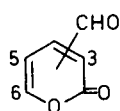


2-Pyronecarboxaldehydes

Joseph T. Kurek and George Vogel (1)

Department of Chemistry, Boston College

Because of our interest in new synthetic applications of 2-pyrones (2,3), we have prepared and characterized three of the four possible unsubstituted 2-pyronecarboxaldehydes.



Repeated attempts to obtain the aldehydes by reduction of the corresponding acid chlorides with lithium tri-*t*-butoxyaluminum hydride (5) resulted only in tarry mixtures, probably involving opening of the pyrone ring (2). However, all three aldehydes were obtained smoothly by Rosenmund reduction of the acid chlorides.

While the 3-carboxaldehyde rapidly decomposed spontaneously in air, the 5- and 6-isomers proved to be relatively stable crystalline substances, though sensitive to alkali, particularly the 5-isomer.

The infrared spectra of both of the stable aldehydes show two carbonyl bands: at 1765 and 1702 cm^{-1} in the 5-isomer, and at 1745 and 1708 cm^{-1} in the 6-isomer. Since 2-pyrones quite generally show at least one carbonyl band between 1730 and 1704 cm^{-1} (6), the lower-frequency bands may be assumed to be due at least in part to the ring carbonyl. However, the higher-frequency bands may equally well be due at least in part to the ring carbonyl also, since most 2-pyrones and other α,β -unsaturated lactones show a second carbonyl band in this region (6,7). It is not possible at present to assign the aldehyde carbonyl bands with certainty. Although the values of 1702 and 1708 cm^{-1} are reasonable for α,β -unsaturated aldehydes (1710-1685 cm^{-1}), the much greater relative intensities and widths of the higher-frequency bands suggest that the aldehyde carbonyl stretching may in fact be located in these higher bands, especially since in chloroform solution the lower band in 2-pyrones and other α,β -unsaturated lactones is normally the more intense of the two (7). Such unusually high aldehyde carbonyl frequencies could be the result of a tightening of the bond by the considerable positive charge carried by the partially aromatic pyrone ring.

EXPERIMENTAL (8)

General Procedure.

In a 200-ml. round-bottomed flask equipped with a thermometer, a reflux condenser, and a gas inlet tube were placed 5 g. (0.032 mole) of the acid chloride, 25 ml. of dry xylene, and 0.5 g. of a 5% palladium-barium sulfate catalyst (9). The mixture was stirred magnetically at 110° while hydrogen was passed through slowly. When evolution of hydrogen chloride was practically complete (5-7 hours), the hot solution was filtered from the catalyst, 5 ml. of hexane was added, and after allowing the mixture to stand overnight in a refrigerator the crystals were filtered off, pressed dry, and sublimed in a vacuum at 80-90° (2-3 mm.).

2-Pyrone-6-carboxaldehyde.

Yield 1.4 g. (35%), m.p. 124-125°; infrared: 1745, 1708, 1625 cm^{-1} ; ultraviolet: λ max 298 $\text{m}\mu$ (ϵ , max 13,100); n.m.r. (δ): H₃, 6.65(dd); H₄, 7.80(dd); H₅, 7.24(dd); CHO, 9.60(s). $J_{34} = 9.5$; $J_{45} = 6.7$; $J_{35} = 1.2$ Hz.

Anal. Calcd. for C₆H₄O₃: C, 58.07; H, 3.25. Found: C, 58.0; H, 3.3.

Semicarbazone, m.p. 227-234° dec. (from aqueous ethanol).

Anal. Calcd. for C₇H₇N₃O₃: C, 46.43; H, 3.90; N, 23.21. Found: C, 46.2; H, 3.9; N, 23.0.

2,4-Dinitrophenylhydrazone, m.p. 279-284° (from ethyl acetate).

2-Pyrone-5-carboxaldehyde.

Yield 1.7 g. (44%), m.p. 93-94° (from ethanol); infrared: 1765, 1702, 1642, 1567 cm^{-1} ; ultraviolet: λ max 260 $\text{m}\mu$ (ϵ , max 11,000); n.m.r. (δ): H₃, 6.45(dd); H₄, 7.85(dd); H₆, 8.61(dd); CHO, 9.79(s). $J_{34} = 9.8$; $J_{46} = 2.6$; $J_{36} = 1.0$ Hz.

Anal. Calcd. for C₆H₄O₃: C, 58.07; H, 3.25. Found: C, 58.1; H, 3.2.

2,4-Dinitrophenylhydrazone, m.p. 273-275° (from ethyl acetate).

Anal. Calcd. for C₁₂H₈N₄O₆: C, 47.38; H, 2.65; N, 18.41. Found: C, 47.43; H, 2.85; N, 18.36.

2-Pyrone-3-carboxaldehyde.

Yield 1.0 g. (25%). White solid turning into a brown gummy material after a few minutes in air. M.p. 88-89° (under nitrogen in sealed capillary, liquid bath).

2,4-Dinitrophenylhydrazone, m.p. 270-271° dec. (from ethyl acetate).

Anal. Calcd. for C₁₂H₈N₄O₆: C, 47.38; H, 2.65; N, 18.41. Found: C, 47.33; H, 2.54; N, 18.03.

Acknowledgment.

This work was supported in part by grants provided by the Public Health Service and the National Science Foundation. We are also grateful to Dr. Gerald J. Kent for directions for the synthesis

of 2-pyrone-3-carboxylic acid and its chloride.

REFERENCES

- (1) To whom enquires should be addressed.
- (2) G. Vogel, *Chem. Ind. (London)*, 268 (1962).
- (3) G. Vogel, *J. Org. Chem.*, 30, 203 (1965).
- (4) C. A. Salemink, *Rec. Trav. Chim.*, 78, 364 (1959), reported the preparation in very low yield of 4,6-dimethyl-2-pyrone-5-carboxaldehyde.
- (5) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, 80, 5377 (1958).
- (6) K. Yamada, *Bull. Chem. Soc. Japan*, 35, 1329 (1962).
- (7) R. N. Jones, C. L. Angell, T. Ito, and R. J. D. Smith, *Can.*

J. Chem., 37, 2007 (1959).

(8) Melting points were determined with a Fisher-Johns apparatus calibrated with standard substances. Elemental analyses were by Dr. Carol K. Fitz and M-H-W Laboratories. Infrared spectra were recorded in chloroform solution using a Perkin-Elmer 421 spectrophotometer, ultraviolet spectra in 95% ethanol on a Perkin-Elmer 202 spectrophotometer, and n.m.r. spectra by Mr. Gerald M. Saluti with a Varian HA-60 instrument, in hexadeuterioacetone solution (internal TMS).

(9) R. Mozingo, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p. 685.

Received December 18, 1967

Chestnut Hill, Mass. 02167