

# (Cyanovinyl)ketenes From Azafulvenones. An Apparent Retro-Wolff Rearrangement

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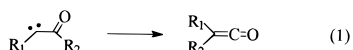
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**Abstract:** Flash vacuum pyrolyses or pulsed pyrolysis of azole esters **1b** and **20** and their carboxylic acids **1a** and **19** or acid chloride **1c** give five-membered ring ketenes (azafulvenones) **2** and **24** which dimerize to diketopiperazines **3** and **21** but also undergo efficient rearrangement to (cyanovinyl)- and (*o*-cyanophenyl)ketene (**6** and **27**). The same products are obtained by elimination of alcohol from esters of these (cyanovinyl)ketenes. Both types of ketenes are observed directly by IR spectroscopy and are trapped by alcohols to give the corresponding azole esters or (cyanovinyl)acetates. 1-Carbonyl-1*H*-isoindole (**34**) is a highly reactive ketene, dimerizing at 50 K. All ketene IR spectra are in good accord with ab initio calculations. The mechanism of this apparent retro-Wolff rearrangement is discussed.

## Introduction

There is considerable current interest in the chemistry of ketenes.<sup>1</sup> A number of unexpected rearrangements has been discovered, including the ketoketene–ketoketene rearrangement<sup>2</sup> and a series of transformations of methyleneketenes<sup>3</sup> and imidoylketenes.<sup>4</sup>

The Wolff rearrangement of  $\alpha$ -oxocarbenes to ketenes is well known<sup>5</sup> (eq 1). The question of intermediacy of oxirenes in this reaction has been the subject of intensive investigation.<sup>5c,6</sup> While the involvement of singlet  $\alpha$ -oxocarbenes as discrete



intermediates in the Wolff rearrangement is still under debate,<sup>7</sup> there is no doubt that the triplet carbenes exist as they have been observed by ESR<sup>8,9</sup> and in some cases also by matrix IR spectroscopy.<sup>9</sup>

While there exist several examples of photochemical “retro carbene reactions”, i.e., the reversion of alkenes to alkylcarbenes and of allenes to vinylcarbenes,<sup>10</sup> as well as the thermal reversion of acetylenes to vinylidenes,<sup>11</sup> a retro-Wolff rearrangement is rare.<sup>12</sup> We now wish to describe two series of intriguing rearrangements of ketenes, the outcome of which corresponds to the operation of a thermal retro-Wolff rearrangement. We also report the direct observation of some of the intermediates.

## Results and Discussion

**1. Preparative FVP of Pyrrole-2-carboxylic Acid (**1a**) and Its Methyl Ester (**1b**).** We have previously reported that the flash vacuum pyrolysis (FVP) of pyrrole-2-carboxylic acid (**1a**) and its methyl ester (**1b**) gives rise to 2-carbonyl-2*H*-pyrrole (**2**).<sup>13</sup> Under preparative conditions, the ketene dimer pyrocoll (**3**) is obtained<sup>13</sup> (Scheme 1). However, it was subsequently discovered that pyrocoll is not the only product formed when **1** is pyrolyzed at higher temperatures, and that a second ketene intermediate is also detectable. The present work was undertaken in order to elucidate the mechanism of its formation.

Preparative FVP of methyl pyrrole-2-carboxylate (**1b**) at 700–850 °C gave the ketene dimer **3** in 90% yield, the remainder being unchanged starting material. At higher temperatures, the yield of dimer **3** was reduced and three further products, **8**, **9**, and **10** (Scheme 1), were isolated. The yield of these products could be improved by trapping the pyrolysis product in a methanol matrix on a cold finger (77 K). In this way, pyrolysis of **1a** at 950 °C resulted in 30% yield of the dimer **3** (partially isomerized to **15** and **16**; see Scheme 2 below), together with a 15% overall yield of a mixture of **1a**,

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, April 1, 1996.

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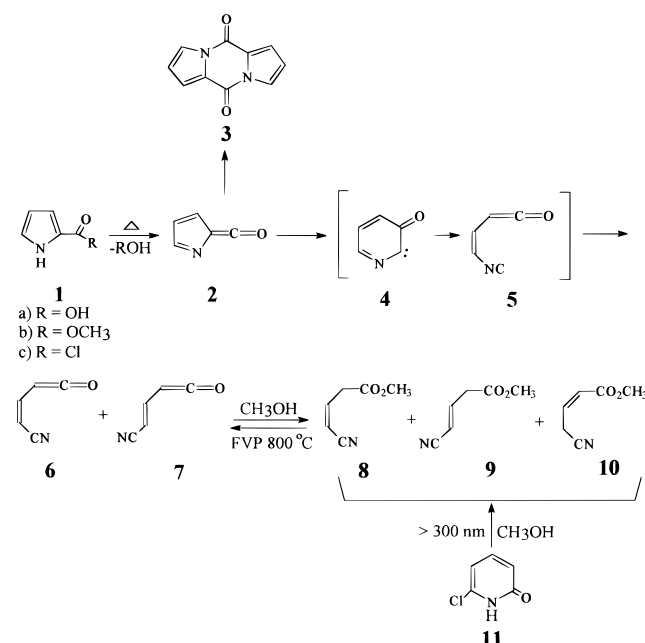
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## Scheme 1

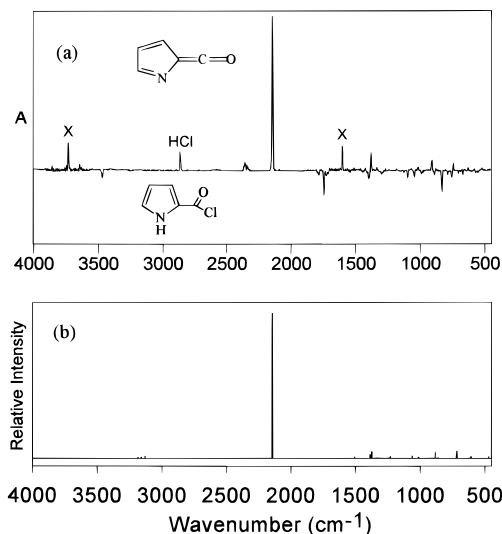


**8**, **9**, and **10** in a 2:7:5:3 ratio. While compounds **8**, **9**, and **10** were not easily separated by column chromatography, they were identified by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and GC–MS. A similar mixture of compounds **8**, **9**, and **10** was also synthesized according to the literature,<sup>14</sup> i.e., photolysis of 6-chloro-2-pyridone (**11**) (Scheme 1). Direct comparison demonstrated the identity of the three compounds **8**, **9**, and **10** in the two mixtures.

In order to understand the formation of dimers **15** and **16** at higher temperature, dimer **3** was isolated after FVP of ester **1b** at 800 °C and pyrolyzed again at different temperatures. Dimer **3** is completely stable up to 850 °C. At 950 °C, 10% of isomerized product was isolated. Flash chromatography of this mixture gave a mixture of four dimers, **A**, **B**, **C**, and **D**. The first fraction contained **A** and **B** (10% combined yield), and rechromatography of this fraction gave almost pure **B**. The second fraction contained the red dimers **C** and **D** (ca. 0.1% yield), and rechromatography of this fraction gave pure dimer **D**. From the <sup>1</sup>H and <sup>13</sup>C NMR data, dimers **A** and **B** are **15** and **16**, and **D** is **18**. A very small amount of **C** was formed; this compound is tentatively assigned structure **17**.<sup>15</sup> The isomerization of **3** is readily explained in terms of 1,5-sigmatropic shifts (Scheme 2), first to 2*H*-pyrrole **12**, and then to 3*H*-pyrroles **13** and **14**.<sup>16</sup> The red dimers **17** and **18** would be formed by a double rearrangement of the type depicted in Scheme 2.

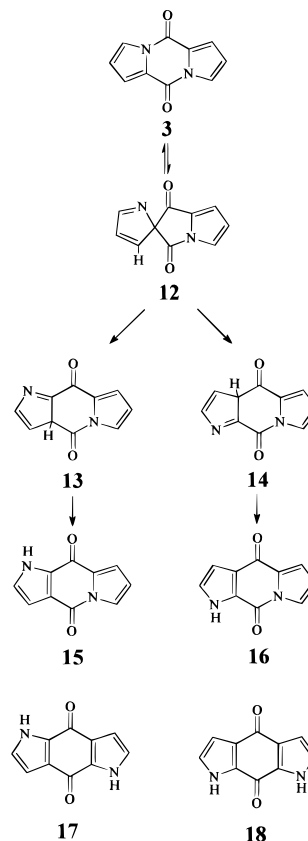
It seemed likely that the cyanovinyl esters **8**, **9**, and **10**, obtained at higher temperatures, were due to trapping of an intermediate formed by rearrangement of ketene **2**. To further elucidate the mechanism, low-temperature Ar and N<sub>2</sub> matrix isolation was carried out.

**2. Matrix Isolation of 2-Carbonyl-2*H*-pyrrole (2) and Its Rearranged Product (Cyanovinyl)ketenes 6 and 7.** (a) FVP. Flash vacuum pyrolysis of pyrrole-2-carboxylic acid (**1a**), its



**Figure 1.** (a) IR spectrum of 2-carbonyl-2*H*-pyrrole (**2**) (positive peaks) at 12 K in an Ar matrix, generated by FVP of pyrrole-2-carboxylic acid chloride (**1c**) at 650 °C. Negative peaks are due to **1c**, arising from a subtraction of the spectrum of **1c** from the FVP spectrum. Bands marked X are due to H<sub>2</sub>O. All peaks assigned to **2** vanished on UV photolysis ( $\lambda > 220$  nm). (b) IR spectrum of 2-carbonyl-2*H*-pyrrole calculated at the MP2/6-31G\* level (scaling factor 0.9427). [IR values of **2**: exptl  $\nu$  (intensity), 2145.7 (vvs), 1376.9 (w), 907.0 (w), 738.5 (w) cm<sup>-1</sup>; calcd  $\nu$  (rel. intensity): 2097.2 (1), 1351.6 (0.110), 885.9 (0.042), 663.1 (0.071) cm<sup>-1</sup>.]

