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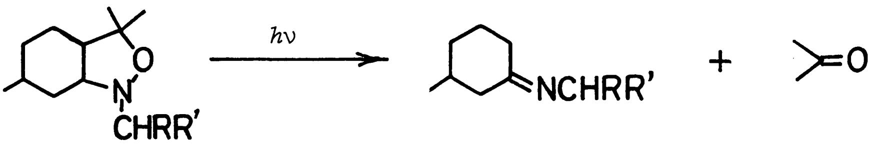
PHOTOFRAGMENTATION OF OXAZOLIDINES.[1] A NEW METHOD FOR THE GENERATION OF AZIRIDINES

Otohiko TSUGE,* Kōji OE, and Noriyuki KAWAGUCHI
Research Institute of Industrial Science, Kyushu University 86, Hakozaki, Higashi-ku, Fukuoka 812

Irradiation of 4,5-cis-2,3,4,5-tetraaryloxazolidines and 3-aryl-3a,9b-dihydroacenaphth[1,2-d]oxazolidines generates the corresponding aziridine intermediates with elimination of aldehyde formed by fissions of the C_2-O and C_4-C_5 bonds in the former and the C_2-O and C_2-N bonds in the latter, respectively. The intervention of aziridine intermediates was proved by photo-cycloadditions.

Photofragmentations of appropriate heterocyclic compounds provide a valuable means of generating reactive species or strained small-ring compounds.[2] Concerning the photolysis with loss of carbonyl fragments from five-membered heterocyclic compounds, however, so far only the 1,2-dioxolanes[3], 1,3-dioxolanes[4], and bicyclic isoxazolidines[5] have appeared in the literature. Since the photo-decarbonylation of bicyclic isoxazolidines afforded the imine as shown below,[5] we were interested in studying photochemical behaviour of oxazolidines. In the present paper we wish to report the photofragmentation of oxazolidines leading to the generation of aziridine intermediates.

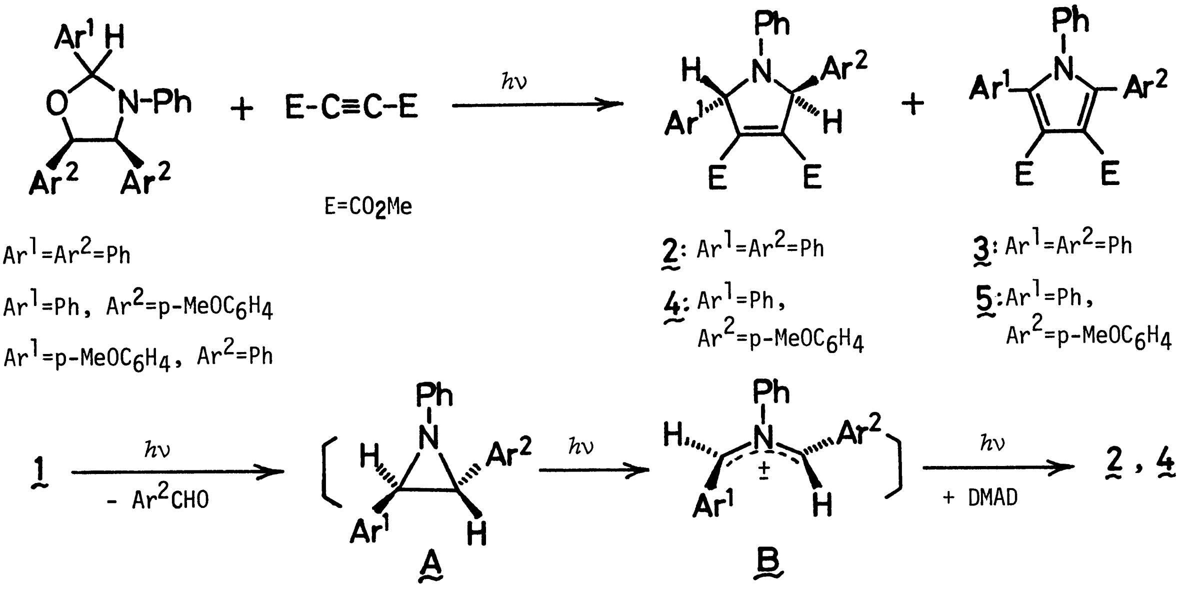


A solution of 1.13 g (3 x 10^{-3} mol) of 4,5-cis-2,3,4,5-tetraphenyloxazolidine (1a)[6] and 1.42 g (10^{-2} mol) of dimethyl acetylenedicarboxylate (DMAD) in 250 ml of benzene was irradiated, under nitrogen, with Pyrex-filtered light from a 300 W high-pressure mercury lamp below 20°C for 3 h. The reaction mixture was concentrated in vacuo at room temperature, and the residue was chromatographed on alumina using benzene as the eluent to give 3,4-bis(methoxycarbonyl)-2,5-trans-1,2,5-triphenyl-3-pyrroline (2) and its dehydrogenated pyrrole 3 in 16 and 4% yields.[7] Irradiation of a benzene solution of 1a and DMAD with a 15 W low-pressure mercury lamp below 20°C for 20 h afforded 2 and 3 in 14 and 8% yields, respectively.[8] The spectral data of 2 were in agreement with those of the compound obtained from the thermal reaction of 2,3-cis-1,2,3-triphenylaziridine with DMAD.[9]

