

Retro-Ene Reactions in Acylallene Derivatives

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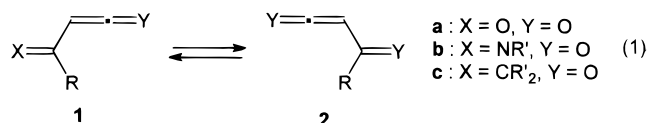
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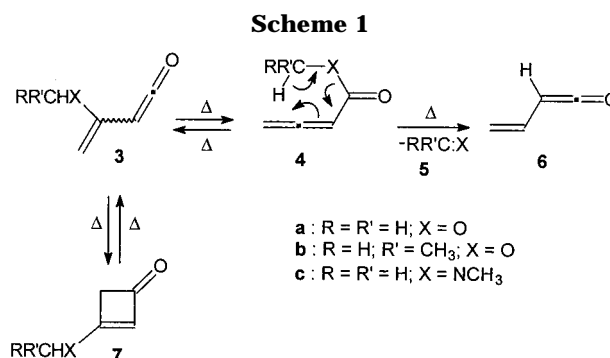
Allenic esters and amides **4** undergo a retro-ene reaction to vinylketene (**6**) and an aldehyde or imine (**5**) under the conditions of flash vacuum thermolysis (FVT). The same products are obtained by FVT of cyclobutenones **7** via electrocyclic ring opening to alkoxy- or aminovinylketenes **3** and 1,3-rearrangement of ketenes **3** to allenes **4**. All the intermediates and products were characterized by matrix isolation IR spectroscopy, and in the case of **4c** the reaction was also monitored by online mass spectrometry. A lower temperature for the retro-ene reaction of **4c**, eliminating an imine, than for **4a**, eliminating formaldehyde, is in agreement with a lower calculated activation barrier (167 and 181 kJ mol⁻¹, respectively, at the G2(MP2,SVP) level of theory). The allenic amide **11** undergoes an analogous retro-ene reaction to the (unobserved) vinylketene **13**, the latter isomerizing to cyclohexenylacrolein **16** in a 1,5-H shift (calculated barrier 125 kJ mol⁻¹; G2 (MP2, SVP)).

Introduction

In recent papers we have described the thermal 1,3-migrations of groups R in the interconversions of α -oxoketenes (**1a** \rightarrow **2a**),¹ imidoalkenes and α -oxoketenimines (**1b** \rightarrow **2b**),² and vinylketenes and acylallenes (**1c** \rightarrow **2c**) (eq 1).³ As observed experimentally, these reac-



tions are highly facilitated by electron rich migrating groups R, especially those possessing lone pairs, due to a favorable interactions between a high-lying orbital of the migrating group and the low-lying ketene-type LUMO, which has a large coefficient at the central cumulenonic carbon atom in the plane of the molecule.^{3a,4} The calculated migratory aptitudes are in the order NMe₂ > SMe > SH > Cl > NH₂ > OMe > OH > F > H > Ph > Me (G2(MP2,SVP) theory).^{3a,4} The activation barriers for the 1,3-shifts are, therefore, related to the LUMO energies and to the exothermicities or endothermicities of the reactions.^{3a,5} The calculated activation barriers for the 1,3-H shift increase in the series α -oxoketene < α -ox-



oketenimine < imidoalkene < acylallene < vinylketene (this ordering can be influenced by substituents). Therefore, in the vinylketene/acylallene system (**1c/2c**), one can only expect to observe this migration for the most electron-donating substituents, i.e., dialkylamino, alkylthio, chloro, and alkoxy. Indeed, these are the reactions that have been documented.^{3,6} They take place under flash vacuum thermolysis (FVT) conditions in the temperature range 370–630 °C. The calculated activation barriers, starting from vinylketenes **1c**, are 129 (NMe₂), 147 (SMe), 157 (Cl), and 169 (OMe) kJ mol⁻¹, respectively.³ The facile 1,3-chlorine migration (**1c/2c**; R = Cl; R' = H) takes place above 370 °C prior to loss of HCl to give butatrienone, H₂C=C=C=O.^{3a} In the case of ethoxyvinylketene/ethyl allenecarboxylate (**1c/2c**; R = OEt), the 1,3-ethoxy shift takes place prior to elimination of ethene to give acetylketene.³

We now report conclusive evidence for a retro-ene reaction operating in this system, which at higher FVT temperatures causes loss of formaldehyde (**1c/2c**; R = OMe) or *N*-methylmethanimine (R = NMe₂) with formation of the unsubstituted vinylketene (**6**; Scheme 1). The ene- and retro-ene reactions are well-known in hydrocarbon chemistry.⁷ For example, the retro-ene reaction of pentene produces propene and ethene. The experimental^{7c} and calculated^{7d,e} (MP2/6-31G*) activation energies are of the order 35–38 kcal mol⁻¹ (140–160 kJ

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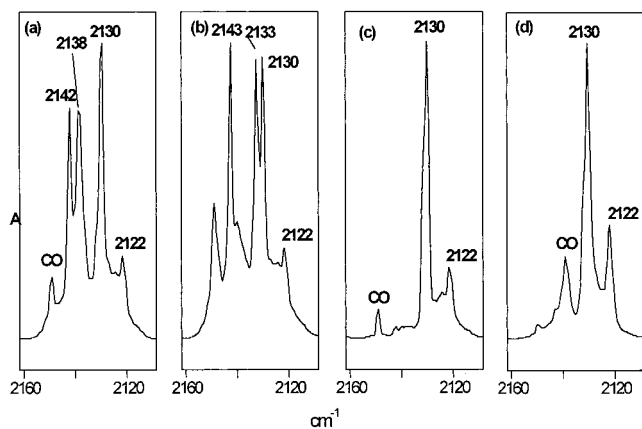


