The Cycloaddition of the 1,3-Butadiene Radical Cation with Acrolein and Methyl Vinyl Ketone

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The 1,3-butadiene radical cation reacts with acrolein and methyl vinyl ketone to produce 'stable' adducts. The nature of the reaction and the structures of the adducts were investigated by collisional activation decomposition (CAD) combined with tandem mass spectrometry (MS/MS), and also by Fourier transform mass spectrometry. The CAD spectra of gas-phase adducts were compared with those of suitable model compounds. On that basis, it was determined that the 1,3-butadiene radical cation undergoes a cycloaddition with these α , β -unsaturated carbonyl compounds. The butadiene radical cation serves as the 'ene', and the acrolein and methyl vinyl ketone react as dienes, forming cycloadducts having 2-ethenyl-2,3-dihydropyran radical cation structures.

INTRODUCTION

Cycloadditions constitute one of the largest classes of organic reactions. The simplest conjugated diene (1,3)butadiene) reacts with itself to produce a mixture of products from different cycloadditions. The [2 + 2], [4 + 2], and [4 + 4] cycloadditions give divinylcyclobutenes, 4-vinyl-cyclohexene, and 1,5-cyclooctadiene, respectively. In addition to dimers of butadiene, mixtures of dimers, trimers, and in some cases polymers are formed at high temperature. In contrast with the chemistry of the neutrals, the gas-phase reaction of the 1,3butadiene radical cation with 1,3-butadiene occurs by a two-step cycloaddition to produce principally the radical cation 4-vinyl cyclohexene.¹

Radical cation cycloadditions have other advantages with respect to neutral cycloadditions. For example, the reaction of neutral 1,3-butadiene with neutral vinyl methyl ether does not take place in the condensed phase. The gas-phase reaction between 1,3-butadiene and the vinyl methyl ether radical cation, however, proceeds efficiently by a two step [4 + 1] cycloaddition to form 4-methoxycyclohexene radical cation.^{2(a)} The 1,3butadiene radical cation also reacts with simple alkenes by mechanisms that are not yet established.^{2(b)}

Radical cation cycloadditions have also been reported to occur in the condensed phase.³ These reactions reveal another advantage of radical cation cycloadditions; that is, they take place for systems in which the dienophile is not activated with electron withdrawing groups. The 1,3-cyclohexadiene radical cation reacts with its neutral precursor via either a [3 + 2] or [4 + 1] cycloaddition.^{3(a)} Radical cation cycloadditions also take place when the dienophile is deactivated with electron donating groups. Hence, the reaction of 1,3-cyclohexadiene with vinyl phenyl ether in the presence of triaryl aminium salts affords a Diels-Alder product.^{3(b)}

These results have led to conjecture on the subject of

0030-493X/89/080637-10 \$05.00 © 1989 by John Wiley & Sons, Ltd. mechanisms for radical cation cycloadditions. The results of theoretical studies point to a non-synchronous concerted cycloaddition^{3(c)} whereas experimental data support a two-step process.^{1,2,4} The condensed-phase reaction of spiro-[2,4]-heptadiene radical cation with its neutral precursor, monitored by ¹H NMR, was also interpreted to occur by means of a two-step cyclo-addition.⁴

Radical cation reactions are also unusual because the diene need not be activated with electron donating groups as is typical of Diels-Alder reactions of closed shell species.

We report here the gas-phase radical cation reactions of 1,3-butadiene and acrolein, and 1,3-butadiene and methyl vinyl ketone. Both acrolein and methyl vinyl ketone have double bonds that are activated by electron withdrawing groups. The study of these two related systems is motivated by the following questions: (i) do radical cation cycloadditions take place when the 'ene' is activated as in neutral cycloadditions? and (ii) if so, which species reacts as a radical cation and which species reacts as the diene? The last question involves two possibilities that are illustrated in Eqns (1) and (2).



Radical-cation Diels-Alder reactions can be conducted in high-pressure (approximately 1 Torr) chemical ionization (CI) sources, and the structures of adducts determined by collisional-activation decomposition

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(CAD) mass spectrometry.^{1,2} The capacity to determine structure by CAD is well known.⁵ Reaction adducts have also been studied in the cell of Fourier transform (FT)-mass spectrometers.^{1,2,6} Here the chemistry at low pressure (approximately 10^{-6} torr) can be examined under single-collision conditions, and the features of FTMS such as ion storage, ion ejection, pulsed values, and the ability to examine the chemistry as a function of time can be used efficaciously.⁷ The structural insights of CAD spectrometry and the kinetic information obtainable by using FTMS make an effective combination to study bimolecular gas-phase radical-cation reactions.

We are pleased to devote this paper to Professor Allan Maccoll, who has devoted his career to an understanding of ion chemistry. The potential for gas-phase radical cation cycloadditions is one of our longest standing research interests, dating from 1972.^{2(b)} Thus, this work is a particularly appropriate dedication.