## Scheme 2

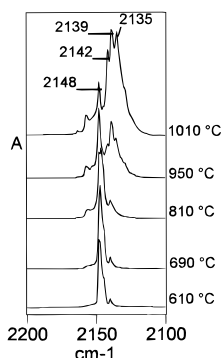


methyl ester (**1b**), or the acid chloride (**1c**) gave 2-carbonyl-2*H*-pyrrole (**2**), which was isolated in an Ar or N<sub>2</sub> matrix at 12 K and detected by IR spectroscopy (Figure 1a). Ketene **2** has a strong IR absorption at 2148 cm<sup>-1</sup> (N<sub>2</sub> matrix) as well as peaks at 1377 (w), 1333 (vw), 908 (w), and 737 (w) cm<sup>-1</sup>. Ab initio calculations of the structure and IR spectrum of ketene **2** were carried out at both B-LYP and MP2 levels with the 6-31G\*

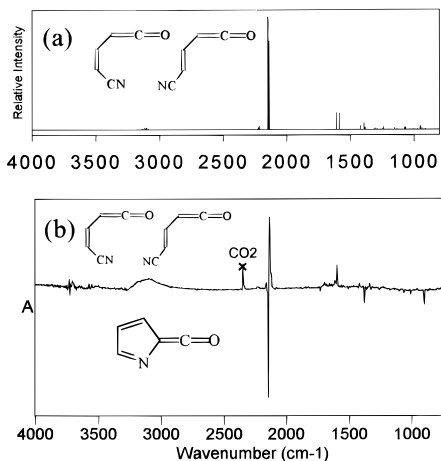
(14) Kaneko, C.; Fujii, H.; Kato, K. *Heterocycles* **1982**, *17*, 395.

(15) (a) Wiersum<sup>15b</sup> has previously mentioned that FVP of the anilide of pyrrole-2-carboxylic acid gave an unsymmetrical dimer, assigned the structure **16**, but no pyrocoll (**3**) was observed at all. It is clear, however, that **16** is a high-temperature rearrangement product of **3**, and that **15** and **16** are formed in a nearly 1:1 ratio. (b) Wiersum, U. E. *Recl. Trav. Chim. Pays-Bas* **1982**, *11*, 365.

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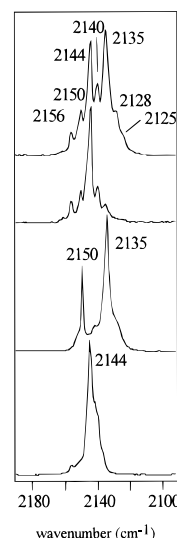
**Figure 2.** IR spectra of isolated product at 12 K in a  $N_2$  matrix following FVP of pyrrole-2-carboxylic acid (**1a**) at various temperatures.



**Figure 3.** (a) Calculated IR spectra of cyano ketenes **6** and **7** (four conformers in equal ratios) at the BLYP/6-31G\* level [ $\nu$  2137, 2139, 2147, 2146 (vs, C=C=O); 2213, 2223, 2219, 2224 (vw, CN); 1586, 1606, 1587, 1606 (w); 1420, 1393, 1423, 1387 (vw); 1385, 1311, 1313, 1302 (vw); 972, 1035, 1066, 1073 (vw)  $cm^{-1}$ ]. (b) IR spectrum of mixture of compounds **6** and **7** in a  $N_2$  matrix as obtained by FVP of pyrrole-2-carboxylic acid (**1a**) at 1000 °C [ $\nu$  2141.8, 2139.3, 2134.7 (vs, C=C=O); 2234 (vw, br, CN); 1596.5 (w); 1421.2 (vw); 1338 (vw); 962.5 (vw)  $cm^{-1}$ ].

basis set. The calculated spectrum (see Figure 1b) agrees well with the experimental results in both absorption frequency and intensity of the peaks. An IR spectrum of **2** derived from **1a** is shown in the supporting information.

At increased pyrolysis temperature (700–1100 °C), the ketene **2** absorption decreases, while a set of new ketene peaks at 2142, 2139, and 2135.5  $cm^{-1}$  ( $N_2$  matrix) appears (Figure 2). The new peaks are assigned to *cis*- and *trans*-(cyanovinyl)ketene (**6** and **7**) (Scheme 1) for the following reasons: (1) Trapping with methanol results in formation of **8**, **9**, and **10**, as described in section 1. Formation of **8** and **9** is readily explained in terms of 1,2-addition of methanol to ketenes **6** and **7**, respectively. **10** could be formed *via* 1,4-addition to ketene **6** or **7**. (2) The *ab initio* calculated IR spectrum (B-LYP/6-31G\*) agrees well with the experimental data (Figure 3). (3) The mixture of **8**, **9**, and **10**, generated by photolysis of **11**, was subjected to FVP at 800 °C.  $N_2$  matrix isolation resulted in the mixture of ketenes **6** and **7** with the main absorptions at 2142, 2139, and 2135.5  $cm^{-1}$  (Scheme 1). These are exactly the same peaks as obtained by FVP of pyrrole-2-carboxylic acid (**1a**) at 1010 °C. The same experiments were also conducted with Ar matrix isolation, whereby an 850 °C pyrolysis of **8**, **9**, and **10** resulted in a mixture of ketenes **6** and **7** with the main IR absorption at 2135  $cm^{-1}$ . Pyrolysis of pyrrole-2-carboxylic acid (**1a**) or the ester **1b** at  $\geq 800$  °C also gave rise to a new ketene peak at 2135



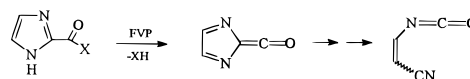
**Figure 4.** Matrix IR spectra of pyrolysis products of pyrrole-2-carboxylic acid methyl ester in Ar. From bottom to top: FVP at 630 °C, FVP at 1000 °C, pulsed pyrolysis at 1000 °C, pulsed pyrolysis at 1400 °C. The bands at 2150 and 2140  $cm^{-1}$  are due to CO.

$cm^{-1}$  (Ar) due to **6** and **7** (cf. Figure 4). **2** absorbs at 2144  $cm^{-1}$  in an Ar matrix.

From these results, it follows that 2-carbonyl-2H-pyrrole (**2**) is the first intermediate formed on FVP of the acid derivatives **1**. At higher temperatures, ketenes **6** and **7** are formed by rearrangement of the first ketene **2**. This kind of rearrangement is unusual. As shown in Scheme 1, this rearrangement suggests the ring expansion of ketene **2** to give an  $\alpha$ -oxocarbene (**4**) followed by ring opening to (isocyanovinyl)ketene (**5**), which then isomerizes to (cyanovinyl)ketenes **6** and **7**. The rearrangement of ketene **2** to  $\alpha$ -oxocarbene **4** constitutes a retro-Wolff rearrangement.<sup>17</sup>

**(b) Pulsed Pyrolysis.** It has not been possible under FVP conditions to obtain any direct evidence for the intermediacy of isocyanide **5**, which would be expected to have both NC and C=C=O vibrations in the 2100  $cm^{-1}$  region and could exist as *Z* and *E* isomers with a total of four conformers. The absence of **5** is not surprising since it is known that the activation barrier for isocyanide–nitrile isomerizations is on the order of 35–38 kcal/mol (146–159 kJ/mol)<sup>18</sup> (see also section 7). However, pulsed pyrolysis<sup>19</sup> (PP) of **1b** gave additional intermediates. In PP, a free jet expansion rapidly cools the products exiting the high-pressure pulsed pyrolysis nozzle, thereby increasing the chances of isolating a short-lived intermediate. The resulting Ar matrix IR spectra show better resolution than the FVP/Ar matrix spectra (Figure 4). Because of the very short pyrolysis tube in PP, much higher temperatures are required than for FVP.

(17) (a) Other mechanisms for formation of **6** and **7** from **2** can be considered. Ring opening of **2** to a nitrene :N=CH=CH=CH=C=O followed by a 1,4-H shift could give **6**. However, evidence that the carbonyl group at C-2 in **2** actually migrates to C-3 is revealed in the analogous rearrangement of 2-carbonyl-2H-imidazole to cyanovinyl isocyanate.<sup>17d,e</sup>

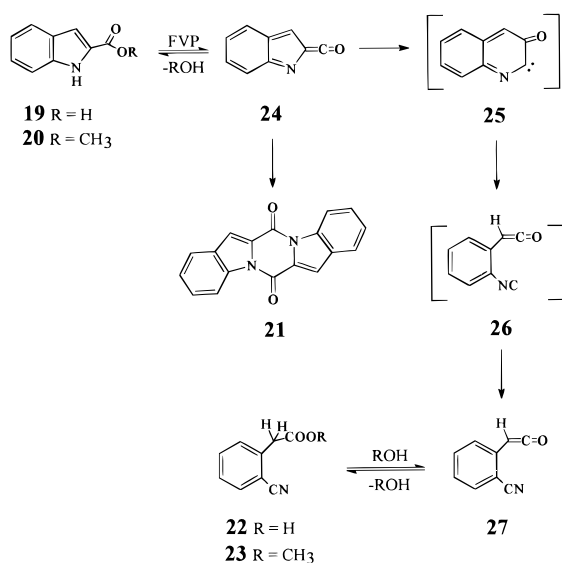


(b) Furthermore, the rearrangement of **20**, described below, requires carbon migration and would not be explained by the nitrene mechanism. (c) The lack of formation of **27** from **34** further mitigates against the ring opening/nitrene mechanism. (d) Bender, H.; Wentrup, C. Unpublished results. (e) Nguyen, M. T.; Hajnal, M. R.; Ha, T.-K.; Vanquickenborne, L. G.; Wentrup, C. J. Am. Chem. Soc. **1992**, *114*, 4387.

(18) Pakusch, J.; Rüchardt, C. Chem. Ber. **1989**, *122*, 1593.

(19) Kohn, D. W.; Clausberg, H.; Chen, P. Rev. Sci. Instrum. **1992**, *63*, 4002.

## Scheme 3



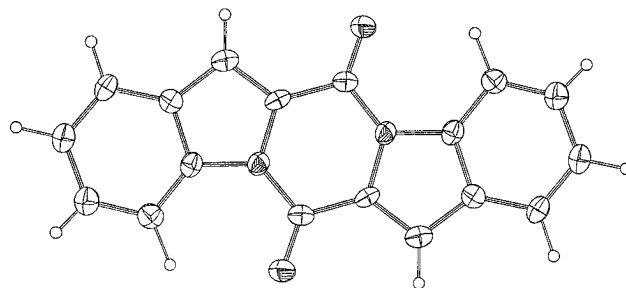
Thus, PP of **1b** at 1000 °C gives a spectrum similar to that of FVP at 630 °C, but with better resolution, consisting largely of ketene **2**. PP at 1150 °C causes formation of ketenes **6** and **7** as well (2140 and 2137 cm<sup>-1</sup>), but new peaks also start appearing at 2128 and 2125 cm<sup>-1</sup>. The latter increase further on PP at 1400 °C (Figure 4). These new peaks appear at wavenumbers where nothing was detectable using FVP. They by no means prove the existence of isocyanide **5**, but the wavenumber would be in agreement with such a structure.<sup>20</sup>

**3. Preparative Pyrolysis of Indole-2-carboxylic acid (19) and Its Methyl Ester (20).** Similar investigations were also carried out on indole derivatives. FVP of indole-2-carboxylic acid (**19**) or its methyl ester (**20**) at 600 °C gave small amounts of the ketene dimer **21**, the remainder being starting material. At higher pyrolysis temperatures, using ester **20**, increasing amounts of methyl (2-cyanophenyl)acetate (**23**) were formed (Scheme 3). The best yield (70%) of **23** was obtained by FVP at 700 °C and trapping with MeOH on the cold finger. A 10% yield of dimer **21** was also obtained under these conditions. Nitrile ester **23** can also be isolated in up to 52% yield by FVP of the acid **19**, while cocondensing the product with MeOH. Dimer **21** is the first product at lower pyrolysis temperature; it is most likely due to the dimerization of ketene **24** formed by elimination of MeOH or water from **20** or **19**. Formation of nitriles **22** and **23** can be due to the trapping of a rearranged ketene intermediate (**27**) (Scheme 3). Dimer **21**<sup>21</sup> was characterized by NMR, MS, and X-ray crystallography (Figure 5).