All other photochemical reactions in the present paper were performed by irradiation with a 300 W high-pressure mercury lamp below 20°C.

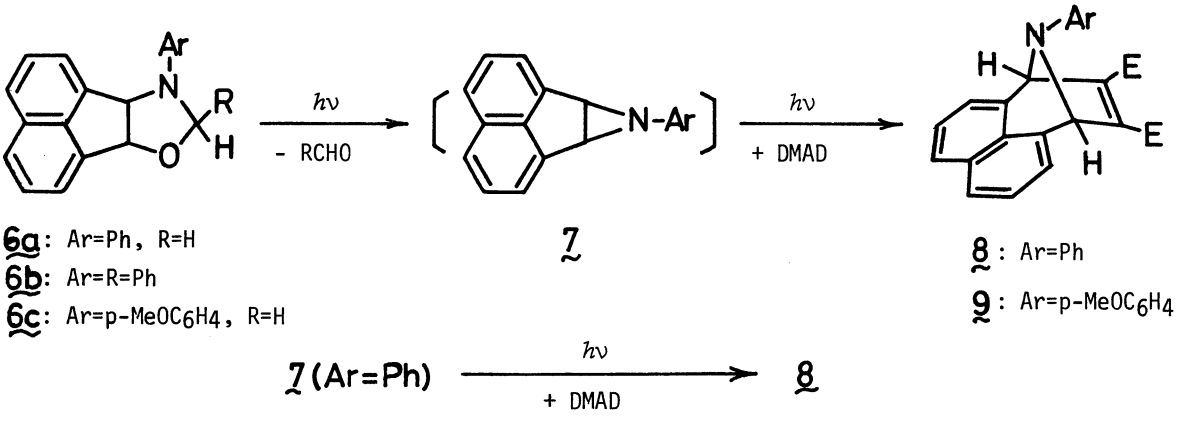
Upon irradiation of cis-4,5-bis(p-methoxyphenyl)-2,3-diphenyloxazolidine (1b) in the presence of DMAD under similar conditions, 2,5-trans-2-(p-methoxyphenyl)-1,5-diphenyl-3-pyrroline (4) and its dehydrogenated pyrrole 5 were obtained in 16 and 4% yields. The same products, 4 and 5, were also formed in 9 and 1% yields from the photochemical reaction of 4,5-cis-2-(p-methoxyphenyl)-3,4,5-triphenyloxazolidine (1c) with DMAD. Structural elucidation of products, 2 - 5, was accomplished on the basis of spectral data.[10]

As described above, the same products, 4 and 5, were formed in both the photochemical reactions of 1b and 1c with DMAD. This fact indicates that p-methoxybenzaldehyde or benzaldehyde was photochemically extruded from 1b or 1c, respectively. Thus, the pathway for the photochemical reaction can be explained as illustrated in Scheme 1. The reaction proceeds via an initial formation of trans-aziridine intermediate A with elimination of aldehyde (Ar^2CHO) from oxazolidine 1. This is followed by disrotatory ring opening of A to trans-azomethine ylide B, which reacts with DMAD to give 2,5-trans-3-pyrroline 2 or 4. This is comparable to the formation of 3-pyrroline 2 in the thermal reaction of 2,3-cis-1,2,3-triphenylaziridine with DMAD.[9]



