CHEMISTRY LETTERS, pp. 39-42, 1972. Published by the Chemical Society of Japan

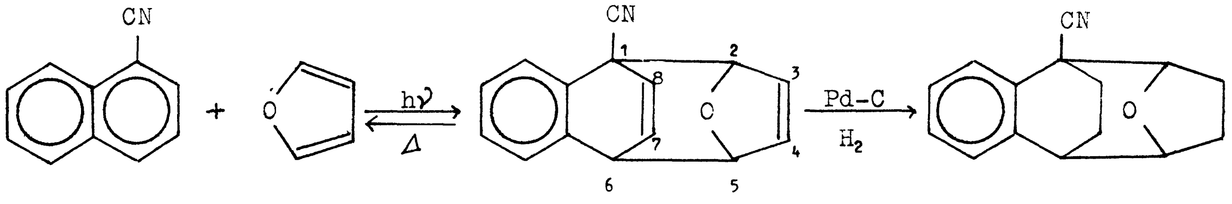
THE PHOTOCHEMICAL (4 + 4) CYCLOADDITION OF FURAN TO α-NAPHTHONITRILE

CHYONGJIN PAC, TAIZO SUGIOKA and HIROSHI SAKURAI
THE INSTITUTE OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OSAKA UNIVERSITY
SUITA-SHI, OSAKA, JAPAN

The photochemical reaction of α-naphthonitrile with furan affords a (4 + 4) cycloadduct, 1-cyano-9,10-benzo-11-oxatricyclo[4,2,2,$1^{2,5}$]-undeca-3,7,9-triene (I), in a good yield, and an exciplex intermediacy is suggested on kinetic and spectroscopic grounds.

The (4 + 4) cycloaddition reactions which are of theoretical interest1) have been well investigated on the photochemical dimerization reactions of anthracene derivatives,2) 2,6-dimethylcoumaline,3) N-methyl-2-pyridone,4) 2-aminopyridine,4) and 2-methoxynaphthalene.5) The intramolecular photo-addition of 1,3-di(α-naphthyl)-propane is of interest in relation to excimer intermediacy.6) In contrast to the photodimerization, cross (4 + 4) cycloaddition reactions between two different molecules have been less investigated; there have been reported two typical examples, the photochemical addition of acyclic 1,3-diene to benzene or naphthalene7) and the photochemical cross dimerization between tetracene and anthracene derivatives.8) The present paper deals with a novel photochemical (4 + 4) cycloaddition reaction of furan to α-naphthonitrile (α-NN) and describes kinetic and spectroscopic results.

Irradiation of a benzene solution of α-NN containing a large excess of furan through a Pyrex glass with a high pressure mercury arc gave a sole 1:1-adduct having mp 86.5 - 87 °C in 70 - 80% isolated yield. The adduct was thermally unstable and quantitatively decomposed into the starting materials above ca. 150 °C.



(I) (II)

The structure of the adduct was determined from the elementary analyses and the following spectral data: ν_{max} (KBr) 3030, 3020, 2990, 2950, 2810, 2220, 1640 and 1180 cm^{-1}; λ_{max}^{MeOH} (ϵ) 260 (543), 268 (550) and 276 nm (483); m/e 153 (100%), 126 (20%) and 68 (30%); δ_{CCl_4} (60 MHz) 3.5 (d-t, $J_{5,6} = J_{6,7} = 6$ Hz, $J_{6,8} = 2$ Hz, C_6-H), 4.35 (d, C_5-H), 4.5 (s, C_2-H), 5.72 (s, C_3- and C_4-H), 6.47 (d-d, $J_{7,8}$ = 8 Hz, C_8-H), 6.78 (d-d, C_7-H) and 6.8 - 7.9 ppm (m, aromatic protons). The coupling constants were determined by a spin decoupling method.

The UV data exhibit a simple non-conjugated benzene chromophore and thus eliminate an 1,2-dihydronaphthalene structure. Since the two vinylic protons at 6.47 and 6.78 ppm and the methine proton at 3.5 ppm consist of an ABX system, an 1,4-dihydronaphthalene structure can be assigned to the adduct. That the adduct has a 2,5-dihydrofuran ring is exemplified by the observation that the signal at 5.72 ppm appears as a singlet at a quite close chemical shift to that of the vinylic protons of 2,5-dihydrofuran (s, 5.84 ppm). Therefore, the (4 +4) cycloadduct structure can be assigned to the adduct.

