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# Reactivity of Carbenes and Ketenes in Low-Temperature Matrices. Carbene CO Trapping, Wolff Rearrangement, and Ketene–Pyridine Ylide (Zwitterion) Observation

Peter Visser, Ralf Zuhse, Ming Wah Wong, and Curt Wentrup\*

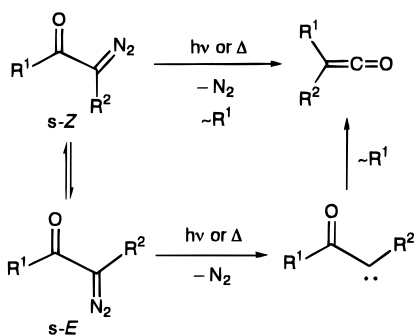
Contribution from the Department of Chemistry, The University of Queensland, Brisbane Qld 4072, Australia

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**Abstract:** Dicarboxyketenes **8a** and **8b** are obtained by photolysis of diazo esters **7** in cryogenic matrices or by FVT of **7** followed by matrix isolation. The photochemical Wolff rearrangement of diazomalones **1** in Ar matrix at temperatures as low as 6.5 K produces alkoxy(alkoxycarbonyl)ketenes **3**, also obtained by FVT of **1**. Photolysis of **1** in CO matrix at  $\geq 6.5$  K produces the dicarboxyketenes **8**. Ketenes **3**, **8**, and **12** react with pyridine above 40 K to produce ketene–pyridine ylides (zwitterions) **9**, **10**, and **13**, respectively.

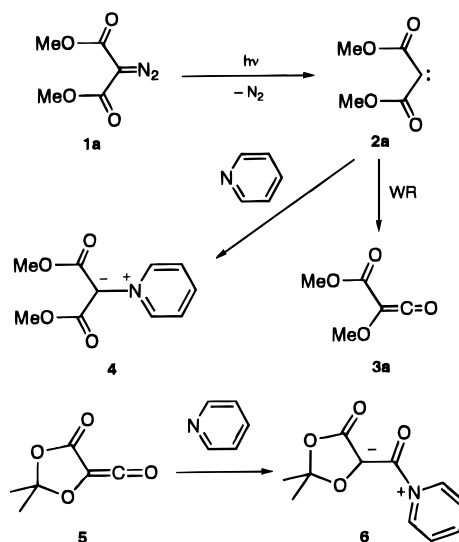
## Introduction

The detailed mechanism of the Wolff rearrangement (WR)<sup>1</sup> is a matter of much current interest. Kaplan *et al.*<sup>2</sup> suggested that *s*-Z diazo carbonyl compounds undergo WR to ketenes concerted with N<sub>2</sub> elimination, whereas the *s*-E forms react in a stepwise manner via the (singlet) carbenes. This view has been adopted by other authors,<sup>3</sup> sometimes to the extent that the existence of singlet oxocarbenes as discrete intermediates was denied.<sup>3d,e</sup>



Important evidence for the existence of (singlet) (di)carboxyketenes as discrete intermediates was reported recently.<sup>4</sup> Laser flash photolysis (LFP) at room temperature demonstrated that singlet dicarbomethoxycarbene (**2a**), formed by photolysis of diazomalonnate **1a**, was trappable with pyridine in competition with WR, so that each carbene molecule was captured when [pyridine] > 0.4 M. The rate constant for WR could be estimated to be of the order of 10<sup>9</sup> s<sup>−1</sup>. Intersystem

crossing to the triplet carbene was negligible under these conditions. No carbene was directly observed. The pyridine trapping reaction led to an ylide **4**, detected by UV–vis spectroscopy. There was no evidence for the alternative trapping of ketene **3a** by pyridine. In contrast, in the case of photolysis of diazo-Meldrum's acid, WR was faster than carbene–pyridine trapping, with the result that ketene **5** was being trapped, giving a so-called ketene–pyridine ylide (correctly: zwitterion) **6**, the latter detected via its UV absorption.<sup>4</sup>



So far, the detection of carbene–pyridine and ketene–pyridine ylides of types **4** and **6** has been by transient UV–vis spectroscopy.<sup>4,5</sup> It is of interest to obtain infrared spectroscopic data for such ylides for better structural information. We have recently demonstrated that carbocyclic ketene–pyridine ylides can be generated and observed in low-temperature matrices.<sup>6</sup> We now report the first IR spectroscopic observation of ylide