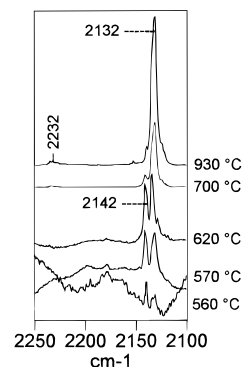
**4. Matrix Isolation of 2-Carbonyl-2H-Indole (24) and (2-Cyanophenyl)ketene (27).** FVP of ester **20** at 560 °C with matrix isolation of the products at 12 K in a N<sub>2</sub> matrix showed a very weak peak at 2142 cm<sup>-1</sup> in the IR spectrum (Figure 6)

(20) (a) The calculated IR spectra (B-LYP/6-31G\*) of conformers of **5** predict absorptions at 2074–2084 cm<sup>-1</sup> (–NC; 60–90 km mol<sup>-1</sup>) and 2136–2148 cm<sup>-1</sup> (C=C=O; 500–1000 km mol<sup>-1</sup>). However, these calculations underestimate the wavenumber for isocyanides by ca. 23 cm<sup>-1</sup> (e.g., vinyl cyanide: exptl,<sup>20b</sup> 2125 cm<sup>-1</sup>; calcd (B-LYP), 2102 cm<sup>-1</sup>). Thus, the isocyanide absorption of **5** may be expected at 2100–2110 cm<sup>-1</sup>. There are several examples of vinyl isocyanides known to absorb in the range 2115–2135 cm<sup>-1</sup>.<sup>20c,d</sup> (b) Bolton, K.; Owen, N. L. *Spectrochim. Acta* **1970**, *26*, 909. (c) Juchnowski, I. N.; Binev, I. G. In *The Chemistry of Triple-Bonded Functional Groups*; Patai, S., Rapoport, Z., Eds.; Wiley: Chichester, 1983; Vol. 1, Part 1, p 130. (d) Nunami, K.-i.; Yamada, M.; Fukui, T.; Matsumoto, K. *J. Org. Chem.* **1994**, *59*, 7635.

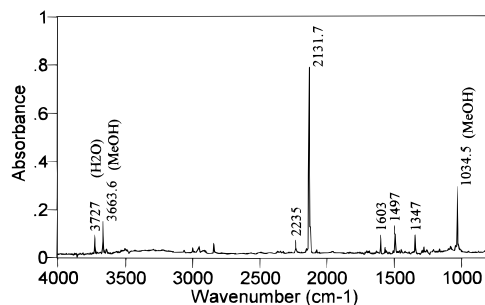
(21) (a) Boatman, R. J. and Whitlock, H. W. *J. Org. Chem.*, **1976**, *41*, 3050. (b) Ciamician, G. L. and Zatti, C. *Ber. Dtsch. Chem. Ges.* **1888**, *21*, 1929. (c) Coffen, D. L.; Katonak, D. A.; Nelson, N. R. and Sancilio, F. D. *J. Org. Chem.* **1977**, *42*, 948.



**Figure 5.** ORTEP drawing of diindolo[1,2-*a*:1',2'-*d*]pyrazine-8,16-dione (**21**) (30% probability level).



**Figure 6.** Partial IR spectra of the isolated products in a N<sub>2</sub> matrix at 12 K by pyrolysis of methyl indole-2-carboxylate (**20**) at various temperatures.



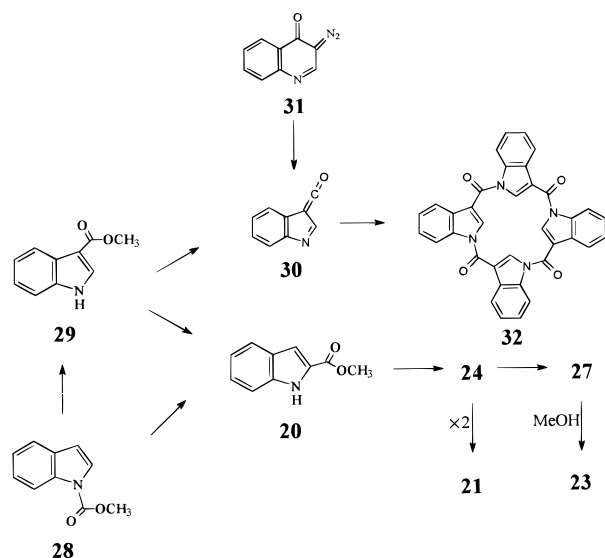
**Figure 7.** IR spectrum of (2-cyanophenyl)ketene (**27**) isolated in a nitrogen matrix at 12 K as formed by FVP of methyl indole-2-carboxylate (**20**) at 930 °C.

together with unchanged starting material. Increasing the temperature to 620 °C resulted in a stronger 2142 cm<sup>-1</sup> peak, while a peak at 2132 cm<sup>-1</sup> appeared and increased significantly. When the temperature reached 700 °C, the 2132 cm<sup>-1</sup> peak became much stronger, and a weak nitrile absorption appeared at 2232 cm<sup>-1</sup> as well. Meanwhile, the 2142 cm<sup>-1</sup> peak became weak. On further raising of the temperature to 930 °C, the 2132 cm<sup>-1</sup> peak dominated the spectrum, and no starting material remained (Figure 7). The MeOH eliminated from ester **20** was also observed in the matrix (1034.5 and 3727 cm<sup>-1</sup>, N<sub>2</sub> matrix). The 2142 cm<sup>-1</sup> band is assigned to ketene **24**, and the 2132 cm<sup>-1</sup> band to the rearranged ketene **27** in accord with the preparative pyrolysis results (Scheme 3). As in the pyrrole case, the rearrangement is postulated to proceed *via* oxocarbene **25** and (2-isocyanophenyl)ketene (**26**) (Scheme 3). The 2142 cm<sup>-1</sup> band is unlikely to be due to **26**. Phenyl isocyanides absorb at 2130–2105 cm<sup>-1</sup>.<sup>20c,22</sup>

Ar matrix isolation gave similar results. FVP of ester **20** at 650–700 °C gave a sharp absorption of 2128 cm<sup>-1</sup>; no nitrile absorption was detectable under these conditions. FVP of ester **20** at 850 °C gave a strong absorption at 2128 cm<sup>-1</sup> together

(22) Walborsky, H. M.; Niznik, G. E. *J. Org. Chem.* **1972**, *37*, 187.

Scheme 4



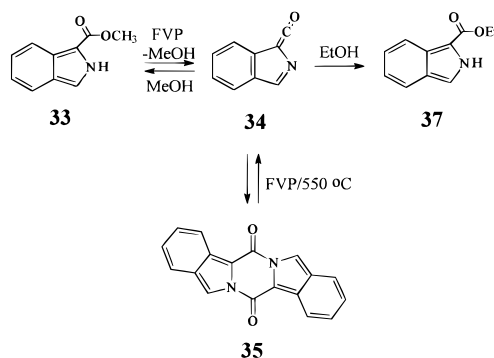
with a weak CN absorption at  $2230\text{ cm}^{-1}$ . The complete IR spectrum of ketene **27** from  $4000$  to  $800\text{ cm}^{-1}$  could be identified by comparison with the  $\text{N}_2$  matrix. The  $2128/2230\text{ cm}^{-1}$  peaks are due to **27**. Most likely the first formed ketene **24** also absorbs at  $2128\text{ cm}^{-1}$  in an Ar matrix. The fact that the main absorptions of ketenes **24** and **27** are close to each other agrees well with B-LYP/6-31G\* calculated spectra ( $2137/2139\text{ cm}^{-1}$ ; vide supra).

FVP of **19** gave ketene **27** as well as indole. Methyl ester **23** also gave **27** by FVP at  $800\text{ }^\circ\text{C}$ ; the Ar matrix IR spectrum was identical with that described above.

In a separate experiment, the product was isolated in a U-tube so that the MeOH formed as a byproduct could be removed by distillation. Subsequent warming to room temperature resulted in a polymer of **27** (mass range up to ca. 5000). This material featured CN and C=O groups in IR and is therefore formulated as a ketene polymer with *o*-cyanophenyl side chains.

**5. Preparative FVP and Matrix Isolation of Methyl Indole-1- and -3-carboxylates.** It is known<sup>23</sup> that substituents in position 1, 2, or 3 in indole will undergo 1,5-shifts (with concomitant 1,5-H shifts) under thermolysis conditions. Esters **28** and **29** were therefore subjected to FVP in the expectation to observe the same pyrolysis products as from **20**. Methyl indole-1-carboxylate (**28**) was pyrolyzed, and the products were trapped as a neat film on a cold window at  $77\text{ K}$ , followed by IR spectroscopic detection. With an FVP temperature of  $700\text{ }^\circ\text{C}$ , a small absorption at  $2123\text{ cm}^{-1}$  was observed together with starting material. When the temperature was raised to  $800\text{ }^\circ\text{C}$ , the  $2123\text{ cm}^{-1}$  band became much stronger and was accompanied by a weak absorption at  $2223\text{ cm}^{-1}$  (CN). On further increase to  $900$  and  $1000\text{ }^\circ\text{C}$ , the species absorbing at  $2123$  and  $2223\text{ cm}^{-1}$  and MeOH became the only products. By careful comparison with the spectrum of cyano ketene **27** from the FVP of **20** under the same conditions (neat film), it was clear that the same compound was produced. Therefore, the ester group in **28** migrates to the 2-position under FVP conditions. Loss of MeOH leads to ketene **27** via the retro-Wolff rearrangement described above (Scheme 4). In order to confirm this, **28** was preparatively pyrolyzed at  $750\text{ }^\circ\text{C}$ . The isolated products were identified as 56% unchanged starting material, 28% **29**, 6% dimer **21**, and 28% cyano ester **23**. Thus, under these conditions, the ester group at the 1-position in **28** migrated to

Scheme 5



both the 2- and 3-positions. The 3-ester **29** remained unchanged (or in equilibrium with **20** and **28**), and the 2-ester reacted to give the isolated products.

