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EFFECT OF GUEST CATION ON THE PHOTOREACTIVITY OF THE PYRAZINE DERIVATIVES HAVING CROWN ETHER MOIETY[1)]

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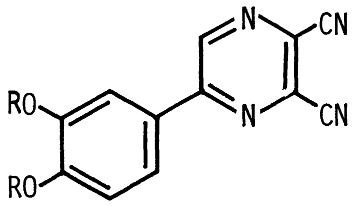
Irradiation of the acetonitrile solution of 4'-(5,6-dicyanopyrazin-2-yl)benzo-15-crown-5 (1) or 4-(5,6-dicyanopyrazin-2-yl)-1,2-dimethoxybenzene (2) in the presence of triethylamine gave monodecyano-derivative (3 or 4) and bisdecyano-derivative (5 or 6). Sodium ion stimulates the reaction of the crown ether derivative.

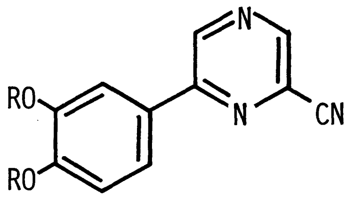
A guest cation shows a diversed effect on the photoreactivity of crown ether derivatives. We have counted up "a pairing effect",[2)] "the effect on oxidation potential",[3)] "the effect on the quantum yield of the triplet state",[4)] and "the stabilization effect of a transition state".[5)] Here we report another type of effect, "the effect on reduction potential", on the photoreactivity of a crown ether derivative, 4'-(5,6-dicyanopyrazin-2-yl)benzo-15-crown-5 (1).[6,7)]

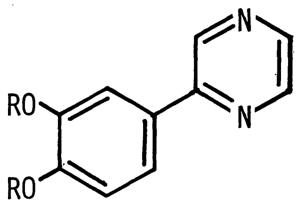
A pyrazine derivative having electron attractive substituents is a good mimicry of an oxidation-reduction coenzyme such as flavin, in which the aromatic system containing nitrogen plays a leading part of the redox system.

An acetonitrile solution of benzo-15-crown derivative (1) (1.4×10^{-2} mol/dm^3) was irradiated in the presence of triethylamine (5.6×10^{-2} mol/dm^3), and 4'-(6-cyanopyrazin-2-yl)benzo-15-crown-5 (3)[7)] was obtained in 80% yield.[8)] 4-(5,6-Dicyanopyrazin-2-yl)-1,2-dimethoxybenzene (2) reacted in a similar way and gave 4-(6-cyanopyrazin-2-yl)-1,2-dimethoxybenzene (4) in 80% yield. The structures of the products (3 and 4) were easily assigned from NMR spectra. A new aromatic hydrogen at the pyrazine ring (δ=8.95 for 3 and 8.94 for 4) shows meta coupling (J=2 Hz) with the original hydrogen on the pyrazine ring (δ=9.20 for 3 and 9.18 for 4). Prolonged irradiation in the presence of large excess of triethylamine gave bisdecyano-pyrazine derivatives (5 and 6).[9)]

