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Carboxyketenes from 4-Hydroxy-1,3-oxazin-6-ones and Meldrum's Acid Derivatives

Lisa George,[†] Rakesh Naduvile Veedu,[†] Hassan Sheibani,[†,‡] Avat Arman Taherpour,[†,‡] Robert Flammang,[§] and Curt Wentrup*[,†]

Chemistry Building, School of Molecular and Microbial Sciences, The University of Queensland, Brisbane, Qld 4072, Australia, and Laboratoire de Chimie Organique, Université de Mons-Hainaut, B-7000 Mons, Belgium

wentrup@uq.edu.au

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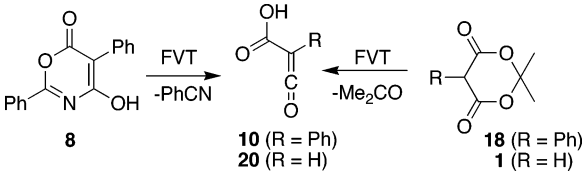

New 4-hydroxy-1,3-oxazin-6-ones **8** and **16** were prepared from chlorocarbonyl(phenyl)ketene and amides. The flash vacuum thermolysis (FVT) reactions of these compounds and the 4-methoxy derivative **17** were investigated by Ar matrix isolation IR spectroscopy and online mass spectrometry including MS/MS analysis. Carboxy(phenyl)ketene **10** is formed as the major product by thermal fragmentation of 4-hydroxy-1,3-oxazin-6-one **8**. This takes place via the unstable 6-hydroxy tautomer **9**. Another tautomer, the 5*H*-isomer **12**, leads to the formation of benzoyl isocyanate **13** as a minor product together with phenylketene **14**. Carboxy(phenyl)ketene **10** remains detectable at high FVT temperatures but undergoes thermal decarboxylation to phenylketene **14**. The same carboxy(phenyl)ketene **10** is also produced in significant amounts by FVT of 5-phenyl-Meldrum's acid **18** via the unstable enol tautomer **19**. A small amount of the unsubstituted carboxyketene **20** is observable on FVT of Meldrum's acid **1** itself.

Introduction

Derivatives of Meldrum's acid (1,3-dioxane-4,6-dione) **1** are excellent precursors for the production of a variety of ketenes, propadienones, iminopropadienones, and other reactive molecules by flash vacuum thermolysis (FVT).[1] Tautomerizable 5-alkylidene derivatives **2** can react via the enol tautomers **3**, which in a 6-electron cycloreversion reaction of the retro-Diels–Alder-type fragment to the little known carboxyketenes (ketene carboxylic acids) **4**.[2,3] Fragmentation of the keto forms **2** leads to methyleneketenes **5**, and decarboxylation of the carboxyketenes **4** can lead to either methyleneketenes **5** or vinylketenes **6**. In some cases, the carboxyketenes have been shown to cyclize to isolable and lower-energy 3-methyleneoxetane-2,4-dione **7** prior to fragmentation to **5** (Scheme 1).[4]

Although the FVT reactions of Meldrum's acids have been examined by several groups for over 30 years, it has not been realized that carboxyketenes are formed as observable intermediates from simple derivatives such as Meldrum's acid **1** itself and its 5-phenyl derivative. We now report that this is the case. Moreover, we have discovered a new route to carboxyketenes from the title compounds, 4-hydroxy-1,3-oxazin-6-ones.

Results and Discussion

1. Oxazinones. 4-Hydroxy-1,3-oxazin-6-ones were prepared by reaction between chlorocarbonylketenes and amides. FVT

[†] University of Queensland.

[‡] H.S. was a visiting scholar from the Chemistry Department, Shahid Bahonar University of Kerman (2004–2005), and A.A.T. is a visiting scholar from the Chemistry Department, Graduate Faculty, Azad University, Arak, Iran (2006–2007).

[§] Université de Mons-Hainaut.

