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PHOTOCHEMICAL REACTION OF NAPHTHYL α-NITROACRYLATES[1]

Seiko Hirotani and Shonosuke Zen*
School of Pharmaceutical Sciences, Kitasato University,
Shirokane, Minato-ku, Tokyo 108, Japan

Photolysis of 2-nitro-3-(1-naphthyl)acrylates (1) in acetone gave novel naphtho[1,2-b]furan-2-carboxylates (2) and 2-(alkoxyoxalylaminomethylene)naphthalen-1-ones (3). 2-Nitro-3-(2-naphthyl)acrylate also produced the furan derivative 2 on irradiation. A mechanism for this new photorearrangement reaction is described.

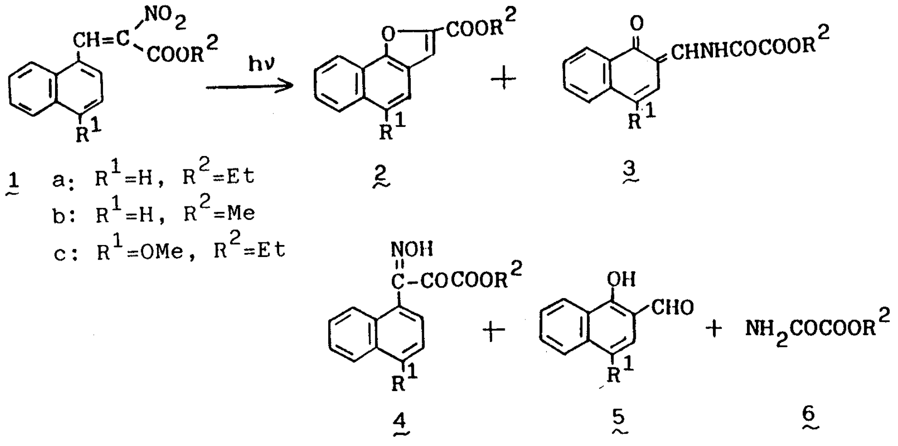
KEYWORDS——photochemical rearrangement; naphthyl α-nitroacrylate; naphtho[1,2-b]furan-2-carboxylate; 2-(ethoxyoxalylaminomethylene)naphthalen-1-one; α-keto-β-hydroxyiminoester

From a growing interest in the photochemical reactions of naphthyl α-nitroacrylates (1) in which their nitro group is attached to conjugated system, the compounds 1 were irradiated with a high pressure mercury lamp through a Pyrex filter in organic solvent.

We wish to report here that novel photochemical products,[2] naphtho[1,2-b]furan-2-carboxylates (2a:R^1=H,R^2=Et, 2b:R^1=H,R^2=Me, 2c:R^1=OMe,R^2=Et) and 2-(alkoxyoxalylaminomethylene)naphthalen-1-ones (3a:R^1=H,R^2=Et, 3b:R^1=H,R^2=Me, 3c:R^1=OMe,R^2=Et) could be obtained by the irradiation of 1 in acetone. More remarkable is the formation of 2a also from the irradiation of ethyl 2-nitro-3-(2-naphthyl)acrylate[3] (7). The reaction sequences are shown in Charts 1 and 2.

This observation suggests that the compound 1a[3] causes a rearrangement under the reaction condition employed, that is, a carbon atom (C-3) of the acrylate group attached to the 1-position of naphthalene ring rearranges to the 2-position, to yield 2 and 3 respectively.