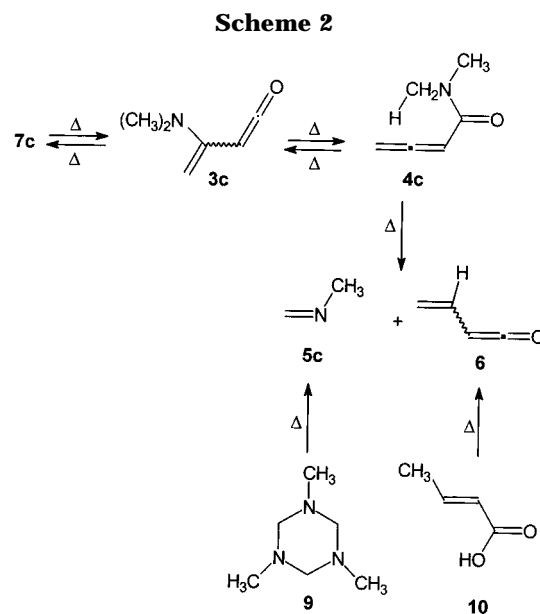
Figure 1. Partial Ar matrix FTIR spectra (12 K) of the results of FVT of (a) **4a** at 1000 °C, (b) **4b** at 850 °C, (c) **4c** at 750 °C, and (d) **10** at 850 °C. The bands at 2130 and 2122 cm^{-1} belong to **6**. Those at 2142 and 2138 cm^{-1} are due to *s-trans*-**3a** (see ref 3a). The peaks at 2143 and 2133 cm^{-1} are assigned to *s-cis*- and *s-trans*-acetylketene (see refs 3 and 10). The variable peaks at 2148 and/or 2138 cm^{-1} are due (in part in Figure 1a) to CO.³⁹

mol^{-1}) for the ene reaction and $\sim 50 \text{ kcal mol}^{-1}$ (200 kJ mol^{-1}) for the retro-ene reaction.^{7d} There has been a single prior report of a retro-ene reaction taking place in *N,N,N,N*-tetraethylallene-1,3-dicarboxamide on heating to 180–200 °C during distillation (0.1 mbar), which caused formation of an α -pyrone via a hypothetical ketene intermediate.⁸

Results and Discussion

1. FVT Experiments. In the system alkoxyvinylketene (**3a,b**), -acylallene (**4a,b**), -cyclobutenone (**7a,b**) (Scheme 1) the interconversions **7** \rightleftharpoons **3** and **3** \rightleftharpoons **4** have been established by matrix isolation FTIR spectroscopy.³ The interconversion of **3a** and **4a** takes place at ca. 650 °C under FVT conditions. FVT of allene **4a** above 780 °C caused formation of unsubstituted vinylketene (**6**) as evidenced by Ar matrix isolation of the ketene at 12 K. The characteristic bands of **6** are at 2130 and 2122 cm^{-1} (Figure 1a) as further elaborated below. It appears that the band at 2122 cm^{-1} is due to either a site or another conformer of **6** as the ratio between these two bands remained nearly constant, even when other precursors were employed (Figure 1). This 2130/2122 cm^{-1} species became dominant above 900 °C. A set of bands due to formaldehyde⁹ (**5a**) appeared concomitantly with those of **6** (2995, 2816, 2864, 2798, 1742, 1738, 1499, 1174 cm^{-1}).

These results can be understood in terms of a retro-ene reaction of the allenic ester **4a** (Scheme 1). In further support of this, FVT of 3-methoxycyclobutenone (**7a**) was performed. At 400 °C, this causes ring opening to the observable vinylketene **3a**.³ From 800 °C onward, the



unsubstituted vinylketene **6** was again observed with the emergence of bands at 2130 and 2122 cm^{-1} .

Further investigation was performed on the ethyl analogues **4b** and **7b**. FVT/matrix isolation of ethyl 2,3-butadienoate (**4b**) between 570 and 800 °C caused partial conversion to the vinylketene **3b**.³ At 850 °C, the unsubstituted vinylketene **6** (2130, 2122 cm^{-1}) as well as acetylketene^{3,10} were observed (Figure 1b). On neat deposition at 77 K, two bands at 2137 and 2118 cm^{-1} were observed due to acetylketene and unsubstituted vinylketene (**6**), respectively. The value of 2118 cm^{-1} for neat **6** is in agreement with a previous report.¹¹ The formation of acetylketene is due to elimination of ethene from **3b** as previously elucidated.³

FVT of 3-ethoxycyclobutenone¹² (**7b**) at 400–700 °C gave the observable ketene **4b**.³ At 800 °C, weak bands due to vinylketene **6** were observed at 2130 and 2122 cm^{-1} (Ar, 12 K). The weakness of the bands due to **6** in the ethoxy case contrasts the strong signals in the methoxy case (**4a** and **7a**) and is due to competing reactions leading to the formation of acetylketene, propyne, and CO₂ from the ethoxy derivatives **4b** and **7b** at high FVT temperatures.

To confirm the generality of the reaction and to give further evidence for the formation of vinylketene **6**, the dimethylamino derivatives **7c** and **4c** were investigated. Here, although the aminovinylketenes **3c** are not directly observable under FVT conditions, **7c** and **4c** were shown to interconvert, starting from both sides, at ca. 470 °C.³ FVT/matrix isolation of allenic amides **4c** gave rise to bands due to vinylketene **6** starting already at 500 °C, becoming very strong at 700 °C (Figure 1c).

