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Flash Vacuum Pyrolysis of *tert*-Butyl β-Ketoesters: Sterically Protected α-Oxoketenes.[†]

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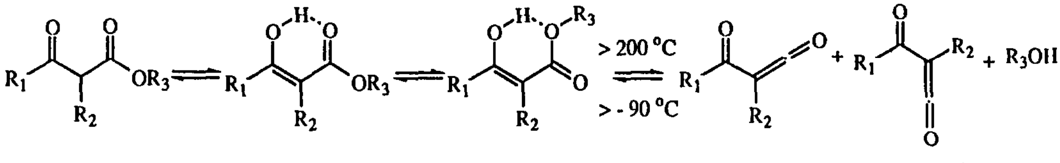
Abstract: Infrared spectroscopic analysis of the products showed that flash vacuum pyrolyses (FVP) of dimethyl *tert*-butylmalonate (**1b**) and methyl *tert*-butyl(pivaloyl)acetate (**1d**) at ca. 550 °C afforded the corresponding *tert*-butyl(carbomethoxy)ketene (**4b**) and *tert*-butyl(pivaloyl)ketene (**4d**), respectively, with loss of methanol, together with unreacted **1b** and **1d** (Ar matrix, 12 K or neat at 77 K; 10^{-5} mbar). Monitoring by IR spectroscopy showed that **4b** reacted with methanol at ca. -50 °C to give **1b**. Ketene **4d** does not react with methanol at room temperature, but afforded ester **1d** on refluxing for 8 h. FVP of **1b** and **1d** at temperatures above 650 °C gave the α-oxoketenes **4b** and **4d**, respectively, unsubstituted dimethyl malonate (**1a**) and methyl 4,4-dimethyl-3-oxo-pentanoate (**1c**), respectively, due to retro-ene reactions with elimination of isobutene, as well as pyrolysis products derived from **1a** and **1c**, respectively. FVP of α-unsubstituted β-ketoesters **1a** and **1c** at ca.500 °C (10^{-5} mbar) with argon matrix isolation of the products at 12 K afforded the ketenes **4a** and **4c** as mixtures of s-*Z* and s-*E* conformers together with mixtures of unreacted keto (**1a,c**) and enol forms (**2a,c**). On warming to temperatures between -90 and -50 °C, back-reaction of ketenes **4a,c** with methanol resulted in the re-generation of enols **2a,c**, without increasing the amounts of the keto forms **1a,c**.

INTRODUCTION

In a previous report,[1] it was shown that flash vacuum pyrolysis (FVP) of β-ketoesters **1** allowed the direct IR spectroscopic observation of α-oxoketenes **4**, presumably via the enol intermediates **3**, and that open-chain α-oxoketenes **4** can exist in the s-*E* and s-*Z* forms (Scheme 1). Independently, strong evidence for the intermediacy of α-oxoketenes **4** in the decarbonylation of 2,4-dioxoacids and esters was also reported.[2]

Scheme 1



1 2 3 s-Z-4 s-*E*-4

[†] This paper is dedicated to Professor Charles W. Rees, Imperial College, London, on the occasion of his 65th birthday.

FVP of the ethyl β-ketoesters[1] at 200-400 °C gave ketenes **4** as well as a mixture of unreacted keto (**1**) and enol (**2**) forms, but at higher temperatures (ca. >700 °C) elimination of ethylene and decarboxylation occurred. The ease of formation of ketenes **4** was directly related to the ease of enolization of the starting ester; α-substituted ketoesters **1** exist largely in the keto form and require high pyrolysis temperatures for ethanol elimination and ketene formation.

In order to gain further insight into the FVP of β-ketoesters, we have investigated the methyl esters **1a-d** (Table I). It was of particular interest to observe the ketenes directly and to monitor their reactions with methanol to regenerate the keto or enol forms of the starting materials.[1] It will be shown that, due to the steric hindrance, the α-*tert*-butylated esters **1b** and **1d**, which exist largely in the keto forms, give rise to the s-*E* ketene conformers of **4b** and **4d**. These are persistent species,[3,4] and their back reactions with methanol are shown to give ketoesters **1**, without any enol being detectable. In contrast, ketenes **4a** and **4c** exist as mixtures of s-*E* and s-*Z* forms, and enols are detectable in their reactions with methanol.

