though its hydrogen bonds cannot be ideal.

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Supplementary Material Available: Spectroscopic and analytical data for compounds 1 and 4 and tables of atomic coordinates, bond distances and angles, and anisotropic temperature factors (6 pages). Ordering information is given on any current masthead page.

Direct Observation of α-Oxo Ketenes Formed from 1,3-Dioxin-4-ones and the Enols of β-Keto Esters

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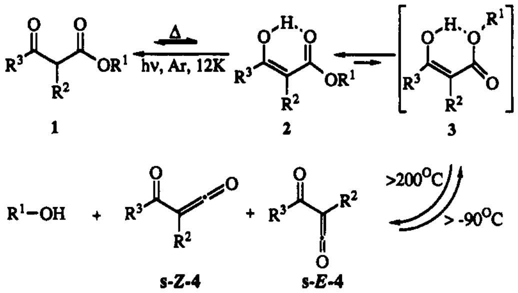
Summary: The enol forms of β-keto esters thermolyze to alcohols and α-oxo ketenes, which are characterized by low-temperature IR spectroscopy and on warming regenerate the β-hydroxy-α,β-unsaturated esters. The matrix isolated s-*Z* and s-*E* forms of α-oxo ketenes are characterized and photochemically converted into other conformers or sites. Matrix photolysis of 2,2,6-trimethyl-1,3-dioxin-4-one gives the s-*Z* acetylketene initially. α-Oxo ketenes polymerize in the cold and dimerize only at elevated temperatures.

There has been considerable recent interest in α-oxo ketene (acylketene) chemistry.[1-3] In connection with our studies of the keto ketene–keto ketene[3a] and related rearrangements,[3c] we needed ready access to spectroscopically observable α-oxo ketenes as a prelude to ^{13}C labeling experiments. Here we report direct evidence that (i) it is the enol forms of β-keto esters which on flash vacuum pyrolysis (FVP) decompose to α-oxo ketenes and alcohols;[4] (ii) the ketenes react again with alcohols to regenerate the enols; (iii) in the absence of nucleophiles, the α-oxo ketenes do not dimerize in the cold, but polymerize; (iv) open-chain α-oxo ketenes can exist in s-*Z* and s-*E* forms, which are resolved and characterized by Ar matrix IR spectroscopy; (v) photolysis of the matrix isolated α-oxo ketenes produces new conformers or sites, a process which is partially reversed on warming.

Scheme I



The keto (1) and enol (2) forms of β-keto esters[5] are readily distinguishable by IR spectroscopy, the C=O groups of the former appearing at the higher frequencies[6] (e.g. **1b** (Ar, 12 K), 1748, 1683, 1157 cm^{-1}; **2b** (Ar, 12 K), 1655, 1643, 1246 cm^{-1}).

FVP of the esters 1 at temperatures above 200 °C (10^{-4} mbar) with Ar matrix isolation of the products at 12–18 K gave the ketenes 4 (Table I) together with mixtures of the unreacted keto and enol forms (1 and 2). Similar results were obtained on neat deposition of the products at 77 K, except that the bands due to the individual s-*Z* and s-*E* isomers of the ketenes (Table I) were not resolved due to the inherently broader bands obtained under such conditions (e.g. for **4a**: 2137 (s) cm^{-1}). It was particularly noticeable that those esters that do not readily enolize react very sluggishly; the reaction product containing the ketene is rich in the keto form 1 and depleted of enol 2. The keto forms are unreactive, and hence the reaction will not go

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(1) (a) Hyatt, J. A.; Feldman, P. L.; Clemens, R. J. *J. Org. Chem.* **1984**, *49*, 5105. (b) Clemens, R. J.; Witzeman, J. S. *J. Am. Chem. Soc.* **1989**, *111*, 2186. (c) Witzeman, J. S. *Tetrahedron Lett.* **1990**, *31*, 1401.

