 1.677) is linked through a two-bond coupling to another olefinic carbon C9 (δ 143.85), which in turn is two-bond coupled to H10a and H10b. These results are consistent with a propen-2-yl group. ^{1}H$-$^{13}C HMBC also showed that the methyl singlets H12 (δ 0.792) and H13 (δ 0.961) are correlated to C4 (δ 28.51) through two-bond couplings, establishing that the two methyl groups are attached to C4. Similarly, the methyl singlet H7 (δ 1.164) and methyl doublet H8 (0.798) are connected to C1 (δ 30.66) and C2 (δ 42.42), respectively; the latter is further supported by the observation of a ^{1}H$-$^{1}H COSY cross-peak between H8 and H2 (δ 1.982).

The rest of the molecule was assembled by HMQC, starting from the three methine protons H3, H2, and H5. Two-bond couplings between these protons and the various carbon atoms established the bicyclo[3.1.0] ring and linked the propen-2-yl group to the C3 position on the 5-membered ring. The coupling constants between H5 and H6 and between H3 and H2 are consistent with their *trans* configurations (Table 4). The relative configuration of the isopropyl group and the propen-2-yl group in structure **5** is indicated by the existence of a cross-peak between H3 and H6 in the ^{1}H$-$^{1}H COSY spectrum.

Discussion

Both photoionization and photosensitized electron transfer have been used to generate and characterize a number of conjugated diene radical cations. Photoionization is relatively limited in scope since only the more easily oxidized dienes give sufficient radical cation yields for kinetic measurements. However, it does provide a clean source of the radical cation and can be used at diene concentrations where addition of the radical cation to its precursor is minimized. The photosensitization method is more generally applicable to a variety of dienes, although it suffers from the limitation of overlapping absorptions of the diene radical cation with sensitizer- or cosensitizer-derived radical ions and requires higher concentration of dienes. As noted above there are also significant limitations in terms of the potential quenchers that can be studied using photosensitization as a method for generation of the radical cation.

All of the conjugated diene radical cations have λ_{max} in the 340−400 nm region with a substantially broader and weaker absorption in the visible, as shown in Table 1. Literature data for $\mathbf{1}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ generated by γ-irradiation in a freon matrix at low temperature are also included for comparison.[26] Electronic absorption spectra for 1,3-butadiene and a number of methyl-substituted derivatives in a variety of rigid media have been reported.[26] The data indicate that the UV absorption band for the radical cations shifts to progressively lower energy with increasing methyl substitution, with λ_{max} values of 295, 305, and 363 nm for 1,3-butadiene, *trans*-1,3-pentadiene, and 2,5-dimethyl-2,4-hexadiene, respectively. The cyclic dienes all have λ_{max} values in the 365−400 nm region, at slightly lower energy than the acyclic systems. Thus, the spectroscopic data shown in Table 1 for conjugated diene radical cations in acetonitrile at room temperature are in good agreement with the matrix data. By contrast, substantially different λ_{max} values (440 and 450 nm) have been reported for *cis*- and *trans*-1,3-pentadiene radical cations generated by pulse radiolysis in *n*-butyl chloride.[48] These results are analogous to some of the early matrix results for 1,3-butadiene which had shown additional absorption bands at 425 and 1200 nm at high diene concentrations.[49] It is now well established that these additional absorptions arise from dimer cations and secondary products formed through interaction with matrix molecules.[28,50,51] It is likely that the pulse radiolysis results are also complicated by absorptions due to solvent-related ions, although it should be noted that the reported λ_{max} of 400 nm for the 1,3-cyclohexadiene radical cation produced by this method is in good agreement with the low-temperature matrix data. We have been unable to find suitable conditions to observe this radical cation, although the tetramethyl-substituted derivative can be easily detected (Table 1).[39]

There are several reactions that may account for the decay of the diene radical cation in the absence of added nucleophiles or alkenes. For experiments in which $\mathbf{1}^{\bullet+}$ is generated by photoionization at relatively low diene concentrations, the radical cation decays by reaction with either traces of water in the acetonitrile or the solvated electron or its products. However, the decay kinetics for the radical cations generated by photosensitization are determined largely by their reaction with the precursor diene, as shown in Figure 4. Product studies demonstrate that a dimeric product (**5**) is formed when $\mathbf{1}^{\bullet+}$ is generated using a stable triarylaminium radical cation as the electron transfer catalyst. Radical cation-mediated dimerizations of 1,3-dienes are well documented in the literature and generally lead to either cyclobutane or Diels−Alder adducts or mixtures of both, depending on reaction conditions and diene structure.[14,15] It is clear that the major product isolated from the radical cation-mediated dimerization of **1** is not the expected cyclobutane or Diels−Alder product, although these may be responsible for some of the minor dimeric products observed by GC/MS. However, dimer **5** may arise from rearrangement of an initial cyclobutane adduct or its radical cation.[52] In fact the steric bulk of diene **1** and literature precedent would argue in favor of a preference for [2 + 1] addition to generate a cyclobutane radical cation rather than a [3 + 2] Diels−Alder addition.[53] Dimer **5** is not formed under photosensitized conditions, at least using 1,4-dicyanonaphthalene/biphenyl. It is interesting to note that similar results have been reported for the mixed cycloaddition between **1** and 1,3-cyclohexadiene.[54] Although this reaction can be carried out using a triarylaminium salt as the electron transfer catalyst, the photosensitized reaction using 9,10-dicyanoanthracene did not produce any cycloadduct. Variations in the rate constants for reactions involving the sensitizer or catalyst with the initial dimer radical cation may account for the discrepancies between the two methods for initiating radical cation cycloaddition chemistry.