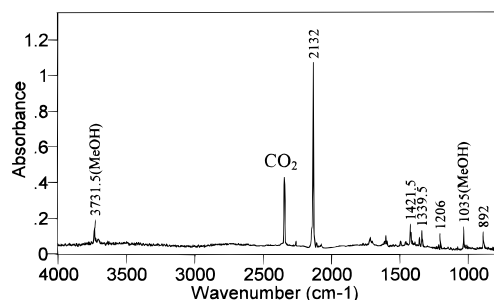
Methyl indole-3-carboxylate (**29**) was hence pyrolyzed, and the intermediates were isolated in an Ar matrix. With the pyrolysis temperature below  $700\text{ }^\circ\text{C}$ , ester **29** remained unchanged as observed by IR spectroscopy. At  $740\text{ }^\circ\text{C}$ , a new peak at  $2137\text{ cm}^{-1}$  appeared, together with a weak one at  $2128\text{ cm}^{-1}$ . Raising the temperature to  $860\text{ }^\circ\text{C}$  caused the  $2128\text{ cm}^{-1}$  peak to become stronger. The eliminated methanol could also be seen in the IR. When the temperature was increased to  $880\text{ }^\circ\text{C}$ , no  $2137\text{ cm}^{-1}$  peak could be seen, but the  $2128\text{ cm}^{-1}$  band became the strongest in the spectrum. By comparison with the previous spectra, we assign the  $2128\text{ cm}^{-1}$  peak to the cyano ketene **27**. By comparison with our earlier work,<sup>24</sup> the initially formed  $2137\text{ cm}^{-1}$  absorption is assigned to a very small amount of 3-carbonyl-3H-indole (**30**), formed by elimination of methanol from the 3-ester **29** or its 2H- or 3H-tautomer. This 3-carbonyl-3H-indole (**30**) exhibits a strong absorption of  $2137\text{ cm}^{-1}$  when formed by photolysis of 4-oxo-3-diazoquinoline (**31**) in an Ar matrix at  $12\text{ K}$  and tetramerizes to **32** on warming.<sup>24</sup> The amount of **30** formed in the FVP of **29** was too small to allow the isolation of tetramer **32**.

In order to confirm the formation of ketene **30**, **29** was also pyrolyzed with  $\text{N}_2$  matrix isolation. FVP at  $750\text{ }^\circ\text{C}$  resulted in three small absorptions,  $2142$ ,  $2140.5$ , and  $2132\text{ cm}^{-1}$ , in the  $\text{N}_2$  matrix. The  $2132\text{ cm}^{-1}$  band became much stronger with increasing FVP temperature. As seen before in the  $\text{N}_2$  matrix of the pyrolysis products of ester **20**, the  $2132\text{ cm}^{-1}$  band is due to the formation of ketene **27**. The  $2142\text{ cm}^{-1}$  band is assigned to 3-carbonyl-3H-indole (**30**). The photolysis of **31** demonstrated that ketene **30** absorbs at  $2142\text{ cm}^{-1}$  in an  $\text{N}_2$  matrix. Therefore, in analogy with the indole 2-ester case, the remaining  $2140.5\text{ cm}^{-1}$  band is assigned to the formation of ketene **24**. Accordingly, preparative pyrolysis of **29** at  $800\text{ }^\circ\text{C}$  gave, besides 78% of starting material, dimer **21** (9%) and cyano ester **23** (8%). FVP at  $900\text{ }^\circ\text{C}$  with MeOH gave less dimer **21** (1%), but more cyano ester **23** (52.5%), together with 46.5% of unreacted starting material.

**6. Preparative Pyrolysis of Methyl Isoindole-1-carboxylate (33) and Matrix Isolation of 1-Carbonyl-1H-Isoindole (34).** Methyl isoindole-1-carboxylate (**33**) was subjected to FVP at different temperatures. Pyrolysis at  $500\text{ }^\circ\text{C}$  with Ar matrix isolation of the product gave a strong IR absorption at  $2132\text{ cm}^{-1}$ . This absorption together with other absorptions in the fingerprint region was assigned to 1-carbonyl-1H-isoindole (**34**) (Scheme 5). Methanol was observed ( $1034.5$  and  $3731.5\text{ cm}^{-1}$ ) at the same time. High-temperature FVP ( $700\text{--}900\text{ }^\circ\text{C}$ ) gave the same result without any rearrangement of ketene **34** (Figure 8). As the absorption of ketene **34** is close to that of CO ( $2137/$

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**Figure 8.** IR spectrum of 1-carbonyl-1H-isoindole (**34**) in an argon matrix at 12 K by FVP of methyl 1-isoindolecarboxylate (**33**) at 720 °C.

2149  $\text{cm}^{-1}$  in Ar), the spectrum of CO itself in an Ar matrix and that of ketene **34** in an Ar matrix with 1% CO were generated under the same pyrolytic conditions. Comparison of the spectra ascertained that the 2132  $\text{cm}^{-1}$  peak was not due to CO.

Preparative FVP was then carried out in the temperature range 500–800 °C with and without trapping reagent. Pyrolysis at 750 °C without trapping reagent gave a 95% yield of ketene dimer **35** and 5% unchanged ester **33**, the latter isolated on a 77 K cold finger. Pyrolysis of **33** at 650 °C followed by condensation of ethanol on the cold finger (77 K) gave the same results. No product arising from the trapping of ketene **34** with ethanol could be found. This is in agreement with the warmup experiments conducted on low-temperature matrices. Ketene **34** was isolated at 12 K in a Xe matrix (2123.5  $\text{cm}^{-1}$ ) following FVP of ester **33** at 700 °C; subsequent warmup of the matrix demonstrated that ketene **31** is only stable till ca. 50 K. This unusual instability is thought to be due to the  $\alpha$ -nitrogen atom which, as a built-in nucleophile, promotes dimerization. Obviously, it is not possible to trap the ketene with ethanol at 77 K. We have discovered this kind of instability in other, similar types of ketenes.<sup>25</sup>

For the above reason, an apparatus employing a coaxial ethanol inlet tube inside the normal FVP tube was used. The ester **33** was pyrolyzed at 500 °C with a stream of ethanol vapor passing through the inner tube. The length of the inner tube was first adjusted to be two-thirds of the heated zone. In this experiment, 90% of dimer **35** and a 10% mixture of methyl and ethyl esters (1:6.6 by NMR integration) were obtained. When the inner tube was allowed to pass through the whole length of the heated zone, ending just before the cold finger, 95% of dimer **35** together with only 4% of the mixture of methyl and ethyl esters (7:1) was obtained. While these experiments do not prove that ketene **34** is being trapped, they indicate that, under the preparative FVP conditions, most of the dimerization (**34**  $\rightarrow$  **35**) takes place before the end of the pyrolysis tube.

The dimer **35** was used as a second precursor of ketene **34**. Firstly, it was pyrolyzed at different temperatures, and the ketene **34** formed was matrix isolated (Scheme 5). At 550 °C, only a weak ketene absorption at 2132  $\text{cm}^{-1}$  was observed, most of the starting material being unchanged. At 720 °C, ketene **34** was observed with the strongest absorption at 2132  $\text{cm}^{-1}$ , together with unchanged **35**. Preparative FVP of dimer **35** at 800 °C with ethanol trapping at the entrance of the oven gave 50% of dimer and 50% of ethyl ester **37**.

The conclusion is that the ketene **34** is highly reactive, dimerizing even at very low temperature (50 K). However, **34** is thermodynamically stable, and no products of a retro-Wolff rearrangement are observed. This is thought to be due to the

impossibility of formation of any such products without invoking unfavorable *o*-quinoid structures. The possibility of reversible ring expansion of **34** to  $\alpha$ -oxocarbenes cannot be excluded, however.<sup>17c</sup>

**7. Calculated Reaction Profiles.** The retro-Wolff rearrangement of 2-carbonyl-2H-pyrrole (**2**) was studied previously by Nguyen et al. at the CISDQ/6-31G\*\*//HF/6-31G\*\* level.<sup>26</sup> Here, we have examined the rearrangement with a high level of theory, G2(MP2,SVP):<sup>27</sup> (1) Optimized geometries were obtained at the correlated MP2 level, and (2) the energies were determined with an improved treatment of electron correlation, the QCISD(T) level,<sup>28</sup> and a significantly larger basis set (6-311+G(3df,2p)).<sup>29</sup> Consistent with the earlier calculations,<sup>26</sup> we find the involvement of oxocarbene **4** and (isocyanovinyl)-ketene (**5**) in the transformation of 2-carbonyl-2H-pyrrole (**2**) to (cyanovinyl)ketene (**6**). Thus, the retro-Wolff rearrangement involves the sequence of reactions **2**  $\rightarrow$  **TS1**  $\rightarrow$  **4**  $\rightarrow$  **TS2**  $\rightarrow$  **5**  $\rightarrow$  **TS3**  $\rightarrow$  **6** (Figure 9a). Rearrangement of **2** to **6** is calculated to be nearly thermoneutral. The cyclic  $\alpha$ -oxocarbene **4** is found to be a stable equilibrium structure, confirmed by frequency calculations at the MP2/6-31G\* level. This oxocarbene is predicted to lie in a shallow potential well and, therefore, is unlikely to be observable in FVP experiments. Rearrangement of **4** to **2**, via transition structure **TS1**, requires an energy barrier of 30  $\text{kJ mol}^{-1}$  (G2(MP2,SVP)), while ring opening of **4** to form (isocyanovinyl)ketene (**5**), via **TS2**, has a barrier of only 21  $\text{kJ mol}^{-1}$  (G2(MP2,SVP)). It is interesting to note that the C–N bond length in **4** is very short (1.222 Å; Figure 10 in the supporting information), comparable to that of a typical C $\equiv$ N multiple bond. The triplet  $\alpha$ -oxocarbene is predicted to lie 72  $\text{kJ mol}^{-1}$  (G2(MP2,SVP)) above the singlet ground state. Rearrangement of **5** to the final product **6**, via transition structure **TS3**, involves a barrier of 137  $\text{kJ mol}^{-1}$  (G2(MP2,SVP)). This is in agreement with experimental values for isocyanide–cyanide rearrangements (~140–160  $\text{kJ mol}^{-1}$ ).<sup>18</sup> **TS3** lies substantially higher in energy than **TS1** and **TS2**. Hence, the isocyanide–cyanide rearrangement is the rate-determining step for the retro-Wolff arrangement of **2**. In summary, oxocarbene **4** is a stable (but fleeting) intermediate in the transformation of **2** to **6**. The overall barrier for the retro-Wolff rearrangement is 237  $\text{kJ mol}^{-1}$  (G2(MP2,SVP)). This result is consistent with the experimental observation of (cyanovinyl)ketene, and the drastic FVP conditions (ca. 1000 °C) necessary for its formation. Under these reaction conditions, the direct observation of the  $\alpha$ -oxocarbene **4** will be impossible. Observation of isocyanide **5** is difficult under FVP conditions due to the high energies involved (**2**  $\rightarrow$  **TS1**, 179  $\text{kJ mol}^{-1}$ ), so that the barrier to **6** (**5**  $\rightarrow$  **TS3**, 137  $\text{kJ mol}^{-1}$ ) is easily crossed. Note also that the return path **5**  $\rightarrow$  **2** requires only 79  $\text{kJ mol}^{-1}$ ! This is in agreement with the experimental observations (section 3b) that bands possibly ascribable to **5** are observed only under pulsed pyrolysis (PP) conditions. The final product **6** will be highly excited vibrationally (ca. 225  $\text{kJ mol}^{-1}$ ), in agreement with the observation of several isomeric and rotameric forms of **6** and **7** and a considerable improvement in the resolution under PP conditions. Finally, we note that DFT calculations at the B-LYP/6-311+G(2df,2p)+ZPVE level (Figure 9a) are in qualitative agreement with the G2(MP2,SVP) results.

