Synthesis of *N*-Confused Porphyrin Analogues by *β*-Azafulvenone Tetramerization

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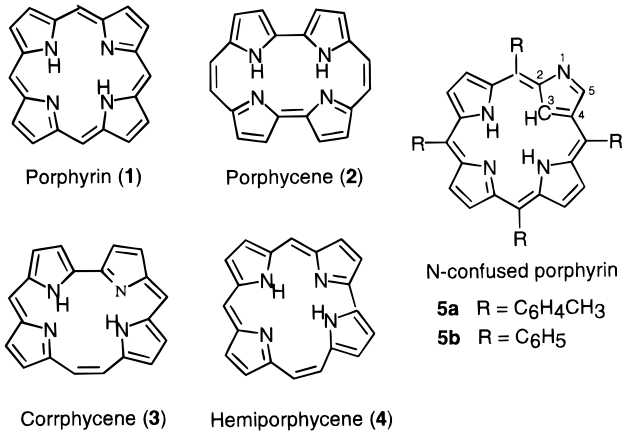
β-Azafulvenones **16** and **33** were generated from **14** or **18** and **31** or **37**, respectively, and directly observed by IR spectroscopy. These heterocyclic ketenes tetramerize to the macrocycles **20** and **34**.

Introduction

Porphyrins are important macrocycles for most organisms.[1] Lately, there has been considerable interest[2,3] in the preparation of non-natural analogues and isomers of the porphyrin system, including porphycene (**2**),[4] corrphycene (**3**),[5] hemiporphycene (**4**),[6] benziporphyrins,[7] and "*N*-confused"[8] porphyrins **5**. The isomers **5**, synthesized by the groups of Furuta[8] and Latos-Grazynski,[9] are particularly interesting, as one of the pyrrole subunits has been rotated ("confused" or "inverted") with respect to its normal position in conventional porphyrins. The inner C−H bond in **5a** is readily metalated with the formation of a Ni(II) metal complex involving three pyrrole nitrogens and C-3 of the fourth ring.[9b,10,11]



It is well known that simple ketenes prefer to dimerize by way of a [2+2] cycloaddition reaction.[12] Our previous work[13] has shown that in heterocyclic ketenes possessing an α-nitrogen atom (α-azafulvenones) such as 2-carbonyl-2*H*-indole (**6**) and 2-carbonyl-2*H*-pyrrole (**8**), this nitrogen atom acts as a nucleophile toward the ketene moiety of another molecule, thus leading to the dimers diindolo-[1,2-*a*;1′2′-*d*]pyrazine-8,16-dione (**7**) and dipyrrolo[1,2-*a*;1′2′-*d*]pyrazine-5,10-dione (**9**), respectively (Scheme 1). It was the purpose of the present study to investigate the behavior of heterocyclic ketenes **10** (X = hydrogen or carbocyclic or heterocyclic ring) possessing a *β*-nitrogen atom (*β*-azafulvenones). Instead of dimerization, oligomerization should lead to the macrocycles **11**. On the basis of ring strain arguments, the tetramer may be expected to be the most stable compound.[14] Such tetramers (**20** and **34**) will have four C−H bonds inside the macrocyclic ring and thus constitute "tetra-*N*-confused" porphyrin analogues.

Results and Discussion

1. Generation and Observation of 3-Carbonyl-3*H*-indole. (a) From 3-Diazo-4-oxo-3,4-dihydroquinoline (14). 3-Nitro-4-hydroxyquinoline was reduced to 3-amino-4-hydroxyquinoline (**12**) according to Süs' method.[15] Diazotization of **12** afforded 4-oxo-3-diazo-3*H*-dihydroquinoline (**14**)[15] after neutralization of the diazonium salt **13**. The diazo compound **14**, purified by vacuum sublimation, was then sublimed onto a 12 K window with Ar matrix isolation and subsequently photolyzed at 254 nm. The photolysis caused elimination of nitrogen, formally to give an α-oxo carbene **15**, which underwent Wolff rearrangement to 3-carbonyl-3*H*-indole (**16**) (Scheme 2). Ketene **16** has a very strong peak at 2140 cm^{-1}. In the fingerprint region, the main peaks are at 1473, 1448, and 1459 cm^{-1}. The reacted diazo compound **14** features a diazo absorption at 2110 cm^{-1} and a carbonyl absorption at 1662 cm^{-1}.[14a] The experimental IR spectrum of **16** is in very good agreement with the BLYP/6-31G* calculated spectrum (Figure 3 in the supporting information).

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(3) Vogel, E. *Pure. Appl. Chem.* **1990**, *62*, 557. Vogel, E. *Ibid.* **1993**, *65*, 143.

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(7) Lash, T. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2533.

(8) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767.

(9) (a) Chmielewski, P. J.; Latos-Grazynski, L.; Rachlewicz, K.; Glowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779. (b) Chmielewski, P. J.; Latos-Grazynski, L. *J. Chem. Soc., Perkin Trans. 2* **1995**, 503.

(10) For other efforts to synthesize C-coordinated porphyrin analogues, see: Kernbach, U.; Ramm, M.; Luger, P.; Fehlhammer, W. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 310.

(11) For theoretical calculations relating to the complexation of **5** by Ni^{2+}, see: Ghosh, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1028.

(12) (a) Hyatt, J.; Raynolds, P. W. *Org. React.* **1994**, *45*, 159. (b) Wentrup, C.; Heilmayer, W.; Kollenz, G. *Synthesis* **1994**, *12*, 1219. (c) Tidwell, T. T. *Ketenes;* Wiley-Interscience: New York, 1995.

(13) (a) Qiao, G. G.; Meutermans, W.; Wong, M. W.; Träubel, M.; Wentrup, C. *J. Am. Chem. Soc.* **1996**, *118*, 3852. (b) Gross, G.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1982**, 360.

(14) (a) Preliminary communication on **16** and **20**: Qiao, G. G.; Wentrup, C. *Tetrahedron Lett.* **1995**, *22*, 3913. (b) For the structure and a different synthesis of **20**, see: Oliver, J. E.; Lusby, W. R. *J. Heterocycl. Chem.* **1991**, *28*, 1565.