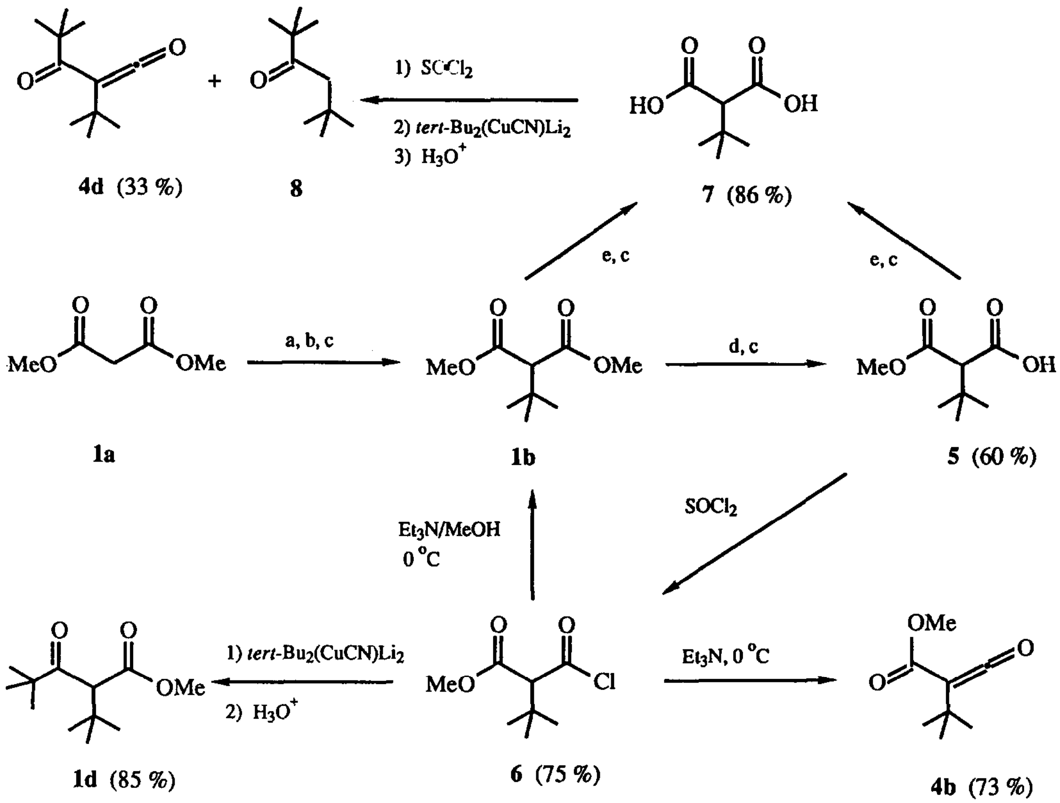
RESULTS AND DISCUSSION

The experimental procedures for the ethyl esters analogues were adapted for the preparation of **1b**,[5] **1d**[4a] and **4b**.[3] *tert*-Butyl(pivaloyl)ketene (**4d**) was prepared according to the procedure described by Savage[4a] (Scheme 2). In our hands, dimethyl *tert*-butylmalonate (**1b**), obtained in two steps from commercially available dimethyl malonate (**1a**), was contaminated with ca. 5% of dimethyl isopropylidenemalonate and 2% of **1a**. Attempts to purify **1b** by distillation or chromatography (preparative GC or column) failed and resulted in heavy loss of **1b**. However, the monoacid **5**, obtained from the hydrolysis of **1b** with one equivalent of methanolic potassium hydroxide followed by acidification, could be purified by flash chromatography[6] using chloroform as eluent. **5** was converted to *tert*-butyl(carbomethoxy)acetyl chloride (**6**) with thionyl chloride, and this was added to two equivalents of triethylamine in methanol. Vacuum distillation afforded pure **1b** (> 98% by GC).

Dehydrochlorination of the acid chloride **6** with triethylamine in dry ether at 0 °C afforded *tert*-butyl(carbomethoxy)ketene (**4b**) after distillation. **4b** was reasonably stable as a neat liquid and could be stored at -10 °C for prolonged periods in a sealed container under nitrogen. Monitoring by IR spectroscopy of the reaction between **4b** and methanol revealed that the reaction started at ca. -50 °C and was complete at -25 °C, with formation of ketoester **1b** ($\nu_{C=O}$ 1733, 1756 cm^{-1}). No enol **2b** was detectable under these conditions. There are several likely reasons for this: (i) **4b** exists in the s-*E* conformation for steric reasons and cannot, therefore, give enol in a concerted 1,4-addition (**4b**→**3b**→**2b**); (ii) even if formed, steric hindrance in the planar enol **2b** would destabilize it vis à vis the keto form **1b**; (iii) At the relatively high temperature of reaction with methanol (-50 to -25 °C) enol-keto tautomerism could be rapid, causing any enol conformers to escape detection (contrast the detection of **2a** and **2c** below).

It is interesting to note that the IR frequencies (ν_{CCO} and ν_{CO}) of **4b** are very dependent on the medium: 2121 and 1721 cm^{-1} (CCl_4); 2127 and 1738 cm^{-1} (gas phase); 2124 and 1718 cm^{-1} (77 K); 2129 and 1730 cm^{-1} (Ar, 12 K). Other examples of the dependence of IR frequencies on the medium have been described.[7]

Scheme 2



a) CH_3COCH_3, $(CH_3CO)_2O$, $ZnCl_2$, Δ b) CH_3MgBr c) H_3O^+ d) 1 eq. KOH/MeOH e) excess KOH/MeOH

Table I. α-Oxoketenes 4 Obtained by FVP of β-Ketoesters 1.

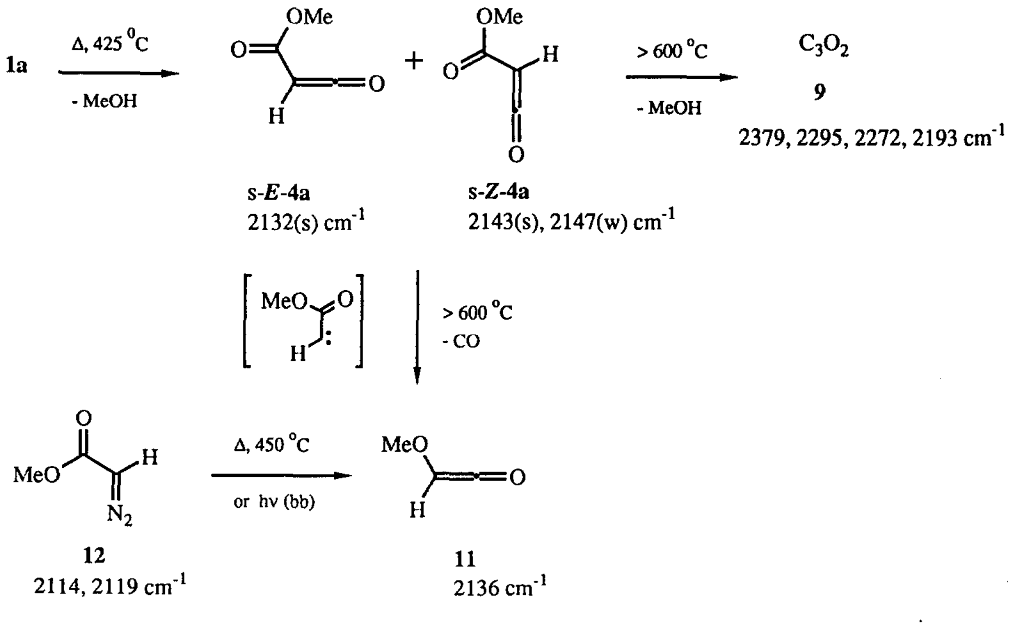
ESTERS 1				PYROLYSIS TEMPERATURE	KETENES 4 (Ar, 12 K; cm^{-1})			
					$\nu_{C=C=O}$		$\nu_{C=O}$	
	R_1	R_2	R_3	°C	s-*Z*	s-*E*	s-*Z*	s-*E*
a	MeO	H	Me	400	2143(s) 2147(m)	2132		
b	MeO	*tert*-Bu	Me	500		2129		1730
c	*tert*-Bu	H	Me	400	2142	2134	1667	1681
d	*tert*-Bu	*tert*-Bu	Me	400		2104		1661

tert-Butyl(pivaloyl)ketene (**4d**) was prepared by the reaction of *tert*-butylmalonyl chloride with four equivalents of *tert*-$Bu_2(CuCN)Li_2$.[4a] **4d** was very stable to air and chromatography (GC and column). Furthermore, **4d** was stable in methanol at ambient temperature for days without noticeable formation of methyl *tert*-butyl(pivaloyl)acetate (**1d**). However, formation of **1d** was complete on refluxing for 8 h at 70 °C.[8] (No enol **2d** is observable under these conditions for the same reasons as given above for **2b**). On prolonged exposure to air and moisture, **4d** slowly decomposed to 2,2,5,5-tetramethylhexan-3-one (**8**) presumably via the acid which then decarboxylated.[4a] The IR frequencies (ν_{CCO} and ν_{CO}) for **4d** are: 2100 and 1655 cm^{-1} (CCl_4);[4b] 2104 and 1667 cm^{-1}(gas phase); 2101 and 1645 cm^{-1} (77 K); and 2104 and 1661 cm^{-1} (Ar, 12 K).