(2) (a) Sato, M.; Ogasawara, H.; Yoshizumi, E.; Kato, T. *Chem. Pharm. Bull.* **1983**, *31*, 1902. (b) Sato, M.; Yoneda, N.; Kaneko, C. *Ibid.* **1986**, *34*, 621; **1986**, *34*, 4577. (c) Yamamoto, Y.; Watanabe, Y.; Ohnishi, S. *Ibid*, **1987**, *35*, 1860. (d) Berkowitz, W. F.; Ozorio, A. A. *J. Org. Chem.* **1971**, *36*, 3787. (e) Leyendecker, F. *Tetrahedron* **1976**, *32*, 349. (f) Maier, G.; Reisenauer, H. P.; Sayrac, T. *Chem. Ber* **1982**, *115*, 2192. (g) Emerson, D. W.; Titus, R. L.; Gonzales, R. M.; *J. Org. Chem.* **1990**, *55*, 3572. (h) Coleman, R. S.; Grant, E. B. *Tetrahedron Lett.* **1990**, *31*, 3677.

(3) (a) Wentrup, C.; Winter, H.-W.; Gross, G.; Netsch, K.-P.; Kollenz, G.; Ott, W.; Biedermann, A. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 800. Wentrup, C.; Netsch, K.-P. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 802. Ben Cheikh, A.; Chuche, J.; Manisse, N.; Pommelet, J. C.; Netsch, K.-P.; Lorencak, P.; Wentrup, C. *J. Org. Chem.* **1991**, *56*, 970. (b) Kappe, C. O.; Evans, R. A.; Kennard, C. H. L.; Wentrup, C. *J. Am. Chem. Soc.* In press. (c) Wentrup, C.; Gross, G.; Berstermann, H.-M.; Lorencak, P. *J. Org. Chem.* **1985**, *50*, 2877. Wentrup, C.; Lorencak, P. *J. Am. Chem. Soc.* **1988**, *110*, 1880. Maquestiau, A.; Pauwels, P.; Flammang, R.; Lorencak, P.; Wentrup, C. *Org. Mass Spectrom.* **1986**, *21*, 259.

(4) This confirms earlier suggestions made by Campbell, D. S.; Lawrie, C. W. *J. Chem. Soc., Chem. Commun.* **1971**, 355. Berkowitz (footnote 30 in ref 2d), and Leyendecker, F.; Bloch, R.; Conia, J. M. *Tetrahedron Lett.* **1972**, 3703.

(5) Materials: the esters **1a**, **1b**, **1e**, **1g**, **1i**, and **1j** were obtained from Aldrich Chemical Co., purified by fractional vacuum distillation, and checked by ^1H NMR. **1c** was prepared from **1b** (1.7 mmol) by exchange with D_2O (99.7%; 110 mmol) for 1 h at room temperature, extraction with ether, drying over Na_2SO_4 and vacuum distillation; 64% deuteration by ^1H NMR. **1d** was prepared according to Vlassa, M.; Barabas, A. *J. Prakt. Chem.* **1980**, *322*, 821. **1f** and **1l** according to Levine, R.; Houser, C. R. *J. Am. Chem. Soc.* **1944**, *66*, 1768. **1h** according to Savage, G. P. Ph.D Thesis, The University of Queensland, 1988; cf. Ito, Y., Nakatsuka, M.; Kise, N., Saegusa, T. *Tetrahedron Lett.* **1980**, *21*, 2873; and **1k** according to ref 6. **5** was obtained from Tokyo Kasei Kogyo Co. Ltd. and purified by distillation at 64–65 °C (3 Torr). **6** was prepared according to Arndt, F. *Org. Synth.* **1940**, *20*, 27.

(6) Rhoads, S. J.; Gilbert, J. C.; Decora, A. W.; Garland, T. R. *Tetrahedron* **1963**, *19*, 1625.