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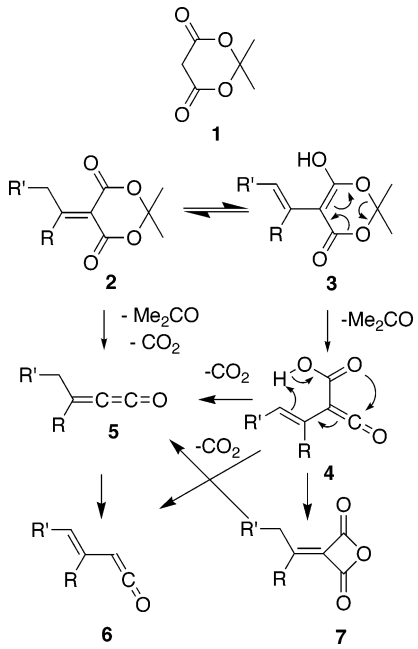
SCHEME 1



of 4-hydroxy-2,5-diphenyl-1,3-oxazin-6-one **8** at 830 °C with isolation of the products in an Ar matrix at 20 K resulted in phenylketene **14** as the major product, together with benzoyl isocyanate **13**, benzonitrile **11**, and CO_2, absorbing at 2121, 2244, 2236, and 2345 cm^{-1}, respectively, in the Ar matrix IR spectra. Phenylketene was identified by comparison with known spectroscopic data.[5] Furthermore, it was trapped with methanol in a preparative FVT experiment, and the resulting methyl phenylacetate was identified by GC-MS. The formation of benzoyl isocyanate was confirmed by GC-MS and by hydrolysis to benzamide. Furthermore, both phenylketene (*m*/*z* 118) and benzoyl isocyanate (*m*/*z* 147) were rigorously identified by the collisional activation mass spectra (CAMS) by using online FVT mass spectrometry (FVT−MS). CAMS data are shown in the Supporting Information. However, the abundance of phenylketene was always far greater than that of benzoyl isocyanate, even though the calculated vibrational extinction coefficient of the isocyanate is larger than that of the ketene. This demonstrates that the isocyanate and the ketene cannot be formed in just one fragmentation reaction of **8**. B3LYP/6-31G* calculated vibrational data: phenylketene, 2128 cm^{-1} (941 km/mol); benzoyl isocyanate, 2251 cm^{-1} (1489 km/mol).

Detailed monitoring of the FVT products as a function of temperature, using both matrix isolation IR spectroscopy and online FVT−MS revealed the formation of carboxy(phenyl)-ketene **10** and benzonitrile **11** as the first thermolysis products. Carboxy(phenyl)ketene is characterized by its mass spectrum (*m*/*z* = 162), which appears together with benzonitrile (*m*/*z* 103), both rising rapidly at 350−450 °C (Figure 1). In the IR spectrum, the carboxyketene features an OH band at 3576 cm^{-1} (coincident with the OH band of the starting material **8** but still present when **8** has been consumed by FVT), a strong ketene band at 2136 cm^{-1} in good agreement with the calculated spectrum derived from B3LYP/6-31G* calculations, and a C═O band at 1755 cm^{-1} (Figure 2). At a FVT temperature of 300 °C, only unchanged **8** was present. At 400−600 °C, the carboxyketene **10** (3575, 2136, and 1755 cm^{-1}) was the major product, but increasing amounts of phenylketene **14** (2121 cm^{-1}) were formed by decarboxylation as the temperature increased. At 700 °C, the peaks due to carboxy(phenyl)ketene and phenylketene were of equal intensity, and at higher temperatures, phenylketene became the major product. IR spectra obtained by FVT at different temperatures are shown in the Supporting Information.

