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Isomeric differentiation of conjugated diene epoxides by polar [4 + 2$^+$] Diels–Alder cycloaddition of acylium ions in an ion trap mass spectrometer

M. Sharifi[1], J. Einhorn*

INRA, Unité de Phytopharmacie et Médiateurs Chimiques, Route de St. Cyr, 78026 Versailles, France

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Abstract

Polar [4 + 2$^+$] Diels–Alder cycloaddition is performed using acylium cations as reagent ions for the characterization and differentiation of isomeric conjugated diene epoxides. The [M + RCO]$^+$ cycloadduct that is produced is unstable and dissociates not by retrocycloaddition, but by pathways favored by the epoxide ring that lead mainly to substituted pyrilium ions. These product ions display *m/z* ratios that correlate with either the epoxide (R_1) or diene (R_2) substituents, thus serving as structurally diagnostic ions for isomeric differentiation. The multiple tandem mass spectrometric (MS^n) capabilities of the quadrupole ion trap mass spectrometer (QITMS) were particularly useful for designing multistep procedures sometimes required for reagent-ion preparation and isolation. They were also appropriate when an additional collisionally induced dissociation (CID) stage was desired to provide further information on any product ion or for additional selectivity. (Int J Mass Spectrom 190/191 (1999) 253–264) © 1999 Elsevier Science B.V.

Keywords: Isomer differentiation; Conjugated diene epoxides; Diels–Alder reaction; Acylium ion; Ion–molecular reaction; Ion trap mass spectrometer

1. Introduction

Gas-phase ion–molecule reactions can provide decisive information regarding the characterization and location of functional groups in aliphatic compounds or for isomeric differentiation in many types of structures [1,2]. To perform such reactions, the quadrupole ion trap mass spectrometer (QITMS) has become of increasing importance because of its ability to control reaction times and its multistage operating sequence (MS^n) features [3,4]. The flexibility of the ion trap in implementing efficient sequences through the use inter alia of convenient radiofrequency waveforms [5] make it suitable to achieve ion–molecule reactions for structural determinations [6–10] including isomer differentiation [11–13]. Moreover, interesting strategies may result from the use of the QITMS as a device to perform mass-selected ion–molecule reactions [14–16]. This approach is essential for better control of ion energetics and to facilitate investigations on specific ion reactivities.

Our current effort to investigate ion–molecule reactions for the practical structure characterization of

* Corresponding author. E-mail: einhorn@versailles.inra.fr

[1] Present address: Trent University, Department of Chemistry, Peterborough, ON K9J 7B8, Canada.

Dedicated to J.F.J. Todd and R.E. March in recognition of their original contributions to quadrupole ion trap mass spectrometry.

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natural microsubstances (insect "semiochemicals") [17] led us to define a number of efficient agents and strategies particularly adapted to the ion trap instrumentation [18]. Of most interest were our findings concerning the reactivity of the $C_2H_5^+$ cation towards conjugated diethylenic epoxide systems [18a]. Under these conditions, an acylium ion is formed through the regioselective decomposition of the MH^+ ion and the fragment ion can further react by [4 + 2$^+$] cycloaddition with the diene moiety of a second neutral molecule. The same process has been shown by Eberlin and Cooks [19] to occur, in general, between acylium ions and conjugated dienes (i.e. isoprene) and was considered as a tool [19,20] to differentiate the ion species from any isomeric form. In the present study, our aim will be to demonstrate the utility of the process to characterize isomeric forms of neutral conjugated diene epoxides through the production of diagnostic-ion products resulting from the adduct. For better control of the reaction, the reagent ion will be produced "externally" (and thus independently) instead of being made in situ from the same substrate. The experiments will be done using a series of C_{15} diene epoxides as model compounds and $C_4H_9CO^+$, CH_3CO^+ and isotope labeled analogues as reagent ions. The latter species will be prepared and finally mass selected through strategies optimally designed for the QITMS.

2. Experimental techniques

2.1. Instrumentation

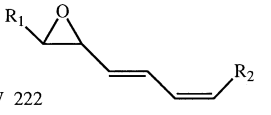
The experiments were performed on a Varian (Walnut Creek, CA) Saturn II GC/MS quadrupole ion trap mass spectrometer. Saturn revision C software was used for data acquisitions, whereas QISMS research version software was utilized to implement the necessary rf and dc voltage sequences for the preparation and mass selection of reagent ions and product–ion analysis. Electron ionization times of reagent gases ranged between 0.3 and 0.6 ms and pressures were set up at 1–2 $\times$ 10^{-5} Torr. The trap manifold temperature was held constant at 130 °C and the He buffer gas pressure was set at 1 mTorr in the ion trap cavity.

Isolation of parent product ions was achieved by the rf/dc apex technique [21,22] and collision-induced dissociation (CID) was performed by resonant excitation [23,24]. The parent ions were irradiated during 10 ms at a q_z 0.2 working point with a single-frequency sinusoidal waveform (153.6 kHz) of variable amplitude (optimized between 0.5 and 0.7 V_{p-p}) applied across the endcap electrodes.

Samples (~10 ng in hexane) were introduced in the mass spectrometer through a Varian Model 4200 gas chromatograph equipped with a DB-5 MS column (32 m $\times$ 0.25 mm inner diameter (i.d.), 0.25 μm film thickness) (J&W Scientific, Folson, CA) and a Ros needle injector (Chrompack, Middelburg, Netherlands).

