CHEMISTRY LETTERS, pp. 45-46, 1975. Published by the Chemical Society of Japan

A NOVEL TYPE OF ADDUCTS IN THE PHOTOCHEMICAL REACTIONS OF 2-PYRIDONES WITH CYANOETHYLENES

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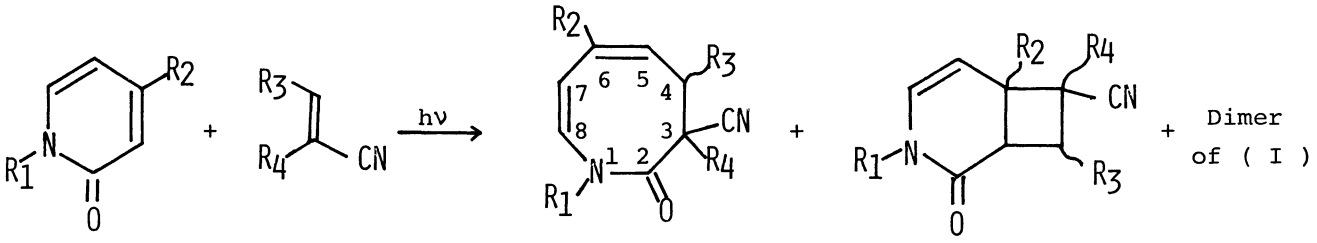
Irradiation of mixtures of 2-pyridones and cyanoethylenes gave a novel type of adducts, 3-cyano-1,2,3,4-tetrahydro-azocin-2-ones, and [2+2]cycloadducts. 2-Pyridones used were 2-pyridone, 4-methyl-2-pyridone, and N-methyl-2-pyridone, and cyanoethylenes used were acrylonitrile, crotononitrile. and methacrylonitrile. The structures of these photoadducts were mainly determined by PMR and mass spectra.

There are many reports in photochemical reactions of α, β-unsaturated carbonyl compounds with olefins but few reports in photoreactions of α,β,γ,δ-unsaturated carbonyl compounds with olefins.[1)]

We have found that the photoreactions of 2-pyridones(I) with cyanoethylenes(II) gave a novel type of photoadducts, 3-cyano-1,2,3,4-tetrahydro-azocin-2-ones(III).

All the photoreactions and the results which have been examined are shown by the following equation.



(I) (II) (III) (IV)

	R_1	R_2
a ;	H	H
b ;	H	CH_3
c ;	CH_3	H

	R_3	R_4
a ;	H	H
b ;	CH_3	H
c ;	H	CH_3

	R_1	R_2	R_3	R_4
a ;	H	H	H	H
b ;	H	H	CH_3	H
c ;	H	CH_3	H	H
d ;	CH_3	H	H	H

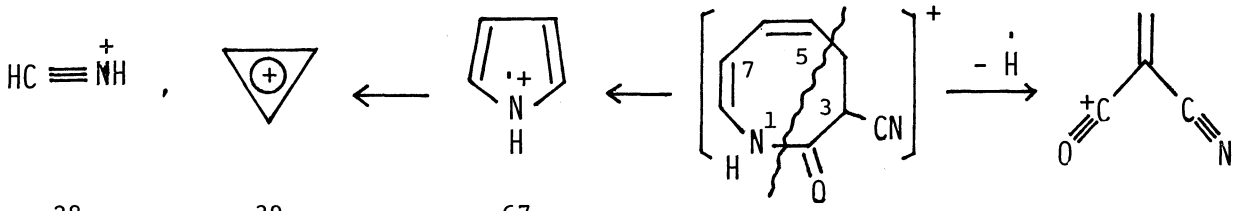
	R_1	R_2	R_3	R_4
a ;	H	H	H	H
b, b' ;	H	H	CH_3	H
c ;	H	CH_3	H	H
d ;	CH_3	H	H	H
e, e' ;	H	H	H	CH_3

Melting points(uncorr.) and yields of these products are as follows: IIIa(158-160°C, 4%), IVa(94-96°C, 41%), IIIb(153-156°C, 6%), IVb(162-164°C, 16%), IVb'(153-156°C, 10%), IIIc(162-166°C, 9%), IVc(153-156°C, 34%), IIId(liquid, 12%), IVd(liquid, 25%), IVe(155-156°C, 9%), IVe'(166-168°C, 12%). Elemental analyses of all these photoproducts were respectively consistent with the values calculated for 1:1-adducts of I with II.

