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Reactions of gaseous acylium ions with 1,3-dienes: further evidence for polar [4 + 2+] Diels–Alder cycloaddition

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A novel reaction of acylium and thioacylium ions, polar [4 + 2+] Diels–Alder cycloaddition with 1,3-dienes and *O*-heterodienes, has been systematically investigated in the gas phase (Eberlin MN, Cooks RG. *J. Am. Chem. Soc.* 1993; 115: 9226). This polar cycloaddition, yet without precedent in solution, likely forms cyclic 2,5-dihydropyrylium ions. Here we report the reactions of gaseous acylium ions [$(CH_3)_2N$—C^+=O, Ph—C^+=O, $(CH_3)_2N$—C^+=S, CH_3—C^+=O, CH_3CH_2—C^+=O, and CH_2=CH—C^+=O] with several 1-oxy-substituted 1,3-dienes of the general formula RO—CH=CH—$C(R^1)$=CH_2, which were performed to collect further evidence for cycloaddition. In reactions with 1-methoxy and 1-(trimethylsilyloxy)-1,3-butadiene, adducts are formed to a great extent, but upon collision activation they mainly undergo structurally unspecific retro-addition dissociation. In reactions with Danishefsky's diene (*trans*-1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene), adducts are also formed to great extents, but retro-addition is no longer their major dissociation; the ions dissociate instead mainly to a common fragment, the methoxyacryl cation of *m/z* 85. This fragment ion is most likely formed with the intermediacy of the acyclic adduct, which isomerizes prior to dissociation by a trimethylsilyl cation shift. Theoretical calculations predict that *meta* cycloadducts bearing 1-methoxy and 1-trimethylsilyloxy substituents are unstable, undergoing barrierless ring opening induced by the charge-stabilizing effect of the 1-oxy substituents. In contrast, for the reactions with 1-acetoxy-1,3-butadiene, both the experimental results and theoretical calculations point to the formation of intrinsically stable cycloadducts, but the intact cycloadducts are either not observed or observed in low abundances. Both the isomeric *ortho* and *meta* cycloadducts are likely formed, but the nascent ions dissociate to great extents owing to excess internal energy. The *ortho* cycloadducts dissociate by ketene loss; the *meta* cycloadducts undergo intramolecular proton transfer to the acetoxy group followed by dissociation by acetic acid loss to yield aromatic pyrylium ions. Either or both of these dissociations, ketene and/or acetic acid loss, dominate over the otherwise favored retro-Diels–Alder alternative. The pyrylium ion products therefore constitute compelling evidence for polar [4 + 2+] cycloaddition since their formation can only be rationalized with the intermediacy of cyclic adducts. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: acylium ions; ion–molecule reactions; mass spectrometry; polar Diels–Alder cycloaddition reactions; gas-phase ion chemistry

INTRODUCTION

Diels–Alder cycloadditions are classical reactions of vast use in chemistry.[1] Many synthetic routes to cyclic compounds are made possible through these [4 + 2] cycloadditions, which are favored for a large variety of dienes and dienophiles. Diels–Alder cycloadditions usually employ uncharged or dipolar components, but many positively

or negatively charged activated dienes or dienophiles are also advantageously used in reactions known as polar cycloadditions.[2]

The high-vacuum solvent-free environment of mass spectrometers provides a convenient medium in which to study the intrinsic reactivity of isolated long-lived ionic species, to measure their properties, to prove their participation as key ionic reaction intermediates, to explore the use of ion–molecule reactions as analytical structurally diagnostic tools and to study the intrinsic feasibility of new reactions involving charged species (for recent reviews on analytical, synthetic and mechanistic applications of ion–molecule reactions, see Ref. 3; for recent general examples, see Ref. 4). In the gas phase, acylium ions (R—C^+=O) are stable, long-lived,

very versatile and reactive cations, and a variety of new reactions of gaseous acylium ions of synthetic and analytical importance have been described (for recent examples, see Ref. 5).

In the gas phase, many polar cycloadditions have been observed, and their synthetic and analytical applications explored (for recent examples, see Ref. 6). Whether these gas-phase reactions occur in a concerted or stepwise fashion is difficult to determine experimentally, hence this mechanistic detail has been a subject of debate,[7] but the potential of cycloadditions for the structural elucidation of gaseous ions and neutrals and as a test of the intrinsic feasibility of novel polar cycloadditions is unquestionable, yet not fully explored. We have reported a novel cycloaddition reaction of gaseous acylium and thioacylium ions: polar $[4 + 2^+]$ Diels–Alder cycloaddition with 1,3-dienes.[8] This gas-phase reaction, yet without precedent in solution, likely yields cyclic 2,5-dihydropyrylium ions (Scheme 1), and experimental and theoretical evidence on some special cases for cyclic adducts has been collected. Although whether a concerted or stepwise-like process operates could not yet be determined, theoretical calculations predict cycloaddition as the most thermodynamically favored reaction: cycloadducts have been shown on average to be 20–30 kcal mol^{-1} (1 kcal = 4.184 kJ) more stable than the respective acyclic adducts.[8]
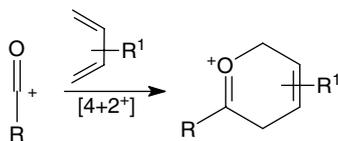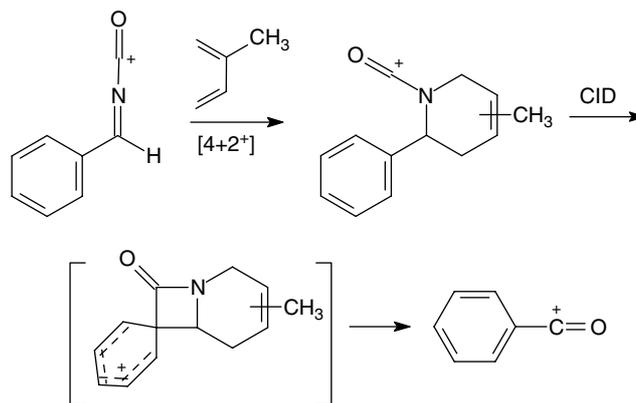

Scheme 1

The first evidence that cyclic adducts are indeed formed was provided by reactions of α,β-unsaturated acylium ions.[8a] For $CH_2=CH-C^+=O$, for instance, cycloaddition occurs predominantly and site-selectively across the $C=C$ bond followed by prompt CO loss, and the resulting cycloadduct shows characteristic collision-induced dissociation (CID) (Scheme 2).
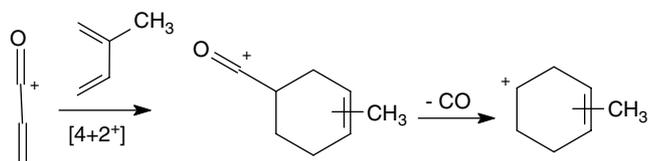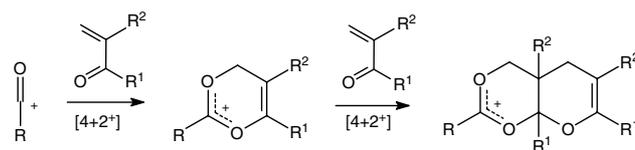

