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THE PHOTOCYCLOADDITION OF 9-CYANOPHENANTHRENE AND 9-CYANOANTHRACENE WITH VINYL ETHERS AND FURAN[1]

Kazuhiko MIZUNO, Chyongjin PAC, and Hiroshi SAKURAI
The Institute of Scientific and Industrial Research, Osaka University
Suita-shi, Osaka

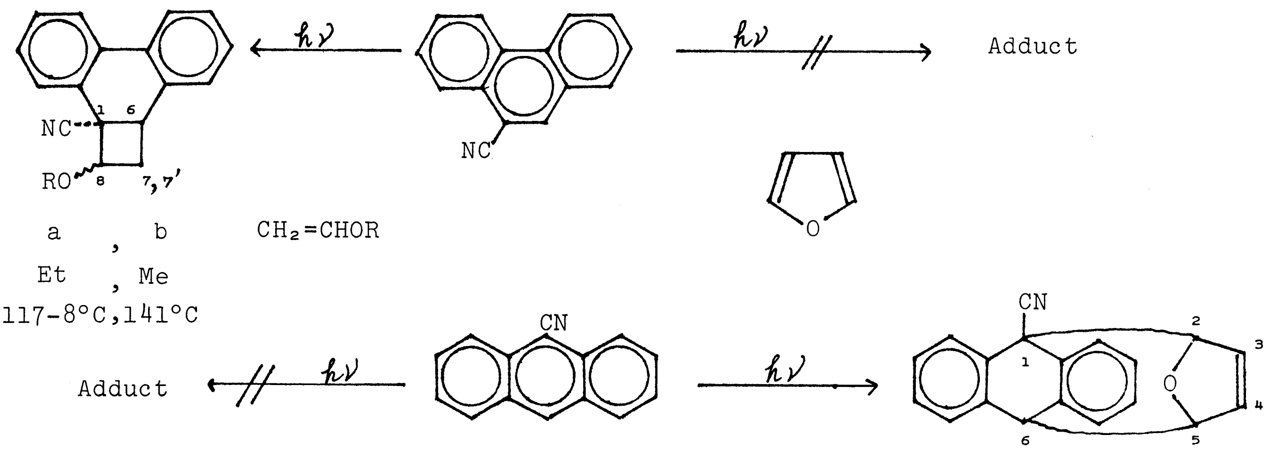
The photocycloaddition of 9-cyanophenanthrene with a vinyl ether affords a (2 + 2) cycloadduct, 1-cyano-8-alkoxy-2,3;4,5-dibenzobicyclo-[4.2.0]octa-2,4-diene (I), but no 1:1-adduct can be obtained with furan, whereas irradiation of 9-cyanoanthracene in the presence of furan gives a (4 + 4) cycloadduct, 1-cyano-7,8;9,10-dibenzo-11-oxatricyclo-[4.2.2.$1^{2,5}$]undeca-3,7,9-triene (III), but no 1:1-adduct is given by the irradiation in the presence of vinyl ethers.

The photocycloaddition to aromatic rings involving exciplexes as intermediates has been of current interest. The configuration of exciplexes can be expected to reflect the stereoselectivity of the cycloaddition[2-7] and the addition-modes,[7] i.e. (2 + 2), (2 + 4), (4 + 4) additions and so on. In previous papers, we have repoted that the photoreaction of α-naphthonitrile with ethyl vinyl ether (VE) affords only (2 + 2) adducts,[2] whereas that with furan (F) gives only a single (4 + 4) adduct.[3] If 9-cyanophenanthrene (9-CP) and 9-cyanoanthracene (9-CA) having the reactive sites fixed on the C_9 and C_{10} positions are used instead of α-naphthonitrile, the possible photocycloaddition will be expected to occur in (2 + 2) and (2 + 4) types for 9-CP and in (4 + 2) and (4 + 4) types for 9-CA. In order to investigate the addition-modes, we carried out the photoreactions of 9-CP and 9-CA with VE and F, though the photocycloaddition of olefinic compounds to phenanthrene,[8] anthracene[6] and 9-CA[7] have been published.

