species except bowlane, for which the HF/6-31G* harmonic vibrational frequencies of Table I, scaled by 0.9, were employed), yielding ΔH_{298} for reaction (2) of −693 kJ mol^{-1}.

Our estimated strain energy for bowlane of 693 kJ mol^{-1} is large but not out of line with values for known highly strained hydrocarbons of comparable size. For example, the strain energies of [3]prismane (7) and cubane (8) have been estimated to be 622 and 690 kJ mol^{-1}, respectively,[15] and yet 7[16] and 8[17] have both been synthesized. Using our calculated enthalpy change for reaction (2) and experimental[18] heats of formation for all species in this reaction except bowlane, the heat of formation of bowlane, ΔH_{f298}, emerges as 492 kJ mol^{-1}. Previous work[19] has shown this type of approach to yield heats of formation for a variety of strained and unstrained hydrocarbons to within about 13 kJ mol^{-1}.

Finally, the predicted infrared spectrum of bowlane, based on scaled (by 0.9) HF/6-31G* harmonic vibrational frequencies, is shown in Figure 2. The CH stretching modes in the 2800–3000 cm^{-1} region are much more intense than the skeletal modes in the ca. 600–1600 cm^{-1} region; the latter are weak but probably observable.

Concluding Remarks

The ab initio calculations presented in this paper predict a C_{2v} structure (**3b**) for bowlane in which the bonds at the quaternary carbon are approaching coplanarity, the average deviation being 10.2°. The calculated strain energy of 693 kJ mol^{-1} is comparable to that of other systems that are highly strained but that have already been synthesized. Our predicted infrared spectrum will hopefully aid in the identification of bowlane during the course of its attempted synthesis.

Acknowledgment. We thank Professor E. D. Jemmis for helpful comments. H.F.S. was supported in part by the U.S. National Science Foundation Grant CHE-8718469 and thanks the Australian National University for a Visiting Fellowship. A generous allocation of time on the Fujitsu VP-2200 of the Australian National University Supercomputer Facility is gratefully acknowledged.

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Direct Observation of α-Oxo Ketenes from the Photolysis of α-Diazo β-Diketones

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Monitoring by IR spectroscopy of the broad-band irradiation of the symmetrically substituted 2-diazocyclohexane-1,3-dione (**11**), 3-diazopentane-2,4-dione (**19**), and 4-diazo-2,2,6,6-tetramethylheptane-3,5-dione (**24**) in Ar matrices at 12 K showed the formation of 2-carbonylcyclopentanone (*s-Z*-**12**), acetyl(methyl)ketene (*s-E*-**20**), and *tert*-butyl(pivaloyl)ketene (*s-E*-**25**), respectively, in less than 10 min. On increasing the photolysis time to >3 h, the α-oxo ketenes **12**, **20**, and **25** decarbonylated to the corresponding oxocarbenes which underwent Wolff rearrangement to carbonylcyclobutane (**15**), dimethylketene (**23**), and di-*tert*-butylketene (**28**), respectively. The reaction of 2-carbonylcyclopentanone (**12**) with CH_3OH was monitored by IR spectroscopy. Thus, it was found that the reaction started at ca. 100 K and was essentially complete at 140 K, involving the initial formation of the enol form (**9**) of methyl 2-oxocyclopentanecarboxylate.

Introduction

There has recently been considerable interest in the chemistry of α-oxo ketenes **1**.[1] Typical precursors to these species (Scheme I) include dioxinones **2**,[1b-f] furandiones **3**,[1a,j,k] β-keto esters **4**,[1b,i] 2,4-dioxoacids and esters **5**,[1c] acid chlorides **6**,[1i,2a,b] and α-diazo β-diketones **7**.[2c-f,3,4]

α-Oxo ketenes are highly reactive species and have usually been generated and trapped in situ.[2b,c,4] A few examples of sterically stabilized α-oxo ketenes that have been isolated include dipivaloylketene,[1k] *tert*-butyl(pivaloyl)ketene (**25**),[3] and *tert*-butyl(carbethoxy)ketene.[2a]

Our group has been actively involved in the studies of these species, and the use of low-temperature FT-IR

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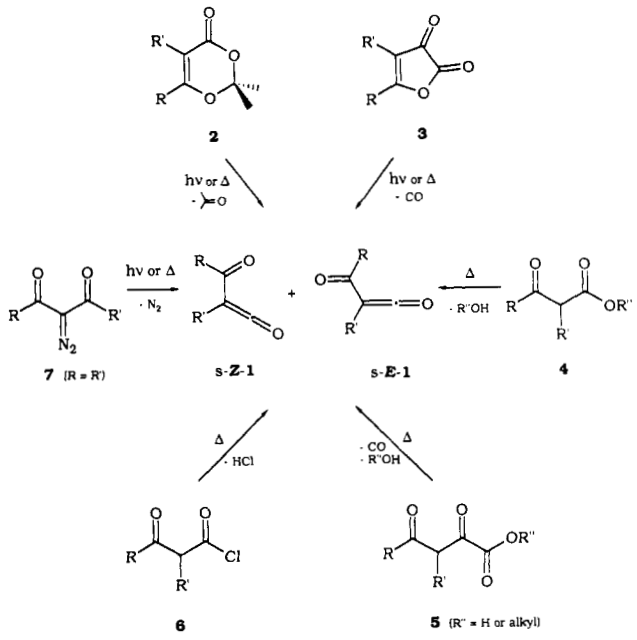
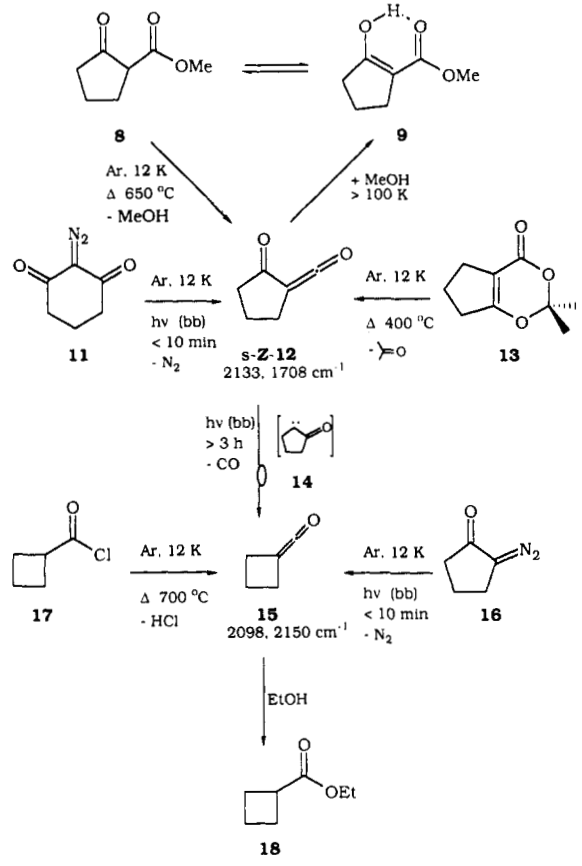
Scheme I



Scheme II



spectroscopic techniques has permitted their direct observation.[1a,b,i,j,k] In our previous work, it was shown that pyrolysis of β-keto esters **4**,[1b,i] dioxinones **2**,[1b,j] and furandiones **3**[1a,j,k] afforded the α-oxo ketenes **1** which were observed in Ar matrices at 10 K or as solid films at 77 K. However, substituted β-keto esters **4** (R′ = alkyl) which do not enolize readily react very sluggishly,[1b,i] and when high pyrolysis temperatures are used, cleavage of the substituent becomes a significant side reaction.[1i] Furandiones **3**[1a,j,k] on pyrolysis or photolysis provide a convenient and clean route to α-oxo ketenes. However, the CO byproduct absorbs in the ketene region (Ar, 12 K, 2138 and 2148 cm^{-1}) and thus may be a problem when the ketene generated has absorptions close to that of CO. In the case of dioxinones **2**,[1b,d,e,j] acetone (Ar, 12 K, 1721 cm^{-1}) is also produced along with the ketene and may mask the carbonyl group absorbtion ($\nu_{C=O}$) of the α-oxo ketene **1**, and this may be a problem for the assignment of the *s*-*E* and *s*-*Z* conformers of the ketene.[1b,j]

