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# PHOTOCHEMICAL (2 + 2 + 2 + 2) CYCLOADDITION OF FURAN TO β-NAPHTHONITRILE[1)]

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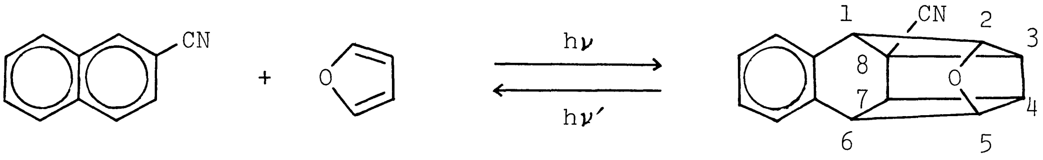
The photochemical reaction of β-naphthonitrile with furan affords a cage-adduct, 8-cyano-9,10-benzo-11-oxapentacyclo[$4,2,2,1^{2,5}0^{3,8}0^{4,7}$] undec-9-ene (I), in good yield.

In a previous paper,[2)] we reported a novel photochemical (4 + 4) cross-cycloaddition of α-naphthonitrile (α-NN) with furan via an exciplex intermediate.[3)] In the present paper, we wish to report the (2 + 2 + 2 + 2) photocycloaddition of furan to β-naphthonitrile (β-NN) giving a novel cage adduct (I). On the cycloaddition involving more than four π-bonds, only a few examples have been known so far.[4)]



(I)

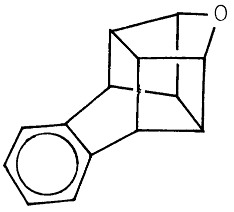
Irradiation of a benzene solution of β-NN containing a large excess of furan through a Pyrex glass with a high pressure mercury arc gave a sole 1:1-adduct[5)] having mp 78 - 78.5 °C in good yield. Although the adduct was thermally fairly stable, irradiation at 254 nm led to the quantitative decomposition into the starting materials.

The structure determination was carried out by IR, UV, NMR and mass spectral data: $\nu_{max}$ (KBr) 3020, 2990, 2960, 2220, 1070 and 870 $cm^{-1}$; $\lambda_{max}^{MeOH}$ ($\epsilon$) 252 (193), 257 (264), 264 (331), 269 (253) and 276 nm (303); m/e 221 (vw), 153 (100%), 68 (53%); $\delta_{CDCl_3}$ (60MHz) 3.15 (br., $C_7$-H), 3.67 (d-t, $C_4$-H), 3.96 (d-d-d, $C_3$-H), 4.05 (t, $C_6$-H), 4.17 (d, $C_1$-H), 4.95 (d-d-d, $C_5$-H), 4.99 (d-d, $C_2$-H) and 7.27 ppm (m, aromatic protons); coupling constants $J_{1,2}=J_{3,4}=J_{5,6}=J_{6,7}=$ 7 Hz, $J_{2,3}=J_{4,5}=J_{4,7}=$ 5 Hz, $J_{3,7}=$ 2 Hz and $J_{5,7}=$ 3 Hz.

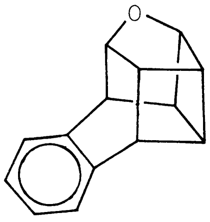
The IR band at 870 $cm^{-1}$ may be tentatively assigned to cyclobutane ring.[6)] A structure of 1:1-cycloadduct is strongly suggested from the mass spectra which show a very weak parent peak at m/e 221 and strong fragments corresponding to the two components along with the other far less important fragments. Possible (2 + 2) adduct-structures having an 1,2-dihydronaphthalene chromophore can be eliminated by the UV-spectra exhibiting a simple non-conjugated benzene chromophore for (I).[7)] Lack of olefinic bonds is unambiguously confirmed by the absence of the IR bands at 1650 and 690 $cm^{-1}$ region[8)] and of the signals due to olefinic protons in the NMR spectra, and especially by quantitative recovery of (I) on catalytic hydrogenation over Pd-charcoal.

The NMR data are fully consistent with the assigned structure (I). The chemical shifts and the coupling constants were determined by the first order analyses of 60 MHz spectra comparing with 100 MHz data and a spin decoupling method (60 MHz). The integral of the spectrum shows four aromatic protons and seven methine protons. The complex signals at $\delta$4.8 - 5.1 are clearly due to the $C_2$- and $C_5$-protons. The broad signal at $\delta$3.0-3.3 can be ascribed to the $C_7$-proton.[9] In the very complex signals at $\delta$3.5 - 4.3 a doublet and a triplet at lower field, attributable to benzylic protons ($C_1$- and $C_6$-H), can be distinctly differentiated from the signals of the other protons. Irradiation at $\delta$3.15 ($C_7$-H) changes the triplet at $\delta$4.05 ($C_6$-H) into a doublet, the doublet of triplets at $\delta$3.67($C_4$-H) into doublet of doublets, and results in disappearance of a small coupling of 3 Hz at $\delta$4.80 - 5.05 ($C_5$-H), whereas the doublet at $\delta$4.17 ($C_1$-H) and the quartet at $\delta$4.99 ($C_2$-H) remain unchanged. On irradiation at $\delta$4.95, the doublet at $\delta$4.17 collapses into a singlet, the triplet at $\delta$4.05 into a doublet, the doublet of triplets at $\delta$3.67 into doublet of doublets, and the very broad signal at $\delta$3.15 into a broad triplet. Moreover, irradiation at $\delta$4.17 changes the quartet at $\delta$4.99 into a doublet, whereas the signal of the $C_5$-proton results in no essencial change. On irradiation at the center of a triplet of the $C_4$-proton ($\delta$3.72) the complex signal of the $C_5$-proton collapses into a broad doublet, whereas the quartet of the $C_2$-proton remains unchanged.

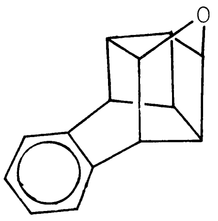
Thus, the NMR results firmly establish the structure of the adduct. The complex pattern of NMR signals can eliminate all the symmetrical structures for the adduct. The other possible structures such as (II), (III), and (IV) can be rigorously eliminated from the NMR data verifying the vicinal coupling of $C_1$-H with $C_2$-H, $C_4$-H with $C_7$-H, $C_6$-H with $C_5$- and $C_7$-H, and the long range coupling of $C_5$-H with $C_7$-H.



(II)



(III)



(IV)

The full results containing the photoaddition of the other furan derivatives to β-NN will be published in a separate paper.

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