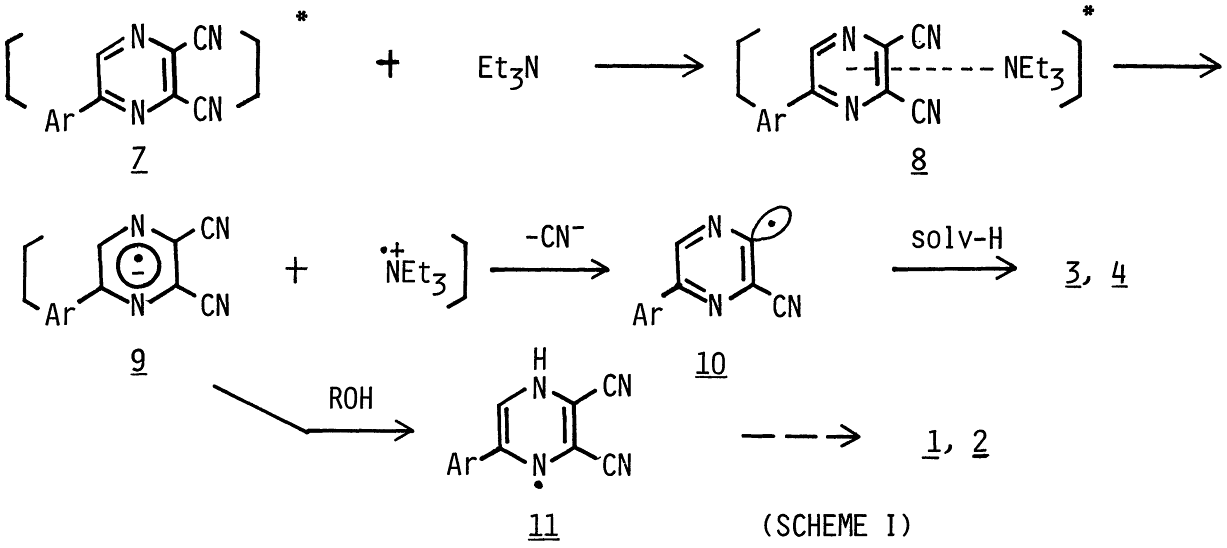
The photolysis of aromatic halides in the presence of triethylamine causes the reductive cleavage of halogen on benzene ring.[10)] Photoreaction of dicyanobenzene in the presence of triethylamine, however, gives substitution products through a single electron transfer from the amine to the excited aromatics.[11)] The photosubstitution of dicyanobenzene must involve a proton transfer in the excited complex corresponding to 8 or the radical ion pair corresponding to 9, but the radical anion of dicyanopyrazine derivative (1) is considered to be stable enough to escape the cage of the radical ion pair (9)(Scheme 1). The escaped radical anion looses a cyanide ion to give a radical (10) which abstracts a


1, 2


3, 4


5, 6

1, 3, 5: RR= $O(CH_2CH_2OCH_2CH_2)_2$ 2, 4, 6: R= CH_3



(SCHEME I)

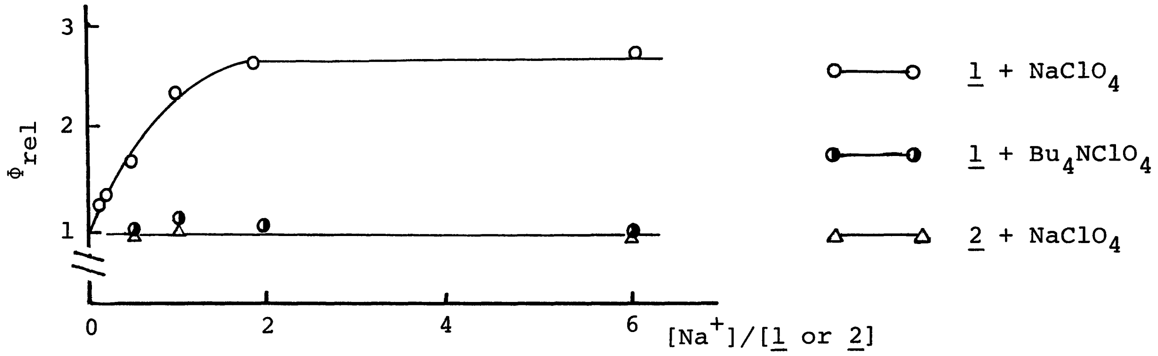


Fig. I. Effect of $NaClO_4$ on the relative quantum yield(Φ_{rel}) of photolyses of 1, and 2 (1.4×10^{-2} mol/dm^3 in CH_3CN).

hydrogen from the solvent to give the reduction products (3 and 4). The formation of radical (10) from radical anion (9) has many similar examples as seen in photochemical dehalogenation of aromatic halides$^{10)}$ or in photochemical $S_{RN}1$ reaction.$^{12)}$ In these reactions the anion radicals are formed by the electron transfer from the electron donors such as amine and organic or inorganic anions.