Scheme 2

The α,β-unsaturated acylium ion $Ph-CH=N-C^+=O$ also reacts with isoprene by cycloaddition, and does so site-selectively across its $C=N$ bond. The cycloadduct dissociates under CID by retro-Diels–Alder (RDA) reaction[9] only to a small extent, and CO loss is suppressed since a highly energetic nitrenium ion would be formed. Therefore, it has been suggested that the cycloadduct dissociates via a tricyclic

Scheme 3

four-membered ring phenonium ion intermediate[8a] to yield $Ph-C^+=O$ (Scheme 3).

More recently, acylium and thioacylium ions have also been shown to undergo both mono and 'charge-remote' tandem polar $[4 + 2^+]$ cycloaddition with O-heterodienes, namely α,β-unsaturated ketones (Scheme 4).[10]

Scheme 4

Although several pieces of evidence for cycloaddition have been collected, it would be useful to investigate more extensively whether cyclic or acyclic adducts are formed in these novel acylium ion cycloaddition reactions. More compelling evidence for cycloaddition is desirable particularly for the reactions occurring across acylium ion $C=O$ bonds (Scheme 1), since such cycloadducts often undergo nearly exclusively the structurally unspecific RDA dissociation. Here we report a systematic study of polar $[4 + 2^+]$ cycloaddition of acylium ions with several 1-oxy substituted s-cis-1,3-dienes of the general formula $RO-CH_2=CH-C(R^1)=CH_2$. In particular, reactions with 1-acetoxy-1,3-butadiene have provided additional and compelling evidence for cycloaddition.

EXPERIMENTAL

The gaseous ions were produced, reacted and their products analyzed via double-stage (MS^2) and triple-stage (MS^3) mass spectrometric experiments performed with an Extrel (Pittsburgh, PA, USA) pentaquadrupole ($Q_1q_2Q_3q_4Q_5$) mass spectrometer.[11] Appropriate precursors were used to form the reactant acylium ions by 70 eV electron ionization: tetramethylurea forms $(CH_3)_2N-C^+=O$ (**1**), acetophenone forms both $Ph-C^+=O$ (**2**) and $CH_3-C^+=O$ (**3**), tetramethylthiourea forms $(CH_3)_2N-C^+=S$ (**4**), 2-butanone forms $C_2H_5-C^+=O$ (**5**), and ethyl vinyl ketone forms $CH_2=CH-C^+=O$ (**6**). In the MS^2 experiments via which

ion–molecule reactions were performed, Q_1 was used to mass-select the ion of interest, the neutral reagent was added to q_2, and ion–molecule reactions occur at translational energy near 1 eV, as calculated from the m/z 39 : 41 ratio in neutral ethylene–ionized ethylene reactions.[12] Product ion mass spectra were acquired by scanning Q_5, while operating Q_3 in the broad band r.f.-only mode. The target gas pressure in q_2 caused typical beam attenuation of 50–80%, that is, multiple low-energy collision conditions were used in q_2 to increases reaction yields and to promote collisional quenching of both the reactant and product ions, although lower yields but essentially the same set of products with small variations on relative abundances were always observed under single collision conditions.[3c]

For the MS^3 experiments, Q_3 was used to mass select a q_2 product ion of interest either for further 10 eV collision dissociation with argon or reactions with a second neutral molecule at near 1 eV collisions in q_4, while scanning Q_5 for spectral acquisition. The 15 eV CID energies were taken as the voltage difference between the ion source and the collision quadrupole. The indicated pressure in each differentially pumped region was typically 2×10^{-6} (ion source), 8×10^{-6} (q_2), and 8×10^{-5} (q_4) Torr, respectively (1 Torr = 133.3 Pa).

RESULTS AND DISCUSSION

As reference ions, we selected two of the least acidic and most reactive[13] acylium ions: the dimethyl carbamyl cation **1**, $(CH_3)_2N$—C^+=O, and the benzoyl cation **2**, Ph—C^+=O. As the mass spectrum of Fig. 1 exemplifies for **1**, both of these acylium ions react readily with alkyl-substituted dienes by polar [4 + 2$^+$] cycloaddition, and their cycloadducts display a high proclivity to dissociate by RDA upon collisional activation (Scheme 5).
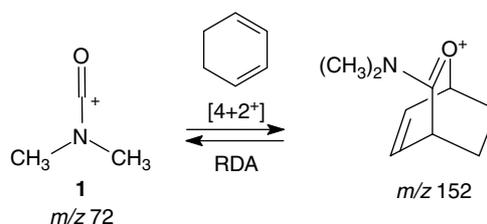
Scheme 5