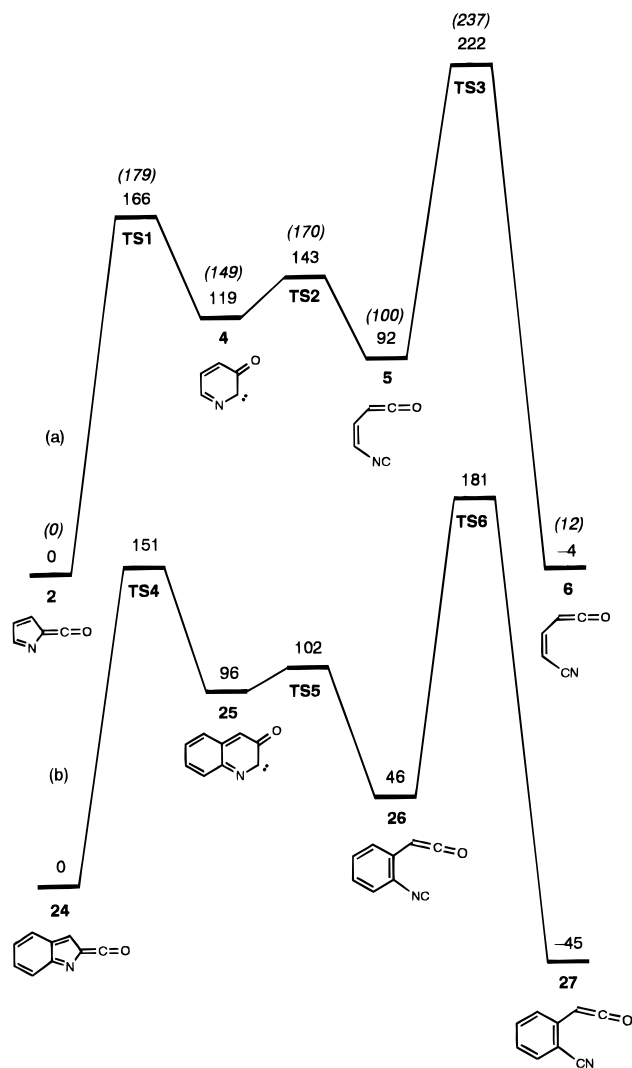
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**Figure 9.** Schematic potential profiles showing retro-Wolff rearrangements of (a) 2-carbonyl-2H-pyrrole (**2**) and (b) 2-carbonyl-2H-indole (**24**) (B-LYP/6-311+G(2d,p)+ZPVE, with G2(MP2,SVP) values in italics, kJ mol<sup>-1</sup>).

The rearrangement of 2-carbonyl-2H-indole (**24**) to (2-cyanophenyl)ketene (**27**) is calculated to be mildly exothermic, by ca. 45 kJ mol<sup>-1</sup>. Both oxocarbene **25** and isonitrile–ketene **26** are predicted to be stable intermediates on the rearrangement pathway, **24** → **TS4** → **25** → **TS5** → **26** → **TS6** → **27** (Figure 9b). Rearrangement of **25** to **24**, via transition structure **TS4**, requires a barrier of 55 kJ mol<sup>-1</sup>, while ring opening to isonitrile **26**, via transition structure **TS5**, has a barrier of just 6 kJ mol<sup>-1</sup>, thus making **25** unobservable. The structure of oxocarbene **25** (Figure 11 in the supporting information) is similar to that of **4**, with a short C–N bond length (1.214 Å) and a long adjacent C–C bond (1.546 Å). Isonitrile **26** is calculated to be more stable than the corresponding isonitrile in the pyrrole case (**5**). It lies in a moderate energy well, with a 105 kJ mol<sup>-1</sup> barrier toward rearrangement to **24**. As with the pyrrole case, the isocyanide–cyanide rearrangement (**26** → **27**), via transition **TS6**, is the rate-determining step of the retro-Wolff rearrangement of **24**. The calculated isocyanide–cyanide barrier for the indole case is similar to that found for the pyrrole case. The overall barrier for the transformation of **24** to **27** (181 kJ mol<sup>-1</sup>) is significantly less than that calculated for the pyrrole system, in excellent agreement with the experimental finding that rearrangement of **24** to **27** takes place under milder FVP conditions (≥620 °C; cf. 1000 °C for the reaction **2** → **6**). Isonitrile **26** lies in a deeper well (105 kJ mol<sup>-1</sup>), but this is

still easily traversed under FVP conditions. Unfortunately, the volatility of the precursors **19** and **20** is insufficient for pulsed pyrolysis experiments. The data in Figure 9b indicate, however, that on direct generation of isocyanide **26** from other precursors, it might be found to rearrange to ketene **24**. Such experiments are being planned.

## Conclusion

The results reported here provide strong evidence for the retro-Wolff rearrangements of **2** and **24** to **6** and **27**, respectively. In both pyrrole and indole series, at low FVP temperatures, the initially formed azafulvenones **2** and **24** can be isolated in matrices at cryogenic temperatures and observed by IR spectroscopy. Both **2** and **24** easily dimerize to piperazinediones **3** and **21**, respectively. At higher FVP temperatures, the rearranged cyano ketenes **6**, **7**, and **27** can be isolated at low temperature or trapped by alcohol to form the respective esters **8**, **9**, **10**, and **23**. The transformation of **2** to **6** is found to require a higher pyrolysis temperature than the corresponding reaction **24** → **27**. Azafulvenone **2** could be formed easily at 700 °C. Very harsh conditions (FVP temperature ca. 1000 °C) were required to generate the cyano ketenes **6** and **7**. In the indole case, on the other hand, it was difficult to isolate the first-formed isoindolic ketene **24** which easily rearranged to the (2-cyanophenyl)ketene **27** at 700 °C.

The proposed retro-Wolff rearrangement of **2** and **24** is supported by ab initio calculations. In both pyrrole and indole series, oxocarbenes **4** and **25** and isocyanide ketenes **5** and **26** are predicted to be distinct but short-lived intermediates on the reaction pathways, and the isocyanide–cyanide rearrangement is the rate-determining step. The retro-Wolff rearrangement of **24** requires a smaller overall activation barrier, in accord with the experimental observations.

## Experimental and Computational Section

**Computational Details.** Standard ab initio molecular orbital calculations<sup>29</sup> were carried out with the GAUSSIAN 92/DFT<sup>30</sup> series of programs. The structures and energies of the pyrrole system were examined at the G2(MP2,SVP) level of theory.<sup>27</sup> This corresponds effectively to QCISD(T)/6-311+G(3df,2p)/MP2/6-31G\* energies together with zero-point vibrational and isogyric corrections. The G2(MP2,SVP) theory is different from the standard G2 theory<sup>31</sup> in two aspects: (1) The basis-set extension energy contributions are obtained at the MP2 level, and (2) the QCISD(T) energies are evaluated using the 6-31G\* basis set. It has been shown that the accuracy of the G2(MP2,SVP) method is comparable to that of the G2(MP2) theory<sup>32</sup> but computationally more efficient.<sup>27</sup> The frozen-core approximation was employed for all MP2 and QCISD(T) calculations.

For the indole system, it is not feasible to carry out calculations at the G2(MP2,SVP) level, and it was examined by the B-LYP formulation<sup>33</sup> of density functional theory (DFT), i.e., the Becke exchange functional<sup>33a</sup> and the Lee–Yang–Parr correctional functional.<sup>33b</sup> For both systems, geometry optimizations were carried out at the B-LYP/6-31G\* level. Harmonic vibrational frequencies and infrared intensities were computed at these equilibrium geometries. A recent study has shown that the unscaled B-LYP/6-31G\* frequencies are suitable for

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**Table 1.** Calculated Total Energies (hartrees) and ZPVE (kJ mol<sup>-1</sup>)

| species       | G2(MP2,SVP) | B-LYP/6-31G* | B-LYP/6-311+G(2d,p) <sup>a</sup> | ZPVE <sup>b</sup> |
|---------------|-------------|--------------|----------------------------------|-------------------|
| ketene 2      | -321.730 45 | -322.162 11  | -322.267 55                      | 173.1             |
| <b>TS1</b>    | -321.662 13 | -322.099 23  | -322.202 03                      | 167.2             |
| oxocarbene 4  | -321.673 56 | -322.116 59  | -322.220 81                      | 169.8             |
| <b>TS2</b>    | -321.665 55 | -322.104 27  | -322.210 10                      | 165.3             |
| isocyanide 5  | -321.692 55 | -322.121 68  | -322.229 84                      | 165.9             |
| <b>TS3</b>    | -321.640 33 | -322.069 20  | -322.178 11                      | 160.1             |
| nitrile 6     | -321.725 79 | -322.158 44  | -322.267 06                      | 167.5             |
| ketene 24     |             | -475.733 03  | -475.879 46                      | 291.8             |
| <b>TS4</b>    |             | -475.677 12  | -475.820 07                      | 286.8             |
| oxocarbene 25 |             | -475.696 75  | -475.841 65                      | 288.6             |
| <b>TS5</b>    |             | -475.691 69  | -475.838 02                      | 285.3             |
| isocyanide 26 |             | -475.711 40  | -475.859 91                      | 286.4             |
| <b>TS6</b>    |             | -475.657 13  | -475.805 91                      | 280.1             |
| nitrile 27    |             | -475.746 58  | -475.895 32                      | 288.1             |

<sup>a</sup> Based on B-LYP/6-31G\* optimized geometries. <sup>b</sup> B-LYP/6-31G\* values.

prediction of experimental frequencies.<sup>34</sup> Improved relative energies were obtained through B-LYP/6-311+G(2d,p) calculations, based on the B-LYP/6-31G\* optimized geometries. Unless otherwise noted, the relative energies mentioned in the discussion refer to the B-LYP/6-311+G(2d,p)/B-LYP/6-31G\* values, with zero-point energy contributions (evaluated from the B-LYP/6-31G\* vibrational frequencies).

