

Reactivity of Ketenes in Matrices. Direct Observation of Ketene–Pyridine Ylides

Greg GuangHua Qiao, John Andraos, and Curt Wentrup*

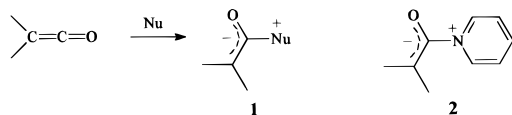
Contribution from the Department of Chemistry, The University of Queensland, Brisbane, Queensland 4072, Australia

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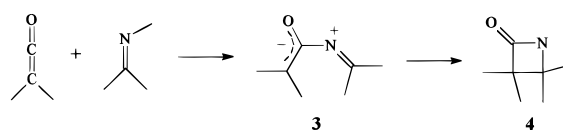
Abstract: Ketenes **7**, **14**, and **17** have been generated in pyridine matrices and observed by infrared spectroscopy to react with pyridine at temperatures between 15 and 50 K to form ketene–pyridine ylides **12**, **15**, and **18**. Azaheterocyclic ketenes **20**, **23**, and **26** dimerize or tetramerize at *ca.* 50 K, whereby one ketene molecule acts as a nucleophile toward the other, forming a transient ketene–imine ylide.

Introduction

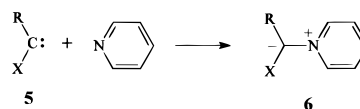
The chemistry of ketenes is of considerable current interest.¹ The interaction between ketenes and nucleophiles in solution at room temperature has been studied extensively using conventional or laser flash photolysis (LFP) methods with UV spectroscopic detection of intermediates.^{2,3} In general, a ketene–nucleophile ylide of type **1** is expected to be formed initially. The reaction with pyridine would give rise to ketene–pyridine ylides of type **2**.³ Such intermediates undoubtedly play



a role in several ketene reactions catalyzed by tertiary amines or pyridines.⁴ Likewise, the Staudinger reaction between ketenes and imines, leading to β -lactam **4**, is believed to take place via an initial ketene–imine ylide, **3**.⁵ Carbenes, too, react with pyridine to form ylides **6**.⁶ Since **6** is much longer lived than carbene **5**, this reaction can be used to trap carbenes that

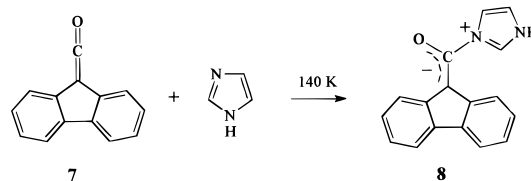


are too short lived for direct observation under LFP conditions,



thus making the carbenes indirectly observable.⁶ Because either α -oxocarbenes or the diazoketone precursors can undergo a rapid Wolff rearrangement to ketenes, the latter forming ylides of type **2**, it is important to be able to distinguish ylides of type **2** and type **6**.^{3c}

Infrared spectroscopy would seem to be an ideal method for the detection of both ketenes and ylides of types **1** and **2**, but it is difficult to apply to very fast reactions under the conditions usually prevailing in LFP studies.⁷ Here we report the direct IR-spectroscopic observation of ketenes reacting in very low temperature matrices, some reactions taking place at temperatures as low as 15–40 K. Only one example of a similar reaction has been reported, viz., the reaction between dibenzopentafulvenone (**7**) and imidazole in a phenolic resin at 140 K, giving ylide **8**, the latter characterized by an absorption at 1635 cm^{-1} in the IR.⁸



Our study was motivated by the discovery that some nitrogen-containing ketenes of type **9** undergo self-reaction (dimerization or tetramerization) at surprisingly low temperatures, thus making

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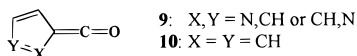
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them unobservable at 77 K; the carbocyclic analogs **10** are much more stable in the absence of an external nucleophile.