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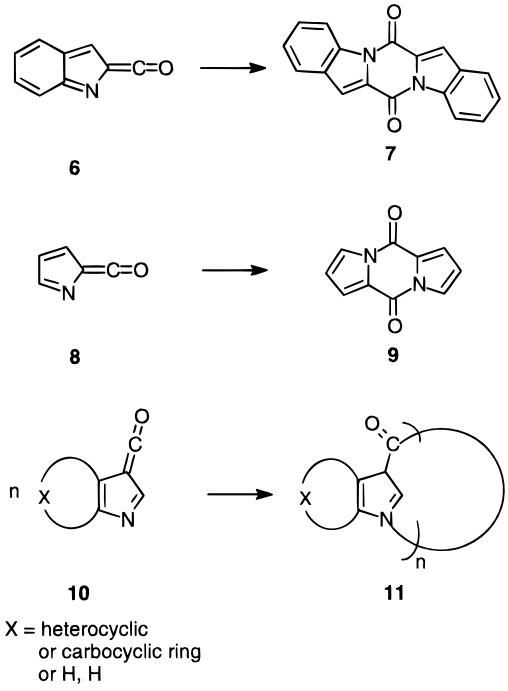
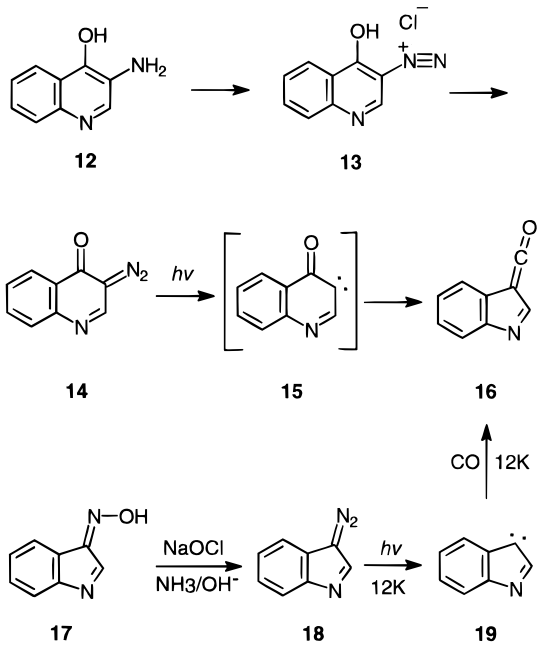
Scheme 1



Scheme 2

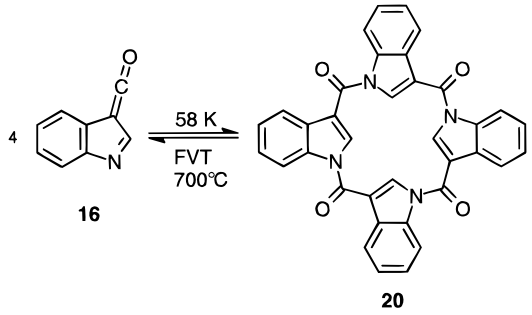


Flash vacuum thermolysis (FVT) of the same α-oxo diazo ketone **14** at 650 °C gave the same ketene, isolated in Ar matrix at 12 K.

(b) From 3-Diazo-3*H*-indole (18). Treatment of indole with amyl nitrite in absolute EtOH/NaOEt afforded 3-oximino-3*H*-indole (**17**).[16] This oxime **17** was dissolved in degassed NaOH solution together with concentrated ammonia and treated with NaOCl. 3-Diazo-3*H*-indole (**18**) thus formed is stable in ether solution at room temperature for several days. It can be sublimed onto a 12 K deposition window under vacuum with Ar as a carrier gas. The Ar matrix isolated **18** has a very strong diazo absorption at 2092 cm^{-1} together with a strong absorption at 1429 cm^{-1} in the fingerprint region.

(16) Madelung, W. *Justus Liebigs Ann. Chem.* **1914**, *504*, 58.

Scheme 3



18 can also be matrix isolated in the presence of CO. In this case, photolysis at 254 nm gave rise to the same ketene **16** as observed by IR spectroscopy.[14a] Although the ketene region around 2100 cm^{-1} was obscured by the large CO absorption, the fingerprint absorptions at 1473, 1448, and 1062 cm^{-1} clearly demonstrate the formation of ketene **16**. The diazo compound **18** was consumed during the photolysis. Obviously, photolysis caused the elimination of nitrogen from **18**, forming carbene **19**, which was then immediately trapped by CO in the matrix to generate ketene **16** (Scheme 2).[17]

2. Tetramerization of 16 to 1,3′-tetrakis(indolylmethanone) (20). Isolation of ketene **16** at 12 K and subsequent warmup revealed that this ketene is only stable below 58 K. This instability is due to the imine function which acts as a nucleophile toward another ketene molecule.[18] IR spectroscopy showed that the product of this thermal matrix reaction is a carbonyl compound. The same product can be obtained preparatively in 75% yield by FVT of diazo compound **14** at 550 °C. When the product of the 58 K reaction was warmed to rt and dissolved in DMSO-d_6, it was shown by ^{1}H NMR spectroscopy to be identical with the product from preparative FVT. The molecular mass of 529 amu by mass spectrometry indicates a tetramer of ketene **16** (Scheme 3). In the mass spectrum, ions due to one, two, three, and four monomer units are seen. Both ^{1}H and ^{13}C NMR demonstrate that the tetramer is a symmetrical molecule with four identical indolecarboxamide subunits. This tetramer was therefore assigned as 1,3′-tetrakis-(indolymethanone) (**20**).[14] The NMR signal assignment was confirmed by two-dimensional ^{13}C−^{1}H correlations (COLOC) with both short- and long-range couplings. MM3 calculations of the structure indicate that **20** is the most stable oligomer compared to the trimer, pentamer or hexamer.[19] The tetramerization of **16** to **20** was directly monitored at $T \leq 70$ K by IR spectroscopy (Figure 5 in the supporting information).

