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Carboxy(vinyl)ketene intermediates in the thermolysis of methylthio- and methoxy-substituted Meldrum's acid derivatives

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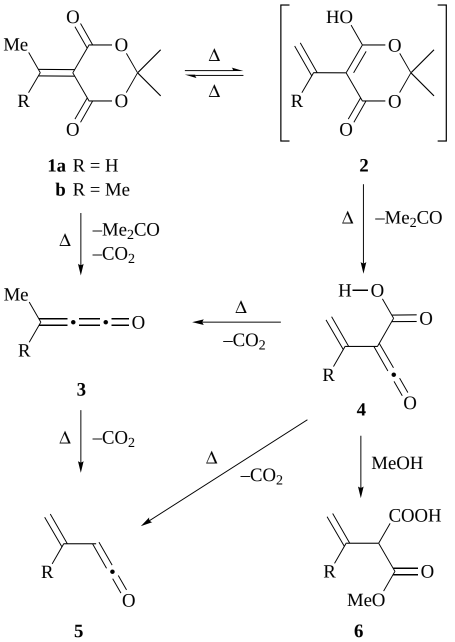
Methylthio- and methoxy-substituted carboxy(vinyl)ketenes 10 and 16a have been identified by Ar matrix isolation FTIR spectroscopy following flash vacuum thermolysis (FVT) of Meldrum's acid derivatives 7 and 13a. Methylthio(methyl)methyleneketene 9 and alkoxy(methyl)methyleneketene 15 are formed concurrently at high FVT temperatures. The alkoxy(methyl)methyleneketenes 15 do not isomerise to alkoxy(vinyl)ketenes 18, which have been generated and identified in other reactions. Ethoxy(methyl)-methyleneketene 15b readily eliminates ethene in a retro-ene type reaction to produce acetylketene 22. Ketenes 15 react with alcohols and amines to produce 3-alkoxybutenoic acid derivatives 21.

Introduction

In previous work it was demonstrated that flash vacuum thermolysis (FVT) of 5-alkylidene-Meldrum's acid derivatives (2,2-dimethyl-1,3-dioxane-4,6-diones, **1**) involved the formation of carboxyketene intermediates (**4**) which subsequently decarboxylated to methyleneketenes (propadienones, **3**) and/or vinylketenes (**5**), and the alkylmethyleneketenes themselves isomerised to vinylketenes at elevated temperatures [1–3] (Scheme 1).



Scheme 1

Carboxy(imino)ketenes [RN=CH–C(COOH)=C=O] were also detected by both IR and photoelectron (PE) spectroscopy in the FVT of 5-alkylaminomethylene-Meldrum's acid derivatives, prior to formation of alkylaminomethyleneketenes (RNH–CH=C=C=O) and iminoketenes (RN=CH–CH=C=O).[4] Whereas alkyl- and aryl-methyleneketenes are reactive intermediates, only detectable at low temperatures or in the gas phase, electron donating substituents strongly stabilise these compounds, so that amino-, alkylthio- and alkoxy-methyleneketenes are stable at or near room temperature.[5,6] Using PE spectroscopic monitoring of the formation of ketenes on FVT of the methylthio- and methoxy(methyl)methylene-Meldrum's acid derivatives **7** and **13a**, a carboxyketene intermediate could not be observed in the case of **7**, and was only tentatively identified in the case of **13a**.[7,8] By analogy with the known chemistry of alkylmethyleneketenes (Scheme 1), it was further suggested that methoxy(methyl)methyleneketene (**15a**) underwent isomerisation to (1-methoxy)vinylketene (**18a**) at elevated temperatures, giving rise to weak bands in the PE spectrum at 923 K.[7] However, PE spectroscopy alone does not permit a definitive identification of transients in such a complex system.

We now wish to report direct evidence for the formation of methoxyvinyl- and methylthiovinyl-(carboxy)ketenes (**16a** and **10**) upon FVT of the appropriate Meldrum's acid derivatives (**7** and **13**) as well as the absence of rearrangement of alkoxymethyleneketenes (**15**) to vinylketenes **18**.

Results and discussion

FVT of 2,2-dimethyl-5-[1-(methylthio)ethylidene]-1,3-dioxane-4,6-dione (7)

The Meldrum's acid derivative **7** was synthesized according to the literature[9] and subjected to FVT at temperatures from 350 to 640 °C with Ar matrix isolation of the products at 12 K. At 380 °C, although the starting material remained mostly undecomposed, two bands were observed in the ketene region at 2139 and 2121 cm^{-1} [Fig. 1(*a*)]. These bands are assigned to the carboxyketene **10** and methyleneketene **9** respectively (Scheme 2) as described below.

