

## Thermal, Photochemical and Mass Spectral Reactions of 2-Ethyl-5-methyl-1-pyrroline

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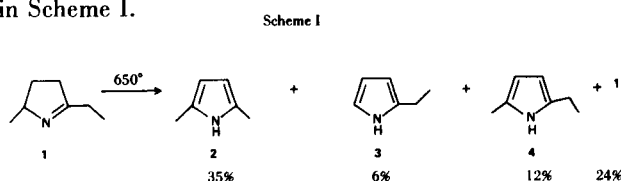
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Pyrolysis of 2-ethyl-5-methylpyrroline (**1**) results in formation of 2,5-dimethylpyrrole, 2-ethyl-5-methylpyrrole, 2-ethylpyrrole and other minor products. Loss of a hydrogen atom or methyl radicals is suggested as the first step in these reactions. Support for the former comes from hydrogen atom abstraction by photo-excited benzophenone. The mass spectral reactions of **1** are briefly considered.

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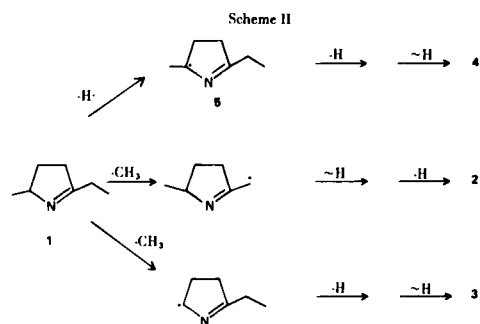
The thermal and photochemical reactions of many pyrroles (**1**) have been studied. Corresponding reactions of pyrrolidines (**2**) and especially of pyrrolines (**3**) are less well studied. We report here on the initial results of our study of the thermal, photochemical and mass spectral reactions of 2-ethyl-5-methyl-1-pyrroline (**1**).

Pyrroline **1** was prepared by the Grignard method of Etienne and Correia (**4**) from 5-methyl-2-pyrrolidinone. Compound **1** was pyrolyzed at 600-675° in a gold chamber and helium atmosphere with a 7 second contact time. At 650° with 87% mass balance, the products are as shown in Scheme I.



The 13% of **1** not converted to **2**, **3** and **4** is largely made up of dimers of these compounds (less 2H), 2-methylpyrrole, pyridine, ethylene, acetonitrile, and propanitrile.

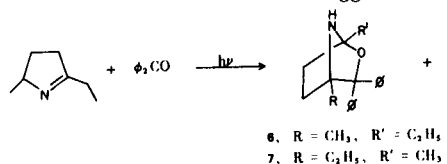
The products in Scheme I are accounted for in the following formal mechanistic scheme.



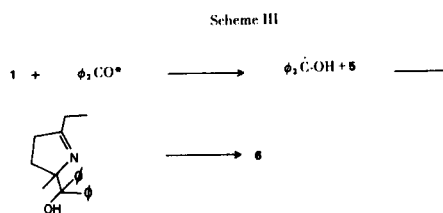
At higher temperature (675° and above), the yields of minor products and especially of dimers (from **5** and related intermediates) and oligomers increased.

Intermediate **5**, which results from loss of a hydrogen atom  $\alpha$  to nitrogen could be generated from a photochemical H-atom abstraction by benzophenone (**8**).

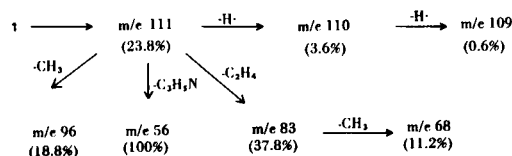
Photolysis (wavelength > 290 nm) of **1** in benzene with benzophenone (which absorbed 98% of the light) cleanly produced two adducts, **6** and **7** (3:2), and a small amount of **4**. This addition reaction and the suggested mechanism



(Scheme III) have precedent (**9**).



The mass spectral fragmentation of **1** suggests processes similar to those occurring thermally. For example,



### Acknowledgement

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### EXPERIMENTAL

With the following exceptions all reagents and solvents were purchased from Aldrich Chemical Co. Diethyl ether (hereafter ether), benzophenone, toluene, and magnesium were purchased from Fisher Scientific Co. All other inorganic reagents were supplied by J. T. Baker Co.