Tetramer **20** forms a light-yellow powder with melting point above 290 °C. It is insoluble in most organic solvents. FVT of **20** at 700 °C regenerates ketene **16** as the only product as evidenced by the strong IR spectrum of the Ar matrix isolated material (Scheme 3).

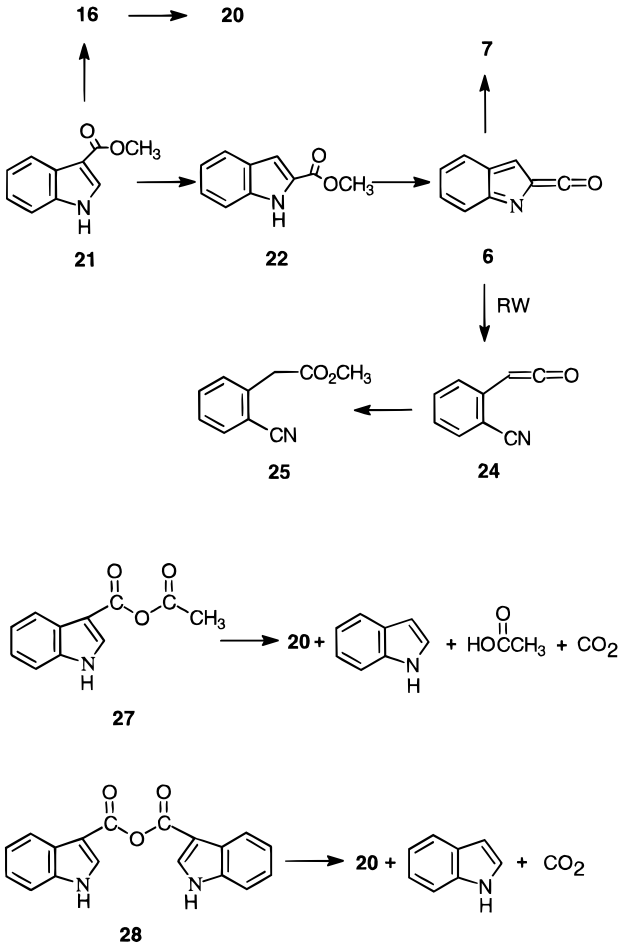
3. Other Percusors for Tetramer 20. We have reported[13a] that under FVP conditions methyl indole-

(17) For other examples of carbene trapping by CO in matrices, see: Sander, W. *Chem. Rev.* **1993**, *93*, 1583.

(18) The reaction between ketenes and pyridine gives directly observable ylides: Qiao, G. G.; Andraos, J.; Wentrup, C. *J. Am. Chem. Soc.* **1996**, *118*, 5634.

(19) Force field calculations performed by Dr. D. J. Brecknell with the MM3(92) molecular mechanics program (Allinger, N. L.; Yuh, Y. H.; Lii, J.-h. *J. Am. Chem. Soc.* **1989**, *111*, 8551. Lii, J.-h.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8566, 8576). Calculated strain energy per monomer unit, for tetramer: $E_s = 32.6$ kcal/mol; trimer: $E_s = 45.7$ kcal/mol; pentamer: $E_s = 35.7$ kcal/mol; hexamer: $E_s = 35.8$ kcal/mol.

Scheme 4



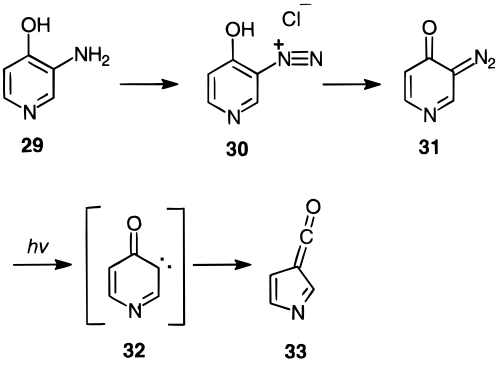
3-carboxylate (**21**) rearranges to methyl indole-2-carboxylate (**22**), which subsequently eliminates methanol to form 2-carbonyl-2*H*-indole (**6**). Ketene **6** is highly unstable and undergoes either dimerization to **7** or retro-Wolff rearrangement to cyanoketene **24**. Ketene **24** is trapped by MeOH to give the ester **25** as the final product (Scheme 4).[13a] In the matrix isolation work, we observed a small absorption ascribable to ketene **16,** formed by direct elimination of MeOH from ester **21** before any ester group migration takes place. Because the amount of ketene **16** is so small, the tetramer **20** is not isolable from a preparative FVT of **21**.

It was thought that anhydrides such as **27** and **28** might be more useful precursors of ketene **16**. Anhydride **27** (Scheme 4) can be easily obtained in quantitative yield by stirring indole-3-carboxylic acid in acetic anhydride solution. Preparative FVT of **27** at 500 °C gave 80% of indole-3-carboxylic acid, together with 10% of a mixture of indole and 3-acetylindole in the ratio of 3:2 (GC-MS). On raising the temperature to 750 °C, the yield of indole increased to 85%, and 10% of tetramer **20** was isolated from the solid residue at the entrance to the oven. The tetramerization takes place in the solid as shown in the following experiment.

Better results were obtained with the anhydride of indole-3-carboxylic acid (**28**), prepared by reaction of indole-3-carboxylic acid with DCC/Et_3N in acetone solution.[20] FVP of **28** at 700 °C afforded 87% of tetramer **20** with indole as a byproduct, thus indicating that ketene **16** and indole-3-carboxylic acid were formed initially.

(20) Suvorov, N. N.; Golubev, V. E. *Pharm. Chem. J.* **1967**, *1*, 440.

Scheme 5



Ketene **16** then tetramerized to **20**. It should be pointed out that these are not FVT reactions since the tetramer was isolated from the residue of the tube containing the starting material. Furthermore, heating of **27** or **28** at *ca*. 200 °C in a Kugelrohr distillation apparatus under vaccum also gave tetramer **20,** isolated from the solid residues.

