

## Notiz/Note

Direct Observation and Trapping of a Heterocyclic  $\alpha$ -Oxo Ketene: 3-Carbonyl-1,3-dihydro-1-methyl-2*H*-indol-2-oneC. Oliver Kappe<sup>a,b</sup>, Gerald Färber<sup>c</sup>, Curt Wentrup<sup>\*b</sup>, and Thomas Kappe<sup>\*a</sup>Institute of Organic Chemistry<sup>a</sup> and Institute of Physical Chemistry<sup>c</sup>,  
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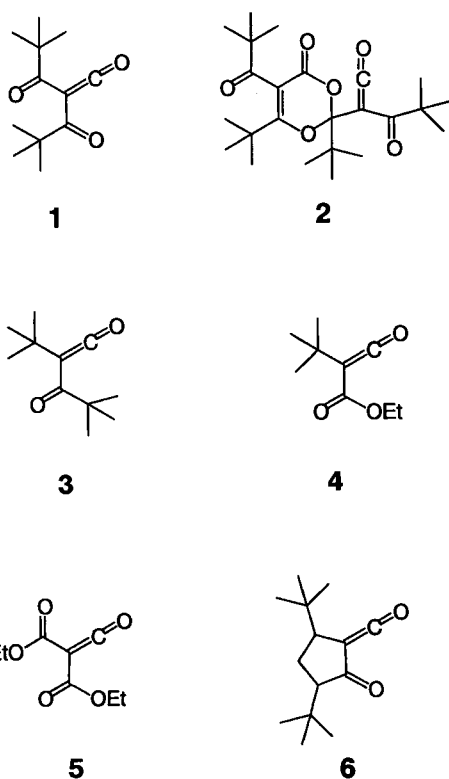
The title compound **8a** was generated by both flash vacuum pyrolysis and matrix photolysis of diazoquinolone **7** and identified by Ar-matrix IR spectroscopy and mass spectrometry.

Trapping of the highly reactive  $\alpha$ -oxo ketene **8a** with methanol leads to  $\beta$ -keto ester **9**, whereas dimerization of **8a** furnishes spiro compound **10**.

Recently, much interest has been focused on the chemistry of  $\alpha$ -oxo ketenes<sup>[1a]</sup>. Usually, this type of conjugated ketenes is highly reactive and cannot be isolated or observed under ordinary reaction conditions, since in most cases rapid dimerization or reaction with atmospheric moisture takes place<sup>[1a]</sup>. A few examples of sterically or electronically stabilized  $\alpha$ -oxo ketenes that have been isolated in substance at room temperature include dipivaloylketene (**1**)<sup>[1]</sup>, its dimer **2**<sup>[1]</sup>, *tert*-butyl(pivaloyl)ketene (**3**)<sup>[2]</sup>, *tert*-butyl(ethoxycarbonyl)ketene (**4**)<sup>[3]</sup>, and bis(ethoxycarbonyl)ketene (**5**)<sup>[4]</sup>. Ketene **3** is

permanently stable and indifferent towards methanol at room temperature<sup>[2]</sup>. One reason for the unreactivity of such crowded  $\alpha$ -oxo ketenes is the energetically preferred *s*-*E* conformation these species adopt<sup>[5]</sup>, that not only prevents [4 + 2] dimerization<sup>[1a]</sup>, but also makes a six-membered transition state for 1,4-addition of nucleophiles<sup>[6]</sup> inaccessible. Cyclic  $\alpha$ -oxo ketenes, which are constrained to the *s*-*Z* conformation, are generally more reactive, even if substituted by bulky groups (e.g. **6**)<sup>[7]</sup>.

Therefore, it is not surprising that heterocyclic  $\alpha$ -oxo ketenes are very unstable, and — with very few exceptions<sup>[8a,b]</sup> — have not been identified so far, although such ketenes were proposed as intermediates in a variety of reactions<sup>[8]</sup>. Here we report on the generation and characterization of such a ketene, employing e.g. low-temperature FT-IR spectroscopy which has proved to be a useful tool in the identification of other reactive  $\alpha$ -oxo ketenes<sup>[9]</sup>.



