

SHORT
COMMUNICATIONS

Selective Thermal Oxidation of 2,3-Dimethyl-5-(phenyldiazenyl)-1-vinyl-1*H*-pyrrole to the Corresponding Pyrrole-2-carbaldehyde: Stabilization of the Pyrrole Ring by Phenylazo Substituent

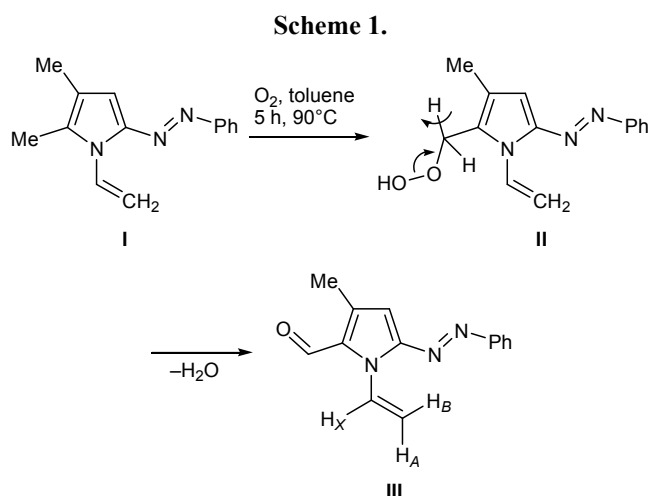
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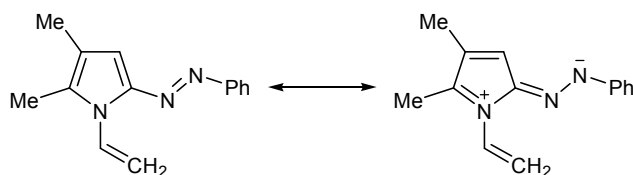
It is known that pyrroles are readily oxidized on exposure to atmospheric oxygen with decomposition of the pyrrole ring [1–3]. We have revealed unusual selective oxidation of methyl group in the pyrrole ring to aldehyde with conservation of the pyrrole ring and such highly reactive substituents as vinyl and azo groups. Heating of 2,3-dimethyl-5-phenyldiazenyl-1-vinyl-1*H*-pyrrole (**I**) in toluene for 5 h at 90°C on exposure to air resulted in the formation of 3-methyl-5-phenyldiazenyl-1-vinyl-1*H*-pyrrole-2-carbaldehyde (**III**) (Scheme 1). Presumably, the oxidation process involves intermediate formation of hydroperoxide **II** which decomposes into aldehyde **III** and water.



It was surprising that the phenylazo group and especially vinyl group in the pyrrole ring remained

unchanged; it is known that the exocyclic double bond in *N*-vinylpyrroles is characterized by enhanced reactivity [4, 5]. Obviously, this is the result of profound electron density transfer from the pyrrole ring to the azo group, which was noted previously [6] (Scheme 2). The sensitivity of the pyrrole ring and double bond in the *N*-vinyl group to electron-deficient reagents (oxidants and acids) decreases, and the mobility (CH acidity) of hydrogen atoms in the methyl group increases, i.e., the methyl group becomes more readily oxidizable.

Scheme 2.



3-Methyl-5-phenyldiazenyl-1-vinyl-1*H*-pyrrole-2-carbaldehyde (III**).** A mixture of 0.1 g (0.47 mmol) of pyrrole **I** and 3.5 ml of toluene was heated for 5 h at 90°C. The solvent was removed under reduced pressure to leave 98 mg of a brown tarry material which was subjected to column chromatography on basic aluminum oxide (pH 8.25) using hexane–diethyl ether (3:1) as eluent to isolate 14.4 mg of compound **III** and 39 mg of initial pyrrole **I**. Yield 23%, orange crystals, mp 90–92°C. IR spectrum, ν , cm^{-1} : 3118, 3064, 2953, 2924, 2852, 1704, 1659, 1651, 1598, 1525, 1495, 1481, 1476, 1441, 1428, 1398, 1372, 1335, 1304,

1199, 1154, 1123, 1103, 1072, 1020, 999, 945, 919, 898, 821, 769, 688, 583, 554, 515, 495. ^1H NMR spectrum, δ , ppm: 2.43 s (3H, Me), 5.40 d (1H, H_A , $^3J_{AX} = 8.9$ Hz), 5.48 d (1H, H_B , $^3J_{BX} = 15.7$ Hz), 6.57 s (1H, 3-H), 7.48 m (3H, *p*-H, *m*-H), 7.74 d.d (1H, H_X , $^3J_{BX} = 15.7$, $^3J_{AX} = 8.9$ Hz), 7.84 m (2H, *o*-H), 9.97 s (1H, CHO). ^{13}C NMR spectrum, δ_C , ppm: 12.2 (Me), 102.4 (C^3), 113.5 (C^b), 123.3 (C^o), 129.5 (C^5), 129.8 (C^m), 129.9 (C^a), 131.9 (C^p), 134.6 (C^4), 149.5 (C^2), 153.8 (C^i), 180.4 (C=O). Found, %: C 70.12; H 5.19; N 17.38. $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}$. Calculated, %: C 70.28; H 5.48; N 17.56.

The IR spectrum was recorded on a Bruker IFS 25 instrument. The ^1H and ^{13}C NMR spectra were measured on a Bruker DPX-400 spectrometer from solutions in CDCl_3 using hexamethyldisiloxane as internal reference.

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