

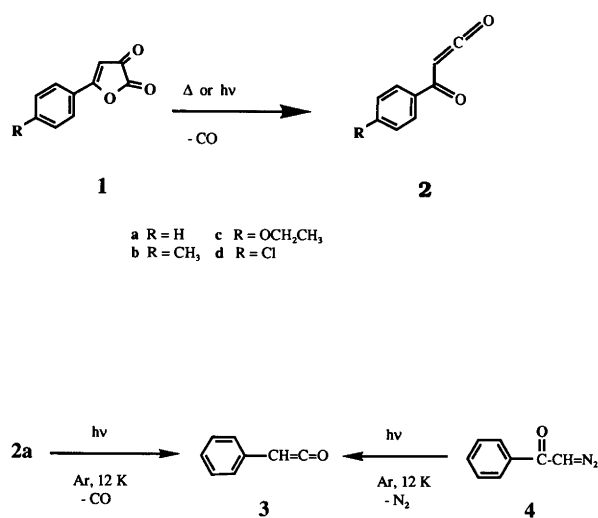
Direct Observation of Benzoylketenes

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Dedicated to Professor Lars Skattebøl on the occasion of his 65th birthday.

α -Oxo ketenes (acylketenes) are versatile intermediates in organic synthesis, usually generated by thermolysis of 2,3-dihydrofuran-2,3-diones,^{1–3} thermolysis or photolysis of 1,3-dioxin-4-ones,^{4,6} or thermolysis of β -keto esters.^{6,7} In connection with our studies on the photoisomerization of α -oxo ketenes⁶ and of the degenerate, thermal acylketene–acylketene rearrangement ($R-CO-CH=C=O \rightleftharpoons O=C=CH-CO-R$) which takes place for $R = \text{aryl}$ ⁸ but not for $R = \text{CH}_3$,⁹ it was mandatory to develop methods for the clean and independent generation of α -oxo ketenes of known initial stereochemistry.



Scheme 1.

Here we report the generation of simple benzoylketenes **2** by both flash vacuum pyrolysis (FVP) and matrix photolysis of furandiones **1** (Scheme 1). The ketenes were identified by their low temperature IR spectra and by high resolution mass spectrometry. Chemical proof for the identity

of the ketenes has been given by trapping in [2 + 4] cycloaddition reactions in solution,^{2,3} but the ketenes are not directly observable under such conditions. Indeed, α -oxo ketenes are extremely unstable except when kinetically stabilized by sterically protecting groups.¹⁰

FVP of **1** at 400–500 °C (10^{-4} mbar) with isolation of the products as neat solids at 77 K for IR spectroscopy permitted the observation of strong bands due to the ketenes **2** near 2136 cm^{-1} . The C=O stretching vibrations were far less prominent, giving rise to bands in the range 1600–1680 cm^{-1} (full spectra are listed in the Experimental section). Similar pyrolysis of **1a** with Ar matrix isolation of the product at 15 K gave **2a**, featuring an extremely strong $\nu_{\text{C}=\text{C}=\text{O}}$ at 2147 cm^{-1} and much weaker bands at 1665, 1648, 1602, 1600, and 1384 cm^{-1} (Fig. 1). The shift of ca. 10 cm^{-1} on going from the neat solid to the matrix-isolated substance is normal. Most importantly, the shape of the 2147 cm^{-1} ketene band (Fig. 1) was identical with that of benzoylketene produced by FVP of methyl benzoylacetate.⁶ The main band at 2147, 2144 cm^{-1} is ascribed to *s-cis*-benzoylketene (**2a**), and the small shoulder at 2134, 2132 cm^{-1} to *s-trans* benzoylketene.⁶ The ketene **2a** is a far stronger absorber than carbon monoxide, which appears at ca. 2139 cm^{-1} and is barely visible in the spectrum shown in Fig. 1 (this CO peak increases on photolysis, *vide infra*). The shape of the ¹³C satellite of the C=C=O band with maximum at 2090 cm^{-1} (not shown) was virtually identical with that of the main band at 2147 cm^{-1} , and also identical in shape and position with the $\nu_{^{13}\text{C}=\text{C}=\text{O}}$ band in the ¹³C labelled compound, Ph–CO–¹³CH=C=O, generated by rearrangement^{8b} of Ph–¹³CO–CH=C=O at 850 °C (10^{-4} mbar) with Ar matrix isolation at 15 K. The present method of FVP of **1a** is far superior to ester pyrolysis⁶ for the generation of IR spectra of acylketenes; the spectrum shown in Fig. 1 is essentially due to pure **2a**. All the bands below 2147 cm^{-1} are also present in the spectrum generated by ester pyrolysis, but their assignment to **2a** was not possible previously.