Direct evidence for the formation of ketene **16** from **28** was, however, obtained by IR spectroscopy of the product from a 940 °C FVT of **28** with Ar matrix isolation at 12 K. **16** was identified by comparison with the spectrum shown in Figure 3 (in the supporting information). However, at this high FVT temperature, a strong absorption at 2127 cm^{-1} was also seen. The latter is due to the formation of ketene **24**, the product of migration from position 3 to position 2 of the indole ring followed by retro-Wolff rearrangement (Scheme 4).[13a] The possibility that **24** is formed by direct ring opening of ketene **16** was ruled out in FVT experiments with **14**. FVT of **14** at 400 to 1000 °C and subsequent Ar matrix isolation of the products at 12 K afforded ketene **16** as the only product according to IR spectroscopy. No absorption due to ketene **24** (2127 cm^{-1}) could be detected.

Compared to diazo compound **14**, anhydride **28** is much easier to synthesize and high yields of tetramer **20** can be achieved from this simple precursor.

4. Generation and Observation of 3-Carbonyl-3*H*-pyrrole (33). 4-Hydroxy-3-aminopyridine (**29**), obtained by reduction of 3-nitro-4-hydroxypyridine with Raney Ni in EtOH solution, was diazotized with isoamyl nitrite in dry EtOH containing HCl. The diazonium salt **30** thus obtained was stirred with solid sodium carbonate in dry ether to give 4-oxo-3-diazopyridine (**31**), which is quite stable in ether solution (Scheme 5). Ether was evaporated and the isolated solid **31** was quickly placed in the cryostat deposition tube. Compound **31** is not stable as a neat solid, and part of it decomposed during this transfer operation. Compound **31** was then sublimed in the cryostat system at 60 °C (10^{-6} mbar) with Ar or N_2 as carrier gas for deposition on a 12 K BaF_2 window. The matrix isolated **31** showed a typical strong diazo absorption at 2130 cm^{-1} (Ar) or 2144 cm^{-1} (N_2). **31** was subsequently subjected to 254 nm UV photolysis for 5 min. Under these conditions, nitrogen is eliminated and an oxocarbene **32** is probably formed. A rapid Wolff rearrangement transforms **32** to 3-carbonyl-3*H*-pyrrole (**33**). In Figure 1, the positive spectrum (b) is due to the formed ketene **33**, and the negative spectrum the reacted diazo compound **31**. Ketene **33** has a very strong C=C=O stretching absorption at 2146 cm^{-1} (Ar matrix; 2150 cm^{-1} in N_2 matrix) together with

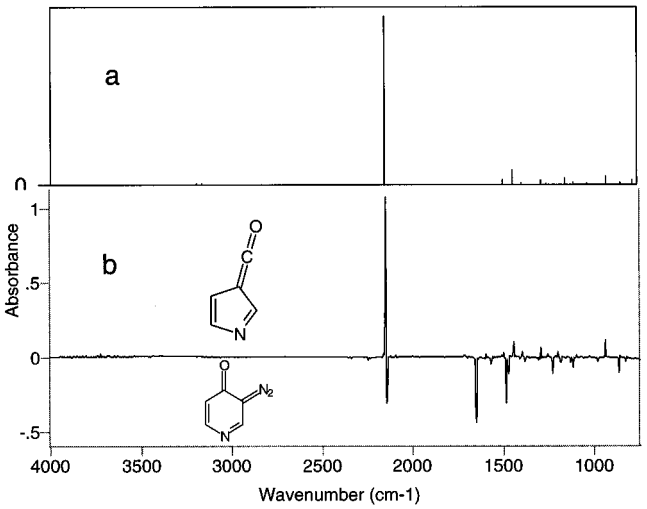
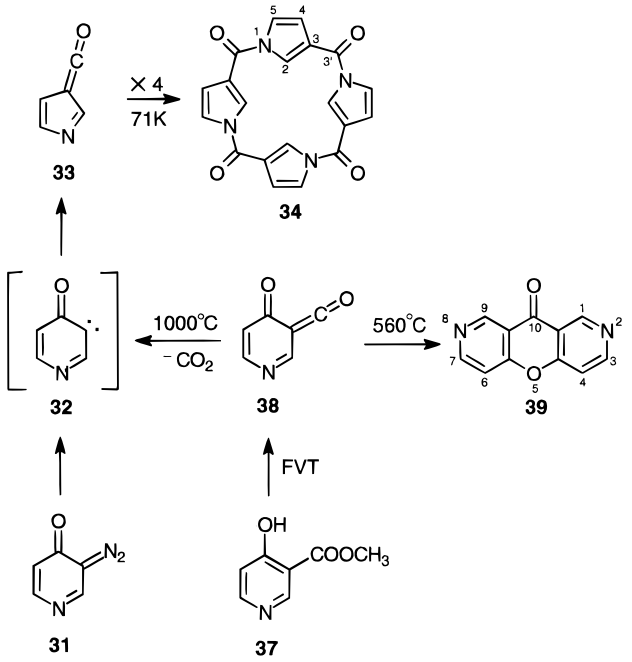


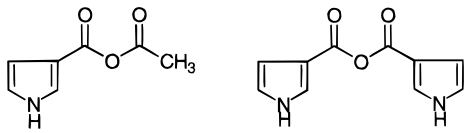
Figure 1. (a) Calculated IR spectrum of ketene **33** (BLYP/6-31G*; unscaled). (b) Positive spectrum: formed spectrum from photolysis of **31** with 254 nm lamp for 2 min; negative spectrum: reacted diazo compound **31** isolated in N_2 matrix at 12 K.

Scheme 6



another three weak peaks in the fingerprint region. The observed IR spectrum is in very good agreement with the ab initio calculated spectrum (Figure 1a) at the BLYP/6-31G* level. Electron correlation at the MP2 level gave similar results, but with better intensity agreements. The MP2/6-31G* spectrum is shown in the supporting information.

