## PHOTOFRAGMENTATION OF OXAZOLIDINES.<sup>1</sup> A NEW METHOD FOR THE GENERATION OF AZIRIDINES

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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  $C_2-0$  and  $C_4-C_5$  bonds in the former and the  $C_2-0$  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.<sup>2</sup> Concerning the photolysis with loss of carbonyl fragments from five-membered heterocyclic compounds, however, so far only the 1,2-dioxolanes<sup>3</sup>, 1,3dioxolanes<sup>4</sup>, and bicyclic isoxazolidines<sup>5</sup> have appeared in the literature. Since the photo-decarbonylation of bicyclic isoxazolidines afforded the imine as shown below,<sup>5</sup> 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  $(\underline{1a})^6$  and 1.42 g  $(10^{-2} \text{ mol})$  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<sup>0</sup>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-3pyrroline (2) and its dehydrogenated pyrrole  $\underline{3}$  in 16 and 4% yields.<sup>7</sup> Irradiation of a benzene solution of la 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.<sup>8</sup> The spectral data of <u>2</u> were in agreement with those of the compound obtained from the thermal reaction of 2,3-cis-1,2,3-triphenylaziridine with DMAD.<sup>9</sup>

All other photochemical reactions in the present paper were performed by irradiation with a 300 W high-pressure mercury lamp below 20<sup>0</sup>C.

Upon irradiation of cis-4,5-bis(p-methoxypheny1)-2,3-diphenyloxazolidine (1b) in the presence of DMAD under similar conditions, 2,5-trans-2-(p-methoxyphenyl)-1,5-diphenyl-3-pyrroline ( $\frac{4}{2}$ ) 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.<sup>10</sup>

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  $\underline{b}$  or  $\underline{b}$ , 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-



Scheme 1

aziridine intermediate <u>A</u> with elimination of aldehyde (Ar<sup>2</sup>CHO) from oxazolidine <u>1</u>. This is followed by disrotatory ring opening of <u>A</u> to trans-azomethine ylide <u>B</u>, which reacts with DMAD to give 2,5-trans-3-pyrroline <u>2</u> or <u>4</u>. This is comparable to the formation of 3-pyrroline <u>2</u> in the thermal reaction of 2,3-cis-1,2,3-triphenylaziridine with DMAD.<sup>9</sup>

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.<sup>11</sup> 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 Z, which reacted with



DMAD to give 3-pyrroline g or g. In fact, the photochemical reaction of aziridine  $\chi$  (Ar=Ph)<sup>9</sup> with DMAD under similar conditions afforded g in 52% yield (Scheme 2). Structural elucidation of g and g

was accomplished on the basis of spectral data.<sup>12</sup>

In addition, the intervention of aziridine intermediate  $\underline{7}$  was supported by the following evidence. Irradiation of oxazolidine <u>6a</u> alone in MeCN below 20<sup>o</sup>C afforded a mixture of two products, <u>10</u> and <u>11</u>, whose relative yields depended on the irradiation time (Table 1). The product <u>10</u> was identical with an aziridine dimer (Ar=Ph) formed from thermal dimerization of aziridine  $\underline{7}$  (Ar=Ph)<sup>9</sup>, and another product <u>11</u> which corresponded to an isomer of <u>6a</u> was assigned as <u>6</u>,8-oxazabicyclo[3.2.1]octane derivative on the basis of spectral data<sup>13</sup> (Scheme 3). Irradiation of other oxazolidines, <u>6b</u>, <u>6d</u>, <u>6e</u> and <u>6f</u>,



3	
	3

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.<sup>14</sup> 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.

	Oxazolidin Ar	e R	Irradiation time, h	Product, %				Recovery of روچ %
<u>6a</u>	Ph	Н	1	10	39	11	12	19
<u>6a</u>	Ph	н	2	10	10	11	30	19
<u>6a</u>	Ph	н	3	10	5	11	45	—
<u>6</u> b	Ph	Ph	1	10	21			
<u>6d</u>	p-MeC <sub>6</sub> H4	н	1	12	15	13	23	19
<u>6e</u>	Ph	Me	1	10	13			_
<u>6</u> f	Ph	Et	1	10	11		—	7

Table 1. Irradiation of Oxazolidines <u>6</u> in MeCN<sup>a</sup>

<sup>a</sup>Intractable materials were formed in all cases.