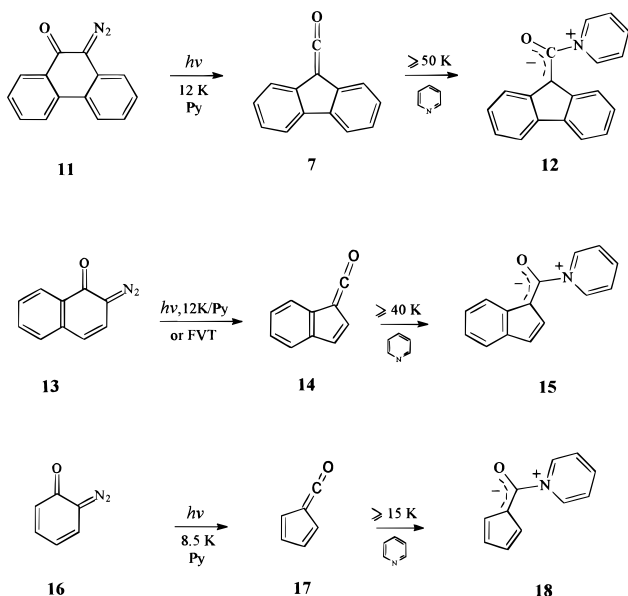


Results and Discussion

1. Ketene–Pyridine Ylide Formation. Ketenes **7**, **14**, and **17** (Scheme 1) are thermodynamically quite stable; they are readily generated in Ar matrices or as neat films by photolysis or flash vacuum thermolysis (FVT) of the diazoketones **11**, **13**, and **16**, respectively. In the absence of external nucleophiles, ketenes **14** and **17** are easily observable by IR spectroscopy at *ca.* 200 K. Ketene **7** is isolable at room temperature.^{1a,9}

The three diazo compounds **11**, **13**, and **16** were deposited together with pyridine on the cold tip of a cryostat at 8.5–12 K. Subsequent irradiation (broad band; high-pressure Xe–Hg lamp) produced ketenes **7**, **14**, and **17** in the pyridine matrices, identified by comparison with the spectra obtained in Ar or neat films. The characteristic ketene absorptions in pyridine are 2115 cm^{-1} (**7**), 2128 cm^{-1} (**14**), and 2126 cm^{-1} (**17**).

Scheme 1



Warmup of the ketenes in a pyridine matrix caused disappearance of the ketene absorptions in concert with development of new, strong bands in the 1650 cm^{-1} region of the spectra. Thus, ketene **7** started reacting at 50 K, giving a species absorbing at 1653 cm^{-1} . IR monitoring of the reaction at 60 K demonstrated that the ketene disappeared with the same rate as that of the formation of the new compound (Figure 1). Bands due to pyridine were observed to decrease at the same time, and the 1653 cm^{-1} absorption is therefore assigned to ylide **12**.

The reaction does not follow pseudo-first-order (or strict second-order) kinetics, but can be described by the equation $[A]_t = [A]_0 \exp(-kt)^\beta + C$ which is typical of reactions in low-temperature matrices,¹⁰ where the exponent β has the value $0 < \beta < 1$ and C is the residual ketene concentration at infinite time at temperature T . The “stretched exponential” decay arises from the fact that the ketene will rapidly react at the lowest temperature with those pyridine molecules that are most favorably oriented. The reaction then stops completely until

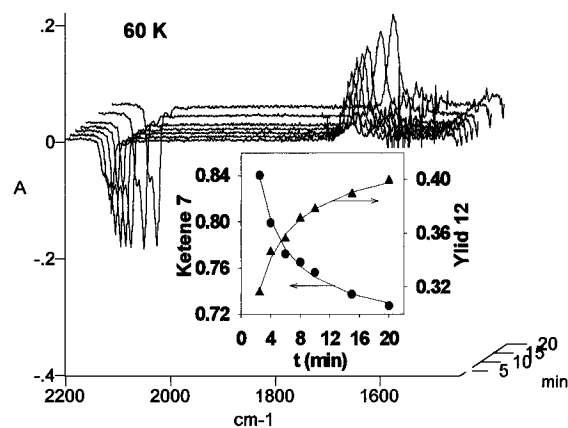


Figure 1. IR difference spectra showing the decreasing (increasingly negative) absorbance of ketene **7** at 2115 cm^{-1} and increase of the ylide **12** at 1653 cm^{-1} in a pyridine matrix at 60 K for 20 min. Inset: decay of ketene absorption at 2115 cm^{-1} and increase of ylide at 1653 cm^{-1} during that 20 min. Absorbance values for the spectra are difference values; for the inset they are absolute values.