2.2. Chemicals

Nitrous oxide (>99.9%; Alphagaz, Paris, France) was used to provide NO^+ cation. Valeraldehyde (>98%; Fluka, Buchs, Switzerland), acetone (99.8%, Fluka), and ^{2}H- or ^{13}C-labeled acetone (CD_3COCD_3 and $CH_3{}^{13}COCH_3$) (>99.95%; Fluka and >99%; Cambridge Isotope Laboratories, Baumgarten, Switzerland, respectively) were used as sources of acylium reagent ions and therefore introduced in the ion trap via mass calibration sample inlet. The model conjugated diene epoxides were synthesized starting from E-3-alkenols through conventional methods [25] e.g. epoxidation followed by tetrapropylammonium perruthenate (TPAP) oxidation [26] into aldehydes and two consecutive Wittig reactions. The E,Z-diunsaturated *trans*-epoxides (see formulas) were obtained as major compounds.



MW 222

Compound	1	2	3	4	5	6
R_1	CH_3	C_2H_5	C_3H_7	C_4H_9	C_5H_{11}	C_6H_{13}
R_2	C_8H_{17}	C_7H_{15}	C_6H_{13}	C_5H_{11}	C_4H_9	C_3H_7

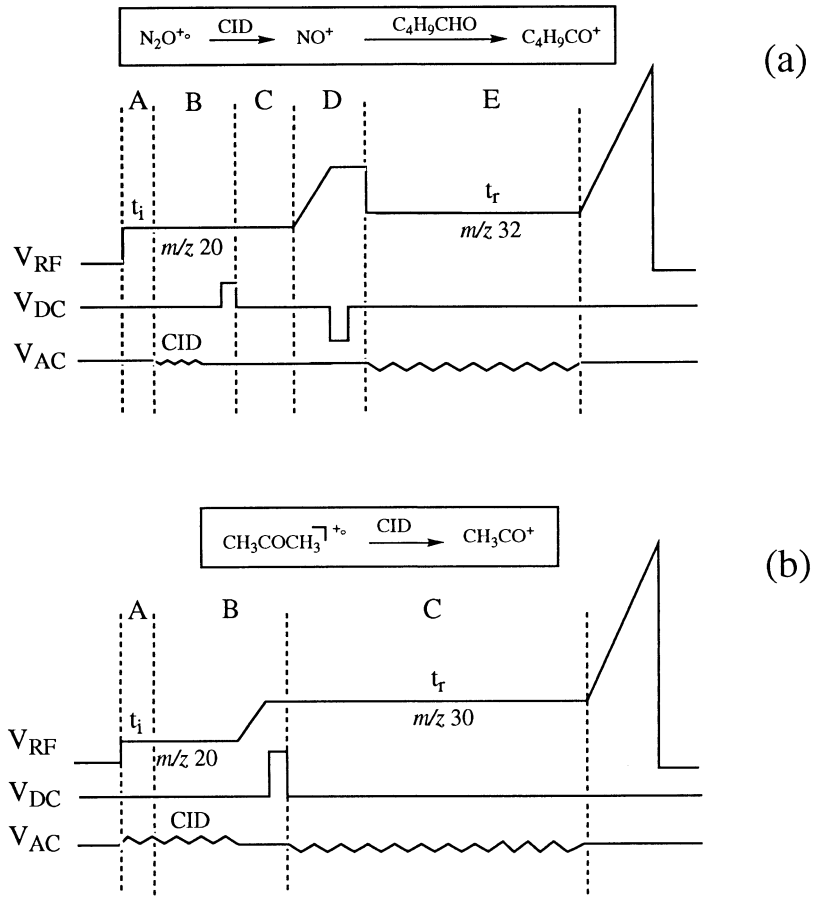


Fig. 1. Scan functions used for reagent ion preparation and mass selection for $C_4H_9CO^+$ from valeraldehyde (NO^+/CI conditions) (a) and CH_3CO^+ from acetone (EI conditions) (b) t_i = ionization time; t_r = reaction time with the substrate.

2.3. Acylium reagent-ion mass selection procedures

Acylium reagent ions once prepared (see below and Fig. 1) were mass selected using the QISMS software according to either rf/dc isolation [21,22] or resonance ejection/broadband ejection [27,28].

2.4. $C_4H_9CO^+$ cation preparation and mass selection

The hydride abstraction properties of NO^+ (hydride-ion affinity (HIA) = 246 kcal/mol) [1] were considered to prepare the acylium reagent ion $C_4H_9CO^+$ from valeraldehyde (C_4H_9CHO). In order to overcome the practical inconvenience associated with nitric oxide (NO) as a neutral source for this species [29], NO^+ was instead prepared from nitrous oxide (N_2O). However, to get an optimal yield and also higher production of the reactive $C_4H_9CO^+$ cation (85 Th), the NO^+ cation initial content (ionized N_2O gives rise to a mixture of NO^+ and $N_2O^{+\circ}$) was improved by a subsequent collisionally induced dissociation (CID) step that transformed some of the $N_2O^{+\circ}$ population into NO^+ (cf. Eq. 1). The latter (likely energetically cool after a 50 ms preparation time because it allows a large number of collisions with He and N_2O to occur) was then allowed to react with valeraldehyde to give $C_4H_9CO^+$ ions through a hydride abstraction process [Eq. (2)]. The structure of $C_4H_9CO^+$ versus isomeric forms was verified under