## Results and Discussion

For the generation of  $\alpha$ -oxo ketene **8a**, 3-diazo-1-methylquinoline-2,4(1*H*,3*H*)-dione (**7**) was chosen as precursor, since pyrolysis or photolysis of  $\alpha$ -diazo- $\beta$ -dicarbonyl compounds usually provides a clean route to  $\alpha$ -oxo ketenes<sup>[9]</sup>. Monitoring by IR spectroscopy of the flash vacuum pyrolysis (FVP) of diazo compound **7** at 600 °C with product isolation in an Ar matrix at 18 K (Figure 1a) revealed the formation of ketene **8a** as the only reaction product (see below). The IR frequencies (2151, 1709  $\text{cm}^{-1}$ ) of this species are in good agreement with the values obtained for other  $\alpha$ -oxo ketenes<sup>[1–5,7,9,10]</sup>.

In a similar experiment ketene **8a** was deposited as neat film at 18 K (2151, 1688  $\text{cm}^{-1}$ ) and the intensity of the ketene absorption constantly monitored by IR spectroscopy on subsequent warm-up of the spectroscopic window. Under these conditions ketene **8a** remained stable until ca. 140 K. Similarly, the broad-band irradiation (1000 W Hg-Xe lamp) of diazo compound **7** in an Ar matrix at 14 K was followed by IR spectroscopy (Figure 1b, difference spectrum). After 3 min of irradiation, **7** ( $\nu_{\text{C-N}}$  2211, 2167, 2151  $\text{cm}^{-1}$ ) was completely converted to  $\alpha$ -oxo ketene **8a** ( $\nu_{\text{C=O}}$  2151  $\text{cm}^{-1}$ ).

