PHOTOPRODUCTS FROM 5-ARYLPYRAZINE-2,3-DICARBONITRILE, STRUCTURE REVISION FOR THE MAIN PRODUCT

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Photoproduct from 5-(3,4-dimethoxyphenyl)pyrazine-2,3-dicarbonitrile was determined to be a mixture of 2-decyano and 3decyano derivative. The similar results were obtained with 5-[(benzo-15-crown-5)-4'-yl]pyrazine-2,3-dicarbonitrile.

In a series of photochemical studies on crown ether derivatives we have reported the enhancing effect of sodium ion on the photoreactivity of 5-[(benzo-15crown-5)-4'-yl]pyrazine-2,3-dicarbonitrile (1).¹⁾ The photochemical reaction of 5-(3,4-dimethoxyphenyl)pyrazine-2,3-dicarbonitrile (2), a reference compound of 1, was also studied. In the previous paper¹⁾ we reported the photoreactions of 1 and 2, and structures 3 and 4 were erroneously given to the photoproducts. Detailed analyses, however, clarified that the photoproduct was a mixture in each case. In this paper we like to revise the structures of the main products.



Irradiation¹⁾ of 2 in the presence of triethylamine gave the product which was assigned the structure 4 in the previous paper.¹⁾ We succeeded in the separation of crude product into two components 4 and 6 (1:6)³⁾ by repeated chromatography on preparative TLC plate of silicagel. The major product 6 shows a strong absorption at 2245 cm⁻¹ and H-NMR signals of the pyrazine protons at δ 8.87 and 9.09 as doublets (J=2 Hz). On the other hand, the minor product 4 shows a weak absorption at 2250 cm⁻¹ and the pyrazine protons resonate at δ 8.75 and 9.19 as singlets. In a series of studies on the derivatives of 5-arylpyrazine-2-carbonitrile and 5-arylpyrazine-3-carbonitrile,⁴⁾ the nitrile of the former always shows stronger IR-absorption at lower wave number since the nitrile group of the former has more polar character by conjugation with the para-aryl group. A paracoupling constant of the protons on pyrazine is reported to be <u>ca</u>. 2 Hz, whereas a meta-coupling constant is nearly zero.⁵⁾ The product 6 has a similar UV-spectrum to that of known 3-amino-5-(3,4-dimethoxyphenyl)pyrazine-2-carbonitrile (7).⁴⁾



Fig. 1. UV-spectra of 4 (----), 6 (----), and 7 (-----) in acetonitrile.

Both spectra have strong absorption band at 350-370 nm region whereas the corresponding absorption of **4** reduces its intensity(Fig.1). These bands may be assigned to an intramolecular CT-band and the location of nitrile group at the para-position of aryl group should promote the transition in the observed trend.

Irradiation of the crown ether derivative 1 under the same conditions gave essentially the same results but the product mixture could not be separated into pure 3and 5. The spectroscopic characteristics described for the analyses of 4 and 6 are observed in the spectra of the product mixture from 1.

The structures 3 and 4, which were erroneously given to the major products, are proved to be the structures of the minor products from 1 and 2 respectively. The descriptions in the previous paper,¹⁾ including the mechanism (Scheme 1) and the effect of alkali metal ion on the photoreactivity, are essentially valid by substituting 5-arylpyrazine-3-carbonitrile (3 and 4) with 5-arylpyrazine-2-carbonitrile (5 and 6) as the structure of the major products.

$$(2)^{*} + Et_{3}^{N} \xrightarrow{i) S. E. T.}_{ii) H^{+}-transfer} \xrightarrow{Ar}_{Ar} N \xrightarrow{V}_{CN} CN \xrightarrow{V}_{N} V \xrightarrow{CN}_{H} CN \xrightarrow{V}_{N} V \xrightarrow{CN}_{H} CN \xrightarrow{V}_{H} CN$$

Scheme 1.

References

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- 2) Irradiations were carried out by a 450 w high pressure mercury lamp mounted in a rotary irradiation apparatus (Rikosha RH-400) through Pyrex reaction tubes. A solution of 1 or 2 $(1.4\times10^{-2} \text{ mol/dm}^3)$ was irradiated for 10 h.
- 3) 4, mp 179-180 °C; IR(CHCl₃) 2250 cm⁻¹; H-NMR(CDCl₃) & 3.96(3H, s), 4.01(3H, s), 7.04(1H, d, J=9 Hz), 7.56-7.70(2H, m), 8.75(1H, s), 9.19(1H, s).
 6, mp 141-142 °C; IR(CHCl₃) 2245 cm⁻¹; H-NMR(CDCl₃) & 3.96(3H, s), 3.98(3H, s), 7.01(1H, d, J=9 Hz), 7.59-7.75(2H, m), 8.87(1H, d, J=2 Hz), 9.09(1H, d, J=2 Hz).
- 4) H. Hirano, R. Lee, and M. Tada, J. Heterocycl. Chem., 19, 1409 (1982).
- 5) R. H. Cox and A. A. Bothner-By, J. Phys. Chem., <u>72</u>, 1642 (1968); L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, London (1969), p. 307.

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