RESULTS AND DISCUSSION

The ion-molecule reactions occurring in an ionized mixture of 1,3-butadiene and methyl vinyl ketone, or of 1,3-budadiene and acrolein, give rise to adducts of $[C_8H_{12}O]^+$ and $[C_7H_{10}O]^+$, respectively, in a CI source at pressures between 0.03 and 0.5 Torr. The structures of the adducts were investigated by obtaining CAD mass spectra with a three-sector tandem mass spectrometer.⁸ Assignment of the adduct sturcture is based on comparison of adduct CAD spectra with those of suitable model compounds.^{1,2} The ion-molecule reactions were also conducted in the cell of an FT-mass spectrometer where fragments of the adduct were monitored as a function of time after ionization.⁶

FT-mass spectrometry

An FT-mass spectrometer was used to study the reactions of $1,3-C_4H_6/CH_2=CHCOCH_3$ (1:1) and $1,3-C_4H_6/CH_2=CHCHO$ (1:1) systems at a pressure of 4×10^{-7} Torr. In the FT-mass spectrometer, no ionmolecule adducts were detected, as was expected. At this low pressure collisional stabilization cannot take place; thus, an adduct, which forms with excess energy, decomposes before a stabilizing collision can intervene. Nevertheless, some evidence for the structure of the adducts come from the pattern of ions that are decompositions products of the transient adduct.

The ions of $[C_4H_6]^{+}$ (m/z 54), and of $[CH_2 = CHCHO]^{+}$ (m/z 56), which are the reactants, and the ions of m/z 95, 92 and 81, which are apparently fragments of the adduct, were monitored as a function of delay time between ionization and detection. At first, the relative abundance of $[CH_2=CHCHO]^{+}$ decreases rapidly. This is the result of self CI between ionized and neutral acrolein, giving rise to the $[M + H]^+$ ion of m/z 57 (see Fig. 1). The relative abundance of $[C_4H_6]^{+}$ decreases steadily throughout the entire experiment, indicating that it is being consumed by some reaction process. In contrast, the abundance of ions of m/z 95, 92 and 81 increase steadily but slowly. The ultimate decrease in the abundance of $[C_4H_6]^{+}$, and the increase of the ions of m/z 95, 92 and 81, are evidence that the precursor ion is the 1,3-butadiene radical cation.

The reaction between methyl vinyl ketone and the 1,3-butadiene radical cation was conducted under the same conditions as those described for the acrolein/ The reactant $1,3-C_4H_6$ butadiene system. and $CH_2 = CHCOCH_3$ radical ions (m/z 54 and m/z 70), and the ions of m/z 43, 79, 80, 81 and 109, the likely fragments of the adduct, were monitored as a function of Both time (see Fig. 2). $[C_4H_6]^+$ and $[CH_2 = CHCOCH_3]^+$ disappear over time; hence, both are reactive ions. A semilog plot of the abundance of the ion of m/z 54 as a function of time reveals that the rate of disappearance increases after the ion of m/z70 has reacted away. This and the rapid disappearance of the ion $[CH_2=CHCOCH_3]^+$ indicate that charge exchange takes place between $[C_4H_6]^+$ and $[CH_2=CHCOCH_3]^+$ (see Eqn (3)). In contrast, the abundances of the fragments of the adduct, of m/z 43, 79, 80, 81 and 109, rise steadily, indicating that the principal reaction is between the 1,3-butadiene radical cation and neutral methyl vinyl ketone (see Eqn (4) and Fig. 2).

There are also side reactions that take place between the 1,3-butadiene radical cation and its nuetral precur-



Figure 1. The time-dependent relative abundance of product ions (formed from an ionized mixture of 1,3-butadiene and acrolein at a pressure of 4×10^{-7} Torr) vs. time.



Figure 2. The time-dependent relative abundances of product ions (formed from an ionized mixture of 1,3-butadiene and methyl vinyl ketone at a pressure of 4×10^{-7} Torr) vs. time.



sor as well as between the methyl vinyl ketone radical cation and its neutral precursor. The latter reaction does not interfere with the outcome of the cross-chemistry because its adduct doesn't generate any fragment ions at the same nominal masses as those of the cross-chemistry adduct. The reaction of the 1,3-butadiene radical cation and neutral 1,3-butadiene does yield some of the same fragments as those of the cross-chemistry; for example, the ions of m/z 80 and 79.

For the reactions in the 1,3-butadiene and methyl vinyl ketone system, double resonance experiments were performed to establish conclusively which species reacts as a radical cation to give the cross-chemistry. Separate experiments were performed in which first the m/z 54 ion and then the m/z 70 ion were ejected. When the m/z 54 ion was ejected, no fragment ions of cross-chemistry were observed. When the m/z 70 ion was ejected, the cross-chemistry took place as previously described. Thus, the principal reactive radical cation in the reaction between 1,3-butadiene and methyl vinyl ketone is the 1,3-butadiene radical cation.

