

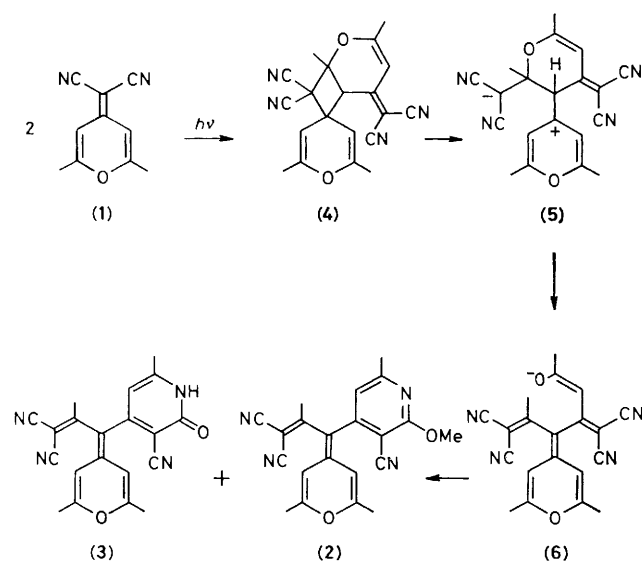
An Unusual Photodimerisation of a Pyrone Analogue; X-Ray Crystal Structure of the Principal Product

Nathaniel W. Alcock and Christopher J. Samuel*

Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL, U.K.

Irradiation of 4-dicyanomethylene-2,6-dimethyl-4*H*-pyran (1) in methanol leads to the dimers (2) and (3); the structure of (2) has been determined by X-ray crystallography.

Recent studies of the photochemistry of 4-pyrones¹⁻³ have shown a wide variety of end-products, depending upon the solvent and the substitution pattern, but all the reactions can be accommodated within a fairly simple mechanistic scheme¹ involving, initially, either formation of a bond between the 2- and 6-positions or [2 + 2]-cycloaddition to the 2,3-double bond. A number of analogues⁴ fit into the same pattern. This report describes an unusual dimerisation which occurs for (1)



Scheme 1

in which the exocyclic oxygen has been replaced by a dicyanomethylene group which has a similar electron-withdrawing effect, but for which $n\pi^*$ excited states cannot be involved.⁵

Irradiation of the dicyanomethylene-pyran⁶ (1) in methanol (0.02 mol dm⁻³, medium-pressure mercury lamp, Pyrex immersion well) led, after preparative layer chromatography, to an orange crystalline product (30%, m.p., from MeOH, 217–217.5 °C). Elemental and mass spectrometric analysis indicated the formula C₂₁H₁₈N₄O₂ corresponding to two molecules of pyran plus one of methanol minus water. Single-crystal X-ray analysis was necessary to show that the structure was (2), as in Figure 1.† The spectroscopic data‡ are in accord with this structure.

Small quantities of a second orange product (<10%, m.p. >330 °C) were also isolated by p.l.c. This was tentatively

† *Crystal Data*: C₂₁H₁₈N₄O₂, orthorhombic, space group *Pccn* with $a = 20.312(8)$, $b = 25.512(11)$, $c = 8.842(4)$ Å, $U = 4582(4)$ Å³, $M = 358.4$, $Z = 8$, $D_c = 1.04$ g cm⁻³. Mo- K_α radiation ($\lambda = 0.71069$ Å). $R = 0.078$ for 925 reflections [$I/\sigma(I) > 3.0$] corrected for Lorentz and polarisation and absorption effects. All non-hydrogen atoms were refined with anisotropic temperature factors. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ ¹H N.m.r. data for (2): δ (CDCl₃) 6.59 (1 H, s), 6.01 (1 H, s), 5.55 (1 H, s), 4.09 (3 H, s), 2.53 (3 H, s), 2.35 (3 H, s), 2.27 (3 H, s), and 2.09 (3 H, s); i.r. (CHCl₃) ν_{\max} 2210s, 1670s, and 1582s cm⁻¹; u.v. (MeOH) λ_{\max} 449 nm (ϵ 13 800), (cyclohexane) λ_{\max} 424 nm; m/z 358 (100%), 357 (23), and 172 (11); M^+ , 358.1410 (calc. 358.1429).