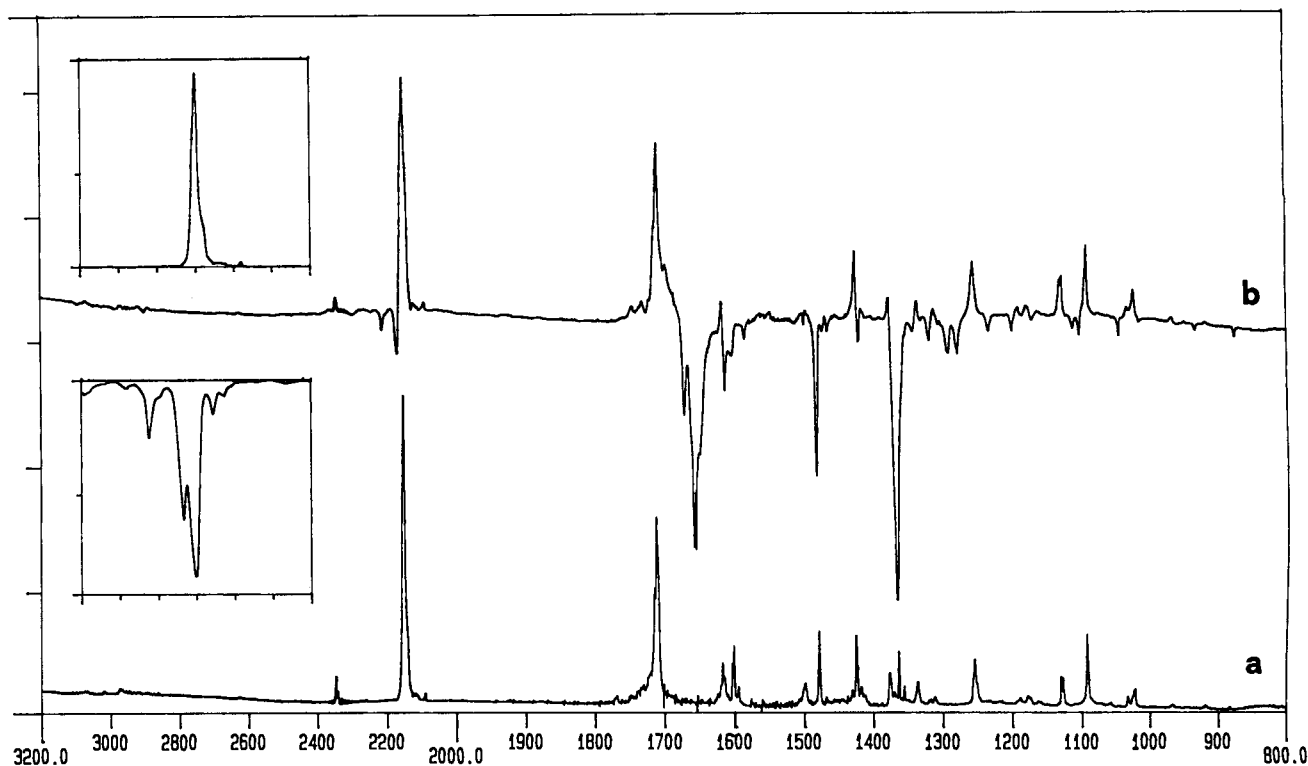
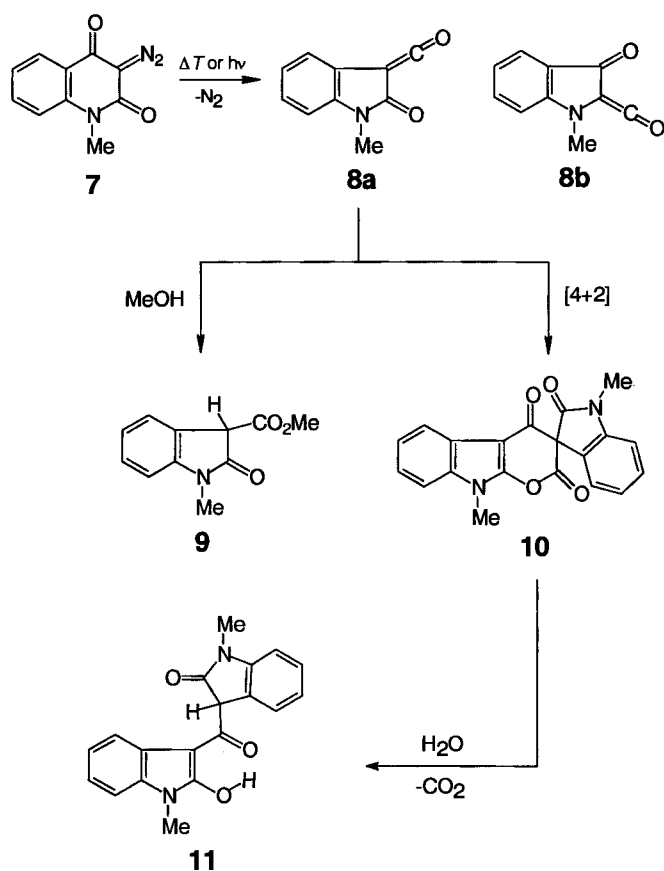


Figure 1. a) IR spectrum of **8a** (Ar matrix, 18 K) produced by FVP (600 °C,  $5 \cdot 10^{-5}$  mbar) of **7** (for exact values see Experimental). b) IR difference spectrum (Ar matrix, 14 K) showing the broad-band photolysis of **7** (bottom) to **8a** (top); the inset (top) shows the expanded ketene region (2000–2300  $\text{cm}^{-1}$ ). The strong band at 2151  $\text{cm}^{-1}$  in the  $\nu_{\text{C}=\text{N}}$  region does not appear in the difference spectrum due to its coincidence with the  $\nu_{\text{C}=\text{O}}$  of **8a** at 2151  $\text{cm}^{-1}$ . These bands are shown in the lower and upper insets, respectively (2000–2300  $\text{cm}^{-1}$  region)