The condensed-phase reactions of neutral 1,3-butadiene with neutral methyl vinyl ketone or with neutral acrolein produce the compounds 3-(cyclohexenyl)-1-ethanone (1) and 3-cyclohexene carboxaldehyde (2), respectively (see Eqn (1)). If radical-cation cycloadditions of this type take place, then the adducts should decompose similarly to the radical cations of these cyclohexene model compounds (see Fig. 3 for CAD spectra). There is qualitative agreement between the fragmentation patterns of the radical cations of compounds 1 and 2 and the adducts formed in the ion-molecule reactions. These patterns will be discussed in more detail later.

The time-dependent disappearance of the reactants and the appearance of fragments that are similar to those of a cycloaddition product are consistent with but do not prove that cycloadditions take place between the 1,3-butadiene radical cation and acrolein, and between the butadiene radical cation and methyl vinyl ketone.

Semilog plots of the abundance of the m/z 54 ion as a function of time reveal that the rate constants for each reaction are not the same. The reaction of the 1,3-butadiene radical cation and methyl vinyl ketone occurs more rapidly than that of the 1,3-butadiene radical cation and acrolein (for a qualitative picture, compare the disappearance of the ion of m/z 54 in Fig. 1 against that of Fig. 2).

CAD mass spectrometry

In addition to the low-pressure experiments performed in the FT-mass spectrometer, the reactions were also conducted in a CI source in which the pressure was varied in the range of 0.02 to 0.5 Torr. Under these conditions, the adducts undergo stabilizing collisions that allow them to be observed directly. Tandem mass spectrometry was used to 'isolate' these adducts for CAD analysis to determine their structures.

The reaction of the butadiene radical cation and acrolein was conducted at high pressure (approximately 0.5 Torr), yielding the ion-molecule adduct $[C_7H_{10}O]^+$ of m/z 110. The fragments ions of m/z 95, 92 and 81, which correspond to the losses of CH₃, H₂O and CHO, respectively, must be generated from a covalently bound species.

These results are consistent with those of the FTMS study. A detailed examination of the fragment ions of m/z 56, 55 and 54 shows that all may not correspond to a covalently bound species. Examination of the peak widths at half height shows that the kinetic energy release accompanying the formation of these ions is smaller than that for the other fragment ions of the



Figure 3. The CAD spectra of the reference compounds (a) 3-(cyclohexenyl)-1-ethanone (1) and (b) 3-cyclohexene carboxaldehyde (2).

adduct. The relative abundances of these ions change dramatically as a function of the pressure in the source. Either the adduct is very sensitive to collisional stabilization or, because it is formed slowly, it is susceptible to interference from other reactions. The former characteristic is indicative of an ion-dipole complex. The fragments of both a covalently bound species such as a cycloadduct and an ion-dipole complex may be represented in the CAD spectra of the adducts.

Comparison of the 1,3-butadiene/acrolein adduct CAD spectrum with that of model compound 2 shows that some of the fragment ions are common. The ions of m/z 85, 92 and 81, which are generated from the adduct, are characteristic of the cycloaddition product. The relative abundances of the fragment ions of 2, however, are not the same as those of the adduct.

The problem of interference arises because both 1,3butadiene and acrolein radical cations react with their neutral precursors, and those systems give ions at the same nominal masses as those of the adduct. Thus, high mass resolution is necessary to 'isolate' the adduct. The combination of low rate of reaction, interferences, and the difficulty of maintaining constant partial pressures makes it difficult to obtain CAD spectra with good signal-to-noise ratios (S/N). The data obtained by FTMS support the conclusion that the reaction is slow for the time/pressure frame of a CI source. For these reasons, we chose the adduct formed in the reaction of the 1,3-butadiene radical cation and methyl vinyl ketone for a more careful examination under highpressure conditions (i.e. in the CI source of the tandem mass spectrometer).

The reaction of the 1,3-butadiene radical cation and methyl vinyl ketone produces a readily detectable adduct $[C_8H_{12}O]^{+}$ of m/z 124. The ion-molecule chemistry of methyl vinyl ketone alone also produces product ions of $[C_8H_{12}O]^{+}$ that interfere with studies of the cross-chemistry of 1,3-butadiene and methyl vinyl ketone. The reaction of the d_6 -1,3-butadiene radical cation and methyl vinyl ketone, which generates an adduct of $[C_8D_6H_6O]^{+\cdot}$ of m/z 130, was chosen so that the adduct is free from any interference from the methyl vinyl ketone chemistry.