The use of α-diazo β-diketones **7**[2c-f,3] as precursors for the generation and direct observation of α-oxo ketenes **1**[2d,e] seems most appropriate since the other product formed, N_2, will not interfere in the IR spectrum. Several methods for the synthesis of the diazo compounds **7** are available.[4] In this study, the symmetrically substituted α-diazo β-diketones **11**,[5] **19**,[6] and **24**[7] were chosen, since only one α-oxo ketene with defined stereochemistry is expected in each case, i.e., due to geometry constraints 2-carbonylcyclopentanone (s-*Z*-**12**) is expected from **11**, acetyl(methyl)ketene (s-*E*-**20**) from **19**, and *tert*-butyl(pivaloyl)ketene (s-*E*-**25**) from **24**. However, no attempts are made here to distinguish between a concerted or stepwise Wolff rearrangement[4,8a] from the diazo compounds to the α-oxo ketenes.

Results

2-Carbonylcyclopentanone (12). Three precursors for the generation of the α-oxo ketene **12** were employed, namely 2-diazocyclohexane-1,3-dione (**11**),[5] methyl 2-oxocyclopentanecarboxylate (**8**), and 4,5,6,7-tetrahydrocyclopenta-1,3-dioxinone (**13**)[2b] (Scheme II). Monitoring by IR spectroscopy of the flash vacuum pyrolysis (FVP) of the β-keto ester **8** at 650 °C with product isolation in an Ar matrix at 12 K showed the formation of 2-carbonylcyclopentanone **12** (2133 and 1708 cm^{-1}) and methanol (1034, 3526 cm^{-1}), as well as the presence of a small amount of unreacted **8** (1717 and 1740 cm^{-1}). Similarly, the IR spectrum of the product of the 400 °C FVP of dioxinone **13** in Ar matrix at 12 K revealed the formation of **12** (2133, 1708 cm^{-1}) and acetone (1721 cm^{-1}). The broad-band irradiation of diazo compound **11** in Ar matrix at 12 K was monitored by IR spectroscopy. After 10 min of irradiation, **11** (1668 and 2137 cm^{-1}) was completely converted to the α-oxo ketene **12** (Figure 1). This latter method gave the cleanest IR spectrum of 2-carbonylcyclopentanone (*s*-*Z*-**12**), and most of the frequencies were obtained from a difference spectrum.

The formation of **12** was further substantiated by trapping with CH_3OH (Scheme II). Thus, in a preparative pyrolysis experiment (650 °C, 10^{-4} mbar), the pyrolyzate of dioxinone **13** was condensed on a N_2 cooled cold-finger previously sprayed with a solution of methanol in CCl_4. On warming, the reaction mixture was collected and analyzed by GC, IR, and NMR spectroscopies. The major product was found to be methyl 2-oxocyclopentanecarboxylate (room-temperature IR enol **9** 1622, 1668 cm^{-1}, and keto **8** 1735, 1762 cm^{-1}; ^1H NMR ($CDCl_3$), enol **9** δ 3.44 (*OMe*), and keto **8** 3.51 (*OMe*); ratio keto **8**:enol **9** = 92:8) which had spectral data identical with those of the authentic material.[9]

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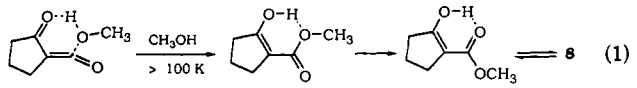
Low-temperature IR monitoring of the reaction between α-oxo ketene **12** and CH_3OH provided compelling evidence for the initial formation of the enol **9** (eq 1). Thus, α-oxo



(1)

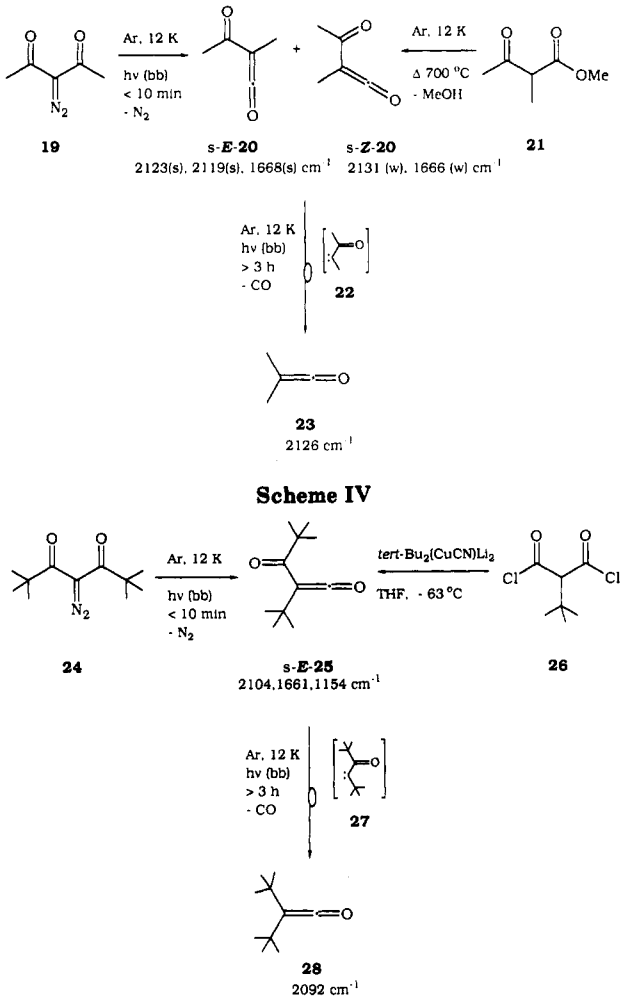
10 **9**

ketene **12** was initially generated in an Ar matrix at 12 K from the photolysis of diazo compound **11**. The matrix was then sprayed with a layer of CH_3OH, and the reaction mixture was allowed to warm while being monitored by IR spectroscopy. The reaction started at ca. 100 K, with initial formation of the enol **9** (1619, 1665 cm^{-1}). A small amount of the keto form **8** (1726 and 1752 cm^{-1}) was also detected. The reaction was essentially complete at ca. 140 K, with the near-exclusive presence of enol **9** whose frequencies had now moved to 1627 and 1672 cm^{-1}; on further warming to 200 K, the IR spectrum demonstrated that enol **9** was the major component present along with a small amount of the keto form **8** (1725, 1753 cm^{-1}) (cf. Figure 2). It is well-documented that IR frequencies are very dependent on the medium,[10,11] and for comparison purposes, the frequencies of authentic **8** in different media were recorded: (CCl_4) keto **8** 1734, 1763; enol **9** 1622, 1667 cm^{-1}; (film) **8** 1725, 1757; **9** 1622, 1659 cm^{-1}; (77 K) **8** 1720, 1748; **9** 1619, 1658 cm^{-1}. The results obtained thus showed direct evidence for the initial formation of enol **9** during the reaction of an alcohol with an α-oxo ketene, presumably via the initial rotamer **10** (eq 1).[12] **9** finally tautomerized to the keto form **8** at above 200 K.

On further irradiation (3 h) of the 2-carbonylcyclopentanone (**12**) generated from **11** in Ar matrix at 12 K, the IR spectrum showed that the intensity of the peak corresponding to α-oxo ketene **12** had decreased with concomitant formation of CO (2138 cm^{-1}) and carbonylcyclobutane (**15**, 2150 and 2098 cm^{-1}) (Scheme II). The presence of CO_2 (2343 cm^{-1}) was detected as well. After 20 h of broad-band photolysis, the IR spectrum demonstrated complete absence of **12**, but the presence of CO_2, CO, ketene **15**, and a new weak band at 2234 cm^{-1}.