CID by the easy elimination of CO and the absence of loss of water

$$N_2O^{+\circ} \xrightarrow{CID} NO^+ \quad (1)$$

$$C_4H_9CHO + NO^+ \rightarrow C_4H_9CO^+ + HNO \quad (2)$$

Fig. 1 (a) reports the complete scan function that was designed in this case. The rf voltage is held at 224 V (corresponding to a low-mass cutoff value of *m/z* 20) during electron ionization of nitrous oxide (segment A). To increase the NO^+ ion population, an ac voltage that corresponds to $N_2O^{+\circ}$ ion motion frequency (151.8 kHz) is applied. The latter ions are thus resonantly excited and fragment into NO^+. The remaining $N_2O^{+\circ}$ ions are then axially ejected (segment B) by application of a positive dc voltage (26 V; 0.5 ms). After the required reaction time (C) between NO^+ and the aldehyde, the $C_4H_9CO^+$ reagent ion is mass selected using the rf/dc apex technique (D). During the next step (E), the [4 + 2^+] cycloaddition process between the acylium ion and the substrate is allowed to occur for a variable reaction period (t_r) at a constant rf level (low-mass cutoff value of *m/z* 32). An ac voltage is applied during this period to resonantly eject protonated valeraldehyde that could be formed concurrently.

2.5. Acetylium ion preparation and mass selection

The acetylium cations CH_3CO^+ (43 Th), $CH_3{}^{13}CO^+$ (44 Th) and CD_3CO^+ (46 Th), were prepared by CID of the $[CH_3COCH_3]^{+\circ}$ (cf. Eq. 3), $[CH_3{}^{13}COCH_3]^{+\circ}$ or $[CD_3COCD_3]^{+\circ}$ radical cation, respectively and their reactivity towards dienic epoxides was investigated after mass selection

$$(CH_3)_2CO^{+\circ} \xrightarrow{CID} CH_3CO^+ + H_3C^\circ \quad (3)$$

The corresponding scan function is shown in Fig. 1 (b). The rf level is set at a low cutoff value of 20 Th during ionization (A). To optimize the production of the acetylium cation, a supplementary ac voltage corresponding to the secular frequency of acetone (labeled or unlabeled) molecular ion is applied to induce its collisional activation (10 ms, A and B). In the next step, mass selection of the acetylium reagent ion is completed by increasing the rf level (low-mass cutoff at *m/z* 30) and applying a positive dc voltage to eliminate residual $[acetone]^{+\circ}$. The isolated acetylium cation is then allowed to react with a dienic epoxide during a variable reaction time (C). A supplementary multiple-frequency ac voltage (173.1–186.5 kHz) is applied continuously during this step to avoid the eventual formation of protonated acetone and $[acetone]^{+\circ}$.

3. Results and discussion

The product ion spectra of the isomeric conjugated diethylenic epoxides taken as models were recorded using various acylium cations as reagent species added independently. The latter were prepared, mass selected, and then allowed to react with neutral substrates during a variable reaction time. Depending on the number of ion isolation steps involved, such procedures correspond to MS^2 (acetylium or labeled analogue) or MS^3 ($C_4H_9CO^+$) experiments. Moreover, an additional isolation step may be introduced when structural information on any ion product is required.

3.1. Reactions induced by $C_4H_9CO^+$ cation

The mass-selected $C_4H_9CO^+$ product ion spectra (Fig. 2) of the diene-epoxides **3**–**6** were recorded using a 200 ms reaction time. These spectra exhibit a few peaks that correspond to product ions such as MH^+ (*m/z* 223)/$[MH - H_2O]^+$ (*m/z* 205) and the adduct ion $[M + C_4H_9CO]^+$ (*m/z* 307)/$[M + C_4H_9CO - H_2O]^+$ (*m/z* 289), reflecting two alternative reaction channels (proton transfer and condensation, respectively) between the acylium reagent ion and the conjugated system.

Besides the occurrence of the above mentioned species, some fragment ions are produced: (1) an ion of high relative abundance (40–70%) named A^+ appearing at *m/z* 123, 137, 151, and 165, respectively, for epoxides **3**–**6**, this *m/z* value being dependent on the size of R_1 (alkyl substituent of the oxiranne ring), and (2) an ion

