

The Dye-Sensitized Photooxygenation of *N*-Phenylpyrrole

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Although phenyl substituted pyrroles have been among the most completely studied in their dye-sensitized photooxidation reactions (1-3) there has been only one report on the photooxidation of *N*-phenylpyrrole (**1**) (4). Whereas the photooxidations of polyphenylpyrroles appear to give products rather unlike the usual products from alkylpyrroles (5,6), Franck and Auerbach's (4) reported product from *N*-phenylpyrrole could be predicted on the basis of De Mayo and Reid's (7) study of *N*-methylpyrrole. We have explored the photooxygenation of *N*-phenylpyrrole more fully and report here on the new products and reaction mechanisms.

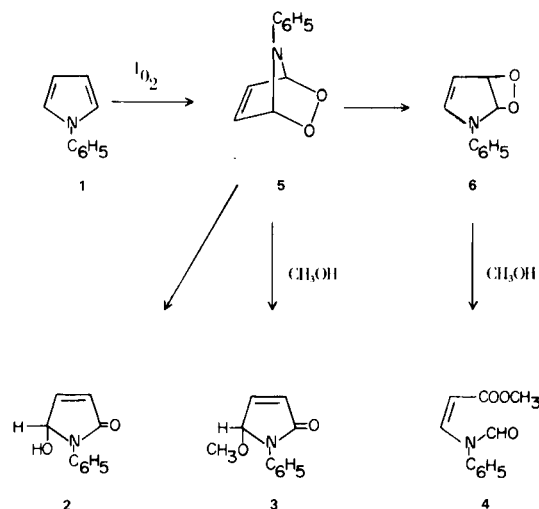
When an oxygenated, dilute methanolic solution of *N*-phenylpyrrole (**1**) containing a small amount of rose bengal (singlet oxygen, 1O_2 , sensitizer) is photolyzed, three major products (**2-4**) are obtained. The hydroxylactam compound (**2**) was previously isolated by Franck and Auerbach (4) in 14% yield from photo-oxygenation in a pyridine-water-tetrahydrofuran solvent mixture or in about 7% yield in a chemically (H_2O_2-OCl) generated 1O_2 reaction. Our yield of **2** from photooxidation of **1** in methanol solvent is comparable to that obtained by Franck and Auerbach using aqueous solvent, and we believe that the majority of our product **2** arises *via* intramolecular rearrangement rather than reaction with water [Scheme 1], *e.g.*, **2** arising in non-aqueous solvents is derived by internal reorganization of an *endo*-peroxide intermediate (**5**). This speculation is reinforced by the observation that *N*-methylpyrrole in chloroform or benzene saturated with ^{18}O -water gives a hydroxylactam with no ^{18}O incorporation (8).

Evidence for *endo*-peroxide **5** and its subsequent reactions is provided by photooxygenation of an acetone- d_6 or Freon 11 solution of **1** at -78° and observation of the complete conversion of **1** to a new substance (**5**) which is observed in the nmr. It also is extremely interesting that **5** formed in acetone- d_6 or Freon-11 solvent at -78° upon warming to -20° slowly liberates O_2 and returns nearly quantitatively to **1** in the absence of a nucleophile. The oxygen liberated was shown to be 1O_2 in a trapping experiment by adding 2,3-dimethyl-2-butene to a solution

of **5** at -78° or -20° and observing the formation of the "ene" reaction product, 2,3-dimethyl-3-butene-1-hydroperoxide, by nmr (9). Even at -78° in methanol solvent, however, **5** is too rapidly transformed to **2**, **3**, **4** and other products and cannot be observed in the nmr. Addition of a nucleophile, *e.g.*, water to **5** formed in acetone- d_6 or Freon-11 at -78° leads to formation of **2** and other products with no oxygen evolution.

As shown in Scheme 1, we rationalize the formation of **2** and **3** principally by internal reorganization and methanolysis of *endo*-peroxide **5** respectively. We suggest that **4** arises from cleavage of dioxetane structure **6** [which itself may be formed by rearrangement of **5** or 1,2-addition of 1O_2 to **1**]. Cleavage of the pyrrole 2,3-bond(s) is unusual in their photooxygenation reactions and has previously been observed only when both positions were substituted with alkyl groups (5).

Scheme 1



EXPERIMENTAL

Photooxygenation of *N*-Phenylpyrrole (**1**).

In a typical experiment, a solution prepared from 500 mg. (3.5 mmoles) of *N*-phenylpyrrole (Aldrich) and 16 mg. of Rose Bengal (Matheson) dissolved in 750 ml. of anhydrous methanol

was placed in a water-cooled immersion well photolysis apparatus (10) and photolyzed using a 500 Watt Sylvania tungsten-halogen quartz lamp No. Q/CL run at 80V. The photo-oxidation was allowed to proceed with monitoring of oxygen uptake until the rate of uptake slowed to *ca* zero and 70% of one mole equivalent was consumed. The reaction was complete in 11 minutes and the rate of oxygen uptake was 7.5 ml./minute. The methanol solvent was removed at 40° using a rotatory evaporator to yield 669 mg. of crude photoproducts. The crude mixture was partially separated by column chromatography on silica gel [M. Woelm, Eschwege, 70-325 mesh ASTM] using ethyl acetate eluent and further purified by preparative thin layer chromatography [Silica Gel F. M. Woelm, Eschwege, 1 mm, ethyl acetate or ether] to give the following photoproducts:

5-Hydroxy-*N*-phenyl-3-pyrrolin-2-one (2).