Analysis of the IR spectrum (Ar, 12 K) of the pyrolysate from dimethyl malonate (**1a**) at 425 °C showed the presence of carbomethoxyketene (**4a**) as a mixture of s-*Z* (2143 cm^{-1}) and s-*E* (2132 cm^{-1}) conformers,[9] as well as unreacted **1a** (1769 and 1717 cm^{-1}) (Scheme 3). Above 600 °C, in addition to α-oxoketene **4a** (s-*E* and s-*Z*), CO_2 (2339, 2343 cm^{-1}), C_3O_2 (**9**; 2378, 2284, 2272, 2193 cm^{-1}), methoxyketene (**11**; 2136 cm^{-1}) and CO (2138, 2148 cm^{-1}) were also detected.[10]

Methyl diazoacetate (**12**) was also employed as a precursor to **11**. Broad band irradiation with unfiltered light for 5 min of a sample of **12** in Ar matrix at 12 K caused the formation of methoxyketene[14] (**11**; 2136 cm^{-1}) and CO, as monitored by IR spectroscopy. Possible pathways rationalizing the observed products are outlined in Scheme 3. Thus, at or below 425 °C, **1a** loses methanol, presumably via the intermediacy of **3a** (Scheme 1) to give ketene **4a** (s-*Z* and s-*E*). Above 600 °C, C_3O_2 (**9**) is also formed by either stepwise loss of methanol (**1a**→**4a**→**9**) or directly from **1a**

Scheme 3



with loss of 2 molecules of methanol. It should be noted that C_3O_2 (**9**) is usually generated from malonic acid and P_2O_5.[11] Decarbonylation of α-oxoketene **4a** under the pyrolytic conditions employed resulted in the formation of the oxo-carbene which underwent the Wolff rearrangement to methoxyketene (**11**). Decarbonylation of ketenes under pyrolytic conditions is well documented.[12-14]

FVP of dimethyl *tert*-butylmalonate (**1b**) below 400 °C gave only unreacted starting material (1743, 1763 cm^{-1}) in agreement with previously reported results[1] that α-substituted β-ketoesters reacted rather sluggishly. At 650 °C, a single isomer of *tert*-butyl(carbomethoxy)ketene (s-*E*-**4b**, 2129, 1730 cm^{-1}) as well as unreacted **1b** were observed (Ar, 12 K) by IR spectroscopy. However, above 750 °C, the IR spectrum of the pyrolysate of **1b** was very similar to that obtained from unsubstituted dimethyl malonate (**1a**) above 600 °C, the only difference being the presence of α-oxoketene s-*E*-**4b** when **1b** was employed as a precursor (Scheme 4). Thus, above 750 °C, **1b** undergoes a retro-ene type cleavage to give enols **13** or **14**, which under the FVP conditions employed afforded products typical of **1a**.

Scheme 4

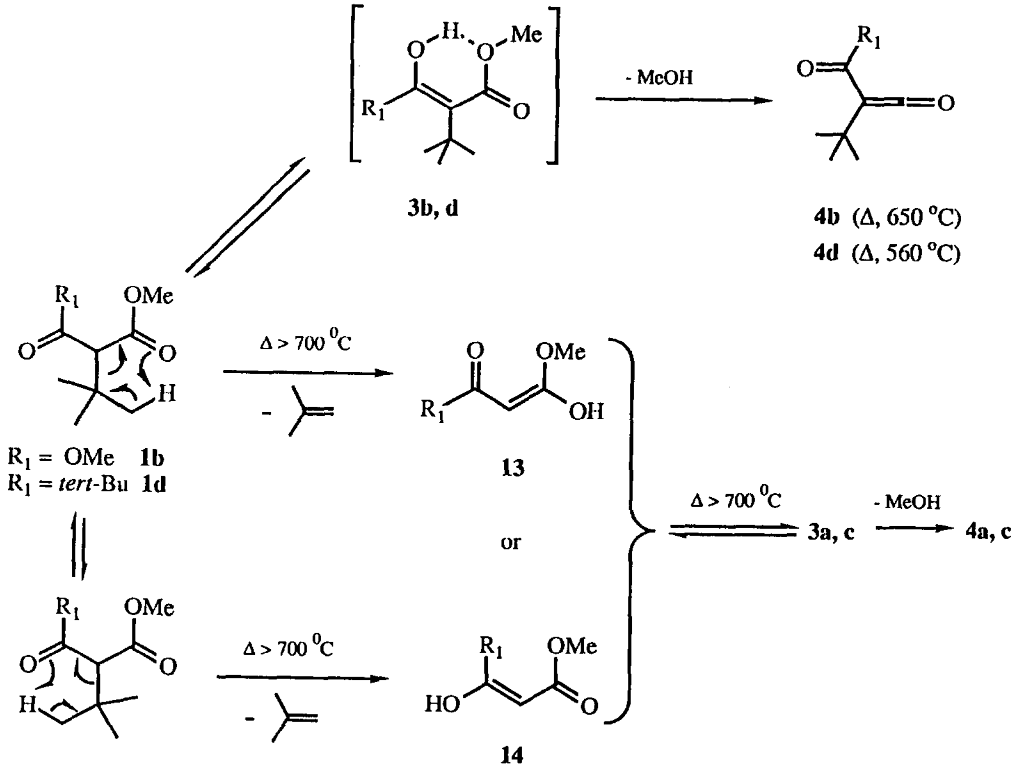


Figure 1. (i) (bottom) Spectrum of the FVP of **1d** at 650 ° with product deposition at 77 K demonstrating the formation of **4d** (2101 cm^{-1}) and **4c** (2134 cm^{-1}) as well as unreacted **1d**. (ii) (top) Warming to 150 K: Diminishing of the band corresponding to **4c** (shifted to 2122 cm^{-1}) and formation of enol **2c** (1621, 1654 cm^{-1}) now observable [1620, 1644 cm^{-1} at 77 K].