Ketene **15** was also generated from other precursors, namely 2-diazocyclopentanone (**16**)[13] and cyclobutylcarbonyl chloride (**17**). IR monitoring of the broad-band photolysis of **16** in an Ar matrix at 12 K demonstrated the formation of ketene **15** in less than 10 min. **15** had a pair of doublets at 2090, 2101 and 2145, 2151 cm^{-1} in the ketene region. On warming to 60 K, the pair of doublets coalesced and shifted to 2084 and 2133 cm^{-1} while decreasing in intensity in concert and disappeared at 110 K. IR monitoring of the FVP of **17** at 700 °C with product isolation at 12 K in Ar showed the presence of **15** as a doublet of

Scheme III



Scheme IV

triplet peaks (2085, 2089, 2099 and 2133, 2137, 2149 cm^{-1}), which coalesced to a pair of peaks (2082 and 2131 cm^{-1}) at 50 K and disappeared at 110 K. This is evidence that the pairs of peaks are associated with ketene **15**, and the small splittings observed at 12 K are probably due to site effects in the Argon matrices.[11a] It should be noted that carbonylcyclopropane also gives rise to a pair of peaks (2135 and 2154 cm^{-1}) in the ketene region at 77 K which decreased in concert on warming.[14] Further evidence for the identity of ketene **15** was adducted from a trapping experiment. Thus, preparative pyrolysis of **17** at 700 °C with condensation of the pyrolyzate in a solution of EtOH in CCl_4 gave ethyl cyclobutylcarboxylate (**18**) as the major product on warming to room temperature (Scheme II).

Acetyl(methyl)ketene (20). Analysis of the IR spectrum of the pyrolyzate of methyl 2-methyl-3-oxobutanoate (**21**) in argon matrix at 12 K indicated the formation of α-oxo ketene **20** as a mixture of *s-E* (2123 (s), 2119 (s), and 1686 (s) cm^{-1}) and *s-Z* (2131 (w) and 1666 (w) cm^{-1}) conformers as well as unreacted **21** (Scheme III). However, IR monitoring of the broad-band photolysis of 3-diazopentane-2,4-dione (**19**) revealed that **19** had completely decomposed to give a single conformer, namely α-oxo ketene *s-E*-**20** in less than 10 min. The difference spectrum (Figure 4) shows a clean IR spectrum of *s-E*-**20**. On increasing the photolysis time to 3 h, the presence of **20**, CO_2 (2345 cm^{-1}), CO (2137, 2149 cm^{-1}), and dimethylketene (**23**, 2126 cm^{-1} [lit. (Ar) 2124;[15] 2128[10] cm^{-1}]) (Scheme III) as

(9) (a) Rappoport, Z., Ed. *The Chemistry of Enols*; John Wiley & Sons: Chichester, 1990. (b) The enol content of the ethyl ester analogue in CCl_4 at room temperature is 11.5 ± 2.0%; see: Rhoads, S. J. *J. Org. Chem.* **1966**, *31*, 171. (c) The enol (**9**) content of **8** is 5% in 95% ethanol; see: Schwarzenbach, G.; Zimmerman, H.; Prelog, V. *Helv. Chim. Acta* **1951**, *34*, 1954.

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(11) (a) Pimentel, G. C.; Charles, S. W. *Pure Appl. Chem.* **1963**, *7*, 111. (b) Moore, C. B.; Pimentel, G. C. *J. Chem. Phys.* **1963**, *38*, 2816.

(12) A preliminary account of the direct observation of enol intermediates in the FVP of β-keto esters to ketenes, and in the reaction of the ketenes with alcohols to regenerate the β-keto esters, is given in ref 1b. Our results directly confirm previous proposals of enol intermediates in the elimination of alcohols from β-keto esters as cited in ref. 1b. See also: Campbell, D. S.; Lawrie, C. W. *J. Chem. Soc., Chem. Commun.* **1971**, 355. Leyendecker, F.; Bloch, R.; Conia, J. M. *Tetrahedron Lett.* **1972**, 3703. Emerson, D. W.; Titus, R. L.; Gonzales, R. M. *J. Org. Chem.* **1990**, *55*, 3572.

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(14) Maquestiau, A.; Pauwels, P.; Flammang, R.; Lorenčak, P.; Wentrup, C. *Org. Mass Spectrom.* **1986**, *21*, 259.

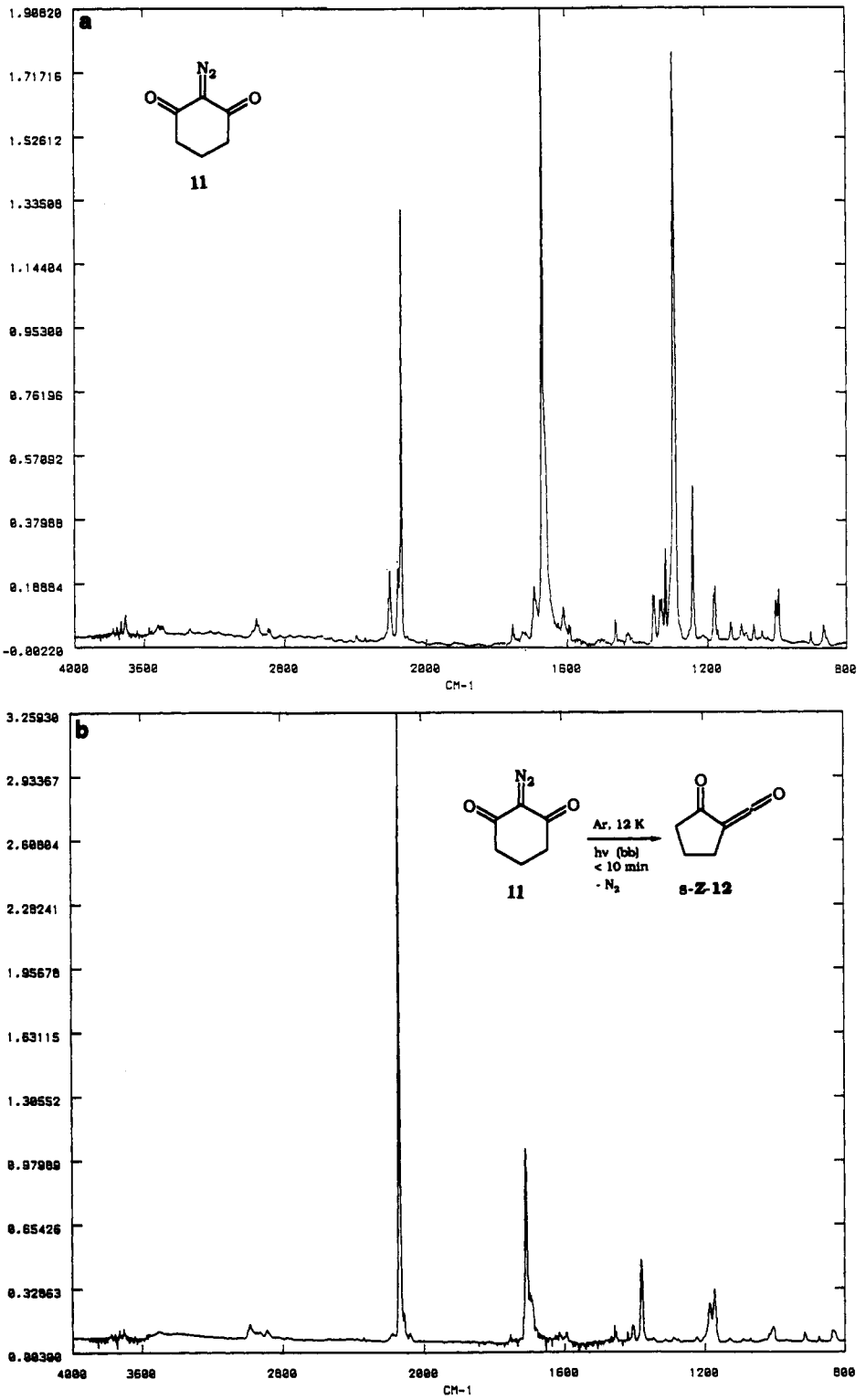


Figure 1. (a) IR spectrum of 11 in argon matrix at 12 K. (b) IR spectrum of *s*-*Z*-12 in argon matrix at 12 K.

well as a new and weak band at 2235 cm^{-1} was observed. Further irradiation for more than 22 h resulted in the complete destruction of **20** with concomitant increases in the peaks due to CO_2, CO, and **23**, as well as the medium-intensity band at 2234 cm^{-1}.