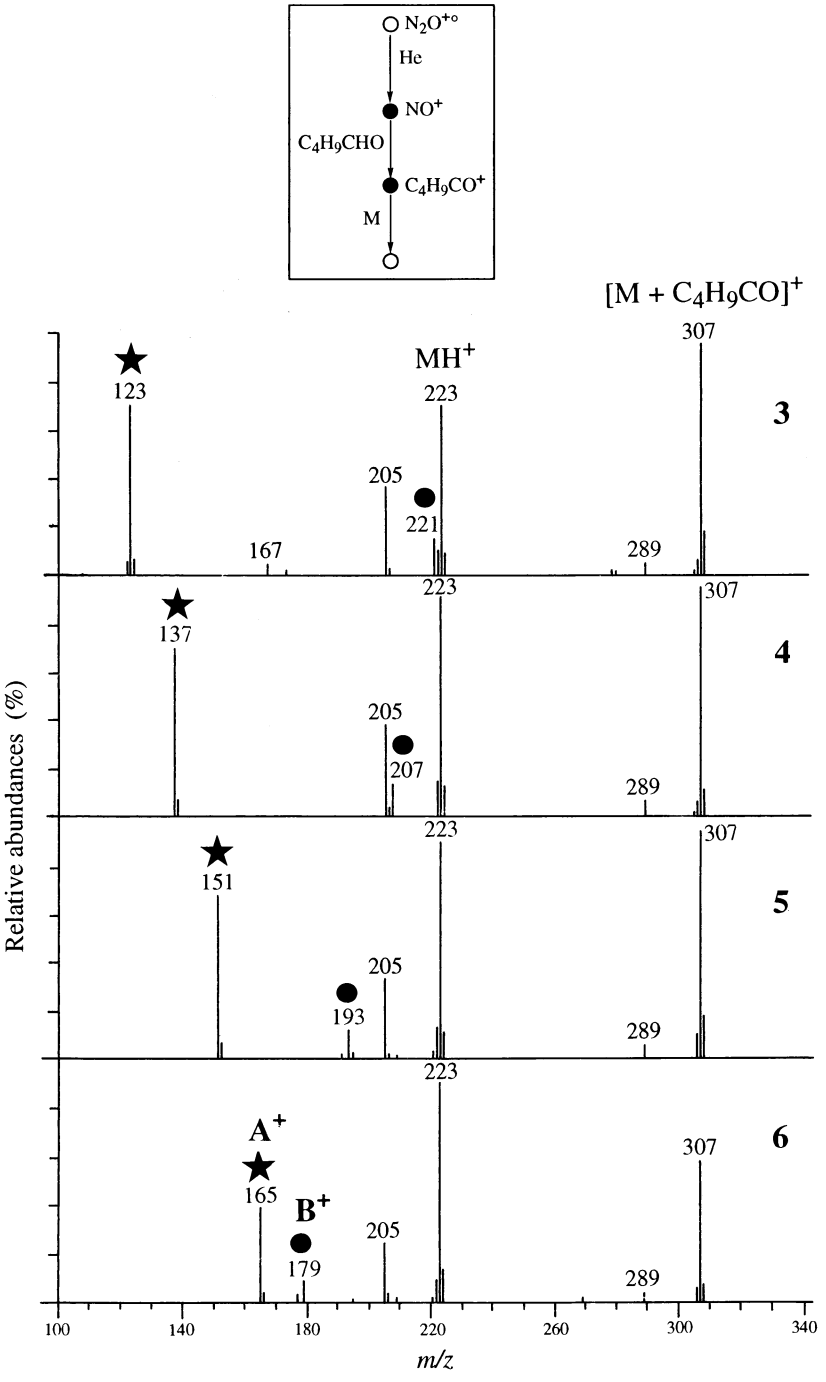


Fig. 2. $C_4H_9CO^+$ product ion spectra of the conjugated diene epoxides **3**–**6**. (Reaction time = 200 ms.) Diagnostic product ions A^+ and B^+ are labeled. Black circles in the insert indicate ion selection steps whereas white circles denote no selection (see [31]).