In addition, a new set of bands was observed in the range 2800–3100 cm^{-1} , increasing in intensity in concert with those due to ketene **6**. These characteristic bands are due to *N*-methylmethanimine (**5c**) (Scheme 2). Proof of the presence of **5c** was secured by comparing the Ar

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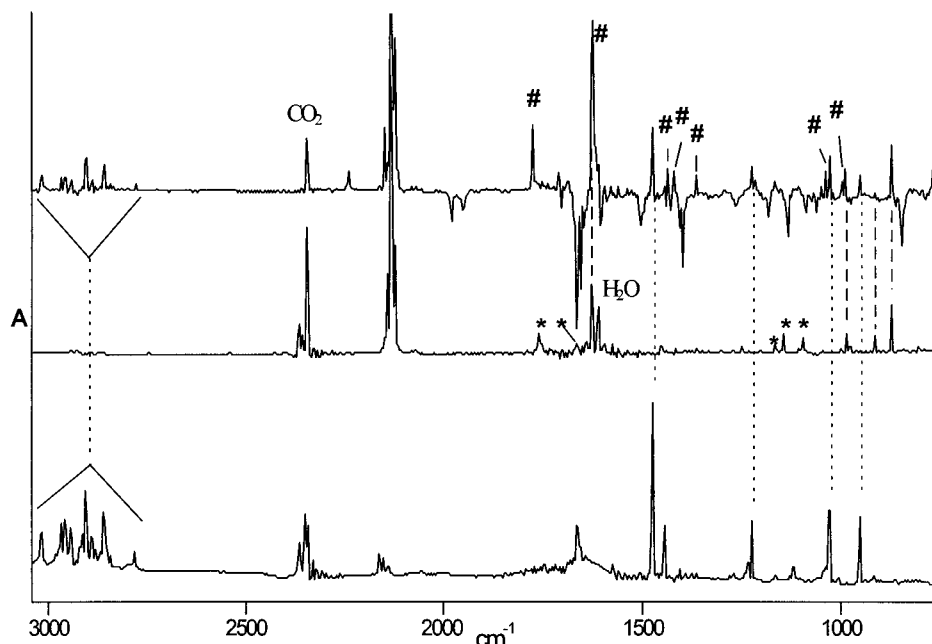


Figure 2. FTIR spectra (Ar, 12 K) of **6** and **5c**. (Top) Spectrum of **6** and **5c** (positive peaks) obtained after subtracting the spectrum resulting from FVT of the allenic amide **4c** at 750 °C from the spectrum of **4c** itself (negative peaks); #: absorptions due to 3-(*N,N*-dimethylamino)cyclobutenone (**7c**). The peaks in the 2100 cm^{-1} region are not shown with their correct intensities. For details of the ketene region see Figure 1c. (Middle) Ar matrix spectrum (12 K) of **6** obtained after FVT of **10** at 850 °C; *: bands due to **10**. (Bottom) Ar matrix spectrum (12 K) of **5c** obtained after FVT of **9** at 850 °C.

matrix IR spectrum with literature values,¹³ and by generating an authentic sample of **5c** by thermolysis of 1,3,5-trimethyl-1,3,5-triazine^{13,14} (**9**) above 800 °C with matrix isolation of the product at 12 K. Very good agreement is observed (Figure 2). Likewise, direct comparison between the thermolysis spectrum from **4c** and an authentic sample of **6** (obtained by thermolysis of (*E*)-2-butenic acid¹⁵ (**10**)) also shows excellent agreement (Figures 1c,d, 2).

The thermolysis of **4c** was also monitored by mass spectrometry (FVT-MS) between 475 and 850 °C (Figure 3). From 525 °C to 750 °C the peak at m/z 68 increased in intensity due to the formation of **6**, whereas the peak at m/z 72 ($\text{M}^+ - \text{C}_3\text{H}_3$), characteristic of **4c**, decreased. A new peak at m/z 42 due to imine **5c** developed concomitantly ($[\text{M} - \text{H}]^+$; α -cleavage; not shown).

The (dimethylamino)cyclobutenone **7c** was thermolyzed analogously, and again the bands due to **6** and **5c** were observed already at an FVT temperature of 550 °C (Ar, 12 K). An explanation for the early appearance of **6** in comparison with the use of alkoxy precursors (**7a,b**) is a lower barrier for the retro-ene reaction, as confirmed by theoretical calculations (section 2).

Although vinylketene **6** was observed already at ca. 550 °C on Ar matrix isolation (12 K), it was not detectable when either allene **4c** or cyclobutenone **7c** were thermolyzed between 500 and 800 °C with product isolation at 77 K. This is explained by a very high reactivity of ketene **6** toward the imine **5c**, even at 77 K.

To confirm this, **4c** and **7c** were separately thermolyzed at 600 °C with neat deposition at 12 K. On

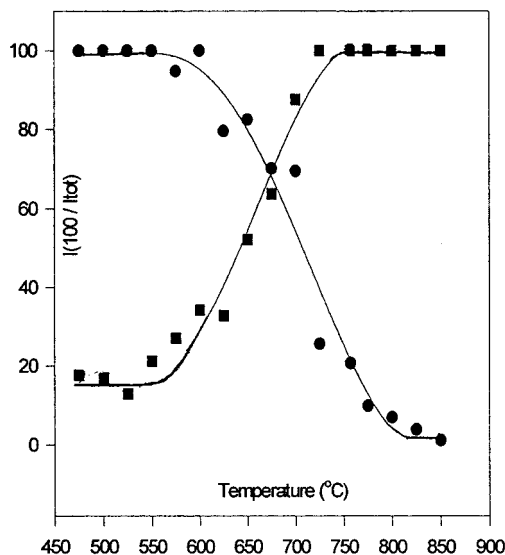


Figure 3. Results of the FVT-MS of **4c**. Relative intensities of ions are shown. ●: m/z 72 (characteristic peak of **4c** (α -cleavage; $\text{M}^+ - \text{C}_3\text{H}_3$)). ■: m/z 68 (vinylketene (**6**)).