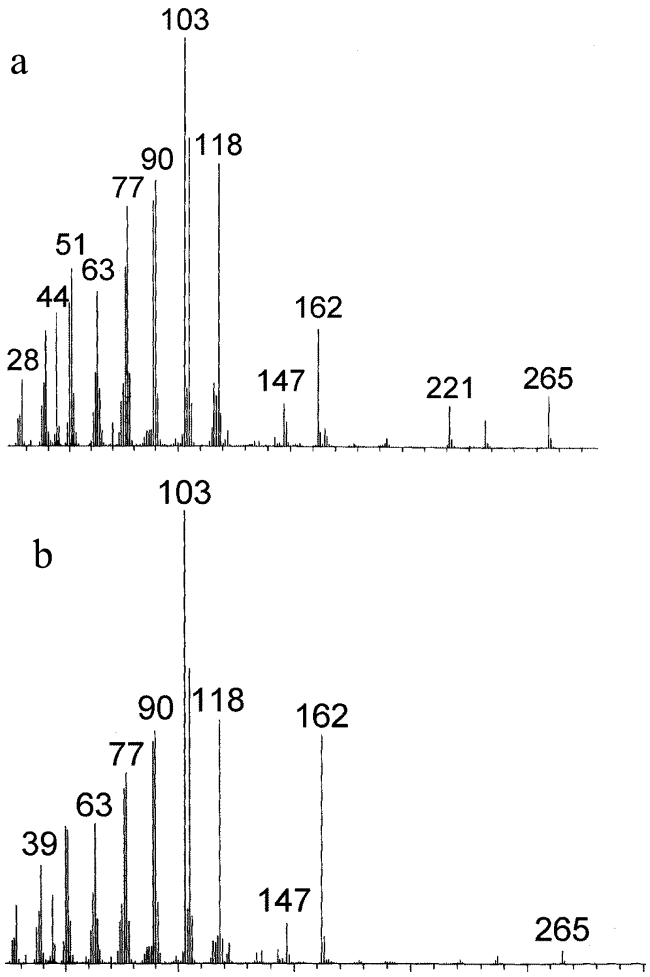


FIGURE 1. FVT of the oxazinone **8**. 70 eV EI mass spectra obtained at (a) 350 °C and (b) 450 °C oven temperatures.

We have calculated the IR spectra of several carboxy(vinyl)-ketenes and vinylketenes observed previously[2] and found that the C═C═O stretching frequencies are generally higher for the carboxyketenes (see the Supporting Information).

The results are explained in terms of Scheme 2. Oxazinone **8** exists in the hydroxy-lactone form shown in the solid state and in solution at ordinary temperatures, but there are two other energetically accessible tautomers, **9** and **12**, ca. 15 and 5 kcal/mol above **8**, respectively, according to B3LYP/6-31G* calculations. The transition structures for formation of **12** by means of a 1,3-H shift in **8** lies at ca. 58 kcal/mol above **8**, but it is likely that the reactions forming both **9** and **12** are in fact intermolecular H transfers taking place in the solid state during sublimation or on the quartz surface. There are many examples of the existence of enols in the gas phase,[6] and equilibrium constants for enolization of carboxylic acid derivatives have been evaluated.[7] The two tautomers **9** and **12** can undergo retro-

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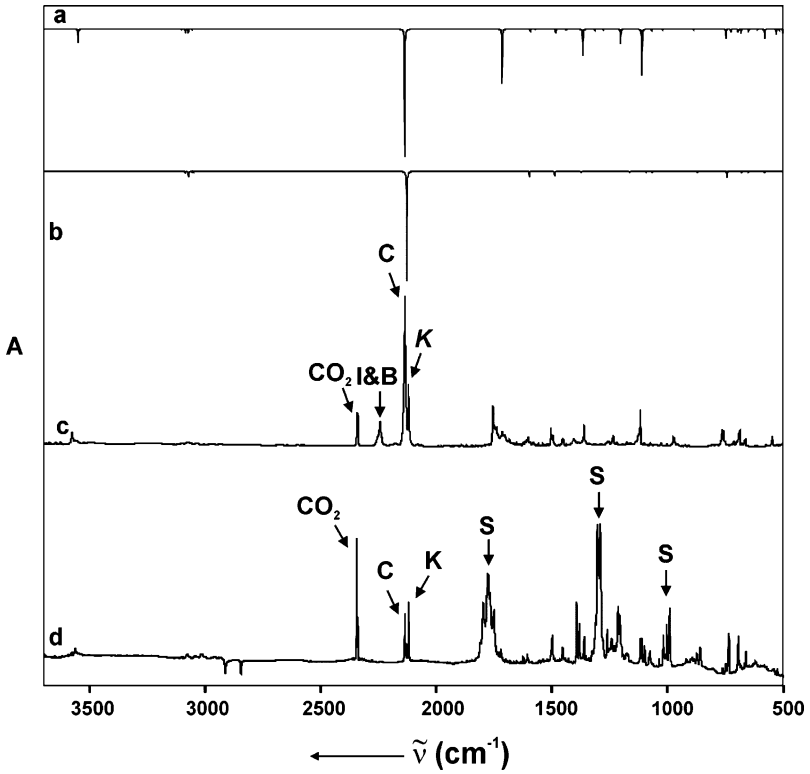
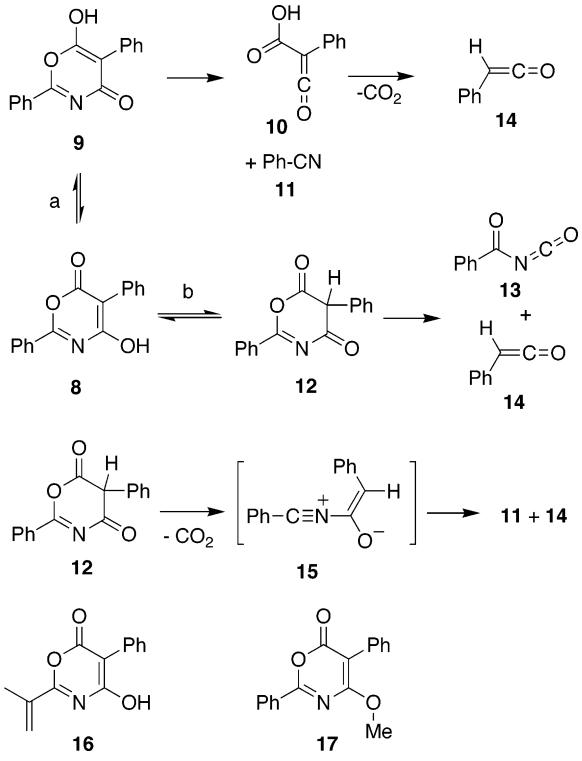


