Primary Photoproducts of Furan-2-carbonitrile and *N*-Methylpyrrole-2-carbonitrile: Trapping by Methanol Addition

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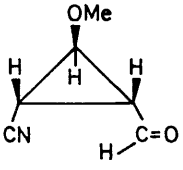
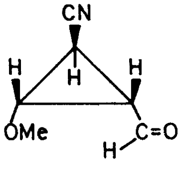
Summary Irradiation of furan-2-carbonitrile and of *N*-methylpyrrole-2-carbonitrile in methanol yielded, respectively, *trans*-3-formyl-2-methoxycyclopropane-1-carbonitrile and *N*-methyl-3-methoxy-5-azabicyclo[2,1,0]pentane-1-carbonitrile as primary photoproducts, indicating as intermediate species a cyclopropenecarboxaldehyde for furan and an azabicyclopentene for pyrrole.

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] pyrazole,[4] and pyrrole[5] series. Except in a few cases,[1,4] however, intermediate species in these reactions have never been isolated. I report that trapping of the transient species by methanol demonstrates the entirely different nature of the photochemical primary reactions of furans and pyrroles.

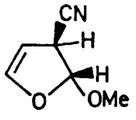
After irradiation of furan-2-carbonitrile in methanol with a low-pressure mercury lamp, the presence of aldehydes was indicated by the formation of yellow crystals upon addition of 2,4-dinitrophenylhydrazine. The primary photoproducts were isolated by evaporation at room temperature *in vacuo*. They showed i.r. absorptions (in $CHCl_3$) indicative of aldehyde groups: ν_{max} 2820, 2725 ν(H-CO), and 1720 ν(C=O) cm^{-1}. Their n.m.r. spectrum in $CDCl_3$ indicated the presence of two major aldehyde products (doublets at τ 0·50 and 0·84; the large splittings are characteristic of cyclopropanecarboxaldehydes.)[6] Structures (I) [J(H$^{\alpha}$–CHO) 4·5 Hz; τ 0·84] and (II) [J(H$^{\alpha}$–CHO) 2·5 Hz; τ 0·50] are assigned on the basis of the following evidence. (i) A smaller coupling constant, 2·5 Hz for (II), can be attributed to the effect of the neighbouring methoxy-group, while a coupling constant normal for a cyclopropanecarboxaldehyde is expected for (I); (ii) the neighbouring methoxy-group shifts the n.m.r. absorption of the aldehyde proton of (II) downfield in comparison with that in (I); (iii) both isomers thermally rearrange to the *trans*-dihydrofuran (III),



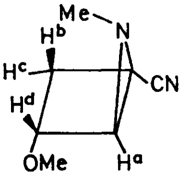
(I)



(II)



(III)



(IV)

as described later. The dihydrofuran was previously reported as a major photoproduct of furan-2-carbonitrile in methanol, but the mechanism of its formation was not clearly understood.[7] When the mixture of (I) and (II) was heated for 28 h at 117 °C, the n.m.r. signals of the cyclopropanecarboxaldehydes [in $CDCl_3$; τ 0·50 (d), 0·84 (d), 6·2 (m), 6·9 (s), and 7·7—8·2 (m)] disappeared, and were replaced by the absorptions of *trans*-2-methoxy-2,3-dihydrofuran-3-carbonitrile [τ 3·55 (t), 4·48(d), 4·98 (t), 6·45 (q), and 6·53 (s)]. In a g.l.c. separation, the *trans*-dihydrofuran was the main product, and its *cis*-isomer (identified from n.m r. doublet splittings: 3 Hz for the *trans*- and 7 Hz for the *cis*-isomer) was obtained only in small amount. Beside its n.m.r. spectrum, the mass spectrum (*M* 125), and i.r. (3090, 2910, 2810, 2220, and 1625 cm^{-1} in CCl_4) and u.v. absorptions (no absorption peaks down to 2000 Å) of the main product were consistent with the structure (III). Hydrolysis of the *trans*-dihydrofuran in aqueous methanol quantitatively yielded furan-3-carbonitrile, while pyrolysis at 250 °C yielded its *cis*-isomer in addition to furan-3-carbonitrile and methanol. Essentially similar results were obtained for the photochemical addition of ethanol and t-butyl alcohol to furan-2-carbonitrile.

The photolysis of *N*-methylpyrrole-2-carbonitrile in methanol with a low-pressure mercury lamp at 40—60 °C yielded a methanol adduct together with *N*-methylpyrrole-3-carbonitrile and 2-methyl-2*H*-pyrrole-2-carbonitrile. The methanol adduct had the following spectroscopic data: mass spectrum (*M* 123), i.r. (2230, 1210, 1160, 1130, 1120, and 1100 cm^{-1} in CCl_4), u.v. (no absorption peaks down to 2000 Å), and n.m.r. (C_6D_6) τ 6·58 (t, H^d), 7·30 (s, MeO), 7·91 (t, H^b), 8·01 (d, H^a), 8·20 (q, H^c), and 8·38 (s, MeN). In its n.m.r. spectrum in C_6D_6, there is no absorption downfield of the triplet at τ 6·58. On the basis of these data and chemical evidence, the photoadduct has the structure (IV). The photoadduct with MeOD showed (n.m.r. spectrum) that deuterium replaced H^b in (IV). A 10% increase of the H^d signal in an NOE experiment indicated spatial interaction between Me and H^d, while decoupling experiments yielded the following coupling constants: $J_{ac} = J_{bc} = J_{bd} = 3·0$ Hz, J_{cd} 2·15 Hz, J_{ad} 0·30 Hz. Smaller coupling constants, J_{bc}, J_{bd}, and J_{cd} compared to those for a cyclobutane system can be attributed to the effect of the polar substituents. Pyrolysis of the photoadduct at 186 °C for 2 h yielded only *N*-methylpyrrole-3-carbonitrile and methanol. This result indicated that NMe approached the 3-carbon atom from the opposite side at the same time as OMe was removed, thus resulting in the formation of *N*-methyl-5-azabicyclo[2,1,0]pent-2-ene-2-carbonitrile, which spontaneously rearranged to *N*-methylpyrrole-3-carbonitrile. Hydrolysis in aqueous methanol yielded both *N*-methylpyrrole-2- and -3-carbonitrile. This result could be explained only by assuming that both isomeric pyrroles derived from the same precursor, *N*-methyl-3-hydroxy-5-azabicyclo[2,1,0]pentane-1-carbonitrile.

In conclusion, these results confirm the photochemical ring contraction mechanism exhibited by furans,[2] while they demonstrate the predominance of a distinctly different mechanism, *i.e.* photochemical bicyclization, for pyrroles.

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