The adduct was generated in the CI source at pressures in the range of 0.3 to 0.5 Torr. To study the adduct as a function of its internal energy, the adduct was also generated in the presence of a variable amount of a bath gas of CS_2 . The stabilization that the adduct receives is twofold: (i) the adduct collides with CS_2 and loses some of its internal energy, and (ii) the non-ionized reactants (methyl vinyl ketone or 1,3-butadiene) undergo charge exchange with CS_2^+ to produce molecular ions with less internal energy than would be formed by direct electron ionization (EI).^{1,2} The CAD spectrum of the adduct does not change when the adduct is collisionally stabilized with a bath such as CS_2 . Thus, the adduct is stable and not sensitive to isomerization.

Although the CAD spectra of 1 and of the adduct are similar, there are notable differences in fragmentation patterns (compare Figs 3 and 4). The radical cation of 1 decomposes by the loss of CH₃⁺ to give an ion of m/z109, whereas the deuterium labelled adduct fragments to give ions of m/z 115 and 113 arising by losses of CH₃⁺ and CD₂H⁺, respectively. The loss of methyl must arise via two different pathways. The reference compound 1 also gives an ion of m/z 81, whereas the adduct produces an ion of m/z 87; both ions arise from the loss of C₂H₃O⁺. The ion of m/z 43 arises by the losses C₆D₆H₃⁻ and C₆H₉⁺, from the adduct and the molecular ion of 1, respectively, and is likely to be the side chain [CH₃CO]⁺.

The ion of m/z 54, $[C_4H_6]^{+*}$, however, is not formed in the decompositions of 1, whereas the most abundant fragment of the adduct is the ion of m/z 60, $[C_4D_6]^{+*}$. The fragment ion of m/z 60, arises by reversion to starting materials. One possible explanation is that a portion of the adduct exists as an ion-dipole complex, which splits apart upon CA to regenerate $[C_4D_6]^{+*}$. The width of the peak at half height for the ion of m/z 60, however, is as large as any other peak in the CAD spec-



Figure 4. The CAD spectrum of the adduct formed from the reaction of d_{e} -1,3-butadiene and methyl vinyl ketone.

trum of the adduct. This suggests the production of a fragment from a covalently bound species. If this is true, then the fragment is a signature of a covalently bound adduct and indicates that the hypothesis of a cyclo-addition to give 3-(cyclohexenyl)-ethanone is not correct.

Alternative cycloaddition

On the basis of cycloaddition of neutral molecules, one expects that the 1,3-butadiene radical cation plus methyl vinyl ketone would result in production of the radical cation of 3-(cyclohexenyl)-ethanone. Condensed-phase radical-cation cycloadditions, however, do not follow the same rules as those of their neutral counter-parts.³ Because both acrolein and methyl vinyl ketone are conjugated dienes, these species can also react as the diene in a cycloaddition.

The reactions of the 1,3-butadiene radical cation with acrolein or methyl vinyl ketone, in which acrolein and methyl vinyl ketone react as the diene, produce the radical cations of 2-ethenyl-3,4-dihydropyran (3) and 2ethenyl-3,4-dihydro-6-methylpyran (4), respectively (see Eqn (2)). A cycloaddition of this type is unusual because neutral 1,3-butadiene 'cycloadds' with methyl vinyl ketone or acrolein to form structures 1 and 2, respectively.

In the condensed phase, it is known that 2substituted pyran compounds such as 3 and 4 can undergo the Claisen rearrangement to form a 3substituted cyclohexene ring if the substituent is a vinyl or substituted vinyl group (see Eqn (5)).⁹ Sarraf,



Morizur and Audier¹⁰ showed that upon EI, 2substituted-2,3-dihydro pyran compounds undergo a specific rearrangement prior to fragmentation. More specifically, the two radical cation isomers, 2-ethenyl-2, 3-dihydropyran (3), and 3-cyclohexenecarboxaldehyde (2), isomerize to a common structure and decompose to give a similar array of fragments (see Table 1).

The compounds 2 and 3 are the models for the two possible cycloadditions between 1,3-butadiene and acrolein (see Eqns (1) and (2)). They are also related because 3 can isomerize to 2 via the Claisen rearrangement (see Eqn (5)). Comparison of their CAD spectra reveals that only one fragment ion is not common to both structures, and that is the ion of m/z 54. This ion is only produced upon CA of 3. The radical cations of 2 and 3 are indistinguishable by their metastable decompositions; under these conditions, the ion of m/z 54 is not a fragment of either structure. When the radical cations of compounds 2 and 3 are ionized by charge exchange with CS_2^+ and stabilized with the neutral bath gas CS_2 , their CA fragmentations change consistently with respect to the ions of m/z 95, 92, 81 and 79. Again, the only difference is the ion of m/z 54 which decreases from 65% relative abundance when unstabilized to 32% relative abundance when the adduct is stabilized at high pressure (i.e. 0.5 Torr) (see Fig. 5 for the extremes).