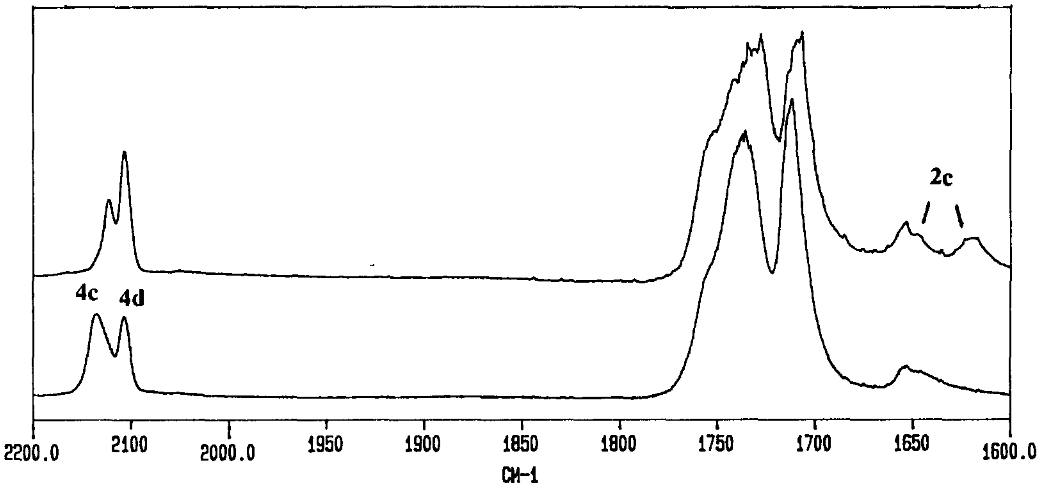
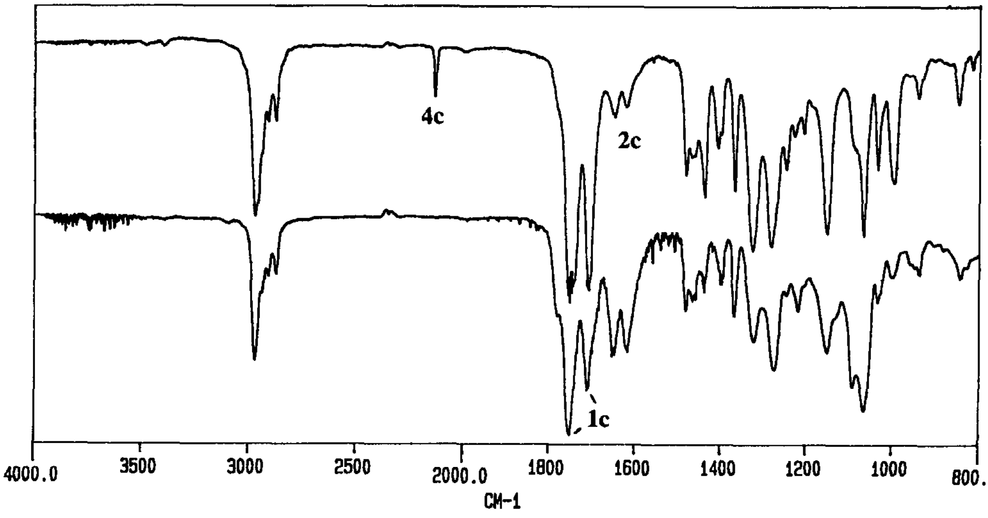


Figure 2. (i) (top) Spectrum of the FVP of **1c** at 500 °C with product deposition at 77 K demonstrating the formation of **4c** (2134 cm^{-1}); enol **2c** (1620, 1644 cm^{-1}) and keto forms **1c** (1708, 1751 cm^{-1}) are also present. (ii) (bottom) On warming to 250 K, the band corresponding to **4c** disappeared with concomitant increase in the intensity of bands due to enol **2c** (1618, 1652 cm^{-1}).

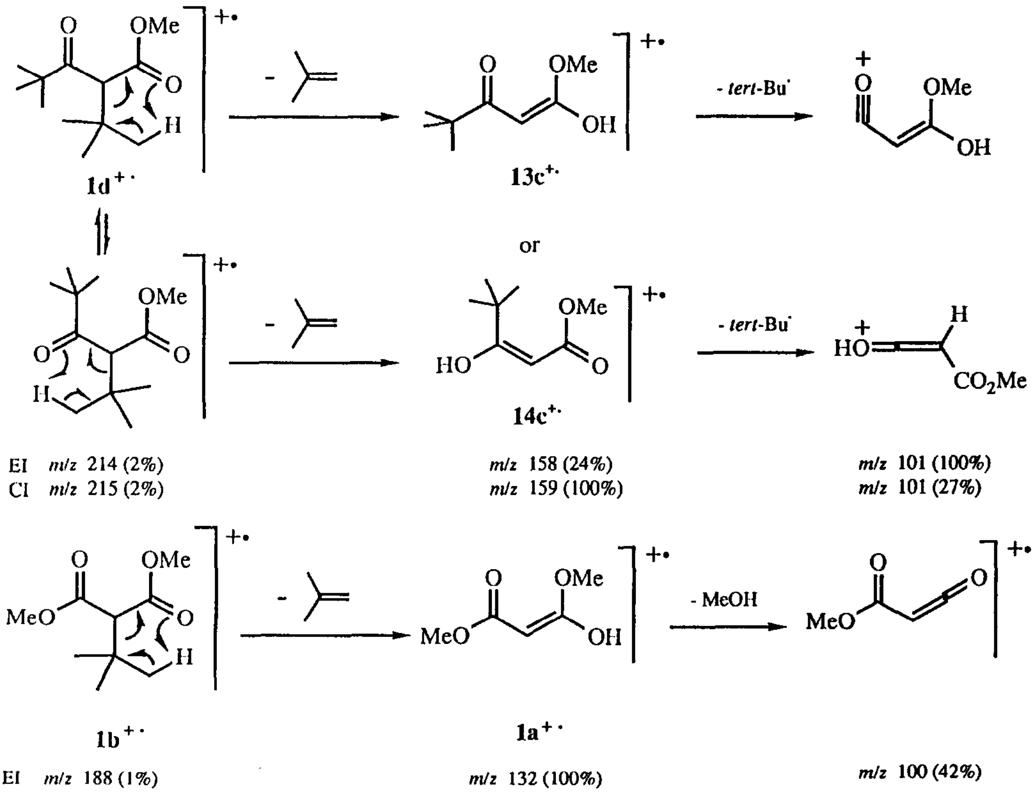


A similar behaviour was observed for methyl *tert*-butyl(pivaloyl)acetate (**1d**). Thus, pyrolysis of **1d** below 550 °C with product isolation at 77 K, gave *tert*-butyl(pivaloyl)ketene **4d** (2101, 1645 cm^{-1}) as well as unreacted **1d** (1737, 1710 cm^{-1}). Above 640 °C, in addition to **1d** and **4d**, pivaloylketene (**4c**) (2134, 1675 cm^{-1}) and enol **13c** or **14c** (1644, 1620 cm^{-1}) were also detected (Scheme 4). On warming to 150 K, the IR intensity of pivaloylketene (**4c**) had decreased by nearly half and shifted to 2122 cm^{-1}; at the same time, formation of methyl 4,4-dimethyl-3-oxo-pentanoate (**1c**) (1755, 1712 cm^{-1}) had started; enol **2c** (1621, 1654 cm^{-1}) was now observable, and the IR intensity of α-oxoketene **4d** (2101 cm^{-1}) had not changed (Figure 1). This is consistent with the finding that **4d** was stable in methanol at ambient temperature (*vide supra*). At 250 K, **4c** had disappeared with concomitant increase of enol **2c** while the IR intensity of **4d** remained virtually unchanged.