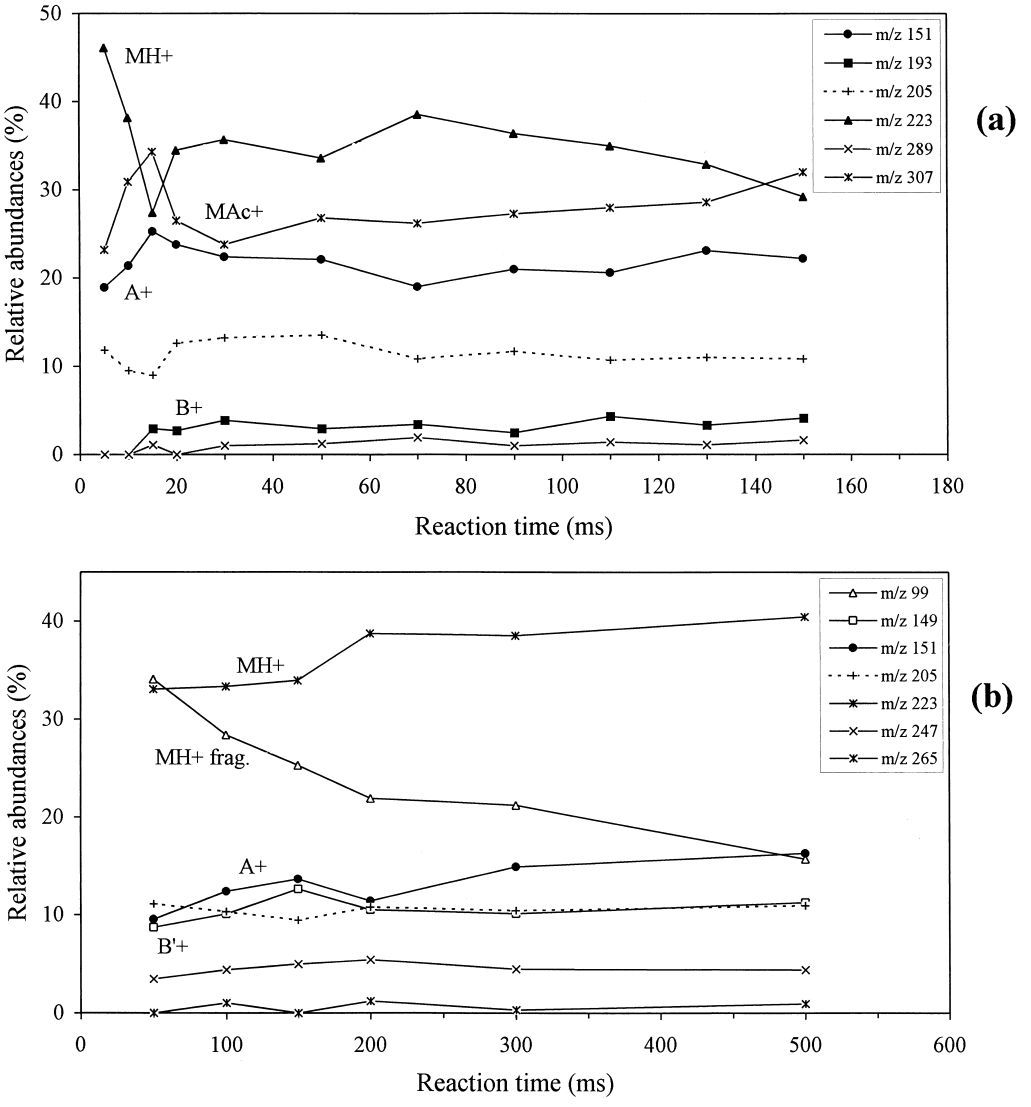


Fig. 3. Evolution of main ion abundances versus reaction time under $C_4H_9CO^+$ (a) or CH_3CO^+ (b) ion–molecule reaction conditions for diene epoxide **5**.

of lower abundance (B^+, ~10%) at *m/z* 221, 207, 193, and 179, respectively, for **3**–**6**. According to its *m/z* value, ion B^+ contains R_2 (alkyl substituent of the diene) and therefore must be considered as a complementary diagnostic ion versus A^+ for the differentiation of these conjugated diene epoxides.

Fig. 3 (a) shows the effect of reaction time on ion relative abundances. MH^+ and the adduct $[M + C_4H_9CO]^+$ display symmetrical evolutions that are particularly noticeable in the 5–50 ms interval. At short reaction times (5 ms), spectra are dominated by the MH^+ ion whereas the $[M + C_4H_9CO]^+$ ion is moderately abundant. When reaction duration is higher the competition between both processes appears less severe, probably as a consequence of the increased number of collisions with neutrals that can stabilize the excited adduct. In most of the intervals studied (20–150 ms) ions A^+ and B^+ appear of

Table 1
CID spectral data of the $[M + C_4H_9CO]^+$ adduct ion resulting from the mass-selected $C_4H_9CO^+$ reaction with diene epoxides **3–6**

	Species *m/z* (relative abundance)			
Compound	A^+	B'^+	MH^+	$[M + Ac - H_2O]^+$
3	123 (*100*)	219 (*16*)[a]	n.d.[b]	289 (*95*)
4	137 (*94*)	205 (*19*)	n.d.	289 (*100*)
5	151 (*100*)	191 (*26*)	223 (*15*)	289 (*47*)
6	165 (*100*)	177 (*29*)	223 (*35*)	289 (*40*)

[a] B^+ at *m/z* 221 (*12*) also present.
[b] Not detected. Ac: C_4H_9CO.

almost constant abundances, indicating a remarkable stability for the species under these ion–molecule reaction conditions.

In order to determine the possible relationships between the adduct ion and the fragment ions, CID of the former was recorded (chosen reaction time = 50 ms). The low-energy CID spectra of $[M + C_4H_9CO]^+$ for epoxides **3–6** are compared in Table 1 (MS^4 experiments). In these spectra, the A^+ cation appears as a major product ion. The B^+ ion is rarely detected (at *m/z* 221 for epoxide **3**) because under these conditions the adduct ion fragments preferably in giving B'^+ an ion that corresponds at least formally to $[B - H_2]^+$. The other ions resulting from the resonant excitation of $[M + C_4H_9CO]^+$ are $[M + C_4H_9CO–H_2O]^+$ and MH^+. These results thus indicate a preeminent role of the $[M + C_4H_9CO]^+$ excited adduct ion in the formation of the major observed product ions. CID was also performed on A^+. This ion did not dissociate under resonant excitation, confirming its stability.

Regarding our previous results obtained with $C_2H_5^+$ as reagent (conditions that produce an acylium ion of R_1CO^+ structure and in situ further "derivatization" of a neutral conjugated diene epoxide) [18a], the present observations exclude the aforementioned pathway of formation for A^+. The *m/z* value of this ion does not correlate with the acylium reagent whereas it does with the alkyl substituent (R_1) of the epoxide.

