# Vinylketene—Acylallene Rearrangement

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The chemistry of ketenes has been of much interest recently.[1] In previous work, we have shown that α-oxoketenes (acylketenes) **1a** undergo a degenerate thermal rearrangement involving a 1,3-shift of the group R (eq 1).[2,3] This migration is dramatically

    a: X=O, Y=O
    b: X=NR', Y=O   (1)
    c: X=CR'₂, Y=O
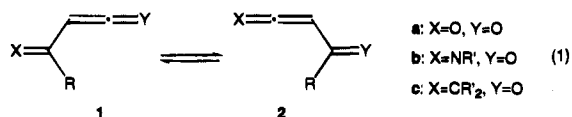
accelerated for electron-donating substituents R (OR', SR', and NR'₂) due to a favorable overlap between the lone pair of the migrating atom and the vacant central carbon p orbital of the ketene LUMO.[3] A similar reaction interconverts imidoylketenes **1b** and α-oxoketenimines **2b**.[4]

Further computational work indicates that the activation barriers are related to the electrophilicities of the carbon atoms where the migration occurs.[5] Thus, for 1,3-H migration, the activation barrier increases in the series α-oxoketene < α-oxoketenimine < imidoylketene < acylallene < vinylketene. An excellent correlation ($R^2 = 0.99$) is observed between the barrier height and the energy difference between the ketene LUMO and the highest occupied orbital involving the migrating group. Accordingly, one can expect to observe the vinylketene—acylallene rearrangement (**1c** ⇌ **2c**) for only the most favorable migrating groups, i.e., alkoxy, thioalkoxy, and amino groups. We now wish to report the first direct evidence for this latter reaction using alkoxy- and (dialkylamino)vinylketene precursors and the corresponding allene carboxylic acid derivatives.

Ab initio molecular orbital calculations[6] were performed using the GAUSSIAN 92 series of programs.[7] Geometry optimizations for vinylketenes [RC(=CH₂)CH=C=O], acylallenes [RC(=O)CH=C=CH₂], and the 1,3-migration transition structures were carried out at the MP2/6-31G* level.[6] Higher-level relative energies were obtained at the QCISD(T)/6-311+G(2d,p)//MP2/6-31G*+ZPVE level[8,9] by using an additivity approximation.[10] A summary of the results is presented in Table 1.

Table 1. Calculated Relative Energies[a] (kJ mol⁻¹)

R	*s-trans*-vinylketene (**1c**)[b]	*s-trans*-acylallene (**2c**)[b]	1,3-shift TS
H	0	43.1	272.9
CH₃	0	31.7	331.3
NH₂	0	−22.0	167.0
OH	0	−26.4	185.5
SH	0	5.7	147.0
OCH₃	0	−25.6	169.4
NHCH₃	0	−20.7[c]	146.4[c]
SCH₃	0	3.5[c]	129.8[c]
N(CH₃)₂	0	−20.6[c]	107.2[c]

[a] QCISD(T)/6-311+G(2d,p)+ZPVE values. [b] Except for R = N(CH₃)₂, the *s-trans* conformation is more stable than the *s-cis* form. [c] Based on an empirical correction to the MP3/6-311+G**+ZPVE value (refs 3 and 5).

As with α-oxoketene[3] and imidoylketene,[5] substitutents with an unshared pair of electrons (NH₂, OH, SH, OCH₃, and N(CH₃)₂) lead to lower barriers while a methyl group destabilizes the four-center transition structure (Table 1). The migratory aptitudes decrease in the order N(CH₃)₂ > SCH₃ > NHCH₃ > SH > OCH₃ > NH₂ > OH > H > CH₃. The stabilizing effect of the electron-rich substituents is readily understood in terms of the favorable interaction between the R group and the vacant central carbon p orbital of the ketene (or allene) moiety in the molecular plane (this is illustrated in Figure 2 in the supporting information).

For all the R substitutents, the 1,3-migration barrier is in the order α-oxoketene < imidoylketene < vinylketene. This can be explained by the energy ordering of the ketene acceptor orbital (LUMO) in the series of ketenes. 1,3-H and 1,3-CH₃ shifts in **1c** are calculated to have high activation barriers and are therefore unlikely to be observable processes. On the other hand, rearrangement of methoxyvinylketene to (methoxycarbonyl)allene is predicted to have an energy barrier of 169 kJ mol⁻¹, comparable to that calculated for the 1,3-phenyl shift in benzoylketene (165 kJ mol⁻¹),[3] which has been observed in a ¹³C labeling experiment.[2a] Thus, we predict the 1,3-OCH₃ shift in vinylketenes to be an observable process. 1,3-Dimethylamino and alkylthio migrations are predicted to be facile processes (cf. Table 1) and should be accessible by experiment.