At 460 °C, most of **7** had disappeared, and the ratio between the ketene peaks was roughly 1 : 1 [Fig. 1(*b*)]. Absorptions due to acetone were also observed at 1721 and 1364 cm^{-1} in the IR spectrum. From 460 to 510 °C, the ketene absorption at 2139 cm^{-1} (**10**) decreased while the band at 2121 cm^{-1} (**9**) first increased, then decreased [Fig. 1(*c*)–(*e*)]. The bands due to CO_2 and acetone increased concomitantly with those of **9**. The absorptions due to the starting material (**7**) disappeared completely above 500 °C. Above 600 °C, the band at 2139 cm^{-1} vanished, the CO_2 absorptions became the most intense, and a new band started to appear in the carbonyl region at 1708 cm^{-1} [Fig. 1(*d*)]. This new peak is due to the formation of the thiophenone derivative **11** as verified by isolation and independent deposition (*vide infra*).

Similar FVT carried out with trapping of the intermediates as a neat film (77 K) was also investigated. The results confirmed the earlier ones. Indeed, at 400 °C, two bands at 2126 and 2093 cm^{-1} assigned to **10** (major) and **9**, respectively, were observed. At higher temperatures, the absorption at 2126 cm^{-1}

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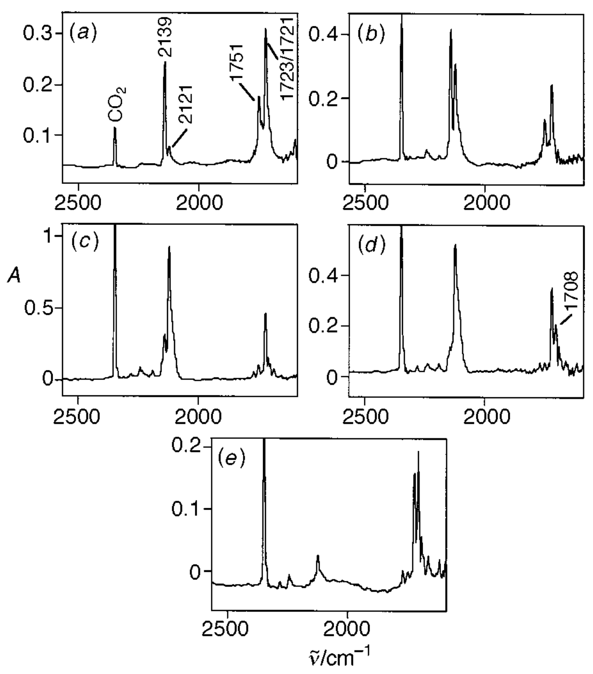
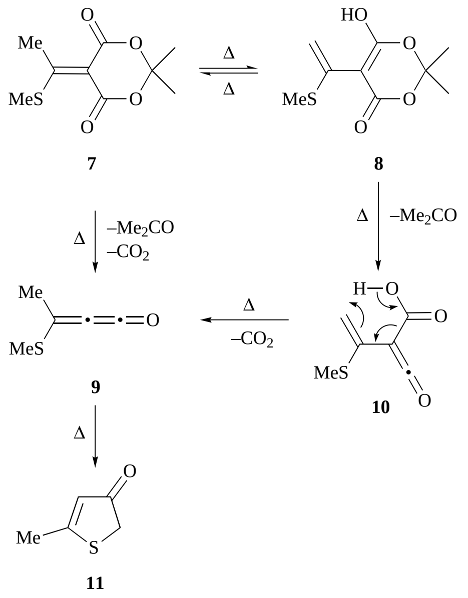


Fig. 1 Partial FTIR spectra (Ar, 12 K) of the results of FVT of **7** at (*a*) 380, (*b*) 460, (*c*) 510, (*d*) 550 and (*e*) 640 °C. Peak assignments: 2139 and 1751 cm^{-1}, **10**; 2121 cm^{-1}, **9**; 1723 cm^{-1}, **7**; 1708 cm^{-1}, **11**; 1721 cm^{-1}, acetone.



Scheme 2

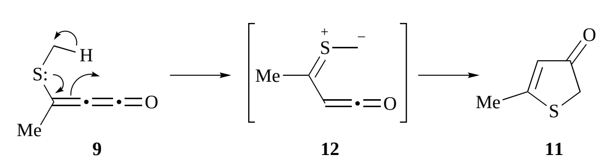
decreased whereas the one at 2093 grew. Above 500 °C a new band at 1686 cm^{-1} due to **11** was observed. The shift to lower wavenumbers in the neat spectra compared with the Ar matrix values is a common observation.

The assignment of the different ketenes is based on the critical analysis of the Ar matrix isolation spectra. The CO_2 absorption at 2340 cm^{-1} is so weak in Fig. 1(*a*) that the band at 2139 cm^{-1} must be due to a species that has not yet eliminated CO_2. Indeed, the CO_2 produced from the thermal decomposition of Meldrum's acid derivatives usually absorbs strongly in the IR spectrum (*cf.* the methoxy and ethoxy cases below). Thus, the ketene band at 2139 cm^{-1} must belong to the carboxyketene **10**. Furthermore, other bands at 3554, 3504 and 1751 cm^{-1} are associated with the one at 2139 cm^{-1} (and on FVT above 460 °C they all disappeared at the same rate). These peaks are characteristic of carboxylic acid monomers[10] [ν(OH) and ν(C=O), respectively]. At higher FVT temperatures, the band at 2121 cm^{-1} increased in intensity, together with those of CO_2 and acetone. This is easily understood in terms of formation of the methyleneketene **9**, obtained by the loss of CO_2 and acetone from **7**. Furthermore, the 2093 cm^{-1} value observed for **9** when isolated neat at 77 K is characteristic of methyleneketenes.[2,6,11]