***tert*-Butyl(pivaloyl)ketene (25).** Photolysis of 2,2,6,6-tetramethylheptane-3,6-dione (**24**)[7] in an Ar matrix at 12 K resulted in the clean formation of α-oxo ketene **25** (2104, 1661, 1154 cm^{-1}), assigned as the *s*-*E* conformer due to steric constraints (vide infra) (Figure 5a and Scheme IV). This is an example of the remarkable migrating ability of a *tert*-butyl group in the Wolff rearrangement.[3,4,15] After 3 h of broad-band irradiation, the IR spectrum showed the presence of CO_2 (2345 cm^{-1}), CO (2137 and 2148 cm^{-1}), and di-*tert*-butylketene (**28**, 2092 cm^{-1} [lit. (Ar) 2104 (s), 2090 (m);[15] 2095[10] cm^{-1}]). After 22 h photolysis, all the α-oxo ketene **25** had been destroyed with concomitant increases in the CO_2, CO, and ketene **28**. A weak absorption band at 2234 cm^{-1} was also present.

α-Oxo ketene *s*-*E*-**25** was also generated in the reaction of 2-*tert*-butylmalonyl chloride (**26**) and *tert*-Bu_2-

(15) (a) Maier, G.; Reisenauer, H.-P.; Sayraç, T. *Chem. Ber.* **1982**, *115*, 2192. (b) Maier, G.; Schäfer, U. *Liebigs Ann. Chem.* **1980**, 798.

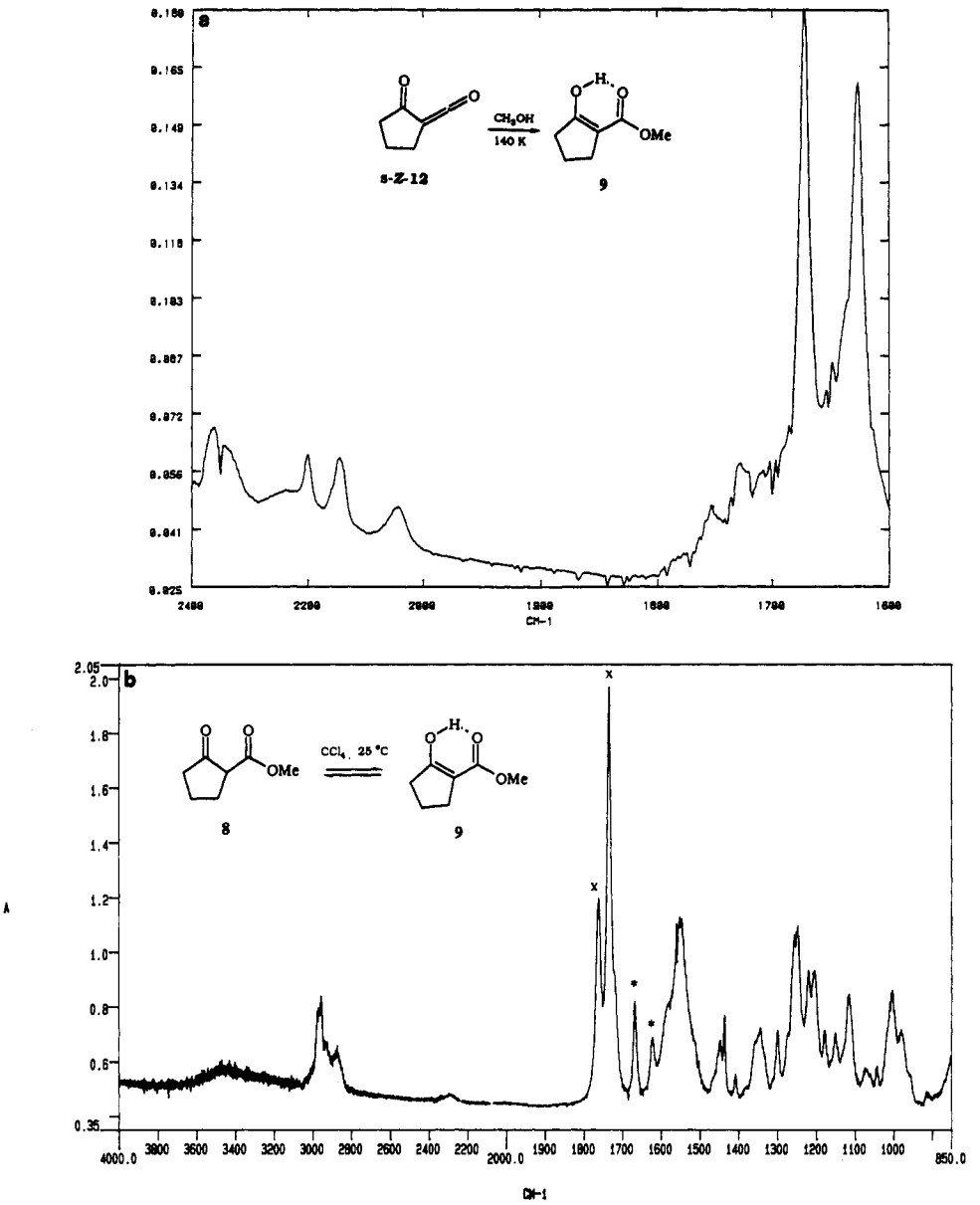
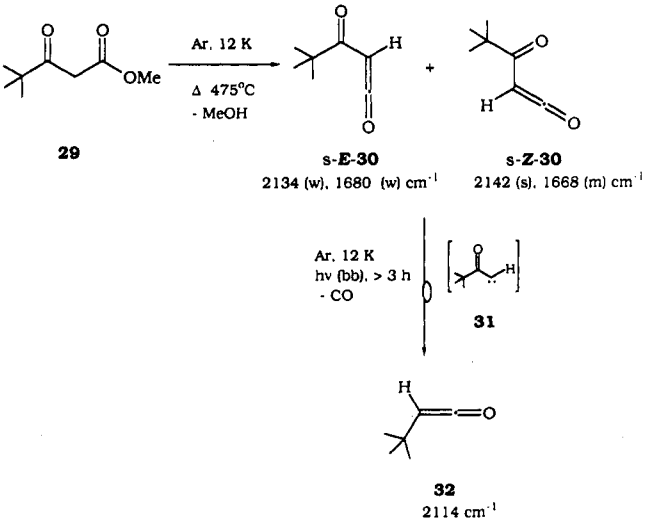


Figure 2. (a) IR spectrum of the reaction of **12** with methanol at 140 K which demonstrates the presence of enol **9** (1627, 1672 cm^{-1}). (b) IR spectrum of authentic **8** in CCl_4 showing the keto (**8**)(x)/enol (**9**)(*) mixture at room temperature (ratio 8:9 = 92:8 by ^1H NMR).

$(CuCN)Li_2$,[11i,16] (Figure 5b and Scheme IV), and results similar to those described above were obtained on prolonged irradiation.