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, November 15, 1996.  
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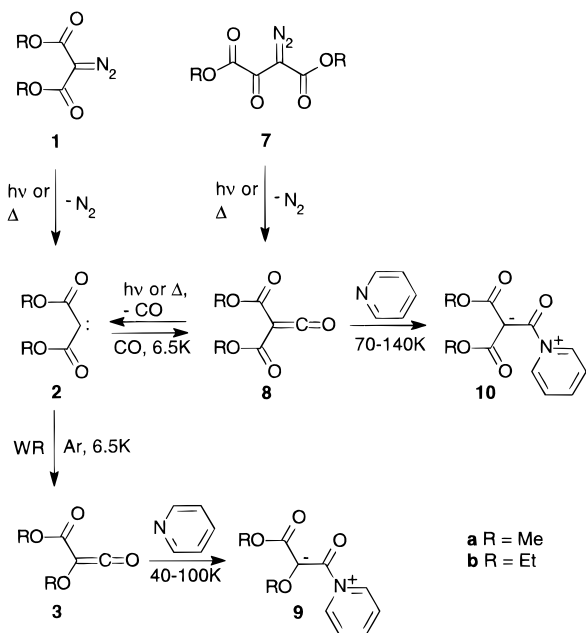
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## Scheme 1



formation from  $\alpha$ -oxoketenes in pyridine matrices (**9**, **10**, and **13**).

In addition, we report definitive proof for the trapping of carbenes **2** with carbon monoxide to produce ketenes **8**. McCluskey and Dunkin reported photolyses of **1a** in Ar and CO matrices.<sup>7</sup> In Ar matrix, WR to **3a** ( $\nu = 2135 \text{ cm}^{-1}$ ) occurred as expected. In pure CO or Ar–CO matrices containing  $\geq 5\%$  CO, the WR was apparently suppressed, and a new ketene absorbing at  $2166 \text{ cm}^{-1}$  was observed instead. It was suggested that the  $2166\text{-cm}^{-1}$  absorption was due to **8a** (see Scheme 1), formed by trapping of carbene **2a** with CO. **2a** itself was not observable. These workers did not generate matrices of authentic ketene **8a**, and therefore the proof that carbene **2a** is really being diverted to **8a** still eludes us.

We have shown elsewhere that  $\alpha$ -oxoketenes are subject to pronounced photoinduced matrix site effects.<sup>8</sup> This makes a proof of the identity of ketene **8a** all the more essential. Note also that the  $2135\text{-cm}^{-1}$  band of **3a**, if extant, is not observable in the presence of CO, which absorbs strongly near  $2138 \text{ cm}^{-1}$ . In connection with our interest in  $\alpha$ -oxoketenes,<sup>9</sup> we have carried out matrix isolation studies of the stable (but exceedingly reactive) dicarbethoxyketene (**8b**), prepared from diazo ester **7b** according to Staudinger.<sup>10</sup> We have investigated the matrix photolyses as well as the flash vacuum thermolyses<sup>11</sup> (FVT) of diazo compounds **1** and **7** and established the identity of ketenes **8** from these two sources.

## Results and Discussion

Photolysis of Ar matrix isolated **1a** at temperatures as low as 6.5 K, but usually at 10–13 K, generated the WR ketene

**Table 1.** Infrared Spectroscopic Data ( $\text{cm}^{-1}$ ) of **3a** in Ar and CO Matrices

photolysis of <b>1a</b> <sup>a</sup>	Ar matrix		CO matrix
	FVT of <b>1a</b> <sup>b</sup>		FVT of <b>1a</b> <sup>c</sup>
3015 w	3014 w		3011 vw
2986 w	2985 w		2982 vw
2966 w	2966 w		2962 w
2947 w	2947 w		2942 vw
2847 w	2846 w		2844 vw
2136 vs	2136 vs		2135 <sup>d</sup> s
2123 m	2123 m		2120 s
	2121 m		
1745 s	1746 s		1737 vs
1709 m	1741 m		1718 m
1443 m	1442 m		1443 m
1346 m	1345 m		1345 m
1311 m	1313 m		1313 m
1198 m	1201 m		1202 m
1131 s	1134 s		1131 s
1023 w	1022 w		1018 w
1008 w	1008 w		1006 w
755 w	756 w		756 w

<sup>a</sup> 30 min broadband irradiation of **1a** matrix isolated in Ar at 13 K.

<sup>b</sup> FVT of **1a** with Ar at 400 °C and matrix isolation in Ar at 13 K.

<sup>c</sup> FVT of **1a** with CO at 400 °C and matrix isolation in CO at 13 K.

<sup>d</sup> This band was obscured by the absorptions of CO in the spectrum, but was revealed after evaporation of the CO on warming to ca. 75 K.