3.2. Reactions induced by CH_3CO^+ cation

The mass-selected CH_3CO^+ product ion spectra of the same isomeric diene epoxides **3–6** (Fig. 4) display again two main species in the high mass region, i.e. the adduct $[M + CH_3CO]^+$ (*m/z* 265) ion and the MH^+ ion (*m/z* 223) and thus confirm the two competitive reaction channels observed for $C_4H_9CO^+$. However, in contrast with the latter, the MH^+ ion is produced in much higher relative abundance since the adduct ion may not even be detected (epoxide **3**). Further, many fragments are likely produced by decomposition of the molecular species. $[M + CH_3CO]^+$ yields the $[M + CH_3CO–H_2O]^+$ ion at *m/z* 247 and should be responsible for the two series of diagnostic ions, that is A^+ (*m/z* 123 to *m/z* 165 for the diene epoxides **3–6**, respectively) appearing at the same *m/z* values as for $C_4H_9CO^+$ and B'^+ or $[B - H_2]^+$. In this case, ion B'^+ is preferable to B^+ (the presence of the latter is not excluded but its abundance is very low) and might indicate that a higher amount of internal energy is deposited into the excited $[M + CH_3CO]^+$ ion as a precursor that allows a subsequent step of decomposition (loss of H_2 from B^+). Moreover, from the observed *m/z* values, e.g. at *m/z* 177, 163, 151, and 135 for **3–6**, respectively, such ions must not only correlate with the size of R_2 but would also depend on the size of the acylium that is used as reagent (−42 u shift when replacing $C_4H_9CO^+$ by CH_3CO^+). On its side, MH^+ gives $[MH–H_2O]^+$ at *m/z* 205, an R_1-containing fragment (from *m/z* 71 to *m/z* 113 for **3–6**, respectively) and a number of ubiquitous ions of alkyl and alkenyl types. The R_1-containing ion must be of R_1CO^+ structure as was demonstrated in a previous study [18a].

These CH_3CO^+ product ion spectra were obtained using a 200 ms reaction time. For shorter reaction times [Fig. 3 (b)] the spectra exhibit a R_1CO^+ ion (e.g. MH^+ fragment) of higher abundance, to the detriment of MH^+. The same behaviour was noticed previously [18a] and was attributed to a possible cooling effect for MH^+ because of an increased number of collisions with the neutrals (He buffer gas, substrate) when increasing the reaction period. In the same interval A^+ and B'^+ ions display increasing yields as a result of a higher competitive production of the $[M + CH_3CO]^+$ adduct. However, this ion appears much more unstable than $[M + C_4H_9CO]^+$ and gives rise to fragments. Also remarkable, the A^+/B'^+