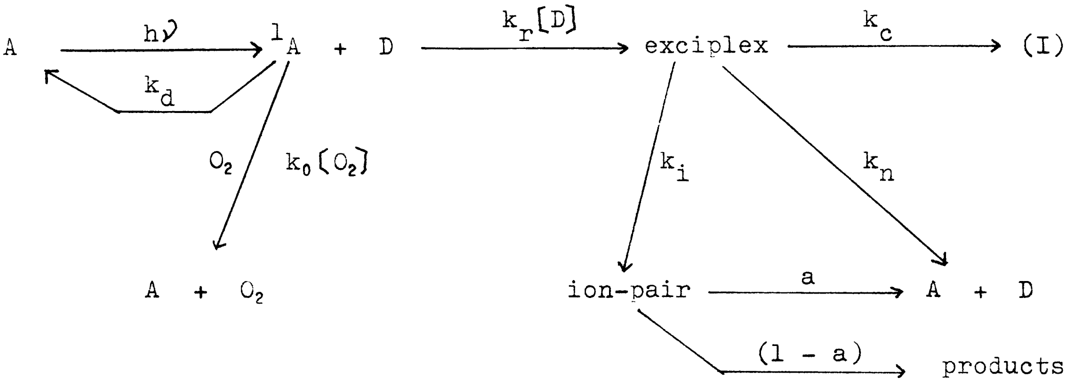
For the adduct (I), however, two stereo-isomers are possible, the one with endo-location of the benzo-ring to the dihydrofuran ring and the other with the exo-location. The C_3 and C_4 protons of the adduct (I) revealed the signal at 0.12 ppm higher field than the vinylic protons in 2,5-dihydrofuran. Moreover, the C_3 and C_4 protons of the hydrogenated isomer (II) appeared at δ 1.68 ppm (center of m), which was 0.17 ppm higher field than the chemical shift of the C_3 and C_4 protons of tetrahydrofuran (δ 1.85 ppm, center of m). These NMR results may be interpreted by the anisotropic effect of the benzo-ring to the vinylic or methylene protons of the endo-located dihydrofuran or tetrahydrofuran ring. Since the anisotropic effect can not be expected for the exo-isomer, the endo-configuration may be preferable, but is not conclusive. X-Ray analyses are now under investigation.

Selective formation of the adduct (I) was confirmed by VPC analyses. When the photolysate was subjected to VPC analyses, no important components except α-NN could be detected. However, hydrogenation of the photolysate on Pd-C yielded only a compound having the same retention time as the hydrogenated isomer (II).

This photochemical reaction was remarkably solvent-dependent. The photolysis of a methanol solution gave a complex mixture in which 10% or less (I) was present. Acetonitrile was a poor solvent for the formation of (I), as well.

In order to clarify the reaction mechanism, the fluorescence spectra of α-NN in the presence of furan were recorded. As furan was added to a cyclohexane solution of α-NN, the fluorescence of α-NN was quenched with blurring of the vibrational structure and broadening of the spectrum. A furan solution of α-NN exhibited a weak and broad fluorescence, quite different from the fluorescence of a tetrahydrofuran solution. Appearence of new emission and endothermic fluorescence quenching are characteristic phenomena for the exciplex formation.$^{9-11)}$ Also with 3-methylfuran, 2-methylfuran and 2,5-dimethylfuran, new emissions appeared with the respective maxima of 390, 390 and 405 nm, which were shifted to longer wavelength with number of methyl substituent. In the case of 2,5-dimethylfuran, an isoemissive point appeared at 375 nm. On the other hand, when methanol was used as solvent, only fluorescence quenching could be observed and no new emission appeared.

In contrast to the fluorescence spectra, the UV spectra of α-NN in furan were essentially identical to those of tetrahydrofuran solutions. All of these spectroscopic results clearly show the exciplex formation between the lowest excited singlet α-NN and ground state furan and may suggest that the fluorescence quenching is due to the exciplex formation. Therefore, a mechanism involving an exciplex as an intermediate was suggested.