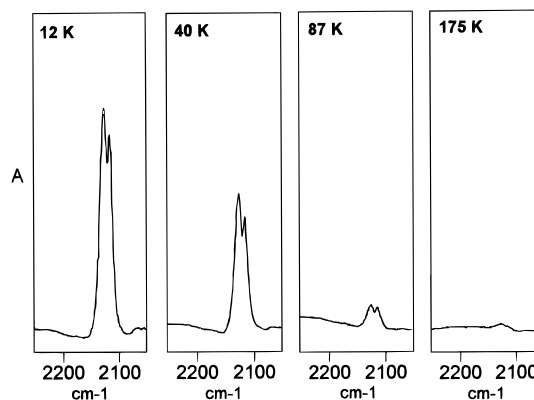


Figure 2. Partial IR spectra of ketene **14** (2128 and 2117.5 cm^{-1}) on the same absorbance scale, recorded during warmup of the window from 12 to 175 K in the presence of pyridine. The warmup took 61 min.

the temperature is raised; the next most favorable sites will now react, and so on. Consequently, a classical Arrhenius analysis and evaluation of activation parameters in terms of k vs T^β are not physically meaningful, and we will report separately on an alternative analysis of activation parameters. The reactions described here have typically very low β values on the order of 0.2.

Ketene **14** similarly reacted with pyridine, starting at *ca.* 40 K; the ketene peak had completely vanished at 175 K during a 61 min warmup period (Figure 2). Constant temperature monitoring of the reaction at 60 K again demonstrated disappearance of the ketene in concert with formation of ylide **15**, absorbing at 1675 cm^{-1} (Figure 3). The ketene and pyridine peaks also disappeared in concert (Figure 4).

The smallest ketene **17** was generated in a pyridine matrix at 8.5 K and found to react with pyridine already at 15 K to form a species (**18**) absorbing at 1687 cm^{-1} (Figure 5). The decay of the ketene at 40 K in concert with the formation of the ylide and disappearance of pyridine is shown in Figure 6. The reaction was observable between 15 and 120 K, again due to the fact that “fast” sites react first and “slow” sites react only at higher temperatures. The extraordinarily low onset of reaction at 15 K implies that this ketene is as reactive as some carbenes.^{10b,11}

We have observed related reactions between ketenes and other

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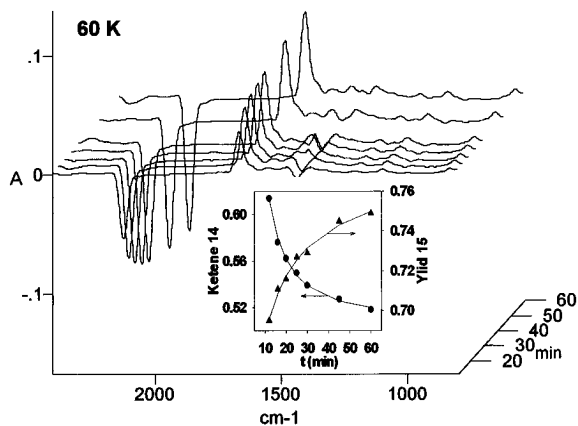


Figure 3. IR difference spectra showing the decreasing absorbance (increasingly negative) of ketene **14** and increase of the ylide **15** at 60 K from 12 (initial time) to 60 min (final time). Inset: decay of the ketene absorbance and increase of ylide during this 48 min. Absorbance values for the spectra are difference values; for the inset they are absolute values.

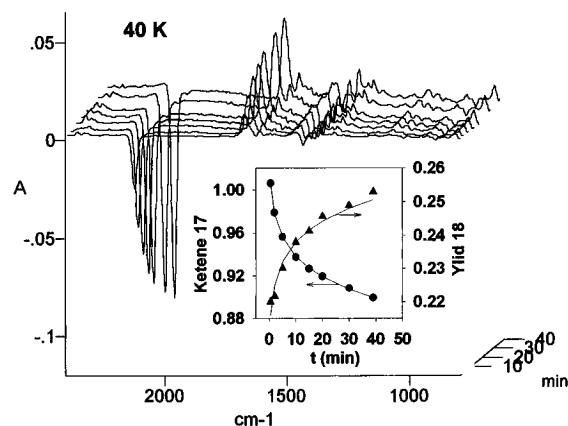


Figure 6. IR difference spectra showing the decreasing absorbance of ketene **17** at 2126 cm^{-1} and increase of the ylide **18** at 1687 cm^{-1} in a pyridine matrix at 40 K for 39 min. Inset: decay of ketene **17** and increase of ylide **18** during 39 min. Absorbance values for the spectra are difference values; for the inset they are absolute values.

