CHEMISTRY LETTERS, pp. 187-188, 1973. Published by the Chemical Society of Japan

THE STEREOSELECTIVE PHOTOCYCLOADDITION OF INDENE AND PHENYL VINYL ETHER TO α-NAPHTHONITRILE[1)]

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The photoreactions of α-naphthonitrile with indene and phenyl vinyl ether afford 1-cyano-4,5;10,11-dibenzotricyclo[$5.4.0.0^{2,6}$]undeca-4,8,10-triene (I) and 1-cyano-8-phenoxy-2,3-benzobicyclo[4.2.0]octa-2,4-diene (IIa) as a single (2 + 2) cycloadduct respectively, which are shown to have an endo-configuration by the consideration of their NMR data.

In previous papers, we have repoted that the photoreaction of α-naphthonitrile (α-NN) with alkyl vinyl ethers affords both the endo-cycloadduct (IIb-c) and the exo-isomer (IIIb-c),[2)] whereas the (4 + 4) photocycloaddition of furan to α-NN is highly stereoselective and remarkably dependent on solvents used.[3)] The difference between the above two photoreactions may be interpreted by the stability and/or the configuration of the exciplexes, since such a planer molecule as furan can be expected to form more stable and rigid exciplexes than linear alkyl vinyl ethers. If this is the case, more conjugated olefins will undergo the photocycloaddition to α-NN with an enhanced stereoselectivity.

Irradiation of α-NN in the presence of an excess of indene gave a single product (I) at an initial stage.[4)] The structure of (I) was determined by the following data:[5)] ν_{max} (nujol) 2240 (C≡N) and 1640 cm^{-1}(C=C); $\lambda_{max}^{CH_3CN}$(ε) 302 (sh), 273 (7.69×10^3) and 265 nm (7.69×10^3); m/e 269 (M^+, vw), 153 and 116; δ_{CCl_4} (60 MHz) 2.75 (d-d, endo C_3-H), 3.18 (d-d, exo $C_{3'}$-H), 3.85 (d-d-d-d, C_2-H), 4.1 (d-d-d, C_7-H), 4.36 (d-d, C_6-H), 5.38 (d-d, C_8-H), 6.0 (d, C_9-H) and 6.6 - 7.3 (m, aromatic protons, 8H); $J_{3,3'}$= 19, $J_{2,3}$= 3.2, $J_{2,3'}$= $J_{2,6}$= $J_{6,7}$= 8, $J_{7,8}$= 4.5, $J_{8,9}$= 10 and $J_{2,7}$= 1.5 Hz.

The complex NMR-signals at δ 3.7 - 4.6 consist of a downfield triplet and two triplets with further splittings. Upon irradiation at δ 2.95 (or 5.38), the triplet at δ 3.85 (or 4.1) collapses into a doublet with splittings. These spin-decoupling results and the first order-analysis in comparison with 100 MHz data establish the vicinal couplings of the C_2-proton with C_6-, C_3- and $C_{3'}$-protons and of the C_7-proton with the C_6- and C_8-protons and a long range coupling between the C_2- and C_7-protons. Thus, all the spectral data support the skeletal arrangement for (I) figured in Chart. It is interesting to note that (I) is not an expected product derived from a stable 1,4-biradical.

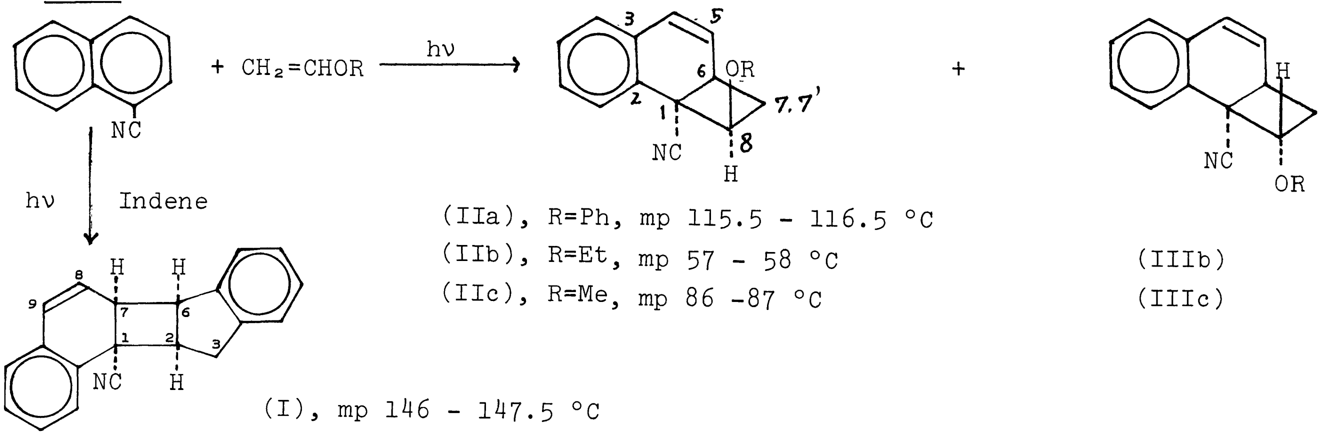
The fact that the C_8- and C_9-protons exhibit the signals at unusually high field than the corresponding protons in any similar compounds[6)] can be reasonably interpreted in terms of anisotropic effect of the endo-located benzene ring of the indane part as being observed in a benzotricyclic compound.[7)] In fact, molecular models of (I) with the endo-configuration show that the benzene ring is just located over the C_8-C_9 bond.