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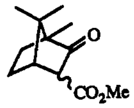
Table I. α-Oxo Ketenes Generated by Flash Vacuum Pyrolysis[5]

	compounds 1			temperatures,[a] °C		ketenes 4 (Ar, 18 K; cm^{-1})[b]			
						$\nu_{C=C=O}$		$\nu_{C=O}$	
	R^3	R^2	R^1	T_1	T_2	s-*Z*	s-*E*	s-*Z*	s-*E*
a	Me	H	Me	250	−90	2147 w 2143 s	2138 w 2133 s[c]	1681 m	1698 m[d]
b	Me	H	Et	250	−80	2147 w 2143 s	2138 w 2133 s[c]	1681 m	1698 m[d]
c	Me	D	Et	250	−80	2136 s	2126 s[e]	1681 m	1698 m[d]
d	*t*Bu	H	Et	>200		2142 s	2132 m	1668 s	1680 w
e	Ad[f]	H	Et	>300	−80	2146 sh 2143 s 2140 sh	2127 w	1666	
f	Ph	H	Me	250	−80	2146 s 2143 sh	2136 w, sh	1632	
g	Me	Me	Et	200	−90	2131 w	2123 s 2120 s	1666 w	1684 s
h	*t*Bu	*t*Bu	Et	>400			2114[g]		
i	$-(CH_2)_3-$		Et	200	−70	2133 s[h]		1708 m	
j	$-(CH_2)_4-$		Et	250	−90	2124 s		1657 m	
k	$-(CH_2)_5-$		Et	200	−80	2127 s			
l				200	−55	2124 s[i]		1716 m	

[a] T_1 denotes the onset of pyrolysis, T_2 the temperature of disappearance of the ketene (isolated at 77 K) due to reaction with the alcohol on warmup. [b] m, medium; s, strong; sh, shoulder; w, weak. [c] One single band is observed at 2137 cm^{-1} at 45 K. [d] The CH_3 sym. def. is at 1378 cm^{-1} for both conformers. [e] Minor bands unobservable due to incomplete deuteration.[5] [f] Ad = adamantyl. [g] Move to 2110 cm^{-1} at 60 K. At room temperature in CCl_4 solution 2109, 1661 cm^{-1}: Nikolaev, V. A.; Frenkh, Yu.; Korobitsyna, I. K. *J. Org. Chem. USSR* **1978**, *14*, 1338. At room temperature (phase not reported): 2105, 1658 cm^{-1}. Wolff, S.; Agosta, W. C. *Can. J. Chem.* **1984**, *62*, 2429. [h] Stays at 2133 cm^{-1} at 45 K; 2127 cm^{-1} at 77 K. [i] 2124, 1715 cm^{-1} at 77 K; 2122 cm^{-1} by FVP of acid chloride; 2128 cm^{-1} in CCl_4 at room temperature.

to completion in such cases, even at temperatures as high as 900 °C.[7] This is true particularly for **1g** and **1h**, which exist largely in the keto forms at room temperature and at 250 °C. (**1h**, 1743, 1718 cm^{-1}; **2h**, 1683 cm^{-1}). For **1h**, reaction only sets in above 400 °C and in both cases it is still very incomplete at 650 °C. This can be due to conformational effects, steric hindrance preventing the formation of the reactive enol form **3**. In the cyclic series, it is known that **1i** enolizes very slightly to **2i**, but **1j** very much to **2j** at room temperature,[6,8] a fact which is also reflected in the IR spectra. At 200 °C **1i** exists largely as the ketone (1766, 1739 cm^{-1}; Ar, 12 K) and conversion to the ketene **4i** is still very incomplete at 500 °C. **1j** gives much enol (**2j**) at 200 °C, the ketene **4j** is formed much more readily, and the reaction is complete at 500 °C. For **1l**, no enol (**2l**) is seen at all at 500–700 °C, and the pyrolysis is, therefore, very incomplete. The ketene **4l** can, however, be produced by Staudinger's method.[9] **1a** and **1b** enolize easily at room temperature (**1b**:**2b** ~ 47:53 in the gas phase at 298 K[10]). The amount of enol at equilibrium decreases with rising temperature,[10] as we confirmed by gas-phase IR spectroscopy. Enolization is rapid in these cases, and both **1a** and **1b** gave acetyl ketene (**4b**)[1c] cleanly at 550 °C (Figure 1, parts b and d).