The thiophenone **11** was isolated in 80% yield and fully characterised following preparative thermolysis of **7** at 600 °C and purification by column chromatography. This material was previously isolated from the FVT of **7** by Chuche[6] and by McNab and co-workers[12] (75% yield). The neat FTIR spectrum (77 K) of the characterised thiophenone **11** was compared directly with the one resulting from thermolysis of **7** at 600 °C. Identical spectra were observed, thus allowing the assignment of the 1686 cm^{-1} band (neat, 77 K; 1708 cm^{-1} in Ar matrix) to **11**.

The formation of carboxyketene **10** can be understood in terms of electrocyclic loss of acetone from the enol tautomer **8** of **7** (Scheme 2). The alternative fragmentation of **7** itself leads to methyleneketene **9**, acetone and CO_2. Another likely route to **9** involves a retro-ene type decarboxylation of **10**, also *via* a cyclic six-electron transition state (Scheme 2).[1,2]

The formation of the thiophenone **11** has been described by Chuche[6] and McNab and co-workers[12] in terms of a sulfur-ylide type intermediate **12** (Scheme 3). Although no direct evidence for such an intermediate has been adduced, **9** seems to be a reasonable precursor to thiophenone **11**: the signals due to thiophenone **11** kept increasing in intensity above 600 °C, whereas both **7** and **10** had already disappeared at *ca.* 500 °C. Thus **9** appears to be the only species remaining that can cyclise to **11**.



Scheme 3

FVT of alkoxy derivatives (13a, b)

The FVT/Ar matrix isolation of the methoxy analogue **13a** (Scheme 4) was studied from 300 to 900 °C using FTIR spectroscopy. At 350 °C, most of **13a** remained unchanged, and the IR spectrum showed two peaks in the ketene region at 2153 and 2150 cm^{-1} due to the carboxyketene **16a** [Fig. 2(*a*)]. The same rate of decrease (when the temperature increased) for the bands at 2153 and 2150 cm^{-1} indicates that these bands belong to the same species (two conformers or sites). A third band at 2130 cm^{-1} is assigned to the methyleneketene **15a** (which always appears at a lower wavenumber, *vide supra*). At higher temperatures, the intensities of the bands ascribed to the carboxyketene **16a** decreased unlike the band at 2130 cm^{-1} [Fig. 2(*b*)]. At a FVT temperature of 500 °C the methyleneketene is the only species observed, **16a** and **13a** having completely disappeared [Figs. 2(*b*), 3].[13] Similar experiments with neat isolation of the intermediates at 77 K gave bands at 2140 and 2106 cm^{-1} due to **16a** and **15a**, respectively.

As in the previous case, the assignment to the different intermediates is based on the analysis of the matrix isolation spectra. The band at 2153 and 2150 cm^{-1} is due to the only species (carboxyketene **16a**) which does not involve CO_2 formation while the band at 2130 cm^{-1} corresponds to the methyleneketene **15a** for which CO_2 is eliminated during the thermal process. While it was quite clear in the case of the methylthio derivative **10**, it is less obvious here because the formation of **15a** commences at 350 °C [Fig. 2(*a*)]. Nevertheless, bands at 3577, 3498 and 1769 cm^{-1} typical of the carboxylic acid moiety disappeared at the same rate as those at 2153 and 2150 cm^{-1} when the temperature increased, thus supporting the assignment of these bands to carboxyketene.

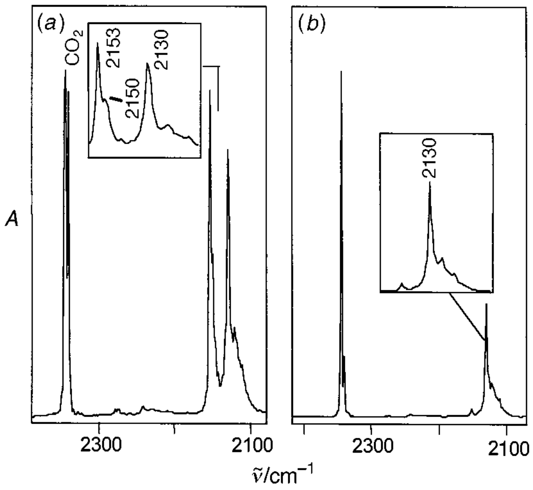
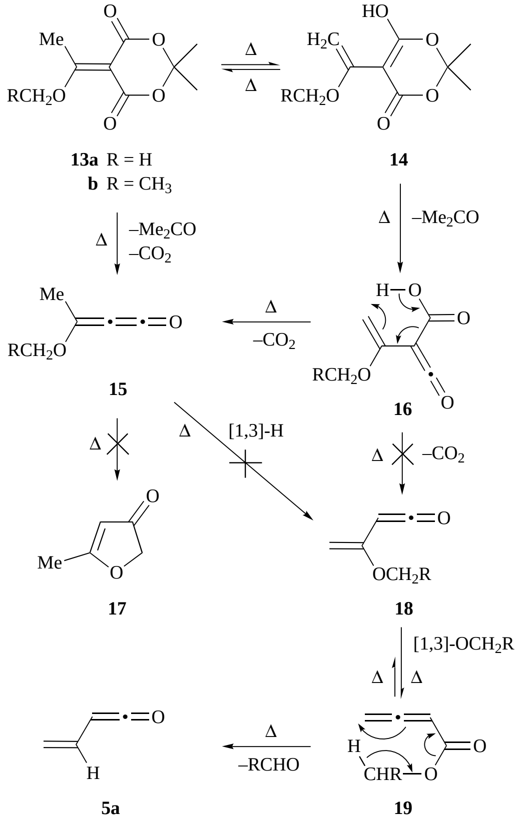