Irradiation of α-NN in the presence of phenyl vinyl ether gave a sole (2 + 2) cycloadduct (IIa) in 70 - 80% yields along with the formation of a 2:2-adduct.[4,8] The spectral data for (IIa): ν_{max}(KBr) 2220 (C≡N), 1630 (C=C) and 1240 cm^{-1}(Ar-O-); $\lambda_{max}^{CH_3CN}$ (ε) 300 (5.6 x 10^2), 273 (7.8 x 10^3) and 265 nm (8.9 x 10^3); m/e 273 (M^+, vw), 153 and 120; δ_{CDCl_3}(60 MHz) 2.27 (d-d-d, $C_{7'}$-H), 2.7 (d-d-d, C_7-H), 3.2 (d-d-d, C_6-H), 5.22 (d-d, C_8-H), 5.72 (d-d, C_5-H), 6.36 (d, C_4-H), and 6.75 - 7.5 (m, aromatic protons, 9H); $J_{4,5}$= 10, $J_{5,6}$= 6, $J_{6,7}$= $J_{7,8}$= 8, $J_{6,7'}$= $J_{7,7'}$= 10.5 and $J_{7',8}$= 8.5 Hz.

The spectral data support the skeletal arrangement for (IIa) figured in Chart. For structural elucidation, it is notable that the NMR spectrum of (IIa) is very similar to that of (IIb) rather than that of (IIIb) except the signals of ethoxyl group and aromatic protons and downfield shifts in the signals of (IIa). The spectral similarity may suggest the endo-configuration for (IIa), though the structure of (IIa) has not been firmly established yet. The exact structure are now under the X-ray analysis. At any rate, indene and phenyl vinyl ether, more conjugated olefins than alkyl vinyl ethers, undergo the photocycloaddition to α-NN in a stereoselective manner.

In contrast to the photoreactions of benzene solutions, irradiation of methanolic and acetonitrile solutions of α-NN containing indene or phenyl vinyl ether gave complex mixtures. The fluorescence from cyclohexane solutions of α-NN was quenched by indene with a diffusion-controlled rate. The results obtained may suggest exciplex intermediacy and may support our prediction. Details are now under investigation.

Chart



(IIa), R=Ph, mp 115.5 - 116.5 °C
(IIb), R=Et, mp 57 - 58 °C
(IIc), R=Me, mp 86 -87 °C

(IIIb)
(IIIc)

(I), mp 146 - 147.5 °C

REFERENCES

1) Photochemical Reactions of Aromatic Compounds. XV. Part XIV. Chemistry Lett., submitted.
2) C.Pac, T.Sugioka, K.Mizuno, and H.Sakurai, Bull. Chem. Soc. Japan, 46, in press (1973).
3) C.Pac, T.Sugioka, and H.Sakurai, Chemistry Lett., 1972, 39.
4) Unless otherwise noted, the solvent was benzene. Irradiation was carried out through a glass filter (>300 nm) with a high pressure-mercury arc. Over-irradiation led to the formation of untractable materials in substantial amounts.
5) Sufficient analytical data for the new compounds were obtained.
6) The normal chemical shifts of the protons corresponding to the C_8- and C_9-protons of (I) are in the range of δ 5.7 - 6.32 and 6.2 - 6.63 respectively. For examples, see, ref. 2; "VARIAN NMR spectra Catalog" compiled by N.S.Bhacca, L.F.Johnson, and J.N.Shoolery, Varian Associates (1962), Chart No. 592 ; W.Herz and G.Caple, J. Amer. Chem. Soc., 84, 3517 (1962); J.J.McCullough, C.Carlo, and C.W.Huang, Chem. Commun., 1968, 1176.
7) H.E.Simmons, J. Amer. Chem. Soc., 83, 1657 (1961).
8) The 2:2-adduct melts at 268 - 269 °C. Although the structure has not been firmly established yet, it appears to be a dimer of (IIa) as judged from the spectral data.

(Received December 6, 1972)