Isolation of the ketenes **4** at 77 K (together with any unreacted β-keto ester **1**) followed by warming of the samples to temperatures between −90 and −50 °C resulted in the reaction with the cocondensed alcohols, *regenerating the enols* **2** without increasing the amount of keto form **1** present, as shown by difference spectroscopy. In the case of **2i**, for example, this is a method of generating a sample enriched in enol (1673, 1623, 1248 cm^{-1}). These results demonstrate that it is the enols **2** that react to ketenes, presumably via **3**, that the ketenes regenerate the enols **2** on reaction with alcohols, and that the keto esters **1** are relatively unreactive.[7]

Preparative pyrolyses of the esters **1** at 500 °C with isolation of the products on a cold finger at 77 K, followed by warming to room temperature, gave only the starting materials (**1**/**2**), demonstrating efficient back-reaction between ketenes and alcohols on warming.[7] When the alcohol was removed from the ketenes by condensation in a cold trap, the latter no longer reverted to esters but instead polymerized on warm up.[10]

The 1,3-dioxin-4-one ring system constitutes another source of acylketenes,[1,2] and there is precedence in the direct observation of carboxyketene formation from 5-hydroxy-1,3-dioxin-4-ones (enols of Meldrum's acids).[3c] The dioxinone **5** was therefore subjected to FVP at 280–300 °C with product isolation at 77 K. The same acetylketene (**4a**) was again obtained (2137, 1676, cm^{-1} at 77 K), together with acetone, and warm up to room temperature gave the same polymer as above,[10b] with only a 3% yield of the ketene dimer, dehydroacetic acid (**6**).[5] Pyrolysis of **5** at a pressure of 5 mbar and collecting the product at 0 °C gave **6** in 70–80% yield and no polymer. Thus, a high-temperature reaction is required for acetylketene to dimerize; the reaction will not take place in a low-pressure FVP experiment. Nor does the back reaction between acetylketene and acetone take place in the cold.

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(7) Only methyl esters should be used at high temperatures since the nonenolized ethyl β-keto esters eliminate ethylene and decarboxylate above 700 °C. Thus, **1a** gives 94% recovery at 900 °C (back-reaction between ketene and methanol). **2a** gives 99% recovery at 450 °C, but at 900 °C only 15% of **2a** together with 70% of acetone.

(8) Schwarzenbach, G.; Zimmerman, M.; Prelog, V. *Helv. Chim. Acta* **1951**, *34*, 1954. cf. ref 6.

(9) Staudinger, H.; Schotz, S. *Ber. Dtsch. Chem. Ges.* **1920**, *53*, 1105. We repeated this experiment with IR detection: treatment of camphorcarboxylic acid chloride with triethylamine in CCl_4 gave a yellow solution exhibiting a ketene band at 2128 cm^{-1} ($t_{1/2}$ ~10 min at room temperature). FVP of the acid chloride at 800 °C gave a ketene band at 2122 cm^{-1} (77 K) disappearing on warm up to −30 °C. FVP of **1l** at 700 °C gave a weak ketene band at 2128 cm^{-1} (18 K) disappearing at −50 °C (back-reaction with methanol).

(10) Folkendt, M. M.; Weiss-Lopez, B. E.; Chauvel, J. P., Jr.; True, N. S. *J. Phys. Chem.* **1985**, *89*, 3347.

(11) (a) For polymerization and depolymerization of α-oxo ketenes, see: Nikolaev, V. A.; Frenkh, Yu.; Korobitsyna, I. K. *J. Org. Chem. USSR* **1978**, *14*, 1069. (b) Polymer of **4a**: IR 3084 w, 2996 w, 1745 s, 1658 s, 1079 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.0–2.4 (broad).