Pyrolysis of commercially available **1c** at 500 °C also gave pivaloylketene **4c** (2134 cm^{-1}; 77 K) together with unreacted keto (**1c**; 1751, 1708 cm^{-1}) and enol (**2c**; 1620, 1644 cm^{-1}) forms. On warming to 250 K, the IR intensity of the enol form **2c** (1618, 1652 cm^{-1}) had increased relative to the keto form (**1c**), while the ketene band had disappeared (Figure 2). This is further evidence that back-reaction of pivaloylketene **4c** with methanol involved the enols **2c** (and **3c**) initially.

Analysis of the mass spectra of the β-ketoesters **1b** and **1d** demonstrated that, in analogy with the thermal retro-ene reactions, the McLafferty rearrangement[15] is very important in these two

Scheme 5



compounds (Scheme 5). Thus, under electron ionization (EI) conditions, the peak at *m/z* 101 is the base peak for **1d**$^{+\cdot}$, and the peak at *m/z* 158 (**13c**$^{+\cdot}$ or **14c**$^{+\cdot}$) corresponding to loss of isobutene from the molecular ion has an abundance of 24%.[15d] Under the milder chemical ionization (CI) conditions, the loss of isobutene from the protonated molecule $[M + H - C_4H_8]^+$ is responsible for the base peak at *m/z* 159. Similarly, in the EI spectrum of **1b**, the base peak corresponds to loss of isobutene from the molecular ion to give **1a**$^{+\cdot}$ (*m/z* 132) (Scheme 5).

Supporting evidence for the importance of loss of isobutene during the pyrolysis of **1d** came from the preparative FVP of **1d** over the temperature range 400 - 900 °C. The pyrolysate was collected and analyzed by GC-IR and GC-MS and the relevant data are collected in Table II.

Thus, at temperatures below 400 °C, only unreacted **1d** was recovered (IR (gas phase) 1721, 1756 cm^{-1}; m/z 214). Between 500 and 600 °C, **1c** (ca. 8%; IR (gas phase) 1770, 1724, 1624 cm^{-1}; m/z 158) was now present as well as methyl 3-methylbuten-2-oate (**15**, ca. 23%; IR (gas phase) 1736, 1664 cm^{-1}; m/z 114). **15** was also prepared from the reaction of 3-methylbuten-2-oic acid in acidic methanol, and the spectral data (IR, NMR, MS) are in agreement with those of **15** obtained from the FVP of **1d**. As the pyrolysis temperature was increased, the amount of **1d** decreased whereas the amounts of the retro-ene product **1c** and **15** increased. At temperatures above 600 °C, small amounts of **1a** (ca. 3%; IR (gas phase) 1768 cm^{-1}; m/z 132) and methyl 3,3-dimethylbutanoate (**16**, ca. 2%; IR (gas phase) 1762 cm^{-1}; m/z 130) were obtained as well. Formation of **1a** corresponds to trapping of C_3O_2 by methanol, and both **15** and **16** may have their origin in a homolytic α-cleavage of **1d**.

Table II. Products Obtained from the FVP of Methyl *tert*-Butylpivaloylacetate (1d) and Identified by GC-IR and GC-MS.

PYROLYSIS TEMPERATURE	RELATIVE YIELD OF PRODUCTS (Area %)				
(°C)	**15**[a]	**16**[b]	**1a**	**1c**[c]	**1d**
400	-	-	-	-	98
500	2	-	-	1	93
550	5	-	-	3	86
600	23	1	1	8	45
700	33	1	2	17	36
750	58	2	3	12	6
900	32	24	0	0	0

[a] 15: methyl 3-methylbuten-2-oate; [b] 16: methyl 3,3-dimethylbutanoate; [c] isobutene also identified by GC-MS of the pyrolysate from 600 °C and above.

CONCLUSION

α-tert-Butyl *β*-ketoesters (**1b** and **1d**) exist predominantly in the keto forms, and therefore eliminate methanol only sluggishly to afford *tert*-butyl *α*-oxoketenes **4b** and **4d** on FVP at temperatures below 550 °C. The *α*-oxoketenes **4b** and **4d** are sterically stabilized and exist essentially in the s-*E* form. At higher pyrolysis temperatures (> ca. 600 °C), loss of isobutene from **1b** and **1d** in a retro-ene reaction competes efficiently with direct ketene formation. This generates the *α*-unsubstituted *β*-ketoesters **1a** and **1c** directly in the enol forms, *i.e.* in a form predisposed for ketene generation. Therefore, under these FVP conditions, the products expected from the *α*-unsubstituted esters **1a** and **1c** are observed. When the enolizable *α*-unsubstituted *β*-ketoesters **1a** and **1c** are used directly as the starting materials, reaction starts already at 500 °C to afford the *α*-oxoketenes **4a** and **4c** as mixtures of s-*E* and s-*Z* conformers together with unreacted keto (**1a** and **1c**) and enol forms (**2a** and **2c**). On warming, back-reaction of the ketenes (**4a** and **4c**) with methanol regenerates the enols **2a** and **2c**, respectively. No enol **2b** is detected in the reaction of the highly sterically hindered *tert*-butyl(carbomethoxy)ketene (**4b**) with methanol at -50 to -25 °C. The most likely reason for this is the sterically enforced s-*E* conformation of **4b**, making the transition state for the 1,4-addition (*cf.* **3b**) inaccessible. Furthermore, the planar enol would be disfavored with respect to the keto form due to steric hindrance. Similarly, *tert*-butyl(pivaloyl)ketene (s-*E*-**4d**) does not react with methanol at ordinary temperatures and does not, therefore, give any detectable amount of enol.