The losses of CH_3 , H_2O and CHO' to give the fragments of m/z 95, 92 and 81, respectively, from the radical cation of 3 are not possible unless the parent compound undergoes some kind of isomerization. This leads us to propose that cleavage of the bond between the oxygen and carbon (2) takes place, resulting in an acyclic distonic ion. Cleavage of the bond between carbons (2) and (3) of the radical cation of 2 results in the same structure 5 (see Eqns (6) and (7)).



Table 1. The relative abundances of CAD ions of C₇H₁₀O reference compounds

m/z	2	3
109	7.2	8.9
108	1.8	1.3
107	2.0	1.4
95	13.8	12.2
92	11.8	12.9
91	4.7	3.0
81	13.4	12.6
79	15.3	12.6
78	4.0	4.0
77	6.9	2.7
67	2.3	3.2
54	0.9	8.2
41	1.5	1.9



Figure 5. The CAD spectra of the reference compound 2-ethenyl-2,3-dihydropyran: (a) without a bath gas, and (b) with a bath gas of CS_2 added.

Therefore, both cycloadditions produce radical cations that may be related. Many of the fragmentations are the same and occur in similar proportions. Thus, their relationship needs to be explored further.

To estimate the potential energy surface (see Fig. 6) for the reaction system, the appearance energies of the ions of m/z 110, 95, 92, 81 and 54 were measured for compounds 2 and 3 (see Table 2).¹⁸ The ions of m/z 95, 81 and 54 have similar critical energies for formation from both structures, and the heats of formation for the radical cations of both compounds are within 2 kcal/mol (1 kcal = 4.184 kJ) of each other. The critical

energy barrier for the ion of m/z 92, formed by the loss of H₂O, is 5 kcal/mol (l kcal = 4.184 kJ) less for 2 than for 3. The loss of H₂O from structure 2 without a ringopening, is conceivable, whereas for 3 it is not. The ion of m/z 95, resulting from the loss of CH₃[•] is not possible from either structure without ring-opening. The ion of m/z 81, formed by the loss of CHO[•] is possible from 2 without a rearrangement, but not from 3. The highresolution EI spectra of 2 and 3 confirm that the ions of m/z 81 are from the loss of CHO[•] rather than of C₂H₅[•]. The ion of m/z 54, which occurs by the retro-Diels– Alder (RDA) reaction, can be formed from both struc-



Figure 6. Schematic potential energy surface for the ion-molecule reaction of the 1,3-butadiene radical cation with acrolein. The numerical values are estimates in kcal/mol (kcal \equiv 4.184 kJ).

 Table 2. Thermochemistry¹⁸ of two cycloaddition products for the ion-molecule reaction between the 1,3-butadiene radical cation and acrolein

3-Cyclohexenecarboxaldehyde $\Delta H_{f} = -26.77 \text{ kcal/mol}^{a}$ $AE_{110} = 8.9 \pm 0.1 \text{ eV}$ $AE_{95} = 9.8 \pm 0.1 \text{ eV}$ $AE_{92} = 9.3 \pm 0.1 \text{ eV}$ $AE_{91} = 10.0 \pm 0.1 \text{ eV}$ $AE_{54} = 11.3 \pm 0.1 \text{ eV}^{b}$ 2-Ethenyl-2.3-dihydropyran $\Delta H_{f} = -7.97 \text{ kcal/mol}^{a}$ $AE_{110} = 8.2 \pm 0.1 \text{ eV}$ $AE_{95} = 9.0 \pm 0.1 \text{ eV}$ $AE_{92} = 8.8 \pm 0.1 \text{ eV}$ $AE_{81} = 9.1 \pm 0.1 \text{ eV}$ $AE_{54} = 10.8 \pm 0.1 \text{ eV}$

 $a 1 \text{ kcal} \equiv 4.184 \text{ kJ}.$

^b The ionization efficiency curves for the m/z 54 ions are not parallel to those of standards but instead decrease more slowly. The *AE* is an upper estimate at best.

tures without any rearrangement prior to fragmentation.

The close correlation between the critical energies for the ions of m/z 95, 81 and 54 may indicate that they are fragments originating from a common structure. Upon CA of the radical cation of 2, however, the ion of m/z 54 is not formed whereas it is for 3.

Rationalization of this key result may come from considering the competition between the rate of ring opening and that of double-bond isomerization. Deuterium labeling experiments show that the loss of methyl from the cyclohexene radical cation occurs after complete scrambling.¹¹ Thus, the barrier for double-bond migration in a cyclohexene ring is less than that of ring opening. For the radical cation of **2**, the rate of doublebond migration is expected to be larger than that of ring-opening to give an acyclic distonic ion. After appropriate double-bond migrations occur, the resulting structure cannot undergo the RDA reaction to give the m/z 54 ion (see Eqns (8) and (9)). Thus, the ions



of m/z 95, 92 and 81 are probably formed by different fragmentation pathways for structures 2 and 3, and the close correlation in fragmentation of 3 is fortuitous. See Fig. 6 for a diagram of the potential energy surface derived from these data.

