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THE PHOTOINDUCED POLAR ADDITION OF METHANOL TO 2H-PYRROLES

John M. Patterson, Robert L. Beine and Michael R. Boyd

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

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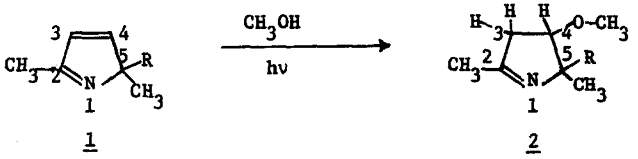
The direct or sensitized photoinduced ionic addition of alcohols to cyclohexenes and cycloheptenes but not cyclopentenes is well documented (1,2). Instead of the addition reaction cyclopentenes undergo either double bond isomerization and reduction (sensitized photolysis) (3) or polymerization (direct photolysis) (2). Cycloalkenes containing a carbonyl group conjugated with the double bond exhibit similar behavior. While cyclopentenone (4) and cyclohexenone (5) show no evidence for polar addition, cycloheptenone (6), substituted cyclohexenones (7), acylcyclohexenones (8) and pyrimidines (9) do. The reported (10) photoreaction of acylcyclopentenes with alcohols probably involves a radical addition since the products are alcohols rather than ethers.

The photoaddition also has been reported to occur at the exocyclic double bond in isopropylidenephthalide (11) and at the double bond in the alicyclic system, benzoylacrylic acid (12).

The photoaddition of alcohols to an azomethine group (C=N) has been observed with a variety of heterocyclic systems such as pyrimidines (13), purines (14), and quinolines (15), however the additions to these systems appear to follow a nonpolar pathway since the products obtained arise from the addition of carbon to the unsaturated system.

We wish to report that methanol undergoes photoaddition (at 254 nm) to substituted 2H-pyrroles (1) which contain both the conjugated double bond and azomethine (C=N) system.



a, R = allyl; b, R = n-propyl

The 2H-pyrroles 1a and 1b were synthesized by the procedure previously described (16) for 2-benzyl-2,5-dimethyl-2H-pyrrole. The compounds (17) exhibited characteristic 2H-pyrrole absorption in the infrared at 1615 and 1525cm^{-1} and an AB pattern at *ca.* 6.2 and 7.2 ppm (see Table I).

Table I. Proton Chemical Shifts (δ,CDCl$_3$) of the 5-Substituted 2,5-Dimethyl-2H-pyrroles.[a]

Compd	CH$_3$ at C-5	H at C-4	H at C-3	CH$_3$ at C-2
1a	1.27 (s,3)	6.25 (d,1;J=5Hz)	7.25 (d,1;J=5Hz)	2.25 (s,3)
1b	1.29 (s,3)	6.19 (d,1;J=5Hz)	7.21 (d,1;J=5Hz)	2.15 (s,3)

(a) Chemical shifts for the allyl and propyl groups were typical and are not reported.

Irradiation (18) of 1a or 1b in methanol (25% solution, w/w) at 254 nm for 6 hr resulted in the formation of 2a and 2b respectively as indicated by the loss of the AB pattern in the nmr spectra and in the shifting of the azomethine absorption from 1615 to 1640 cm^{-1}. Both adducts exhibited in addition, methoxy absorption at 2838 cm^{-1} and C-O absorption at 1105 cm^{-1}. The conversion to adducts (2a and 2b) was > 90% as determined from the nmr spectra (19). Addition of methanol to 1a or 1b did not occur in the dark at 35° or in the dark in the presence of catalytic amounts of 1N H_2SO_4 or NaOMe after 20 hrs.

The nmr spectra of 2a and 2b (see Table II) indicated that the adducts are mixtures of diastereomers and this is confirmed by glpc analysis (20). The diastereomers of 2a were separated by glpc (20) and were obtained in the ratio of *ca.* 1.4:1. Since the diastereomers of 2b were incompletely resolved by the glpc column, the mixture was collected and the properties derived from it. The adducts, 2a and 2b showed molecular ions at 167.131 and

Table II. Proton Chemical Shifts (δ,CDCl$_3$)[a] of the 5-Substituted 4-Methoxy-2,5-dimethyl-1-pyrrolines.