Irradiation of a benzene solution of 9-CP containing a large excess of VE through a glass filter (>300 nm) with a high pressure mercury arc gave a sole 1:1-adduct (Ia) along with the dimer of 9-CP (II).[9] In contrast, the irradiation in the presence of a large excess of F for a longer time gave no adduct, but only resulted in the formation of the dimer (20%) and the recovery of 9-CP (70 - 80%). The structure of (Ia) was determined by the following spectral data[10]: ν_{max} (KBr) 2230 (C≡N) and 1130 cm^{-1} (C-O-C); $\lambda_{max}^{CH_3CN}$ (ε) 272 nm (12200); m/e 275 (M^+, vw), 203 (100%) and 72 (4%); δ_{CDCl_3} (100 MHz) 2.08 (d-t, C_7-H), 2.57 (d-t, $C_{7'}$-H), 3.56 (d-d, C_6-H), 4.61 (d-d, C_8-H), 7.1 - 7.6 (m, aromatic protons, 6H) and 7.9 - 8.1 (m, aromatic protons, 2H); $J_{6,7}= J_{6,7'}= J_{7,7'}= J_{7',8}=$ 11 Hz and $J_{7,8}=$ 10 Hz. Although the stereochemistry of the ethoxyl group has not been firmly established yet, the trans-configuration between the ethoxyl and cyano groups may be assigned from the consideration of the chemical shift of the C_8-proton.[11] At any rate, it is noteworthy that the photoaddition of VE to 9-CP is stereoselective unlike that of electron deficient olefins to phenanthrene.[8]

The photoreaction of 9-CA with F gave the (4 + 4) cycloadduct (III) along with the dimer of 9-CA (IV), while the irradiation of 9-CA in the presence of a large excess of VE resulted in the quantitative formation of (IV). The structure of (III) was determined by the following spectral data[10]: ν_{max} (KBr) 2240 (C≡N), 1630 (C=C), 1050 and 1040 cm^{-1} (C-O-C); $\lambda_{max}^{CH_3CN}$ (ε) 277 (1640), 269 (1130) and 262 nm (720); m/e 203 (100%) and 68 (15%); δ_{CDCl_3} (100 MHz) 4.07 (d, C_6-H), 4.71 (d-d, C_5-H), 4.86 (d, C_2-H), 5.88 (d-d, C_4-H), 5.96 (d-d, C_3-H) and 7.0 - 7.7 (m, aromatic protons, 8H); $J_{2,3}= J_{4,5}=$ 1 Hz, $J_{3,4}=$ 6 Hz and $J_{5,6}=$ 6.5 Hz.

The present results are in sharp contrast to those of the photoreactions of α-naphthonitrile with VE and F. Since the fluorescence of 9-CP or 9-CA was quenched with both VE and F,[12] it is surprising that 9-CP and 9-CA have the distinct and reverse substrate-selectivity in the photoreactions with VE and F. At the present stage, therefore, the substrate-selectivity may be possibly interpreted as being caused by the life and/or the configuration of exciplexes; in the case of the exciplex between 9-CP and F or 9-CA and VE, the life is too short for the reaction to occur and/or the configuration is unfavorable for the cycloaddition. Details are now under investigation.



I a , b

R Et , Me

mp 117-8°C,141°C

III mp 144.5 °C

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10) Sufficient analytical data for all the new compounds were obtained. The NMR signals of ethoxyl group of (Ia) are omitted. The interpretation of the spectral data will be published elsewhere.
11) For structual elucidation, it should be noted that the chemical shift of the C_8-proton of (Ia) is lower than those of both cis- and trans-1-cyano-8-ethoxy-2,3-benzobicyclo[4.2.0]octa-2,4-dienes (δ 4.16 and 4.45).[2]
12) For instance, in the case of 9-CA, the slopes of the Stern-Volmer plots were found to be 0.25 (F) and 0.19 M^{-1} (VE) for the benzene solutions.

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