Acyclic models

The studies of the 1,3-butadiene radical cation with 1,3butadiene, and the vinyl methyl ether radical cation with butadiene, show that both reactions occur as twostep cycloadditions.^{1,2} These reaction adducts, generated at high pressure, undergo fragmentation characteristic of an acyclic structure. This was determined by comparison of the CAD spectra of the adducts with those of suitable model compounds. Less than perfect matches are found. This is consistent with the formation of an acyclic distonic radical cation as the reaction intermediate (see Eqns (10) and (11)). The intermediate cannot be appropriately modeled by ionizing



stable, synthetic model compounds. Nevertheless, a series of acyclic model compounds of the formula $C_8H_{12}O$ were prepared; the fragments formed upon CA of the molecular radical cations are listed in Table 3.

There are two classes of acyclic model compounds that were investigated. The first class is the octadiene-2ones, which represent the carbon skeleton of an adduct in which the butadiene radical cation adds to the 4position of methyl vinyl ketone (see Eqn (12)). Ionization of the model compounds forms conventional



radical cations that may be analogs of any intermediate distonic ions. A comparison of the CAD spectrum of the adduct with those of 5 and 6 shows two major differences: (i) the radical cations of both 5 and 6 lose C_2H_5 to give ions of m/z 95, and (ii) the radical cations of 5 and 6 do not form the ion of m/z 54.



The second class of acyclic compounds are the 3methylene heptene-2-ones, which are comprised of a carbon skeleton that mimics the adduct in which the 1,3-butadiene radical cation adds to the 3-position of

Table 3.	The relative abundances of CAD ions of C ₈ H ₁₂ O ref-
	erence compounds

		-			
m/z	1	5	6	7	8
123	4.5	1.6	6.8	5.5	6.6
109	15.4	13.2	11.7	34.2	28.9
95	3.6	15.4	35.6	1.4	2.0
81	24.5	15.6	14.6	16.4	17.1
80	8.8	5.7	5.7	3.0	5.2
79	6.4	6.7	5.0	4.4	5.8
77	4.2	4.4	2.5	3.4	3.5
43	13.0	13.7	4.6	14.4	13.0

$$\xrightarrow{\gamma} \xrightarrow{\gamma} \qquad \xrightarrow{\gamma} \qquad \xrightarrow{\gamma} \qquad (13)$$

methyl vinyl ketone (see Eqn (13)). Comparison of the CAD spectra of 7 and 8 with that of the adduct shows that the ions of m/z 109, 81 and 43 are common fragments, but their relative abundances are different. Moreover, the radical cations of 7 and 8 do not form the ion of m/z 54.



These comparisons yield no evidence for an acyclic structure for the adduct. The comparisons do reveal, however, that the various isomers are differentiable by CAD analysis, which rules out an interpretation that the adduct and its cyclic models are two examples of a large class of $C_8H_{12}O$ isomers that give common CAD spectra (see Table 3).

Mechanism

In the FT-mass spectrometer, where there is no opportunity for collisional stabilization of an ionmolecule adduct, it is expected that collisions with the right orientation would result in formation of an adduct followed by either decomposition or rearrangement and decomposition. This situation makes it impossible, from the experiments described, to obtain any direct structural information about the adducts from the FTMS experiments.

The high-pressure experiments, performed in the CI source, allow for direct observation of the adduct. These experiments aid in the determination of structure, but are of little help in determining the sequence of events that lead to formation of the reaction adduct.

Considering the results from the high-pressure experiments and from low-pressure measurements and the schematic potential energy surface, which is drawn in accord with the appearance energies, however, gives the necessary information for proposing a mechanism.

The 1,3-butadiene/acrolein reaction produces fragment ions of m/z 95, 92 and 81 that are consistent with cycloadditions to give either or both structures 2 and 3, but the evidence is not strong. For example, it is difficult to determine by means of FTMS experiments whether the adduct decomposes to give the highly characteristic m/z 54 ion because this ion is also reactant. These same arguments can be made about the 1,3butadiene/methyl vinyl ketone system. Thus, it is not possible to differentiate between the two cycloadditions from the FTMS experiments alone.

Comparison of the CAD spectra of the model compounds 2 and 3 reveals that the only distinguishing fragment is that of m/z 54 which is formed in the RDA reaction of 3. Audier and co-workers¹⁰ showed that the distinguishing characteristic between the radical cations of the isomers of 2-vinyl-2,3-dihydropyran systems and 3-cyclohexene aldehydes or ketones systems is the RDA reaction. 3-(Cyclohexenyl)ethanolie, 1, and 2-ethenyl-2, 3-dihydro-6-methylpyran, 4, (the two cycloaddition products possible from the butadiene-methyl vinyl ketone system) are isomers distinguishable by this characteristic. We were unsuccessful in our attempts to prepare the compound 2-ethenyl-2,3-dihydropyran; thus, that comparison cannot be made at this time. On the basis of the literature¹⁰ and the results obtained from the CAD spectra of compounds 2 and 3, however, it is likely that the radical cation of structure 4 would undergo the RDA reaction upon CA to produce the ion of m/z 54.

