79. Photoinduced Reactions of Aryl-2*H*-azirines with Carbonyl Compounds[1]

Preliminary Communication[2]

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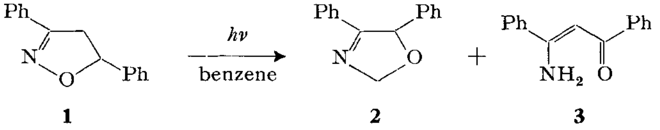
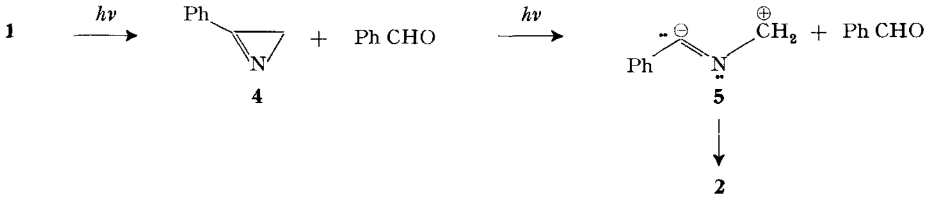
(7. V. 71)

Summary. Irradiation of 3-phenyl-(**4**), 2-methyl-3-phenyl-(**8**), and 2,3-diphenyl-2*H*-azirine (**10**), in benzene solution in the presence of aldehydes, yields the corresponding aryl-3-oxazolines. Photochemical reaction of **4** and **10** with carbon dioxide leads to the formation of 4-phenyl- (**15**) and 2,4-diphenyl-3-oxazolin-5-one (**16**), respectively.

In course of the investigation of photochemical behaviour of 2-isoxazolines, we observed that the irradiation of 3,5-diphenyl-2-isoxazoline (**1**), in benzene solution, gave 4,5-diphenyl-3-oxazoline (**2**) and *β*-amino-chalcone (**3**) in 7 and 5% yield, respectively [2].



Since irradiation of **1** in the presence of [^{14}C]-benzaldehyde yielded labelled **2** we rationalized the formation of **2** by a photoinduced decomposition of **1** into 3-phenyl-2*H*-azirine (**4**) and benzaldehyde. Photochemical ring opening of **4** would give a 1,3-dipole, benzonitrile methylene ylide (**5**), which would add to benzaldehyde in a ground state cycloaddition to form **2**. Cycloadditions of nitrile ylides and aldehydes with formation of 3-oxazolines are known [3].



In fact, the irradiation of 3-phenyl-2*H*-azirine (**4**) [4] in benzene solution ($c = 0{,}046$ M, mercury high pressure lamp, argon, quartz vessel, 6 h) in the presence of equimolar

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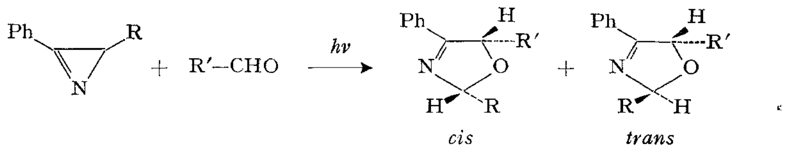
[1] 15. Communication about photoreactions of heterocyclic compounds. Parts of this communication were lectured (H. S.) at: Deuxième Congrès International de Chimie Hétérocyclique, Montpellier, 1969. 14. Communication: see [1].

[2] A full paper will be submitted to this Journal.