Fig. 2 Partial FTIR spectra (Ar, 12 K) of the results of FVT of **13** at (*a*) 350 and (*b*) 460 °C. Peak assignments: 2153, 2150 cm^{-1}, **16a**; 2130 cm^{-1}, **15a**. The spectra shown in (*a*) and (*b*) are on different absorbance scales; spectrum (*b*) is strongly attenuated in order to show the highly increased CO_2 peak.



Scheme 4

Table 1 Calculated and experimental IR data for methoxy(methyl)-methyleneketene **15a**

Calculated[a]		Experimental[b]	
ν/cm^{-1}	Int[c]/km mol^{-1}	ν/cm^{-1}	Int[d]
925	16	942	w
1021	7		
1050	46	1060	m
1134	22	1148	w
1136	1		
1202	52	1241	w
1261	476	1270	s
1372	21	1372	w
1436	17	1433	w
1444	5		
1448	4		
1450	9	1442	w
1461	25	1457	w
1492	147	1689	s
2154	1462	2130	vs
2938	8		
2951	26	2953	w
2991	8		
3023	18	2996	w
3055	19	3042	w
3057	8		

[a] B3LYP/6-31*, scaled by 0.9613.[14] [b] **15a** generated by FVT of **13a** at 510 °C with matrix isolation in Ar at 12 K. [c] Intensity. [d] Relative intensity: w = weak, s = strong, vs = very strong.

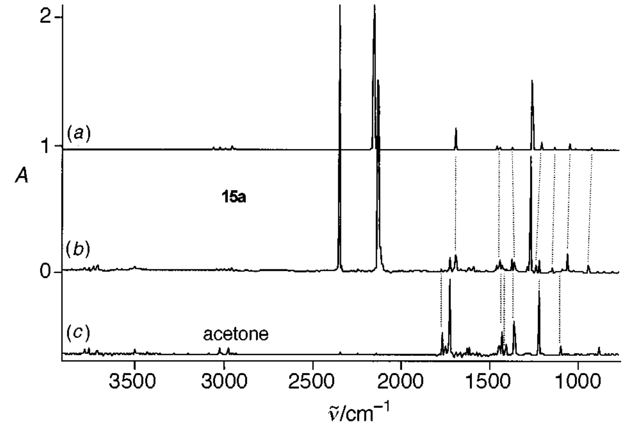
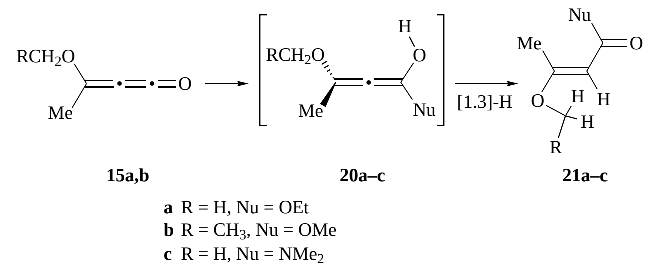


Fig. 3 IR spectra of **15a**. (*a*) Calculated IR spectrum of **15a** at the B3LYP/6-31G* level, (*b*) Ar matrix IR spectrum (12 K) obtained after FVT of **13a** at 510 °C, (*c*) Ar matrix spectrum of acetone at 12 K.



Scheme 5

Further proof for the identity of **15a** is given by its calculated IR spectrum (B3LYP/6-31G*)[14] which is compared with the experimental one in Fig. 3 and Table 1. An excellent agreement is observed, demonstrating that the sample contained only **15a** and acetone. Additional evidence was obtained by trapping of **15a** with ethanol or dimethylamine in preparative experiments. In both cases, only one major compound was isolable by chromatography. NMR analysis demonstrated the formation of ethyl (*E*)-3-methoxybut-2-enoate (**21a**) with ethanol or *N*,*N*-dimethyl-(*E*)-3-methoxybut-2-enamide (**21c**) with dimethylamine (Scheme 5). The NMR data for **21a** are in excellent agreement with those reported in the literature.[15] For **21c** the NMR spectrum is also in good agreement with data for known ester analogues.[15] To confirm the stereochemistry of the trapping products, NOE experiments were carried out on **21c**. As expected, the results indicated a spatial interaction between the OCH_3 group and the vinyl hydrogen.