Compd	CH$_3$ at C-2	H at C-3	H at C-4	CH$_3$O at C-4	CH$_3$ at C-5
2a(major)	1.99 (s,3)	2.61 (t,2)	3.58 (q,1)	3.30 (s,3)	1.10 (s,3)
2a(minor)	1.98 (s,3)	2.59 (t,2)	3.68 (q,1)	3.30 (s,3)	1.18 (s,3)
2b[b]	2.01 (s,3)	2.64 (m,2)	3.60,3.70 (q,1)	3.31 (s,3)	1.14,1.19 (s,3)

(a) Chemical shifts for the allyl and propyl groups are typical and are not reported.

(b) Mixture of diastereomers.

169.146 respectively (theory, 167.131 and 169.147). Heating 2a (diastereomeric mixture or individual diastereomers) or 2b (diastereomeric mixture) at ca.130° produced the corresponding 2H-pyrrole and methanol in approximately a 1:1 ratio as determined by nmr spectroscopy. The nmr chemical shift assignments were verified by deuterium exchange and decoupling experiments. In the 2H-pyrroles 1a and 1b only the methyl group attached to C-2 underwent exchange in deuteromethanol; in both the adducts, 2a and 2b, exchange was observed at C-3 and at the methyl group attached to C-2. In the decoupling experiments with both 2a and 2b, it was found that protons at C-3 and C-4 were coupled and that protons at C-3 were fine coupled to the methyl protons at C-2. No fine coupling was observed between the proton at C-4 and the methyl-group protons at C-2.

Adduct formation is not inhibited by oxygen. Simultaneous irradiation of identical samples (one saturated with oxygen and the other degassed with nitrogen) both produced the adduct in ca. 40% conversion after 1 hr.

Similarly, water undergoes photoaddition to the 2H-pyrrole system. The irradiation of 0.5g of 1a in 2g of a tetrahydrofuran-water mixture (1:1) for 7 hr resulted in almost complete conversion to the hydroxy-1-pyrroline. The excess water was removed by azeotropic distillation (benzene) *in vacuo* to produce a mixture of diastereomers: ir (neat), 3100-3400(OH), 1641(C=N), 1090 cm^{-1}(C-O);nmr ($CDCl_3$), 1.07 and 1.23 (s,3), 2.02 (s,3), 2.40-3.10 (complex asymmetric multiplet, 2), 3.10 (s,1), 4.11 (m.1) and typical allyl absorption; mass spectrum parent, 153. Heating the adduct at 120° for 30 min converted it into a mixture of water and 1a as determined by nmr analysis.

This report as well as the recent report by Kropp (2) describing the direct photolytic addition of methanol to 1,2-dimethylcyclopentene demonstrates that photo-induced ionic additions occur at the endoyclic double bond in appropriately substituted 5-membered ring systems.

In view of the data available, only limited speculation about the mechanistic path is possible. A path involving a transoid excited ground state such as has been postulated for 6- and 7-membered ring compounds (1,2) seems unlikely because of the high energy associated with such a species in a 5-membered ring system. The insensitivity of the photoaddition to oxygen suggests that the reaction proceeds by way of an excited singlet followed by electrophilic or nucleophilic attack by solvent on the excited species.

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(17) Satisfactory elemental analyses were obtained.

(18) Photolyses were carried out in a Rayonet reactor with the sample solution (in 6 mm o.d. quartz tubes) placed in a quartz water-jacketed thermostat centered in the reactor.

(19) Irradiation of 1a in tetrahydrofuran for 6 hr produced less than 10% of high molecular weight material as determined by glpc analysis using an internal standard.

(20) Glpc analyses were carried out using an 8 ft x 0.375 in. 3% Carbowax 20M on KOH-treated Anakrom column at 80°.