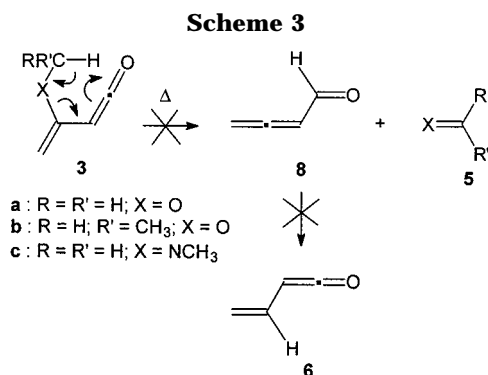
subsequent warm-up, the ketene band at 2118 cm^{-1} (the value for neat ketene **6**, also obtained in the alkoxy cases) had completely disappeared at 75 K. A facile reaction of the imine **5c** with the ketene moiety of **6** (Staudinger reaction¹⁶) is in agreement with previous observations from this laboratory, where it was demonstrated that nucleophiles such as pyridine react well below 77 K with ketenes to give ketene-pyridine zwitterion inter-

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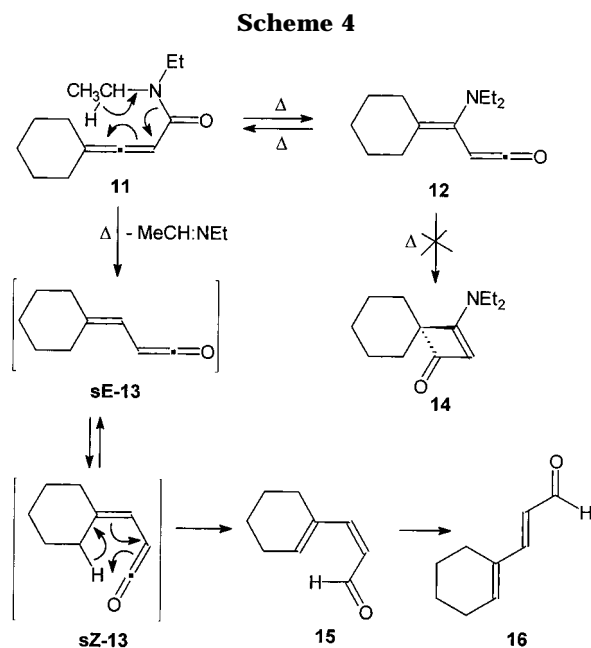
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mediates.^{17a,b} Moreover, vinylketene **6** itself has been reported to be stable at 77 K.¹⁸ We confirmed this by generation of **6** by FVT of **10** with neat isolation at 12 K. In the absence of the imine, ketene **6** remained stable above 80 K.¹⁹

To obtain further evidence on the reaction between **5c** and **6**, these were generated by thermolysis (850 °C) of **9** and **10**, respectively, deposited simultaneously on the cold window (neat, 12 K), observed by their characteristic IR spectra, and subsequently warmed. Again, at 75 K both ketene and imine bands vanished, but further studies would be required for an identification of the products formed.²⁰ Reactions between ketene **6** and imine **5c** could be expected to lead to zwitterionic intermediates which subsequently cyclize to β or δ -lactam, as has been found in many related reactions.¹⁶ However, no direct IR spectroscopic evidence for the formation of such a zwitterion (**17**, see below) or δ -lactam was obtainable due to the strong absorptions of **4c**, **5c** and **7c** in the 1650–1690 cm⁻¹ region. Also no evidence for the formation of a β -lactam was found (expected absorptions^{16b,c} ca. 1760 cm⁻¹).

It was a priori possible that the vinylketenes **3** could also undergo a retro-ene reaction, as illustrated in Scheme 3. This would generate the same aldehyde, ketone, and imine **5**, together with 2,3-butadienal (**8**). However, no new bands were observed in the allenic region or the 1700–1600 cm⁻¹ region that could be ascribed to 2,3-butadienal in any of these experiments on FVT of acylallenes **4** or cyclobutenones **7**. It is also inconceivable that an initially formed formylallene **8**



would easily isomerize to **6**. Allene **8** has a higher calculated energy than the isomeric vinylketene (**6**), but the 1,3-H shift required in the process **8** → **6** has a very high computed activation energy (272.5 kJ mol⁻¹ at the G2(MP2, SVP) level of theory).^{3a} Thus, there is no evidence for the reactions of Scheme 3 occurring.

When 2-cyclohexylidene-*N,N*-diethylethenecarboxamide²¹ (**11**) was thermolyzed between 400 and 760 °C with product isolation in Ar at 12 K, a band ascribed to the vinylketene **12** was observed at 2120 cm⁻¹ above 450 °C (Scheme 4). The formation of **12** is ascribed to the facile 1,3-shift of the diethylamino group in the allenic amide. An electrocyclicization of this ketene to give a spiro compound **14** was not observed, as testified by the absence of bands in the 1700–1800 cm⁻¹ region which could correspond to a conjugated carbonyl group in this strained compound (the carbonyl band for 3-(dimethylamino)cyclobutenone (**7c**) is at 1772 cm⁻¹ in Ar matrix³). The absence of **14** can be ascribed to increased ring strain, making this compound slightly less stable than ketene **12**. An analogous case is 3-chlorovinylketene, which on warmup fails to cyclize to 3-chlorocyclobutenone.^{3a}

Above 700 °C, the band at 2120 cm⁻¹ decreased in intensity and a new set of bands in the 2800 cm⁻¹ region and at 1679 and 1630 cm⁻¹ increased. These are characteristic of an aldehyde, e.g. **16** (Scheme 4).

Chemical evidence for the structure **16** was obtained by generation at 700 °C with product isolation on a coldfinger at -196 °C, both with and without trapping agent (methanol). After warming to room temperature, **16** was isolated in 70% yield, and the ¹H NMR spectrum was in excellent agreement with literature values.²² At FVT temperatures below 700 °C, only starting material **11** was recovered. The formation of **16** is understood in terms of formation of an unobserved ketene **13** via the retro-ene pathway. A subsequent 1,5-H shift causes

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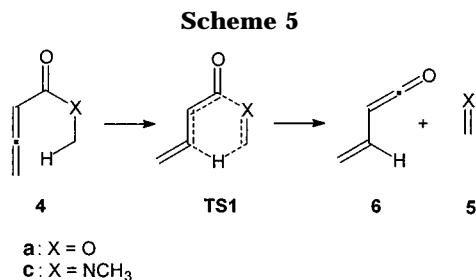
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(19) (a) When vinylketene (**6**) is generated by FVT of butenoic acid **10**, it is isolated in the presence of water ice at 77 K. We have shown elsewhere that ketenes can be stable at -40 °C (and above) in the presence of water-ice,^{19b} whereas the same ketenes react at -100 to -90 °C with MeOH,^{19b} and other ketenes react at temperatures as low as 15–75 K (-258 to -198 °C) with amines (pyridine).^{17a,b} Birney et al. have also reported a high selectivity for reaction of acetylketene with an amine vis-à-vis alcohols.^{19c} (b) Gross, G.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1982**, 360. (c) Birney, D. M.; Xu, X.; Ham, S.; Huang, X. *J. Org. Chem.* **1997**, *62*, 7114.