**3a**. The conversion was complete in 30 min using broadband irradiation from a high-pressure Hg–Xe lamp. Identification of all the bands in the IR spectrum due to **3a** was based on three criteria: (i) ketene **3a** could be bleached on extensive irradiation (11 h) with concomitant formation of CO ( $2139 \text{ cm}^{-1}$ ); (ii) the same IR spectrum of **3a** was obtained by FVT of **1a** at 400 °C with Ar matrix isolation of the product; (iii) the observed IR spectrum is in good agreement with density functional calculations at the B-LYP/6-31G\* level of theory. The experimental spectra are tabulated in Table 1; the theoretical spectra are given in Table 6 in the Supporting Information. Since the ketenes can exist in several different conformations, IR spectra were calculated for three major forms. Our experimental data do not permit an evaluation of conformational preferences. All the major calculated bands are matched by observed ones. Some additional experimental bands, particularly in the  $\nu_{\text{C}=\text{C}=\text{O}}$  region, are undoubtedly due to matrix site effects.<sup>8</sup> Small shifts due to different matrix hosts and different methods of matrix preparation (photolysis versus FVT) are to be expected. The major  $\nu_{\text{C}=\text{C}=\text{O}}$  of **3a** at  $2136, 2124 \text{ cm}^{-1}$  (Ar) and some of the other bands due to **3a** are in agreement with the observations of McCluskey.<sup>7</sup>

The Ar matrix IR spectrum of **8a** was obtained by (i) matrix photolysis of **7a** (broadband, 15 min) and (ii) FVT of **7a** (Ar, 500 °C). Due to the extreme sensitivity of ketene **8a** toward moisture, the above methods were preferable to the isolation of neat **8a** followed by matrix deposition. The IR data for **8a** are given in Table 2 and show good agreement with the calculated spectra for three different conformers given in Table 7 in the Supporting Information. As predicted by theory, the  $\nu_{\text{C}=\text{C}=\text{O}}$  of **8** is found at higher wavenumbers than those of **3**.

The Ar matrices of the ethyl analogs **3b** and **8b** were similarly prepared by photolysis and FVT of **1b** and **7b**, respectively. Since **8b** is isolable as a neat liquid<sup>10b</sup> (albeit extremely sensitive), this compound was also itself deposited as a pure substance in Ar. The experimental IR spectra are given in Tables 4 and 5 and the theoretical spectra in Tables 8 and 9 in the Supporting Information.

Photolysis of **1a** and **1b** in CO and Ar–CO matrices generated the CO-trapped ketenes **8** rather than the WR ketenes

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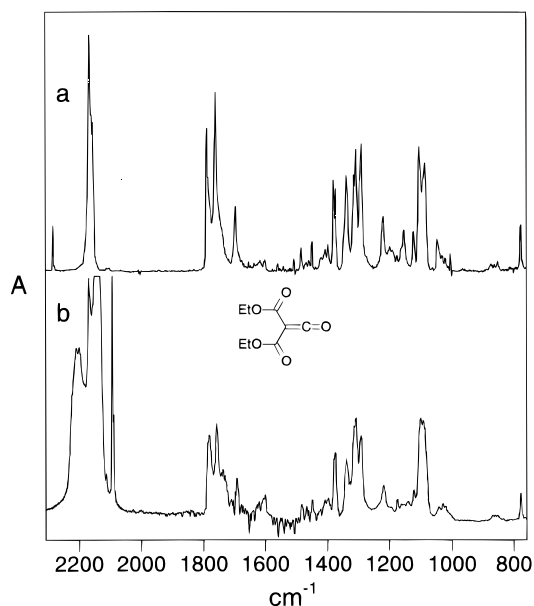
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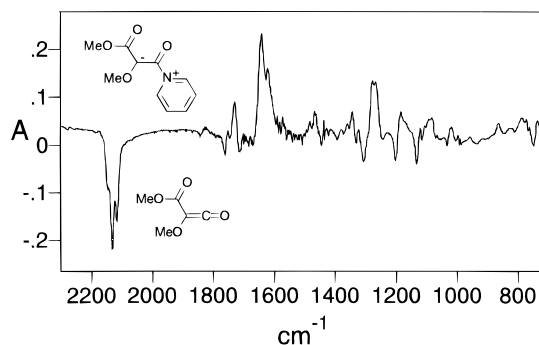
**Table 2.** Infrared Spectroscopic Data ( $\text{cm}^{-1}$ ) of **8a** in Ar and CO Matrices