Photocycloaddition of aryl-2H-azirines and aldehydes



Azirine (10^{-2} mol/l)	Aldehyde (10^{-2} mol/l)	Reaction Time h; conditions		3-Oxazolines[a])		Yield (%)	m.p. (°C)
4 R = H (4.63) [4]	R' = Ph (4.73)	6	A[b])	**2** R = H, R' = Ph		62	82,5–83,3°
4 R = H (4.21)	R' = p-CH_3—C_6H_4 (4.24)	6	A	**6** R = H, R' = p-CH_3—C_6H_4		54	85,3–85,7°
4 R = H (3.62)	R' = n-C_3H_7	9	A	**7** R = H, R' = n-C_3H_7		32	b.p. 70–75°/0,1 Torr
8 R = CH_3 (2.29) [4]	R' = Ph (2.36)	5,5	A	*cis*-**9** R = CH_3 R' = Ph		18	76–77°
					trans-**9** R = CH_3 R' = Ph	9	80–81°
10 R = Ph (1.48) [4]	R' = Ph (13.4)	1	B[b])	*cis*-**11** R = R' = Ph		27	30°
					trans-**11** R = R' = Ph	8	107–109°
10 R = Ph (1.48)	R' = p-Cl—C_6H_4 (13.4)	1	B	*cis*-**12** R = Ph R' = p-Cl—C_6H_4		19	110–111°
					trans-**12** R = Ph R' = p-Cl—C_6H_4	7	139–141°
10 R = Ph (1.48)	R' = C_2H_5 (13.4)	1	B	*cis*-**13** R = Ph R' = C_2H_5		32	oil
					trans-**13** R = Ph R' = C_2H_5	13	oil
10 R = Ph (1.48)	R' = i-C_3H_7 (13.4)	1	B	*cis*-**14** R = Ph R' = i-C_3H_7		35	oil
					trans-**14** R = Ph R' = i-C_3H_7	9	oil

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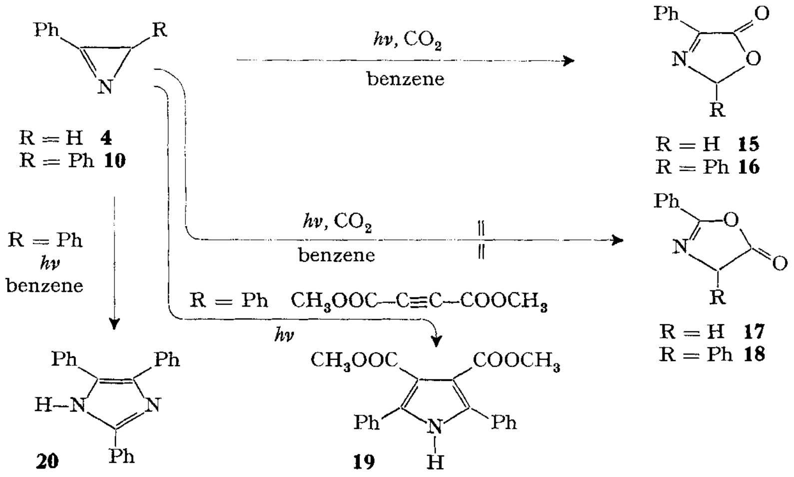
[a]) All new substances showed correct elemental analysis, NMR., IR., UV., and mass spectra. The assignment of the *cis*- and *trans*-configuration of the 3-oxazolines is based on chemical shifts and coupling constants; $J_{2,5}$ is in the range of 4.1 Hz for the *cis*-compounds and 5.3 Hz for the *trans*-compounds [5]. Yields refer to isolated, purified material.

[b]) A = Mercury high pressure lamp, quartz vessel, benzene solution; B = as A but pyrex vessel.

amounts of benzaldehyde, produces **2** in 62% yield. Hydrolysis of **2** with 2N hydrochloric acid gives benzoin, which proves the structure of **2** (*cf.* footnote a) in Table) and determines the direction of the addition of **5** to benzaldehyde (cf. [3]). This new type of photocycloaddition occurred using various aldehydes and aryl-2*H*-azirines (see Table); in all cases cycloaddition appears to follow the same course, indicating a common intermediate of type **5**. Where *cis*- and *trans*-isomers are possible (oxazolines **9**–**14**) the *cis*-isomer is favoured.

No distinct photoreaction was observed with 2-methoxycarbonyl-3-phenyl-2*H*-azirine and benzaldehyde in benzene solution.