5. Tetramerization of Ketene 33 to 1,3′-Tetrakis(pyrrolylmethanone) (34). Preparative FVT of diazo compound **31** at 550 °C yielded a light brown compound with a molecular weight of 372 amu. In analogy with the indole case, this compound is considered to be a tetramer of ketene **33**, namely 1,3′-tetrakis(pyrrolylmethanone) (**34**) (Scheme 6). Because of the instability of **31**, the yields of preparative FVT reactions were, however, extremely low (~1%). Hence, an alternative precursor was needed for further investigation.



35 **36**

In analogy with the indole case (vide supra), it was thought that the anhydrides **35** or **36** could be useful precursors. Both **35** and **36** were synthesized and subjected to preparative FVT investigation. Unlike the indole case, unfortunately, FVT of **35** and **36** gave none of the tetramer **34**. In search of a better thermal precursor of **33**, methyl 4-hydroxynicotinate (**37**) was chosen and synthesized according to known procedures.[21]

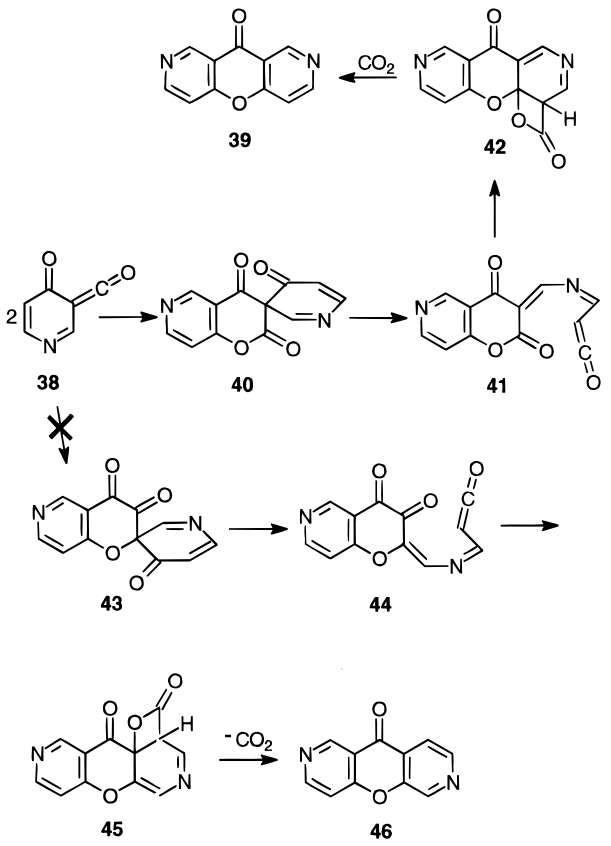
FVT of 37 in the Low-Temperature Range. Isolation of 39. Thermal reaction of ester **37** in the temperature range 500−700 °C is expected to cause elimination of methanol, forming α-oxo ketene **38**. It is also know that oxo ketenes usually dimerize in a specific [2 + 4] cycloaddition manner.[12b] When ester **37** was subjectd to FVT at 560 °C, a new compound, 10-oxo-10*H*-pyrano[3,2-*c*:5,6-*c*′]dipyridine (**39**) was isolated in 61% yield. The specific formation of **39** is readily explained in terms of [2 + 4] cyclodimerization as shown in Scheme 7. The initial dimer **40** undergoes ring opening to an iminoketene **41**. The latter recyclizes to **42**, which under FVT conditions eliminates CO_2 to afford the stable product **39**. The ring opening of another spirodienone derivative to a ketene, which subsequently cyclizes and eliminates CO_2 to give a dibenzofuran derivative has been reported by Sugawara et al.[22]

Compound **39** is a symmetrical molecule. In the ^1H NMR spectrum, the signal due to H(C-1) and H(C-9) appear at a very low field (9.35 ppm). This is typical for xanthone-type heterocycles.[23,24] It is interesting to note that the unsymmetrical compound **46**,[23] which would have resulted from the alternative dimer **43** in a similar manner, was not detectable by NMR of the FVT product. This is in agreement with orientations usually observed in α-oxo ketene dimerizations.[12b]

FVT of 37 in the High-Temperature Range. Isolation of 34. When ester **37** was subjected to FVT at 1000 °C, tetramer **34** was isolated in 90% yield without any **39** being produced. In this experiment, a liquid N_2 cooled U-tube was used as a cold trap. This causes the methanol and ketene to condense in different parts of the trap, thus avoiding their recombination. The result clearly indicates that, under these severe thermolysis conditions, the first-formed α-oxo ketene **38** underwent further elimination of CO and Wolff rearrangement to ketene **33**, the latter cyclizing to tetramer **34** in good yields in the absence of other nucleophiles (Scheme 6). This thermal reaction is very clean, and tetramer **34** is the only product isolated in high yield (90%). On FVT of **37** at 1100 °C with Ar matrix isolation of the product, ketene **33** together with peaks due to methanol and a large absorption due to CO were identified by IR spectroscopy.

(21) Ross, W. C. J. *J. Chem. Soc. C* **1966**, 1816. Kitagawa, T.; Satoshi, M.; Hirai, E. *Chem. Pharm. Bull.* **1978**, 26, 1403.
(22) Izuoka, A.; Miya, S.; Sugawara, T. *Tetrahedron Lett.* **1988**, *29*, 5673.
(23) Trécourt, F.; Quéguiner, G. *J. Chem. Res., Synop.* **1982**, 76.
(24) Compound **39** has properties different from the previously reported isomer, 5-oxo-5*H*-pyrano[2,3-*c*:6,5-*c*′]dipyridine: Trécourt, F.; Marsais, F.; Güngör, T.; Quéguiner, G. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2409.