CO matrix		Ar/CO matrix	Ar matrix	CO matrix	Ar matrix
photolysis of <b>1a</b> <sup>a</sup>	photolysis of <b>7a</b> <sup>b</sup>	photolysis of <b>1a</b> <sup>c</sup>	photolysis of <b>7a</b> <sup>d</sup>	FVT of <b>7a</b> <sup>e</sup>	FVT of <b>7a</b> <sup>f</sup>
3044 vw	3047 w	3045 vw	3041 w	3041 w	3039 w
3013 vw	3014 vw	3015 vw	3014 w	3011 w	3016 w
2963 w	2964 w	2967 w	2965 m	2963 m	2962 w
2852 vw	2853 vw		2852 w	2851 vw	2852 vw
	2174 s				
2166 vs	2167 vs	2165 vs	2167 vs	2165 vs	2163 vs
1798 m	1798 w	1798 m	1805 m	1793 w	1805 m
1782 s	1782 m	1783 s	1789 s	1782 s	1791 s
1763 m	1761 s	1762 m	1768 s	1763 s	1771 s
1700 w	1699 m	1701 w	1702 m	1698 w	1703 m
1442 m	1444 m	1443 m	1442 m	1442 m	1442 m
1322 s	1322 s	1322 s	1323 m	1322 m	1323 m
1195 m	1195 m	1194 m	1192 m	1194 m	1194 m
1104 m	1104 m	1105 m	1105 m	1104 m	1104 s
1093 m	1094 m	1094 s	1097 m	1091 m	1092 m
780 m	780 m	780 m	778 m	779 m	779 m

<sup>a</sup> 45 min broadband irradiation of **1a** matrix isolated in CO at 13 K.<sup>b</sup> 20 min broadband irradiation of **7a** matrix isolated in CO at 13 K.<sup>c</sup> 15 min broadband irradiation of **1a** matrix isolated in an Ar/CO (5%) doped matrix at 6.5 K. <sup>d</sup> 15 min broadband irradiation of **7a** matrix isolated in Ar at 13 K. <sup>e</sup> FVT of **7a** with CO at 500 °C and matrix isolation in CO at 13 K. <sup>f</sup> FVT of **7a** with Ar at 500 °C and matrix isolation in Ar at 13 K.**Figure 1.** FTIR spectra of (a) authentic **8b** in Ar at 13 K; (b) **8b** generated by photolysis of **1b** (20 min) in a CO doped (5%) Ar matrix at 6.5 K. The sharp peak at  $2167\text{ cm}^{-1}$  is due to the  $\text{C}=\text{C}=\text{O}$  stretching vibration of ketene **8b**.

**3.** This is clearly seen by comparison with the authentic ketenes (Figure 1 and Table 2 as well as Table 5 in the Supporting Information). The data for **8a** (Table 2) reveal that this was indeed the species observed by McCluskey.<sup>7</sup> FVT of **7** with codeposition of the product in CO matrix also allowed the preparation of CO matrices of **8**. Similar FVT of **1** with CO as carrier gas (*ca.*  $10^{-3}$  mbar) gave the WR product **3** and none of the trapped ketenes **8**.

Continued irradiation of **8** (11 h) in Ar matrix caused elimination of CO ( $2139\text{ cm}^{-1}$ ) with the IR spectrum of **8** vanishing. This suggests the formation of carbene **2** and consequently the WR ketene **3** on photolysis of **8**. Since **3** itself is destroyed on extensive photolysis, only the photodecomposition products of **3** were observed, *inter alia* a small peak at  $2235\text{ cm}^{-1}$ . Ketenes **8a** and **8b** also eliminate CO on FVT

**Figure 2.** Difference FTIR spectrum showing formation of ylide **9a** (positive peaks) after warmup (40–100 K) of photochemically generated ketene **3a** (negative peaks) in the presence of pyridine.

above  $500\text{ °C}$ , causing the appearance of new signals at  $2139\text{ cm}^{-1}$  (CO) and  $2134\text{ cm}^{-1}$  (**3a**) or  $2126\text{ cm}^{-1}$  (**3b**).

When **8a** is extensively irradiated for 19 h in CO matrix, a small peak due to **3a** is observed at  $2135\text{ cm}^{-1}$ . This peak was made observable by warming the matrix to 75 K in order to let the CO evaporate. We interpret this as follows: photolysis of **8** causes CO elimination and formation of carbene **2**. Most of carbene **2** is again trapped by the CO matrix, regenerating and preserving **8**. In the long run, the Wolff rearrangement of **2** becomes detectable, generating small amounts of **3**. **3** itself photodecarbonylates (leading to decomposition products in Ar matrix), but the resulting carbene is again trapped by CO, thereby preserving **3** for IR spectroscopic observation.