When **7** was irradiated at  $\lambda = 366$  or  $254$  nm for 20 min ketene **8a** appeared to be formed in three different sites<sup>[11]</sup> (2158, 2151, 2147  $\text{cm}^{-1}$ ), which collapsed to a single peak (2151  $\text{cm}^{-1}$ ) on annealing at ca. 30 K for 5 min, or on irradiation with unfiltered output of the 1000 W Hg-Xe lamp for 3 min. The IR spectra obtained from pyrolysis and photolysis (annealed) of **7** were virtually identical, and most of the frequencies of **8a** could be obtained by comparison of the spectra (the small peak at 2090  $\text{cm}^{-1}$  is due to the  $^{13}\text{C}$  satellite)<sup>[10]</sup>. Thus, although a priori the Wolff rearrangement of *unsymmetrically* substituted  $\alpha$ -diazo- $\beta$ -dicarbonyl compounds may lead to two isomeric  $\alpha$ -oxo ketenes (here **8a** and **8b**)<sup>[12]</sup>, the IR spectroscopic evidence strongly suggest that only one ketene is formed.

In addition to IR investigations, the thermolysis of diazoquinolone **7** was also monitored by mass spectrometry, using a FVP apparatus directly attached to the ion source of a mass spectrometer. As the FVP temperature was increased above 300 °C, the ion current due to the molecular ion of **7** ( $m/z$  201) decreased rapidly, ultimately falling to zero. Correspondingly, the molecular ion due to  $m/z$  173 (loss of  $\text{N}_2$ ) increased sharply, reaching a maximum at ca. 650 °C<sup>[13]</sup>, providing additional evidence for the generation of i.e. ketene **8a**, formed by thermal Wolff rearrangement from **7**. The elemental composition of that species was confirmed by exact mass measurement.

However, since neither MS nor IR spectroscopy permitted us to decide conclusively which of the two ketenes, **8a** or **8b**, had been formed, trapping experiments were carried out. Photolysis of diazo compound **7** in methanol solution with a high-pressure mercury lamp for 72 h provided ester **9** in 90% yield. The trapping product was unambiguously identified as ester **9** (and not as the isomer

resulting from the reaction of **8b** with methanol) by IR and  $^{13}\text{C}$ -NMR spectroscopy (see Experimental), in addition to comparison with data for the authentic material<sup>[14]</sup>.

The formation of **8a** was further substantiated by a self-trapping reaction. Thus, from a preparative pyrolysis experiment (400 °C,  $10^{-3}$  mbar), dimer **10** was isolated as the only product in 74% yield. Since it was shown recently that  $\alpha$ -oxo ketenes can form three different types of dimers<sup>[11]</sup> it was mandatory to confirm the structure of **10** by X-ray crystallography (Figure 2). In the case of ketene **8a**, dimerization proceeds by [2 + 4] cycloaddition of one  $\alpha$ -oxo ketene molecule to the C=C bond of another to furnish the hitherto unknown spiro[indole-3,3'-pyrano[2,3-*b*]indole] skeleton. Again, this dimer can only result from ketene **8a** and not from **8b**. Heterocycle **10** is a colorless solid, insoluble in most organic solvents. If treated with aqueous acetone at room temperature, hydrolysis by ring-opening of the lactone ring with subsequent decarboxylation occurs, affording bisindolyl ketone **11**.