FIGURE 2. (a) Calculated IR spectrum of carboxy(phenyl)ketene **10**. (b) Calculated IR spectrum of phenylketene **14** (B3LYP/6-31G*; frequencies scaled by 0.9613). (c) IR spectrum of the product of FVT of oxazinone **8** at 600 °C (Ar matrix, 15 K). (d) IR spectrum of the product of FVT of phenyl-Meldrum's acid **18** at 400 °C (Ar matrix, 15 K). C: carboxy(phenyl)ketene **10**. K: phenylketene **14**. I: benzoyl isocyanate **13**. B: benzonitrile **11**. S: starting material **8**.

SCHEME 2



Diels−Alder-type fragmentations to carboxyketene **10** plus benzonitrile **11** (path a) and to benzoyl isocyanate **13** and phenylketene **14** (path b), respectively. The calculated barriers for these two fragmentations are 44 and 31 kcal/mol, respectively. Both pathways, a and b, are endothermic (by 27 and 20 kcal/mol, respectively). It is not uncommon to see FVT reactions proceeding via thermally populated, unstable tautomers.[8]

The carboxy(phenyl)ketene **10** evidently decarboxylates at elevated temperatures to yield CO_2 and phenylketene **14**, which become by far the major products above 800 °C. The formation of phenylketene by path b is a minor process. The majority of the phenylketene is formed by path a via decarboxylation of **10**. The preferred mechanism of decarboxylation of **10** to **14** is as described in Scheme 1 (**4** to **6**; R′CH═CR = Ph). In carboxy(vinyl)ketenes, the route from **4** to **7** to **5** is preferred, but the presence of the phenyl group in **10** makes this cyclization route unfavorable here. It is noteworthy that the carboxyketene **10** remains observable on FVT above 700 °C. When the FVT products of **8** are condensed at 50 K without Ar, subsequent warmup of the solid matrix causes an initial isocyanate/nitrile band at 2244 to split into two at 2241 and 2239 cm^{-1} due to **13** and **11**, respectively. The band due to carboxy(phenyl)ketene **10** remains at first constant, but its intensity is reduced at 170 K. At 190 K, the intensity of **10** is drastically reduced, and at 200 K, it has all but disappeared. At this temperature, the bands due to phenylketene **14** also disappeared, but those of **11** and **13** still remained. No new bands were discernible. Calculations indicate that the dimerization of **10** by addition of the OH function of one molecule to the C═C═O function of another

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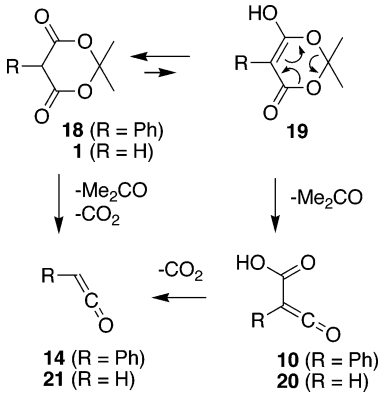
SCHEME 3



is exothermic by 14−20 kcal/mol; hence, polymerization of **10** is a very likely process. We have not prepared derivatives of **10** by addition of nucleophiles to the C═C═O function in this work, but we have shown previously that esters of carboxyketenes are readily isolable from their reactions with alcohols.[2]

One more thermolysis product with a mass of 221 Da was seen in the FVT−MS at the very low FVT temperatures of 350−375 °C only (see Figure 1a). It corresponds to loss of CO_2 from **8**, which would suggest the formation of the zwitterionic structure **15** (Scheme 2) or a cyclization product thereof. It was not formed in sufficient quantity to be characterized in the IR spectra. The calculated activation barrier for formation of **15** from **12** is 41.6 kcal/mol, and the reaction is endothermic by 15 kcal/mol. Zwitterion **15** is calculated to fragment again to benzonitrile and phenylketene with a barrier of 46 kcal/mol (B3LYP/6-31G* SCRF calculations are necessary for charged species). However, the CAMS of *m*/*z* 221 features a strong signal at *m*/*z* 165, normally associated with the 9-fluorenyl cation. This obviously requires a deep-seated rearrangement, and the structure of the *m*/*z* 221 species remains unknown.