During the irradiation of **8a** in CO matrix, the band at  $2174\text{ cm}^{-1}$  decreased faster than the one at  $2167\text{ cm}^{-1}$ ; this indicates that the two peaks are due to different conformers or sites of **8a**.

Ketenes **3a** also decarbonylated on FVT above  $500\text{ °C}$ . CO formation was testified by absorptions at  $2139$  and  $2149\text{ cm}^{-1}$ . The bands due to ketene **3a** decreased dramatically in intensity, but no new ketene (dimethoxyketene<sup>11a</sup>) was observed.<sup>12</sup>

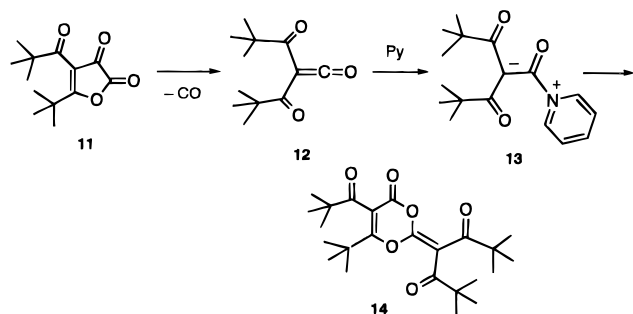
We now turn to the trapping of ketenes **3** and **8** with pyridine. For this purpose, diazo compound **1a** was deposited in a pyridine matrix at 6.5 K. Irradiation for 1.5 h generated the WR ketene **3a** ( $2134\text{ cm}^{-1}$ ) with the usual intensity relative to **1a**. There was no evidence of the carbene **2a** being trapped to form an ylide **4**. In contrast, warming of the pyridine matrix of **3a** above 40 K caused slow reaction with the generation of a new species absorbing at  $1730$ ,  $1643$ , and  $1279\text{ cm}^{-1}$  in the IR (Figure 2). The rate of reaction increased on further warming to 90 K. At 100 K all the ketene had reacted with pyridine. We ascribe the new absorptions to the ketene ylide **9a**. We have recently observed the reaction of other ketenes with pyridine at temperatures as low as 15 K.<sup>6</sup> These reactions have very low activation enthalpies and large, negative activation entropies due to the matrix environment. The absorptions of ylide **9a** vanished again on further heating above 160 K. Ketene **3b** ( $2122\text{ cm}^{-1}$ ) formed an analogous ylide, absorbing at  $1728\text{ cm}^{-1}$  and vanishing on heating to 130–170 K.

Ketene **8a** was similarly generated in pyridine matrix by photolysis of **7a** (1 h, broadband; 6.5 K). The ketene stretch of **8a** appeared at  $2163\text{ cm}^{-1}$  under these conditions. Subsequent warming above 70 K caused the ketene to disappear in concert with the emergence of new bands ascribed to ylide **10a** ( $1727$ ,  $1688$ ,  $1649$ , and  $1620\text{ cm}^{-1}$ ). This process was complete

(12) (a) **1a** and **1b** were also photolyzed in pure ethene matrices. The normal WR to **3** still occurred. None or little of the ethene trapping products were formed. Contrast the ethene trapping of cyclopentadienyldiene: Zuev, P. S.; Nefedov, O. M. *Russ. Chem. Rev.* **1989**, 98, 636. (b) **1a** was also photolyzed in a  $\text{CO}_2$  matrix at 12 K. The normal WR to **3a** was observed.

at 120 K. The analogous ylide **10b** absorbed at 1721, 1681, 1641, and 1619  $\text{cm}^{-1}$ .

It is also possible to co-condense a ketene with pyridine without noticeable reaction taking place in the low-pressure gas phase. Thus, dipivaloylketene **12**<sup>13</sup> was generated by FVT of furandione **11** at 400 °C, co-condensed with pyridine vapor at 30 K, and identified<sup>13</sup> by its IR absorption at 2121  $\text{cm}^{-1}$  (CO was observed at 2134  $\text{cm}^{-1}$  and escaped from the matrix on warming to 70–80 K). Warming to 100 K caused reaction of the ketene with pyridine, giving new bands at 1677, 1605, 1596, and 1579  $\text{cm}^{-1}$ , which we ascribe to ylide **13**. This process was complete at 140 K. As is common for the ketene–pyridine ylides, warming above 160 K caused deterioration of the matrix so that no further spectroscopic studies were possible. However, this example allows us to determine what happens to the ylide on further warming, at least in this one case.<sup>14</sup> After warming to room temperature, the ketene dimer **14** could be isolated. In a preparative scale experiment in which the colorless **12** and pyridine were condensed at 77 K, a pale yellow matrix formed. Warming above 77 K first caused intensification of the yellow color, ascribed to **13**, but above 160 K the color disappeared again. After the matrix was warmed to room temperature and the pyridine removed in vacuo, the colorless dimer **14**<sup>13</sup> was isolated in 70% yield. The most likely interpretation is that, on warming above ca. 160 K, the ketene–pyridine ylide dissociates in part to the components; a molecule of free ketene then reacts with a molecule of ylide to form the dimer.<sup>13</sup> Since a different dimer is formed in the absence of pyridine (and other bases),<sup>13</sup> the nucleophile must be involved in the formation of dimer **14**.