A = α-NN and D = furan.

$$F_0/F = 1 + k_r\tau[D] \quad (1); \quad 1/\phi = \left(1 + \frac{1}{k_r\tau[D]}\right)\left(\frac{k_c + k_n + k_i}{k_c + (1 - a)k_i}\right) \quad (2)$$

$$\tau = 1/k_d \text{ for de-gassed runs and } 1/(k_d + k_0[O_2]) \text{ for air saturated runs} \quad (3)$$

The fluorescence quenching constants ($k_r\tau$) were determined to be 0.57 M^{-1} for de-gassed samples of cyclohexane solutions of α-NN (1.3 x 10^{-4} M) and 0.35 M^{-1} for air saturated samples of the solutions. Quantum yields for the disappearence of α-NN at 313 nm were determined by potassium ferrioxalate actinometry.12) From plots of the reciprocals of the quantum yields versus the reciprocals of furan concentrations, the slopes and the intercepts of the straight lines were determined to be respectively 130 M and 90 for de-gassed samples and 230 M and 90 for air saturated samples ([α-NN] = 1.3 - 1.75 M). On application of these values to the equation (2), k_r/k_d and $k_r/(k_d + k_0[O_2])$ were calculated to be respectively 0.7 M^{-1} and 0.4 M^{-1} which were in a practical agreement with the respective fluorescence quenching constants for de-gassed and air saturated samples. These kinetic results unambiguously establish that the photochemical (4 + 4) cycloaddition reaction takes place in the lowest excited singlet state of α-NN and suggest the exciplex intermedicy, since the fluorescence quenching may be ascribed to the exciplex formation.

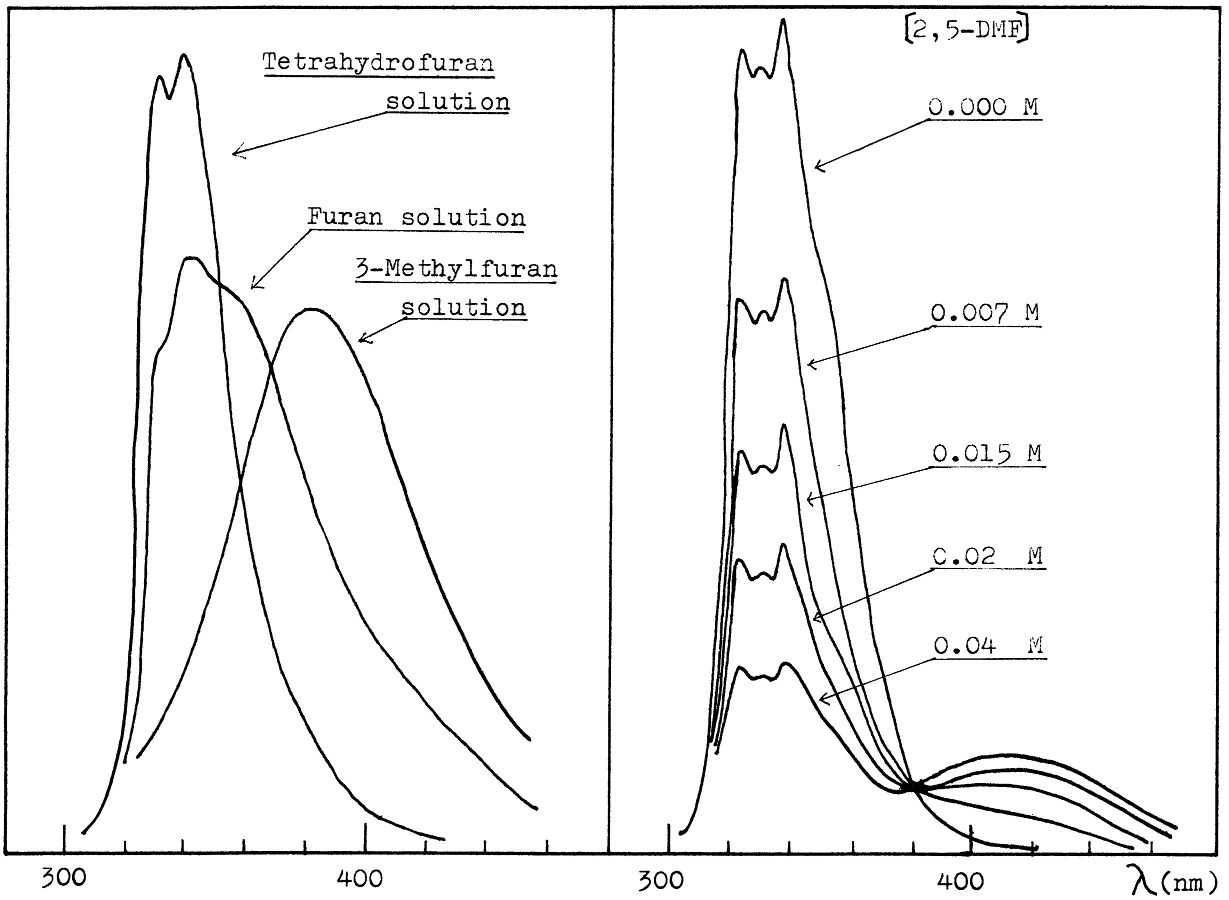
The solvent-dependent character of the photochemical reaction as well as the solvent dependency of the fluorescence quenching may also reflect the exciplex intermediacy. It is well known that electron transfer is dominant over the other processes ($k_i \gg k_n + k_c$) in polar solvents, while $k_n > k_c \gg k_i$ in non-polar solvents.9, 10, 13) In methanol, therefore, an ion-pair is formed exclusively and leads to other products than the adduct (I).