For instance, 2-pyridone(Ia)(0.06 mol) and acrylonitrile(IIa) (0.6 mol) in 200

ml of ethanol were irradiated with a 100 W high-pressure mercury lamp through Pyrex filter for 30 hr under N_2. After concentration, the residue was passed through a silica gel column to give two kinds of 1:1-adducts, IIIa and IVa, together with a small amount of a dimer of Ia.[2]

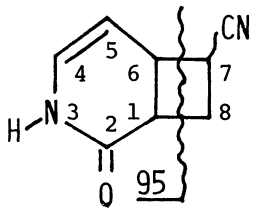
The structure of IIIa was determined to be a novel type of adduct, 3-cyano-1,2,3,4-tetrahydro-azocin-2-one, by the following data: ν_{max}(KBr) 3190(N-H), 2240(C≡N), 1676 (C=O) and 1648 cm^{-1}(C=C); λ_{max}(log ε) 252 nm(3.84)(in ethanol); m/e 148(M^+, 7%), 80($C_4H_2NO^+$, 92%), 67($C_4H_5N^+$, 100%), 39($C_3H_3^+$, 73%) and 28(CH_2N^+, 83%);[3] δ(100MHz, TMS, in $CDCl_3$) 2.98(broad d, 2H, 4-H), 4.45(t, 1H, 3-H, disappeared with hot D_2O), 5.8(m, 3H, 5,6,7-H), 6.04(broad d, 1H, 8-H) and 8.40 ppm(broad s, 1H, N-H, disappeared with hot D_2O); $J_{3,4}$= $J_{7,8}$= 8, $J_{1,8}$= $J_{4,5}$= 2 Hz. The position of the cyano group was determined to be the 3-position by the sharp triplet of 3-H at δ 4.45. The analysis of the mass spectrum is shown below:



28 39 67 148 (IIIa) 80

The characteristic strong peak of m/e 80 supports the structure IIIa.

The structure of IVa was determined to be a [2+2]cycloadduct by the following data: ν_{max}(KBr) 3230(N-H), 2240(C≡N), 1671(C=O), and 1635 cm^{-1}(C=C); λ_{max}(log ε) 265 nm(3.76)(in ethanol); m/e 148(M^+, 15%), 95($C_5H_5NO^+$, 100%; characteristic cleavage along the wavy line), 67($C_4H_5N^+$, 98%), 39($C_3H_3^+$, 93%), and 28(CH_2N^+, 60%);[3] δ(IVa/ Eu(DPM)$_3$[4]= 1.0 mol ratio, TMS, in $CDCl_3$) 7.85(q, 7-H). 8.36(d-d, 5-H), 8.85(broad d, 4-H), 9.25(broad, 6-H), 10.87(q-d, 8-H), 11.76(q, 8-H'), 21.11(q, 1-H) and 22.71 ppm(broad s, N-H); $J_{1,6}$= $J_{1,8}$= $J_{1,8'}$= $J_{8,8'}$= 9, $J_{7,8}$= $J_{7,8'}$= $J_{4,5}$= 8, $J_{3,4}$= 4, $J_{5,6}$= 3 and $J_{6,8}$= 2 Hz. As 1-H coupled with three protons of 6-H, 8-H, and 8-H', the position of the cyano group was determined to be the 7-position.



(IVa)

The structures of other photoproducts were mainly determined by strong resemblances of IIIb, IIIc, and IIId to IIIa, and IVb, IVb', IVc, IVd, IVe, and IVe' to IVa on the patterns of those PMR and mass spectra.

The mechanism of the formation of III, the stereochemistry of IV, etc. are now under investigation.

The authors are grateful to professor Taku Matsuo, Faculty of Engineering, Kyushu University, for his useful suggestion.

References

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(Received October 22, 1974)