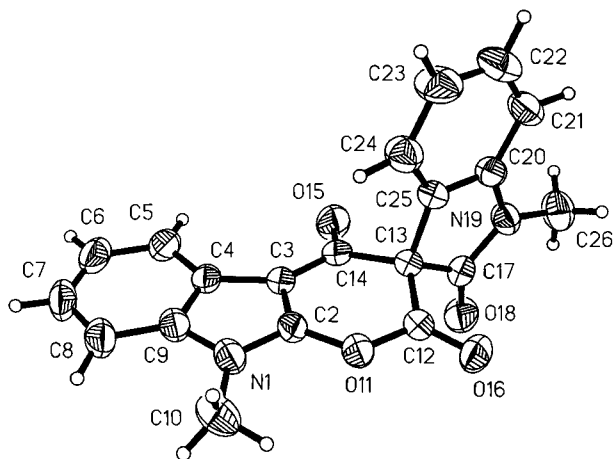


Figure 2. ORTEP drawing of **10**. Thermal ellipsoids are drawn at the 50% probability level, hydrogens are drawn as open circles. Selected bond distances [Å] and bond angles [°]: C2–O11 1.357(3), C3–C14 1.412(3), C12–C13 1.508(3), C13–C14 1.540(3), C13–C25 1.514(3), C17–O18 1.213(3), N19–C20 1.398(3), C2–C3 1.372(3), O11–C12 1.391(3), C12–O16 1.181(3), C13–C17 1.542(3), C14–O15 1.221(3), C17–N19 1.363(3), C20–C25 1.382(3), C12–C13–C17 108.0(2), C12–C13–C25 109.1(2), C17–C13–C25 102.0(2), C12–C13–C14 117.3(2), C14–C13–C25 109.3(2)

In conclusion, we have shown that the photochemical and thermal Wolff rearrangement of diazo compound **7** proceeds with remarkable regioselectivity to produce the heterocyclic  $\alpha$ -oxo ketene **8a**, although no explanation of the very high selectivity can be given at present<sup>[12]</sup>. Restricted to the *s*-*Z* conformation, **8** is extremely unstable and readily dimerizes or reacts with nucleophiles. Nevertheless, the ring constriction of diazoquinolone **7** described herein provides an easy entry into the chemistry of functionalized or fused indoles, which are otherwise not available.

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## Experimental

The FVP apparatus contained a 10 cm length (0.8 cm i.d.) quartz tube in housings flanged to Leybold-Heraeus closed-cycle liquid He cryostats for Ar matrix isolation (14–18 K). Pressures were  $10^{-3}$ – $10^{-5}$  mbar. For matrix isolation, samples were codeposited with ca. 200 mbar of Ar in 20 min on BaF<sub>2</sub> disks. IR spectra were

recorded on a Perkin-Elmer 1700X FT-IR spectrometer at a resolution of  $1\text{ cm}^{-1}$ . Further details and apparatus for preparative FVP were as previously described<sup>[15]</sup>. Matrix photolysis experiments were carried out using a high-pressure Xe-Hg lamp (1000 W, Hanovia) equipped with a water filter for broad-band irradiation or a monochromator (Schoeffel GM250) for irradiation at 366 nm. Irradiation at 254 nm employed a 75-W "Flächenstrahler" from Grätzel (Karlsruhe). For solution photolysis a high-pressure Hg lamp (TQ 150, Hanau) was used. FVP/MS was carried out in an apparatus similar to the one used for matrix isolation, employing a 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). —  $^1\text{H}$  NMR (200 MHz) and  $^{13}\text{C}$  NMR (50 MHz): Varian XL-200. — EI MS: Kratos MS25RFA. — Microanalyses: C,H,N Automat Carlo Erba 1106. — Melting points: uncorrected. — Diazoquinolone **7** was prepared according to ref.<sup>[16]</sup>.

**FVP of 7: Generation of 3-Carbonyl-1,3-dihydro-1-methyl-2H-indol-2-one (8a):** A sample of **7** was sublimed at ca. 80 °C through a hot quartz tube (600 °C) and codeposited with Ar on a BaF<sub>2</sub> window to give **8a**: IR (Ar matrix, 18 K):  $\tilde{\nu} = 2151\text{ cm}^{-1}$  (vs), 2090 (w), 1709 (s), 1615 (m), 1602 (m), 1497 (w), 1476 (m), 1423 (m), 1374 (m), 1336 (w), 1253 (w), 1191 (w), 1177 (w), 1128 (m), 1091 (m), 1024 (w). — IR (neat, 18 K):  $\tilde{\nu} = 2151$  and  $1688\text{ cm}^{-1}$ , stable till 140 K.