Photolysis of Ar matrix isolated **1a** with the unfiltered

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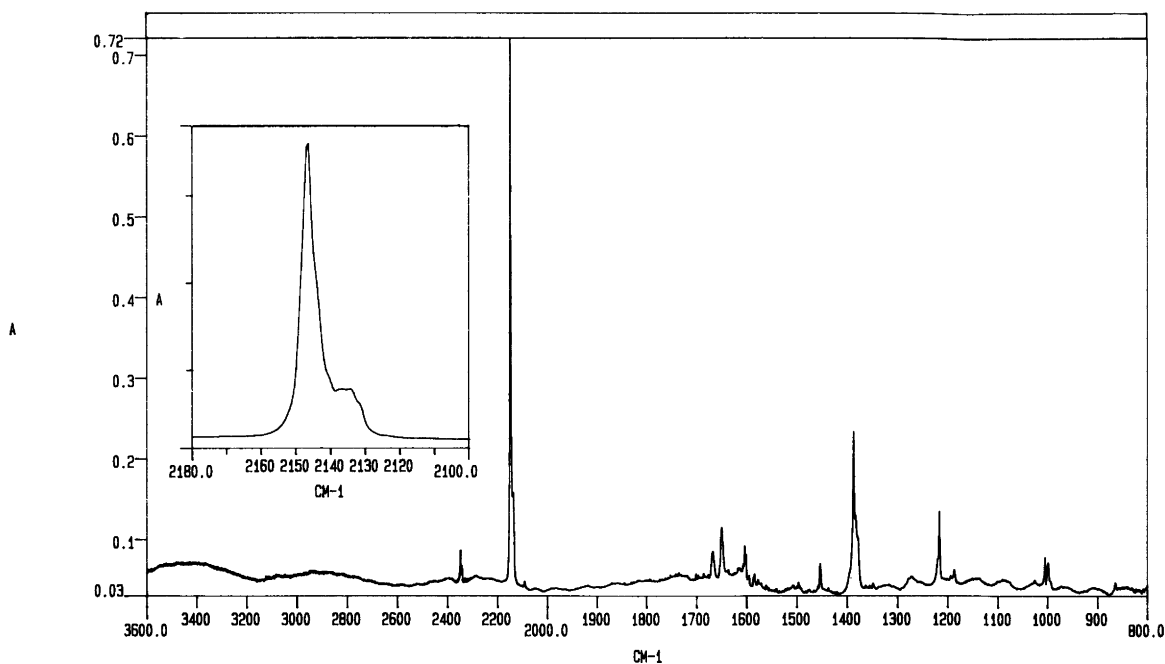


Fig. 1. FT-IR spectrum (Ar, 15 K) of benzoylketene (**2a**) produced by FVP of **1a** at 500 °C (10^{-5} mbar). Inset: detail showing the structure of the $\nu_{\text{C}=\text{O}}$ band near 2147 cm^{-1} (maximum).

light of a high-pressure Xe–Hg lamp also produced **2a**, with the main $\nu_{\text{C}=\text{O}}$ at 2147 cm^{-1} and its shape much like the one shown in Fig. 1. This confirms that the high frequency portion (2147 cm^{-1}) of the band is due to the *s-cis* isomer.⁶ However, **2a** is photochemically unstable. Ar matrix isolation of thermally produced **2a** followed by broad-band photolysis at 12 K for 16 h caused complete conversion of **2a** into phenylketene (**3**) and CO. The shoulder around 2134 cm^{-1} ascribed to the *s-trans* form of **2a** (see Fig. 1) initially increased in intensity relative to the 2147 cm^{-1} band on photolysis, but both then disappeared due to conversion into **3** and CO. Phenylketene (**3**) ($\nu_{\text{C}=\text{O}}$ 2120 cm^{-1} ; ^{13}C satellite at 2067 cm^{-1}) was identified by comparison with an authentic sample, produced¹¹ by matrix photolysis of diazoacetophenone (**4**) (Ar, 12 K).

While the experiments described above provide compelling evidence that the benzoylketenes **2** have been identified, they fall short of absolute proof. Additional strong evidence was adduced by real-time monitoring of the pyrolysis reactions of **1** by mass spectrometry, using a reactor situated immediately in front of the ion source of the spectrometer. As the FVP temperature was increased above 200 °C, the ion currents due to the molecular ions of **1** decreased rapidly, falling to zero at ca. 400 °C. At the same time, the molecular ion due to **2** increased sharply, *m/z* 146 for **2a** reaching a maximum at 350 °C, and decreasing only slightly on further heating to 650 °C. Since all of the starting furandiones **1** had disappeared above 350 °C, it is obvious that the neutral ketenes, **2**, were being detected. Their compositions were confirmed by exact mass measurements near the optimal FVP temperatures (400 °C).

We are using the same methodology to generate *s-cis*

acetylketene and study its photo-conformers. The results will be presented elsewhere in due course.