With 3-methylfuran, an 1:1-adduct was obtained also in a good yield. On the other hand, the photochemical rection with 2-methylfuran was very slow to give only a small amount of an adduct. With thiophene, no reaction took place, while the photochemical reaction with pyrrole gave a mixture of products.

Details will be published in a separate paper.

REFERENCES

1) R.Hoffman and R.B.Woodward, J. Amer. Chem. Soc., 87, 2046 (1965).
2) D.J.Trecker, "Organic Photochemistry" ed. by O.L.Chapman, Marcel Decker, New York, 1969, vol. 2, p. 85.
3) P.DeMayo and R.W.Yip, Proc. Chem. Soc., 1964, 84.
4) E.C.Taylor, R.O.Kan and W.W.Paudler, J. Amer. Chem. Soc., 83, 4484 (1961); E.C.Taylor and R.O.Kan, ibid., 85, 776 (1963).
5) J.S.Bradshaw and G.S.Hammond, ibid., 85, 3953 (1963); J.S.Bradshaw, W.B.Nielson and D.P.Rees, J. Org. Chem., 33, 259 (1968).
6) E.A.Chandros and C.J.Dempster, J. Amer. Chem. Soc., 92, 703 (1970).
7) G.Koltzenburg and K.Kraft, Tetrahedron Lett., 1966, 389; K.Kraft and G.Koltzenburg, ibid., 1967, 4357; 4723.
8) H.Bouas-Laurent and A.Castellan, Chem. Commun., 1970, 1648.
9) A.Weller, Pure Appl. Chem., 16, 115 (1968); H.Knibbe, D.Rehm and A.Weller, Z. Bunsenges. Physik. Chem., 72, 257 (1968).
10) N.Mataga, T.Okada and N.Yamamoto, Chem. Physics Lett., 1, 119 (1967).
11) H.Yamashita and M.Koizumi, Bull. Chem. Soc. Japan, 41, 2313 (1968).
12) C.G.Hatchard and C.A.Parker, Proc. Roy. Soc. (London), A235, 518 (1956).
13) K.Kaneta and M.Koizumi, Bull. Chem. Soc. Japan, 40, 2254 (1967).



Figures. The left; the fluorescence spectra of α-NN solutions (ca. 1.3 x 10^{-4}M). The intensities of the respective spectra are in arbitrary units. The right; the fluorescence spectra of cyclohexane solution of α-NN (ca. 2.5 x 10^{-4}M) in the presence of 2,5-dimethylfuran.

(Received October 6, 1971)