Pivaloylketene (30). Analysis of the IR spectrum of the pyrolyzate of methyl 4,4-dimethyl-3-oxopentanoate (**29**) at 475 °C, condensed in an argon matrix at 12 K, revealed the presence of pivaloylketene (**30**) as a mixture of *s-Z* (2142 (s) and 1668 (m) cm^{-1}) and *s-E* conformers (2134 (w) and 1680 (w) cm^{-1}) as well as unreacted **29**. Broad-band photolysis of this mixture for 1.5 h resulted in the formation of *tert*-butylketene (**32**, 2114 cm^{-1} [lit.[15] (Ar) 2113 cm^{-1}) together with other unidentified absorptions in the ketene region. The formation of **32** corresponds to loss of CO (observed at 2137, 2149 cm^{-1}) from **30** followed by Wolff rearrangement of the resulting oxocarbene **31**. On warming to 200 K, all the peaks in the ketene region disappeared.

Scheme V



Discussion

Broad-band irradiation of the diazo compounds **11**, **19**, and **24** in argon matrices at 12 K cleanly afforded the corresponding α-oxo ketenes **12**, **20**, and **25**, respectively,

(16) Savage, G. P. Ph.D Thesis, The University of Queensland, 1988.

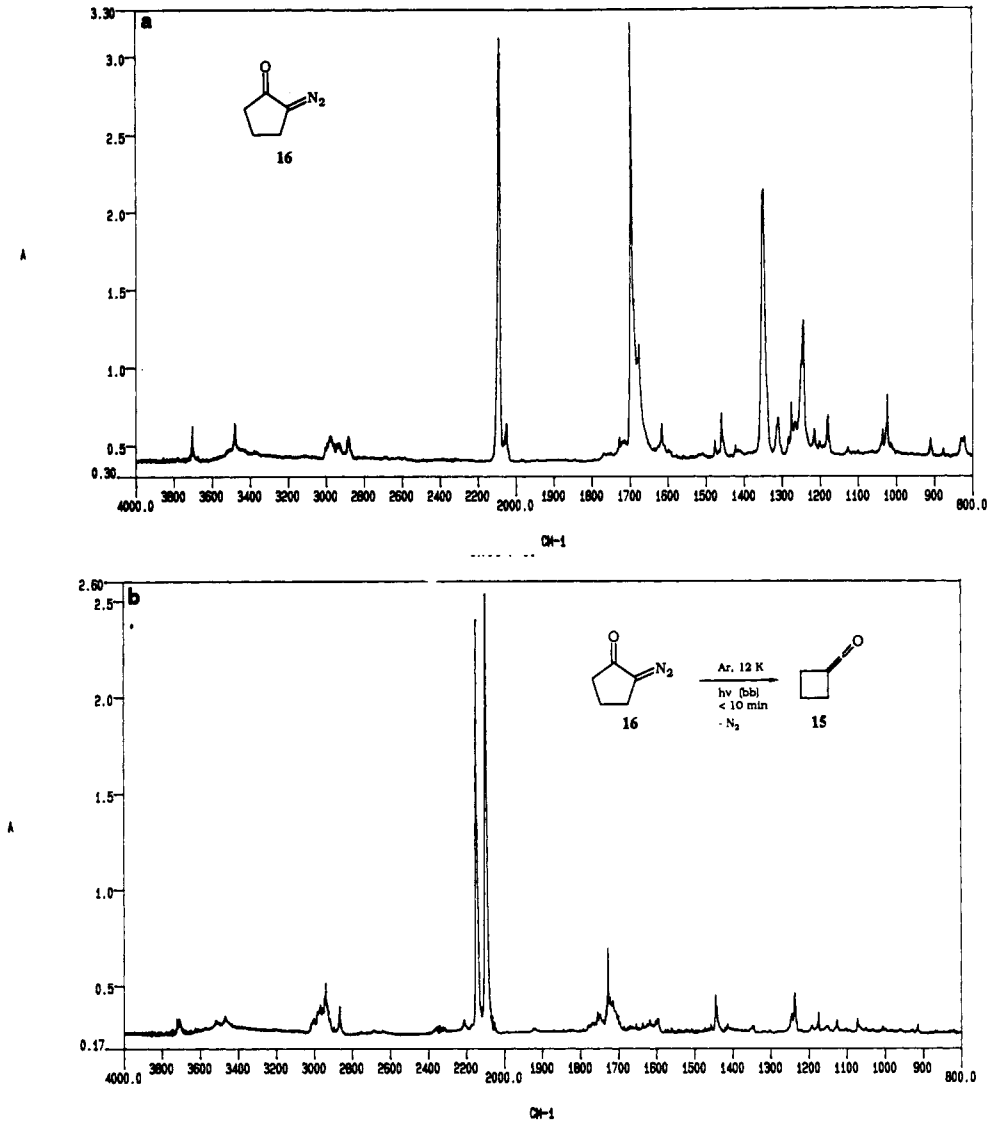


Figure 3. (a) IR spectrum of **16** in argon matrix at 12 K. (b) IR spectrum of **15** in argon matrix at 12 K.

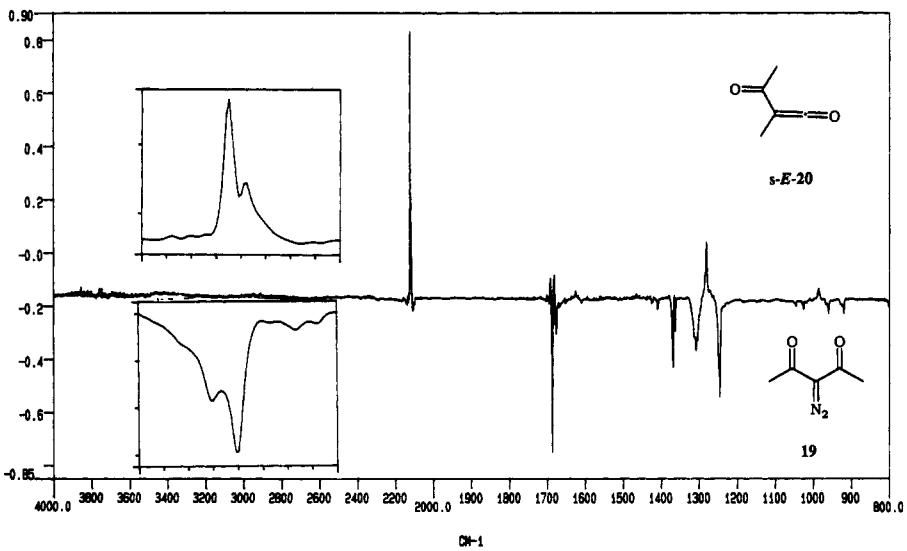


Figure 4. IR difference spectrum of *s*-*E*-**20** (top) and **19** (bottom); the inset (top) shows the expanded ketene region (2100–2140 cm^{-1}). The ν_{CNN} 2121 (s), 2125 (m) cm^{-1} does not appear in the negative difference spectrum due to its near coincidence with the ν_{CCO} of *s*-*E*-**20** at 2123 (vs), 2119 (m) cm^{-1}. These two bands are shown in the lower and upper insets, respectively.

in less than 10 min as monitored by low-temperature IR spectroscopy (Figures 1b, 4, and 5a). The difference spectra allowed the assignment of most of the frequencies associated with the α-oxo ketenes. The results obtained are very useful for the assignment of bands to the individual *s*-*Z* and *s*-*E* conformers of open-chain α-oxo ket-