We have calculated the IR spectra of ylides **9a** and **10a** in the gas phase ( $\epsilon = 1$ ) and in a solvent of high dielectric constant ( $\epsilon = 80$ ), using the self-consistent reaction field (SCRF) method.<sup>15</sup> The calculations for the gas-phase molecules show very poor agreement with the experimental observations: the highest-frequency carbonyl group absorption is calculated to be 100–200  $\text{cm}^{-1}$  above the highest experimental one (Table 3). It is important to note that these ketene–pyridine ylides are highly polar molecules, e.g. the calculated dipole moment of **10a** is 7.1 D ( $\epsilon = 1$ ). Thus, the matrix environment where these ylides are observed is similar to a solute molecule in the presence of a strong dielectric field. The introduction of the solvent reaction field has a strong influence on the molecular geometries as well as the IR spectra of the ylides. On going from the gas phase to a polar medium of  $\epsilon = 80$ , the C–N bond lengths in **9a** and **10a** are shortened by 0.438 and 0.074 Å, respectively, and the calculated (highest) carbonyl stretching

**Table 3.** Experimental and Calculated (B-LYP/6–31G\*) Characteristic IR Data ( $\text{cm}^{-1}$ ) for Ketene–Pyridine Ylides **9a** and **10a**

9a			10a		
	calcd			calcd	
exp	$\epsilon = 1$	$\epsilon = 80^a$	exp	$\epsilon = 1$	$\epsilon = 80^b$
1730	1966	1753	1727	1834	1767
1643	1690	1603	1688	1691	1674
1279	1298	1276	1649	1648	1629
	1239	1212	1620	1603	1603
				1459	1458
				1325	1310
				1230	1231

<sup>a</sup> SCRF calculation ( $a_0 = 4.50$  Å). <sup>b</sup> SCRF calculation ( $a_0 = 5.00$  Å).

vibration is displaced to a lower frequency (red shift), by 213 and 77  $\text{cm}^{-1}$  for **9a** and **10a**, respectively (Table 3). The calculated IR spectra of **9a** and **10a** in the polar medium ( $\epsilon = 80$ ) are now in very good accord with experiment (Table 3). This phenomenon applies also to the carbocyclic ketene–pyridine ylides described previously.<sup>6</sup>

## Conclusion

Ar matrix photolysis of **1a,b** produces the Wolff rearrangement (WR) products **3**, also generated by FVT of **1**. Ketenes **8** are obtained by matrix photolysis or FVT of **7**. Photolysis of **1** in CO matrices generates the unobserved carbenes **2**, or species mimicking the carbenes, which are immediately trapped, even at 6.5 K, by CO to give **8**, to the exclusion of the Wolff rearrangement to **3**, thus confirming a postulate by McCluskey and Dunkin.<sup>7</sup> Extensive photolysis of **3** or **8** causes decomposition with CO loss, but a 19-h photolysis of **8** in CO matrix gives detectable amounts of **3**.

In contrast to room temperature solution chemistry, where pyridine traps carbene **2a** efficiently,<sup>4</sup> the WR occurs unabated in a solid pyridine matrix. The resulting ketenes **3** form ketene–pyridine ylides **9** on warming above 40 K. Similarly, dicarbalkoxyketenes **8** form ketene–pyridine ylides **10** above 70 K. Theoretically calculated IR spectra of ketene–pyridine ylides are in agreement with experiments only when a polar reaction field ( $\epsilon = 80$ ) is included in the calculations. Both calculations and experiments indicate that the enthalpies of activation for ketene–pyridine ylide formation are extremely small, and the ketenes can be formed and observed in the presence of pyridine only because of high entropy barriers in the solid matrices. These entropy barriers also prevent pyridine from trapping the carbenes **2** under low temperature matrix conditions.<sup>16</sup>

**Computational Details.** Density functional calculations<sup>17</sup> were carried out using the Gaussian 92/DFT series of programs.<sup>18</sup> Harmonic vibrational frequencies and infrared intensities were calculated using the B-LYP<sup>19</sup> formulation of density functional theory, i.e. with the Becke's exchange functional<sup>19a</sup>

(16) From work on simple  $\alpha$ -oxoketenes it can be concluded that the normal activation barrier for WR is no more than 2–3 kcal mol<sup>-1</sup>: Toscano, J. P.; Platz, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 4712.