EXPERIMENTAL SECTION

General. Glassware was dried in an oven at 250 °C and cooled in a desiccator prior to use. Sensitive reactions were carried out under a nitrogen atmosphere. Unless otherwise indicated, materials were from commercial suppliers and were used without further purification. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenoneketyl under N_2. Butyllithium (BuLi) was standardized[16] with a solution of diphenylacetic acid in THF of known concentration at 0 °C under N_2. Triethylamine (Et_3N) was dried over KOH pellets and distilled. Dimethyl malonate (**1a**) and methyl 4,4-dimethyl-3-oxo-pentanoate (**1c**) were from Aldrich Chemical Co.

Apparatus. The FVP apparatus employed 10-cm length (0.8-cm i.d.) quartz tubes in housings flanged to Leybold-Heraeus closed-cycle He cryostats (for matrix isolation; 10-20 K) or Air Products liquid N_2 cryostats (for isolation at 77 K). Pressures were 10^{-3}-10^{-5} mbar. Unless otherwise indicated, samples were pre-cooled to -10 to -20 °C before vacuum deposition on KBr or BaF_2 discs. For matrix isolation (12 K), samples were co-deposited with ca. 100 mbar Ar in 15 min and for solid film (77 K) the samples were deposited in ca. 10 min. Further details and apparatus for preparative FVP were as previously described.[17] Known pyrolysis products were identified by direct spectral comparison with authentic materials, deposited and/or recorded under the same experimental conditions.

Gas chromatographic (GC) analyses were conducted on SE-32 columns using He as a carrier gas and are reported as relative peak areas without correction for detector response. The GC employed for GC-FTIR analysis was equipped with a flame ionization detector (FID) and arranged so that the effluent could be directed via a heated transfer line to a Perkin-Elmer 1700X FTIR spectrometer having a resolution of 4 cm^{-1} for the gas phase spectra. The column (SE-32) was programmed to start at 50 °C and increased by 10 °C/min to 120 °C, held for 2 min at 120 °C, then increased by 10 °C/min to 250 °C and held for 10 min. GC-MS analyses were also performed using the same type of temperature program as the GC-FTIR on a SE-32 column. Chromatographic separations were performed using flash chromatography[6] on silica gel, and preparative GC using a 10% OV-101 column.

NMR spectra were recorded on a JEOL GX400 spectrometer (400 MHz for ^{1}H, 100.6 MHz for ^{13}C); UV spectra were run on a Varian Cary 1. IR spectra were recorded on a Perkin-Elmer 1700X FTIR spectrometer at a resolution of 1 cm^{-1} (except for the gas phase, see above), and mass spectra were obtained using a Kratos MS25RFA mass spectrometer. Irradiations were carried out with a high-pressure Xe-Hg lamp (1000 W, Hanovia).

Dimethyl isopropylidenemalonate was prepared according to the procedure described for the diethyl ester analogue.[5] Yield: 47%; Bp: 60-63 °C/5 Torr. ^{1}H-NMR ($CDCl_3$) δ 2.2 (s, 6H, 2OCH_3), 3.8 (s, 6H, $C(CH_3)_2$); IR (film) 1062, 1246, 1436, 1642 (C=C), 1727 (C=O) cm^{-1}.

Dimethyl *tert*-butylmalonate (1b) was obtained following the procedure reported.[4a] Analytical GC showed that **1b** was contaminated with ca. 5% of dimethyl isopropylidenemalonate and 2% of **1a**. Attempts to purify **1b** by fractional distillation or by chromatography (preparative GC or flash) failed.

However, pure **1b** was obtained from the reaction of *tert*-butyl carbomethoxyacetyl chloride (**6**, see below) with Et_3N in CH_3OH. Thus, 6.12 g (32 mmol) of **6** in 15 mL of dry Et_2O was added dropwise to an ice-cooled solution of 50 mL CH_3OH and 10 mL (75 mmol) Et_3N, with immediate formation of a thick white precipitate. The resulting mixture was stirred for 5 h, then poured onto 50 mL of water and extracted with 2x50 mL of ether. The combined ether layer was then washed successively with aq. $NaHCO_3$, brine and water. After drying over $MgSO_4$ and filtration, the organic phase was concentrated in vacuo to give a colourless oil. Vacuum distillation afforded **1b** (5.5 g, 93%, bp 48-49 °C/0.4 Torr) which was >98% pure by GC analysis. IR (film) 1050, 1148, 1239, 1327, 1435, 1733, 1769, 2957 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.0 (s, 9H, *tert*-Bu), 3.1 (s, 1H, CH), 3.6 (s, 6H, 2OCH_3); ^{13}C-NMR ($CDCl_3$) δ 27.8 ($C(\underline{C}H_3)_3$), 33.4 ($\underline{C}(CH_3)_3$), 51.6 (OCH_3), 60.9 (CH), 168.5 (C=O); mass spectrum, m/z (relative intensity) 188 (0.5; M^+), 173 (1; $M^{+\cdot}$-CH_3), 157 (9), 141 (8), 132 (100; $M^{+\cdot}$-C_4H_8), 113 (19), 101 (39), 100 (42), 83 (10), 73 (10), 69 (54), 59 (10), 57 (59), 41 (25).

***tert*-Butyl(carbomethoxy)acetic acid (5)** was prepared according to the procedure described by Newman and Zuech.[3] The acid **5** was purified by flash chromatography on silica gel using $CHCl_3$ as eluent in 60% yield. IR (film) 1738, 3486 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.1 (s, 9H, *tert*-Bu), 3.2 (s, 1H, CH), 3.7 (s, 3H, OCH_3), 10.7 (br s, 1H, OH); ^{13}C-NMR ($CDCl_3$) δ 27.9 ($C(\underline{C}H_3)_3$), 33.8 ($\underline{C}(CH_3)_3$), 52.0 (OCH_3), 60.9 (CH), 169.2 ($\underline{C}O_2CH_3$), 173.1 (COOH).

***tert*-Butyl(carbomethoxy)acetyl chloride (6)**[3] was obtained from **5** and $SOCl_2$ in 75% yield. Bp 46-47 °C/0.7 Torr. IR (CCl_4) 1745, 1811 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.1 (s, 9H, *tert*-Bu), 3.8 (s, 1H, CH), 3.8 (s, 3H, OCH_3).

***tert*-Butylmalonic acid (7)** was obtained in 86% yield from **1b** in excess methanolic NaOH, and in 82% yield from **5** and excess methanolic NaOH. Mp 157-158 °C [Lit[4a] 156-157 °C]. IR (nujol)

1713, 3418 cm^{-1}; ^{1}H-NMR (CD_3OD) δ 1.2 (s, 9H, *tert*-Bu), 3.3 (s, 1H, CH), 5.8 (br s, 2H, 2OH); ^{13}C-NMR (CD_3OD) δ 28.5 ($C(\underline{C}H_3)_3$), 32.8 ($\underline{C}(CH_3)_3$), 62.2 (CH), 172.2 (C=O).