The presence of **21a** and **21c** can be understood in terms of formation of the allene-1,1-diol derivatives **20a** or **20c** (nucleophilic addition to ketenes often involves enol formation[16]) (Scheme 5). The latter undergoes a [1,3]-H shift (inter- or intra-molecular) toward the central carbon atom of the allene to give **21a** or **21c**. The stereospecificity of the reaction would be due to a greater thermodynamic stability of the *E* isomer compared to the *Z* one. Indeed, since the methyl and

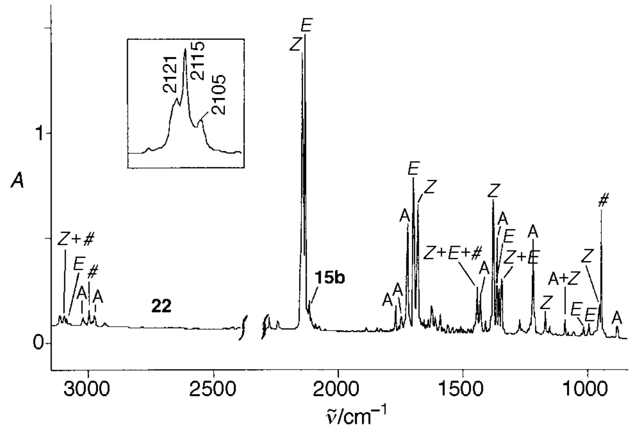


Fig. 4 FTIR spectrum (Ar, 12 K) of *s-cis-* and *s-trans*-acetylketenes (**22**) obtained by FVT of **13b** at 750 °C. *Z*: *s-cis*-**22**; *E*: *s-trans*-**22**; A: acetone; #: ethane. Inset: Partial FTIR spectrum (Ar, 12 K) of the results of FVT of **13b** at 250 °C. The bands at 2121, 2115 and 2105 cm^{-1} are due to ethoxy(methyl)methyleneketene **15b**.

methoxy groups are perpendicular to the hydroxy moiety in the allenes **20a** and **20c**, either *E* or *Z* isomers could be obtained. As the *E* isomers have a lower enthalpy of formation, they are preferentially formed.

It has been postulated in the photoelectron spectroscopy work[7] that in addition to **15a** and **16a**, another species, the methoxyvinylketene (**18a**, Scheme 4), was also formed.[6] Our results demonstrate that such a compound is actually not formed. In fact, in a previous paper[17a] we have independently generated and characterised (1-methoxyvinyl)ketene **18a** by Ar matrix isolation. The characteristic bands are at 2142/2138 and 2134 cm^{-1}. None of these bands were observed on FVT/matrix isolation of **13a**. Furthermore, we have proven that **18a** rearranges to methyl buta-2,3-dienoate (**19a**) *via* a [1,3]-MeO shift, above 650 °C[17] (Scheme 4). No trace of such an allene was detected using **13a** as the starting material. Finally, no bands belonging to the unsubstituted vinylketene (**5a**) and formaldehyde, resulting from the retro-ene reaction[17a,18] of **19a** taking place at temperatures above 800 °C (Scheme 4), were observed.

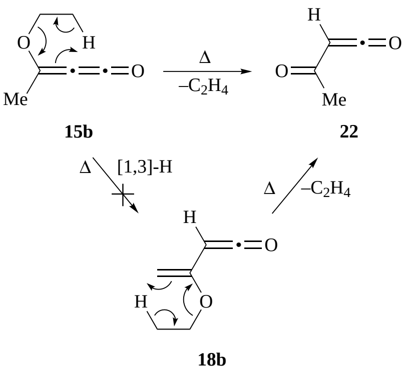
The formation of the carboxyketene **16a** is again explained in terms of fragmentation of the enol form **14a** of the Meldrum's acid **13a** (Scheme 4).