Scheme 1

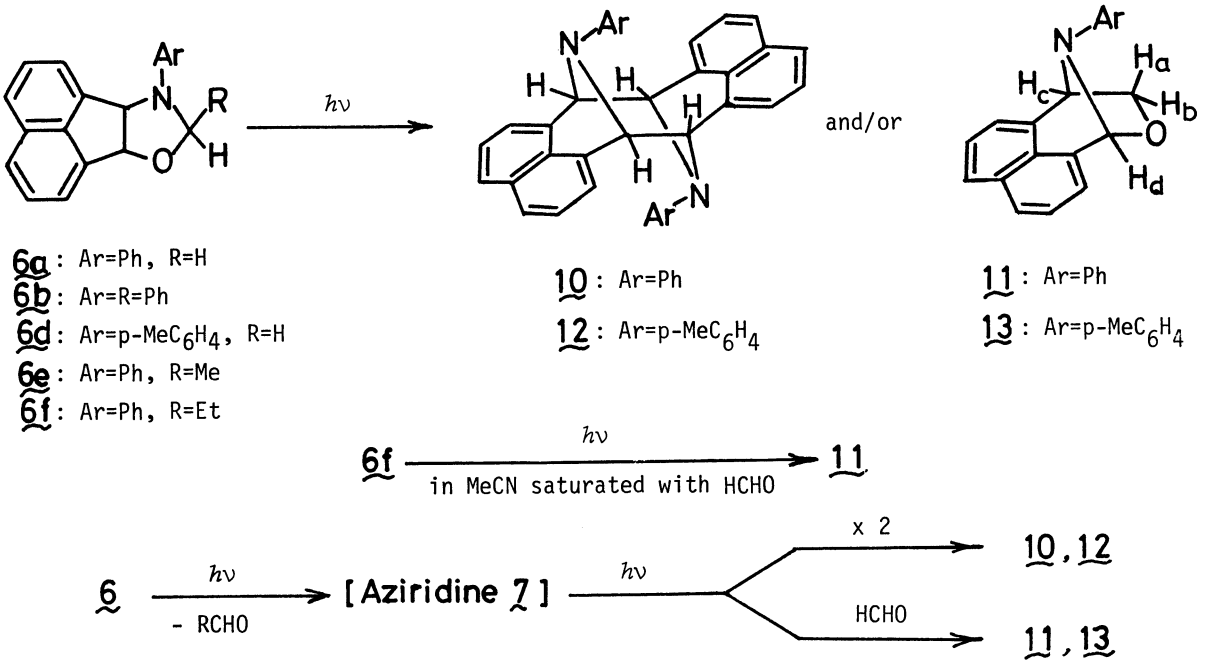
Next, photofragmentations of 3-aryl-3a,9b-dihydroacenaphth[1,2-d]oxazolidines 6 have been investigated. The photochemical reactions of 3-phenyloxazolidine 6a and 2,3-diphenyloxazolidine 6b with DMAD afforded a 50% yield of the same bicyclic 3-pyrroline derivative 8, together with a small amount of unidentified product.[11] Similarly, irradiation of 3-(p-methoxyphenyl)oxazolidine 6c in the presence of DMAD gave the corresponding 3-pyrroline derivative 9 in 52% yield. The formation of 8 and 9 indicates that aldehyde (RCHO) was extruded from 6 to yield aziridine intermediate 7, which reacted with DMAD to give 3-pyrroline 8 or 9. In fact, the photochemical reaction of aziridine 7 (Ar=Ph)[9] with DMAD under similar conditions afforded 8 in 52% yield (Scheme 2). Structural elucidation of 8 and 9



Scheme 2

was accomplished on the basis of spectral data.[12]

In addition, the intervention of aziridine intermediate 7 was supported by the following evidence. Irradiation of oxazolidine 6a alone in MeCN below 20°C afforded a mixture of two products, 10 and 11, whose relative yields depended on the irradiation time (Table 1). The product 10 was identical with an aziridine dimer (Ar=Ph) formed from thermal dimerization of aziridine 7 (Ar=Ph)[9], and another product 11 which corresponded to an isomer of 6a was assigned as 6,8-oxazabicyclo[3.2.1]octane derivative on the basis of spectral data[13] (Scheme 3). Irradiation of other oxazolidines, 6b, 6d, 6e and 6f, was performed under similar conditions, and the results are also shown in Table 1. Oxazolidine 6d gave a mixture of dimer 12 and oxazabicyclooctane 13.[14] In the cases of oxazolidines, 6b, 6e and 6f, having a substituent at 2-position, however, dimer 10 was obtained as the sole isolable product.



Scheme 3

Table 1. Irradiation of Oxazolidines 6 in MeCN[a]

Oxazolidine	Ar	R	Irradiation time, h	Product, %				Recovery of 6, %
6a	Ph	H	1	10	39	11	12	19
6a	Ph	H	2	10	10	11	30	19
6a	Ph	H	3	10	5	11	45	—
6b	Ph	Ph	1	10	21		—	—
6d	p-MeC$_6$H$_4$	H	1	12	15	13	23	19
6e	Ph	Me	1	10	13		—	—
6f	Ph	Et	1	10	11		—	7

[a] Intractable materials were formed in all cases.

It has also been found that irradiation of oxazolidine **6f** in MeCN saturated with formaldehyde gave a 52% yield of oxazabicyclooctane **11**. It is thus evident that dimer (**10** or **12**) and oxazabicyclooctane (**11** or **13**) are formed via dimerization of aziridine **7** and cycloaddition of **7** to formaldehyde, respectively (Scheme 3).