The behavior of the 2-isopropenyloxazinone **16** on FVT was similar to that of **8** as studied by Ar matrix IR spectroscopy, giving rise to new signals at 2345 (CO_2), 2259, 2138, and 2121 cm^{-1} (phenylketene), and it is assumed, therefore, that its fragmentation reactions are analogous to those of **8**. The 6-methoxy derivative **17** was prepared by methylation of **8** with diazomethane. Because **17** cannot undergo any tautomerization reactions of the types described in Scheme 2 (paths a and b), no ketenes were formed on FVT at 300−900 °C. An X-ray crystal structure of **17** is available.[9]

2. 5-Phenyl-Meldrum's Acid 18. The identification of carboxy(phenyl)ketene as described above prompted us to investigate the possibility of forming the same compound by FVT of 5-phenyl-Meldrum's acid **18** (Scheme 3). Indeed, FVT of **18** at 360 °C resulted in the now familiar peaks at 3576 and 2136 cm^{-1} (**10**) and 2121 cm^{-1} (**14**) (Figure 2d). On increasing the temperature to 400 °C, the relative intensity of phenylketene **14** doubled, and at higher FVT temperatures, phenylketene **14** became by far the major product, with only a trace of **10** being observable at 500 °C (IR spectra resulting from FVT at different temperatures are shown in the Supporting Information).

The same reaction was monitored by FVT−MS. Dissociative ionization of **18** to carboxy(phenyl)ketene **10** is observed at *m*/*z* 162 but only to a very low extent, less than 2% of the base peak due to **14** at *m*/*z* 118. The *m*/*z* 162 ions disappeared completely at elevated temperatures, and after complete consumption of the starting material **18**, phenyl ketene **14** remained as the main product. The CAMS of the *m*/*z* 162 ions (**10**) from **8** and **18** were identical within experimental error (Figure 3). These observations are rationalized in Scheme 3. The enol tautomer **19** was not observed directly, but we have demonstrated the existence of enols of other Meldrum's acid derivatives previously.[2a]

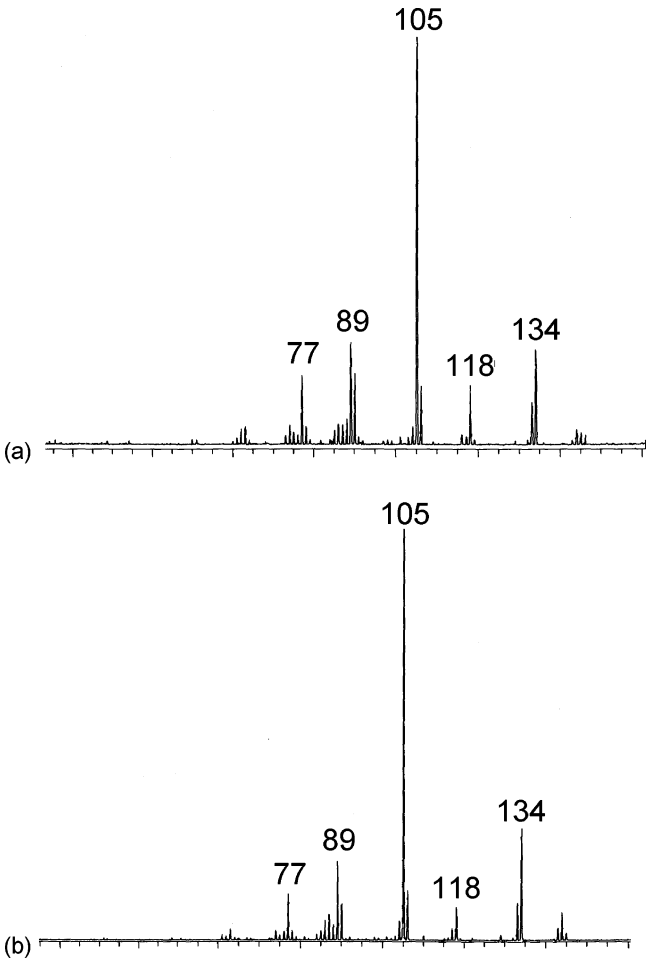


FIGURE 3. Collisional activation mass spectrum (oxygen collision gas, B/E mode) of the *m*/*z* 162 ions (carboxy(phenyl)ketene **10**) from (a) **8** and (b) **18**.