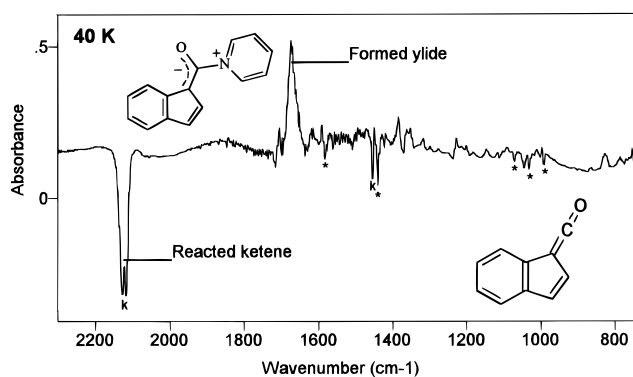


Figure 4. IR difference spectrum on warmup from 12 to 40 K, converting ketene **14** to ketene ylide **15**. Positive spectrum: formed ketene ylide (1675 cm^{-1}). Negative spectrum: reacted ketene (2128, 2117.5 cm^{-1}) (bands marked k) and pyridine (marked with *).

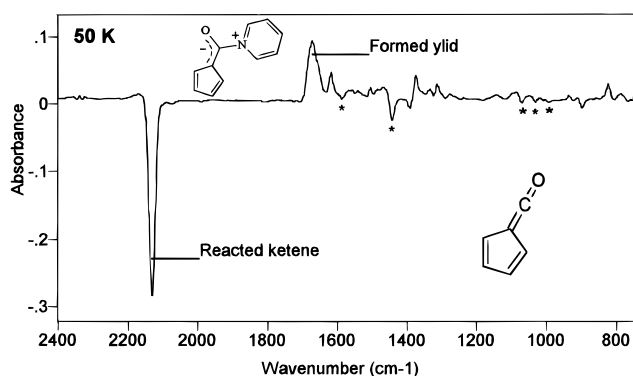


Figure 5. IR difference spectrum on warming of the window at 50 K for 20 min, converting ketene **17** to ketene ylide **18**. Positive spectrum: formed ketene ylide **18** (1683 cm^{-1}). Negative spectrum: reacted ketene **17** (2126 cm^{-1}) and pyridine (marked with *).

amines. For example, **7** reacts with triethylamine at 50 K. We will report more detailed investigations of such reactions in due course.

2. Dimerization, Tetramerization, and Reaction with Alcohols. 1-Carbonyl-1H-isoindole (20) and 2-Carbonyl-2H-pyrrole (23). The facile reactions between ketenes and pyridine or other amines offer an explanation for the extraordinary

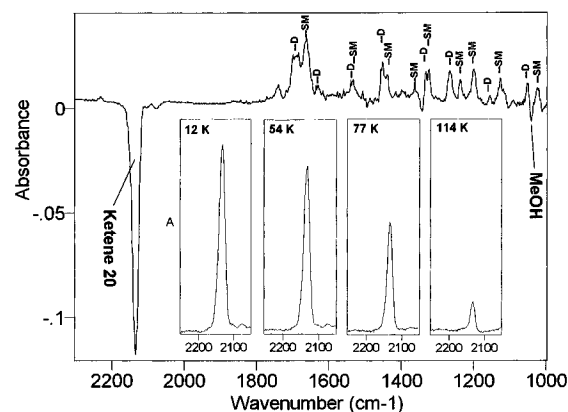


Figure 7. IR difference spectrum on warming from 47 to 78 K of the neat pyrolysate produced by FVT of ester **19** at 500 °C neat. Positive spectrum: the formed dimer **21** (D) and ester **19** (SM). Negative spectrum: the disappearance of ketene **20** and methanol. Inset: decay of ketene **20** on warming from 12 to 114 K in the course of 47 min. The 2133 cm^{-1} band is shown.

