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THE PHOTOCHEMICAL BEHAVIOR OF CYCLIC IMINO ETHERS. THE N-O BOND FISSION AND SYN-ANTI ISOMERIZATION IN THE C=N-O CHROMOPHORE(1)

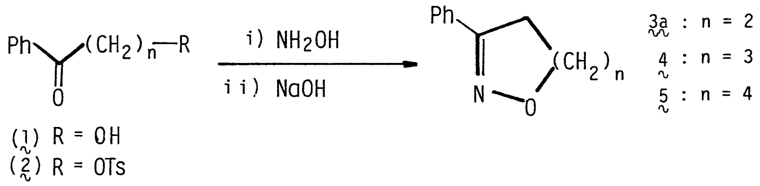
Hiroshi SAIKI and Toshio MUKAI*

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

Six-, seven-, and eight-membered cyclic imino ethers (3, 4, and 5) were synthesized and their photoreactions were investigated to compare with those of isoxazoline derivatives. The derivatives of 3 upon irradiation afforded ring-cleaved products, whereas 4 and 5 were found to be inert to irradiation.

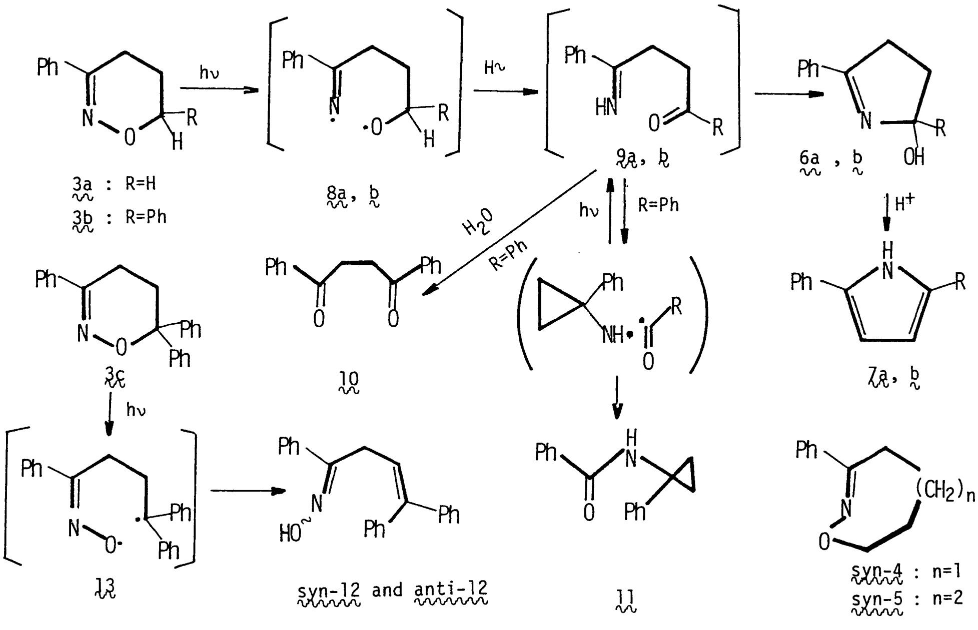
The photochemistry of compounds containing the C=N bond has not developed as rapidly as that of carbonyl compounds because the facile radiationless decay due to twisting around the C=N bond results in low reactivity of the excited imino compounds.2) In some compounds containing the Ph-C=N-O chromophore (e.g. the O-methyl ether of acetophenone oxime) a decay process consisting mainly of syn-anti isomerization was also found to be responsible for the photostability of the compounds.3) In contrast to this, it is well known that 3-phenyl-isoxazoline, the simplest cyclic imino ether, easily undergoes photolysis, mainly N-O bond fission.4) This sharp contrast in the photochemical behavior of constrained and non-constrained imino ethers prompted us to study the photoreactions of six-, seven-, and eight-membered compounds with the Ph-C=N-O chromophore.

Syntheses of the starting materials, 3-phenyldihydro-1,2-oxazine (3a), 3-phenyl-tetrahydro-1,2-oxazepine (4) and 3-phenyl-1-oxa-2-aza-2-cyclooctene (5) were shown in Scheme 1. Tosylates 2 obtained from alcohols 15) were converted to the corresponding oximes and cyclized by treatment with base to give the cyclic imino ethers (yields: 3a, mp 70°C, 70%; 4, mp 45-46°C, 80%; 5, oil, 45%). The other two derivatives, (3b) (mp 161-162.5°C) and (3c) (mp 194°C) were also synthesized according to the procedure6) reported.