Experimental

Flash vacuum pyrolysis (FVP) was carried out in unpacked quartz tubes (10 cm length; 0.8 cm i.d.) using the apparatus previously described.¹² Pyrolysis products were condensed in an Ar matrix at 12–22 K or neat at 77 K.

Matrix photolysis was carried out using a 1000 W high pressure Xe–Hg lamp. FT-IR spectra were recorded on a Perkin-Elmer 1720X spectrometer at a resolution of 1 cm^{-1} .

FVP/MS was carried out in an apparatus similar to the one used for matrix isolation, employing a 10 × 0.8 cm quartz tube directly connected to the ion source of a Kratos MS25RFA mass spectrometer. There was a ca. 3 cm unheated length of quartz tube between the pyrolysis zone (200–1000 °C) and the ion source (200 °C).

5-Aryl-2,3-dihydrofuran-2,3-diones (**1**) were prepared according to the literature.³

FVP of 5-arylfuran-2,3-diones (**1**) was carried out at 400–500 °C (10^{-4} mbar) with isolation of the products on a KBr disk at 77 K for IR spectroscopy. The following spectra were obtained. **2a** (R = H): 3062, 2135 (vs), 1622, 1613, 1598, 1577, 1449, 1384, 1221, 1000, 705 cm^{-1} . **2b** (R = CH₃): 3046, 2136 (vs), 1618, 1605, 1569, 1409, 1384 cm^{-1} . **2c** (R = C₂H₅O): 2982, 2135 (vs), 1671, 1604, 1571, 1425, 1383, 1259, 1177, 1045 cm^{-1} . **2d** (R = Cl): 3061, 2148 (vs), 1681, 1618, 1590, 1569, 1490, 1409, 1381, 1219, 1096, 1010, 865, 843, 746, 503 cm^{-1} .

Matrix isolation of 2a. **1a** was pyrolyzed at 500 °C (5×10^{-5} mbar) and the products isolated in Ar matrix at 15 K. The IR spectrum (Fig. 1) showed the following bands assigned to **2a**: 2147 (vs), 2144 (sh), 2137 (sh), 2134 (sh), 2132 (sh), 2090 (w, ^{13}C satellite), 1665 (w), 1648 (w), 1602 (w), 1600 (w), 1451 (w), 1384 (m), 1216 (m), 1004 (w), 998 (w), 700 (w) cm^{-1} . Bands at 2345 and 2340 cm^{-1} were due to CO_2 , and a band at 2139 cm^{-1} to CO.

The same bands due to **2a** were obtained on pyrolysis of methyl benzoylacetate at 850 °C,⁶ but the spectrum was much less clean in this case.

Matrix photolysis of 2a. A sample of **2a** prepared as described above was photolyzed unfiltered in an Ar matrix at 12 K over a 20 h period. The low-frequency ketene bands around 2134 cm^{-1} initially increased in intensity relative to the main 2147 cm^{-1} band, as did the band at 2139 cm^{-1} ascribed to CO. Further irradiation caused all bands of **2a** to disappear (16 h), with concomitant increase in the CO band and formation of a new ketene absorbing at 2120 (vs) and 2067 (w, ^{13}C satellite) cm^{-1} . The CO disappeared when the temperature was raised to 40 K, but the new ketene remained. This new ketene was identified as phenylketene by direct comparison with a sample prepared by matrix photolysis of diazoacetophenone¹¹ (Ar, 15 K, 10 min, unfiltered light): 2120 (vs), 2067 (w, ^{13}C satellite), 1604 (m), 1505 (m), 1239 (w) cm^{-1} .

Matrix photolysis of 1a. **1a** was deposited with Ar at 12 K and photolyzed with the (unfiltered) light of the high-pressure Xe–Hg lamp for 15 min. The ketene formed initially showed a strong absorption at 2147 cm^{-1} , with a less well developed shoulder at 2132–2137 cm^{-1} . This indicates that the major band at 2147 cm^{-1} is due to the *s-cis* isomer of **2a**.

FVP/mass spectrometry of 1. The molecular ions of **1a–c** and **2a–c** were monitored by mass spectrometry as a function of temperature. The intensities of the molecular ions of **1a–c** decreased to zero when going from 200 to 400 °C, and those of **2a–c** reached a maximum at 350–400 °C. The high resolution mass spectra of thermally produced **2** were measured at an FVP temperature of 400 °C.

2a: Calc. for $\text{C}_9\text{H}_6\text{O}_2$ 146.03674; found 146.0367. **2b:** Calc. for $\text{C}_{10}\text{H}_8\text{O}_2$ 160.05238; found 160.0532. **2c:** Calc. for $\text{C}_{11}\text{H}_{10}\text{O}_3$ 190.06293; found 190.0626. Low resolution MS of **2a**: 146 (70, M^+), 105 (100), 77 (60), 51 (15), 28 (10).

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