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The Preparation of Pyrazinealdehyde by Ozonolysis of Vinylpyrazine

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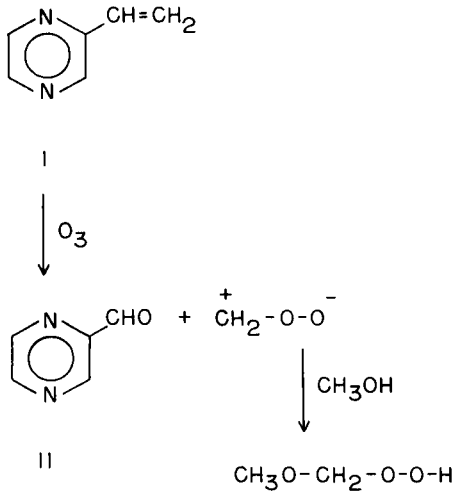
The recent report by Rutner and Spoerri (2) describing the synthesis of pyrazinealdehyde (II) by the lithium aluminum hydride reduction of methyl pyrazinoate prompts us to report our synthesis of this aldehyde by ozonolysis of vinylpyrazine (I) (3).

Treatment of a methanolic solution of vinylpyrazine at -30° with ozone following a procedure outlined by Calligham and Wilt for the ozonolysis of vinylpyridines (4), afforded a 73% yield of a material which proved to be pyrazinealdehyde (II), as determined by mixture melting point and comparison of infrared spectra (5). As the yield obtained by this procedure more than favorably compares with the yield obtained by Rutner and Spoerri (2), this procedure affords an alternate method of preparing this valuable intermediate.

Although no study was made of the mechanism of the reaction it appears likely that the ozonolysis involves the cleavage of the vinyl compound producing pyrazinealdehyde (II) and an alkyl zwitterion stabilized by methanol, a hydroxylic solvent (4, 6).



EXPERIMENTAL (7)

2-Vinylpyrazine (I).

This compound was prepared by a procedure described by Kamal, Neubert and Levine (3), in 65% yield, b.p. 62-64° (21 mm.), n_D^{26} 1.5535.

Pyrazinealdehyde (II).

A solution of 10.6 g. (0.1 mole) of vinylpyrazine (I) in 125 ml. of methanol in a Dreschel bottle was placed in an ethanol-dry ice bath with the temperature maintained between -40 and -60°. A second Dreschel bottle filled with a potassium iodide-starch solution was connected to the exhaust of the reaction vessel, and served as an indicator solution. Ozonized oxygen was then passed through the system at a flow rate of 0.035 standard cubic feet per minute (0.07 moles of ozone per hour). Upon completion of the ozonolysis, as evidenced by the indicator solution (approximately ninety minutes), the reaction mixture was cooled to -60° and a solution of 12.6 g. (0.1 mole) of sodium sulfite in 50 ml. of water was cautiously added with constant stirring so as to prevent the reduction from becoming too exothermic. The temperature was then allowed to rise to room temperature and the methanol evaporated under reduced pressure. This procedure yielded a yellow liquid to which was added 100 ml. of a saturated aqueous solution of sodium chloride. The resulting solution was then extracted with eight 50 ml. portions of chloroform. The combined chloroform extracts were combined, dried over magnesium sulfate, and filtered through decolorizing carbon. After evaporation of the chloroform under reduced pressure, the remaining yellowish liquid was distilled, using Ansul ether 181 as a chaser solvent. This procedure yielded 6.8 g. (73.5%) of pyrazinealdehyde, b.p. 57-59° (6 mm.), as a light yellow liquid. Redistillation gave 4.7 g. of pure pyrazinealdehyde, b.p. 57-58° (6 mm.), m.p. 31-33°, [lit. (2) m.p. 31-33°].

REFERENCES

(1) To whom all inquiries should be sent.
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(3) M. Kamal, H. Neubert and R. Levine, *ibid.*, 27, 1365 (1962).
(4) R. H. Callighan and M. H. Wilt, *ibid.*, 26, 4912 (1961).
(5) The authors are indebted to Prof. P. E. Spoerri for kindly supplying us with a sample of this material.
(6) R. Creigee, *Record Chem. Progr.*, 18, 111 (1957).
(7) All melting points are uncorrected and were taken on a Mel-Temp apparatus. Infrared spectra were obtained using a Perkin-Elmer Infracord Spectrophotometer. Ozonolyses were carried out using a Welsbach, Model T-23 laboratory ozonolysis unit.

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