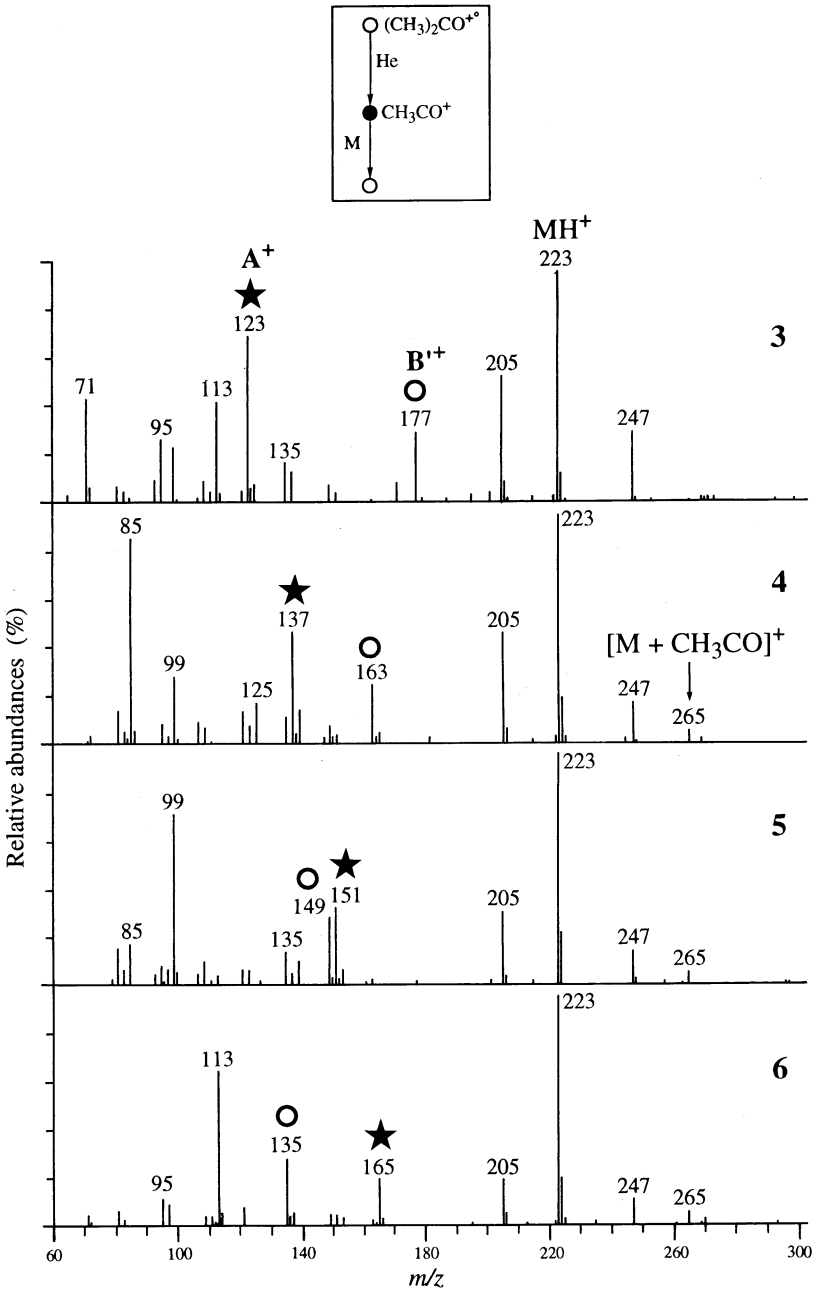


Fig. 4. CH_3CO^+ product ion spectra of the conjugated diene epoxides **3**–**6**. (Reaction time = 200 ms). Diagnostic product ions A^+ and B'^+ are labeled. The black circle in the insert indicates an ion selection step whereas white circles denote no selection (see [31]).

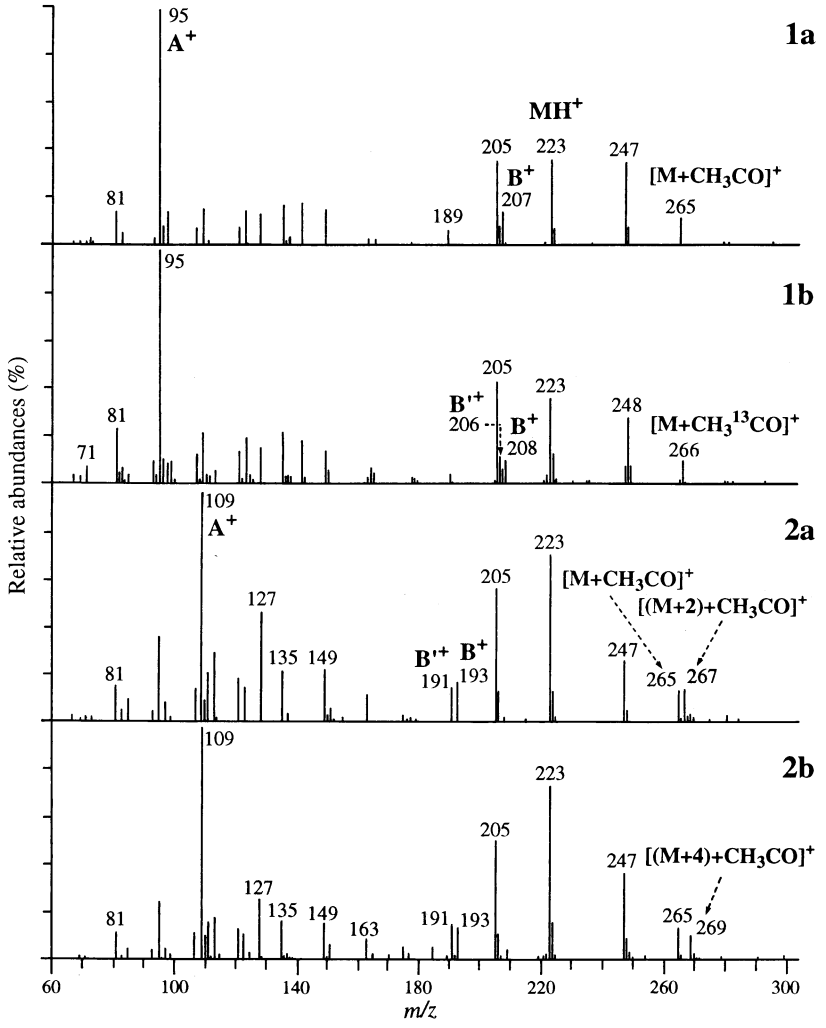


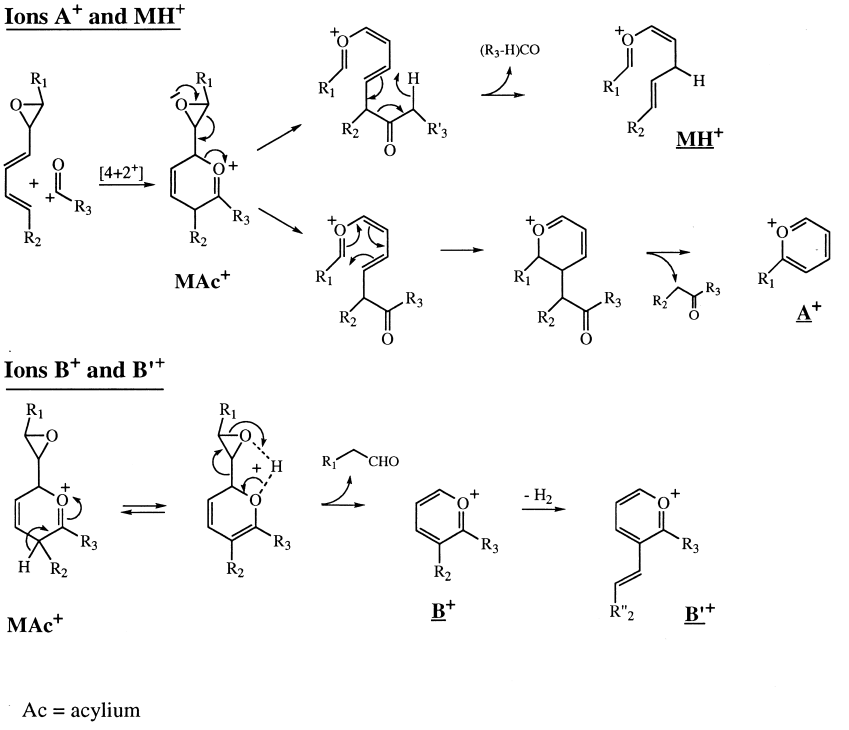
Fig. 5. Product ion spectra obtained with CH_3CO^+ (1a) or CH_3–$^{13}CO^+$ (1b) for diene epoxide **1** (reaction time = 50 ms) and with CH_3CO^+ for diene epoxide **2** after 50 ms (2a) or 200 ms (2b) reaction time.