Scheme 7



NMR spectroscopy of **34** reveals a symmetrical structure. In the ^{1}H NMR, the H(C-2) in the pyrrole rings inside the macrocyle give rise to a low-field signal at 8.78 ppm. In the mass spectrum, ions due to tetramer, trimer, dimer, and monomer are seen. The structure of tetramer **34** was investigated theoretically by density functional theory at the B-LYP/6-31G* level. **34** is predicted to have a symmetrical geometry, with S_4 symmetry (Figure 2). The four inner C−H bonds inside the macrocyclic ring are in the arrangement of a (not fully regular) tetrahedron (D_{2d}, with H−H distances 2.408 and 2.565 Å; see Figure 2). The cavity described by the four central carbons atoms has C−C cross-ring distances of 4.306 Å, similar to those in normal porphyrins. Finally, we note that the formation of tetramer **34** from four molecules of ketene **33** is calculated to be highly exothermic, by 533 kJ mol^{-1} (BLYP/6-31G*).

As ester **37** is easy to synthesize and purify; it is the ideal precusor for the preparation of tetramer **34**.

Experimental Section

Apparatus. Preparative FVT was carried out in electrically heated quartz tubes, either 32 or 40 cm long, of 2 cm diameter. Samples were sublimed into the horizontal pyrolysis tube using a sublimation oven. The system was evacuated to *ca.* 10^{-5} mbar and continuously pumped during thermolysis using a turbomolecular pump. The product was trapped at 77 K on a cold finger or in a U-tube. For trapping of the products with methanol, the pyrolysate was cocondensed with methanol vapor on the 77 K cold finger, whereby methanol was introduced between the exit of the oven and the cold finger. In reactions where removal of methanol was desired, products were condensed in a U-tube at 77 K, and methanol was removed by continuous pumping during warmup. Further details of the FVT apparatus have been published.[25]

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 closed cycle liquid He crystat.[25] Ar and N_2 were used as matrix media, which were passed over the sample while it was sublimed and co-condensed as a matrix at *ca.* 12 K on a BaF_2 window for IR spectroscopy.

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).

Matrix FTIR, ^{1}H and ^{13}C NMR, mass spectra (70 eV; direct insertion), GC−MS, and UV spectra were recorded as previously indicated.[13a] Melting points are uncorrected.

Computational Details. Density functional theory calculations were performed with the Gaussian 92/DFT[26] programs. Geometry optimizations were carried out with the B-LYP formulation[27] of density functional theory, i.e., the Becke exchange functional (B)[27a] in combination with the Lee−Yang−Parr correlation functional (LYP),[27b] using the 6-31G* basis set.[28] Harmonic vibrational frequencies and infrared intensities were computed at these equilibrium geometries. A recent study has shown that unscaled B-LYP/6-31G* frequencies are suitable for prediction of experimental fundamental frequencies.[29]

3-Diazo-4-oxodihydroquinoline (14). This compound was synthesized according to the literature procedure[15] with modifications. The diazonium chloride of 3-diazo-4-oxodihydrdquinoline (**13**) was obtained by diazotization of 3-amino-4-oxoquinoline (**12**) in aqueous HCl/EtOH solution with $NaNO_2$.[15] After being dried *in vacuo* overnight, **13** (690 mg; 3.32 mmol) was mixed with excess Na_2CO_3 powder in dry ether. The suspension was stirred in the dark for 3 h before filtering. The ether solution was evaporated and diazo compound **14** purified by sublimation (460 mg; 2.69 mmol, 81%): mp 128 °C dec (lit.[15] mp 129−130 °C); IR (KBr) 2156 vs, 1627.5 vs, 1606 s, 1585.5 s, 1546 s, 1466.5 m, 1329 w, 1278 m, 1248 m, 1176 m, 1148 w, 864 w, 765 m, 747 w, 684.5 m cm^{-1}; IR (12K, Ar matrix) 2137 m, 2110 vs, 1662 s, 1611 w, 1580 m, 1567 w, 1549.5 s, 1470 w, 1386 w, 1319 w, 1277 m, 1251.5 s, 1238 w, 1200 w, 1180 m, 1145.5 w, 965 w, 951 w, 906 w, 863 w, 773 m cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 8.65 (s, 1H), 8.27 (dd, J = 7.79, 1.35 Hz, 1H), 7.81 (dd, J = 7.26, 0.8 Hz, 1H), 7.77 (td, J = 6.98, 1.62 Hz, 1H), 7.50 (td, J = 7.66, 1.36 Hz, 1H); ^{13}C NMR ($CDCl_3$, 400 Hz) δ 164.4, 140.1, 138.0, 127.6, 123.5, 121.5, 118.9, 118.7; UV (Ar matrix, 12 K) λ_{max} 244, 361 nm; MS *m*/*z* 171 (M^+; 32), 143 (100), 115 (79), 88 (26), 62 (11).

3-Diazo-3*H*-indole (18). 3-Oximino-3*H*-indole (**18**)[16] (5 g, 0.034 mol) was dissolved in 240 mL of degassed H_2O together with 36 mL of 1 N NaOH (0.0030 mol) at 0 °C under N_2. Concd (12.5%) NH_3 solution (12 mL) was added with stirring. NaOCl (60 mL, 5.25%) was then added dropwise over a 15 min period. Stirring continued for a further 30 min before leaving the mixture in the refrigerator (4 °C) overnight. The solution was then extracted with ether, washed with water, and dried. 3-Diazo-3*H*-indole thus obtained was stable in ether solution at room temperature for several days: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.60 (s, 1H), 7.83−7.87 (d, J = 6.9 Hz, 1H), 7.50−7.55 (d, J = 5.9 Hz, 1H), 7.31 (m, 2H); IR (12K, Ar matrix) 2092 vs, 1462 m, 1428.5 s, 1424.5 vs, 1385.5 w, 1271 s, 1199 m, 1113.5 w, 1063.5 w, 846.5 w, 763 w, 759 w cm^{-1}. This compound decomposed partially during the measurement of the ^{1}H NMR spectrum, and a ^{13}C NMR spectrum or elemental analysis were not obtainable.