The CAD spectrum of the adduct formed by the reaction in an ionized mixture of d_6 -1,3-butadiene and methyl vinyl ketone shows quite clearly that it is a cycloadduct having the pyran structure, 4 (see Eqn (2)). The presence of the ion of m/z 60, which is formed by reversion to starting material, is substantial evidence that the adduct structure is the 2-ethenyl-2,3-dihydro-6methylpyran radical cation.

The results point to a general conclusion that the 1,3butadiene radical cation reacts with α,β -unsaturated aldehydes and ketones in a cycloaddition to give radical cations of 2-ethenyl-2,3-dihydropyran substituted accordingly at the 6-position (see Eqn (14)). The 1,3butadiene reacts as the 'ene' and methyl vinyl ketone as



the diene. This mode of reaction is in strong contrast to the corresponding neutral cycloaddition, and the radical-cation reaction may be of synthetic value as a method for the synthesis of 2,3-dihydropyran compounds. We were unable to determine whether the cycloaddition takes place by a concerted or stepwise mechanism.

EXPERIMENTAL

Mass Spectrometry

Collision-activated dissociation mass spectra were measured with a Kratos MS-50 triple analyzer mass spectrometer,¹² which consists of a Nier–Johnson geometry high-resolution mass spectrometer followed by an electrostatic analyzer (ESA-II). An ion of interest formed in the ion source was selected at a mass resolution of 3000–5000 (10% valley) by using MS-1 (ESA-I and the magnetic sector). ESA-II was scanned to give the metastable ion or CAD spectra of the mass selected ion. In a typical CAD experiment, 5–10 scans were acquired, and the signals were averaged.

Ion-molecule reactions were run in a commercially available (Kratos Scientific Instruments, Mark II) chemical ionization source, which was operated at 280 eV, a total emission current of 500 μ A, and at a temperature setting of 100 °C. Source pressure was esti-

mated by using an ion gauge located in the source pumping manifold. The ion gauge was not calibrated for these experiments. However, the pressures we report are based on the results of calibrations made for previous studies.^{1,2} The ion acceleration voltage was 8000 V.

The 1,3-butadiene (Matheson instrument grade) and d_6 -1,3-butadiene (Merck Isotopes) were admitted through a commercially available (Kratos Scientific Instruments) reagent gas inlet system operated at 100 °C. Carbon disulfide (Matheson Coleman and Bell reagent grade) was admitted through a custom-fabricated all glass heated system. Both the acrolein and methyl vinyl ketone (Aldrich Chemical Company) were admitted to the source via a home-built reservoir probe operated at ambient temperature. Gases were leaked into the source through a needle valve.

Fourier-transform mass spectra were recorded by using a home-built FT-mass spectrometer operating in the heterodyne mode,¹³ and controlled by a Nicolet 1000 data system and associated electronics. The 1,3butadiene and both the acrolein and methyl vinyl ketone were admitted through a metal inlet system held at ambient temperature. All reagents were put through a number of freeze-pump-thaw cycles. Typical operating pressures were 2×10^{-7} Torr for experiments involving one reagent and 4×10^{-7} Torr for experiments involving two reagents. Two reagents were always admitted separately to give a 1:1 mixture in the cell. Time delay experiments were performed by acquiring spectra at times varying from 1 to ~1500 ms post ionization.

Reference compounds

The reference compounds that were synthesized were characterized by mass spectrometry (Kratos MS-50 double analyzer) and ¹H NMR spectroscopy (Nicolet NIT-360).

3-(Cyclohexenyl)-1-ethanone(1)

This compound was synthesized by the reaction of 1,3butadiene and methyl vinyl ketone by the method of Diels and Alder.¹⁴ The mixture of 1,3-butadiene and methyl vinyl ketone in benzene was heated in a sealed glass tube for 48 h at 100 °C. The solvent was removed under reduced pressure, and the product was isolated via vacuum distillation. ¹H NMR: 1.55 (s, 2H), 1.95 (m, 1H), 1.99 (d of d, 2H), 2.10 (d of t, 1H), 2.18 (s, 3H), 2.55–2.65 (m, 1H), 5.69 (s, 2H). Mass spectrum (full scans at a resolution of 10 000, 70 eV) (found: M⁺⁺ = 124.0886, C₈H₁₂O requires M⁺⁺ = 124.0888) (67%), m/z 109 (15%), m/z 95 (4%), m/z 81(100%), m/z 79 (39%), m/z 77 (11%), m/z 67 (5%), m/z 53 (27%).