The cycloadducts of acylium ions with 1,3-dienes are C-protonated forms of 2H-pyrans. Accordingly, as the sequential product ion mass spectrum in Fig. 2 exemplifies for the adduct of the acetyl cation CH_3—C^+=O (**3**) with 2,3-dimethyl-1,3-butadiene, these cycloadducts readily transfer
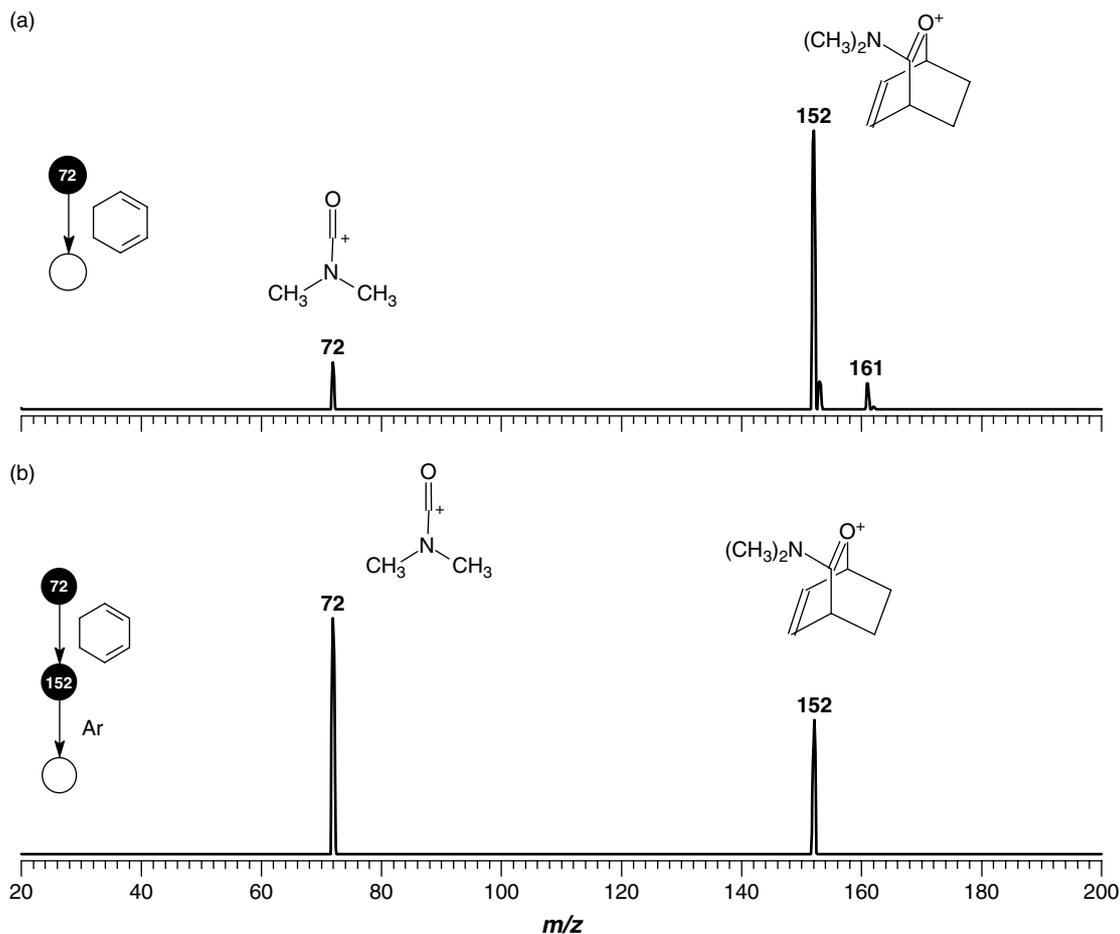

Figure 1. (a) Product ion mass spectrum for reactions of **1** of m/z 72 with 1,3-cyclohexadiene (M, 80 u). (b) Sequential product ion mass spectrum for CID of the cycloadduct of m/z 152. The product ion of m/z 161 is the 1,3-cyclohexadiene (M) proton-bound dimer, M$_2$H$^+$.
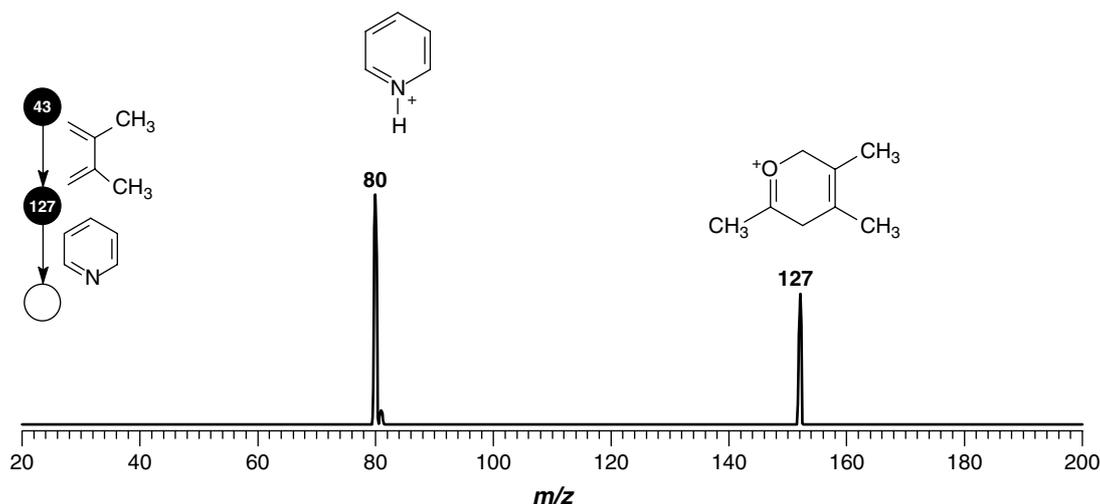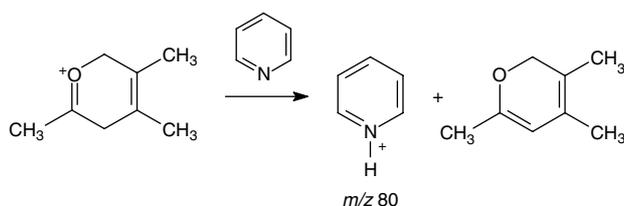
Figure 2. Sequential product ion mass spectrum for reactions with pyridine of the [4 + 2⁺] cycloadduct formed in reactions of the acetyl cation **3** of *m/z* 43 with 2,3-dimethylbutadiene (84 u).

a proton to pyridine to form protonated pyridine of *m/z* 80 and, probably, the neutral 2H-pyrans (Scheme 6).

Scheme 6

Are cyclic adducts indeed formed?

To probe via a CID structural investigation whether cyclic adducts are formed, one could try to form cycloadducts that dissociate by structurally diagnostic pathways other than the structurally unspecific RDA dissociation. Such cycloadducts should be formed from 1,3-dienes bearing substituents able to minimize or suppress the RDA dissociation. The use of 1-oxy-substituted 1,3-dienes therefore appeared appropriate since the polar [4 + 2⁺] cycloadducts could form stable and aromatic pyrylium ions (Scheme 7(b)) via ROH loss after intramolecular proton transfer to the RO group. This favored dissociation could then suppress or at least prevail over the otherwise favored RDA dissociation. Note, however, that this strategy would work only if the regioselectivity favors the *meta* cycloadduct[14] because the *ortho* cycloadduct (Scheme 7(a)) would still be expected to dissociate by RDA.