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and the Lee–Yang–Parr correlation functional,<sup>19b</sup> with the standard 6-31G\* basis set.<sup>20</sup> A recent study has shown that unscaled B-LYP/6-31G\* frequencies are suitable for prediction of experimental fundamental frequencies.<sup>21</sup> The effects of solvent on the ketene–pyridine ylides (**9a** and **10a**) were studied using the self-consistent reaction field (SCRF) method.<sup>15</sup> In this model the solute is taken to occupy a spherical cavity of radius  $a_0$  which is calculated quantum mechanically,<sup>22</sup> and the solvent is represented by a continuous dielectric, characterized by a given dielectric constant ( $\epsilon$ ). Note that the calculated SCRF geometries and IR spectra for other ketene ylides are similar to those obtained with a more refined solvation model, the self-consistent isodensity polarizable continuum model (SCIPCM).<sup>23</sup>

## Experimental Section

Infrared spectra were recorded on a Perkin-Elmer System 2000, and mass spectra on a Kratos MS25RFA spectrometer (source temperature 200 °C, 70 eV, direct insertion, chemical ionisation with isobutane). Matrix isolation was carried out using Leybold-Heraeus ROK 10-300 or Air Products CSW-202-6.5 closed cycle liquid He cryostats with BaF<sub>2</sub> windows, the latter equipped with a Lakeshore Model 330 temperature controller. A Hanovia high-pressure Hg–Xe lamp (1000 W) equipped with a 16 cm water filter with quartz windows (to remove the IR radiation to prevent the matrix from warming) was used for the photolyses (broadband). Matrices for photolysis experiments were prepared by sublimation of the diazo compounds into a stream of the matrix isolation host gas for co-condensation on the cold window. Depositions were made at 13 or 30 K. For the sublimation of **7b**, the matrix host gas was passed over the compound in order to increase the amount of sample deposited on the window. Gas flow was controlled by a needle valve.

In FVT experiments, the matrix isolation host gas was passed over the compound in order to increase the amount of sample deposited on the window. The mixture of matrix gas and sample was led through a 10 cm heated quartz tube, equipped with a heating wire, thermocouple, and a quartz insert to increase the contact time in the hot zone. Matrix isolation gases, Ar (99.999%), CO (95%), C<sub>2</sub>H<sub>4</sub> (>98%), and CO<sub>2</sub> (>99.8%), were used as purchased from BOC Gases Australia Ltd. Mixtures of Ar and CO were prepared on a vacuum line by standard manometric procedures.

**Dimethyl diazomalonate (1a)** was prepared according to literature methods.<sup>24</sup> IR (Ar, 13 K) 3037 w, 3015 w, 2996 m, 2855 w, 2153 w, 2144 s, 2138 m, 2119 w, 1783 m, 1758 vs, 1717 m, 1692 w, 1449 w, 1442 s, 1374 w, 1361 m, 1338 m, 1321 m, 1316 m, 1278 m, 1274 w, 1191 m, 1119 w, 1108 s, 1092 w, 765 m, 762 m cm<sup>-1</sup>; mass spectrum,  $m/z$  (relative intensity) 158 (M<sup>+</sup>, 62), 141 (8), 127 (40), 113 (12), 107 (13), 99 (24), 91 (62), 69 (20), 68 (12), 59 (100), 43 (15), 29 (21), 28 (30). The yellow oil was evaporated at 0 °C for 20 min for photolysis experiments, and 20 min for FVT experiments, and the material was co-condensed with the host gas on the cold window. Photolysis and thermolysis IR data are in Tables 1 and 2.

**Diethyl diazomalonate (1b)** was prepared in the same fashion as **1a**.<sup>24</sup> IR (Ar, 13 K) 3007 w, 3000 w, 2942 vw, 2880 vw, 2150 m, 2144 m, 1777 m, 1750 s, 1708 m, 1699 m, 1481 w, 1461 w, 1446 w, 1397 w, 1375 m, 1327 s, 1319 s, 1278 m, 1101 s, 1030 w, 764 w cm<sup>-1</sup>; mass spectrum,  $m/z$  (relative intensity) 186 (M<sup>+</sup>, 36), 155 (28), 141 (35), 133 (7), 115 (12), 91 (58), 86 (8), 69 (10), 65 (5), 43 (16), 29 (100), 28 (13). The diazo compound, a yellow oil, was evaporated at 0 °C for 45 min in photolysis experiments and for 20 min in the

case of FVT experiments. Photolysis and thermolysis IR data for the resulting matrices are presented in Tables 4 and 5 in the Supporting Information.