instability of ketenes of type **9**. For example, methyl isoindole-1-carboxylate (**19**) eliminates methanol on FVT at 550 °C, but the expected ketene **20** was not observable when the thermolysate was condensed on a 77 K KBr window; only methanol, the ketene dimer **21**,¹² and ester **19** were detected. However, when the thermolysis product was isolated as a neat film at 12 K, ketene **20**¹² was readily detected by its strong absorption at 2133 cm^{-1} together with peaks due to the eliminated methanol. Slow warmup of the sample revealed that ketene **20** started reacting at 47 K (Figure 7, inset) and that dimer **21** together with the starting material **19** was being formed between 47 and 78 K (Figure 7). The dimerization of **20** to **21** can be looked upon as one ketene molecule acting as a nitrogen nucleophile toward the other, generating a new ketene ylide (vide infra). Thus, the reactivities of ketene **20** toward itself and toward methanol are similar to that of the carbocyclic analog **14** with pyridine.

2-Carbonyl-2H-pyrrole (**23**) can be generated by FVT of pyrrole-2-carboxylic acid or its methyl ester **22**.¹² When generated from the acid and deposited at 12 K, warmup to 40 K caused dimerization of **23** to **24**. This product was identified by difference IR spectroscopy as well as isolation at room temperature and comparison with authentic material.¹²

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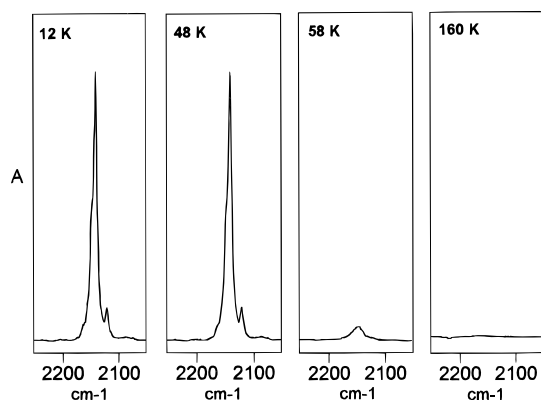
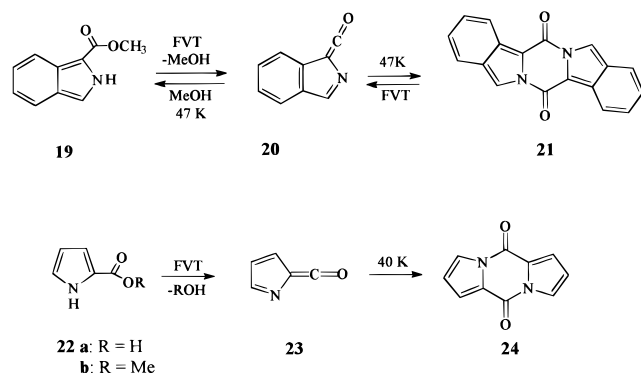


Figure 8. Partial IR spectra of ketene **26** (2142 cm^{-1}) on the same scale recorded during warmup from 12 to 160 K. The warmup took 39 min.

Scheme 2



3-Carbonyl-3H-indole (26). Oxo diazo compound **25**¹³ was sublimed onto a 12 K BaF₂ window as a neat film and irradiated with a low-pressure Hg lamp (254 nm) to generate ketene **26** (2142 cm^{-1}). Full conversion of diazo compound **25** was achieved as monitored by the disappearance of the peak at 2121 cm^{-1} . Subsequent warming of the neat ketene **26** caused no change below 48 K; at 58 K the ketene intensity was dramatically reduced, and at 71 K it had virtually vanished (Figure 8). IR difference spectra and comparison with authentic material demonstrated the formation of tetramer¹³ **27** at 71 K. Furthermore, the identity of the tetramer was verified by ¹H NMR spectroscopy after warming to room temperature and dissolving the deposit on the window in DMSO-*d*₆. Identical results were obtained when **25** was deposited in an Ar matrix and photolytically converted to **26** at 12 K and the matrix gently warmed to *ca.* 40 K to allow Ar to evaporate. The residual ketene absorption again started decreasing at *ca.* 60 K and had vanished at 70 K with simultaneous formation of tetramer **27**. When a KBr pellet containing diazo compound **25** was irradiated at 77 K, only tetramer **27** was observed as a product.