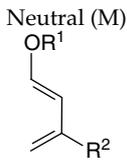### 1-Methoxy- and 1-(trimethylsilyloxy)-1,3-butadiene

Table 1 summarizes the product ion mass spectra for reactions of **1** of *m/z* 72 and **2** of *m/z* 105 with 1-methoxy-1,3-butadiene (entries 1 and 2) and 1-(trimethylsilyloxy)-1,3-butadiene (entries 3 and 4). With these two dienes, both acylium ions form adducts to great extent, but unfortunately these adducts still dissociate nearly exclusively by the structurally unspecific retro-addition pathway (back to the reactant ions of *m/z* 72 and 105, respectively). A low-abundance CH₃OH loss CID fragment (*m/z* 124 of 2% relative abundance; Table 1, entry 1) was observed only for the adduct of
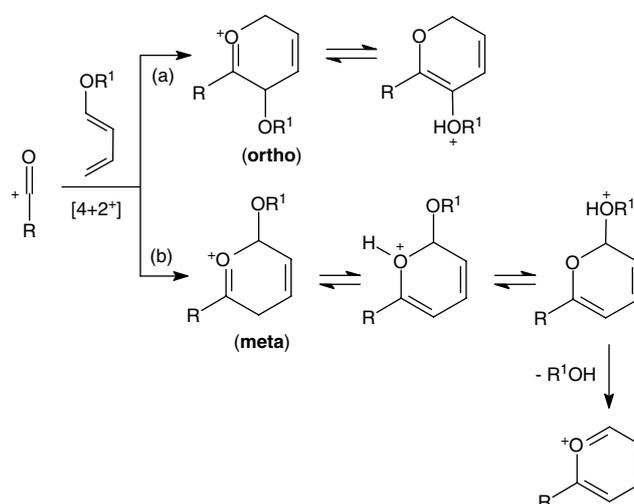
Scheme 7

1 with 1-methoxy-1,3-butadiene. Reasons for the dominance of retro-addition could be (i) cycloaddition with regioselectivity driving the major formation of the undesirable *ortho* cycloadduct (Scheme 7(a)); (ii) the *meta* cycloadduct may be formed but with its 1-oxy group competing unfavorably for the proton with other sites of higher proton affinity (Scheme 7(b)); or (iii) preferential formation of the competing acyclic adduct. Theoretical calculations (M. N. Eberlin, A. B. Lemos and R. Sparrapan, unpublished results) at the B3LYP/6−31G(d,p) level indicate that acyclic adducts are favored: geometry optimization of the *meta* cycloadduct of the acetyl cation (used as a model acylium ion) with both 1-methoxy- and 1-(trimethylsilyloxy)-1,3-butadiene show them to be unstable and to ring open without a barrier to the corresponding acyclic adducts, which are in turn calculated to be −13.5 kcal mol⁻¹ (1-methoxy-1,3-butadiene) and −17.2 kcal mol⁻¹ (1-(trimethylsilyloxy)-1,3-butadiene) more stable than the stable *ortho* cycloadducts. Probably the instability of the *meta* cycloadducts results from the charge-stabilizing effect of the 1-oxy substituents (Scheme 8, R¹ = CH₃ or Si(CH₃)₃, R² = H). (All B3LYP/6−31G(d,p)

Table 1. Main product ions (m/z (relative abundance)) observed in the product ion mass spectra for reactions of (thio)acylium ions $(CH_3)_2N—C^+=O$ (**1** of m/z 72), $Ph—C^+=O$ (**2** of m/z 105), $CH_3—C^+=O$ (**3** of m/z 43), $(CH_3)_2N—C^+ = S$ (**4** of m/z 88), $C_2H_5—C^+=O$ (**5** of m/z 57) and $CH_2=CH—C^+=O$ (**6** of m/z 55) with 1-oxy-substituted 1,3-dienes, and the CID fragments observed in the sequential product ion mass spectra of the main product ions

Entry	Ion R—C⁺=X (Ac⁺)	Neutral (M) OR¹ ⟍ R²	(Cyclo)adduct (MAc⁺)	Proton transfer (MH⁺)	Secondary (cyclo)addition products	CID fragments of major product ions
1	**1**	$R^1=CH_3$, $R^2=H$	**156** (100)	**85** (7)	None	**156**: 124 (2), 113 (3), 111 (4), 72 (100)
2	**2**		**189** (100)	**85** (11)	None	**189**: 105 (100)
3	**1**	$R^1=SiCH_3$, $R^2=H$	**214** (100)	**143** (37)	None	**214**: 72 (100)
4	**2**		**247** (48)	**143** (100)	None	**247**: 105 (100)
5	**1**		**244** (100)	**173** (6)	None	**244**: 85 (100), 72 (22)
6	**2**		**277** (27)	**173** (32)	**85** (62), **257** (100)	**277**: 105 (1), 85 (100)
		$R^1=CH_3$, $R^2=OSi(CH_3)_3$				**257**: 85 (100), 73 (23) **85**: 53 (100)
7	**3**		None	**173** (100)	**85** (37), **257** (22)	**85**: 53 (100) **257**: 85 (100), 73 (32)
8	**4**		**260** (100)	**173** (5)	None	**260**: 215 (12), 88 (100), 85 (32), 73 (27)
9	**1**		**184** (12)	**113** (4)	**142** (100), **124** (31)	**184**: 142 (100), 124 (11), 72 (13) **142**: 72 (100), 46 (78) **124**: 94 (3), 81 (2), 80 (2), 70 (2), 55 (1)[b]
10	**2**	$R^1=COCH_3$, $R^2=H$	None	**113** (2)	**157** (100)	**157**: 129 (8), 128 (21), 127 (4), 115 (1), 73 (1)[b]
11	**3**		**155** (6)	**113** (100)[a]	**95** (58), **113** (100)[a]	**155**: 95 (100) **95**: 67 (3), 41 (1)[b]
12	**5**		None	**113** (58)	**127** (2), **109** (100)	**109**: 83 (11), 79 (5), 77 (4), 57 (3)[b]
13	**6**		None	**113** (100)	**125** (32), **107** (48)	**107**: 77 (100)

[a] In reactions of **3** with 1-acetoxy-1,3-butadiene, the proton transfer product and the ketene loss fragment from the cycloadduct are isobaric (m/z 113).

[b] The pyrylium ions so formed are very resistant towards CID; hence abundances of their fragments are measured relative to the parent ion of 100% abundance.

energies and geometries are available from the authors on request.)
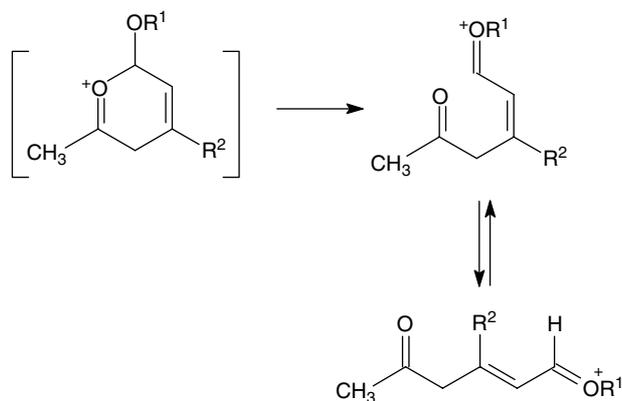
Scheme 8

Danishefsky's diene

As the mass spectrum in Fig. 3(a) exemplifies for **1**, both acylium ions **1** and **2** form adducts with Danishefsky's diene (*trans*-1-methoxy-3-(trimethylsiloxy)-1,3-butadiene) to great extent (Table 1, entries 5 and 6). For **2**, the cycloadduct of

m/z 277 is still formed, but two unexpected ions of m/z 85 and 257 are formed as the major products (Table 1, entry 6). The ion of m/z 257 is likely formed by secondary addition of m/z 85 to Danishefsky's diene (172 u). CID of the adduct of **1** of m/z 244 with Danishefsky's diene (Fig. 3(b)) yields the retro-addition fragment ion of m/z 72, but the ion of m/z 85 is the dominant fragment. The adduct of **2** with Danishefsky's diene (m/z 277) dissociates upon CID nearly exclusively to the ion of m/z 85. The adduct of m/z 85 with Danishefsky's diene (m/z 257) dissociates upon CID predominantly to the ion of m/z 85, likely by retro-addition, and also to $Si(CH_3)_3^+$ (m/z 73). The intriguing product ion of m/z 85 dissociates exclusively likely by methanol loss to an ion of m/z 53 (Table 1, entry 6).