Chart 1



1 a: R^1=H, R^2=Et
b: R^1=H, R^2=Me
c: R^1=OMe, R^2=Et

In a typical experiment, a solution of 1.0 g (3.7 mmol) of 1a in 400 ml of acetone was irradiated under nitrogen atmosphere at 20°C using a 450 W high pressure mercury lamp equipped with a Pyrex filter for 2 h. The solvent was removed and soon a red precipitate of 2-(ethoxyoxalylaminomethylene)naphthalen-1-one[5] (3a), mp 154-156°C(dec.)(yield, 10.0%), separated out. The compound 3a was hydrolyzed by 6N hydrochloric acid to give aldehyde 5a (70%). Purification by chromatography on silica gel (hexane-ethyl acetate 10:1) separated out the following products, ethyl naphtho[1,2-b]furan-2-carboxylate[6] (2a), mp 87.5-88.0°C,(2.2%); ethyl 3-(1-naphthyl)-3-oximino-2-oxopropionate (4a), mp 121-122°C,(1.6%); 1-hydroxy-2-naphthaldehyde[8] (5a),(26.8%); and ethyl oxamate[8] (6a),(15.8%).

The nitro esters, 1b and 1c, reacted in a similar manner to obtain the corresponding 2b, mp 94.5-95.5°C(lit.[7] 95-96°C)(2.2%), 2c, mp 104.5-105.5°C (2.8%), 3b, mp 202-203°C(dec.)(7.7%), 3c, mp 193.5-195.0°C(dec.)(6.8%), 5a (28.1%), and 5c (19.0%), respectively. These results support also the above-mentioned rearrangement. Whereas similar photolysis of 2-naphthyl derivative 7 gave also the corresponding 2a (2.6%), 8, mp 94-96.5°C (22%), and 6 (10.8%) respectively. This reaction is very closely related to that reported by P. M. Crosby et al.,[4] where 2-methyl-phenanthro[9,10-b]furan forms via the corresponding intermediate radical (R-C=C(Me)-O•, R=9-phenanthryl), as shown in Chart 2.

A reaction mechanism can be considered for the formation of 2 based on the above results and by analogy with known reaction pathways as shown Chart 3.

Initially rearrangement of nitroform of 1 (C=C-NO_2) into its nitrite form (C=C-O-NO)and subsequent isomerization to keto-oxime (4) occur as reported by Chapman.[9],[10] Furthermore the nitrite decomposes to radical A[4] together with

Chart 2

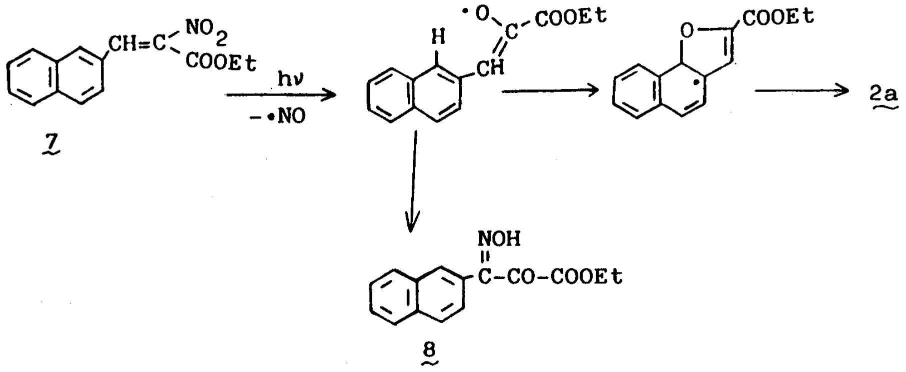
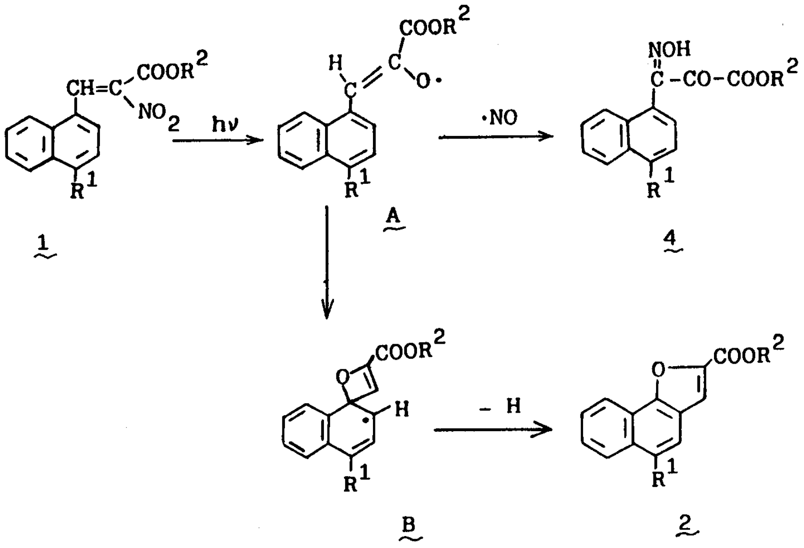


