Photoisomerization of 2-Cyanopyrrole

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Summary Irradiation of 2-cyanopyrrole in methanol yields 3-cyanopyrrole as a major photo-product; this is believed to be the first example of the 2–3 valance isomerization of pyrroles.

PHOTOISOMERIZATIONS involving transfer of a substituent from the 2-position to the 3-position have been reported in the isoxazole,[1] furan,[2] thiophen,[3] and pyrazole[4] series. The specific 2–3 direction of photoisomerization has been correlated with the bond orders of the excited ring systems calculated from simple Hückel-type molecular orbitals.[5] In spite of these findings, the 2–3 valence isomerization of pyrroles has not previously been reported, though thermal[6] and photochemical[7] 1–2 and 1–3 valence isomerizations have been reported. In this last case, however, the 2-isomer is not the precursor of the 3-isomer, because 2-benzylpyrrole does not isomerize to its 3-isomer either photochemically or thermally.

I report that 2-cyanopyrrole photoisomerizes to 3-cyanopyrrole in a methanol solution on irradiation with u.v. light, and that 3-cyanopyrrole does not photoisomerize to the 2-isomer under the same conditions.

2-Cyanopyrrole was first of all prepared by dehydration of pyrrole-2-aldoxime by acetic anhydride,[8] but it was found that its photo-dehydration in methanol was more convenient.† The i.r., n.m.r., and molecular weight of the 2-cyanopyrrole thus obtained agreed completely with those in the literature.[9]

A 0·02% solution of 2-cyanopyrrole in methanol in a quartz tube, after thorough degassing, was placed in the centre of a bank of low-pressure mercury lamps, and was irradiated for 20 hr. The solvent was then removed by distillation. The photo-products were isolated by g.l.c. with a 6 ft Apiezon oil column at 150°. Pyrrole-2-carboxyaldehyde (5% chemical yield) appeared first after the solvent. The single photo-product (55% chemical yield) isolated after the original 2-cyanopyrrole (retention time relative to 2-cyanopyrrole: 2·5) had the following spectral data; *M* 92; i.r. ν_{max} 3430, 3280, 2230, 1250, 1090, and 1060 cm^{-1} in CCl_4; n.m.r. three multiplets at τ 2·65 (1 H), 3·16 (1 H) 3·45 (1 H), and one broad singlet at τ 1·0 (1 H) in CCl_4.

2-Cyanopyrrole does not isomerize to the 3-isomer on heating for 4 hr at 180° in a methanol solution in a sealed tube. Therefore, the 2–3 isomerization is specific to photochemical reactions and different from the 1–2 and 1–3 valence isomerizations of the pyrroles.[6,7]

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† The photo-dehydration has also been observed in furan-2-aldoxime; details will be published later.

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