'Silicon and sulfur labeling'[15]

When the ³⁰Si-labeled Danishefsky's diene adduct of **1** (m/z 246) is mass selected and dissociated (spectrum not shown), the same pair of m/z 72 and 85 fragment ions as observed for the ²⁸Si-labeled cycloadduct of m/z 244 (Table 1, entry 5) is formed; hence the ion of m/z 85 does not contain Si. To follow by 'sulfur labeling' the mechanism leading to the ion of m/z 85 (and then to the ion of m/z 257), reactions of the
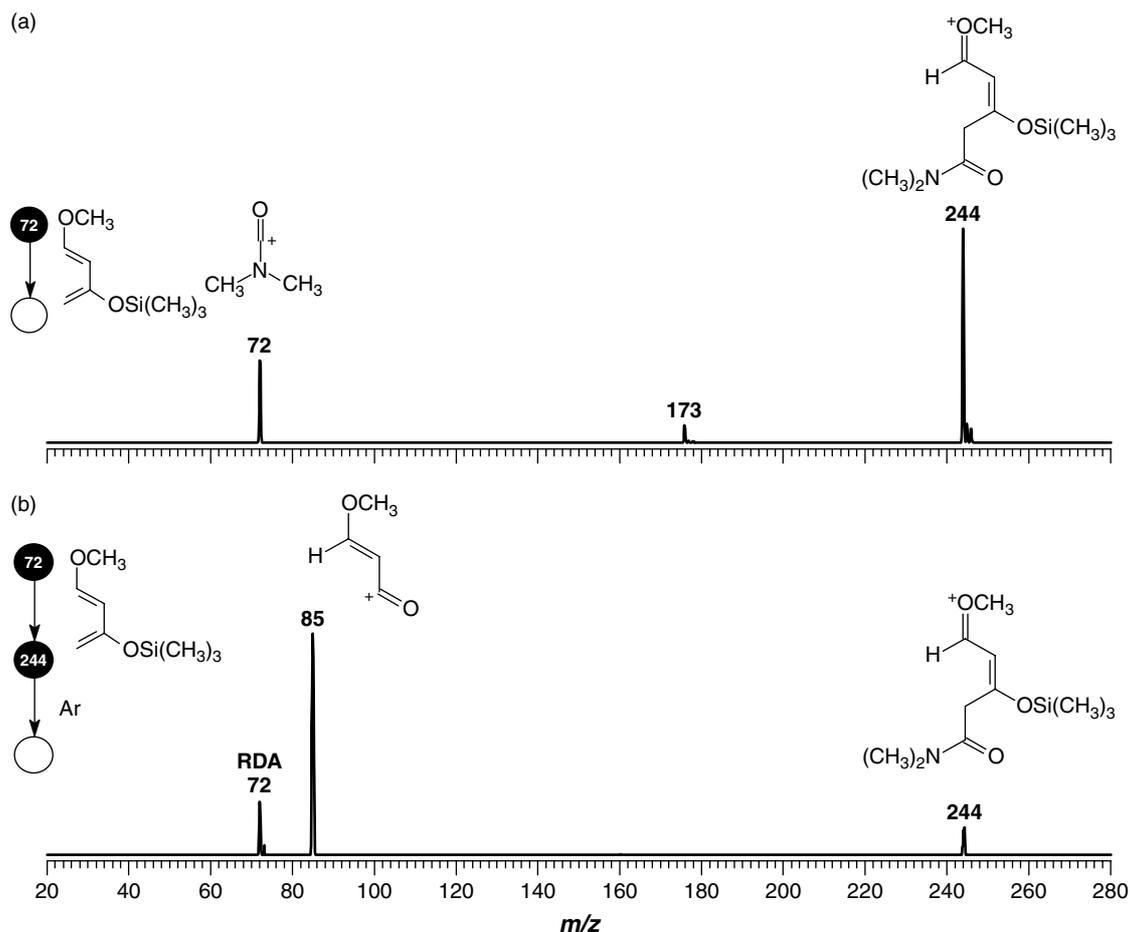
Figure 3. (a) Product ion mass spectrum for the reaction of **1** of *m/z* 72 with Danishefsky's diene (M, 172 u). The product ion of *m/z* 173 is MH$^+$. (b) Sequential product ion mass spectrum for CID of the *m/z* 244 cycloadduct.

thioacylium ion $(CH_3)_2N—C^+=S$ (**4**) were also performed (Table 1, entry 8). As does its oxygen analogue **1** (Fig. 3(a)), **4** adds readily to Danishefsky's diene. When its adduct of *m/z* 260 is subjected to CID, dissociation re-forms mainly the reactant ion **4** of *m/z* 88 by retro-addition, but again the intriguing ion of *m/z* 85 is formed to a considerable extent. Since no 'sulfur shift' (*m/z* 85 to 101) occurs, and since the ion of *m/z* 85 is observed for both the acylium (**1**) and thioacylium (**4**) analogues, it is clear that the ion of *m/z* 85 is formed regardless of the reactant (thio)acylium ion. To confirm this conclusion further, reactions of the acetyl cation $CH_3—C^+=O$ (**3**) were also performed (Table 1, entry 7). As expected, the acidic[13] **3** reacts predominantly with Danishefsky's diene by proton transfer (*m/z* 173). The intact cycloadduct of **3** is not observed, but again the product ions of *m/z* 85 and 257 are both formed, to medium extents.

As for the 1-methoxy- and 1-silyloxy-1,3-butadiene *meta* cycloadducts, theoretical calculations indicate the formation of acyclic adducts with Danishefsky's diene: geometry optimization of the Danishefsky's diene *meta* cycloadduct of **3** shows it to be unstable and to ring open without a barrier to the acyclic adduct, which is in turn calculated to be −24.3 kcal mol^{-1} more stable than the stable *ortho* cycloadduct. Again, the instability of the Danishefsky's diene meta cycloadduct probably results from

the charge-stabilizing effect of the 1-methoxy substituent (Scheme 8, $R^1 = OCH_3$, $R^2 = Si(CH_3)_3$).

