THE PHOTODIMERIZATION OF NAPHTHO[1,2-c]FURAZAN[1]

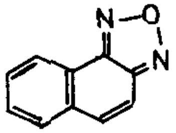
Makoto Nitta, and Toshio Mukai*

Department of Chemistry, Faculty of Science, Tohoku University.

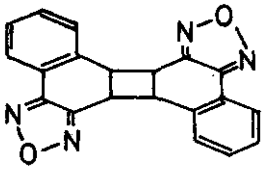
Sendai, Japan

Irradiation of naphtho[1,2-c]furazan (I) afforded two photodimers (II) and (III) accompanied by fragmentation products. The structure of the dimers was assigned on the basis of the solvent dependency for the dimerization as well as the degradation reactions of the dimers. In addition, it was suggested that the photodimerization took place via a triplet state of I.

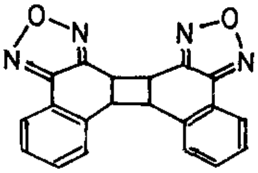
Recently it was reported by Cantrell and Haller[2] and by our group[3] that 1,2,5-oxadiazoles (furazans), upon irradiation, underwent a cycloreversion reaction and afforded a nitrile and a nitrileoxide. Futhermore, we have found that in the presence of an oxygen acceptor, the irradiation of several furazan derivatives led to the formation of 1,4-dinitriles in fairly good yields.[4] It was pointed out that, however, in the case of naphtho[1,2-c]-furazan (I) which contains an styryl chromophore, a photodimer II, mp 309°, was obtained, although in poor yield, in addition to the formation of cis- and trans-o-cyanocinnamonitrile.[4b] We wish to describe here our additional result of the photodimerization of I, which is a new example of the photochemical dimerization of compounds possessing a heterocycle.



I



II (anti or syn)



III (anti or syn)

In order to increase the yield of the photodimer, we carried out the irradiation of I in various solvents and at several concentrations. Also we could isolate another dimer III, mp 261°. The results obtained are shown in Table 1. Increasing the concentration of the solution of I resulted in an increase of the yields of the photodimers II and III, and the ratio of II/III decreased in polar solvents such as methanol and acetonitrile.

Table 1. Irradiation of I in various solvents and concentrations[a)]

Solvent	conc. of I (M)	recovery of I (%)	yield (%) II	III	II/III
C_6H_6	10^{-1}	61.6	10.8	0.4	26.1
CH_3OH[b)]	5×10^{-1}	49.3	14.5	6.8	2.24
CH_3OH	10^{-1}	52.6	13.7	6.4	2.17
CH_3CN[b)]	5×10^{-1}	43.3	22.0	15.7	1.41
CH_3CN	10^{-1}	49.2	9.4	7.1	1.13

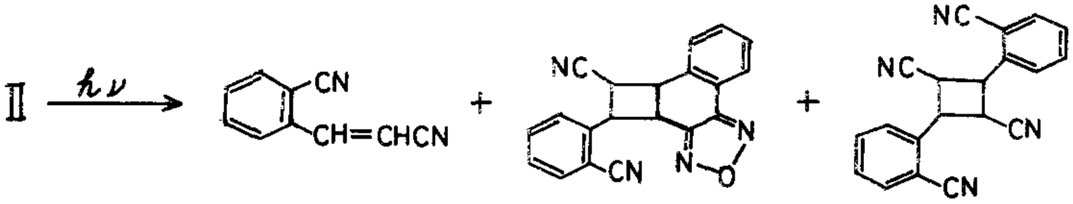
a) Rayonet (MGR-100 RPR-350 nm light), 5 hr irradiation.

b) In methanol or acetonitrile, solvent-incorporated products were also obtained.[4b)]