**Dimethyl 3-diazo-2-oxosuccinate (7a)** was prepared according to Staudinger's method<sup>10a</sup> for the diethyl derivative **7b**. IR (Ar, 13 K) 3042 w, 3014 w, 2965 m, 2910 w, 2857 w, 2177 m, 2153 s, 2134 w, 1763 m, 1741 s, 1729 m, 1671 m, 1461 w, 1442 m, 1360 m, 1341 w, 1321 m, 1300 m, 1225 s, 1197 m, 1187 s, 1035 m, 785 w, 759 w cm<sup>-1</sup>; mass spectrum,  $m/z$  (relative intensity) 187 (M<sup>+</sup> + H, 71), 159 (13), 158 (14), 127 (50), 99 (23), 84 (33), 83 (34), 69 (96), 59 (100), 55 (27), 45 (44), 43 (43), 41 (36), 40 (48), 30 (69), 29 (99), 28 (68); <sup>1</sup>H NMR (CDCl<sub>3</sub>) 3.92 (s), 3.87 (s); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 164.4, 162.4, 160.3, 74.6, 53.1, 52.8 ppm. The compound was evaporated at room temperature for 60 min in photolysis experiments and at 0 °C for 20 min in the case of FVT experiments. Photolysis and thermolysis IR data for the resulting matrices are given in Table 2.

**Diethyl 3-diazo-2-oxosuccinate (7b)** was prepared according to Staudinger.<sup>10a</sup> IR (Ar, 13 K) 3007 w, 2953 w, 2920 w, 2880 w, 2141 m, 1763 m, 1734 s, 1672 m, 1663 m, 1484 w, 1466 w, 1448 w, 1377 m, 1340 m, 1312 m, 1292 m, 1217 s, 1149 m, 1136 w, 1036 m, 754 w cm<sup>-1</sup>; mass spectrum,  $m/z$  (relative intensity) 215 (M<sup>+</sup> + H, 90), 187 (18), 177 (15), 169 (22), 159 (50), 151 (28), 149 (73), 141 (22), 86 (21), 69 (41), 45 (29), 42 (19), 29 (100), 28 (12). The compound was evaporated in a stream of Ar at room temperature for 10 min in photolysis experiments and at 0 °C for 20 min in the case of FVT experiments. Photolysis and thermolysis IR data for the resulting matrices are given in Table 5 in the Supporting Information.

**Dicarbethoxyketene (8b)** was prepared by a method of Staudinger,<sup>10b</sup> involving the reaction of **7b** in the presence of Pt. **8b** was directly deposited on the cold window without any further purification. IR (Ar, 13 K) 2999 m, 2953 w, 2941 w, 2921 w, 2880 w, 2166 s, 2153 m, 1788 m, 1760 s, 1484 w, 1449 w, 1337 m, 1307 m, 1289 m, 1219 w, 1103 m, 1083 m, 777 w cm<sup>-1</sup> (cf. Table 5 in the Supporting Information).

**Generation of Ketene–Pyridine Ylides.** Matrices were prepared by sublimation of the diazo compound in a stream of pyridine vapor, and the mixtures were co-condensed on the cold window at 30 K. Pyridine was distilled over KOH and degassed before use, and the pyridine gas flow was controlled by a needle valve. The photolyses were performed with the sample at 6–6.5 K until complete conversion. The pyridine matrices were warmed up slowly in steps of 10 K until all ketene had reacted. IR data are given in Table 3.

Dimer **14** (mp 140 °C) was isolated in 70% yield (140 mg) from the FVT of **11** (230 mg) at 400 °C following layered deposition with pyridine at 77 K, warming to room temperature, and evaporation of the pyridine; it was identified by comparison of the melting point and <sup>1</sup>H and <sup>13</sup>C NMR spectra with those of an authentic sample.<sup>13</sup>

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**Supporting Information Available:** Tables 4–9 showing observed IR data for **3b** and **8b** in Ar and CO matrices, and calculated IR spectra of the major conformers of **3a**, **3b**, **8a**, and **8b** (B-LYP/G-31G\*) (7 pages). See any current masthead page for ordering and Internet access instructions.

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