Schemes 9 depicts a general mechanism for the reactions of acylium ions with Danishefsky's diene that fits the experimental observations discussed above.

Cycloaddition may compete with or even dominate over simple addition, but the intrinsically unstable *meta* cycloadduct, if formed, is just a transient species that ring opens spontaneously to the acyclic adduct for which an O-to-O(S) trimethylsilyl cation shift is available. After isomerization, dissociation yields, regardless of the reactant acylium ion, the common 2-methoxyacryl cation of *m/z* 85. Upon CID, the ion of *m/z* 85 dissociates by methanol loss to yield the acylium ion of *m/z* 53, whereas it reacts in turn with Danishefsky's diene by simple addition to form the product ion of *m/z* 257. The ion of *m/z* 257 is a special adduct that may dissociate to *m/z* 85 either by retro-addition or by the trimethylsilyl cation shift pathway (Scheme 9).

1-Acetoxy-1,3-butadiene

Table 1 (entries 9–13) summarizes the product ion mass spectra for reactions of **1** and **2** with 1-acetoxy-1,3-butadiene, and also for **3** and two additional acylium ions: **5** ($C_2H_5—C^+=O$) and **6** ($CH_2=CH—C^+=O$). As exemplified in Fig. 4(a), **2** reacts with 1-acetoxy-1,3-butadiene to form a nearly exclusive product ion of *m/z* 157! This major product ion is

$X = O, S$

$[4+2^+]$

$[1,5\text{-Si(CH}_3)_3]$

$m/z\ 257$

$m/z\ 85$

$- CH_3OH$ CID

CID

$m/z\ 53$

Scheme 9

(a)

77

105

113

157

Ph

(b)

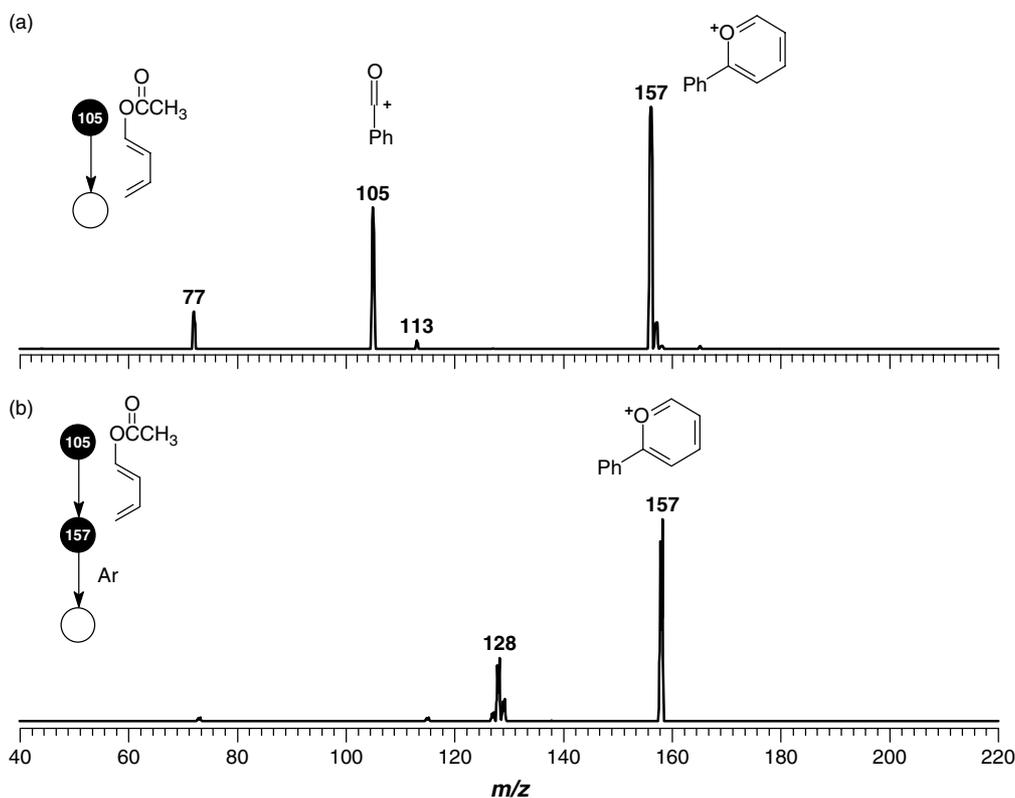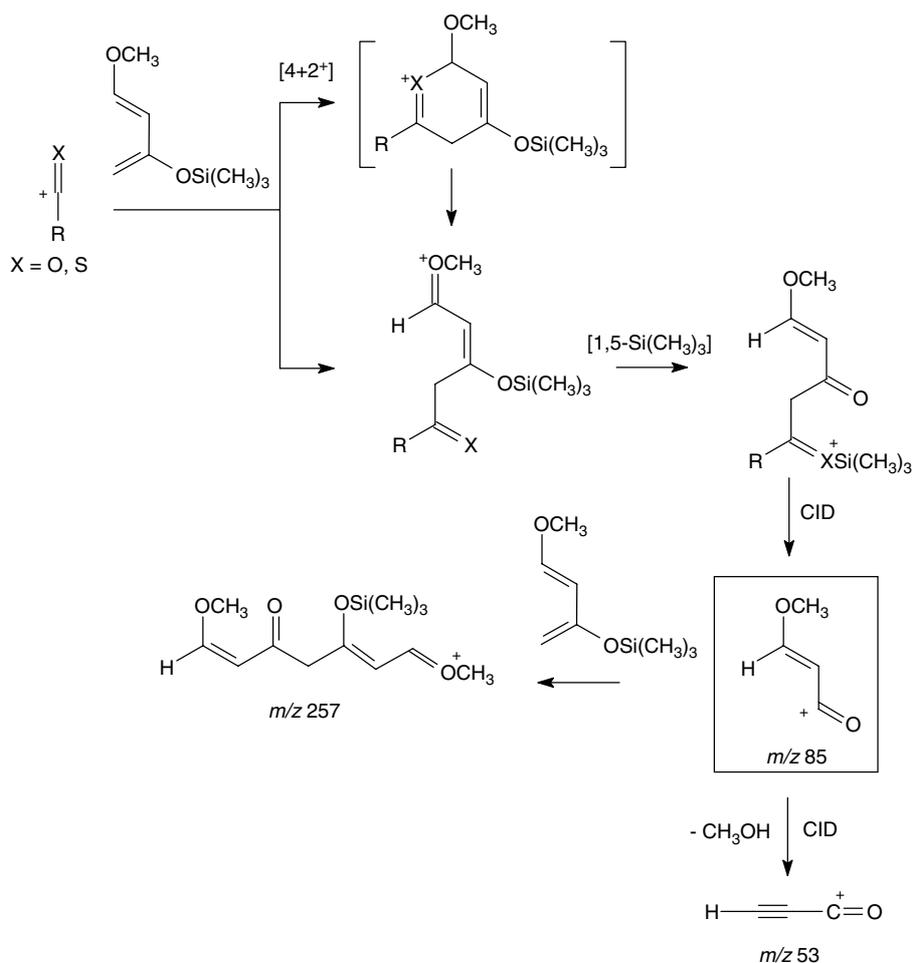**128**

