

THE PHOTOISOMERIZATION OF BENZYLPIRROLES

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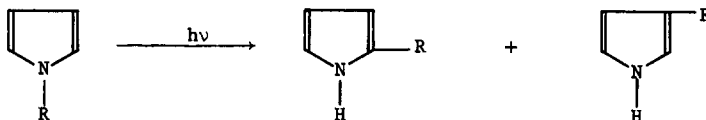
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The production of 2 and 3 substituted pyrroles from the corresponding N substituted pyrrole by a thermally-induced group migration has been shown to occur with 75-85% retention of configuration (1). We wish to report a similar N-to-2 and N-to-3 migration of benzylic groups (R) which is induced photochemically.

The irradiation of N-benzylpyrrole (2g, neat) in quartz tubes (7 mm OD) with a 200 watt Hanova Type S654A lamp for 18 hrs or with a Rayonet reactor (2537Å) for 4.5 hrs produced (glpc analysis) 12.6±0.7% 2-benzylpyrrole and 2.5±0.2% 3-benzylpyrrole. Decomposition and polymerization estimated at less than 5% was also observed. The glpc retention times, infrared and nmr spectra obtained from the photolysis products were identical to those obtained from



the 2 and 3 isomers produced on pyrolysis (2) and from those produced on reaction of pyrrolylmagnesium bromide with benzyl bromide.

Irradiation (2537Å) of a methanolic solution containing 2g of N-benzylpyrrole (2:1) for 4.5 hrs increased the yields to 28.1% 2 isomer and 9.8% 3 isomer.

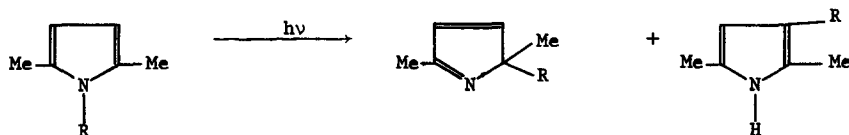
When either 2- or 3-benzylpyrrole were irradiated for 4.5 hrs in methanol (2:1) at 2537Å only recovered starting material and decomposition products were observed. It is concluded that the 2 isomer is not the precursor of the 3 isomer in the photoisomerizations as has been postulated by Jacobson (3) and Pine (4) for the thermal isomerizations.

We have found that optically active groups migrate from the N to the 2 and 3 positions with 54% retention of configuration in the photoisomerization reaction. Thus the irradiation (2537Å) of (+)-N-(1-phenylethyl)pyrrole (2g, neat) for 4 hrs gave 12.5±1.3% 2 isomer and 2.7±0.5% 3 isomer (average of 14 runs.) Decomposition and polymerization was estimated to be less than 5%. The products gave glpc retention times, infrared and nmr spectra which were identical to those previously reported (1). Configurational assignments and optical purities were based upon the values obtained from the pyrolysis reactions (1). The recovered N isomer retained 99.6% of its optical activity in these experiments.

As was observed in the photoisomerization of N-benzylpyrrole, irradiation (2537Å, 6 hrs) of a methanolic solution of N-(1-phenylethyl)pyrrole (2g) resulted in increased conversions -- 20±2% 2 isomer and 6.5±0.3% 3 isomer. On the other hand, migration to the 2 position occurred only with 32% retention of configuration. As before, the N isomer was recovered with 99.7% retention of its optical activity.

In order to determine the effect of 2,5-methyl substituents on the photoisomerization, (+)-N-(1-phenylethyl)-2,5-dimethylpyrrole (15.7g), $[\alpha]_D^{25} + 26.97$, was irradiated (2537Å) neat (5 hrs) in a vessel consisting of concentric quartz tubes joined by a Dewar seal to give a thin layer (ca. 3 mm) of liquid.

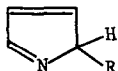
The products were 3-(1-phenylethyl)-2,5-dimethylpyrrole (5.4±1.7%) and 2-(1-phenylethyl)-



2,5-dimethyl-2H-pyrrole (11.9±1.5%, isolated yield 10%); bp 113-4° (9mm); n_D^{25} 1.5282; $[\alpha]_D^{25}$ -18.2±0.3° (c 8.28, CCl₄); λ_{max}^{MeOH} 210 mμ (ϵ 9160); γ^{CCl_4} 1610 cm⁻¹, nmr spectrum (100 MHz), 1.14 ppm (sextet, 6H); 2.13 (doublet, 3H), 3.12 (octet, 1H), 6.05 (quartet, 1H), 7.16 (multiplet, 6H). The elemental analyses were satisfactory and the nmr and infrared spectra of the 2H-pyrrole were identical to those obtained from the basic product resulting from the reaction of 1-phenylethyl bromide and 2,5-dimethylpyrrolmagnesium bromide. Recovered N isomer retained 99.6% of its optical activity.

Pyrolysis of the 2H-pyrrole at 300° produced 3-(1-phenylethyl)-2,5-dimethylpyrrole in 96% yield and with 34.9% optical purity. Thus, combined photoisomerization and pyrolysis (from N to 3) occurred with 36% retention of configuration. These results indicate that there is probably considerable loss of optical activity occurring during the photoisomerization step.

To evaluate the possibility that the 2H-pyrrole was the precursor of the 3 isomer formed in the photoisomerization, 2-(1-phenylethyl)-2,5-dimethyl-2H-pyrrole was irradiated (2537Å) neat for 2.5 hrs. Analysis by glpc showed no evidence of isomerization and it was found that the recovered 2H-pyrrole retained 92.3% of its optical activity. It appears likely then, that in the case of the N-substituted dimethylpyrroles, that the 3 isomer arises from a direct 1,3-migration and not through a 2H-pyrrole intermediate. Likewise, the formation of 3 isomer in the photoisomerization of N-benzylpyrrole also probably involves a direct 1,3 migration. Another possible reaction path, which cannot be ruled out at this time, involves photoisomerization to the 2H-pyrrole I followed by a room temperature thermal isomerization to either 2 isomer or a precursor of 3 isomer.



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References

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