3-Carbonyl-3*H*-indole (16). (a) Diazo compound 14 was matrix isolated in Ar by sublimation (10^{-5} mbar) at 50 °C onto

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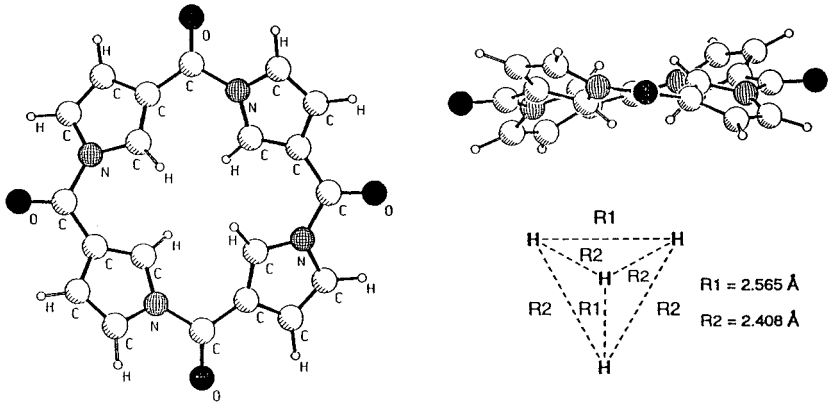

Figure 2. Optimized (B-LYP/6-31G*) geometry of tetramer **34**.

a BaF_2 window with Ar as the carrier gas. On 254 nm photolysis for 13 min, **14** was completely converted to 3-carbonyl-3*H*-indole (**16**): IR (Ar, 12 K) 2139 vs, 1485.5 w, 1473 m, 1448 m, 1331 w, 1284.5 w, 1193.5 w, 1109 w, 1059 m, 868 w, 761 w cm^{-1}; UV (Ar, 12 K) λ_{max} 228, 305.5 nm. Ketene **16** was also matrix isolated by FVT of **14** at 650 °C with Ar as a carrier gas (10^{-3} mbar).

(b) Diazo Compound 18 was sublimed onto a 12 K BaF_2 window *in vacuo* (10^{-5} mbar) at 70 °C with CO as a carrier gas. The resulting matrix of **18** in CO matrix was irradiated at 254 nm for 15 min. Ketene **16** thus formed had IR (CO matrix, 12 K) 1484, 1471.5, 1447, 1062 cm^{-1}.

(c) From Anhydride 28. The anhydride of indole 3-carboxylic acid (**28**)[20] was subjected to FVT at 940 °C, and the products were matrix isolated in Ar on a 12 K BaF_2 window. Ketene **16** was observed by IR spectroscopy (2136 cm^{-1}), together with the rearranged ketene **24** (2127 cm^{-1}).

(d) Tetramer 20 was subjected to FVT at 700 °C with matrix isolation of the product in Ar matrix. By IR spectroscopy, ketene **16** was the only compound observed: IR (Ar matrix, 12 K) 2136 vs, 1487 w, 1473.5 w, 1462 w, 1059 w, 867 w, 766 w, 761 w cm^{-1}.

1,3′-Tetrakis(indolylmethanone) (20). (a) FVT of Diazo Compound 14. A 900 mg (5.26 mmol) sample of **14** was sublimed at 85 °C (10^{-4} mbar) and preparatively thermolyzed at 500 °C. A light yellow compound condensing on the glassware immediately outside the oven was collected and washed with acetone. The insoluble white solid (675 mg, 75 %) was identified spectroscopically as 1,3′-tetrakis(indolylmethanone) (**20**):[14] mp 290−292 °C dec (lit.[14b] mp >300 °C); ^{1}H NMR (DMSO-d_6, 400 MHz, 50 °C) δ 7.50−7.53 (t, H5, J = 7 Hz), 7.53−7.57 (t, H6, J = 6 Hz), 8.16−8.18 (d, H4, J = 8 Hz), 8.38−8.48 (d, H7 J = 7.3 Hz), 9.42 (s, H2); ^{13}C NMR (DMSO-d_6, 400 MHz, 50 °C) δ 112.4 (C3), 115.3 (C7), 120.7 (C4), 124.8 (C5), 125.7 (C6), 128.0 (C3a), 135.6 (C7a), 137.4 (C2), 162.9 (C8).[14] The definitive NMR signal assignments were based on two-dimensional ^{13}C−^{1}H correlations (COLOC) with both short- and long-range couplings: IR (KBr) 1689 vs, 1539.5 m, 1479.5 w, 1450 vs, 1379.5 m, 1326.5 w, 1263 w, 1200 vs, 1151.5 s, 1019 m, 831.5 s, 748.5 s cm^{-1}; MS m/z 572 (M^+, 27), 429 (10), 286 (55), 143 (100), 115 (35), 89 (8).

(b) FVP of Anhydride 27. A 50 mg sample of **27**, obtained in quantitative yield by stirring indole-3-carboxylic acid in acetic anhydride solution, was sublimed at 100−125 °C and preparatively thermolyzed at 750 °C. The compound isolated from the cold finger was examed by GC−MS and NMR and identified as indole (85%). Acetone washing of the residual material in the sublimation tube afforded 4 mg (∼10%) of insoluble white solid, which was identified as tetramer **20** by ^{1}H NMR spectroscopy and comparison with the above sample.

(c) FVP of Anhydride 28. A 100 mg sample of **28** was sublimed at ca. 120 °C and subjected to preparative FVT at 700 °C. Indole (30 mg; 77%) was isolated from the cold finger, and 41 mg (87%) of tetramer **20** was obtained as a white powder from the residue in the sublimation tube after washing with acetone.

(d) Warmup of Ketene 16. Ketene **16** was matrix isolated in Ar by photolysis of **14** as described above. The deposition window was slowly warmed to room temperature and any reaction was monitored by IR spectroscopy. Ketene **16** disappeared at 58 K, and after warming to rt, tetramer **20** was identified by IR and ^{1}H NMR (DMSO-d_6) of the material remaining on the window. In these experiments, the formation of tetramer **20** was detected already below 70 K (Figure 5 in the supporting information).