157

Ph

Ar

m/z

Figure 4. (a) Product ion mass spectrum for reactions of **2** of *m/z* 105 with 1-acetoxy-1,3-butadiene (112 u). (b) Sequential product ion mass spectrum for CID of the main reaction product: the aromatic 2-phenylpyrylium ion of *m/z* 157.

likely formed via polar [4 + 2$^+$] cycloaddition followed by intramolecular proton transfer and fast aromatization by acetic acid loss. Probably, therefore, we have finally formed the designed aromatic ion: the 2-phenylpyrylium ion (Scheme 7(b), R = Ph, R^1 = COCH$_3$). The acylium ion **1** reacts in a similar but not identical fashion (Table 1, entry 9); the 2-dimethylaminopyrylium ion of m/z 124 is formed to a medium extent by methanol loss, but most of the nascent cycloadduct of m/z 184 dissociates more favorably to the fragment ion of m/z 142, likely by ketene loss. In an MS^3 experiment (Table 1, entry 9), m/z 184 dissociates upon CID as expected (from the products observed in the MS^2 product ion mass spectrum), that is, mainly to the ion of m/z 142 (by ketene loss), m/z 124 (by methanol loss) and m/z 72 (by RDA).

Probably, therefore, reaction of **2** with 1-acetoxy-1,3-butadiene occurs predominantly by polar [4 + 2$^+$] cycloaddition, its regioselectivity favors the *meta* cycloadduct, proton transfer to the acetoxy group competes favorably and the acetoxy-protonated form of the intact cycloadduct promptly dissociates by acetic acid loss (60 u) to yield the aromatic 2-phenylpyrylium ion of m/z 157 (Scheme 7(a), R=Ph). For **1**, however, both the *ortho* and *meta* cycloadducts are likely formed; hence the *meta* cycloadduct dissociates by acetic acid loss to form the desired aromatic 2-dimethylaminopyrylium ion of m/z 124 (Scheme 7(b), R = N(CH$_3$)$_2$), whereas the *ortho* cycloadduct dissociates both by ketene loss to the ion of m/z 142 (Scheme 10) and by RDA to the ion of m/z 72. Similar reactivity is observed for **5** and **6** (Table 1, entries 12 and 13); the intact cycloadducts are not detected, but the two respective ketene loss (m/z 127 and 125) and acetic acid loss fragments, the pyrylium ions of m/z 109 and 107, are formed as major product ions. For **3** (entry 11), both the intact cycloadduct of m/z 155 and the acetic acid loss fragment ion (the 2-methylpyrylium ion of m/z 95) are observed, but formation of the ketene loss fragment ion of m/z 113 could not be confirmed because the ion is isobaric with the proton transfer product.
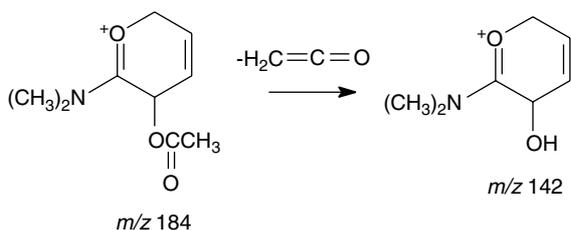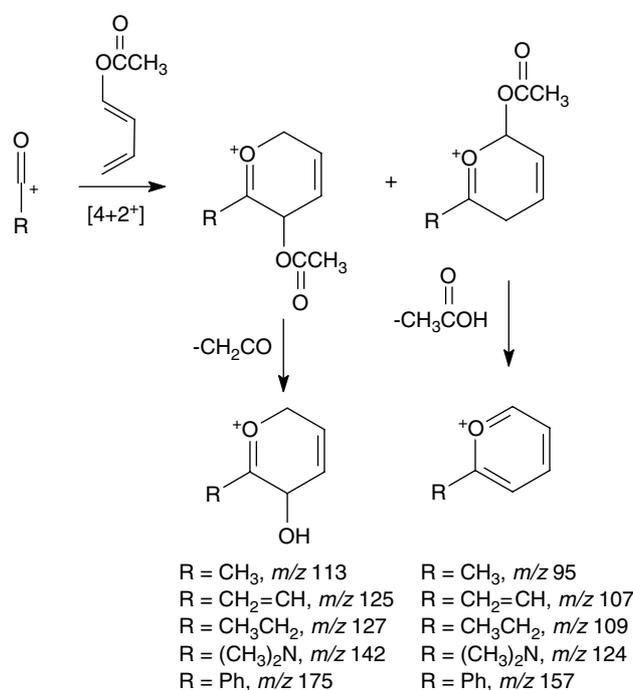

Scheme 10

Theoretical calculations also provide evidence for cycloaddition of acylium ions with 1-acetoxy-1,3-butadiene. For this particular 1,3-diene, the reduced charge-stabilizing effect of the 1-acetoxy substituent (as compared with 1-methoxy and 1-trimethylsilyloxy substituents) helps to stabilize the *meta* cycloadduct, which is therefore found to be intrinsically stable: −13.4 kcal mol^{-1} more stable than the acyclic adduct and −7.0 kcal mol^{-1} more stable than the *ortho* cycloadduct. In addition, intramolecular proton transfer to the acetoxy group within the *meta* cycloadduct is predicted to

form an unstable species that undergoes spontaneous acetic acid loss to yield the final pyrylium ion product. These theoretical predictions are summarized in the potential energy surface diagram in Fig. 5.

Sequential product ion mass spectra (Table 1, entries 9–13) also provide evidence for the formation of pyrylium ions, as exemplified in Fig. 4(b) for that of the 2-phenylpyrylium ion. Under collision activation, the putative pyrylium ions show great resistance towards dissociation, as expected for such aromatic and stable cations, and low-abundance fragments are only formed on increasing the collision energy and argon pressure. Additionally, the spectrum of the 2-methylpyrylium ion of m/z 95 (Table 1, entry 11) matches perfectly that of the authentic ion generated from dimethylfuran (not shown). Scheme 11 summarizes the general trends postulated for the reactions of acylium ions with 1-acetoxy-1,3-butadiene.