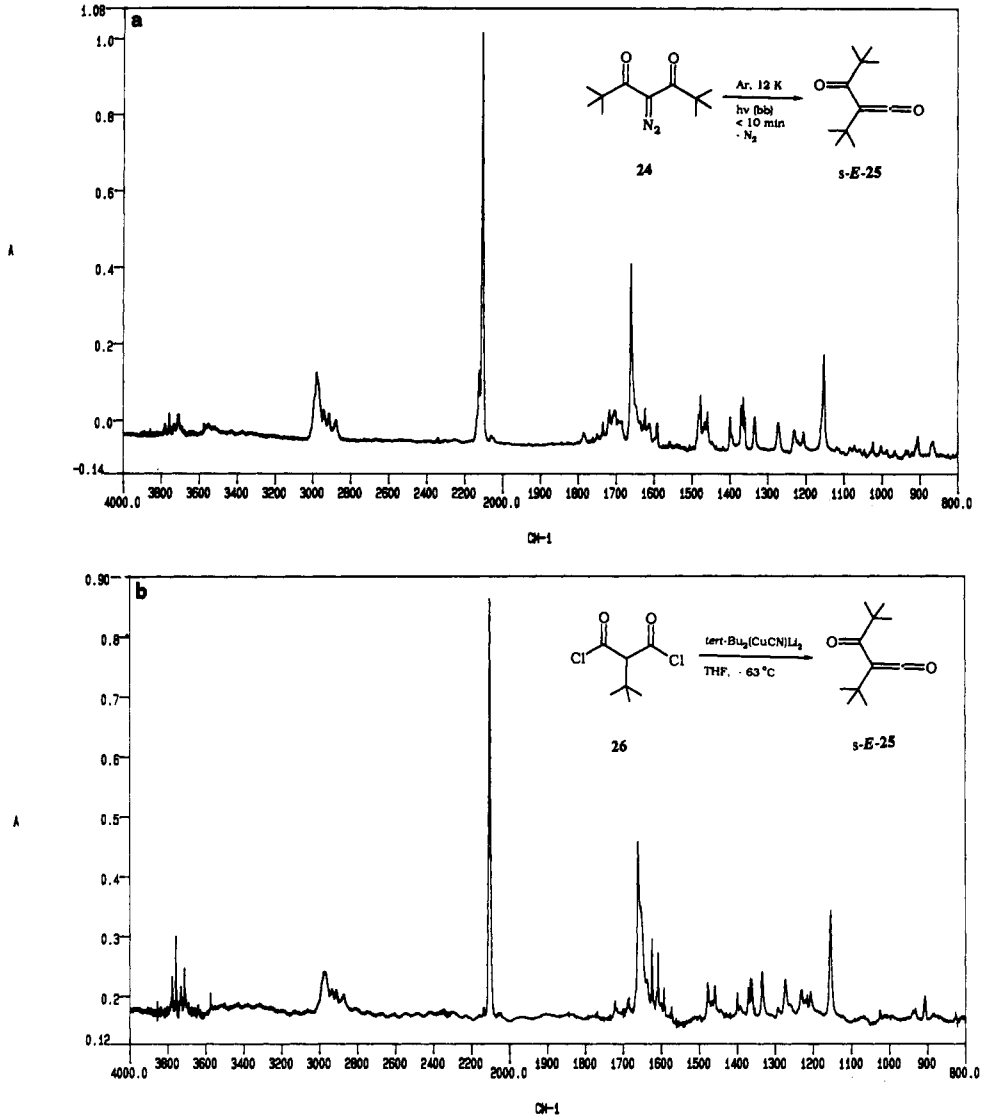


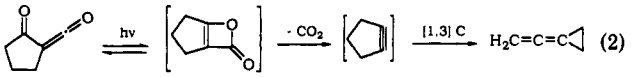
Figure 5. (a) IR spectrum of **25** from the photolysis of **24** in argon matrix at 12 K. (b) IR spectrum of **25** obtained from the reaction of **26** with $Bu_2(CuCN)Li_2$ followed by deposition in argon matrix at 12 K.

enes.[1b] The predominance of the various conformers of the α-oxo ketenes formed in the matrices probably reflects intrinsic thermodynamic preferences caused by steric hindrance. Thus, **12** is restricted by geometry to exist in the *s-Z* form. Steric hindrance makes the *s-E* forms of **20** and **25** the most stable, and these are the major or exclusive conformers seen. In **30**, steric hindrance favors the *s-Z* form, which again is the major conformer observed.

In all cases, prolonged irradiation of the α-oxo ketenes in Ar matrices at 12 K resulted in decarbonylation to the corresponding oxocarbenes, which then underwent Wolff rearrangement to the respective dialkylketenes (Schemes II–V). This supports earlier observations that prolonged broad-band irradiation of benzoylketene afforded phenylketene.[1a]

It was also noted that, in all cases, line broadening of the peaks in the IR spectra occurred on prolonged irradiation. This could be a consequence of the heat generated by photolysis resulting in partial evaporation of the argon with ensuing aggregation of the substrates. For example, the IR spectrum of isolated CO_2 in Ar matrix at 12 K shows two sharp and narrow peaks at ca. 2340 and 2345 cm^{-1}, but a broad peak at ca. 2343 cm^{-1} on aggregation.[11a]

Another possible reaction pathway for the decomposition of the α-oxo ketenes on photolysis is the cyclization to the unsaturated four-membered cyclic lactones which then lose CO_2 to afford acetylenes (eq 2).[17] This pathway would



s-Z-12 33 34 35

require the α-oxo ketenes to be in the *s-Z* form for cyclization. 2-Carbonylcyclopentanone (**12**) has the required *s-Z* geometry for such a reaction (eq 2), but our experimental results do not confirm such a pathway. The resulting acetylene would be the highly strained cyclopentyne **34**[2d,e] which theory predicted to have an IR frequency of 1828 cm^{-1} for the carbon triple bond.[18] Also, while the observation of cyclopentyne (**34**) may be difficult, neither the oxetone **33** (expected IR ca. 1900 cm^{-1}) nor the allene **35**[2e] were detectable in this case.

Acetyl(methyl)ketene (**20**) and *tert*-butyl(pivaloyl)ketene (**25**) are generated in the *s-E* forms from their respective diazo precursors. Isomerization to the *s-Z* forms would be required in order that cyclization to the oxet-2-ones and

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loss of CO_2 to give but-2-yne and di-*tert*-butylacetylene could occur, and we have no direct experimental evidence for such a pathway.

In all cases, on prolonged irradiation, an additional broad peak at 2234 cm^{-1} was observed. The intensity of the band was fairly pronounced during the photolysis of α-oxo ketenes **20** and **25** and fairly weak for **12** and **30**. From the analysis of the different IR spectra obtained, it seemed probable that in all cases the same species having a frequency of 2234 cm^{-1} was being produced on prolonged irradiation. This species could conceivably be C_3O but its intensity is too weak for a secure identification. The IR spectrum of an Ar matrix isolated C_3O is available[19] and shows a narrow peak at 2243 cm^{-1} and weaker bands at 1907 and 580 cm^{-1}.[19a,b] In our case, as stated earlier, it is very likely that on prolonged irradiation, the species under study were no longer isolated but aggregated, and frequency shifts are well documented under such conditions.[1j,10,11] In any event, the main reactions are formation of α-oxo ketenes and their decarbonylation to dialkylketenes.

Monitoring of the reaction of α-oxo ketene **12**, generated at 12 K in an argon matrix, with methanol provided compelling evidence for the initial formation of enol **9**, presumably via the rotamer **10** (eq 1 and Figure 2). Recently, the observation of a different type of carboxylic acid enols in the hydration of ketenes using laser flash photolysis and UV spectroscopy was reported.[20]

Conclusion

α-Oxo ketenes can be generated from the photolysis of symmetrically substituted α-diazo β-diketone precursors and can be directly observed by low-temperature FT-IR spectroscopy. This method is far superior to others (viz. dioxinones **2**, furandiones **3**, or β-keto esters **4**) since the IR spectra of the α-oxo ketenes are clean from other byproducts. On prolonged irradiation, the major reaction pathway is the loss of CO from the α-oxo ketenes to give oxocarbenes which then undergo Wolff rearrangement to afford dialkylketenes.

IR spectroscopic monitoring of the reaction between 2-carbonylcyclopentanone (**12**) and CH_3OH gave direct evidence for the initial formation of the enol **9**, which at higher temperatures (>200 K) tautomerized to the keto form (**8**) of methyl 2-oxocyclopentanecarboxylate (eq 1).