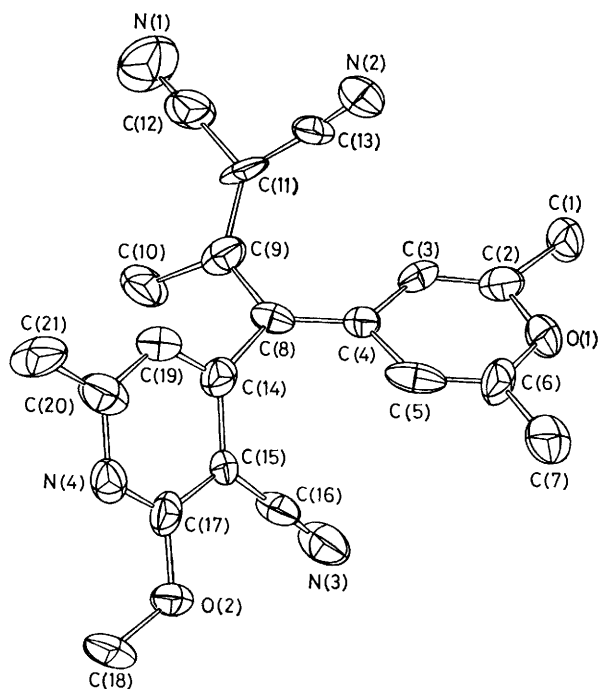
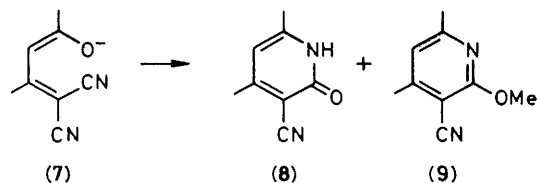


Figure 1. X-Ray structure of (2).

identified as the corresponding pyridone (3) on the basis of the spectroscopic data[§] and by analogy.

The formation of these products is most readily explained by postulating an initial [2 + 2]-cycloaddition to give (4) followed by a deep-seated rearrangement (Scheme 1). Heterolysis of the cyclobutane ring in (4) leads *via* the highly stabilised zwitterion (5) to (6) in which the bottom left portion of the products is complete. The heterolysis is reminiscent of

[§] ¹H N.m.r. data for (3): δ (CDCl₃) 5.99 (2 H, br s), 5.79 (1 H, s), 2.47 (3 H, s), 2.31 (3 H, s), 2.27 (3 H, s), and 2.16 (3 H, s); δ (CD₃SOCD₃) 6.45 (1 H, s), 6.10 (1 H, s), 6.07 (1 H, s), 3.30 (1 H, s, temperature dependent), 2.26 (6 H, s), 2.21 (3 H, s), and 2.17 (3 H, s); i.r. (Nujol mull) ν_{\max} 2208s, 1668s, 1648s, and 1611s cm⁻¹; u.v. (MeOH) λ_{\max} 443 and 352 nm; m/z 344 (100%), 343 (21), and 172 (22); M^+ , 344.1265 (calc. 344.1273).



Huisgen's study⁷ of the addition of tetracyanoethylene to enol ethers in which a similar cleavage of cyclobutanes occurs in polar solvents.

The species (7), a simpler analogue of (6), is an early intermediate in the Knoevenagel condensation of acetylacetone and malononitrile which has been reported to lead to the pyridone (8).⁸ The analogy with (6) \rightarrow (2) + (3) is strengthened by our finding that careful chromatography of the mother liquors from the reaction of acetylacetone and malononitrile in methanol catalysed by triethylamine afforded a *ca.* 1% yield of the methoxypyridine (9). Conversion of (6) and (7) into products thus differs only in the proportions of these products. The mechanism of this type of heterocyclisation has been discussed in detail.⁹

These results illustrate a new facet of the photochemistry of pyrones and their analogues in which an exocyclic double bond is involved in a cycloaddition as well as the 2,3-double bond, and contrasts with 2,6-dimethyl-4-pyrone itself in which the various dimers³ are all derived by cycloadditions at the 2,3-double bond.

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