Further FVT/matrix isolation was carried out on the ethyl derivative **13b** between 200 and 750 °C. At 250 °C, three bands were observed in the ketene region at 2121, 2115 and 2105 cm^{-1} (inset in Fig. 4). They are all assigned to conformers and/or sites of ethoxy(methyl)methyleneketene **15b**. From 250 to 600 °C, these peaks increased in intensity together with the CO_2 absorption. Above 600 °C, two new peaks in the ketene region at 2143 and 2133 cm^{-1} grew in intensity concomitantly with the disappearance of the ethoxy(methyl)methyleneketene bands. They are due to *s-trans-* and *s-cis*-acetylketenes (**22**) respectively[19] (Scheme 6). The characteristic ethylene absorption at 948 cm^{-1} was also observed, increasing together with those of **22** and CO_2. The starting material had completely vanished at 700 °C. The different assignments are now discussed. Since the ratio between the three peaks at 2121, 2115 and 2105 cm^{-1} remained unchanged at different FVT temperatures, all of them belong to the same species. Furthermore, when the temperature was raised, these three absorptions as well as the CO_2 and acetone peaks became more intense. This shows that all the peaks in the ketene region are generated through a process involving CO_2 and acetone formation and therefore are due to ethoxy(methyl)methyleneketene (**15b**). Direct evidence is given by the calculated B3LYP/6-31G* IR spectrum, which is compared with the experimental one in Table 2. A good agreement is observed. Chemical proof for **15b** by trapping with methanol has been investigated previously.[17a] By analogy with the methoxy case discussed above, the trapping product obtained was identified as the methyl (*E*)-3-ethoxybut-2-enoate (**21b**)[17a] (*cf.* Scheme 5). The absence of the carboxyketene **16b** in the matrix IR spectra of the thermolysates of **13b** (whereas it was observed in the methoxy and methylthio derivatives) remains unexplained but is indicative of the fine balance of rate constants required for observation of all the intermediates.

Table 2 Calculated and experimental IR data for ethoxy(methyl)methyleneketene **15b**

Calculated[a]		Experimental[b]	
ν/cm^{-1}	Int[c]/km mol^{-1}	ν/cm^{-1}	Int[d]
785	1		
861	9		
979	6		
1020	6		
1047	94	1056	m
1088	4		
1144	4		
1183	82	1199	m
1252	1		
1260	620	1274	s
1357	0		
1373	28	1374	m
1393	2		
1444	7		
1447	3		
1457	6		
1465	5		
1483	9		
1688	150	1679	s
2152	1522	2121, 2115, 2105	vs
2937	7		
2943	17		
2949	10		
2987	7		
2991	8		
3012	21		
3019	35		
3056	7		

[a] B3LYP/6-31*, scaled by 0.9613.[14] [b] **15b** generated by FVT of **13b** at 350 °C with matrix isolation in Ar at 12 K. [c] Intensity. [d] Relative intensity (see Table 1).

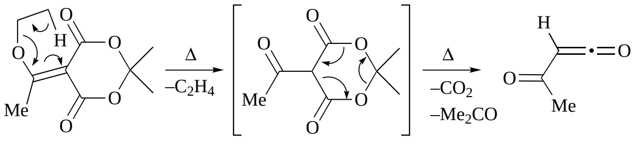


Scheme 6

Evidence for the *s-cis-* and *s-trans*-acetylketenes (**22**) was obtained by comparison of the Ar matrix IR values (from the thermolysis of **13b** at 750 °C; Fig. 4) with the ones obtained using different precursors.[20] Our data are in excellent agreement with previous measurements from this laboratory.[20]

The formation of these ketenes (**22**) is explained by the decomposition of the ethoxymethyleneketene (**15b**) (Scheme 6). The FVT/matrix IR spectra show that bands assigned to **22** and ethene increase concomitantly with the decrease of **15b**. Thus, acetylketene is formed in a retro-ene type pericyclic reaction of **15b** (Scheme 6). We have recently observed facile retro-ene reactions in other extended cumulenes (iminopropadienones, R–N=C=C=C=O).[21]

Another, less probable, route would be the thermolysis of the acetyl-Meldrum's acid derivative **23**, formed in a retro-ene type decomposition of **13b** (Scheme 7). No trace of **23** was observed.



13b **23** **22**

Scheme 7

23 is an isolable compound, whose FVT to **22** we have investigated in other work.[20b]

As in the methoxy case, the ethoxy(vinyl)ketene **18b** was not formed (Scheme 4). Indeed, *s-cis*- and *s-trans*-ethoxy(vinyl)ketene are known to absorb strongly at 2140 and 2136 cm^{-1}, respectively.[17] Although acetylketene **22** can be formed from **18b** (Scheme 6), this pathway cannot be operative here because at this temperature (600 °C) **18b** should still be observed. Furthermore the peaks assigned to the ethyl allenecarboxylate **19b** resulting from a [1,3]-OEt shift[17] in **18b** (Scheme 4) were also absent. Finally, no trace of the unsubstituted vinylketene (**5a**) which would have formed in a retro-ene reaction[18] of **14** was observed at higher temperatures.

Conclusions

Carboxy(vinyl)ketenes **10** and **16a** are detectable intermediates in the FVT reactions of the alkylthio- and methoxy-substituted-Meldrum's acid derivatives **7** and **13a**. They are more transient than the corresponding carboxy(alkylvinyl)-ketenes of type **4** reported previously,[1–3] easily decarboxylating to methylthio- and alkoxy-methyleneketenes **9** and **15**. The carboxy(ethoxyvinyl)ketene **16b** was not detectable. The corresponding ethoxy(methyl)methyleneketene **15b** undergoes a retro-ene type elimination of ethene to give *s-cis*- and *s-trans*-acetylketene **22**. As previously found,[6,12] the methylthio(methyl)-methyleneketene **9** cyclises to a thiophen-3-one (**11**), but the alkoxy analogues **15** do not undergo any such isomerisation to **17**. Contrary to an earlier report,[7] alkoxy(methyl)methyleneketenes **15** do not isomerise to (1-alkoxyvinyl)ketenes **18**. This is in sharp contrast to the alkylmethyleneketenes **3**, where such isomerisation has been established both by direct observation and by chemical trapping.[1–3]