(20) In the low-pressure gas-phase reaction, the vinylketene **6** and the imine **5c** will be prevented from reacting with each other and cyclizing to lactams. β -Lactams are the products expected in solution phase reactions.^{16b,c}

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isomerization to the more stable aldehyde **16** (Scheme 4; cf. Section 2). Even though this known type of sigmatropic shift²³ is reversible, in this particular case the equilibrium is completely displaced toward the aldehyde **16** due to its higher thermodynamic stability. Indeed, semiempirical calculations predict the aldehyde **16** to be more stable than the ketene **sZ-13** by 30 (PM3), or 26 (AM1) kJ mol⁻¹.

In attempted trapping reactions with MeOH at 77 K, mainly starting material **11** was recovered at FVT temperatures below 700 °C. The ketene **12** was not trappable. One explanation for this could be the high reactivity (below 77 K) of the amine moieties in **11** or **12** toward the ketene, resulting in the formation of ketene/amine zwitterions, possibly followed by polymerization.¹⁹

Similarly, when the allene carboxamide **11** was thermolyzed between 500 and 800 °C with product isolation at 77 K, no trace of ketene **12** was observed, probably due to the formation of ketene/nucleophile zwitterions and subsequent reactions well below 77 K. The starting material **11** remained the only identifiable species, until 580 °C, when **16** started to appear.

In this reaction too, there was no evidence for an alternative retro-ene reaction of ketene **12**, which in analogy with Scheme 3 would have yielded an allenic aldehyde, 2-cyclohexylideneacrolein.

2. Theory. 2.1. Retro-Ene Reaction. To gain more insight into the abovementioned retro-ene reactions, G2(MP2,SVP) calculations were performed for allenes **4a** and **4c**, reacting to vinylketene **6** and formaldehyde **5** via transition states **TS1a** and **TS1c**, respectively (Scheme 5). In both cases, **TS1** features the transfer of a hydrogen atom from a methyl group to the central carbon atom of the allene moiety (see Figure 4) together with some lengthening of the CO–X bond compared to the starting material (1.536 Å in **TS1a** (1.359 Å in **4a**); 1.425 Å in **TS1c** (1.370 Å in **4c**). **TS1c** is shown in Figure 4, and that of **TS1a** in Figure S1 in the Supporting Information, where the full computed structural data is also presented. The structure of **TS1** is further discussed in section 2.3. The calculated activation energies, presented in Table 1, give at the highest level, G2(MP2,SVP) theory, a barrier for **TS1a** of 181 kJ mol⁻¹, and for **TS1c** of 167 kJ mol⁻¹ above the allene starting material, in agreement with the experimental observation that the retro-ene reaction takes place significantly more easily for **4c** than for **4a**.

On the basis of previous work, both experimental^{16,17} and theoretical,^{24,25} a zwitterion **17** (Figure 5) may be

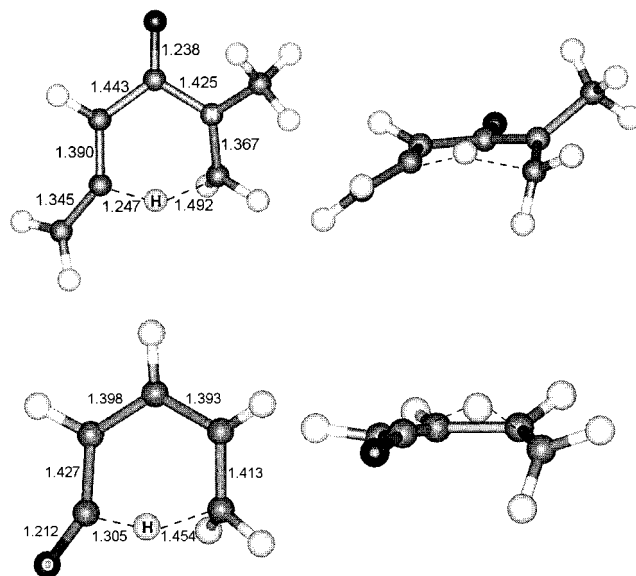


Figure 4. Calculated structures of **TS1c** (upper) and **TS2** (lower) at the MP2/6-31G* level.

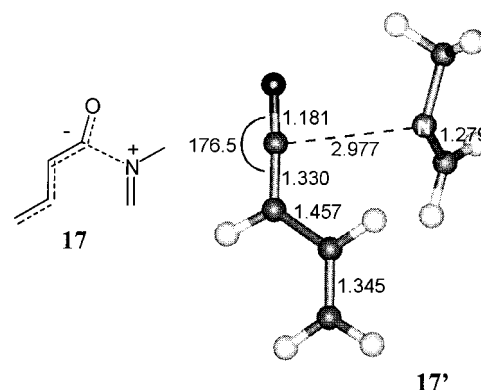


Figure 5. Hypothetical zwitterion **17**, and calculated ketene–imine van der Waals complex **17'** (MP2/6-31G*).

