

PHOTOISOMERIZATION OF SOME SUBSTITUTED N-ACETILPYRROLES

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While the irradiation of N-benzylpyrrole, N-benzyl-2,5-dimethylpyrrole¹ and N-allyl-2,5-dialkylpyrroles² results in group migration from nitrogen to both the 2 and 3 positions of the pyrrole ring, the irradiation of N-acetylpyrrole reportedly gives only 2-acetylpyrrole³ as isomerized product. Because of this apparent difference in behavior and because of our observation that the photolysis⁴ of N-acetyl-2,5-dimethylpyrrole produces 3-acetyl-2,5-dimethylpyrrole⁵, we have reinvestigated the photoisomerization of N-acetylpyrrole and have extended the study to N-acetyl-2-methylpyrrole as well.

We have found that the irradiation⁴ of a 0.05M solution of N-acetylpyrrole in methanol produced⁶ both 2-acetyl- and 3-acetylpyrroles in 59±4 and 6±1% yields respectively. In a similar experiment a 1.5 hr irradiation of N-acetylpyrrole (0.2M in dioxane) produced 54±3% 2-acetylpyrrole and 6±2% 3-acetylpyrrole. Unreacted N isomer was present to the extent of 27±3%. In this and in subsequent experiments, the isomeric pyrrole products were isolated by preparative glpc and identified by comparisons of their glpc retention times and spectral properties (infrared, nmr and mass) with those obtained from authentic samples produced by synthetic methods reported in the literature. Mixture melting points were not depressed.

The influence of solvent on the formation of 2-acetylpyrrole was investigated by simultaneously irradiating⁴ 0.2M solutions of N-acetylpyrrole and analyzing the photolyzate at 0.5 hr intervals. While the extent of photoreaction of N-acetylpyrrole (i.e. disappearance) was about the same for methanol, ethanol and dioxane solvents (ca. 35% recovery after 1.5 hr) the fraction of reacted N isomer converted to 2 isomer was somewhat greater in the dioxane media than in alcohol media (88% as opposed to 62% after 1.5 hr.). The isomerization reaction apparently is favored in dioxane relative to the competing polymerization and photo-

cleavage reactions. These solvent effects support the existence of an intermediate whose decomposition to products is solvent dependent.⁷ The effect of the nature of solvent on the time of formation of product absorption bands in flash photolysis studies prompted Shizuka, Okutsu, Mori and Tanaka³ to propose the valence isomer 1 of the 2H-pyrrole 2 as the intermediate in



this photoisomerization. Since substituted 2H-pyrroles have been isolated in previous pyrolysis studies of N-allyl-² and N-benzyl-2,5-dimethylpyrroles¹, N-acetylpyrrole and alkyl-substituted N-acetylpyrroles were irradiated⁴ simultaneously to obtain direct evidence for this kind of species in the acetylpyrrole isomerizations. The results are summarized in Table I.

The products reported in the table did not undergo isomerization or interconversion after isolation and further irradiation. 2-Acetylpyrrole gave neither 3-acetyl- nor N-acetylpyrrole on photolysis in methanol for 21.5 hr. 2-Acetylpyrrole, 3-acetylpyrrole, 2-methyl-5-acetylpyrrole, 2-methyl-3-acetylpyrrole and 3-acetyl-2,5-dimethylpyrrole showed no evidence of interconversion or isomerization on irradiation in dioxane for 1.5 hr. Likewise thermally-

Table I. Photoisomerization of N-Acetylpyrrole and Alkyl-substituted N-Acetylpyrroles in Dioxane.

<u>N</u> -Acetyl Reactant	Isomeric Pyrroles(wt.%)		Recovered
	2-Acetyl	3-Acetyl	<u>N</u> -Acetylpyrrole
Pyrrole	54	6	27
2-Methylpyrrole	38 ^a	19 ^b	33
2,5-Dimethylpyrrole	0 ^c	36	27

(a) 2-Acetyl-5-methylpyrrole. (b) 3-Acetyl-2-methylpyrrole. (c) 2-Acetyl-2,5-dimethyl-2H-pyrrole (not observed).

-induced isomerizations or interconversions among the N- and C-acetylpyrroles were not observed after 2 hr in dioxane at 46°⁸.

Formation of products by a free radical dissociation process is unlikely since the irradiation of equimolar mixtures of N-acetylpyrrole and 2-methylpyrrole or pyrrole and N-acetyl-2-methylpyrrole failed to produce crossover products.

While the introduction of methyl substituents onto the pyrrole ring does not affect the extent to which the substituted pyrrole undergoes photoreaction (within experimental error),

the substituents do influence both the fraction of molecules undergoing isomerization relative to other competitive paths such as polymerization and cleavage⁹ as well as the relative 2 and 3 isomer yields. Thus the irradiation of N-acetylpyrrole and N-acetyl-2-methylpyrrole produces ca. 60% isomerization while the irradiation of N-acetyl-2,5-dimethylpyrrole produces only 36% isomerization. In addition, the fraction of 3 isomer among the isomerization products increases with increasing methyl substitution. These experiments in which the substituents alter the partitioning among various reaction paths support the existence of an intermediate in the photolyses. Product composition - time dependence studies indicate that both the 2 and 3 isomers are primary products of reaction.

The path or paths by which 3 isomer arises cannot be identified explicitly. By analogy with the N-allyl- and N-benzyl-dimethylpyrrole systems^{1,2}, it might be expected that at least part of the 3 isomer produced arises from a direct N to 3 migration on photolysis. On the other hand, the facts that the 2-acetyl-2-methyl-2H-pyrrole could not be isolated and that the acetyl group has a high migratory aptitude in thermal reactions⁸ suggests that in the methyl-pyrrole systems, some of the 3 isomer arises from a photo-induced formation of 2H-pyrrole followed by a thermally-induced migration (at room temperature) of acetyl to the 3 position. This latter proposal that acetyl-2H-pyrroles undergo a room temperature isomerization even though C-acetylpyrroles are stable under such conditions is a reasonable one since alkyl- and allyl-2H-pyrroles have been observed^{1,2} to isomerize at temperatures considerably lower (ca. 200-300°) than those required for the corresponding alkyl- and allylpyrroles.

References

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- (4) All irradiations were carried out at 254 nm in 6 mm o.d. quartz tubes using a rotating assembly enclosed in a water-cooled quartz jacket (Temp 21-24°) with the assembly placed in the center of a Model 100 Rayonet reactor.
- (5) Irradiation of a 0.2M solution in dioxane for 1.5 hr produced 36% 3-acetyl-2,5-dimethylpyrrole and 27% recovered starting material.
- (6) Products were analyzed by glpc using a 3 ft x 0.25 in. 10% SE-30 column and an internal standard. Peak areas were estimated using the height-times-width at half-height method. Each of the yields is the average of the analysis of two samples irradiated simultaneously.

- (7) The referee points out that similar solvent effects may have arisen also from competing photooxidation reactions, e.g., D. A. Lightner and L. K. Low, J. Heterocycl. Chem., 9, 167 (1972). However no evidence (glpc) for the formation of such products was observed in the present experiments.
- (8) The thermolysis of N-acetylpyrrole in methanol at 60° gave a 6% yield of 2-acetylpyrrole after 9.5 hr.
- (9) Cleavage as measured by formation of deacetylated pyrroles occurred to the extent of ca. 4% and 7% in the photolyses of N-acetyl-2-methylpyrrole and N-acetyl-2,5-dimethylpyrrole respectively.