**Matrix Photolysis of 7:** A sample of **7** was sublimed at ca. 80 °C and codeposited with Ar on a BaF<sub>2</sub> disk. Photolysis by broad-band irradiation was monitored by IR spectroscopy which showed complete conversion of **7** into **8a** in 3 min. **7**: IR (Ar, 14 K):  $\tilde{\nu} = 2211\text{ cm}^{-1}$  (w), 2167 (m), 2151 (s), 1669 (m), 1655 (s), 1645 (m), 1611 (m), 1600 (m), 1498 (w), 1480 (m), 1419 (w), 1363 (vs), 1317 (w), 1291 (w), 1277 (w), 1231 (w), 1198 (w), 1111 (w), 1102 (w), 1045 (w), 934 (w), 876 (w). — IR data for **8a** are identical with those found on pyrolysis (see above). There is no evidence for the formation of isomeric **8b**, and, since the  $^{13}\text{C}$  satellite is detected (ca. 1%), we conclude that the isomeric ketene **8b**, if formed at all, is present in less than 1%.

**FVP/Mass Spectrometry of 7:** The molecular ions of **7** and **8a** were monitored by mass spectrometry as a function of temperature. The intensity of the molecular ion of **7** decreased to zero when going from 300 to 450 °C, and the one for **8a** reached a maximum at ca. 650 °C. The high-resolution mass spectrum of thermally produced **8a** was measured at a FVP temperature of 650 °C. — **8a**: C<sub>10</sub>H<sub>7</sub>NO<sub>2</sub>: calcd. 173.0477; found 173.0478.

**Methyl 2,3-Dihydro-1-methyl-2-oxo-1H-indole-3-carboxylate (9):** A solution of diazo compound **7** (500 mg, 2.49 mmol) in 300 ml of methanol was irradiated at room temp. for 72 h. After evaporation of the solvent, the crude product was recrystallized from methanol/water or CCl<sub>4</sub> to give 460 mg (90%) of pure **9**, m.p. 127–131 °C (ref.<sup>[14]</sup> 129–132 °C). — IR (KBr):  $\tilde{\nu} = 1737\text{ cm}^{-1}$ , 1704. —  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta = 3.22$  (s, 3H, NMe), 3.78 (s, 3H, OMe), 4.43 (s, 1H, 3-H), 6.81–7.39 (m, 5H, aromatic H); accompanied by ca. 10% of enol tautomer:  $\delta = 3.56$  and  $3.96$  (2 s, 2 Me). —  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>):  $\delta = 26.5$  (q, NMe), 52.1 (d, C-3), 53.2 (q, OMe), 108.8–144.7 (6 aromatic C), 167.7 (m, CO), 170.7 (m, CO). — MS (70 eV),  $m/z$  (%): 205 (88) [M<sup>+</sup>], 173 (0.5), 146 (100), 117 (50). — C<sub>11</sub>H<sub>11</sub>NO<sub>3</sub> (205.2): calcd. C 64.38, H 5.40, N 6.83; found C 64.62, H 5.05, N 6.78.

**1,9'-Dimethylspiro[3H-indole-3,3'-(2'H)-pyrano[2,3-*b*]indole]-2,2',4'-(1H,9'H)-trione (10):** A sample of diazo compound **7** (402 mg, 2.00 mmol) was pyrolyzed in the preparative apparatus at 400 °C and  $10^{-3}$  mbar within 2 h (sublimation temp. ca. 120 °C). The product deposited at the end of the hot zone and was collected from there. Digestion of the crude pyrolysis product with dry acetone gave 256 mg (74%) of pure **10**, m.p. 200 °C (dec.). An analytical

sample was obtained by recrystallization from dry nitromethane. — IR (KBr):  $\tilde{\nu}$  = 1802  $\text{cm}^{-1}$ , 1725, 1662. —  $^1\text{H NMR}$  ( $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 3.22 (s, 3H, NMe), 3.85 (s, 3H, NMe), 7.15–7.74 (m, 8H, aromatic H). —  $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_4$  (346.3): calcd. C 69.36, H 4.07, N 8.09; found C 69.01, H 4.23, N 8.22.