3. Meldrum's Acid 1. To demonstrate the generality of carboxyketene formation, we reinvestigated the FVT reaction of Meldrum's acid **1** itself (Scheme 3). Here too, new absorptions at 3574 and 2156 cm^{-1}, ascribed to the parent carboxyketene **20**, were observed by Ar matrix IR spectroscopy following FVT at 360−500 °C (see Supporting Information). Ketene CH_2═C═O **21** was observed at 2142 cm^{-1} and identified by comparison with the well-established literature spectrum. The 2156 cm^{-1} signal is ascribed to the more stable *s*-*Z* form of carboxyketene **20** based on comparison with the calculated value (B3LYP/6-31G*: *s*-*Z*-**20** 2164 cm^{-1}; *s*-*E*-**20** 2136 cm^{-1}; CH_2═C═O 2153 cm^{-1}).

The 70 eV EIMS of **1** is described in the Supporting Information. FVT of **1** at 350 °C showed peaks due to the thermal production of acetone (*m*/*z* 58) and carbon dioxide (*m*/*z* 44), but most of the sample was still not pyrolyzed. At an oven temperature of 450 °C, most of the sample had been pyrolyzed,

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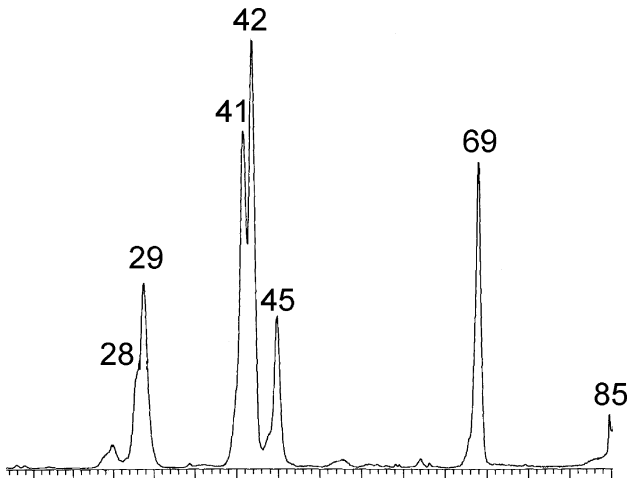

FIGURE 4. CA spectrum of the *m*/*z* 86 ions obtained after FVT of **1** at 450 °C; helium collision gas.

as indicated by the strong intensification of the peaks due to acetone and carbon dioxide and the disappearance of the starting material [*m*/*z* 129 = $M^{+\bullet} - CH_3$]. The base peak at *m*/*z* 43 is due to dissociative ionization of acetone. A careful investigation of the *m*/*z* 85−90 region of the mass spectrum shows the appearance of a new peak at *m*/*z* 86 not present at lower temperatures. This peak is due to the ionization of a compound $C_3H_2O_3$ resulting from the thermal elimination of acetone from **1**.

The structural characterization of this $C_3H_2O_3$ thermolysis product was investigated using the FVT/MS/MS methodology. The CA spectrum using He as the collision gas is shown in Figure 4. CAMS of a beam of mass-selected *m*/*z* 86 ions generates intense fragment peaks at *m*/*z* 69, 45, 42, and 41 readily ascribed to C-protonated[3b,10] carbon suboxide, C_3O_2 (*m*/*z* 69), carbon dioxide (*m*/*z* 45), and ionized ketene (*m*/*z* 42, 41). These fragmentations leave no doubt as to the carboxyketene structure **20** for the $C_3H_2O_3$ thermolysis product.

Thus, we conclude that the thermolysis of Meldrum's acid involves, at least in part, a retro-Diels−Alder-type fragmentation of the enol tautomer **19** to yield carboxyketene **20**. It is probable that the direct fragmentation of **1** to ketene **21** (Scheme 3) is a major route for the parent compound, but stabilization of the enol **19** by conjugation with a phenyl group makes the carboxyketene route more pronounced and easily observable in the case of phenyl-Meldrum's acid **18**.

Conclusion

Carboxy(phenyl)ketene **10** is formed by thermal fragmentation of hydroxyoxazinone **8**. This takes place via the unstable hydroxy tautomer **9**. Another tautomer, **12**, leads to the formation of benzoyl isocyanate **13** and phenylketene **14**. Carboxy(phenyl)ketene **10** undergoes decarboxylation to phenylketene **14** at elevated temperatures.

