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

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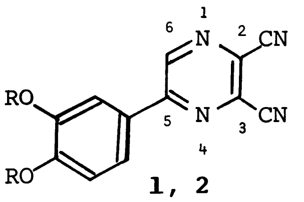
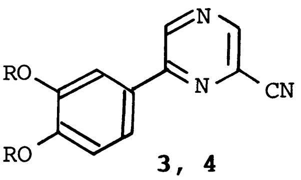
Photoproduct from 5-(3,4-dimethoxyphenyl)pyrazine-2,3-dicarbonitrile was determined to be a mixture of 2-decyano and 3-decyano derivative. The similar results were obtained with 5-[(benzo-15-crown-5)-4'-yl]pyrazine-2,3-dicarbonitrile.

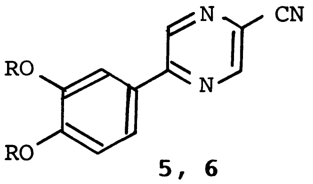
In a series of photochemical studies on crown ether derivatives we have reported the enhancing effect of sodium ion on the photoreactivity of 5-[(benzo-15-crown-5)-4'-yl]pyrazine-2,3-dicarbonitrile (**1**).[1)] The photochemical reaction of 5-(3,4-dimethoxyphenyl)pyrazine-2,3-dicarbonitrile (**2**), a reference compound of **1**, was also studied. In the previous paper[1)] 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.



1, 2



3, 4



5, 6

1, 3, 5 : R=$CH_2CH_2O(CH_2CH_2O)_2CH_2CH_2$ **2, 4, 6** : R=CH_3

Irradiation[1)] 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 para-coupling constant of the protons on pyrazine is reported to be ca. 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)]

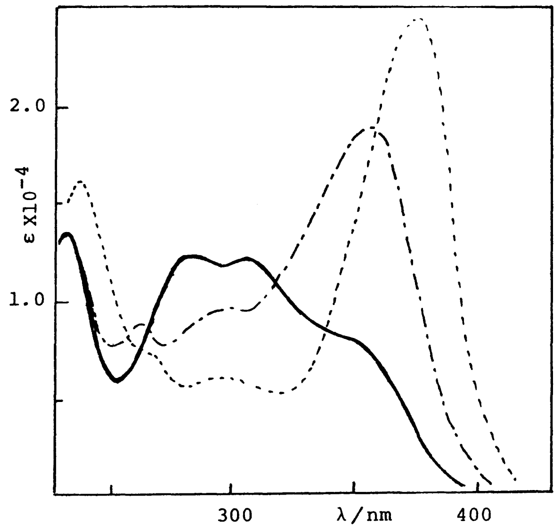
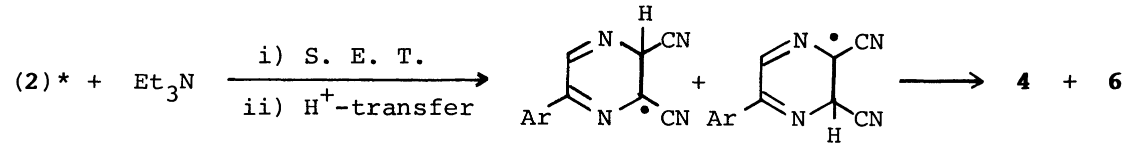


Fig. 1. UV-spectra of **4** (——), **6** (—·—·), and **7** (------) in acetonitrile.

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 **3** and **5**. The spectroscopic characteristics described for the analyses of **4** and **6** are obsereved 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.



Scheme 1.

References

1) M. Tada, H. Hamazaki, and H. Hirano, Chem. Lett., 1980, 921; Bull. Chem. Soc. Jpn., 55, 3865 (1982).
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** (1.4X10^{-2} mol/dm^3) was irradiated for 10 h.
3) **4**, mp 179-180 °C ; IR(CHCl$_3$) 2250 cm^{-1}; H-NMR(CDCl$_3$) δ 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 ℃ ; IR(CHCl$_3$) 2245 cm^{-1}; H-NMR(CDCl$_3$) δ 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., 72, 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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