*Bis(2,3-dihydro-1-methyl-2-oxo-1H-indol-3-yl) Ketone (11)*: 1 ml of water was added to a suspension of dimer **10** (50 mg, 0.14 mmol) in 5 ml of acetone, and the resulting mixture was stirred for 12 h at room temp. After acetone was removed in vacuo, the suspension was diluted with 3 ml of water and filtered to give 40 mg (90%) of pure **11**, m.p. 162–165 °C. An analytical sample was obtained by recrystallization from methanol. — IR (KBr):  $\tilde{\nu}$  = 3450  $\text{cm}^{-1}$  br, 1706, 1662. —  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 3.19 (s, 3H, NMe), 3.26 (s, 3H, NMe), 4.99 (s, 1H, 3'-H), 6.80–7.47 (m, 8H, aromatic H). —  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 25.8 (NMe), 26.6 (NMe), 50.3 (C-3'), 104.2 (C-3), 108.6–144.9 (12 aromatic C), 168.4, 170.9, 171.5 (C-2 + 2 CO). — MS (70 eV),  $m/z$  (%): 320 (13) [ $\text{M}^+$ ], 174 (33), 173 (15), 147 (100). —  $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_3$  (320.3): calcd. C 71.29, H 5.03, N 8.74; found C 71.03, H 5.21, N 8.68.

*X-Ray Structure Determination of 10* ( $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_4$ ,  $M = 346.3$ )<sup>[17]</sup>: A colorless specimen of size 0.24 × 0.26 × 0.56 mm was investigated at 296 ± 2 K on a Siemens P4 diffractometer ( $\text{Cu-K}\alpha$  radiation,  $\lambda = 1.54178$  Å, graphite monochromator). Cell dimensions were determined by a least squares fit to the setting angles of 38 reflections with  $11^\circ \leq 2\theta \leq 52^\circ$ : monoclinic system, spacegroup  $P2_1/c$ ,  $a = 12.396(2)$ ,  $b = 10.561(2)$ ,  $c = 12.544(2)$  Å,  $\beta = 104.65(3)^\circ$ ,  $V = 1588.8(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu = 0.848$  mm<sup>-1</sup>,  $d_c = 1.448$  gcm<sup>-3</sup>. Intensity data were collected for a complete hemisphere of reciprocal space with  $2^\circ \leq 2\theta \leq 114^\circ$ ,  $-1 \leq h \leq 13$ ,  $-11 \leq k \leq 11$ ,  $-13 \leq l \leq 13$  ( $\omega$  scans, width 1.2°, variable speed, ranging from 5°/min to 30°/min, stationary background measurement at each end of the scan for 25% of the total scan time). 5005 Reflections were measured yielding 2147 independent reflections ( $R_m = 0.039$ ) and 1906 with  $F/\sigma(F) > 4$ . Usual LP corrections were applied, but no absorption correction. The structure was solved by direct methods and refined by minimizing the quantity  $\sum w(|F_o| - |F_c|)^2$  (full matrix), all non-hydrogen atoms were refined with anisotropic a.d.p.'s, hydrogen atoms were refined with isotropic a.d.p.'s at observed positions. Final  $R = \sum \|F_o| - |F_c| \| / \sum \|F_o| - |F_c|\| = 0.0436$ ,  $wR = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2} = 0.0400$  for 291 parameters and 1906 observations [weighting scheme  $1/\sigma^2(F)$ ]. The final difference density map shows features up to 0.19 eÅ<sup>-3</sup> and down to -0.22 eÅ<sup>-3</sup>. The Siemens SHELXTL software was used for the calculations. Figure 2 shows a perspective drawing of the molecule.

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- <sup>[13]</sup> At higher temperatures the molecular ion due to **8a** decreases again, and a new compound with  $m/z$  145 (corresponding to loss of CO from **8a**) is formed. Decarbonylation of ketene **8a** with subsequent Wolff rearrangement<sup>[2,8f,9a,10]</sup> would presumably give a second ring-contracted ketene (2-carbonyl-1,2-dihydro-1-methylbenzazete). In fact, IR investigation of the FVP of **7** at 1000 °C confirm the formation of a second ketene in this temperature region ( $\tilde{\nu} = 2120$   $\text{cm}^{-1}$ , Ar matrix). We agree with one of the referees, that this ketene could probably also be formed by prolonged photolysis of matrix isolated **7** at 254 nm.
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- <sup>[17]</sup> Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-400152, the names of the authors, and the journal citation.