The same carboxy(phenyl)ketene **10** is also produced together with phenylketene **14** by FVT of 5-phenyl-Meldrum's acid **18**. These two products are thought to arise from fragmentation of the enol and keto tautomers **19** and **18**, respectively. The ratio carboxy(phenyl)ketene/phenylketene (**10**:**14**) is higher for the oxazinone precursor **8** than for the phenyl-Meldrum's acid **18** (see Figure 2), thereby indicating that the latter fragments in part via the keto form **18** and in part via the higher energy enol tautomer **19**.

A small amount of the unsubstituted carboxyketene **20** is observable on FVT of Meldrum's acid **1** itself, but the main product is ketene **21**, thereby indicating that Meldrum's acid fragments predominantly as the keto form **1**, and only to a small extent via the enol tautomer **19**.

Experimental

The internal quartz thermolysis tube for online FVT−MS[11] and the six-sector mass spectrometer[12] used for electron ionization (EI) and collisional activation (CA) MS have been described previously. The apparatus and procedures for preparative FVT[13] and for Ar matrix isolation[14] were as previously described. The internal oven employed a 10 cm long, 0.7 cm i.d., electrically heated quartz tube suspended in a vacuum chamber directly flanged to the cryostat cold head, with a wall-free flight path of ca. 3 cm between the exit of the quartz tube and the cold target (KBr or CsI for IR spectroscopy). The external oven consisted of a 20 cm (0.7 cm i.d.) quartz tube ending in a quartz flange directly flanged to the cryostat cold head; this tube was heated on a 10 cm length and had an ca. 5 cm unheated length connecting it to the cold head. FVT products were isolated in liquid nitrogen (77 K) in the preparative thermolyses and at 7−22 K with Ar for matrix isolation IR experiments. In a typical matrix isolation experiment, ca. 10 mg of substance is sublimed through the external or internal quartz oven at a vacuum of ca. 10^{-6} to 2×10^{-6} mbar, and the resulting products are codeposited with Ar (5 mbar/min from a 2 L reservoir filled with 1 atm of Ar). IR spectra were recorded with a resolution of 1 cm^{-1}. GC for GC/MS analysis was performed on a 30 m capillary column, with an injector port temperature of 200 °C and a temperature program of 100 °C for 2 min and then 16 °C/min until 270 °C. Melting points are uncorrected. 2,2-Dimethyl-5-phenyl-1,3-oxazine-4,6-dione **18** was prepared according to the literature.[15]

DFT calculations were performed at the B3LYP/6-31G* level.[16] Vibrational frequencies were scaled by a factor 0.9613.[17]

4-Hydroxy-2,5-diphenyl-1,3-oxazin-6-one 8. To a stirred solution of benzamide (242 mg, 2 mmol) in boiling xylene (15 mL)

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was added (chlorocarbonyl)phenylketene[18] (362 mg, 2 mmol). The reaction mixture was then immediately cooled. A precipitate was formed instantly. It was collected and washed with diethyl ether. Recrystallization from dry ethyl acetate−hexane afforded pale yellow crystals (300.9 mg, 85%): mp 218 °C; IR (KBr) cm^{-1} 3200−2500 (broad, OH), 1670, 1620, 1562, 1495, 1403, 1332, 1259, 1170, 1119, 776, 687; MS *m*/*z* (relative intensity), 265 (M^+, 100), 237 (68), 118(15), 105 (16), 77 (10); ^{1}H NMR (500 MHz, DMSO) δ 12.87 (s, 1H), 8.16−7.27 (m, 10H); ^{13}C NMR (DMSO, 125 MHz) δ 17.9, 95.1, 125.8, 126.9, 127.5, 130.1, 131.1, 135.2, 160.4, 162.31, 165.1. Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.45; H, 4.15; N, 5.28. Found: C, 72.48; H, 3.95; N, 5.12.