The instability of ketene **26**, and its efficient tetramerization, can be ascribed to the transient formation of a ketene–imine ylide of type **28** (Scheme 3). In the case of **20** (Scheme 2), a correctly oriented ylide would rapidly cyclize to **21**. In the case of **26**, ring strain prohibits formation of a stable dimer, and so the intermediate ylide **28** could have a longer lifetime and be observable by IR. In fact, careful examination of the IR spectra during warmup of **26** at 40 K reveals the formation of new peaks at 1632 and 1697 cm^{-1} during the first 2 min (Figure 9). The 1632 cm^{-1} peak decreases after 33 min at 40 K, almost vanishes at 120 K, and is absent in the final product **27**. It is possible that the 1632 cm^{-1} peak is due to ylide **28**. Figure 9 illustrates

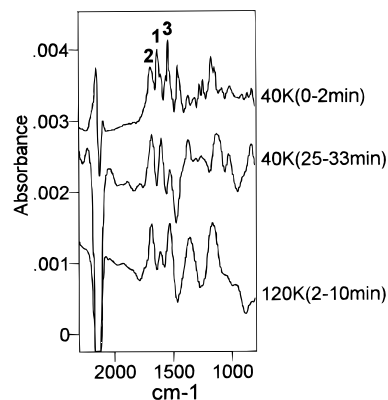
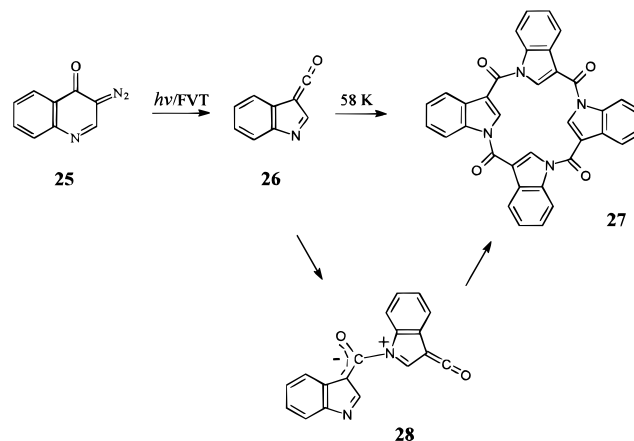


Figure 9. Partial IR difference spectra of the warmup product from 3-carbonyl-3H-indole (**26**) at 40 and 120 K. Peaks 2 and 3 belong to tetramer **27**. 1: 1632 cm^{-1} . 2: 1697 cm^{-1} . 3: 1541 cm^{-1} .

Scheme 3



that a new ketene absorption also appears, as expected for compound **28**, but this has to be interpreted with caution because the first difference spectrum in Figure 9 is taken at very early times when little reaction has occurred. Hence, there is still much unchanged ketene **26** present. A small shift in the maximum of the ketene absorption frequency in the solid film could engender a false positive ketene peak.

Our *ab initio* calculations indicate that the reaction of two molecules of ketene **26** to ylide **28** is exothermic by 4 kJ mol^{-1} . This is similar to the 6 kJ mol^{-1} exothermicity calculated for the reaction **14** + pyridine \rightarrow **15** (BLYP/6-31G*¹⁴). The tetramerization of **26** is calculated to be exothermic by 446 kJ mol^{-1} .¹⁴

Conclusions

Ketenes **7**, **14**, and **17** are observable in pyridine matrices at cryogenic temperatures, but react above 50, 40, and 15 K, respectively, to form ketene–pyridine ylides **12**, **15**, and **18**. The ylides are characterized by strong absorptions at 1650 – 1680 cm^{-1} in the IR, indicative of the strongly delocalized and polarized carbonyl groups. *Ab initio* calculations indicate that ylide formation is mildly exothermic and has a low activation energy.¹⁴

Facile dimerization of azacyclic ketenes **20** and **23** and the tetramerization of 3-carbonyl-3H-indole (**26**) at *ca.* 47, 40, and 58 K, respectively, can also be ascribed to the formation of intermediate ketene–imine ylides, e.g., **28**, whereby one ketene molecule acts as a nucleophile toward the other.

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Experimental Section

Apparatus. The flash vacuum thermolysis (FVT) apparatus was as previously described.¹⁵ FVT was carried out in unpacked quartz tubes (100 mm length, 8 mm i.d.) at 200–1000 °C (*ca.* 10⁻⁴ mbar), and the products were isolated in Ar matrices at 12–20 K or neat at 12 or 77 K. An APD Cryogenics cryostat, CSW-204SL-6.5 K, equipped with KBr or BaF₂ windows and a Lakeshore Model 330-44 temperature controller were used. For bimolecular reactions, diazo compounds were cocondensed with a large excess of pyridine at 8.5–12 K and subsequently converted to ketenes by irradiation at the lowest attainable temperature. Rapid warmup to the indicated temperatures was achieved, and the accuracies of the temperatures given are better than ±1 K.