Melting points are uncorrected and were run on a Thomas-Hoover Unimelt apparatus. Infrared (ir) spectra were run on a Perkin-Elmer 727 Spectrophotometer and were calibrated with polystyrene. Nuclear magnetic resonance (nmr) spectra were run on a Varian EM 360 or a Jeol Minimar-100 spectrometer and are reported relative to TMS at 0.0  $\delta$ . Mass spectra were run on an AEI MS-30 mass spectrometer at 70 eV. Preparative gas chromatography (gc) was carried out on a Varian 920 gas chromatograph with a 5' x 1/4", 15% SE30 column. Analytical gc work was carried out on a Perkin-Elmer 900 gas chromatograph with a 5' x 1/8", 15% SE30 column. Integration was carried out with a Hewlett-Packard model 3380A recording integrator. Ultraviolet (uv) spectra were run on a Beckman DB-GT grating spectrophotometer. CHN analyses were run on a Perkin-Elmer model 240 Elemental Analyzer.

#### Preparation of 2-Ethyl-5-methyl-1-pyrroline (**1**).

5-Methyl-2-pyrrolidinone (20 g., 0.20 mole) in toluene (100 ml.) was added dropwise at 15° to a mixture of ethyl magnesium bromide (prepared from ethyl bromide (87.2 g., 0.8 mole) and magnesium turnings (19.5 g., 0.8 mole) in ether under nitrogen, followed by removal of about 85% of the ether at reduced pressure) in toluene (250 ml.). The mixture was refluxed overnight, cooled, acidified (concentrated hydrochloric acid, 100 ml. in 200 ml. of ice). The aqueous layer was neutralized (potassium carbonate) and steam distilled. The distillate (two layers) was extracted with ether (2 x 30 ml.), made strongly basic with potassium hydroxide, and extracted again with ether (2 x 30 ml.). The ether extracts were combined, dried over potassium hydroxide, filtered and distilled (~760 mm) yielding a fraction (7.3 g., b.p. 120-135°) which contained 83% of **1** contaminated with ether, water, and isomers (?) of **1**. Gc separation (80°, 20 psi He) gave pure ( $\geq 99.6\%$  on CBX 1540 capillary column at 75°) pyrroline **1**: uv max (ether): 228 nm ( $\epsilon$ , 99.2); ir (neat liquid): 2960  $\text{cm}^{-1}$  ( $\text{CH}_3$ ), 2855 ( $\text{CH}_2$ ), 1640 ( $\text{C}=\text{N}$ ); nmr (deuteriochloroform):  $\delta$  4.02 (m, 1H, J = 8 Hz and J = ?,  $\text{HC}=\text{N}$ ), 2.43 (q, 2H,  $\text{CH}_2-\text{CH}_3$ ), 2.37 (m, 2H,  $\text{CH}_2-\text{C}=\text{N}$ ), 1.27 (m, 2H,  $\text{CH}_2-\text{CH}-\text{CH}_3$ ), 1.21 (d, 3H, J = 8 Hz,  $\text{CH}_3-\text{CH}$ ), 1.18 (t, 3H,  $\text{CH}_3-\text{CH}_2$ ); mass spectrum (70 eV) m/e (relative intensity): 112 (1.6), 111 (23.8), 110 (3.6), 109 (0.6), 97 (0.9), 96 (18.8), 96 (1.1), 84 (2.1), 83 (37.8), 82 (10.5), 81 (1.1), 80 (1.1), 70 (0.4), 69 (8.2), 68 (11.2), 67 (1.3), 57 (3.7), 56 (100), 55 (10.1), 54 (6.5), 53 (3.3), 52 (1.4) 51 (0.7), 44 (0.6), 42 (7.2), 41 (38.2), 40 (2.4), 39 (10.0), 38 (0.6).

Anal. Calcd. for  $\text{C}_7\text{H}_{13}\text{N}$ : C, 75.62; H, 11.79; N, 12.60. Found: C, 75.53; H, 11.84; N, 12.67.