4-Hydroxy-2-isopropenyl-5-phenyl-1,3-oxazin-6-one 16. To a stirred solution of methacrylamide (170 mg, 2 mmol) in dry boiling toluene (20 mL) was added (chlorocarbonyl)phenylketene (362 mg, 2 mmol). The reaction mixture was immediately cooled, and the resulting precipitate was collected, washed with diethyl ether, and recrystallized from dry THF−hexane to afford pale yellow crystals (321 mg, 70%): mp 161−162 °C; IR (KBr) 3200−2500 (broad, OH), 1660, 1635, 1605, 1557, 1347, 1174, 1156, 938, 795, 690 cm^{-1}; MS *m*/*z* 229 (M^+, 25%), 118 (100), 91 (56), 77 (24), 69 (37), 41 (72); ^{1}H NMR (DMSO, 500 MHz) 2.06 (s, 3H), 5.86 (s, 1H), 5.27 (s, 1H), 7.24−7.50 (m, 5H), 12.35 (s, 1H); ^{13}C NMR (DMSO, 125 MHz) 17.9, 95.1, 125.8, 126.9, 127.5, 130.1, 131.1, 135.2, 160.4, 162.3, 165.1. Anal. Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found; C, 68.08; H, 4.71; N, 6.02.

4-Methoxy-2,5-diphenyl-1,3-oxazin-6-one 17. A solution of **8** (1.2 g, 5.2 mmol) in THF (20 mL) was added slowly below 0 °C and with stirring to a solution of diazomethane in ether (20 mL, 20 mmol). Stirring was continued for 12 h while the mixture was allowed to warm to room temperature. The resulting yellow product was collected by vacuum filtration and recrystallized from THF−hexane to yield 800 mg of **17** as yellow crystals: mp 192 °C; IR (KBr) cm^{-1} 3051 w, 3032 w, 2947 w, 2866 w, 1742 s, 1724 s, 1612 m, 1578 m, 1543 s, 1496 m, 1441 m, 1379 m, 1327 m, 1298 m, 1199 m, 1175 w, 1116 m, 1077 w, 1069 w, 977 w, 912 w, 871 m, 780 m, 760 m, 706 m, 691 m, 658 w, 599 w, 537 w; GC Rt 16.28 min; MS *m*/*z*, 279 (M^+, 20%), 251 (10), 105(90), 77 (53); ^{1}H NMR ($CDCl_3$, 500 MHz) 4.10 (s, 3H), 7.33−7.63 (m, 8H), 8.31 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) 55.3, 98.2, 127.7, 127.9, 128.7, 128.8, 129.4, 130.0, 130.2, 133.7, 161.0, 162.9, 165.2. HRMS calcd for $C_{17}H_{13}NO_3$: 279.0898. Found: 279.0896. Anal. Calcd for $C_{17}H_{10}NO_3$: C, 73.11; H, 4.69; N, 5.02. Found; C, 73.13; H, 4.72; N, 4.98.

FVT Matrix Isolation of 8. 4-Hydroxy-2,5-diphenyl-1,3-oxazin-6-one **8** (10 mg, 0.038 mmol) was gently sublimed at 80−83 °C and subjected to FVT at a temperature of 830 °C with Ar matrix isolation of the products on a CsI disk at 20 K in the course of 21 min: IR (Ar, 20 K) 3077 w, 2345 s, 2244 m, 2136 m, 2121 vs, 1755 w, 1708 m, 1604 m, 1580 w, 1505 m, 1495 m, 1450 w, 1406 w, 1387 w, 1354 m, 1260 w, 1234 w, 1118 w, 1028 vw, 969 w, 800 w, 758 m, 750 m, 702 w, 687 m, 662 m, 547 w cm^{-1}. The results of analogous experiments at 300−800 °C are described in the text and in Figure 2.

Preparative FVT of 8. A portion of **8** (30 mg, 0.114 mmol) was subjected to FVT at 830 °C. The product was collected at 77 K on a cold finger, which was rinsed with THF after the end of the experiment. GCMS analysis of the resulting mixture revealed three products: Rt 8.21 (*m*/*z* 147), assigned to benzoyl isocyanate by comparison with the literature spectrum;[19] Rt 10.54 (*m*/*z* 121), ascribed to benzamide formed by hydrolysis of benzoyl isocyanate; and Rt 16.73 (*m*/*z* 136), due to phenylacetic acid formed by hydrolysis of phenylketene.

In a similar experiment, the cold finger was rinsed with MeOH after the end of the experiment. GCMS of the resulting mixture showed the major peak at Rt 6.37 (*m*/*z* 150) due to methyl phenylacetate. A minor peak at Rt 10.52 min (*m*/*z* 121) was ascribed to benzamide, formed by hydrolysis of benzoyl isocyanate.

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Supporting Information Available: Mass spectra relating to the FVT/MS and FVT/MS/MS of **1**, **8**, and **18**. IR spectra relating to the FVT matrix isolation of **1**, **8**, and **18**. Cartesian coordinates, energies, and vibrational frequencies of all calculated molecules and transition structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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