Table 1. Calculated Relative Energies (kJ mol⁻¹) for the Retro-Ene Reactions of **4a** and **4c** (Scheme 5)

level of calcn	R = methoxy			R = dimethylamino		
	4a	TS1a	6 + 5a	4c	TS1c	6 + 5c
HF/6-31G*	0	300.8	40.1	0	285.7	86.1
MP2(fc)/6-31G*	0	205.5	48.1	0	177.5	99.0
MP2/6-311+G(3df,2p)	0	186.8	47.9	0	157.2	100.8
QCISD(T)/6-31G*	0	211.2	51.6	0	197.2	93.3
G2 (MP2,SVP)	0	181.4	35.6	0	167.1	80.6

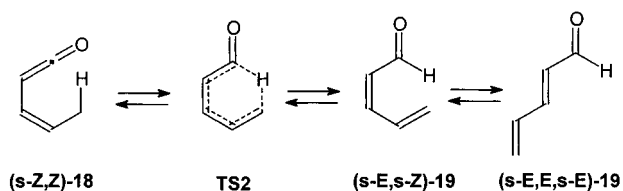
involved in the addition of an imine to a ketene. It is possible, therefore, that this intermediate could also exist on the retro-ene energy surface. At the HF/6-31G* level

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(25) Concerted Staudinger reactions have also been predicted computationally: (a) Yamabe, S.; Minato, T.; Osamuro, Y. *J. Chem. Soc., Chem. Commun.* **1993**, 450. (b) Fang, D. C.; Fu, X. Y. *Int. J. Quantum Chem.* **1992**, *43*, 669.

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Scheme 6



of theory, such an intermediate is indeed found, in a very shallow minimum, $140.4 \text{ kJ mol}^{-1}$ above **4c**. At this level of theory, **TS1c** is 286 kJ mol^{-1} above **4c**, but there is only a 0.4 kJ mol^{-1} barrier for the intermediate to dissociate to **6** + **5c** (transition structure $140.8 \text{ kJ mol}^{-1}$ above **4c**). The intermediate becomes already less favorable than its dissociation transition state **TS1c** when entropy is taken into account, calculating ΔG . There is no corresponding intermediate for the retro-ene reaction of **4a** at the HF/6-31G* level. The abovementioned intermediate **17** in the reaction of **4c** disappears at correlated levels (MP2 and G2), where the retro-ene reaction is concerted in both methoxy (**4a**) and dimethylamino (**4c**) cases. When lengthening the N–CO distance in **TS1c**, no stationary point can be found corresponding to an intermediate zwitterion, but only a loose van der Waals complex **17'** with a very long N...CO contact (2.98 \AA). At the Becke3LYP level it is even longer, about 3.2 \AA . The MP2/6-31G* structure is shown in Figure 5. This species has still an almost linear C=C=O moiety (176.5°) and is best described as a ketene complex rather than a zwitterion. Very recently, calculations on a cyanoketene–formaldimine van der Waals complex have been published.²⁶ Complex **17'** exists in a shallow minimum, 9 kJ mol^{-1} below the separated products, **5** + **6c**. For chemical purposes, the reactions can be regarded as concerted. A more detailed investigation of the potential energy surface, including β - and δ -lactam formation, at ab initio and density functional levels of theory, and including a dielectric field, is in progress and will be published elsewhere.

2.2. 1,5-H Shift. In the case of allene **11**, the vinylketene **13** resulting from the retro-ene rearrangement could not be observed (Scheme 4). Instead, the aldehyde **16**, formed from **13** by a 1,5-hydrogen shift, was isolated. We therefore investigated a model system, the rearrangement of methylvinylketene **18** to penta-2,4-diene-1-al **19** (Scheme 6).

Starting from the required *s-Z,Z* conformer of **18** (6 kJ mol^{-1} above the corresponding *s-E,Z* conformer), the transition state **TS2** for the 1,5-H shift lies 125 kJ mol^{-1} above *s-Z,Z*-**18**. The structure of **TS2** is similar to, but flatter than that of **TS1**, with the hydrogen atom again being transferred nearly in-plane toward the central carbon p orbital of the ketene (Figure 4). For further discussion see section 2.3. The migration initially leads to the aldehyde (*s-E,Z,s-E*)-**19** ($+9.4 \text{ kJ mol}^{-1}$) which then isomerizes to the more stable conformation (*s-E,E,s-Z*)-**19**: $-13.5 \text{ kJ mol}^{-1}$; Table 2). These data clearly illustrate why the vinylketene **13** cannot be observed. Once formed at temperatures which overcome the barrier for the retro-ene reaction ($167\text{--}184 \text{ kJ mol}^{-1}$), the ketene can easily rearrange to the aldehyde **16** via the more facile (125 kJ mol^{-1}) 1,5-hydrogen shift.

2.3. The Nature of the Transition States. The transition structures calculated for the retro-ene reaction,

Table 2. Calculated Relative Energies (kJ mol^{-1}) for the 1,5-H Shift Reaction (**18** → **19**) (Scheme 6)

level of calcn	(<i>s-Z,Z</i>)- 18	TS2	(<i>s-E,Z,s-Z</i>)- 19	(<i>s-E,E,s-E</i>)- 19
HF/6-31G*	0	215.9	-2.2	-26.7
MP2(fc)/6-31G	0	130.7	12.8	-8.7
MP2/6-311+G(3df,2p)	0	119.2	17.5	-5.0
QCISD(T)/6-31G	0	143.9	1.8	-19.4
G2(MP2,SVP)	0	125.0	10.4	-13.5

TS1a and **TS1c**, are shown in Figure 4 and in the Supporting Information. In **TS1c** the hydrogen atom moves ca. 17° out of the plane of the four carbon atoms. The terminal CH_2 group of the allene moiety has twisted to a large extent, so that an essentially planar vinyl group can form when the H atom is fully transferred. This is even more pronounced in **TS1a**, which is more advanced (i.e. "later"), with a forming bond length C3–H = 1.173 \AA . The rough planarity of these transition structures could suggest a pseudopericyclic nature of the reactions,²⁷ but further computational studies of model compounds will be required in order to determine the exact orbital interactions. 1,5- and 1,7-H shifts in conjugated allenes have been investigated by Okamura et al.,²⁸ and the "allene effect" (a lowering of the activation barrier compared to the nonallenic 1,3 pentadiene and 1,3,5-heptatriene systems) has been explained by Jensen in terms of extra conjugation in the TS, which can be formally regarded as biradicaloid.²⁹

The nearly-planar **TS1** with the CH_2 end groups twisted into the plane are in accord with that interpretation, but again model compound calculations are required in order to determine the magnitude of the effect.