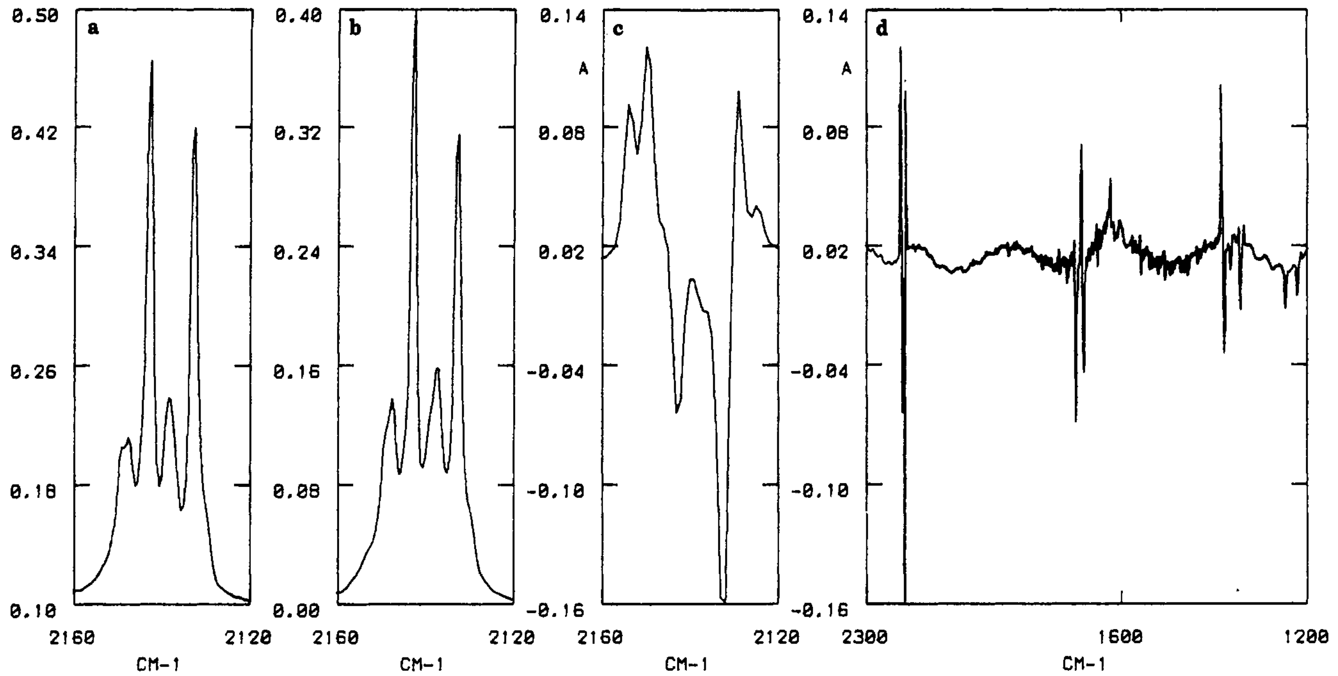

Figure 1. (a) Ketene region of the IR spectrum of **4a** produced by FVP of **5** at 350 °C (Ar, 12 K). Exact values: 2147, 2143, 2138, 2133 cm^{-1}. (b) Ketene region of the IR spectrum of **4a** produced by FVP of **1b** at 500 °C (Ar, 12 K). Exact values: see Table I. An identical spectrum is obtained on FVP of **1a** at 300–900 °C. (c) and (d) Difference spectrum: the result of photolysis of **4a** (254 nm, 60 min; Ar, 12 K). Positive peaks are due to the photoproduct. Negative peaks are due to s-*Z*/s-*E*-**4a** produced by FVP of **1b** at 500 °C and matrix isolated in Ar at 12 K.