Addition of water or methanol to the reaction system depressed the reaction of 1 and 2. The solvent cage consisting of protic solvents can protonate the radical anion (9) to give radical (11), which may revert to the radical anion or give an adduct with the amine. Protonation occurs at ipso-position in the case of dicyanobenzene to give a substitution product.$^{11)}$ The radical anion (9), however, must be protonated at the more basic nitrogen to give radical (11) and 11 or its adduct with the amine cannot eliminate HCN to give a substitution product.

These assumptions of the reaction profile, an electron transfer mechanism, are supported by the effect of sodium ion to the reaction systems. The complex formation between the crown part of 1 and sodium ion ($K_{ass}=2.9 \times 10^3 \text{mol}^{-1}\text{dm}^3$ in acetonitrile, 25°C) must raise the reduction potential of the excited 1 and promote the electron transfer process. The relative quantum yields of the reduction products (3 and 4) in the presence of sodium perchlorate is shown in Fig.1. Since 1 has a strong absorption between 300 - 450 nm; $\lambda_{max}^{CH_3CN}$ (ε), 370 (1.86×10^4) and 356 nm (1.84×10^4) (Na^+- complex), the concentration of 1 for the reaction (1.4×10^{-2}mol dm^{-3}) is enough to absorb the whole light from the lamp in this region. No effect was observed by the addition of tetrabutylammonium perchlorate to the reaction system of crown-derivative (1). The photolysis of dimethoxy-derivative (2) was not affected by sodium perchlorate. These findings clearly show that the effect of sodium ion on the photoreaction of crown-derivative (1) is deeply associated with the formation of host-guest complex between the crown ether and sodium ion.

Formation of bisdecyano-derivatives (5 and 6) must take the same process to the formation of 3 and 4 from 1 and 2 respectively, but 3 and 4 are less reactive than 1 and 2 due to the lower reduction potential.

Monocyano-derivative (3) is strongly fluorescent though the starting dicyano-derivative (1) is non-emissive. The fluorescence of 3, $\lambda_{max}^{emis.}$ 499 nm, is quenched by triethylamine. Stern-Volmer plots of the fluorescence quenching (3, 1.00×10^{-4} mol dm^{-3} in CH_3CN) by triethylamine ($k_q\tau = 0.23 \text{ mol}^{-1}\text{dm}^3$, without $NaClO_4$) is stimulated by the addition of sodium perchlorate ($k_q\tau = 0.83 \text{ mol}^{-1}\text{dm}^3$, [$NaClO_4$] 1.00×10^{-3} mol dm^{-3}). In contrast, sodium perchlorate does not affect the quenching efficiency of fluorescence from dimethoxy-derivative (4) by triethylamine. It is conceivable that the increase of $k_q\tau$ value is due to the increase of τ-value. However, the intensity of fluorescence from 3 increases moderately in the presence of sodium perchlorate. Thus the rate constant of fluorescence (k_f) increases and the life time [$\tau = 1/(k_f + k_d)$] must be diminished when non-radiative decay (k_d) is not much affected. The increase of $k_q\tau$ value, therefore, must be mostly due to the increase of k_q value.$^{13)}$

These results are in good accordance with the electron transfer mechanism of the photochemical behavior of the pyrazine derivatives (1,2,3, and 4). The effect of sodium ion on the photoreactivity of 1 is due to the raise of reduction potential.

REFERENCES AND NOTES

1) Photochemistry of host guest complex, part VI. Part V, H. Hirano, K. Kurumaya, and M. Tada, Bull. Chem. Soc. Jpn., under submission.

2) M. Tada and H. Hirano, Tetrahedron Lett., 1978, 5111.

3) M. Tada, A. Suzuki, and H. Hirano, J. Chem. Soc. Chem. Commun., 1979, 1004.

4) M. Tada, H. Hirano, and A. Suzuki, Bull. Chem. Soc. Jpn., 53, in press (1980).

5) A. Suzuki and M. Tada, Chem. Lett., 1980, 515.