#### Pyrolysis of **1**.

Samples of **1** (99%, 0.100 ml.) were slowly introduced into a CDS-810 reactor (Chemical Data Systems, Oxford, Pa.), vaporized at 175° in a flow system (helium at 20 psi) and pyrolyzed at

650  $\pm$  10° for 7 seconds. The effluent gasses were cooled rapidly to 175° and collected with greater than 95% efficiency at liquid nitrogen temperature. The resulting mixture was separated by gc and gave the following: **1** (24%) identified by its spectral (nmr, ir, and mass spectrum) and chromatographic (SE30) characteristics; 2,5-dimethylpyrrole (**5**) (**2**) (35%); 2-ethylpyrrole (**6**) (**3**) (6%); and **4**, 2-ethyl-5-methylpyrrole (**7**) (12%), each unequivocally identified by its established spectral characteristics; five of nine or more long retention (SE 30 at 200°) products (total yield about 7%) were tentatively assigned as dimeric products of **2** and/or **3** or **4** on the basis of their mass spectra (gc separated) with three compounds each with molecular ions at m/e 188 and two compounds each with molecular ions at m/e 216; nmr (mixture of compounds in deuteriochloroform):  $\delta$  8.2 (broad, NH), 5.5-6.0 ( $\text{C}=\text{C}-\text{H}$ ), 1.2-2.4 (methyl and ethyl); ir (mixture of compounds in carbon tetrachloride): 3450  $\text{cm}^{-1}$  (NH), and 1600 ( $\text{C}=\text{C}$ ). Other minor products (2-methylpyrrole, pyridine, ethylene, acetonitrile and propionitrile) were each present in 1% yield or less, and were identified by their characteristic ir spectra, and, with the exception of ethylene, their mass spectra.

#### Photoinduced Reactions of **1**.

Nitrogen purged benzene solutions (10 ml.) of **1** (0.056 g., 0.05 mole) and benzophenone (0.15 mole) were photolyzed (450 watt, medium pressure Hanovia mercury lamp, through pyrex) for 0.5 hour. The resulting solution contained unreacted **1**, benzophenone, **4**, **6** and **7**. The volatile products were separated and analyzed by gc: unreacted **1** (0.036 g.) and **4** (approx. 0.0006 g., identified by mass spectra), both estimated by gc integration. Non-volatile products were separated by chromatography on silica gel (cyclohexane); Benzophenone was eluted with cyclohexane; benzopinacol (m.p. 178-180°) was eluted with cyclohexane/ether, 20:1; **6** (eluted with cyclohexane/ether, 10:1, 26 mg., 51%, contaminated with some **7**), m.p. 90-97; nmr (deuteriochloroform):  $\delta$  7.2-7.6 (m, 10H, phenyl), 4.3-4.6 (broad, 1H, NH), 2.1-2.3 (m, 6H,  $\text{CH}_2-\text{CH}_2$  and  $\text{CH}_2-\text{CH}_3$ ), 2.0 (s, 3H,  $\text{CH}_3$ ), 0.85 (t, 3H,  $\text{CH}_2-\text{CH}_3$ ); ir (deuteriochloroform): 3400  $\text{cm}^{-1}$  (? very weak, NH), 3060 (aromatic), 2950 ( $\text{CH}_3$ ), 1170 ( $\text{C}-\text{O}$ );

Anal. Calcd. for  $\text{C}_{20}\text{H}_{23}\text{NO}$ : C, 81.87; H, 7.90; N, 4.77. Found: C, 81.80; H, 7.94; N, 4.83.

Compound **7** (eluted with cyclohexane/ether, 10:1, 17 mg., 35% contaminated with some **6**), m.p. 102-106°; nmr (deuteriochloroform):  $\delta$  7.1-7.75 (m, 10H, phenyl), 4.8-5.1 (broad, 1H, NH), 2.3 (q, 2H,  $\text{CH}_2-\text{CH}_3$ ), 2.1-2.3 (m, 4H,  $\text{CH}_2-\text{CH}_2$ ), 1.2 (s, 3H,  $\text{CH}_3$ ), 0.9 (t, 3H,  $\text{CH}_2-\text{CH}_3$ ); ir (deuteriochloroform): 3045  $\text{cm}^{-1}$  (aromatic), 2950 ( $\text{CH}_3$ ), 1180 ( $\text{C}-\text{O}$ ).

Anal. Calcd. for  $\text{C}_{20}\text{H}_{23}\text{NO}$ : C, 81.87; H, 7.90; N, 4.77. Found: C, 81.79; H, 7.97; N, 4.79.

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