Scheme 1

The photoreactions of dihydro-1,2-oxazine derivatives 3a, 3b, and 3c were carried out in dry acetonitrile at room temperature in a Rayonet RPR-100 photoreactor (254nm lamp). Irradiation of 3a gave quantitatively 5-hydroxy-2-phenylpyrroline (6a) (mp 116-118°C), which was unstable in the presence of a trace of acid, converting to 2-phenylpyrrole (7a) (mp 119-120°C). The reaction pathway is rationalized by the initial N-O bond fission (3a → 8a) and hydrogen migration (8a → 9a) followed by cyclization (9a → 6a). A precedent of the reaction sequence such as 9a → 6a → 7a can be found on the photolysis of 2-pyrrolidone dericatives.[8] Irradiation of 3b, on the other hand, afforded 2,5-diphenylpyrrole (7b) (mp 143°C, 15%),[9] 1,4-diphenylbutane-1,4-dione (10) (mp 145°C, 21%),[10] and N(1-phenylcyclopropyl)-benzamide (11) (mp 175°C, 28%). This reaction should proceed in a similar manner to that of 3a, namely, the formations of 7b and 10 can be well rationalized by the dehydoration of 6b and the hydrolysis of 9b, respectively.[11] Similarly 11 can be derived by the α-cleavage of iminoketone 9b followed by recombination of the resulted radicals. The structural assignment of 11 is based on spectral properties such as mass, nmr and ir spectra.



Scheme 2

In contrast with the photolyses of 3a and 3b, that of the diphenyl derivative 3c afforded a mixture of the syn-isomer (mp 143-144°C) and the anti-isomer (mp 108-110°C) of oxime of 1,4,4-triphenyl-but-3-en-1-one (12) (40% yield each). The structures of these two products were established by comparison with authentic samples.[12] The formation of oximes 12 can be explained by the C-O bond fission in 3c followed by hydrogen migration in the resulting cleaved species 13. Theus, dihydro-1,2-oxazine derivatives 3 exhibit different types of photolysis depending on the substituents;

i. e., two phenyl groups at the 6-position lead to C-O bond fission although the N-O bond fission was a favored process as shown for 3a and 3b.[13] The carbon-oxygen bond fission was also observed in the photolysis of 3,5,5-triphenylisoxazoline.[6,14] Therefore, it may be concluded that the primary photoprocesses of five- and six-membered cyclic imino ethers are very similar.

Seven- and eight-membered cyclic imino ethers (4 and 5) were stable upon irradiation and showed no cleavage reaction. The photostability is probably due to a decay process which consists of an equilibrium between (4 and 5) and syn-isomers (syn-4 and syn-5). Addition of methanol or furan to the reaction mixture did not give any solvent addition or cycloaddition products.[15]

In order to prove the existence of the syn-isomers (syn-4 and syn-5), the photochemical behavior of 4 and 5 at -196°C was examined spectroscopically. Independent irradiations of 4 and 5 in 2-methyl-tetrahydrofuran at -196°C resulted in approximately a 25% reduction of the uv absorption coefficient at 243nm. This reduction of the absorption coefficient was almost recovered when the solution was warmed to 50°C, keeping for 15 min, and then cooled again to -196°C. This observation may be explained by the syn-anti isomerization because the syn- and anti-isomers of acetophenone oxime ether are known to show different absorption coefficients at their uv maxima (λ_{max}; 238nm, ε 6080 for syn-isomer and 248nm, ε 10990 for anti-isomer).[4,16] In addition, the nmr spectrum of 5[10] which was obtained by low temperature-irradiation (-70°C), was monitored during the course of warming. The spectrum was complicated at -50°C, but at 23°C showed new peaks at δ 2.0 $\sim$ 2.2ppm (60% of 1H, multiplet) assignable to the hydrogen at the C_6 or C_7 position of the syn-isomer (syn-5). The absorption gradually disappeared at 23°C with a half life of 20 min.