Chart 3



loss of nitrogen(II) oxide simultaneously. And finally, the radical (**A**) rearranges to the compound **2** through oxetene **B** accompanied with hydrogen abstraction.

Further detailed studies on the photoreaction of nitroacrylates are now in progress.

REFERENCES AND NOTES

1) The Synthetic Reaction of Aliphatic Nitro Compounds XXII; Presented in part at the 103rd Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, April, 1983, Abstr. p.160; Also Presented in part at the Symposium on Photochemistry, Tokyo, December, 1979, Abstr. p.200, Chem. Abstr., 93, 45537s (1980). (Part XXI: S. Zen and K. Harada, Chem. Lett., 1982, 1711.)

2) All new compounds gave consistent spectral data and correct elemental analyses.

3) O. S. Wolfeis, Z. Naturforsch. 31b, 594 (1976). These acrylates were employed as a mixture of E and Z in this reaction.

4) P. M. Crosby, K. Salisbury, and G. p. Wood, J. Chem. Soc., Chem. Commun., 1975, 312. 1-(9-phenanthryl)-2-nitroprop-1-ene on irradiation gave 2-methyl-phenanthro[9,10-b]furan (in a 5% yield) and phenanthrene-9-carboxaldehyde (25%) exclusively.

5) MS (m/z, rel.intensity %): 271 (M^+, 31), 198 (M^+-COOEt, 100); UV λmax (in hexane-ether) nm (logε): 266 (4.11), 295 (4.12), 420 (3.15), 446 (3.15); ^{1}H NMR (δ in $CDCl_3$, 90 MHz): 1.44 (3H,t,J=7 Hz,CH_3), 4.46 (2H,q,J=7 Hz,CH_2), 6.68 (2H,s,H-3and H-4), 7.58 (1H,dd,J=8,2 Hz,H-5), 7.86 (1H,d,J=10 Hz,CH-N), 7.36-7.62 (2H,m,H-6and H-7), 8.23 (1H,dd,J=8,2 Hz,H-8), 13.76 (d,J=10 Hz,NH); ^{13}C NMR (δ in $CDCl_3$): 13.9 (CH_3), 63.9 (CH_2), 116.0, 122.7, 127.2 (2C), 127.3 (C-8), 127.7, 130.6, 133.7 (C-5), 137.8, 139.7 (CH-N), 155.8 (C=O), 158.9 (C=O), 186.9 (C=O).

6) This ethyl ester was identical with the authentic sample synthesized independently from 1-hydroxy-2-naphthaldehyde without the need for light source by Duro's method (Ref. 7).

7) F. Duro, G. Scapini, and P. Cordorell, Boll. Sedute Accad. Gioemia Sci. Natur. Catania., 10, 332 (1970). Chem. Abstr., 75, 20065b (1971).

8) Both the compound **5** and **6** were identical with the authentic sample.

9) O. L. Chapman, A. A. Griswold, E. Hoganson. G. Lenz, and J. Reasoner, Pure Appl. Chem., 9, 585 (1964).

10) O. L. Chapman, P. G. Cleveland, and E. D. Hoganson, Chem. Commun., 1966, 101.

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