Infrared spectra were recorded on a Perkin-Elmer 1700X or a System 2000 FTIR spectrometer, the latter with an MCT detector and a resolution of 1–0.5 cm⁻¹.

Photolyses were carried out with a low-pressure Hg lamp (75 W, 254 nm maximum output; Gräntzel, Karlsruhe, Germany) or a high-pressure Xe–Hg lamp (1000 W; Hanovia).

NMR spectra were recorded on Bruker AC 200 (200 Hz) and Jeol GX 400 (400 Hz) spectrometers, MS spectra (70 eV; direct insertion) on a Kratos MS25RFA, and GC–MS spectra on a Hewlett-Packard 5992B instrument. Melting points are uncorrected.

Materials. Pyrrole-2-carboxylic acid (**22a**) was purchased from Aldrich. Methyl isoindole-1-carboxylate (**19**),¹² methyl pyrrole-2-carboxylate (**22b**),¹² 4-oxo-3-diazo-3,4-dihydroquinoline (**25**),¹³ and tetramer **27**¹³ have been described elsewhere. Diazo compounds **11**, **13**, and **16** were prepared according to literature methods, and relevant spectroscopic data are given below.

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9-Diazophenanthrene 10-Oxide (11).¹⁶ Mp 111–112 °C (lit.¹⁶ mp 107–109 °C); ¹H NMR (CDCl₃, 200 MHz) δ 7.2–7.4 (m, 2 H), 8.2–8.3 (m, 2 H), 7.4–7.6 (m, 2 H), 7.66–7.78 (m, 1 H), 8.36–8.44 (m, 1 H); ¹³C NMR (CDCl₃, 300 MHz) δ 78.0 (C=N₂), 120.3, 123.0, 124.0, 125.0, 125.1, 126.3, 127.9, 128.9, 129.6, 133.1, 134.8, 179.5 (C=O); IR (CH₂Cl₂) 1625, 2088, 2104, 2987, 3056 cm⁻¹; IR (pyridine, 8.5 K) 2110 s, 2093 m, 1622.5 s, 1301.5 s, 1319 w, 1274 w, 1241 w, 1183.5 m, 914.5 w cm⁻¹; MS *m/z* 220 (M, 22.2), 192 (68.6), 164 (100).

2-Diazonaphthalene 1-Oxide (13).¹⁷ ¹H NMR (CDCl₃, 200 MHz) δ 6.52 (d, *J* = 9 Hz, 1 H), 6.84 (d, *J* = 9 Hz, 1 H), 7.36–7.45 (m, 2 H), 7.52–7.69 (m, 1 H), 8.25–8.30 (m, 1 H); ¹³C NMR (CDCl₃, 300 MHz) δ 77.2 (C=N₂), 116.2, 117.2, 125.2, 127.1, 128.1, 129.4, 132.6, 137.4, 180.0 (C=O); IR (pyridine, 8.5 K) 2143 s, 2117 vs, 1623 m, 1609 vs, 1584 w, 1578 m, 1569.5 m, 1546 w, 1482.5 w, 1420.5 w, 1325 m, 1274.5 s, 1243 s, 1190.5 w, 1137 m, 948.5 w, 872 w cm⁻¹; MS *m/z* 175 (M, 35), 142 (45), 114 (100), 88 (21).

1-Diazobenzene 2-Oxide (16).¹⁸ ¹H NMR (CDCl₃, 200 MHz) 6.37–6.29 (m, 1 H), 6.74–6.68 (m, 1 H), 7.37–7.58 (m, 2 H); ¹³C NMR (CDCl₃, 200 MHz) δ 77.2 (C=N₂), 115.8, 123.5, 123.9, 138.5, 177.1 (C=O); IR (pyridine, 8.5 K) 2130.5 w, 1622 m, 1600.5 s, 1540 w, 1507 s, 1480 m, 1460 s, 1428 w, 1339 s, 1253 w, 1240 w, 1223 w, 1145 m, 1119 m, 992 w, 859 w cm⁻¹.

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