The estimated rate constants for the reaction of $\mathbf{1}-\mathbf{4}^{\bullet+}$ with their diene precursors are all in the 10^8-10^9 M^{-1} s^{-1} range. These results are in good agreement with previous studies of the radical cation-mediated dimerization of 1,3-cyclohexadiene in which Stern−Volmer product quenching led to an estimate of 3×10^8 M^{-1} s^{-1} for the rate constant for the initial addition of the radical cation to the diene.[55] Rate constants of $\sim 5 \times 10^8$ M^{-1} s^{-1} for dimerization of 1,3-pentadiene and isoprene have also been estimated by pulse radiolysis.[48] Although "dimerization" provides a logical explanation for the observed reaction of the diene radical cations with their precursors, the curved plots shown in Figure 4 are indicative of a more complex mechanism than irreversible addition to generate a dimer radical cation. The isolation of a dimer resulting from substantial rearrangement of the initial starting materials is also consistent with a more complex mechanism. Similar curvature in the plot of the rate constant for radical cation decay as a function of the alkene concentration had been observed earlier for the radical cation-mediated dimerization of 4-methoxystyrene.[56] In this case detailed kinetic and product studies for both the dimerization of the styrene and the

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[52] One possible route for formation of **5** involves initial rearrangement of a 1,3-diisobutenyl-2,2,4,4-tetramethylcyclobutane radical cation to a 1,3-distonic radical cation with the radical center on a cyclopentane ring and the charge on the isopropyl group. Deprotonation of this radical cation gives a cyclopentyl radical that, after a methyl shift and addition of the subsequent radical center to the remaining isobutenyl group, generates the required bicyclo[3.1.0] ring system with an isopropyl radical at the 3-position. This radical can then be reduced to the anion which is protonated to give **5**.

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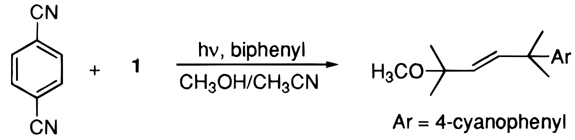
cycloreversion of the product cyclobutane dimer demonstrated that the curvature resulted from competition between rearrangement of the initial dimer radical cation and cycloreversion to neutral 4-methoxystyrene plus its radical cation. Similar detailed mechanistic studies for diene **1** were not possible since only rearranged dimer was isolated and since no adduct radical cations were detected in our time-resolved experiments.

The reactions of alkene radical cations with nucleophiles usually occur by nucleophilic addition or electron transfer, although deprotonation has also been observed for sterically hindered pyridines and amines.[22] The measured rate constants for reaction of $\mathbf{1}-\mathbf{4}^{\bullet+}$ with methanol clearly correspond to nucleophilic addition, based on the fact that electron transfer would be prohibitively endothermic and consistent with product studies by Arnold and co-workers.[11] For example, generation of $\mathbf{1}^{\bullet+}$ by photosensitized electron transfer using dicyanobenzene/biphenyl in methanol/acetonitrile leads to the formation of the photo-NOCAS adduct in 82% yield (eq 5).[11] This product results from addition of methanol to the terminal position of the initial diene radical cation to give a distonic radical cation followed by deprotonation to give an allylic radical. Coupling of the allylic radical with the dicyanobenzene radical anion at the *ipso* position gives an adduct that loses cyanide ion to generate the final product. Similar adducts have been isolated from several other conjugated dienes; in each case the products are consistent with addition of methanol at the terminal position of the more highly substituted double bond.[11] Coupling of the allylic radical with the radical anion generates both 1,2- and 1,4-addition products for dienes that are less highly substituted than **1**.