The C=C=O and C=O stretching vibrations of several open chain α-oxo ketenes give rise to discrete bands for the s-*Z* and s-*E* conformers in Ar matrix (Table I), but not in the neat state at 77 K. The main bands for acetylketene (**4a**) are in good agreement with data reported by Witzeman,[1b,c] but two minor bands appear in the ketene region as well (Table I and Figure 1). The *same* pattern of bands is obtained by FVP of **5** above 280 °C (Figure 1a; **4a** produced from **5** by FVP at 350 °C: IR (Ar, 12 K), 2143, 2133, 1698, 1681, 1378 cm^{-1} plus bands due to acetone: 2973, 1718, 1363, 1230 cm^{-1}). Since the intensities of the minor bands (2147, 2138 cm^{-1} for **4a**) depend on the quality of the matrix, they may be due to site effects. The band due to matrix isolated CO_2 is similarly split by a matrix effect (2344.5 cm^{-1} (major), 2339.5 cm^{-1} (minor)), whereby the intensity of the minor band serves as a measure of the quality of the matrix; increased intensity of the minor ketene bands (2147, 2138 cm^{-1}) correlates with an increase in the minor CO_2 band at 2339.5 cm^{-1}. Conditions could not be found where the minor ketene bands were removed completely.

The assignment of bands to the individual s-*Z* and s-*E* conformers of the ketenes is made on the basis of the following criteria: (i) in the related α,β-unsaturated ketones, the frequency separation of the C=O and C=C bands is larger for the s-*Z* than for the s-*E* forms, and the intensity ratio for the C=O and C=C bands is larger for s-*E*.[12] From the intensity differences observed in different experiments on the same molecules, the correspondence between C=C=O and C=O bands of individual conformers is clearcut. (ii) In **4d–f**, steric constraints favor the s-*Z* conformers, which give rise to the strong C=C=O bands at high frequencies and C=O bands at low frequencies. (iii) In **4g,h**, steric interactions favor the s-*E* forms, which absorb at the appropriate frequencies. (iv) MNDO calculations on **4a** indicate that the s-*Z* form is of lowest energy, and the IR predictions for s-*Z* and s-*E* are in agreement with the experiment.[13] (v) Photolysis of the 1,3-dioxin-4-one **5** in Ar matrix (254 nm; 12 K) gives only the S-*Z* form of **4a** (2143, 2148 cm^{-1}) (together with the photoconformers at 2151, 2155 cm^{-1}, vide infra) and acetone (1719, 1363, 1230 cm^{-1}).[14] (vi) The possibility that the splitting of bands could be due to Fermi resonance is removed because the ^{13}C satellites of the ketene bands appearing at 2070–2090 cm^{-1} have the same shapes and splittings as the main bands.[15]

Photolysis of the matrix isolated acetylketene **4a** at either 245 or 313 nm (Ar, 18 K) did not result in simple *E*–*Z* interconversion, but gave rise to new bands at 2154, 2150, 2130, 1688, and 1385 cm^{-1} (Figure 1, parts c and d). The *E* form (2133, 1699 cm^{-1}) disappeared faster than the *Z* form, and hence these bands appear more negative in Figure 1, parts c and d. The new peaks at 2150 and 2130 cm^{-1} appeared first. A photostationary state appeared to be reached after 2 h, and no further change took place on 254-nm irradiation for 20 h, except for a slow increase in a further band at 2125 cm^{-1}. The rapid photochemical process was partially reversed on warming to 35 K. Further warming to 45 K (allowing Ar to evaporate) caused coalescence of all the bands in the ketene region and generation of the spectrum of "neat" acetylketene (2137 cm^{-1}). Similar irradiation of **5** (254 nm, 15 min; AR, 18 K) gave only the bands due to s-*Z*-**4a** plus the high frequency part of the photoproduct (2155, 2151, 1687, 1385 cm^{-1}). Further irradiation at 313 nm also produced the *E* form (2136, 1698 cm^{-1}), and photolysis at 365 nm for 6

