

Direct Observation of 1-Azafulven-6-one and Annulated Derivatives

Gerhard Gross and Curt Wentrup*

Fachbereich Chemie, University of Marburg, Lahnberge, D-3550 Marburg, West Germany

1-Azafulven-6-one, 2-carbonyl-2*H*-indole, 5-carbonyl-5*H*-furo[3,2-*b*]pyrrole, and thieno- and pyrrolo-analogues are isolated at low temperatures following thermal elimination of water or methanol from the corresponding carboxylic acids or esters; the azafulvenones dimerise at -100 to -40 °C to diketopiperazine derivatives.

1-Azafulven-6-ones (2-carbonyl-2*H*-pyrroles) have been postulated as reaction intermediates in the Wolff rearrangement of diazopyridones¹ and in the base-induced elimination reactions of pyrrole-2-carboxylic acid chlorides,^{2a} but no direct evidence for their existence has ever been obtained. We now report the preparation and direct spectroscopic observation of several such compounds.

Indole-2-carboxylic acid (**1**) was subjected to flash vacuum pyrolysis in an apparatus allowing the direct, low-temperature i.r. spectroscopic observation of the products. At pyrolysis temperatures between 650 and 850 °C a strong keten absorption appeared at 2106 cm^{-1} in the i.r. spectrum of the cold (-196 °C) pyrolysate. On subsequent warming the keten absorption was observable up to ca. -40 °C; at this temperature the i.r. spectrum changed into that of a mixture of the starting material (**1**) and the dimer (**4**) (*vide infra*).

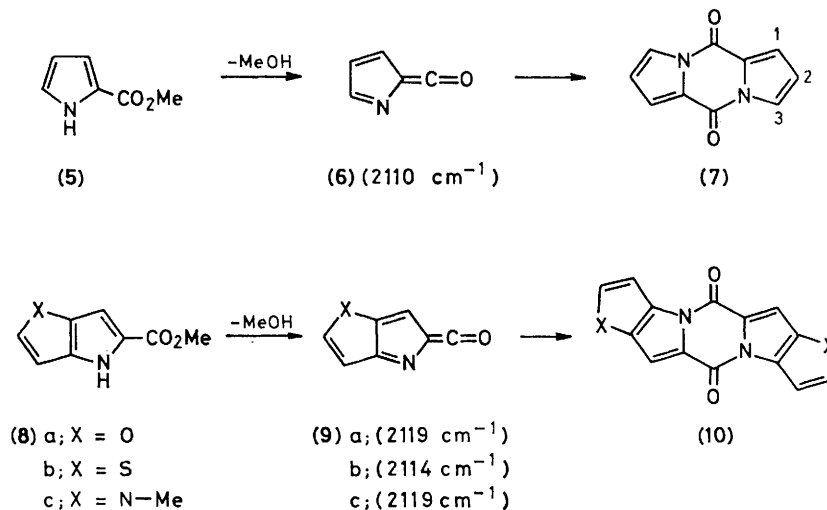
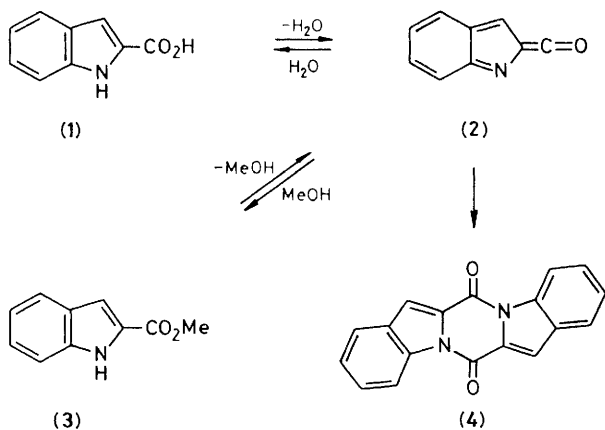
The same keten (**2**) was also formed on pyrolysis of the methyl ester (**3**) at 850 °C; in this case, however, the keten absorption at 2106 cm^{-1} disappeared on warming to -100