Methyl *tert*-butyl(pivaloyl)acetate (1d) was prepared according to the procedure of Savage[4a] from the reaction of **6** with 1.5 eq. of *tert*-$Bu_2(CuCN)Li_2$ in 85% yield. Bp 46-48 °C/0.1 Torr. IR (film) 1714, 1745 cm^{-1}; IR (gas phase) 1723, 1758 cm^{-1}; IR (Ar, 12 K) 1721, 1750 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.0 (s, 9H, *tert*-Bu), 1.1 (s, 9H, *tert*-Bu), 3.6 (s, 3H, OCH_3), 3.7 (s, 1H, CH); ^{13}C-NMR ($CDCl_3$) δ 26.0 ($CHC(\underline{C}H_3)_3$), 28.5 ($COC(\underline{C}H_3)_3$), 34.9 ($CH\underline{C}(CH_3)_3$), 45.9 ($CO\underline{C}(CH_3)_3$), 51.8 (OCH_3), 60.9 ($\underline{C}HC(CH_3)_3$), 168.9 ($\underline{C}O_2CH_3$), 209.5 ($\underline{C}OC(CH_3)_3$); mass spectrum, m/z (relative intensity) EI 214 (2; M^+), 183 (5), 158 (41; $M^{+\cdot}$-C_4H_8), 157 (23), 143 (6), 130 (12), 115 (25), 101 (100), 85 (9), 83 (3), 69 (1), 57(10), 41 (1); CI 215 (2; M^++H), 159 (100), 158 (9), 157 (8), 141 (2), 130 (3), 115 (4), 101 (27), 85 (28), 59 (17), 41 (70).

***tert*-Butyl(carbomethoxy)ketene (4b)** was prepared from **6** and Et_3N in dry Et_2O at 0 °C. Bp 34-35 °C/0.8 Torr, yield 73%. **4b** was a colourless oil which could be stored for prolonged period at 0 °C under N_2. UV (pentane) λ_{max} 228 nm; ^{1}H-NMR ($CDCl_3$) δ 1.2 (s,9H, *tert*-Bu), 3.6 (s, 3H, OCH_3); ^{13}C-NMR ($CDCl_3$) δ 29.3 ($C(\underline{C}H_3)_3$), 30.1 ($\underline{C}(CH_3)_3$), 50.0 ($\underline{C}$=C=O), 50.9 (OCH_3), 167.3 ($\underline{C}O_2CH_3$), 191.8 (C=$\underline{C}$=O); mass spectrum, m/z (relative intensity) 156 (17; M^+), 141 (97), 109 (75), 96 (6), 82 (7), 73 (45), 69 (26), 59 (31), 57 (13), 53 (19), 43 (100); IR (CCl_4) 978, 1008, 1085, 1222, 1275, 1721, 2068 (w), 2121 (vs), 2162 (w), 2959 cm^{-1}; IR (gas phase) 1084, 1216, 1274, 1738, 2127, 2967 cm^{-1}; IR (77 K) 1087, 1189, 1203, 1226, 1281, 1337, 1366, 1436, 1718, 2070 (w), 2124 (vs), 2168 (w), 2959 cm^{-1}; IR (Ar, 12 K) 1091, 1190, 1203, 1227, 1283, 1339, 1367, 1439, 1466, 1730, 2076 (w), 2129 (vs), 2168 (w), 2964 cm^{-1}

Reaction of 4b with methanol. A sample of the ketene **4b** maintained at -24 °C (CCl_4/N_2 slurry) was deposited on a KBr disc at 77 K (10^{-4} mbar) for 5 min. Then a layer of pre-cooled (-24 °C) CH_3OH was deposited and the mixture was allowed to warm up. Monitoring by IR spectroscopy showed that the reaction started at ca. -50 °C with the appearance of the bands at 1733 and 1756 cm^{-1} (**1b**), and diminishing of the band at 2123 cm^{-1} (**4b**). The reaction was complete at ca. -25 °C. The product on the cold finger was collected and was found to be largely **1b** (> 80% by GC) by comparison with an authentic sample.

***tert*-Butyl(pivaloyl)ketene (4d)** was prepared following the procedure described[4a] from *tert*-butyl malonyl chloride (from **7** and $SOCl_2$) and 4 eq. of *tert*-$Bu_2(CuCN)Li_2$. **4d** and 2,2,5,5-tetramethylhexan-2-one (**8**) were obtained in a 7:3 ratio as analysed by GC. **4d** was purified by preparative GC (T 150 °C, 10% OV-101) and isolated in 33% yield. **8**: IR (CCl_4) 910, 1071, 1346, 1365, 1464, 1478, 1710, 2953 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.9 (3, 9H), 1.0 (s, 9H), 2.1 (s, 2H); mass spectrum, m/z (relative intensity) 156 (3, M^+), 99 (23), 85 (8), 71 (14), 57 (100), 41 (31). **4d**: UV (pentane) λ_{max} 219 nm; ^{1}H-NMR ($CDCl_3$) δ 1.06 (s, 9H), 1.13 (s, 9H); ^{13}C-NMR ($CDCl_3$) δ 27.4 ($C{=}C{-}C(\underline{C}H_3)_3$), 29.3 ($COC(\underline{C}H_3)_3$), 32.3 ($C{=}C{-}\underline{C}(CH_3)_3$), 45.5 ($CO\underline{C}(CH_3)_3$), 53.4 ($\underline{C}$=C=O), 196.5 (C=$\underline{C}$=O), 202.2 ($\underline{C}OC(CH_3)_3$); IR ($CCl_4$)[4b] 904, 1007, 1149, 1268, 1331, 1365, 1475, 1655, 2054 (w), 2100 (vs), 2963 cm^{-1}; IR (gas phase) 902, 1143, 1216, 1262, 1329, 1370, 1479, 1667, 2104, 2969 cm^{-1}; IR (77 K) 1070, 1156, 1230, 1272, 1334, 1363, 1477, 1645, 2101, 2958 cm^{-1}; IR (Ar, 12

K) 908, 1155, 1231, 1272, 1335, 1366, 1478, 1661, 2104, 2970 cm^{-1}; mass spectrum, m/z (relative intensity) 182 (4; M$^+$), 167 (1), 154 (2), 125 (7), 83 (4), 69 (3), 67 (5), 57 (100), 41 (31).