The full sets of optimized (B-LYP/6-31G\*) equilibrium and transition structures are displayed in Figures 10 and 11 in the supporting information. G2(MP2,SVP) and B-LYP/6-311+G(2d,p) total energies and ZPVE (B-LYP/6-31G\*) for all species are collected in Table 1. Schematic potential energy profiles for the retro-Wolff rearrangements are shown in Figure 9. Bond lengths are given in angstroms and bond angles in degrees, and refer, unless otherwise noted, to the B-LYP/6-31G\* values.

**Apparatus.** Preparative FVP was carried out in electrically heated quartz tubes, either 32 or 40 cm long, of 2 cm diameter. Samples were sublimed into the pyrolysis tube using a Büchi sublimation oven. The system was evacuated to ca. 10<sup>-5</sup> mbar and continuously pumped during pyrolysis using a Leybold-Heraeus turbomolecular pump, PT150. The pyrolyzed product was trapped on a liquid N<sub>2</sub> cold finger (77 K). For trapping of the products with methanol, the pyrolyzate was cocondensed with methanol vapor on the 77 K cold finger, whereby methanol was introduced between the exit of the pyrolysis oven and the cold finger. In reaction where removal of methanol was desired, products were condensed in a U-tube at 77 K, and methanol was removed by continuous pumping during warming. In reactions with trapping by alcohol at different points in the oven, a coaxial tube carrying the alcohol vapor was fitted inside the pyrolysis tube. Further details of the FVP apparatus have been published.<sup>35</sup>

The pulsed pyrolysis (PP) apparatus employed a solenoid valve (General Valve Corp. Series 9), operating at a frequency of 4 pulses/min. The duration of the pulse was 500 ms. The sample was evaporated at 60–100 °C, with a stream of Ar passed through the sample compartment at a stagnation pressure of 2 atm. The sample compartment was attached directly to the valve, which was held at the same temperature. The exit aperture of the valve led into a quartz tube, which was attached to the valve body by a graphite ferrule. The quartz tube (60 mm long, inner diameter 0.9 mm, exit aperture of 0.3 mm) was heated (Ta wire, 0.25 mm diameter) over a length of 15 mm at the end facing the cold window of the cryostat. Heat radiation toward the cold window was prevented with the aid of two shields (14 and 3 mm orifice diameters). The pyrolysis temperatures were measured by optical pyrometry through a quartz window.

Matrix isolation was carried out using a 10 cm long, 0.8 cm diameter quartz tube in an oven directly attached to the vacuum shroud of a Leybold-Heraeus liquid He cryostat.<sup>35</sup> Argon and nitrogen were used as matrix media, which were passed over the sample while it was subliming and cocondensed as a matrix at ca. 12 K on a BaF<sub>2</sub> window for IR spectroscopy. Neat isolation at 77 K was carried out in a similar apparatus using a liquid N<sub>2</sub> cryostat.<sup>35</sup>

Matrix IR spectra were recorded on Perkin-Elmer 1720X or System 2000 instruments. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL GX400 (400 MHz) or Bruker AC200 (200 MHz), mass spectra (70 eV; direct insertion) on a Kratos MS25RFA, GC-MS spectra on a Hewlett-Packard 5992B, and UV spectra on a Varian Cary 1 instrument.

Melting points are uncorrected. Kugelrohr distillation was carried out using a Büchi apparatus.

**Preparative FVP of Methyl Pyrrole-2-carboxylate (1b). (1) Dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine-5,10-dione (3).** A 0.4 g (3.2 mmol) sample of **1b** was sublimed at 160 °C and pyrolyzed in the 40 cm oven at 800 °C (10<sup>-3</sup> mbar) in the course of 3.5 h. Dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine-5,10-dione (**3**) (0.27 g, 90%) condensed in the air-cooled part of the equipment between the oven and the cold trap and was purified by sublimation at 150 °C (10<sup>-3</sup> mbar): mp 272–273 °C (lit.<sup>36</sup> mp 272–273 °C); identical with a sample prepared according to the literature;<sup>37</sup> IR (KBr) 1705 m, 1650 m, 1630 m, 1560 m, 1460 s, 1425 m, 1330 s cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ 6.55 (dd, *J* = 3.69 Hz, *J* = 3.09 Hz, 1H, H-C<sub>3</sub>), 7.38 (dd, *J* = 3.69 Hz, *J* = 1.5 Hz, 1H, H-C<sub>2</sub>), 7.78 (dd, *J* = 3.09 Hz, *J* = 1.5 Hz, 1H, H-C<sub>4</sub>); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 114.6 (C<sub>3</sub>), 122.7 (C<sub>4</sub>), 124.2 (C<sub>4a</sub>), 150.6 (C=O); MS *m/z* 187 (11), 186 (M<sup>+</sup>, 100), 158 (3), 130 (10), 93 (55), 65 (25); HRMS calcd for C<sub>10</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub> 186.0429, found 186.0435.

(2) Similar experiments at FVP temperatures of 700 and 750 °C gave **3** in yields of 60% and 62%, respectively, the remainder being the unchanged starting material (**1b**).

(3) In an analogous experiment at a pyrolysis temperature of 950 °C with trapping of the products in a methanol matrix on a cold finger at 77 K, dimer **3** condensed as above in 30% yield (contaminated with the rearranged dimers **15** and **16**; see below) in the air-cooled part of the apparatus. High-vacuum distillation of the methanol solution from the cold finger gave a 15% yield of a mixture of four compounds, **1b**, **8**, **9**, and **10** (2:7:5:3), as analyzed by <sup>1</sup>H and <sup>13</sup>C NMR and GC-MS and comparison with the products of photolysis of **11** (*vide infra*).

**Data for Methyl (Z)-4-Cyano-3-butenolate (8):** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.46 (dd, *J* = 7.25 Hz, *J* = 1.6 Hz, 2H, CH<sub>2</sub>), 3.71 (s, 3H, CH<sub>3</sub>), 5.41 (dt, *J* = 11.2 Hz, *J* = 1.6 Hz, 1H, H-C<sub>4</sub>), 6.67 (dt, *J* = 11.0 Hz, *J* = 7.25 Hz, 1H, H-C<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 36.2 (CH<sub>2</sub>), 52.3 (CH<sub>3</sub>), 102.6 (C<sub>4</sub>), 115.2 (CN), 145.7 (C<sub>3</sub>), 169.3 (C=O); GC-MS (150–300 °C) the compound isomerized to **9**.

**Data for Methyl (E)-4-Cyano-3-butenolate (9):** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.25 (dd, *J* = 7.25 Hz, *J* = 1.6 Hz, 2H, CH<sub>2</sub>), 3.70 (s, 3H, CH<sub>3</sub>), 5.48 (dt, *J* = 16.6 Hz, *J* = 1.6 Hz, 1H, H-C<sub>4</sub>), 6.76 (dt, *J* = 16.4 Hz, *J* = 7.25 Hz, 1H, H-C<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 37.7 (CH<sub>2</sub>), 52.3 (CH<sub>3</sub>), 103.3 (C<sub>4</sub>), 115.1 (CN), 146.3 (C<sub>3</sub>), 169.1 (C=O); GC-MS (*t*<sub>R</sub> = 6.14 min) *m/z* 125 (M<sup>+</sup>, 2), 94 (31), 81 (30), 66 (100), 59 (75), 55 (89).

**Data for Methyl (E)-4-Cyano-2-butenolate (10):** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.28 (dd, *J* = 5.4 Hz, *J* = 2 Hz, 2H, CH<sub>2</sub>), 3.74 (s, 3H, CH<sub>3</sub>), 6.21 (dt, *J* = 15.6 Hz, *J* = 2.0 Hz, 1H, H-C<sub>2</sub>), 6.77 (dt, *J* = 15.6 Hz, *J* = 5.4 Hz, 1H, H-C<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 20.2 (CH<sub>2</sub>), 51.9 (CH<sub>3</sub>), 115.5

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(CN), 125.4 (C<sub>2</sub>), 134.8 (C<sub>3</sub>), 165.4 (C=O); GC-MS (*t*<sub>R</sub> = 6.8 min) *m/z* 125 (M<sup>+</sup>, 2), 94 (33), 81 (27), 66 (100), 59 (93), 55 (71).

**Isomerization of Dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine-5,10-dione (3) to 1*H*-Dipyrrolo[1,2-*a*:2',3'-*d*]pyridine-5,9-dione (15) and 6*H*-Dipyrrolo[1,2-*a*:3',2'-*d*]pyridine-5,9-dione (16).** A 0.5 g (2.7 mmol) sample of **3** was pyrolyzed at 850–900 °C in the course of 6 h, giving rise to four new dimers, named **A**, **B**, **C**, and **D**. **A** and **B** were identified as **15** and **16** (or **16** and **15**); **C** and **D** were identified as **17** and **18**, respectively. The four dimers were separated initially by flash chromatography (SiO<sub>2</sub>/ethyl acetate–CH<sub>2</sub>Cl<sub>2</sub>, 1:1), giving a first fraction containing unchanged **3** (0.44 g, 88%). The second fraction (0.05 g, 10%; mp 198 °C) was a mixture of dimers **A** and **B** (ratio 1.2–1.6 in different experiments). The third fraction was a mixture of dimers **C** and **D** (ca. 0.1% yield). Repeated flash chromatography (five times) resulted in (i) a fraction containing **A** and **B**, enriched in **A**, (ii) almost pure **B**, (iii) a fraction enriched in **C**, and (iv) pure **D**. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **A–D** are given in the supporting information.