to -90 °C with simultaneous re-formation of the starting material (**3**). Similar results were obtained preparatively using an apparatus where the products were condensed on a cold finger (-196 °C). When the keten formed by pyrolysis of the acid (**1**) was condensed in a methanol matrix on the cold finger, the methyl ester (**3**) could be isolated after warm-up to room temperature. If the cold finger was replaced by a cold trap (U-tube), however, subsequent isolation at room temperature gave mainly the keten dimer (**4**) [90% from (**3**); m.p. $325\text{--}327$ °C], identified by spectroscopy [¹H n.m.r. [(CD₃)₂SO, 70 °C, 400 MHz] δ 7.45 (t, 1 H, *J* ca. 7.5 Hz), 7.62 (t, 1 H, *J* ca. 7.5 Hz), 7.82 (s, 1 H), 7.88 (d, 1 H, *J* ca. 8 Hz), and 8.49 (d, 1 H, *J* ca. 8 Hz); *m/e* 286.0749, calc. for C₁₈H₁₀N₂O₂ 286.0742] and comparison with literature data.²

These observations are explained as follows. Since water remains solid until 0 °C, but methanol only until -98 °C, diffusion, and therefore reaction, of the keten (**2**) starts at a lower temperature when generated from (**3**) (methanol matrix) than from (**1**) (water matrix). A higher reactivity of the keten towards methanol would have the same effect. When the pyrolysis products are trapped in a U-tube, the less volatile keten (**2**) condenses at the top of the trap where it dimerises, whereas the more volatile water or methanol is drawn into the trap.

Analogous pyrolyses of pyrrole-2-carboxylic acid or its methyl ester (**5**) at 850 °C produced the keten (**6**) (2110 cm^{-1} , -196 °C) which on warming to -100 to -90 °C dimerised to pyrocoll^{2a,3} (**7**) [90%; m.p. $272\text{--}273$ °C (lit.,^{3b} m.p. $272\text{--}273$ °C); ¹H n.m.r. (CD₃OD, 400 MHz) δ 6.554 (C-2-H), 7.381 (C-1-H), and 7.776 (C-3-H), *J*_{1,2} 3.685 Hz, *J*_{1,3} 1.50 Hz, and *J*_{2,3} 3.085 Hz; *m/e* 186.0435, calc. for C₁₀H₆N₂O₂ 186.0429], identical with a sample prepared according to Ref. 3a.

At 850 °C the furo-, thieno-, and pyrrolo-[3,2-*b*]pyrrole carboxylic acid esters (**8a–c**) similarly gave the ketens (**9a–c**), which disappeared at -100 to -80 °C. The dimers



(10a) and (10b) were isolated from preparative pyrolyses [(10a): m.p. 265 °C; ¹H n.m.r. (CDCl₃, 400 MHz) δ 6.980 (dd, 1 H, *J* 0.7 and 2.1 Hz), 7.268 (d, 1 H, *J* 0.7 Hz), and 7.684 (d, 1 H, *J* 2.1 Hz); *m/e* 266.0332, calc. for C₁₄H₆N₂O₄ 266.03276; (10b): subl. 255 °C without melting; ¹H n.m.r. (CDCl₃, 400 MHz) δ 7.61 (d, 1 H, *J* ca. 5 Hz), 7.62 (s, 1 H), and 7.68 (d, 1 H, *J* ca. 5 Hz); *m/e* 297.9874, calc. for C₁₄H₆N₂O₂S₂ 297.98707].

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Received, 22nd December 1981; Com. 1456

References

- 1 O. Süss and K. Möller, *Liebigs Ann. Chem.*, 1955, **593**, 91.
- 2 (a) R. J. Boatman and H. W. Whitlock, *J. Org. Chem.*, 1976, **41**, 3050; (b) G. Ciamician and C. Zatti, *Ber. Dtsch. Chem. Ges.*, 1888, **21**, 1929; (c) D. L. Coffen, D. A. Katonak, N. R. Nelson, and F. D. Sancilio, *J. Org. Chem.*, 1977, **42**, 948.
- 3 (a) G. L. Ciamician and P. Silber, *Ber. Dtsch. Chem. Ges.*, 1884, **17**, 103; (b) A. W. Johnson and W. R. Overend, *J. Chem. Soc., Perkin Trans. 1*, 1972, 2681.