R = CH$_3$, m/z 113   R = CH$_3$, m/z 95
R = CH$_2$=CH, m/z 125   R = CH$_2$=CH, m/z 107
R = CH$_3$CH$_2$, m/z 127   R = CH$_3$CH$_2$, m/z 109
R = (CH$_3$)$_2$N, m/z 142   R = (CH$_3$)$_2$N, m/z 124
R = Ph, m/z 175   R = Ph, m/z 157

Scheme 11

CONCLUSION

Gas-phase reactions of mass-selected acylium ions with 1-oxy-substituted 1,3-dienes of the general formula RO—CH=CH—C(R^1)=CH$_2$ have been studied. Reactions with 1-methoxy-, 1-(trimethylsilyloxy)- and 1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene (Danishefsky's diene) form mainly acyclic adducts. Although cycloaddition may dominate or compete with simple addition, the *meta* cycloadducts are unstable, as shown by B3LYP/6–31G(d,p) calculations. The transient *meta* cycloadducts, if formed, would ring open without a barrier to the acyclic adduct, which is considerably more stable than the intrinsically stable *ortho* cycloadduct. The instability of the *meta* cycloadduct likely results from the charge-stabilizing effect of the 1-methoxy and 1-trimethylsilyloxy substituents. Compelling evidence that cycloadducts are formed via polar [4 + 2$^+$]
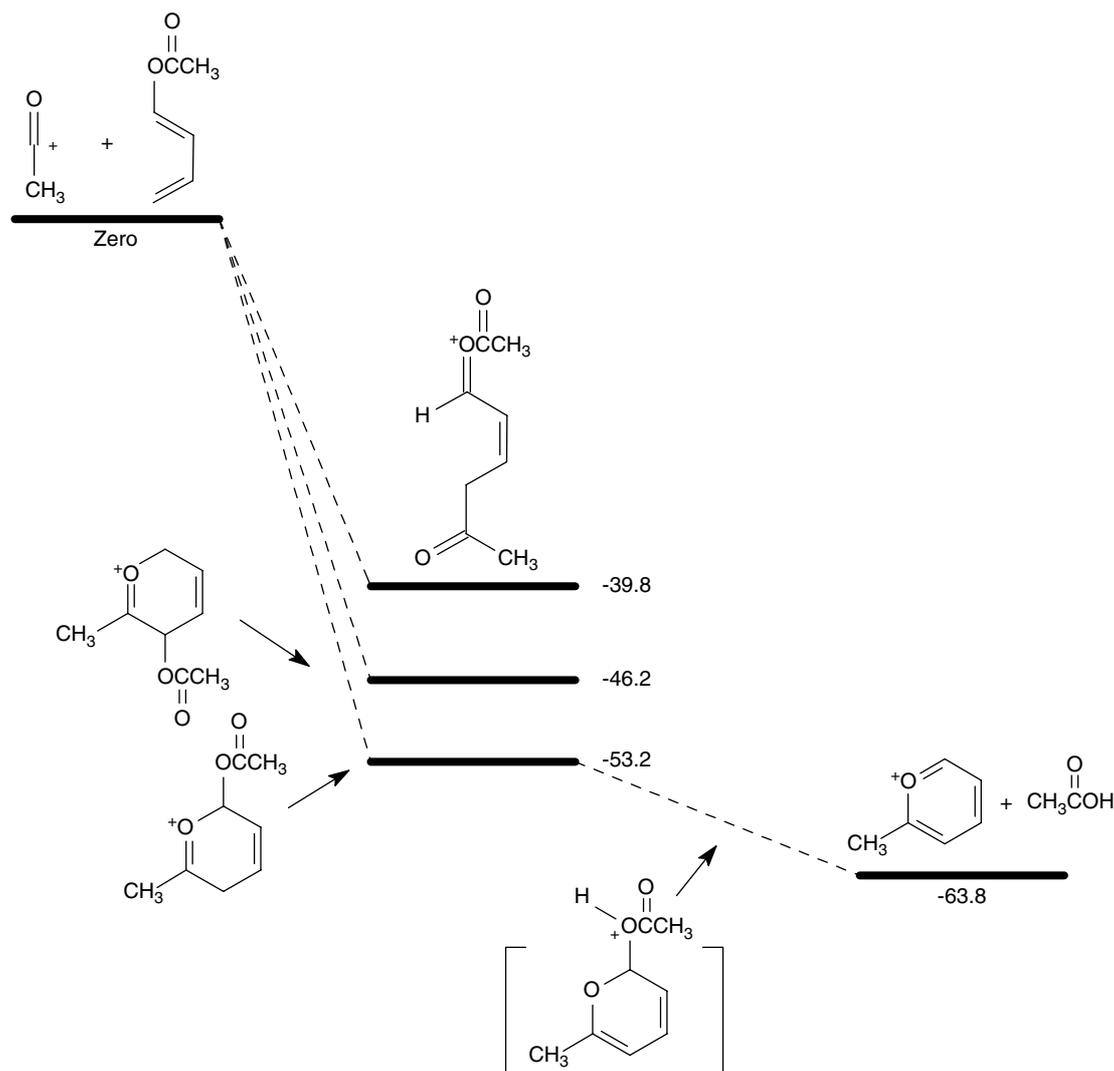
Figure 5. B3LYP/6–31G(d,p) potential energy surface diagram for reactions of **3** ($CH_3 - C^+ = O$) with 1-acetoxy-1,3-butadiene. Energies are given in kcal mol^{-1}. The acetoxy-protonated *meta* cycloadduct is predicted to be unstable, and to dissociate spontaneously by acetic acid loss to yield the 2-methylpyrylium ion. Energy barriers for (cyclo)additions and intramolecular proton transfer were not estimated, and are not indicated. The energies calculated for the species are, in hartrees: **3** (−152.92918); 1-acetoxy-1,3-butadiene (−1383.88156), acyclic adduct (−536.87319), *ortho* cycloadduct (−536.88343), *meta* cycloadduct (−536.89452), 2-methylpyrylium ion (−307.81997) and acetic acid (−229.09148).

cycloaddition has been collected, however, in reactions with 1-acetoxy-1,3-butadiene. The diminished charge-stabilizing effect of the 1-acetoxy substituent helps to stabilize the *meta* cycloadduct, which otherwise forms aromatic pyrylium ions after intramolecular proton transfer and acetic acid loss. Formation of these pyrylium ions can only be rationalized with the intermediacy of the *meta* cycloadducts formed by (either concerted or unsynchronized but the more thermodynamically favored) polar [4 + 2⁺] Diels–Alder cycloaddition.

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