The reason for this and the mechanisms of transformation of carboxy(vinyl)ketenes and of methyleneketenes to vinylketenes are the subject of theoretical investigations to be reported elsewhere.[22] The direct isomerisation of a methyleneketene (*e.g.* **3**) to a vinylketene (*e.g.* **5**) constitutes a 1,3-H shift and has, therefore, a very high calculated energy barrier.[22] It is quite likely that such isomerisations are in fact not intramolecular 1,3-H shifts, but instead wall-catalysed reactions. There are many examples of sensitive compounds (especially carrying O–H or N–H functions) isomerising extremely readily under FVT conditions to more stable tautomers in reactions formally involving 1,3-H shifts; in reality, these reactions are more likely bimolecular or wall-catalysed.[23] The observation that alkylthiomethyleneketenes such as **9** cyclise to thiophenones **11** (Scheme 3), whereas the oxy analogues **15** do not cyclise to furanones **17**, is in good agreement with *ab initio* calculations of the activation barriers and energies of the zwitterionic intermediates (*e.g.* **12**).[22b]

Experimental

Computational method

Harmonic vibrational frequencies and IR intensities were calculated at the B3LYP/6-31G* level. The B3LYP formulation[14] of density functional theory corresponds to Becke's 3-parameter exchange functional[14a] together with the Lee–Yang–Parr correctional functional.[14b] The directly calculated frequencies were scaled by 0.9613 to account for the average overestimation of vibrational frequencies at this level of theory.[24]

Apparatus

Preparative FVT was carried out in electrically heated quartz tubes, 40 cm long, 2 cm diameter. Samples were 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 PT 150. The pyrolysate was, when necessary, co-condensed with methanol, ethanol or dimethylamine vapour on the 77 K cold finger, whereby the trapping reagents were introduced between the exit of the pyrolysis oven and the cold finger. Further details of the FVT apparatus have been published.[20,25]

Matrix isolation experiments were carried out using a 10 cm long, 0.8 cm diameter quartz tube in an oven directly attached to the vacuum shroud of a Leybold–Heraeus or Air Products liquid He cryostat.[20,25] Ar was used as matrix medium, which was passed over the sample while it was subliming and co-condensed as a matrix at *ca.* 12 K on a BaF_2 window for IR spectroscopy. Neat isolation at 77 K was carried out in a similar apparatus using a liq. N_2 cryostat.[25]

IR spectra were recorded on Perkin-Elmer 1720X or System 2000 instruments. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC200 (*J* values are given in Hz), mass spectra (70 eV; direct insertion) on a Kratos MS25RFA, and GC–MS on a Hewlett Packard 5992B instrument.

Materials

Trimethyl orthoacetate and triethyl orthoacetate (1,1,1-trimethoxy- and 1,1,1-triethoxy-methane, respectively) were obtained from Aldrich.

2,2-Dimethyl-5-[1-(methylthio)ethylidene]-1,3-dioxane-4,6-dione 7. **7** was prepared according to the method of Huang and Chen,[9] mp 117–119 °C; δ_H(200 MHz, $CDCl_3$) 2.88 (s, SCH_3), 2.52 (s, CH_3), 1.71 [6 H, s, 2 × (2-Me)]; ν_{max}/cm^{-1} (neat, −196 °C) 3000w, 1727w, 1700s, 1496m, 1440w, 1436w, 1414m, 1393w, 1381w, 1287s, 1272s, 1240m, 1206m, 1192m, 1107w, 1045w, 1019br, 930w, 811w, 799w; (Ar, 12 K) 1750w, 1738w, 1723s, 1520m, 1506m, 1445w, 1420m, 1392m, 1379w, 1324w, 1287s, 1272s, 1238m, 1217w, 1209m, 1196m, 1107br, 1044m, 1022w, 1012br, 999w, 988w, 966br, 936w, 808w, 799w.

FVT of 7: isolation of 5-methylthiophen-3(2*H*)-one[6,12] 11. 200 mg of **7** ($9.2.10^{-4}$ mol) was sublimed at 95 °C (3×10^{-5} mbar) and thermolysed at 600 °C to give **11** (84 mg, 80%); δ_H(200 MHz, $CDCl_3$) 6.03 (1 H, q, *J* 1.1, 4-CH), 3.69 (2 H, q, *J* 0.8, 2-CH_2), 2.38 (3 H, m, 6-CH_3); δ_C(200 MHz, $CDCl_3$) 202.0 (C-3), 180.4 (C-5), 121.7 (C-4), 41.2 (C-2), 19.6 (C-6); ν_{max}/cm^{-1} (neat, KBr) 2968w, 2924w, 2853w, 1686s, 1653s, 1569s, 1432m, 1378m, 1289br, 1196m, 1171w, 1126w, 1025w, 967w, 874w, 780w; *m/z* (EI) 114 (M^+, 100%), 86 (45), 85 (41), 71 (42), 67 (38), 53 (20), 46 (64), 45 (50), 39 (48).

