Synthesis of 1-Methyl-3-pyrrolin-2-one

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The synthesis of 1-methyl-3-pyrrolin-2-one from the oxidative-elimination of 1-methyl-3-phenylselenenyl-2-pyrrolidinone and from the pyrolysis of 3-phenylsulfinyl-2-pyrrolidinone is reported.

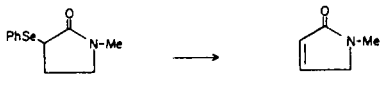
J. Heterocyclic Chem., 14, 681 (1977).

The preparation of 3-pyrrolin-2-ones from alkaline (2) and acidic (3) hydrogen peroxide oxidations, autoxidation (4), and photooxidation (5) of pyrrole derivatives has been reported. These synthetic approaches to 3-pyrrolin-2-ones are generally hampered by low yields and numerous side products. The photooxidations are also of limited value, since in these processes an alkoxy or hydroxy group is introduced into the C-5 position of the pyrrolinone nucleus. The Scheffold-Dubs cyclization procedure (6) can also be utilized in the synthesis of 3-pyrrolin-2-ones; however, in this process a C-5 hydroxy group is also introduced in the pyrrolinone nucleus. Other methods of preparing 3-pyrrolin-2-ones involve the reaction of ethyl azidoformate (7) with furan and the reduction of cyclic imides (8) followed by acid-catalyzed elimination (9).

Recently we reported (10) that α-unsubstituted lactams can be monosulfenylated and monoselenenylated. The studies reported herein show that an α-phenylselenenyl or an α-phenylsulfenyl moiety can be used to introduce a $\Delta^{3,4}$-double bond in an intact 2-pyrrolidinone nucleus under relatively mild reaction conditions as depicted below.

Reaction of the phenylselenenyl lactam (**1**) (10) (Scheme I) with aqueous hydrogen peroxide (11) in methanol at 0° for 2 hours and subsequent distillation afforded 1-methyl-3-pyrrolin-2-one (**2**) (2a,4,9) in 57% yield. The nmr spectrum of (**2**) was identical to that of authentic (**2**) (12).

Scheme I



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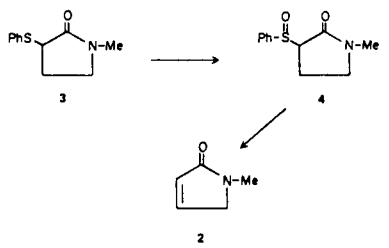
A second route to (**2**) was also realized by utilizing the phenylsulfenyl lactam (**3**) (10) (Scheme II). Reaction of (**3**) with *m*-chloroperbenzoic acid in methylene chloride at 0° for 24 hours yielded the sulfoxide (**4**) in 88% yield. Pyrolysis (13) of the sulfoxide (**4**) in toluene in the presence of solid sodium bicarbonate at 110° for 1.25 hours and subsequent chromatography on silica gel G and distillation afforded 1-methyl-3-pyrrolin-2-one (**2**) in 46% yield.

Scheme II



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EXPERIMENTAL

Nmr spectra were recorded on a Jeolco Model c60HL spectrometer at 60 MHz with TMS as an internal standard. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrometer.

1-Methyl-3-pyrrolin-2-one (**2**) from 1-Methyl-3-phenylselenenyl-2-pyrrolidinone.

1-Methyl-3-phenylselenenyl-2-pyrrolidinone (**1**) (10) (0.30 g., 0.00118 mole) dissolved in 5 ml. of methanol was cooled to 0°. A 30% hydrogen peroxide solution (0.803 g., 0.0071 mole) and 0.85 ml. of water was added and the resulting solution was stirred at 0° for 2 hours.

The reaction was poured into a 10% sodium bicarbonate solution (100 ml.) and extracted with three 100 ml. portions of methylene chloride. The combined methylene chloride extracts were washed with 100 ml. of water. The methylene chloride solution was dried over anhydrous magnesium sulfate, filtered and concentrated on a rotary evaporator, affording a yellow oil. Kugelrohr distillation of the oil yielded (65 mg., 57%) of 1-methyl-3-pyrrolin-2-one (**2**) (2a,4,9,12), b.p. 100° (0.15 mm); nmr (deuteriochloroform): δ 7.07-7.30 (m, 1H), 6.07-6.35 (m, 1H), 4.06 (m, 2H) and 3.06 (s, 3H); ir (neat): 1700 and 1675 (doublet) and 1590 cm^{-1}.

3-Phenylsulfinyl-2-pyrrolidinone (**4**).

1-Methyl-3-phenylsulfenyl-2-pyrrolidinone (**3**) (10) (5.0 g., 0.0242 mole) was dissolved in 75 ml. of methylene chloride and cooled to 0°. *m*-Chloroperbenzoic acid (4.4 g., 0.0253 mole) was added and the reaction was stirred at 0° for 24 hours.

The reaction was poured into a sodium bicarbonate solution (2.9 g., 0.035 mole) and 125 ml. of water and stirred for 0.5 hour. The heterogeneous mixture was extracted with three 100 ml. portions of chloroform. The combined chloroform extracts were dried over anhydrous magnesium sulfate, filtered and concentrated on a rotary evaporator, affording 5.4 g. of an oil. The oil was chromatographed on silica gel G and elution with a methanol-ether solution yielded (4.8 g., 89%) of a white solid, 1-methyl-3-phenylsulfinyl-2-pyrrolidinone (**4**); nmr (deuteriochloroform): δ 7.77 (s, 5H), 2.99 and 2.62 (singlets, *N*-methyls, 3H) and

1.50-4.45 (m, 5H); ir (chloroform): 1695 and 1046 cm^{-1}.

Anal. Calcd. for $C_{11}H_{13}NO_2S$: C, 59.18; H, 5.87; N, 6.27. Found: C, 59.05; H, 5.84; N, 6.12.

1-Methyl-3-pyrrolin-2-one (**2**) from 1-Methyl-3-phenylsulfinyl-2-pyrrolidinone.

1-Methyl-3-phenylsulfinyl-2-pyrrolidinone (4) (0.50 g., 0.00224 mole) was dissolved in 8 ml. of toluene. Sodium bicarbonate (0.23 g., 0.0027 mole) was added and the resulting mixture was heated with an oil bath at 110° for 1.25 hours.

The reaction was cooled to room temperature and filtered through a short column of celite 545. The celite was washed with methylene chloride and the resulting filtrate was concentrated on a rotary evaporator, affording a brown oil. The oil was chromatographed immediately on silica gel G and elution with ether afforded a light yellow oil. Kugelrohr distillation of the oil yielded (100 mg., 46%) of 1-methyl-3-pyrrolin-2-one (**2**). The nmr and ir of (**2**) derived from the sulfoxide were identical when compared to those spectra obtained from the oxidative-elimination of (**1**).

REFERENCES AND NOTES

(1) Undergraduate research participant.

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(12) We would like to thank Prof. L. Chierici for kindly providing us with the nmr spectrum of the pyrrolinone (**2**).

(13) For analogous pyrolysis reactions see: B. M. Trost and A. J. Bridges, *J. Org. Chem.*, **40**, 2014 (1975) and references within.