References

1. Photochemistry of Heterocyclic Compounds. 10. Part 9: O. Tsuge, K. Oe, and H. Inoue, Heterocycles, 12, 217 (1979).
2. N. J. Turro, "Modern Molecular Photochemistry", The Benjamin/Cummings Publishing Co., Inc., 1978, p. 526.
3. W. Adam and N. Duran, Tetrahedron Lett., 1357 (1972).
4. R. L. Smith, A. Manmade, and G. W. Griffin, ibid., 663 (1970).
5. N. A. LeBel, T. A. Lajiness, D. B. Ledlie, J. Am. Chem. Soc., 89, 3076 (1967).
6. Oxazolidines, **1a**, **1b** and **1c**, were prepared from the corresponding triarylaminoethanols and benzaldehydes. **1a**: mp 212-213°C; **1b**: mp 161-163°C; **1c**: mp 183-185°C.
7. A trace amount of 1,2-bis(methoxycarbonyl)cyclooctatetraene [mp 110-112°C] was obtained, together with recovery (18%) of **1a**.
8. The cyclooctatetraene compound was obtained in 20% yield, together with recovery (15%) of **1a**.
9. A. C. Oehlshlager, A. S. Yim, and M. H. Akhtar, Can. J. Chem., 56, 273 (1978).
10. All new compounds in this paper gave satisfactory elemental analyses. IR and NMR spectra were taken in KBr disks and in CDCl3 solutions, respectively.
    2: mp 172-173°C (lit.[9] mp 164-166°C); IR 1735 (sh), 1725 cm^{-1}; NMR δ 3.60 (6H, s), 6.25 (2H, s, $\geq$C$\underline{\mathrm{H}}$), 6.30-7.50 (15H, m); MS m/e 413 (M^+). **3**: mp 210-212°C; IR 1710 (sh), 1700 cm^{-1}; NMR δ 3.70 (6H, s), 6.70-7.30 (15H, m); MS m/e 411 (M^+). **4**: mp 167-168°C; IR 1750, 1730 cm^{-1}; NMR δ 3.59, 3.60, 3.67 (each 3H, s), 6.26 (2H, s, $\geq$C$\underline{\mathrm{H}}$), 6.40-7.40 (14H, m). **5**: mp 166-167°C; IR 1720, 1710 cm^{-1}; NMR δ 3.73 (3H, s), 3.75 (6H, s), 6.70-7.30 (14H, m).
11. Oxazolidines **6** were prepared by the reported method (O. Tsuge, M. Tashiro, and K. Oe, The Reports of Research Institute of Industrial Science, Kyushu University, No. 51, 7 (1971)).
    The unidentified product, mp 187-189°C, was an isomer of **8**. IR 1730, 1710 cm^{-1}; NMR δ 3.70, 3.81 (each 3H, s), 6.70-7.90 (11H, m), 8.00, 8.65 (each 1H, s); MS m/e 385 (M^+).
12. **8**: mp 229-230°C (lit.[9] mp 211-212.5°C); IR 1735 (sh), 1720 cm^{-1}; NMR δ 3.76 (6H, s), 5.79 (2H, s, $\geq$C$\underline{\mathrm{H}}$), 6.50-7.70 (11H, m); MS m/e 385 (M^+). **9**: mp 225-227°C (lit.[9] mp 225-227°C); IR 1740, 1715 cm^{-1}; NMR δ 3.50 (3H, s), 3.70 (6H, s), 5.66 (2H, s, $\geq$C$\underline{\mathrm{H}}$), 6.40-7.60 (10H, m).
13. **10**: mp > 300°C (lit.[9] mp 322-324°C); NMR δ 5.12 (4H, s, $\geq$C$\underline{\mathrm{H}}$), 6.40-7.70 (22H, m); MS m/e 243 ($M^+/2$). **11**: mp 132-133°C; NMR δ 3.93 (1H, d, H_b, J=6.0 Hz), 4.28 (1H, dd, H_a, J=5.0, 6.0 Hz), 5.18 (1H, d, H_c, J=5.0 Hz), 6.43 (1H, s, H_d), 6.70-7.90 (11H, m); MS m/e 273 (M^+).

14: **12**: mp > 300°C; NMR δ 1.96 (6H, s), 5.03 (4H, s, $\geq$C$\underline{\mathrm{H}}$), 6.20-7.80 (20H, m); MS m/e 257 ($M^+/2$). **13**: mp 136-137°C; NMR δ 2.23 (3H, s), 3.92 (1H, d, H_b, J=6.0 Hz), 4.27 (1H, dd, H_a, J=4.5, 6.0 Hz), 5.13 (1H, d, H_c, J=4.5 Hz), 6.41 (1H, s, H_d), 6.90-7.90 (10H, m); MS m/e 287 (M^+).

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