3-Cyclohexene carboxaldehyde (2)

This compound was synthesized by the method of Diels and Alder.¹⁴ A mixture of 1,3-butadiene and acrolein in benzene was heated in a sealed tube for 48 h at 100 °C. The solvent was removed under reduced pressure, and the product was isolated via vacuum distillation. ¹H NMR: 1.60 (m, 1H), 1.94 (d of t, 1H), 2.05 (q, 2H), 2.17 (d of d, 2H), 2.42–2.58 (m, 1H), 5.65 (d of t, 2H), 9.65 (s, 1H). Mass spectrum full scans at a resolution of 10000, 70 eV) (found: $M^{+*} = 110.0731$, $C_7H_{10}O$ requires $M^{+*} = 110.0732$) (39%), m/z 95 (12%), m/z 92 (9%), m/z81 (26%), m/z 79 (100%), m/z 77 (11%), m/z 67 (18%), m/z 53 (11%).

2-Ethenyl-2,3-dihydropyran (3)

This compound was synthesized by the modified Wittig procedure.⁹ ¹H NMR: 1.40–2.20 (m, 4H), 4.30 (m, 1H), 4.65–4.80 (m, 1H), 5.05–5.45 (m, 2H), 5.85–5.95 (d of d of d, 1H), 6.32, (d of t, 1H). Mass spectrum (full scans at a resolution of 10000, 70 eV) found: M^{+*} 110.0730, $C_7H_{10}O$ requires M^{+*} 110.0732) (52%), m/z 95 (12%), m/z 92 (8%), m/z 81 (34%), m/z 79 (22%), m/z 55 (42%), m/z 54 (100%), m/z 53 (28%).

3,7-Octadiene-2-one (5)

This compound was prepared from the reaction of the Grignard reagent of 4-bromo-1-butene with 4-(N,N-diethylamino)-methyl vinyl ketone as described for the Benary reaction.¹⁵ ¹H NMR: 2.23 (s, 3H). 2.30 (m, 4H), 5.00 (m, 2H), 5.80 (m, 1H), 6.10 d of t, 1H), 6.80 (d of t, 1H). Mass spectrum (full scans at a resolution of 10 000, 70 eV) found: $M^{+*} = 124.0886$, $C_8H_{12}O$ requires $M^{+*} = 124.0888$) (25%), m/z 109 (33%), m/z 95 (7%), m/z 81 (100%), m/z 80 (23%), m/z 79 (38%), m/z 67 (22%), m/z 55 (36%).

3,5-Octadiene-2-one (6)

This compound was prepared by using the Wadsworth-Emmons reaction between 2-pentanal and acetonyl diethyl phosphonate as described by Crandall and Mayer.¹⁶ ¹H NMR: 1.06 (t, 3H), 2.31 (s, 3H), 2.38 (d of q, 2H), 5.92 (d of t, 1H), 6.14 (d of d, 1H), 6.16 (d, 1H), 7.48 (d of d, 1H). Mass spectrum (full scans at a resolution of 10 000, 70 eV) (found: $M^{+*} = 124.0893$, C₈ H₁₂O requires $M^{+*} = 124.0888$) (24%), *m/z* 109 (13%), *m/z* 95 (100%), *m/z* 81 (43%), *m/z* 79 (20%), *m/z* 77 (7%), *m/z* 67 (5%), *m/z* 53 (15%).

3-Methylene 6-heptene-2-one (7)

This compound was synthesized via the acetoacetic ester synthesis of ketones by using the reaction between methyl acetoacetate and 4-bromo-1-butene.¹⁷ ¹H NMR: 2.17 (m, 2H), 2.25 (s, 3H), 2.45 (t, 2H), 4.92–5.03 (m, 2H), 5.72–5.83 (m, 1H), 5.79 (s, 1H), 6.05 (s, 1H). Mass spectrum (full scans at a resolution of 10 000, 70 eV) (found M⁺⁺ = 124.0893, C₈H₁₂O requires M⁺⁺ = 124.0888) (5%), m/z 109 (56%), m/z 81 (100%), m/z 79 (14%), m/z 70 (14%), m/z 67 (14%), m/z 55 (26%), m/z 53 (22%).

3-Methylene 5-heptene-2-one (8)

This compound was synthesized via the acetoacetic ester synthesis of ketones by using the reaction between methyl acetoacetate and 4-bromo-2-butene.¹⁷ ¹H NMR: 1.67 (d, 3H), 2.35 (s, 3H), 3.45 (d, 2H), 5.35–5.52 (m, 2H), 5.79 (s, 1H), 6.02 (s, 1H). Mass spectrum (70 eV) (found: $M^{++} = 124.0886$, $C_8H_{12}O$ requires $M^{++} = 124.0888$) (10%), m/z 109 (100%), m/z 81 (79%), m/z 79

(33%), m/z 77 (8%), m/z 67 (5%), m/z 55 (19%), m/z 53 (27%).

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