Emission spectrum was observed at room temperature neither for the seven- and eight-membered cyclic imino ethers (4 and 5) nor for the five- and six-membered compounds such as 3-phenyl-isoxazoline[17] and 3a. The photochemical cleavage of the cyclic imino ethers (3, 4, and 5) was sensitized neither by acetophenone nor by benzophenone, but the photoreduction of benzophenone was quenched by both non-constrained (4 and 5) and constrained compounds (3a and 3-phenyl-isoxazoline).[18] This suggests that the triplet energy of benzophenone was transferred to the imino ethers and, thus, the singlet state could be responsible for the photocleavage and the syn-anti isomerization reactions. The suggestion that syn-anti isomerization of 4 and 5 occurs from the singlet state is also supported by analogy with the acetophenone oxime ether[3] and is compatible with the fact that no emission was observed. We thus conclude that the photoreaction of cyclic imino ethers has two competitive paths probably derived from the singlet excited state : one is photolysis, mainly N-O bond fission. and the other is syn-anti isomerization.

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References

1) Organic Photochrmistry 52. Part 51 ; M. Sawaura and T. Mukai, Bull. Chem. Soc. Jpn., in press.

2)(a) A. C. Pratt, Chem. Soc. Rev., **6**, 63 (1977).

(b) A. Padwa, Chem. Rev., **77**, 37 (1977) and references therein.

3) A. Padwa and F. Albrecht, J. Am. Chem. Soc., **94**, 1000 (1972); **96**, 4849 (1974).

4)(a) H. Giizendanner, H. -J. Rosenkranz, H. -J. Hansen and H. Schmid, Helv. Chim. Acta , **56**, 2588 (1973).

(b) T. Matsuura and Y. Ito, Tetrahedron Lett., 2287 (1973).

(c) T. Mukai and H. Sukawa, Tetrahedron Lett., 1835 (1973).

(d) O. Seshimoto, T. Kumagai, K. Shimizu, and T. Mukai, Chem. Lett., 1977, 1195.

5) H. R. Ward and P. D. Sherman Jr., J. Am. Chem. Soc., **90**, 3812 (1968).

6) R. Fragher and T. L. Gilchrist, J. Chem. Soc., Chem. Commun., 581 (1974).

7) The elemental analyses were satisfied in all unknown compounds.

8) P. H. Mazzochi and J. J. Thomas., J. Am. Chem. Soc., **94**, 8281 (1938).

9) C. F. H. Allen, D. M. Young, and M. R. Gilbert, J. Org. Chem., **2**, 235 (1938).

10) C. Weygand and W. Meusel, Chem. Ber., **76**, 498 (1943).

11) Alcohol **6b** was not able to be isolated, but photolysis of **3b** in methanol gave diketone **10** as single product in good yield, supporting the reaction mechanism shown in Scheme 2.

12) Anti-isomer of **12** was synthesized from 1,4,4-triphenyl -but-3-en-1-one by treating with hydroxylamine and irradiation of the anti-isomer afforded the syn-isomer.

13) Although the chromophore is a little different from **3a**, the photoreaction of 2-phenyl-3,6-dihydro-2H-oxazine exhibits N-O bond fission to give N-phenylpyrrole. See, D. Sheiner, C. L. Chapman and L. D. Lassila, J. Org. Chem., **34**, 813 (1969).

14) Irradiation of 3,5,5-triphenyl-2-isoxazoline afforded 1,1-diphenylethylene in good yield, implying that the reaction also started from C-O bond fission. Other examples are cited in references 4a and 4b .

15) Methanol is regarded as good reagent to trap strained olefins. See, H. Nozaki, M. Kurita, and R. Noyori, Tetrahedron Lett., 2025 (1968); 5433 (1968).

16) G. J. Karabatsons and N. Hsi, Tetrahedron, **23**, 1079 (1967).

17) At -196°C, 3-phenyl-2-isoxazoline was found to exhibit fluorescence but no phosphorescence. See, T. Kumagai, K. Shimizu, Y. Kawamura and T. Mukai, Tetrahedron, in press.

18) The oxime ethers (acetophenone oxime ether, 3-phenyl-2-isoxazoline, **3a** and **4**) quenched the photoreduction of benzophenone in cyclohexanol. When quantum yields for the formation of cyclohexanone were determined in the presence of the oxime ether using VPC, linear Stern-Volmer Plots are obtained. The following $K_q\tau$ values are given for each quencher ($K_q\tau$ = 325 for syn O-methyl ether of acetophenone oxime, and 765 for the anti-isomer; 2150 for 3-phenyl-2-isoxazoline; 1520 for **3a**; 215 for **4**). The oxime ethers also quenched Type II reaction of valerophenone. See, PhD. Thesis of H. Saiki, 1977 (Faculty of Science, Tohoku Univ.)

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