TS2 is much flatter than corresponding transition structures for 1,5-H shifts in 1,3-pentadiene or cyclopentadiene, where the migrating hydrogen atom moves as much as 79° out of plane.^{7e,30} The near-planarity of **TS2** (Figure 4) suggests that the H atom is transferring toward the in-plane ketene p orbital at C3, which is orthogonal to the remaining π backbone. This process therefore has the characteristics of a pseudopericyclic reaction.²⁷ Closely related, nearly planar transition structures have been computed for the 1,5-H shift in 4-formylvinylketene (HCO-CH=CH-CH=C=O ; calc. $E_a \sim 99 \text{ kJ mol}^{-1}$),⁵ and for the 1,5-Cl shift in 4-(chlorocarbonyl)vinylketene (ClCO-CH=CH-CH=C=O ; calc. $E_a \sim 32 \text{ kJ mol}^{-1}$).^{4b}

The calculated barrier separating **18** and **TS2** (125 kJ mol^{-1}) is not particularly low. This is in line with results for related compounds containing a CH_2 group rather than a C=O group, e.g. chloromethyl isocyanate (ClCH_2NCO) compared with chlorocarbonyl isocyanate (ClCONCO); the calculated barrier for the 1,3-Cl shift is 191 kJ mol^{-1} in the former,^{4b} and only 85 kJ mol^{-1} in

(27) (a) Pseudopericyclic reactions were defined by Lemal as those having an orbital disconnection.^{27b} This disconnection or orthogonality^{27c} renders the Woodward–Hoffmann rules inapplicable, and all reactions are allowed, regardless of the number of electrons. The reactions have been investigated extensively by Birney in recent years.^{27d,e} (b) Ross, J. A.; Seiders, R. P.; Lemal, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 4325. (c) Wentrup, C.; Netsch, K.-P. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 802. (d) Birney, D. M.; Ham, S.; Ünruh, G. R. *J. Am. Chem. Soc.* **1997**, *119*, 4509 and references therein. (e) See also Luo, L.; Bartberger, M. D.; Dolbier, W. R. *J. Am. Chem. Soc.* **1997**, *119*, 12366 and references therein.

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the latter.^{4c} While all these reactions can be termed pseudopericyclic, the tremendous effects of ketenes (compared with allenes) and halogens as well as other electron-donating lone-pair groups on lowering the activation barriers are due to better HOMO–LUMO interaction terms,^{4b} which can also be expressed in terms of the nucleophilicity and electrophilicity of the reacting centers.⁵

Other things being equal, we then expect lower activation barriers for ketenes than for allenes and much lower barriers for the transfer of lone-pair groups than hydrogen atoms.

Conclusion

The allenic esters **4a** and **4b** undergo a retro-ene reaction on FVT above 800 °C to give unsubstituted vinylketene (**6**) together with formaldehyde (**5a**) or acetaldehyde (**5b**).

The thermolysis of *N,N*-dimethylallene-carboxamide (**4c**) likewise gives vinylketene **6** and *N*-methylmethanimine (**5c**), starting at lower FVT temperatures (>500 °C).

These observations are in very good agreement with ab initio calculations which predict activation energies for the retro-ene reaction of 181 (R = OMe) or 167 (R = NMe₂) kJ mol⁻¹.

The same acylallenes **4** are formed on FVT of cyclobutenones **7** via vinylketenes **3**.³ At higher FVT temperatures, the retro-ene reactions again lead to the formation of **6**.

In the case of the 2-cyclohexylidene-*N,N*-diethylethenecarboxamide (**11**), Ar matrix isolation indicates the formation of the vinylketene **12**, formed by a 1,3-NEt₂ shift, but the vinylketene **13** expected from the retro-ene reaction is not directly observable. Instead, formation of a conjugated aldehyde **16** occurs by a 1,5-H shift in **13**. Ab initio calculations carried out on 4-methylvinylketene **18** confirm that the 1,5-H shift has a much lower activation barrier (ca. 125 kJ mol⁻¹) than the retro-ene reaction.

Experimental and Computational Section

Computational Methods. Standard ab initio molecular orbital calculations³¹ were carried out using the GAUSSIAN 94 system of programs.³² The structures and energies of all model compounds were examined at the G2(MP2,SVP) level of theory.³³ This corresponds effectively to QCISD(T)/6-311+G(3df,2p)/MP2/6-31G* energies together with zero-point vibrational and isogyric corrections. In the G2(MP2,SVP) theory, the basis-set extension energy contribution is calculated at the MP2 level, and the QCISD(T) energy is evaluated using the 6-31G* basis set. It has been shown that the accuracy of the G2(MP2, SVP) method is comparable to that

of G2(MP2)³⁴ theory but computationally more efficient. The frozen-core approximation was employed for all correlated calculations. Zero-point vibrational energy calculations were performed at the HF/6-31G* level.

General Experimental Methods. Preparative flash vacuum thermolysis (FVT) was carried out in electrically heated quartz tubes, 40 cm long, of 2 cm diameter. Samples were vaporized or sublimed into the pyrolysis tube using a Büchi sublimation oven. The system was evacuated to ca. 10⁻⁵ mbar and continuously pumped during FVT using a Leybold-Heraeus turbomolecular pump PT150. The thermolysates were cocondensed with or without MeOH vapor on the 77 K coldfinger, whereby methanol was introduced between the exit of the pyrolysis oven and the coldfinger. Further details of the FVT apparatus have been published.³⁵

Matrix isolation was carried out using 10 cm long, 0.8 cm internal diameter quartz tubes in an oven directly attached to the vacuum shroud of a Leybold-Heraeus closed cycle liquid He cryostat.^{3b,35} Ar was used as matrix host, which was passed over the sample while it was subliming and cocondensed at ca. 12 K on a BaF₂ window for IR spectroscopy. Neat isolation at 77 K was carried out in a similar apparatus using a liquid N₂ cryostat.³⁵

The FVT-MS combination has been described.³⁶

Materials. 3-Methoxycyclobutenone,³⁷ 3-ethoxycyclobutenone,¹² 3-(*N,N*-dimethylamino)cyclobutenone,^{3a} **4a,b**,³⁸ and **4c**^{3a} were synthesized according to the literature. IR matrix isolation data for these compounds have been described.^{3a} **10** was obtained commercially (Aldrich).