**Data for Dimer A:** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 6.42 (dd, *J* = 3.5 Hz, 1H), 6.76 (dd, *J*<sub>NH</sub> = 2.6 Hz, *J* = 2.7 Hz, 1H), 7.11 (dd, *J* = 3.8 Hz, *J* = 1.8 Hz, 1H), 7.32 (dd, *J*<sub>NH</sub> = 2.6 Hz, *J* = 2.7 Hz, 1H), 7.69 (dd, *J* = 3.1 Hz, *J* = 1.5 Hz, 1H), 13.6 (br s, 1H, NH, exchanging with D<sub>2</sub>O), NH couplings were confirmed by exchange with D<sub>2</sub>O; <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 109.9, 113.4, 119.3, 121.2, 123.5, 127.3, 131.3, 132.7, 156.3, 166.1.

**Data for Dimer B:** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 6.42 (dd, *J* = 3.5 Hz, *J* = 3.2 Hz, 1H), 6.76 (dd, *J*<sub>NH</sub> = 2.6 Hz, *J* = 2.7 Hz, 1H), 7.09 (dd, *J* = 3.6 Hz, *J* = 1.5 Hz, 1H), 7.32 (dd, *J*<sub>NH</sub> = 2.6 Hz, *J* = 2.7 Hz, 1H), 7.66 (dd, *J* = 3.0 Hz, *J* = 1.5 Hz, 1H), 13.17 (br s, 1H, NH, exchanging with D<sub>2</sub>O), NH couplings were confirmed by collapse on exchange with D<sub>2</sub>O; <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 107.9, 113.6, 119.4, 122.8, 126.8, 127.8, 128.4, 132.0, 152.0, 171.6; HRMS calcd for C<sub>10</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub> *m/z* 186.04290, found 186.0428.

**Data for Dimer C:** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 7.68 (m, 1H), 7.85 (m, 1H), 12.7 (br s, 1H, NH, exchanging with D<sub>2</sub>O); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 107.4, 125.1, 125.7, 132.9, 174.0.

**Data for Dimer D:** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 6.48 (d, *J* = 2.6 Hz, 1H), 7.09 (d, *J* = 2.6 Hz, 1H), 12.6 (s, 1H, NH, exchanging with D<sub>2</sub>O); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 107.8, 125.5, 127.3, 131.9, 168.3, 179.3; UV (EtOH) λ<sub>max</sub> 288, 322, 459 nm; HRMS calcd for C<sub>10</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub> *m/z* 186.04290, found 186.0428.

**Photolysis of 6-Chloro-2-pyridone (11).** Photolysis was conducted according to the literature.<sup>15</sup> A 200 mg sample of 6-chloro-2-pyridone (**11**) was dissolved in 200 mL of absolute methanol in a quartz tube. A high-pressure mercury lamp was used to photolyze the solution at room temperature for 24 h until no starting material was left according to monitoring by TLC. The solution was under nitrogen throughout the course of photolysis. After reaction, the solvent was evaporated, and the mixture was subjected to column chromatography (SiO<sub>2</sub>/ethyl acetate). Two fractions were obtained. The first fraction (140 mg) was a mixture of compounds **8**, **9**, and **10** in the ratio 14:15:13 (by <sup>1</sup>H NMR integration). Fraction 2 contained 54 mg of 2-methoxy-6-pyridone:<sup>38</sup> <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 4.30 (s, 3H, CH<sub>3</sub>), 6.65 (d, *J* = 7.8 Hz, 1H, CH), 6.70 (d, *J* = 8.1 Hz, 1H, CH), 8.02 (t, *J* = 7.94 Hz, 1H, CH); <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>) δ 54.0 (OCH<sub>3</sub>), 98.2 (CH), 102.7 (CH), 142.6 (CH), 163.2 (C), 163.7 (C); IR (KBr) 1668 s, 1613 s, 1468 m, 1409 m, 1376 m, 1279 m, 1164 m, 1071 m 937 w, 770 w, 551 m cm<sup>-1</sup>; GC-MS *m/z* 125 (M<sup>+</sup>, 98), 124 (75), 96 (43), 95 (45), 82 (85), 67 (40), 55 (35), 39 (100).

**Matrix Isolation of 2-Carbonyl-2*H*-pyrrole (2) and Cyanovinyl Ketenes 6 and 7.** **Method A: Flash Vacuum Pyrolysis (FVP).** **2-Carbonyl-2*H*-pyrrole (2).** (a) **From Pyrrole-2-carboxylic Acid (1a).** Pyrrole-2-carboxylic acid (**1a**) was pyrolyzed at 690 °C with N<sub>2</sub> as the carrier gas. The pyrolyzed product was trapped on a BaF<sub>2</sub> window (12 K) and assigned as 2-carbonyl-2*H*-pyrrole (**2**): IR (N<sub>2</sub> matrix, 12 K) 2148 vs, 1509 vw, 1418 vw, 1376.5 w, 1333.5 vw, 1264 vw, 1179 vw, 1065.4 vw, 1014 vw, 908 w, 879 vw cm<sup>-1</sup>; UV (N<sub>2</sub> matrix, 12 K) λ<sub>max</sub> 266 nm.

(b) **From Methyl Pyrrole-2-carboxylate (1b).** Methyl pyrrole-2-carboxylate (**1b**) was sublimed (10<sup>-6</sup> mbar) at room temperature and

pyrolyzed at 630 °C with Ar as the carrier gas: IR (Ar, BaF<sub>2</sub>, 12 K) 3731.4 w (MeOH), 2145 vs, 1508 vw, 1420 vw, 1377 w, 1361 vw (MeOH), 1332 vw, 1264.5 vw, 1177 vw, 1053 vw, 1035 w (MeOH), 1013.7 vw, 906.3 w, 877 vw cm<sup>-1</sup>.

(c) **From Pyrrole-2-carboxylic Acid Chloride<sup>24a</sup> (1c).** **1c** was sublimed (10<sup>-6</sup> mbar) at 40 °C and pyrolyzed at 650 °C with Ar as the carrier gas: IR (Ar, KBr, 12 K) 2864.5/2859.6 m (HCl), 2145.5 vs, 1507 vw, 1419.5 vw, 1377 w, 1333 vw, 1264.7 vw, 1177.5 vw, 1067 vw, 1014 vw, 907 w, 877 vw, 738.5 w, 575.5 vw, 518 vw cm<sup>-1</sup>.

(Cyanovinyl)ketenes **6** and **7**. (a) Pyrrole-2-carboxylic acid (**1a**) or its methyl ester (**1b**) was pyrolyzed at 1010 °C with N<sub>2</sub>, and the (cyanovinyl)ketenes **6** and **7** were isolated as a mixture in the matrix: IR (N<sub>2</sub>, 12 K) 2234 w, 2141.8 vs, 2139.3 vs, 2134.7 vs, 1596.5 m, 1421.4 w, 1338 w, 962.5 w cm<sup>-1</sup>. (b) Pyrrole-2-carboxylic acid chloride (**1c**) at 850 °C gave (cyanovinyl)ketenes **6** and **7**: IR (Ar, 12 K): 2226 vw, 2134 vs, 1593 m, 1419 w, 1339 w, 918.7 w cm<sup>-1</sup>. (c) A mixture of compounds **8**, **9**, and **10** generated by photolysis of **11** was pyrolyzed at 850 °C: IR (Ar, 12 K) 2230 broad (CN), 2132 vs (C=C=O) cm<sup>-1</sup>.

**Method B: Pulsed Pyrolysis (PP).** 2-Carbonyl-2*H*-pyrrole (**2**) was generated by PP of **1b** at 1000 °C: IR (Ar, 12 K) 2144 vs, 1377.8 w, 908 w, 737 w cm<sup>-1</sup>. (Cyanovinyl)ketenes **6** and **7** were generated by PP at 1400 °C: IR (Ar, 12 K) 2226 vw, 2135 vs, 1593 m, 1419 w, 1339 w, 919 vw, 857 w 653 vw, 649 vw cm<sup>-1</sup>.

**Preparative FVP of Indole-2-carboxylic Acid (19) and Its Methyl Ester (20).** **Diindolo[1,2-*a*:1',2'-*d*]pyrazine-8,16-dione (21).** Methyl indole-2-carboxylate (**20**) (0.4 g, 2.29 mmol) was sublimed at 60 °C and pyrolyzed in the 32 cm oven at 700 °C. The dimer **21** (33 mg, 10%) condensed on the glassware immediately outside the oven and had properties identical with those of sample prepared according to Ciamician:<sup>39</sup> mp 325–327 °C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 7.44 (t, *J* = 7.48 Hz, 1H), 7.61 (t, *J* = 7.69 Hz, 1H), 7.83 (s, 1H), 7.87 (d, *J* = 7.49 Hz, 1H), 8.46 (d, *J* = 8.3 Hz, 1H); IR (KBr) 1701 vs, 1583 w, 1560 s, 1451 m, 1368 vs, 1345.5 vs cm<sup>-1</sup>; GC-MS *m/z* 286 (M<sup>+</sup>, 100), 143 (47), 115 (45), 114 (21), 88 (12), 62 (8), 44 (6); HRMS calcd for <sup>12</sup>C<sub>18</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> *m/z* 286.0754, found 286.0749. Crystal data: a light yellow crystal from DMSO was subjected to single-crystal X-ray analysis at 298 K, C<sub>18</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>, FW = 286.28 g mol<sup>-1</sup>, space group P2<sub>1</sub>/c, *a* = 5.805(3) Å, *b* = 5.2000(6) Å, *c* = 20.709(11) Å, β = 94.81(2)°, *V* = 622.9 Å<sup>3</sup>, *Z* = 2, *Q*<sub>calc</sub> = 1.526 mg/m<sup>3</sup>, μ(Mo Kα) = 0.102 mm<sup>-1</sup>, number of unique reflections 1090, number of reflections with *I* > 2σ<sub>*I*</sub> = 435, *R* = 0.0598, *wR*<sub>2</sub> = 0.1408. The full data are presented in the supporting information.

The same compound was obtained in similar yield on pyrolysis of indole-2-carboxylic acid (**19**) at 600–850 °C.