ratio is found to be relatively stable (equal to ~1) versus a reaction time in the 20–200 ms interval, but slightly increases at higher values.

3.3. Reactions induced by labeled acetylium cations and further mechanistic pathways

Mass-selected reagent ion experiments were also performed using isotope labeled acylium cations. Methyl-d_3 acetylium (CD_3CO^+) or ^{13}C-labeled one (CH_3–$^{13}CO^+$) applied on the same diene epoxides than above gave rise to the production of $[M + CD_3CO]^+$ or $[M + {}^{13}COCH_3]^+$ and MD^+ or MH^+, respectively, as expected. It was also noticed that under CD_3CO^+ conditions, increasing reaction time from 50–200 ms gave a lower yield of R_1CO^+ (a potential "protonating" agent because it was not deuterium labeled) as expected but the increase of MD^+ abundance was not accompanied by any production of MH^+, thus confirming the above interpretation of collisional thermalization to explain this effect.

More interestingly, the B'^+ ion (and B^+ as well,



Scheme 1. Possible origin of the diagnostic-ion products from the reaction of RCO^+ with conjugated diene epoxides.

when detected) was found to shift by +3 u or +1 u, respectively, with these reactant ions demonstrating a complete integration of the acylium in this type of product ion. In the case of diene epoxide **1** (Fig. 5), the product ion spectrum obtained with the unlabeled reagent exhibits ion B^+ at *m/z* 207 and it cannot be determined whether B'^+ is also produced under these conditions because its signal would be superimposed with $[MH - H_2O]^+$ at *m/z* 205. The spectrum obtained with CH_3–$^{13}CO^+$ clearly ascertains (+1 u shift) the formation of both ions in equal abundances. In contrast, the ion A^+ *m/z* value remained unchanged in the presence of either labeled reagent. This finding thus provided evidence of the noninvolvement of the reagent in this product.

According to these data and to explain the main product ions obtained under reaction conditions or CID, an initial polar $[4 + 2^+]$ Diels–Alder cycloaddition reaction is postulated (Scheme 1). The resulting adduct ion can then decompose through an epoxide assisted ring opening giving rise to a R_1-substituted pyrilium ion (A^+) after recyclisation and elimination of a ketone or to MH^+ (isomeric form) by loss of a ketene. Concurrently, the adduct can isomerize through proton transfer and eliminate an aldehyde to yield a disubstituted pyrilium ion (B^+) or B'^+ (likely α,β-unsaturated pyrilium) after a subsequent loss of H_2. The latter might eventually result from a bimolecular reaction with M yielding $(M + H_2)$ or $(M + 2H_2)$ neutrals because the corresponding addition products with CH_3CO^+ were detected in some cases (Fig. 5). Under reaction conditions, MH^+ is further formed in competition with the adduct by direct protonation of the substrate by the acylium reagent ion. Under CID, MH^+ might be formed to some extent by reactions of the adduct or its fragments with the residual neutral.

The higher fragmentation content issuing from MH^+ observed with the acetylium ion versus $C_4H_9CO^+$ is consistent with the expected proton

affinities (APs) order for these species ($C_4H_9CO^+ > CH_3CO^+$ with AP of $CH_3CO^+ = 198$ kcal/mol) [30]. Also remarkable is the nonrecovery of the acylium ion by decomposition of the cycloadduct in contrast with the results of Eberlin and Cooks [19]. The [4 + 2^+] Diels–Alder cycloaddition process is strongly supported, however, by the failure to observe an addition product in the case of conjugated monoethylenic epoxides, or similar decomposition behaviour when studying homoconjugated diene epoxide corresponding adducts.

4. Conclusion

In this study, a new application of the polar [4 + 2^+] Diels–Alder reaction of acylium ions in the gas phase is reported. The addition of the reagent ion occurs on the diene subunit of conjugated diethylenic epoxides to give rise to a cyclic adduct ion. The cycloaddition process is probably regioselective and thus oriented by the presence of the oxiranne ring. The observed decomposition product ions issuing from the adduct having *m/z* ratios dependent on the substituents of the initial substrate should be considered diagnostic ions for isomer differentiation purposes. These findings confirm the high potential of the ion trap, in particular when using its MS^n capabilities, to perform ion–molecule reactions of high selectivity on natural substrates of unknown structures.

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