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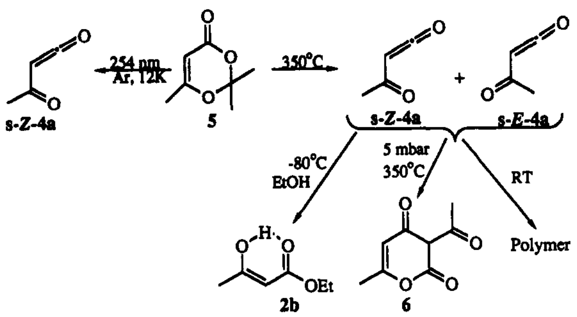
[12] Noack, K.; Jones, R. N. *Can. J. Chem.* **1961**, *39*, 2225.

[13] MDNO calculations (AMPAC program package) for **4a**: ΔH_f (s-*Z*) −51.9 kcal/mol; ΔH_f (s-*E*) −49.2 kcal/mol. Rotational barrier 3.7 kcal/mol. IR (s-*Z*) 3407, 2469, 2082, 1537 cm^{-1}; IR (s-*E*) 3381, 2467, 2087, 1538 cm^{-1}.

[14] Matrix photolysis of keto/enol mixtures of esters **1**/**2** does not produce ketenes but causes slow conversion of the enols to the keto forms. The latter are photostable.

[15] The cyclic α-oxo ketenes **4i–l** are constrained to s-*Z* or skew conformations and do not fit well into the pattern established for the open chain compounds. **4i** and **4l** have surprisingly high, and **4j** a rather low C=O frequency, and for **4k** a C=O band could not be located with certainty. These unexpected results merit further investigation.

Scheme II



h produced all the ketene bands in the photostationary state. (The carbonyl band of s-*Z*-**4a** produced by photolysis of **5** does not appear at 1687 but at 1675 cm^{-1}, presumably due the vicinity of acetone in the matrix cavity). Photolysis of **5** in 3-methylpentane glass (254 nm, 20 min; 18 K) gave acetone (1718 cm^{-1}) and s-*Z*-**4a** (2143, 1675 cm^{-1}) with no fine structure. Photolysis of **5** in pentane (254 nm; 30 °C) gave the same ketene polymer as obtained on FVP, and photolysis in ethanol solution (254 nm; 30 °C) gave ethyl acetoacetate.[16]

The photoproduct still contains a carbonyl group and a methyl group (1688 and 1385 cm^{-1}, respectively) in an environment very similar to that of the starting material (**4a**) (Figure 1d), and since it also behaves like **4a** chemically and is converted to **4a** on warm up, it is reasonable to conclude that the photoproduct is not a different compound but a set of different conformers, presumably skew, arising from the matrix environment adapting to the excited state structures of the ketenes and thus trapping the ground states in "unnatural" conformations.[17] Such photoconformers were seen also for **4d** (2152, 2112 cm^{-1}) and, weakly, for **4i** (2150 cm^{-1}). **4g,h** showed no photoreaction, probably because the predominant ground-state conformers are already skew s-*E* forms.

The phenomenon reported here is of considerable importance for all matrix-photochemical studies involving ketene-forming reactions. The photochemical Wolff rearrangement is a case in point, where not only multiple bands due to dimethyl ketene have been observed but strong bands that would normally have been ascribed to ketenes have been interpreted as the C=C stretch in dimethyloxirene.[18] While we do not wish to cast doubt on the assignment,[18] and dialkyl ketenes may very well behave differently from acylketenes, our results demonstate a need for a thorough investigation of the photoreactions of ketenes, and we plan such a study.

Acknowledgment. This work was supported by the Australian Research Council and The University of Queensland. We thank Dr. R. F. Evans for a sample of **1h**.

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[16] Cf. Sato, M.; Ogasawara, H.; Takayama, K.; Kaneko, C. *Heterocycles* 1987, *26*, 2611.

[17] Evidence for the existence of long-lived excited states of the ketenes is seen, particularly in the case of **4i**, which exhibits extremely strong blue phosphorescence ($\tau > 0.5$ s).