6) Compound (1) was prepared by the following sequence; (1) acetylation of benzo-15-crown-5 with acetic acid in polyphosphoric acid, (2) selenium dioxide oxidation of the resulting 4'-acetylbenzo-15-crown-5, and (3) condensation of the dicarbonyl product with diaminomaleonitrile. Compound (2) was prepared by the same procedure to that for 1.

7) All new compounds described in this report gave correct elemental analyses and spectral data. 1, mp 151°C; IR(nujol), 2249 cm^{-1}; NMR($CDCl_3$)(δ), 3.76(8H, s), 3.96(4H, m), 4.22(4H, m). 6.98(1H, d, J=9 Hz), 7.75(2H, m), and 9.23(1H, s); $\lambda_{max}^{CH_3CN}$ (ε), 370 nm (1.86 X 10^4). 2, mp 203°C; IR(nujol), 2249 cm^{-1}; NMR($CDCl_3$) (δ), 4.01(3H, s), 4.04(3H, s), 7.08(1H, d, J=9), 7.74(2H, m), and 9.25(1H, s); $\lambda_{max}^{CH_3CN}$ (ε), 369 nm (1.93 X 10^4). 3, mp 137°C; IR(nujol), 2248 cm^{-1}; NMR($CDCl_3$) (δ), 3.75(8H, s), 3.93(4H, m), 4.20(4H, m), 7.03(1H, d, J=9), 7.75(2H, m), 8.95(1H, d, J=2), and 9.20(1H, d, J=2). 4, mp 143°C; IR(nujol), 2250 cm^{-1}; NMR($CDCl_3$) (δ), 4.01(3H, s), 4.03(3H, s), 7.07(1H, d, J=9), 7.72(2H, m), 8.94 (1H, d, J=2), and 9.18(1H, d, J=2). 5, mp 109°C; NMR($CDCl_3$)(δ), 3.77(8H, s), 3.92(4H, m), 4.18(4H, m), 6.95(1H, d, J=9), 7.55(1H, dd, J=9 and 2), 7.62(1H, d, J=2), 8.44(1H, d, J=2.5), 8.57(1H, diff. dd), and 8.98(1H, d, J=2). 6, mp 75°C;NMR($CDCl_3$) (δ), 3.94(3H, s), 3.97(3H, s), 6.99(1H, d, J=9), 7.58 (1H, dd, J=9 and 2), 7.67(1H, d, J=2), 8.48(1H, d, J=2.5), 8.60(1H, diff. dd), and 9.02(1H, d, J=2).

8) All irradiations were carried out by a 450 W high pressure Hg lamp mounted in a rotary irradiation apparatus (Rikosha RH-400). Products were isolated by chromatography on silicagel eluted with chloroform or chloroform-benzene.

9) Irradiations of 1 and 2 in CH_3CN-Et_3N (3:1) for 16 h gave 5 and 6 in 40 and 44% yields, respectively.

10) (a) J. Nasielski, A. Kirsch-Demesmae, P. Kirsch, and R. Nasielski-Hinke, J. Chem. Soc., Chem. Commun., 1970, 302; (b) C. Pac, T. Tosa, and H. Sakurai, Bull. Chem. Soc. Jpn., 45, 1169 (1972); and (c) K. Tsujimoto, T. Tasaka, and M. Ohashi, J. Chem. Soc., Chem. Commun., 1975, 758.

11) K. Tsujimoto, K. Miyake, and M. Ohashi, J. Chem. Soc., Chem. Commun., 1976, 386; Bull. Chem. Soc. Jpn., 53, in press (1980).

12) J. F. Bunnett, Acc. Chem. Res., 11, 413 (1978) and references cited therein.

13) Fluorescence of aromatics can be quenched by sodium salts containing counter anions of low oxidation potential such as iodide, but the quenching is negligible by the salt consisting of anion of high oxidation potential. H. Shizuka, T. Saito, and T. Morita, Chem. Phys. Lett., 56, 519 (1978).

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