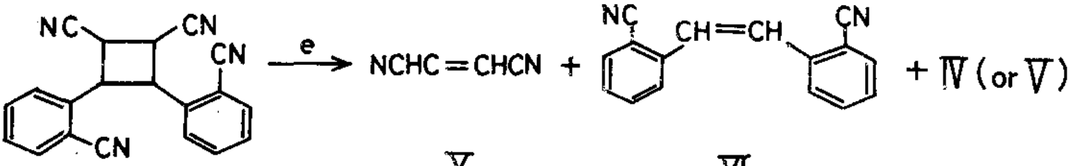
The heating of II and III at their melting point resulted in the thermal decomposition and naphthofurazan I was recovered. In addition, mass spectra of II and III show the peaks due to I (m/e 170, 100%) and its subsequent fragment ions. This evidence along with the following uv and nmr spectra supports that II and III are dimers possessing a cyclobutane ring. The uv and nmr spectra of II and III are as follows: II; uv max in tetrahydrofuran, nm (log ε), 225 (4.60), 260 (4.29), 293 (3.76), 302 (4.08); nmr (100 MHz, DMSO-d_6), τ 4.44 (multiplet, 4H), 1.6-2.45 (multiplet, 8H), III; uv max in tetrahydrofuran, nm (log ε), 234 (4.35) 260 (4.37), 293 (3.76), 302 (3.75), nmr (100 MHz, DMSO-d_6), τ 4.48 (multiplet, 4H), 1.6-2.45 (multiplet, 8H). Usually, nmr splittin constants give useful information concerning the configuration of the cyclobutane ring.[5] However, the dimers II and III are so sparingly soluble in the usual organic solvents that it is difficult to obtain clear nmr spectra or to measure dipole moments for analysis, and therefore a choice of structures for II and III from the four possible structures seemed impossible.

Thus, we applied our method,[4a] in which 1,4-dinitriles should be formed by cleavage of the furazan ring, for the determination of the structure of dimers II and III. When a tetrahydrofuran solution of II was irradiated using a high pressure mercury lamp (Toshiba H400-P) in the presence of triethylphosphite, four products IV, V, VI and VII were obtained in 15, 10, 25, and 9% yields respectively. Two of them, VI mp 230°, and VII mp 315°, are new photo-products[6] and exhibit the following spectra: VI; uv max in tetrahydrofuran, nm (log ε), 225 (4.73), 260 (4.42), 286 (4.02), 299 (3.97); nmr (100 MHz, DMSO-d_6), τ 5.15 (multiplet, 4H), 1.80-2.70 (multiplet, 8H); mass spectrum (m/e), 170 (100 %), 154 (6 %). 140 (58 %), 127 (13 %), VII; uv max in tetrahydrofuran, nm (log ε), 226 (4.67), 277 (3.78), 285 (3.80); nmr (100 MHz, DMSO-d_6) τ 5.21 (singlet, 4H), 1.98-2.53 (multiplet, 8H); mass spectrum (m/e), 154 (100 %), 127 (48 %).

Under the same irradiation condition, VI afforded VII in addition to IV and V, but IV or V did not undergo the dimerization leading to VII, thus indicating that VI and VII may be primary photo-products from II. These facts coupled with elemental analyses[6] suggest that VI is a product resulting from the cleavage of one furazan ring and VII is a product of two furazan ring cleavage. Application of the same irradiation procedure to dimer III did not afford cyclobutane derivatives such as VII and instead a new product VIII, mp 210°, was obtained in 6% yield accompanied by the formation of IV and V (29 and 23% yields). The product VIII is a product of one furazan ring cleavage and exhibits the



IV(cis)and V (trans)   VI   VII



IX   X   XI

following spectral data; uv max in tetrahydrofuran, nm (log ε), 234 (4.41), 261 (4.24), 293 (3.77), 302 (3.72): nmr (100 MHz, DMSO-d_6), τ 5.12 (multiplet, 4H), 1.98-2.53 (multiplet, 8H); mass spectrum is similar to that of VI. If the dimer II had the head-to-head structure, the degradative cyclobutane should have a structure of IX . The mass spectrum of IX is expected to exhibit the peaks ascribed to each of IV (or V), X and XI.[7] However, this was not the case and spectrum of VII exhibits only the peak due to IV or V, indicating that VII has 1,3-dicyanocyclobutane structure. Consequently, the dimer II should be the head-to-tail structure. However, in this stage, our findings did not enable us to determine whether II is of syn or anti type. In addition, it is well known that the formation of the dimer having the larger permanent dipole moment is favored in polar media.[8] As shown in Table 1, the ratio of the dimer III was increased in polar solvents compared with in nonpolar solvents. On the basis of this fact, we would propose the head-to-head structure for the dimer III.

In order to clarify the excited state for the dimer formation, we irradiated a methanolic solution of I (10^{-1} M) in the presence of piperylene (5×10^{-1} M) as a quencher under the same irradiation conditions. The yields of II and III decreased one fifth compared to the case with no quencher present, but the formation of IV and V was not affected.[9] Futhermore, we found that absorption maxima of I which appear at 290, 323, 338 nm in n-hexane shift to 292, 326, 340 nm in methanol. This may suggest that the excited state is probably a π-π^* configuration.

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9 This fact probably suggests that IV and V were formed via a singlet state and dimers II and III via a triplet state. However, it needs more detailed studies to determine the real excited state.

Received, 6th June, 1973