3-Diazo-4-oxopyridine (31). This compound was synthesized by a modification of the literature procedure.[30] The diazonium chloride of 3-diazo-4-oxopyridine (**30**) was obtained by diazotization at 0 °C of 3-amino-4-oxopyridine (**29**) in EtOH solution containing dry HCl with isoamyl nitrite. **30** was dried under vacuum overnight. A 500 mg sample of **30** was mixed with excess Na_2CO_3 powder in dry ether solution. The suspension was stirred in the dark for 3 h before the solid was filtered off. The ether solution of 3-diazo-4-oxopyridine (**31**) thus formed was stable, but the compound slowly decomposed in the solid state: IR (Ar, 12 K) 2129.5 vs, 1657 vs, 1574.5 m, 1492.5 s, 1470.5 w, 1381 w, 1234.5 m, 1228 m, 1188.5 m, 1134.5 m, 1118 w, 981 w, 865.5 m, 832 w, 827 w cm^{-1}; IR (N_2, 12 K) 2144 vs, 1651 vs, 1570 w, 1489 s, 1474 w, 1383 w, 1237 w, 1228 m, 1188 m, 1135 m, 1120 w, 984 w, 867 m, 830 w, 827 w cm^{-1}.

3-Carbonyl-3*H*-pyrrole (33). (a) Diazo compound 31 was matrix isolated in Ar or N_2 by sublimation (10^{-5} mbar) at 60 K onto a BaF_2 window with Ar or N_2 as a carrier gas. On 254 nm photolysis for 5 min, **31** was completely converted to 3-carbonyl-3*H*-pyrrole (**33**): IR (Ar, 12 K) 2145.5 vs, 1504.5 w, 1460 w, 1444.5 m, 1397 w, 1292.5 m, 1258 w, 1200.5 w, 1097.5 w, 937 m, 825 w cm^{-1}; IR (N_2, 12 K) 2150 vs, 1501.5 w, 1445.5 m, 1393.5 w, 1293 m, 1258.5 w, 1202w, 1097 w, 1029 w, 938 m, 862 w cm^{-1}.

(b) From Ester 37. This compound[21] was subjected to FVT at 1100 °C and the product Ar matrix isolated on a 12 K BaF_2 window. The isolated products were identified by IR spectroscopy as ketene **33** (2145.5 cm^{-1}), CO (2139, 2149 cm^{-1}), and MeOH (1034, 3732 cm^{-1}).

1,3′-Tetrakis(pyrrolylmethanone) (34). (a) FVT of Ester 37. A sample of **37** (150 mg; 0.98 mmol) was sublimed at 120−140 °C and pyrolyzed at 1000 °C, using a U-tube as cold trap. The eliminated MeOH was trapped in the U-tube cooled with liq. N_2. A light brown compound depositing immediately outside the oven was collected and washed with acetone, affording 94 mg (90%) of 1,3′-tetrakis(pyrrolylmethanone) (**34**). **34** can be further purified by sublimation at 260 °C (10^{-4} mbar): mp 200−202 °C dec; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.78 (dd, J = 1.9, 1.9 Hz, 1H), 7.66 (dd, J = 3.49, 1.91 Hz, 1H), 6.92 (dd, J = 3.71, 1.59 Hz, 1H); ^{13}C NMR (DMSO-d_6, 400 MHz) δ 161.9, 131.5, 121.35, 118.4, 113.1; IR (KBr) 1711 vs, 1544 s, 1493 s, 1396 m, 1357.5 s, 1316 s, 1158 vs, 837 m, 752 m cm^{-1}; MS m/z 372 (M^+, 10.1), 279 (4.9), 186 (16.2), 94 (100), 93 (25.6), 73 (14.3), 66 (19.1), 44 (12.1), 39

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(25.4), 38 (17.2) cm^{-1}; HRMS calcd for $^{12}C_{20}H_{12}N_4O_4$ 372.0857, found 372.0858.

(b) FVT of Diazo Compound 31. Diazonium salt **30** (100 mg) was neutralized to **31** with Na_2CO_3 in ether solution as described above. The ether was evaporated in the FVT sample tube, and **31** was subjected to FVT at 550 °C. A small amount of brown material was isolated from the tube immediately outside the pyrolysis oven. This compound was identified as tetramer **34** by MS and ^1H NMR (ca. 1% yield).

10-Oxo-10*H*-pyrano[3,2-*c*:5,6-*c*′]dipyridine (39). Ester **37** (50 mg; 0.33 mmol) was subjected to preparative FVT at 710 °C, trapping the products in a U-tube at liquid N_2 temperature. A powder (8 mg) was isolated from the glassware immediately outside the oven, washed with pentane, and identified as 4-hydroxynicotinic acid. The compound isolated from the U-tube was subjected to SiO_2 column chromatography, eluting with acetone, which afforded 23 mg (61%) of 10-oxo-10*H*-pyrano[3,2-*c*:5,6-*c*′]dipyridine (**39**): mp 200−201 °C; ^1H NMR (acetone-d_6, 400 MHz) δ 9.35 (s, 1H), 8.89 (d, J = 5.82 Hz, 1H), 7.62 (d, J = 5.82 Hz, 1H); ^{13}C NMR (acetone-d_6, 400 MHz) δ 162.05, 156.03, 155.00, 150.26, 138.81, 113.75; IR (KBr) 1673 vs, 1612 s, 1599 vs, 1468 m, 1344 m, 1170.5 m, 930 m, 795 m cm^{-1}; MS m/z 198 (M^+, 100), 170 (30), 169 (20), 143 (22), 122 (15), 115 (25), 53 (25), 50 (30); HRMS calcd for $^{12}C_{11}H_6N_2O_2$ 198.0429, found 198.0427. Anal. Calcd for $C_{11}H_6N_2O_2$: C, 66.67; H, 3.05; N, 14.14. Found: C, 66.84; H, 3.065; N, 14.07.[24]

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Supporting Information Available: Copies of ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra of **34**. Figures 3−7 showing observed matrix IR spectra of **16**, **14**, **18**, **20**, **31**, and **33**, calculated IR spectrum (BLYP/6-31G*) of **16**, calculated IR (MP2/6-31G*), and optimized geometries (BLYP/6-31G*) of **16** and **33** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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