(5)

The rate constants shown in Table 2 for methanol addition to $\mathbf{1}-\mathbf{4}^{\bullet+}$ clearly demonstrate the effects of alkyl substitution on the reactivity of the diene radical cation. The reactivity toward methanol decreases with increasing alkyl substitution in the order $\mathbf{1}^{\bullet+} < \mathbf{3}^{\bullet+} < \mathbf{4}^{\bullet+} < \mathbf{2}^{\bullet+}$. These results parallel those observed earlier for nucleophilic addition to arylalkene radical cations in which case the more electron-rich radical cations were less reactive toward nucleophilic addition.[22,35]

By contrast to the methanol additions, the rate constants for reactions of $\mathbf{1}-\mathbf{4}^{\bullet+}$ with anionic nucleophiles are all close to the diffusion-controlled limit and show little selectivity. Both nucleophilic addition and electron transfer are common in reactions of radical cations with anions; the latter usually predominate in cases where electron transfer is exergonic by ≤5 kcal/mol.[35,43,57] However, the relative oxidation potentials for the anionic quenchers and dienes used are such that electron transfer is unlikely to occur with a diffusion-controlled rate constant for any of the anions with $\mathbf{1}^{\bullet+}$ or for nitrate plus $\mathbf{2}-\mathbf{4}^{\bullet+}$. In fact the slower rate constants for reaction of acetate and nitrate with $\mathbf{1}^{\bullet+}$ parallel the changes in nucleophilicity of the anions rather than variations in oxidation potential. Consistent with this hypothesis, there is no evidence for the formation of $Br_2^{\bullet-}$ as a product of the reaction of Br^- with $\mathbf{1}^{\bullet+}$. Product studies are also in agreement with nucleophilic addition since cyanide ion has been shown to add to $\mathbf{1}^{\bullet+}$ to give a photo-NOCAS adduct in a manner analogous to that shown for methanol in eq 5.[11] By contrast $\mathbf{2}-\mathbf{4}^{\bullet+}$ would be expected to react via electron transfer with chloride, bromide, acetate, and cyanide ions. These reactions were not examined due to potential problems with quenching of the sensitizer by the anion. However, the absence of cyanide adducts in reactions of a number of substituted 1,3-butadienes[11] is consistent with an electron transfer reaction for diene radical cations with oxidation potentials higher than that of **1**.

The data in Table 3 demonstrate that the conjugated diene radical cations are relatively unreactive toward simple terminal olefins such as 1-hexene, although rate constants can be measured for some of the more electron-rich alkyl- and alkoxy-substituted ethylenes. For example, the rate constants for reaction with 2-methyl-1-butene follow the order $\mathbf{3}^{\bullet+} < \mathbf{4}^{\bullet+} < \mathbf{2}^{\bullet+}$, as is observed for addition of methanol. Since the oxidation potential for the substrate is 0.7−0.9 V higher than that of any of the dienes, the possibility of electron transfer can be readily excluded and the observed rate constants are those for addition reactions. Although the oxidation potential of 3-methyl-2-pentene is comparable to those of the dienes, the trend in rate constants suggests that the measured rate constant for $\mathbf{2}^{\bullet+}$ corresponds to addition since $\mathbf{4}^{\bullet+}$ would be expected to react more rapidly than $\mathbf{2}^{\bullet+}$ if electron transfer was the dominant mode of reaction. This is supported by the fact that $\mathbf{4}^{\bullet+}$ does react with tetramethylethylene with close to a diffusion-controlled rate constant, presumably via electron transfer. Neither $\mathbf{3}^{\bullet+}$ nor $\mathbf{1}^{\bullet+}$ react with measurable rate constants (i.e., $<1 \times 10^6$ M^{-1} s^{-1}) with any of the simple alkyl-substituted ethylenes, clearly indicating the importance of steric and electronic effects in the radical cation in determining the reactivity toward cycloaddition.

The diene radical cations react more rapidly with the electron-rich alkoxy-substituted alkenes. The more highly substituted radical cation ($\mathbf{1}^{\bullet+}$) is by far the least reactive; both the low oxidation potential of **1** and the fact that the changes in rate constant for the three vinyl ethers do not parallel their relative oxidation potentials suggest that addition is the dominant mode of reaction. By contrast, the oxidation potentials of the dienes and quenchers are comparable for $\mathbf{2}-\mathbf{4}^{\bullet+}$, and both electron transfer and addition reactions are possibilities. Of the three radical cations, $\mathbf{3}^{\bullet+}$ would be predicted to be the least reactive toward both electron transfer (by virtue of its lower oxidation potential) and addition (since it is less reactive to methanol and other alkenes). However, the rate constants for reaction of $\mathbf{3}^{\bullet+}$ with alkoxyethylenes decrease with decreasing oxidation potential (ethyl vinyl ether > 2-methoxypropene > 1-ethoxy-1-propene), which is exactly the opposite to what is expected for an electron transfer reaction. As noted above for the other alkenes, the fact that $\mathbf{2}^{\bullet+}$ is more reactive than $\mathbf{4}^{\bullet+}$ for each of the alkoxyethylenes suggests that addition rather than electron transfer dominates the measured rate constants for these two diene radical cations. By contrast, the trend toward increasing rate constant with decreasing oxidation potential for the three alkoxyethylenes could be construed as evidence for electron transfer, especially since the actual differences in rate constant between $\mathbf{2}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ are not large for any particular substrate. To summarize, it is likely that the measured rate constants

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for reaction of the four diene radical cations with the alkoxyalkenes reflect predominantly addition, although one cannot exclude an electron transfer component in some cases.