R_f 0.64 (ethyl acetate), 109 mg., 18% isolated yield; nmr (11) (acetone-d₆): δ 2.87 (br s, 1H, OH), 6.12 (s, 1H, CH-O), 6.19 (d, 1H, J = 5 Hz, =CH-C=O), 7.15 (d, 1H, J = 5 Hz, CH=C-C-O), 7.5 (m, 5H, aromatic) ppm; mass spectrum (11), *m/e* (relative intensity): 175 [M⁺] (40%), 158 [M-OH] (2%), 121 (52%), 93 (100%), 77 [C₆H₅] (34%); ir (11) (potassium bromide): 1655 cm⁻¹ [lit. (4) 1705 (chloroform)].

Anal. Calcd. for C₁₀H₉NO₂: 175.0633. Found: 175.0640.

5-Methoxy-*N*-phenyl-3-pyrrolin-2-one (3).

R_f 0.75 (ethyl acetate), 148 mg., 22% isolated yield; nmr (deuteriochloroform): δ 3.11 (s, 3H, OCH₃), 6.00 (s, 1H, CH-O), 6.35 (d, 1H, J = 6 Hz, =CH-C=O), 6.98 (d, 1H, J = 6 Hz, CH=C-C-O), 7.45 (m, 5H, aromatic) ppm; mass spectrum, *m/e* (relative intensity): 189 [M⁺] (81%), 174 [M-CH₃] (25%), 158 [M-OCH₃] (100%), 130 (30%), 93 (8%), 77 [C₆H₅] (55%); ir (potassium bromide): 1685 cm⁻¹.

Anal. Calcd. for C₁₁H₁₁NO: 189.0790. Found: 189.0754.

Methyl β-(*N*-Phenyl-*N*-formylamino)acrylate (4).

R_f 0.80 (ethyl acetate), 117 mg., 16% isolated yield; nmr (deuteriochloroform): δ 3.85 (s, 3H, -COOCH₃), 6.20 (d, 1H, J = 6.5 Hz, =CH-COOCH₃), 6.45 (d, 1H, J = 6.5 Hz, N-CH=), 6.84 (s, 1H, N-CHO), 7.4 (m, 5H, aromatic); mass spectrum, *m/e* (relative intensity): 205 [M⁺] (24%), 190 [M-CH₃] (10%), 174 [M-OCH₃] (21%), 173 [M-HOCH₃] (82%), 160 (18%), 146 [M-COOCH₃] (29%), 129 (24%), 113 (78%), 93 (100%), 77 [C₆H₅] (35%); ir (potassium bromide): 1690 cm⁻¹, shoulder 1660 cm⁻¹.

Anal. Calcd. for C₁₁H₁₁NO₃: 205.0729. Found: 205.0739.

N-Phenylpyrrole Endo-peroxide (5).

N-Phenylpyrrole (2 mg., 0.01 mmole) in an nmr tube was dissolved in about 0.3 ml. of either acetone-d₆, Freon-11 with 10% acetone-d₆ or methanol-*O-d* and cooled to -78°. The singlet oxygen sensitizers used in each solvent were: methylene blue in acetone-d₆, 1,8-dinaphthalene-thiophene in Freon-11, and rose bengal in methanol-*O-d*. A slow stream of oxygen was passed through each solution during irradiation [Sylvania Tungsten-halogen lamp, Q/CL, 500 Watt, 80-100 volts] of the solutions which were cooled in a half-silvered Dewar. Irradiated samples were quickly transferred to the pre-cooled probe of the nmr (Varian XL-100). At -78° a complete conversion of 1 to its *endo*-peroxide (5) could be observed in acetone-d₆ or Freon-11, but not in methanol *O-d*. In methanol *O-d* at -78°, 2, 3, 4 and other

products were observed; nmr (acetone-d₆, -78°): 1, δ 6.27 (2H, C-CH-C), 7.22 (2H, C=CH-N), 7.3-7.5 (5H, C₆H₅) ppm; 5, δ 6.79 (2H, C-CH=C), 6.98 (C=CH-N), 7.2-7.4 (5H, C₆H₅) ppm; nmr (Freon-11 + 10% acetone-d₆, -78°): 1, δ 6.21 (2H, C-CH-C), 7.22 (2H, C=CH-N), 7.4 (5H, C₆H₅) ppm; 5, δ 6.58 (2H, C-CH=C), 6.70 (2H, C=CH-N), 6.9-7.3 (5H, C₆H₅) ppm.

Singlet Oxygen Trapping from 5.

N-Phenylpyrrole (10 mg., 0.07 mmole) was irradiated as before in acetone-d₆ at -78°. After complete conversion of 1 to 5, a 2-7 μl sample of 2,3-dimethyl-2-butene was added. Four separate experiments were carried out:

(i) The mixture was warmed gradually by pulling the tube out of the dewar and re-emersing it as soon as bubbles appeared.

(ii) The sample was placed in a sealed tube and placed in an ice methanol bath for 2 hours and then allowed to warm to room temperature.

(iii) The solution was kept overnight in an ice methanol bath.

(iv) The solution was kept at -78° for 48 hours at which time it was allowed to warm to room temperature. Only a few bubbles were observed on warming.

Only experiments (i) and (iv) worked well enough to detect a 1-2% conversion of 2,3-dimethyl-2-butene to 2,3-dimethyl-3-butene-1-hydroperoxide (12); nmr (acetone-d₆, -78°): δ 1.29 (s, 6H, -C(O) (CH₃)₂), 1.77 (s, 3H, -C-CH₃), 4.80 (m, 1H, =CH), 4.89 (m, 1H, =CH) ppm.

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