Experimental Section

Apparatus. The FVP apparatus employed a 10-cm length (0.8-cm i.d.) quartz tube in housings flanged to Leybold–Heraeus closed-cycle He cryostats (for Ar 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 precooled at −10 to −23 °C before vacuum deposition on BaF_2 or KBr disks. For matrix isolation (12 K), samples were codeposited with ca. 100 mbar of Ar in ca. 15 min, and for solid film (77 K), samples were deposited in ca. 10 min. Further details and apparatus for preparative FVP were as previously described.[21]

IR spectra were recorded on a Perkin-Elmer 1700X FT-IR spectrometer at a resolution of 1 cm^{-1}; UV spectra were recorded on a Varian Cary 1 and NMR spectra on a JEOL GX400 spectrometer (400 MHz for ^1H; 100.6 for ^{13}C). Gas chromatographic (GC) analyses were conducted on a SE-32 column and are reported as relative peak areas without correction for detector response. Chromatographic separations were performed using flash chromatography[22] on silica gel. Irradiations were carried out with a high-pressure Xe-Hg lamp (1000 W, Hanovia).

Materials. Unless otherwise indicated, materials were from commercial suppliers and were used without further purification.

3-Diazopentane-2,4-dione (19) was prepared according to the procedure reported by Regitz[6] in 70% yield after purification by flash chromatography using a mixture of hexane and ethyl acetate (4:1) as eluent: IR (film) 817, 932, 965, 1025, 1142, 1240, 1306, 1367, 1667, 2127 (vs), 2264 (w), 3007 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.3 (s).

Methyl 2-methyl-3-oxobutanoate (21) was obtained by transesterification[23] of the corresponding commercial ethyl ester (Aldrich) in acidic methanol: IR (CCl_4) 1723, 1749 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (d, 3 H, J = 7.1 Hz), 2.2 (s, 3 H), 3.5 (q, 1 H, J = 7.1 Hz), 3.7 (s, 3 H, O*Me*).

2-Diazocyclohexane-1,3-dione (11)[5] was prepared from cyclohexane-1,3-dione (Aldrich) and tosyl azide[24] in 60% yield after purification by flash chromatography using a mixture of hexane and ethyl acetate (1:4) as eluent: mp 48–50 °C (lit.[25] mp 47–48 °C); UV (CH_3OH) λ_{max} 229, 258, nm; IR (CCl_4) 997, 1064, 1178, 1237, 1288, 1315, 1349, 1419, 1656, 2134 (vs), 2195 (m), 2957 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.9 (m, 2 H), 2.4 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 18.2 (CH_2CH_2CO), 36.5 (CH_2CH_2CO), 84.4 (*C*=N), 190.1 (C=O).

4,5,6,7-Tetrahydrocyclopenta-1,3-dioxin-4-one (13) was prepared following the procedure described by Jäger[2b] in 60% yield after purification by flash chromatography using a mixture of hexane and ethyl acetate (4:1) as eluent: IR (film) 889, 987, 1012, 1089, 1147, 1202, 1256, 1377, 1418, 1646, 1735, 2945 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6 (s, 6 H, 2Me), 1.9 (m, 2 H, $CH_2CH_2CH_2$), 2.5 (m, 4 H, $CH_2CH_2CH_2$).

2-Diazocyclopentanone (16) was prepared according to the literature procedure[13] and was purified by flash chromatography using a mixture of hexane and ethyl acetate (3:2) as eluent: IR (film) 1022, 1178, 1214, 1243, 1351, 1459, 1698, 2049 (w), 2091 (vs), 2977 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.1 (m, 2 H, $CH_2CH_2CH_2$), 2.4 (t, 2 H, CH_2C=O), 3.1 (t, 2 H, CH_2C=N); ^{13}C NMR ($CDCl_3$) δ 19.5 ($CH_2CH_2CH_2$), 24.1 (CH_2C=N), 37.2 (CH_2C=O), 58.0 (*C*=N), 200.2 (*C*=O).

4-Diazo-2,2,6,6-tetramethylheptane-3,5-dione (24) was prepared in five steps following the procedure described by Nicolaev et al.[7] and was purified by flash chromatography using a mixture of hexane and ethyl acetate (4:1) as eluent: IR (CCl_4) 920, 993, 1010, 1052, 1162, 1199, 1370, 1394, 1465, 1480, 1661, 2111 (vs), 2975 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2 (s); ^{13}C NMR ($CDCl_3$) δ 26.4 ($C(CH_3)_3$), 45.1 ($C(CH_3)_3$), 79.9 (*C*=N), 198.6 (*C*=O).

FVP of 8. A sample of precooled (−10 °C) methyl 2-oxocyclopentanecarboxylate (**8**) (Aldrich) was pyrolyzed at 650 °C and codeposited with ca. 100 mbar of Ar on a BaF_2 disk at 12 K in 15 min. The IR spectrum revealed the formation of 2-carbonylcyclopentanone (**12**, 2133, 1708 cm^{-1}) as well as unreacted **8** (1717, 1740 cm^{-1}) and CH_3OH (1034, 3526 cm^{-1}).

FVP of 13. (i) The IR spectrum of the pyrolyzate at 400 °C of 4,5,6,7-tetrahydrocyclopenta-1,3-dioxin-4-one (**13**) in an Ar matrix at 12 K (10^{-5} mbar) revealed the formation of α-oxo ketene **12** (2133, 1708 cm^{-1}) and acetone (1721 cm^{-1}).

(ii) 50 mg of **13** was pyrolyzed at 650 °C (10^{-4} mbar), and the products were collected on a N_2 cooled cold-finger previously sprayed with a 10% solution of methanol in CCl_4. On warming, the pyrolyzate mixture was collected and analyzed by GC and IR. The major and near-exclusive product (>85% by GC) was found to be methyl 2-oxocyclopentanecarboxylate (**8**) which had spectral data (1622, 1668 cm^{-1} for the enol form **9**, and 1735, 1762 cm^{-1} for the keto form **8**) in agreement with authentic material.

Photolysis of 11. (i) IR monitoring of the broad-band photolysis of 2-diazocyclohexane-1,3-dione (**11**) (Ar, 12 K, 10^{-5} mbar)

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showed that 11 had completely decomposed to the α-oxo ketene (12) in less than 10 min. 11: IR (Ar, 12 K) 995, 1068, 1178, 1240, 1293, 1317, 1609, 1668, 2137 (vs) 2157 (w), 2205 (w) cm^{-1}. 12: IR (Ar, 12 K) 1171, 1186, 1382, 1709, 2134, 2986 cm^{-1}. On increasing the irradiation time to 3 h, inspection of the resulting IR spectrum showed a decrease of the intensity of the peak at 2134 cm^{-1} (12) with concomitant formation of carbonylcyclobutane (15, 2150 (s), 2098 (s) cm^{-1}), CO_2 (2343 cm^{-1}), and CO (2138 cm^{-1}). After 20 h of photolysis, the IR spectrum showed the absence of 12, but the presence of CO_2, CO, 15, and a weak band at 2234 cm^{-1}.

(ii) **Generation of Enol 9.** A sample of 2-diazocyclohexane-1,3-dione (11) was codeposited in a stream of Ar on a BaF_2 disk at 12 K (10^{-5} mbar). Broad-band irradiation for less than 10 min converted 11 to 2-carbonylcyclopentanone (12) as shown by IR spectroscopy. A layer of CH_3OH precooled to −23 °C (CCl_4/N_2 slurry) was vacuum deposited on top of the Ar matrix on the BaF_2 disk. The vacuum line was closed and argon introduced. Then the mixture on the disk was allowed to warm while the reaction was being monitored by IR spectroscopy. At 12 K, the ketene bands were at 2131 and 1689 cm^{-1}. Reaction started at ca. 100 K, and the IR spectrum showed the presence of α-oxo ketene 12 as well as methyl 2-oxocyclopentanecarboxylate in the enol form (9, 1619 and 1665 cm^{-1}) and a small amount of the keto form (8, 1726, 1752 cm^{-1}). At 140 K, all of the ketene had reacted while the peaks corresponding to the enol form 9, now shifted to 1627 and 1672 cm^{-1}, had increased in intensity. At 200 K, the enol 9 was the major component present with a small amount of the keto form 8 (1725, 1753 cm^{-1}).