(2E)-Butenoic acid (10): IR (Ar matrix, 12 K): 3585 (w), 3579 (w), 3570 (sh), 3567 (m), 3562 (w), 3551 (w), 2992 (w), 2963 (w), 2953 (w), 2924 (w), 1755 (s), 1738 (m), 1729 (m), 1710 (m), 1707 (w), 1664 (m), 1449 (m), 1436 (w), 1379 (w), 1366 (w), 1360 (w), 1356 (w), 1346 (w), 1320 (b), 1298 (b), 1294 (w), 1273 (b), 1229 (w), 1201 (w), 1181 (b), 1164 (m), 1160 (w), 1144 (m), 1102 (w), 1093 (m), 1090 (m), 979 (w), 973 (w), 963 (w), 852 (w), 869 (w), 866 (w), 849 (w), 846 (w), 842 (w), 840 (w) cm⁻¹.

1,3,5-Trimethyl-1,3,5-triazine (9). **9** was synthesized according to Graymore.^{14a} Yield 30–50%; bp 160–172 °C. ¹H NMR (60 MHz, CDCl₃): δ 2.30 (s, 9 H), 3.21 (s, 6 H); IR (neat, -196 °C): 2966 (s), 2942 (s), 2892 (m), 2843 (w), 2809 (sh), 2787 (s), 2773 (sh), 2726 (m), 2664 (m), 2649 (m), 2630 (w), 2596 (m), 2572 (w), 2503 (w), 2453 (w), 1471 (s), 1444 (s), 1428 (s), 1386 (m), 1373 (m), 1346 (w), 1305 (w), 1273 (sh), 1262 (s), 1234 (m), 1156 (m), 1116 (s), 1050 (w), 1025 (m), 1003 (m), 981 (w), 915 (s), 898 (w), 860 (m), 836 (w), 627 (w) cm⁻¹; (Ar, 12 K): 2981 (m), 2952 (m), 2901 (w), 2847 (w), 2815 (w), 2793 (m), 2730 (w), 2670 (w), 2636 (w), 2605 (w), 2576 (w), 1475 (m), 1446 (m), 1430 (w), 1425 (w), 1387 (m), 1375 (m), 1277 (m), 1266 (m), 1237 (m), 1163 (m), 1126 (m), 1119 (s), 1052 (w), 1005 (m), 917 (m), 915 (m), 862 (w), 629 (w), 496 cm⁻¹.

Matrix Isolation of *N*-Methylmethanimine (5c). The preparation of a matrix of **5c** was slightly different from the one described by Stolkin and Günthard.¹³ Instead of using a low FVT temperature and an alumina–silica catalyst (90:10), **9** was detrimerized by FVT at 850 °C. The data for **5c** are as follows: IR (neat, 12 K): 3013 (m), 2943 (s), 2896 (s), 2850 (s), 2776 (m), 1653 (s), 1473 (s), 1437 (m), 1405 (w), 1384 (w), 1262 (w), 1232 (m), 1160 (w), 1112 (m), 1046 (m), 1002 (w), 949 (m), 917 (w), 861 (w), 630 (vw), 498 (w) cm⁻¹; IR (Ar, 12 K): 3014 (m), 2964 (m), 2955 (m), 2940 (m), 2902 (m), 2886

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(w), 2878 (w), 2856 (m), 2850 (m), 2839 (w), 2776 (w), 1657 (m), 1470 (vs), 1441 (m), 1222 (m), 1027 (m), 950 (m), 663 (w), 479 (w) cm^{-1} . The Ar matrix IR data are in good agreement with the literature.¹³

2-Cyclohexylidene-*N,N*-diethylethenecarboxamide (11). The synthesis of **11** was described by Parker et Petraitis.²¹ The ¹H NMR data were in good agreement with the literature.^{21a} Purity according to NMR was higher than 98%. ¹³C NMR (400 MHz, CDCl₃): δ 204.3, 165.2, 105.4, 85.9, 42.6, 40.8, 30.3, 26.8, 25.8, 14.6, 13.0; IR (Ar, 12 K): 2981 (m), 2971 (sh), 2941 (m), 2896 (w), 2862 (m), 2848 (w), 1973 (m), 1642 (s), 1481 (m), 1473 (m), 1465 (m), 1460 (m), 1451 (m), 1441 (m), 1431 (m), 1402 (w), 1380 (m), 1364 (w), 1349.5 (w), 1346 (w), 1323 (w), 1315 (w), 1280 (m), 1251 (w), 1237 (m), 1226 (m), 1182 (w), 1155 (w), 1135 (m), 1099 (w), 1090 (w), 1085 (w), 1073 (w), 1027 (w), 1022 (w), 977 (w), 947 (w), 933 (w), 922 (w), 911 (w), 898 (w), 853 (w), 828 (w), 821 (w), 811 (w), 788 (w), 781 (w) cm^{-1} .

**FVT of 11: Isolation of (*E*)-3-(1-Cylohexen-1-yl)prope-
nal (16).** FVT of **11** was carried out at 700 °C and gave, after column chromatography (SiO₂/CHCl₃), **16** (yield: 70%). ¹H NMR data are in excellent agreement with the literature.²²

Purity by NMR was higher than 90%. ¹³C NMR (200 MHz, CDCl₃): δ 194.4, 156.3, 141.3, 135.5, 125.8, 26.7, 24.2, 21.9, 21.8.

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Supporting Information Available: Structure **TS1a** calculated at the MP2/6-31G* level of theory (Figure S1), calculated structural parameters for **4a**, **4c**, **TS1a**, **TS1c**, **17'**, and **6** (MP2/6-31G*) (Table S1), Cartesian coordinates for the calculated structures (Table S2), and IR and GC-MS data for compound **16** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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