[18] Bachmann, C.; N'Guessan, T. Y.; Debu, F.; Monnier, M.; Pourcin, J.; Aycard, J.-P.; Bodot, H. *J. Am. Chem. Soc.* 1990, *112*, 7488.

Total Synthesis of Phenanthroviridin Aglycon: The First Naturally Occurring Benzo[*b*]phenanthridine

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Summary: The first synthesis of a naturally occurring benzo[*b*]phenanthridine has been accomplished via coupling of a cyanophthalide and a substituted bromocinnamate and subsequent transformation of the resulting aryl naphthoquinone carboxylate via formylation, Hoffmann rearrangement, cyclization, and deprotection steps.

The isolation of the first naturally occurring benzo[*b*]phenanthridine, phenanthroviridin (**1**), and its aglycon **2** from *Streptomyces viridiochromgenes* DSM3972 was recently reported.[1] Both compounds are active against lung carcinoma MBA9812 in mice.[1] We had previously predicted that the hypothetical pyridone **3** would be an intermediate in the transformation of dehydrorabelomycin (**4**) during the biosynthesis of the kinamycin antibiotics (kinamycin D (**5**), Scheme I).[2] It would be quite reasonable to also consider **2** as a potential intermediate in this remarkable pathway.[3,4] We now report the first synthesis of **2** by an efficient route that should also allow introduction of glycosyl moieties at the C-1 phenol for synthesis of **1** and analogues, as well as strategically placed isotopic labels for biosynthetic studies.

In order to obtain the angular tetracyclic ring system, we envisioned that the ABD rings could be constructed via coupling of a cyanophthalide with a substituted cinnamate. Cyanophthalide (**6**)[5] has been frequently used for the construction of linear tetracycles[5,6] (e.g., anthracyclinones).

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[1] Fendrich, G.; Zimmermann, W.; Gruner, J.; Auden, J. A. L. Eur. Pat. Appl. EP 304,400 C1 C07D221/18), 22 Feb 1989, CH Appl. 87/3, 196, 20 Aug 1987 (*Chem. Abstr.* 1990, *112*, 752959).

[2] Seaton, P. J.; Gould, S. J. *J. Am. Chem. Soc.* 1988, *110*, 5912-5914.

[3] Seaton, P. J.; Gould, S. J. *J. Am. Chem. Soc.* 1987, *109*, 5282-5284.

[4] Sato, Y.; Gould, S. J. *J. Am. Chem. Soc.* 1986, *108*, 4625-4631.

[5] (a) Li, T.; Wu, Y. L. *J. Am. Chem. Soc.* 1981, *103*, 7009-7011. (b) Li, T.; Wu, Y. L.; Walsgrove, T. C. *Tetrahedron* 1984, *40*, 4701-4710. (c) Freskos, J. N.; Morrow, G. W.; Swenton, J. S. *J. Org. Chem.* 1985, *50*, 805-810.

[6] (a) Russell, R. A.; Pilley, B. A.; Irvine, R. W.; Warrener, R. N. *Aust. J. Chem.* 1987, *40*, 311-323. (b) Chenard, B. L.; Dolson, M. G.; Sercel, A. D.; Swenton, J. S. *J. Org. Chem.* 1984, *49*, 318-325. (c) Swenton, J. S.; Freskos, J. N.; Morrow, G. W.; Sercel, A. D. *Tetrahedron* 1984, *40*, 4625-4632. (d) Kraus, Y. A.; Cho, H.; Crowley, S.; Roth, B.; Sugimoto, H.; Pruch, S. *J. Org. Chem.* 1983, *48*, 3439-3446. (e) Keay, B. A.; Rodrigo, R. *Can. J. Chem.* 1983, *61*, 637-639. (f) Li, T.; Walsgrove, T. C. *Tetrahedron Lett.* 1981, *22*, 3741-3744. (g) Kraus, G. A.; Sugimoto, H. *Tetrahedron Lett.* 1978, 2263-2266.