For comparison purposes, the IR and NMR spectra of authentic methyl 2-oxocyclopentanecarboxylate (Aldrich) were recorded: IR (CCl_4) keto 8 1734, 1763; enol 9 1622, 1667 cm^{-1}; IR (film) 1725, 1757; 1622, 1659 cm^{-1}; IR (77 K) 1720, 1748; 1619, 1658 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.51 (OMe of the keto form 8); 3.44 (OMe of the enol form 9). The ratio of the integrated peaks is 8:9 = 92:8.

Photolysis of 16. Monitoring by IR spectroscopy of the broad band photolysis of 2-diazocyclopentanone (16) (Ar, 12 K, 10^{-5} mbar) revealed that 16 had completely decomposed to carbonylcyclobutane (15) in less than 10 min. 15: IR (Ar, 12 K) 1072, 1125, 1174, 1237, 1444, 1594, 2090, 2101, 2145, 2151, 2939 cm^{-1}. 16: IR (Ar, 12 K) 910, 1021, 1179, 1215, 1243, 1349, 1459, 1615, 1698, 2050 (w), 2089 (vs), 2936 cm^{-1}. On warming, the IR spectrum showed a gradual shift of the ketene bands which at the same time diminished in intensity in concert. Thus, at 60 K, the pairs of peaks corresponding to 2090, 2101 and 2145, 2151 cm^{-1} at 12 K had coalesced and shifted to 2084 and 2133 cm^{-1} while diminishing in intensity in concert; at 90 K, the peaks were at 2078 and 2129 cm^{-1}; and at 110 K they had completely vanished.

FVP of 17. (i) The pyrolyzate of cyclobutylcarbonyl chloride (17; Aldrich) at 700 °C was codeposited with Ar (ca. 100 mbar, 15 min) on a BaF_2 disk at 12 K (10^{-5} mbar). The IR spectrum showed the presence of CO_2 (2338 cm^{-1}) and carbonylcyclobutane (15) (2085, 2089, 2099, 2133, 2137, 2149 cm^{-1}) as well as a small amount of 17 (1761, 1799 cm^{-1}). On warming to 50 K, the two triads at 2133, 2137, 2149 and 2085, 2089, 2099 cm^{-1} at 12 K had coalesced to a pair of peaks at 2131 and 2082 cm^{-1}, and the intensity diminished in concert as observed in the case described above for the photolysis of 16. At 110 K, the ketene bands disappeared.

(ii) 50 mg of cyclobutylcarbonyl chloride (17) was pyrolyzed at 700 °C over a period of 1.5 h (10^{-4} mbar). The pyrolyzate was condensed in a trap containing a 10% solution of EtOH in CCl_4, cooled to −63 °C ($CHCl_3/N_2$ slurry), connected to a second trap cooled in liquid N_2. On warming, the pyrolyzate mixture in the first trap was collected, and a white insoluble solid was filtered off. The filtrate was concentrated in vacuo and the residue analyzed by GC, IR, and NMR. It was found to be essentially (>90% by ^1H NMR) ethyl cyclobutylcarboxylate (18) which had spectral data (IR, NMR) in agreement with authentic material.

Photolysis of 19. A sample of precooled (−23 °C) 3-diazopentane-2,4-dione (19) was codeposited with ca. 100 mbar Ar in 15 min at 12 K (10^{-5} mbar) on a BaF_2 disk. Photolysis by broad-band irradiation was monitored by IR spectroscopy which showed complete decomposition of 19 to give acetyl(methyl)ketene (*s-E*-20) in less than 10 min. 19: IR (Ar, 12 K) 919, 1245, 1308, 1363, 1368, 1686, 2121 (s), 2125 (m) cm^{-1}. *s-E*-20: IR (Ar, 12 K) 913, 986, 1281, 1362, 1686, 2119 (m), 2123 (vs) cm^{-1}. After 3 h of photolysis with broad-band irradiation, the IR spectrum showed the presence of CO_2 (2345 cm^{-1}), CO (2137, 2149 cm^{-1}), and a band at 2235 cm^{-1}. After 16 h of photolysis, the IR spectrum revealed that all the α-oxo ketene 20 had been destroyed, while the amount of CO_2 and the band at 2234 cm^{-1} had increased. Also present were CO (2137, 2149 cm^{-1}) and dimethylketene (23, 2126 cm^{-1}) [lit. (Ar) 2124[15] cm^{-1}; 2128[10] cm^{-1}].

FVP of 21. The pyrolyzate of methyl 2-methyl-3-oxo-butanoate (21) at 700 °C was deposited in a stream of Ar (100 mbar in 15 min) on a BaF_2 disk at 12 K (10^{-5} mbar). Analysis of the IR spectrum showed the presence of acetyl(methyl)ketene (20) as a mixture of *s-E* (2123 (s), 2120 (s), 1684 (s) cm^{-1}) and *s-Z* (2131 (w), 1666 (w)) isomers as well as unreacted 21 (1751, 1717 cm^{-1}). The matrix mixture was irradiated with broad-band UV light for 16 h, and the resulting IR spectrum was similar to the one described for the photolysis of 3-diazopentane-2,4-dione (19; see above).

Photolysis of 24. A sample of 4-diazo-2,2,6,6-tetramethylheptane-3,5-dione (24) was codeposited with Ar at 12 K (10^{-5} mbar) and photolyzed by broad-band irradiation for 10 min. The IR spectrum demonstrated complete decomposition of 24 to *tert*-butyl(pivaloyl)ketene (*s-E*-25). 24: IR (Ar, 12 K) 1156, 1676, 2117 cm^{-1}. 25: IR (Ar, 12 K) 1154, 1365, 1479, 1661, 2104 cm^{-1}. After 3 h of photolysis, CO_2 (2345 cm^{-1}), CO (2137, 2148 cm^{-1}), di-*tert*-butylketene (28, 2092 cm^{-1} [lit. (Ar) 2104 (s), 2090 (m)[15] cm^{-1}; 2095[10] cm^{-1}]) and 25 were present. After 22 h of photolysis, 25 was completely destroyed, while the intensity of the peaks corresponding to CO_2, CO, and di-*tert*-butylketene (28) had increased. A weak peak at 2234 cm^{-1} was detected as well. Similar results were obtained with 25 prepared from *tert*-butyl malonyl chloride (26) and *tert*-$Bu_2(CuCN)Li_2$.[1i,16]

FVP of 29 and Photolysis of 30. The pyrolyzate of methyl 4,4-dimethyl-3-oxopentanoate (29) at 475 °C was deposited in a stream of Ar on a BaF_2 disk at 12 K (10^{-5} mbar). The IR spectrum showed the formation of pivaloylketene (30) as a mixture of *s-Z* (2142 (s), 1668 (m) cm^{-1}) and *s-E* (2134 (w), 1680 (w) cm^{-1}) conformers as well as unreacted 29 (1717, 1764 cm^{-1}).

The matrix mixture was irradiated with broad-band UV light for 1.5 h, after which time the presence of 30, CO_2 (2345 cm^{-1}), CO (2149, 2137 cm^{-1}), and *tert*-butylketene (32, 2114 cm^{-1} [lit.[15] (Ar) 2113 cm^{-1}]), as well as a weak band at 2234 cm^{-1} were observed. On warming to 200 K, all the bands in the 2000–2400 cm^{-1} region had vanished.

Acknowledgment. This research was supported by the Australian Research Council.