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

## References

- Photochemistry of Heterocyclic Compounds. 10. Part 9: 0. Tsuge, K. Oe, and H. Inoue, Heterocycles, <u>12</u>, 217 (1979).
- 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., <u>89</u>, 3076 (1967).
- Oxazolidines, <u>la</u>, <u>lb</u> and <u>lc</u>, were prepared from the corresponding triarylaminoethanols and benzaldehydes. <u>la</u>: mp 212-213<sup>o</sup>C; <u>lb</u>: mp 161-163<sup>o</sup>C; <u>lc</u>: mp 183-185<sup>o</sup>C.
- A trace amount of 1,2-bis(methoxycarbonyl)cyclooctatetraene [mp 110-112<sup>0</sup>C] was obtained, together with recovery (18%) of <u>la</u>.
- 8. The cyclooctatetraene compound was obtained in 20% yield, together with recovery (15%) of <u>la</u>.
- 9. A. C. Oehlshlager, A. S. Yim, and M. H. Akhtar, Can. J. Chem., <u>56</u>, 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 (1it.<sup>9</sup> mp 164-166°C); IR 1735 (sh), 1725 cm<sup>-1</sup>; NMR δ 3.60 (6H, s), 6.25 (2H, s, \$CH), 6.30-7.50 (15H, m); MS m/e 413 (M<sup>+</sup>). 3: mp 210-212°C; IR 1710 (sh), 1700 cm<sup>-1</sup>; NMR δ 3.70 (6H, s), 6.70-7.30 (15H, m); MS m/e 411 (M<sup>+</sup>). 4: mp 167-168°C; IR 1750, 1730 cm<sup>-1</sup>; NMR δ 3.59, 3.60, 3.67 (each 3H, s), 6.26 (2H, s, \$CH), 6.40-7.40 (14H, m). 5: mp 166-167°C; IR 1720, 1710 cm<sup>-1</sup>; NMR δ 3.73 (3H, s), 3.75 (6H, s), 6.70-7.30 (14H, m).
- 11. Oxazolidines <u>6</u> were prepared by the reported method (0. 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<sup>o</sup>C, was an isomer of <u>8</u>. IR 1730, 1710 cm<sup>-1</sup>; 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<sup>+</sup>).
- 12. <u>8</u>: mp 229-230<sup>o</sup>C (lit.<sup>9</sup> mp 211-212.5<sup>o</sup>C); IR 1735 (sh), 1720 cm<sup>-1</sup>; NMR & 3.76 (6H, s), 5.79 (2H, s, ≥CH), 6.50-7.70 (11H, m); MS m/e 385 (M<sup>+</sup>). <u>9</u>: mp 225-227<sup>o</sup>C (lit.<sup>9</sup> mp 225-227<sup>o</sup>C); IR 1740, 1715 cm<sup>-1</sup>; NMR & 3.50 (3H, s), 3.70 (6H, s), 5.66 (2H, s, ≥CH), 6.40-7.60 (10H, m).
- 13. <u>10</u>: mp > 300<sup>o</sup>C (lit.<sup>9</sup> mp 322-324<sup>o</sup>C); NMR  $\delta$  5.12 (4H, s,  $\geq$ C<u>H</u>), 6.40-7.70 (22H, m); MS m/e 243 (M<sup>+</sup>/2). <u>11</u>: mp 132-133<sup>o</sup>C; NMR  $\delta$  3.93 (1H, d, H<sub>b</sub>, J=6.0 Hz), 4.28 (1H, dd, H<sub>a</sub>, J=5.0, 6.0 Hz), 5.18 (1H, d, H<sub>c</sub>, J=5.0 Hz), 6.43 (1H, s, H<sub>d</sub>), 6.70-7.90 (11H, m); MS m/e 273 (M<sup>+</sup>).
- 14: 12; mp > 300<sup>o</sup>C; NMR  $\delta$  1.96 (6H, s), 5.03 (4H, s, ≽C<u>H</u>), 6.20-7.80 (20H, m); MS m/e 257 (M<sup>+</sup>/2). 13: mp 136-137<sup>o</sup>C; NMR  $\delta$  2.23 (3H, s), 3.92 (1H, d, H<sub>b</sub>, J=6.0 Hz), 4.27 (1H, dd, H<sub>a</sub>, J=4.5, 6.0 Hz), 5.13 (1H, d, H<sub>c</sub>, J=4.5 Hz), 6.41 (1H, s, H<sub>d</sub>), 6.90-7.90 (10H, m); MS m/e 287 (M<sup>+</sup>).

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