3-Methoxycyclobutenone[11] (**3a**) underwent flash vacuum pyrolysis (FVP)[12] to the *s-cis*- and *s-trans*-methoxyvinylketenes[13] **4a** at temperatures above 400 °C, as evidenced by Ar matrix isolation of the ketenes at 12 K (FTIR 2138 and 2142 cm⁻¹). At FVP temperatures above 650 °C, weak allene bands were observed at 1982 and 1947 cm⁻¹ as well, increasing in intensity up to ~900 °C. Direct comparison with methyl allenecarboxylate (**5a**) confirmed the identity of the bands. Further evidence is given for the ethyl analogue **5b**.

Analogous FVP/matrix isolation of 3-ethoxycyclobutenone[14] **3b** gave *s-cis*-and *s-trans*-ethoxyvinylketenes **4b** above 400 °C. The conversion was complete at 700 °C. The characteristic IR bands of **4b** are at 2136 and 2140 cm⁻¹ (Ar, 12 K) (Figure 1a). These are also generated upon Ar matrix photolysis of **3b** (1000 W high-pressure Hg—Xe lamp; broad band; quartz). The *cis* form absorbing at 2136 cm⁻¹ is generated first but isomerizes

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(10) Δ*E*(QCISD(T)/6-311+G(2d,p)) ≈ Δ*E*(QCISD(T)/6-31G*) − Δ*E*(MP2/6-31G*) + Δ*E*(MP2/6-311+G(2d,p)).

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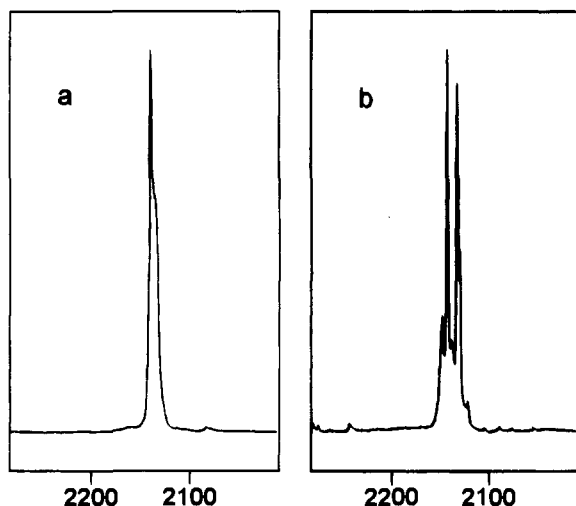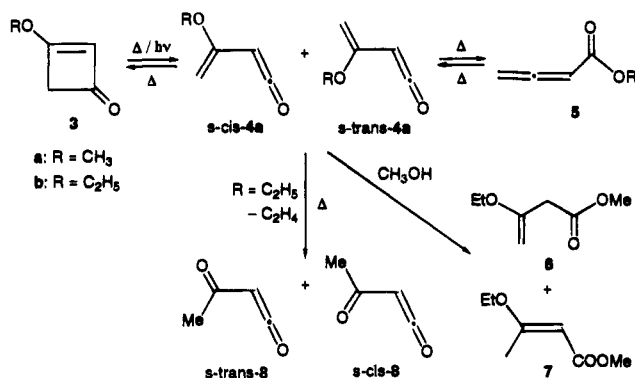
Figure 1. Partial Ar matrix FTIR spectra (12 K) of the results of FVP of **3b**: (a) *s-cis*-**4b** and *s-trans*-**4b** (2136, 2140 cm⁻¹) at 540 °C; (b) *s-cis*-**8** and *s-trans*-**8** at 900 °C.[16]

to the *trans* form (2140 cm⁻¹) on further photolysis (5:1 ratio after 5 min, changing to a 1.9:1 ratio after 85 min photolysis). When the thermally generated ketenes were trapped at −196 °C and subsequently warmed, reversion to the starting material **3b** was observed at −25 °C. Furthermore, ketenes **4b** were again generated at 450 °C and trapped on a cold finger coated with MeOH at −196 °C. After this mixture was warmed to room temperature, ¹H NMR analysis demonstrated the formation of methyl 3-ethoxy-3-butenoate (**6**) and methyl (*E*)-3-ethoxy-2-butenoate (**7**) in a ratio 64:36 (74% yield with 26% **3b** recovered).