**Methyl (2-Cyanophenyl)acetate (23).** Methyl indole-2-carboxylate (**20**) (0.30 g, 1.71 mmol) was pyrolyzed in the 32 cm oven at 700 °C. The volatile product was cocondensed with MeOH on a cold finger at 77 K, MeOH being introduced through a needle valve between the oven exit and the cold finger. The resulting methanol solution was concentrated and subjected to Kugelrohr distillation, giving 210 mg (70%) of nitrile **23**. This compound is known,<sup>40</sup> but no spectral data have been reported. The identity of the pyrolysis product with a sample prepared according to Halford and Weissmann<sup>40a</sup> was established by spectral comparison: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.31 (td, *J* = 7.5 Hz, *J* = 1 Hz, 1H, H-C<sub>4</sub>), 7.34 (d, *J* = 7.8 Hz, 1H, H-C<sub>6</sub>), 7.49 (td, *J* = 7.8 Hz, *J* = 1.3 Hz, 1H, H-C<sub>5</sub>), 7.59 (dd, *J* = 7.5 Hz, *J* = 0.8 Hz, 1H, H-C<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 39.16 (td, CH<sub>2</sub>), 52.24 (q, CH<sub>3</sub>), 113.38 (m, C<sub>2</sub>), 127.74 (dd, C<sub>4</sub>), 130.56 (dq, C<sub>6</sub>), 132.70 (dd, C<sub>3</sub>), 132.81 (dd, C<sub>5</sub>), 137.49 (pent, C<sub>1</sub>), 170.02 (t, CO); the <sup>1</sup>H and <sup>13</sup>C NMR spectra were correlated by a 2D (COLOG) spectrum; IR (film on KBr) 2955 m, 2227 s, 1742 s, 1490 m, 1437 s, 1343 s, 1227 s, 1167 s 760 s cm<sup>-1</sup>; HRMS calcd for <sup>12</sup>C<sub>10</sub>H<sub>9</sub>NO<sub>2</sub> 175.0633, found 175.0634.

**23** was also formed in 24% yield when no additional methanol was used for trapping. **23** was formed in 50–52% yield by FVP of indole-2-carboxylic acid (**19**) at 850 °C with trapping of the product in a MeOH matrix at 77 K.

In experiments with both **19** and **20**, without added methanol, a polymer of (2-cyanophenyl)ketene (**27**) was formed. When the

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pyrolysate from **20** (700–800 °C) was isolated in a U-tube, and the methanol formed as a byproduct removed by distillation, slow warming of the U-tube resulted in polymer formation in the same place where ester **23** would otherwise have been formed. The polymer had the following properties: IR 2225 s, 1767 s  $\text{cm}^{-1}$ ; MS (250 °C)  $m/z$  429 (trimer), 286 (dimer), 116 (2-cyanobenzyl); molecular mass distribution by gel permeability chromatography, 300–5000 amu.

**Matrix Isolation of 2-Carbonyl-2H-indole (24) and (2-Cyanophenyl)ketene (27).** **2-Carbonyl-2H-indole (24).** Methyl indole-2-carboxylate (**20**) was pyrolyzed from 560 to 620 °C with  $\text{N}_2$  carrier gas. The product was examined by IR ( $\text{N}_2$ , BaF<sub>2</sub>, 12 K). The absorption at 2141  $\text{cm}^{-1}$  appeared first at 560 °C, increased at 620 °C, vanished at 700 °C, and was assigned as the C=C=O stretching vibration of 2-carbonyl-2H-indole (**24**).

**(2-Cyanophenyl)ketene (27).** (a) Methyl indole-2-carboxylate (**20**) was pyrolyzed from 700 to 930 °C. (2-Cyanophenyl)ketene (**27**) was isolated in  $\text{N}_2$  and Ar matrices: IR ( $\text{N}_2$ , 12 K) 2234.7 vw, 2131.7 vs, 1609 vw, 1571.7 m, 1497 m, 1347 w, 1284.5 w, 760.5 w  $\text{cm}^{-1}$ ; IR (Ar, 12 K) 2230.5 vw, 2127.5 vs, 1602 m, 1572 w, 1496 m, 1451 vw, 1387 vw, 1283.5 w, 1084 vw, 756 w, 586 vw, 458 vw  $\text{cm}^{-1}$ . (b) Methyl (2-cyanophenyl)acetate (**23**) was subjected to FVP at 800 °C with matrix isolation of the product in Ar at 12 K. The IR spectrum of **27** was identical with the above.

**Preparative FVP of Methyl Indole-1-carboxylate (28) and Methyl Indole-3-carboxylate (29).** (1) A 400 mg sample of methyl indole-1-carboxylate<sup>41</sup> (**28**) was sublimed at 40–50 °C and pyrolyzed in the 32 cm oven at 700 °C. The product was dissolved in MeOH and filtered. The insoluble solid was identified as dimer **21** (24 mg, 6%). The filtrate was evaporated, and the residue (336 mg) was analyzed by <sup>1</sup>H NMR: 56% starting material **28**, 10% methyl indole-3-carboxylate (**29**), and 28% cyano ester **23**. (2) A 200 mg sample of methyl indole-3-carboxylate (**29**), from the reflux of indole-3-carboxylic acid (Aldrich) in MeOH/HCl (dry) solution in the dark for 4 h, was sublimed at 75 °C and pyrolyzed under the above conditions at 800 °C to give dimer **21** (20 mg, 5%). The fraction soluble in MeOH was separated by column chromatography ( $\text{SiO}_2/\text{CHCl}_3$ ) to give 172 mg (78%) of starting material **29** and 18 mg (8%) of cyano ester **23**.

**Matrix Isolation of 1-Carbonyl-1H-isindole (34).** Methyl isindole-1-carboxylate (**33**)<sup>42</sup> was pyrolyzed at 500 °C with Ar as the carrier gas, and the product was isolated in an Ar matrix at 12 K. All the absorptions in the IR spectrum were assigned to the unreacted starting material **33**, MeOH, and 1-carbonyl-1H-isindole (**34**). The latter had IR (Ar, 12 K) 2132.2 vs, 1421.7 w, 1339.3 w, 1205.8 w, 1035 w, 892.2  $\text{cm}^{-1}$ .

Ketene **34** can also be matrix isolated by FVP of dimer **35** at 720 °C with Ar or Xe: IR (Xe, 12 K) 2123.5 vs, 1417.5 w, 1360 w, 1218.5 w, 1032.5 w  $\text{cm}^{-1}$ .

**Preparative FVP of Methyl Isoindole-1-carboxylate (33).** This compound was synthesized according to the literature method:<sup>42</sup> <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.10 (t,  $J$  = 7.08 Hz, 1H), 7.27 (t,  $J$  = 7.48 Hz, 1H), 7.48 (s, 1H), 7.66 (d,  $J$  = 8.72 Hz, 1H), 8.07 (d,  $J$  = 8.31 Hz, 1H), 11.4 (s, br, 1H), 3.99 (s, CH<sub>3</sub>); IR (KBr) 3193.5 b, 1655 vs, 1525 w, 1485 w, 1455.5 s, 1438 m, 1395 m, 1362 w, 1331 s, 1262.5 m, 1233.5 m, 1200 m, 1127.5 s, 1113.5 m, 1037.5 m, 791 m, 770.5 m, 740.5 m, 614 w, 589 w, 581 w  $\text{cm}^{-1}$ ; MS  $m/z$  175 ( $\text{M}^+$ , 77), 143 (100), 132 (60), 115 (95), 104 (10), 89 (40), 77 (20), 63 (18).

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**Diisoindolo[1,2-*a*:1',2'-*d*]pyrazine-8,16-dione (35).** Methyl isindole-1-carboxylate (**33**) (100 mg) was sublimed at 75 °C and pyrolyzed in the 32 cm oven at 700 °C. The dimer **35** (95 mg, 95%) condensed on the glassware immediately outside the oven. Five percent of starting material was collected from the cold finger. Dimer **35** was purified (80 mg, 80%) by sublimation in high vacuum ( $2 \times 10^{-4}$  mbar) at 160 °C: mp 320 °C; <sup>1</sup>H NMR ( $\text{DMSO}-d_6$ )  $\delta$  7.24 (t,  $J$  = 7.66 Hz, 1H), 7.49 (t,  $J$  = 7.66 Hz, 1H), 7.85 (d,  $J$  = 8.59 Hz, 1H), 8.09 (d,  $J$  = 8.59 Hz, 1H), 8.51 (s, 1H); <sup>13</sup>C NMR ( $\text{DMSO}-d_6$ )  $\delta$  119.2 (CH), 119.6 (CH), 123.0 (CH), 124.6 (CH), 125.8 (C), 130.1 (CH), 132.6 (C), 133.7 (C), 149.7 (C=O); IR (KBr) 3131 w, 1677 vs, 1626 m, 1548 m, 1526.5 m, 1455.5 vs, 1445 s, 1388 m, 1353 m, 1335 m, 1242 w, 1198.5 m, 1155.5 w, 1075.5 m  $\text{cm}^{-1}$ ; MS  $m/z$  286 ( $\text{M}^+$ , 72), 143 (100), 115 (77.1), 88 (14.1), 62 (7), 43 (32.2); HRMS calcd for  $\text{C}_{18}\text{H}_{10}\text{N}_2\text{O}_2$   $m/z$  286.0742, found 286.0754. Anal. Calcd for  $\text{C}_{18}\text{H}_{10}\text{N}_2\text{O}_2$ : C, 75.50; H, 3.52; N, 9.79. Found: C, 75.20; H, 3.51; N, 9.76.

**Trapping of Ketene 34 with Ethanol.** (1) A 50 mg sample of methyl isindole-1-carboxylate (**33**) was sublimed at 95 °C and pyrolyzed through the 32 cm oven at 500 °C. At the same time, EtOH vapor was passed through a tube concentric with the pyrolysis tube and running for 3/4 of the length of the oven. After the end of the reaction, a 90% yield (45 mg) of dimer **35** was isolated from inside the pyrolysis tube. A 10% yield (5 mg) of the EtOH trapping product was collected from the cold finger. <sup>1</sup>H NMR showed that the trapped product was a mixture of methyl and ethyl isindole-1-carboxylates in a 1:6.6 ratio. (2) A 10 mg sample of dimer **35** was sublimed at 200 °C and pyrolyzed at 800 °C together with EtOH. The product was 50% dimer **35** and 50% ethyl isindole-1-carboxylate: <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.11 (t,  $J$  = 7.68 Hz, 1H), 7.27 (t,  $J$  = 7.68 Hz, 1H), 7.4 (s, 1H), 7.67 (d,  $J$  = 8.31 Hz, 1H), 8.08 (d,  $J$  = 7.89 Hz, 1H), 10.3 (s, br, NH), 1.46 (t,  $J$  = 7.06 Hz, CH<sub>3</sub>), 4.44 (q,  $J$  = 7.06 Hz, CH<sub>2</sub>); GC–MS  $m/z$  189 ( $\text{M}^+$ , 54%), 161 (7), 143 (100), 115 (75), 89 (35), 63 (16), 39 (7). The NMR data are in good agreement with literature values<sup>43</sup> for the *N*-methyl derivative.

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**Supporting Information Available:** Details of the X-ray crystallographic analysis of **21** and views of the structure, <sup>1</sup>H and <sup>13</sup>C NMR spectra of dimers **15**, **16**, **17**, and **18**, IR spectrum of **2** ( $\text{N}_2$ , 12 K) produced from **1a**, and selected computed geometrical parameters for the ground state and transition structures related to the species in Figure 9 (Figures 10 and 11) (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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