Methyl 3-methylbuten-2-oate (15) was prepared by refluxing commercially available methylbuten-2-oic acid in methanol and conc. sulfuric acid; IR (CCl_4) 1079, 1153, 1232, 1351, 1378, 1663, 1723, 2958; ^{1}H-NMR ($CDCl_3$) δ 1.85 (m, 3H, CH_3), 2.12 (m, 3H, CH_3), 3.68 (s, 3H, OCH_3), 5.63 (m, 1H, C=CH); mass spectrum, m/z (relative intensity) 114 (32; M$^+$), 99 (5), 83 (100), 69 (1), 55 (60), 43 (10), 39 (40).

FVP of methyl *tert*-butyl(pivaloyl)acetate (1d). (i) Pyrolyses were carried out at temperatures between 400 and 900 °C (10^{-5} mbar) and the products were examined by GC-IR and GC-MS. Thus, 200 mg of **1d** was pyrolysed at 600 °C and at least six compounds were identified under these conditions: (i) isobutene [retention time 2.7 min; m/z 56 (42; M$^+$), 55 (14), 53 (7), 50 (8), 41 (100), 39 (57)]; (ii) methyl 3,3-dimethylbutanaote (**16**) [retention time 4.7 min; relative yield ca. 1%; IR (gas phase) 1762 cm^{-1}; m/z 130 (1; M$^+$), 115 (4), 99 (23), 83 (10), 75 (8), 73 (100), 69 (2), 59 (18), 57 (86), 41 (50)]; (iii) methyl 3-methylbuten-2-oate (**15**) [retention time 5.3 min; relative yield ca. 23%; IR (gas phase) 1736, 1664 cm^{-1}; m/z 114 (29; M$^+$), 99 (6), 83 (100), 69 (2), 55 (61), 43 (10), 39 (42)]; (iv) **1a** [retention time 6.2 min; relative yield ca. 1%; IR (gas phase) 1768 cm^{-1}; m/z 132 (4; M$^+$), 101 (100), 74 (54), 69 (14), 59 (89), 57 (33), 44 (28), 43 (22), 42 (45)]; (v) **1c** [retention time 11.5 min; relative yield ca 8%; IR (gas phase) 1724, 1770 cm^{-1}; m/z 158 (1; M$^+$)]; (vi) **1d** [retention time 11.5 min; relative yield ca. 45%; IR (gas phase) 1721, 1756 cm^{-1}; m/z 214 (1; M$^+$)]. The spectral data of these products were also consistent with those of authentic materials. The product distributions for the pyrolyses at 400, 500, 550, 700, 750 and 900 °C are given in Table II.

(ii) Thin film IR spectra of the pyrolysis of **1d** were recorded by deposition at 77 K. At pyrolysis temperatures between 450-550 °C, the IR spectrum showed mainly the presence of **1d** (1710, 1737 cm^{-1}) and a small amount of α-oxoketene **4d** (2101, 1645 cm^{-1}). At 640 °C, **1d**, **4d**, pivaloylketene (**4c**) (2134 cm^{-1}) and enol **2c** (1620, 1644 cm^{-1}) were observed. On warming to 150 K, the band at 2134 (**4c**) shifted to 2122 cm^{-1} and diminished in intensity, while the bands due to enol **2c** now at 1621 and 1654 cm^{-1} increased in intensity. The band at 2101 cm^{-1} (**4d**) remained essentially unchanged. At 250 K, **4c** had completely disappeared with concomitant increase in enol **2c** (1618, 1652 cm^{-1}). The intensity of **4d** remained virtually unchanged even on warming to room temperature.

FVP of 1c at 475 °C with product isolation in Ar matrix at 12 K gave ketene **s-*E*-4c** (2134, 1667 cm^{-1}) and **s-*Z*-4c** (2142, 1681 cm^{-1}). Pyrolysis of **1c** at 500 °C with product isolation at 77 K showed the presence of unresolved **4c** (2134 cm^{-1}) together with unreacted **1c** (1708, 1751 cm^{-1}) and enol **2c** (1620, 1644 cm^{-1}). On warming to 190 K, the ketene band shifted to 2124 cm^{-1}, and disappeared at ca. -250 K with an increase in the intensity of the enol form (**2c**, 1618, 1652 cm^{-1}) relative to the keto form (**1c**, 1708, 1751 cm^{-1}).

FVP of 1b at 400 °C with product isolation in Ar matrix at 12 K showed the presence of unreacted **1b** only (1753, 1763 cm^{-1}). At 650 °C, in addition to **1b**, ketene **4b** (2129, 1730 cm^{-1}) as well as **s-*Z*-4a** (2139(m), 2142(vs) cm^{-1}), methoxyacetylene[10] (**10**; 2152, 2155 cm^{-1}), CO (2148, 2138

cm^{-1}) and CO_2 were detected. At 750 °C, there was a significant increase in the intensity of **10** and formation of C_3O_2 (**9**; 2378, 2287, 2272, 2198 cm^{-1} [lit.[11a] 2380, 2289, 2272, 2195 cm^{-1}). At 850 °C, **10** and C_3O_2 (**9**) were the major products.

FVP of 1a at 400 °C with Ar matrix isolation at 12 K gave ketene s-*E*-**4a** (2132 cm^{-1}) as the minor component, s-*Z*-**4a** (2143 cm^{-1}) as the major component, together with unreacted **1a** (1717 and 1769 cm^{-1}). At 600 °C, in addition to **1a** and ketene **4a**, at least five other compounds were present: C_3O_2 (**9**; 2379, 2285, 2272, 2193 cm^{-1}); methoxyacetylene (**10**; 2152, 2155 cm^{-1}); methoxyketene (**11**; 2136 cm^{-1}); along with CO_2 (2340, 2345 cm^{-1}) and CO (2149, 2138 cm^{-1}). At 850 °C, **1a** and **4a** were the minor components, and the relative intensities of **9** and **10** had increased.

Methyl diazoacetate (12) was prepared according to the procedure described by Hendrickson and Wolf.[18] IR (neat) 972, 998, 1094, 1120, 1183, 1339, 1369, 1438, 1652, 2106, 3059 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.8 (s, 3H), 4.8 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ 45.8 (C=N), 51.6 (OCH_3), 168.0 (C=O). A pre-cooled (-23 °C) sample of **12** was co-deposited with ca. 100 mbar of Ar on a BaF_2 disc at 12 K (10^{-5} mbar) and irradiated for 5 min with unfiltered light. The difference spectrum showed the presence of a band at 2136 cm^{-1} assigned to methoxyketene (**11**) as well as CO (2148, 2138 cm^{-1}).

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