FVP of **3b** above 690 °C also gave rise to allene bands identical with those of ethyl allenecarboxylate (**5b**).[15] The latter was also unambiguously identified by ¹H NMR of the product of a preparative pyrolysis of **3b** at 690 °C. The allene bands in the IR spectrum increased up to an FVP temperature of 730 °C, whereupon they decreased again, disappearing entirely at 920 °C. Throughout this temperature range (∼600−920 °C), a new set of bands belonging to acetylketene **8** grew in intensity (Figure 1b).[16] As we have recently characterized acetylketene very thoroughly,[12] this pattern is readily recognized as the *s-trans* and *s-cis* forms of **8**. Bands due to ethene at 948, 2996, and 3096 cm⁻¹ were also identified. The formation of acetylketene and ethene above 600 °C is readily understood in terms of ethene elimination from the ethoxyvinylketenes **4b**.[17,18]

Proof of the interconversion of vinylketenes **4b** and (ethoxy-carbonyl)allene **5b** was obtained by FVP of the latter at 570−800 °C. Again, the vinylketene bands due to *s-cis*- and *s-trans*-**4b** were observed, as well as those due to *s-cis*- and *s-trans*-**8** and ethene, increasing in intensity with the temperature. The

formation of **8** and ethene by FVP of both **3b** and **5b** was confirmed by direct on-line monitoring of the reactions by mass spectrometry.[19]

Preliminary experiments on other allene and cyclobutenone derivatives confirmed the generality of the rearrangement. Thus, FVP of trimethylsilyl allenecarboxylate at ≥600 °C gave rise to a ketene absorption at 2126 cm⁻¹. FVP of 3-(dimethylami-no)cyclobutenone caused the emergence of new allene absorptions at 1970 and 1950 cm⁻¹ (77 K) already at 500 °C, in agreement with the lower calculated barrier for the 1,3-shift of a dialkylamino group. These experiments are continuing, and further details will be reported later.

The rearrangement described herein may help explain the hitherto mystifying results of cycloaddition of ynamines (and ynols) to ketenes, in which both cyclobutenones **9** and allenes can be obtained,[20] and support the proposed mechanism of the rearrangement of alkylthio-substituted allenes to naphthalenes and cyclobutenone derivatives.[21] It has usually been assumed[20]
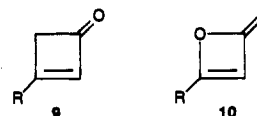
that allene formation is due to initial [2 + 2] cycloaddition to give unobserved 4-methyleneoxetanes **10** followed by ring opening, whereas the [2 + 2] cycloaddition to give cyclobuten-ones **9** is the normal outcome. Our calculations (MP2/6-311+G**//MP2/6-31G*) indicate that the oxetanes **10** (R = OMe or NMe₂) are ∼120 kJ mol⁻¹ higher in energy than **9**. Therefore, in suitable cases, the normal cycloaddition to give **9**, followed by electrocyclic ring opening to vinylketenes and 1,3-rearrangement to allenes, as described herein, may be a lower energy pathway. We are continuing our investigation of these intriguing rearrangements.

Supporting Information Available: Spectroscopic data for compounds **5b**, **6**, and **7**; Figure 2 showing interaction between migrating group and ketene MOs in vinylketenes (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

(15) Data for **5b**, **6**, and **7** are listed in the supporting information.

(16) *s-cis*-Acetylketene: 3095, 2148, 2143, 1681, 1378, 1345, and 1168 cm⁻¹. *s-trans*-Acetylketene: 3083, 2137, 2133, 1699, 1343, and 1221 cm⁻¹.

(17) (a) At still higher temperatures (≥800 °C), acetylketene underwent partial decomposition to CO₂ and propyne (3323 (w) and 2137 (w) cm¹) (also observed when other acetylketene precursors[12] were used). A further possible source of propyne is the elimination of ethene and then CO₂ from **5b**.[16b] However, this does not appear to be a significant process, and only a minute band due to unsubstituted allene (1955 cm⁻¹) was formed from **5b** at 900 °C. In none of the reactions using **3a,b** as precursor was a fragmentation to alkoxyethyne and ketene observed. (b) Bigley, D. B.; Weatherhead, R. H. *J. Chem. Soc., Perkin Trans.* 2 **1976**, 592; 704. Dallinga, J. W.; Nibbering, N. M. M.; Boerboom, A. J. H. *J. Chem. Soc., Perkin Trans.* 2 **1983**, 281.

(18) Compound 3 (R = OH) is computed to be almost isoenergetic with 4 (calculated relative energies (QCISD/6-311+G(2d,p)+ZPVE): 3, 0; *s-cis*-4, −1; *s-trans*-4, −9; *s-cis*-5, −34; *s-trans*-5, −36 kJ mol⁻¹). The transition structure for 3 (R = OH) → *s-cis*-4 lies 94 kJ mol⁻¹ above 3. The transition structure for *s-trans*-4 → *s-trans*-5 lies 176 kJ mol⁻¹ above 3. Thus, under conditions where the reaction 4 ⇌ 5 occurs, the interconversion 3 ⇌ 4 will be rapid.

(19) The FVP-MS technique (Kratos MS25RFA) is described in the following: Wentrup, C.; Kambouris, P.; Evans, R. A.; Owen, D.; Macfarlane, G.; Chuche, J.; Pommelet, J. C.; Ben Cheikh, A.; Plisnier, M.; Flammang, R. *J. Am. Chem. Soc.* **1991**, *113*, 3130.

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