Conclusions

A number of conjugated diene radical cations have been generated photochemically by either photoionization or photosensitized electron transfer and have been spectroscopically and kinetically characterized using laser flash photolysis. The electronic absorption spectra for the diene radical cations in acetonitrile show a strong absorption band in the 340−400 nm region with a broader, weaker absorption band in the visible and are in good agreement with low-temperature data for the same species. The radical cations show typical cationic behavior in that they react with anionic nucleophiles with rate constants that are at or close to the diffusion-controlled limit and are insensitive to oxygen. The measured rate constants for addition to methanol demonstrate that the more highly alkyl-substituted radical cations are substantially less reactive toward nucleophilic addition. In the absence of added alkenes or nucleophiles, the lifetime of the radical cation is determined by its reaction with the precursor diene, with rate constants in the 10^8-10^9 M^{-1} s^{-1} range. Product studies for 2,5-dimethyl-2,4-hexadiene (**1**) using a triarylaminium salt as the electron transfer catalyst demonstrate that this reaction leads to dimerization, although the major isolated product results from substantial rearrangement of the initial adduct radical cation. The rate constants for reaction of the radical cations with a variety of alkyl- and alkoxy-substituted ethylenes were also evaluated and provide some of the first kinetic data for the initial step in mixed cycloaddition reactions for simple conjugated diene radical cations.

Experimental Section

General. HPLC experiments were run on a HP1090 liquid chromatograph equipped with a HP ODS Hypersil (5 μm, 200 × 2.1 mm) column and an UV dectector. Electrochemical measurements were made using an EG&G 273A potentiostat in acetonitrile with 0.1 M tetrabutylammonium perchlorate. Half-wave oxidation potentials were obtained using a platinum electrode and were measured relative to ferrocene and then converted to the SCE standard.

1,1′-Bicyclohexenyl was synthesized according to a literature procedure.[58] All other alkenes and dienes were commercial samples of highest quality available. They were purified by distillation or/and running through a small column of alumina prior to the experiments. Acetonitrile and dichloromethane were purified by distillation over calcium hydride under dry nitrogen.

Laser Flash Photolysis (LFP). Sample solutions were prepared with optical density (OD) of 0.3−0.4 at the excitation wavelength (266 or 308 nm) and were contained in 7 × 7 mm^2 quartz cells (quenching experiments) or in 7 × 7 mm^2 flow cells connected with Teflon tubing to a sample reservoir equipped with a Teflon stopcock for controlling the flow rate (transient spectra). Either a Lumonics HY750 Nd:YAG laser (266 nm, ≤60 mJ/pulse, ∼10 ns/pulse) or an EX530 excimer laser (XeCL, 308 nm, ≤40 mJ/pulse, ∼8 ns/pulse) was used for sample excitation. The laser system has been described previously.[59] Data acquired by a PC-386 computer were transferred to a Macintosh Quadra-700 computer for processing.

Product Studies. Tris(4-bromophenyl)aminium hexachloroantimonate (0.74 g, 0.9 mM) was added to a solution of 2,5-dimethyl-2,4-hexadiene (1 g, 9 mM) in dichloromethane (2 mL) at 0 °C, and the mixture was stirred at room temperature overnight. Dichloromethane (10 mL) was added, and the solid residue was removed by filtration. A colorless oil was obtained after evaporation of the solvent under vacuum. GC/MS of the crude product indicated a 30% conversion of the starting substrate into four dimeric products, with the one with the shortest retention time predominating (≥80%). A number of unidentified products were also observed. The dimeric compounds were isolated by column chromatography (silica gel, hexane, $R_f = 0.7$). Concentration of the first fraction of the eluent gave a product (0.1 g, 20% isolated yield) which was the major dimer in ≥95% purity. ^1H and ^{13}C NMR data for this dimer are listed in Table 4, with additional material available as Supporting Information. HRMS calcd for $C_{16}H_{28}$: 220.2191. Found: 220.2186.

Supporting Information Available: ^1H and ^{13}C NMR spectra and two tables summarizing COSY, NOESY, and HMBC data for **5** (4 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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