2,2-Dimethyl-5-(1-methoxyethylidene)-1,3-dioxane-4,6-dione 13a. **13a** was prepared from trimethyl orthoacetate and Meldrum's acid using the method of Polansky and co-workers[26] (yield 33%); mp 94–96 °C; δ_H(200 MHz, $CDCl_3$) 4.13 (3 H, s, OCH_3), 2.75 (3 H, s, CH_3), 1.66 [6 H, s, 2 × (2-CH_3)]; ν_{max}/cm^{-1} (neat, −196 °C) 2999w, 2957w, 1923w, 1739w, 1702s, 1545m, 1472br, 1414w, 1393w, 1381w, 1333w, 1292m, 1266m, 1239w, 1207m, 1151m, 1069m, 1039br, 1010w, 991w, 931w, 880w, 799w; (Ar, 12 K) 3011br, 2996w, 2957w, 1767w, 1756w, 1725s, 1593w, 1573m, 1554m, 1540m, 1451br, 1420br, 1392m, 1378m, 1329m, 1286s, 1264m, 1240br, 1209m, 1196m, 1188w, 1158br, 1072m, 1051w, 1031w, 1010w, 996w, 935w, 901w, 886w, 880w, 798w.

Trapping of 15a with ethanol and dimethylamine: formation of ethyl (*E*)-3-methoxybut-2-enoate 21a and *N*,*N*-dimethyl-(*E*)-3-methoxybut-2-enamide 21c. 200 mg of **13a** (10^{-3} mol) was sublimed at 65 °C (5×10^{-5} mbar) and thermolysed through the oven at 650 °C onto a cold finger coated with ethanol or dimethylamine and cooled at -196 °C. Once the reaction was complete and the cold finger warmed up to room temperature, the oily residues were purified by column chromatography (SiO_2, $CHCl_3$) to afford **21a** (115 mg, 80%) or **21b** (86 mg, 60%). The spectroscopic data for **21a** are: δ_H(200 MHz, $CDCl_3$) 5.02 (1 H, s, 2-CH), 4.14 (2 H, q, *J* 7.1, 6-CH_2), 3.63 (3 H, s, 5-OCH_3), 2.29 (3 H, s, 4-CH_3), 1.28 (3 H, t, *J* 7.1 H, 7-CH_3); δ_C(200 MHz, $CDCl_3$) 172.9 (C-3), 167.8 (C-1), 90.7 (C-2), 59.2 (C-6), 55.2 (C-5), 18.7 (C-4), 14.3 (C-7); ν_{max}/cm^{-1} (neat, KBr) 2980m, 1713s, 1627s, 1441m, 1398m, 1278m, 1141s, 1054m, 821m; *m*/*z* (GC–MS) 144 (M^+, 17%), 115 (5), 113 (5), 99 (100), 87 (5), 72 (27), 59 (33), 55 (5), 43 (28), 39 (31). The ^1H and ^{13}C NMR data are in good agreement with those described in the literature.[15]

The spectroscopic data for **21c** are: δ_H(200 MHz, $CDCl_3$) 5.18 (1 H, s, 2-CH), 3.61 (3 H, s, 5-OCH_3), 3.01 [6 H, br s, 2 × (6-NCH_3)], 2.20 (3 H, s, 4-CH_3); δ_C(200 MHz, $CDCl_3$) 168.3 (C-1 or C-3), 168.1 (C-3 or C-1), 91.1 (C-2), 54.7 (C-5), 37.7 (C-6), 35.2 (C-6), 18.5 (C-4); ν_{max}/cm^{-1} (neat, KBr) 2900m, 1650s, 1600s, 1250s, 1095s, 880m; *m*/*z* (EI) 143 (M^+, 21%), 123 (3), 112 (3), 99 (100), 85 (5), 77 (5), 69 (8), 59 (11), 55 (9), 43 (26), 41 (12).

2,2-Dimethyl-5-(1-ethoxyethylidene)-1,3-dioxane-4,6-dione 13b. The synthesis of **13b** was described previously;[17a] mp 86–88 °C ν_{max}/cm^{-1} (neat, -196 °C) 2996w, 2945w, 1735w, 1701s, 1540m, 1420m, 1381m, 1332w, 1293m, 1266m, 1238m, 1206m, 1150m, 1116w, 1062m, 1037w, 1013w, 969w, 929w, 896w, 799w; (Ar, 12 K) 3012br, 1769w, 1763w, 1730s, 1573m, 1537br, 1473w, 1423w, 1391w, 1380m, 1377m, 1362w, 1329m, 1290s, 1282m, 1262m, 1240br, 1217m, 1209m, 1159m, 1123w, 1096w, 1065s, 1045w, 1030w, 1012w, 998w, 971m, 929w, 860w, 797w.

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