A clean photoreaction occurred when **4** or **10** was irradiated in benzene solution in the presence of carbon dioxide (mercury high pressure lamp, pyrex vessel); 4-phenyl-3-oxazolin-5-one (**15**, m.p. 86–87°) was formed in 30% yield, 2,4-diphenyl-3-oxazolin-5-one (**16**, m.p. 52–54°) in 60% yield (*cf.* footnote a) in Table)[3]. The occurrence of isomeric 2-phenyl- (**17**) and 2,4-diphenyl-2-oxazolin-5-one (**18**) in the photoreaction mixture of **4** and **10** was excluded by the independent synthesis of **17** and **18** [6]. Compounds **15** and **16** as well as **17** and **18** are stable under the conditions of the photoreaction. As far as we know the cycloaddition of nitrile ylides with carbon dioxide represents new type of 1,3-dipolar cycloaddition. In the photochemical transformation of 3-phenyl sydnone into 4-phenyl-Δ^2-1,3,4-oxadiazolin-5-one a cycloaddition of this type was postulated [7].



Preliminary experiments showed that neither **4** nor **10** react photochemically with acetophenone or acetone. A photoreaction was observed however, when **10** was irradiated in benzene solution in the presence of two mol-equivalents of dimethyl acetylene dicarboxylate. In this case 2,5-diphenyl-3,4-di-methoxycarbonylpyrrole (**19**) [8] could be isolated in 40% yield. Very recently *Padwa* & *Smolanoff* [9] reported that aryl-2*H*-azirines exhibit photocycloadditions with electron-deficient olefines. Photochemical behaviour similar to that shown by aryl-2*H*-azirines is observed in

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[3] The chemistry of this little known class of compounds is under investigation.

the case of 1,3-diaryl-1*H*-diazirines which are intermediates in the photolysis of 3,4-diarylsydnones [10].

Photolysis of **4** yielded 4-phenyl-3-phenylimino-1-azabicyclo[2,1,0]pentane [10], whereas 2,4,5-triphenyl-imidazole (**20**) was formed when **10** was irradiated under the same conditions [1]. **20** was also detected in the pyrolysis products of **10** [12] (*cf.* [13]).

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BIBLIOGRAPHY

[1] *H. Heimgartner, L. Ulrich, H.-J. Hansen & H. Schmid,* Helv. *54,* 2313 (1971).

[2] *H. Giezendanner,* Thesis, University of Zurich, 1971; *H.-J. Hansen & H. Schmid,* Bull. Soc. chim. France *1971*, in press.

[3] *R. Huisgen, H. Stangl, H. J. Sturm & H. Wangenhofer,* Angew. Chem. *74,* 31 (1962).

[4] *G. Smolinsky,* J. org. Chem. *27,* 3557 (1962); *F. W. Fowler, A. Hassner & L. A. Levy,* J. Amer. chem. Soc. *89,* 2077 (1967); *A. Hassner & F. W. Fowler, ibid. 90,* 2869 (1968).

[5] *F. T. Winkler,* Thesis, University of Zurich, 1970.

[6] *J. W. Cornforth* 'The Chemistry of Penicillin', *H. T. Clarke, J. R. Johnson & R. Robinson,* p. 778, Ed. Princeton Univ. Press, Princeton N.J. 1949; *H. Gotthardt, R. Huisgen & H. O. Bayer,* J. Amer. chem. Soc. *92,* 4343 (1970).

[7] *C. H. Krauch, J. Kuhls & H.-J. Piek,* Tetrahedron Letters *1966,* 4043.

[8] *H. O. Bayer, H. Gotthardt & R. Huisgen,* Chem. Ber. *103,* 2356 (1970).

[9] *A. Padwa & J. Smolanoff,* J. Amer. chem. Soc. *93,* 548 (1971).

[10] *M. Märky, H.-J. Hansen & H. Schmid,* Helv. *54,* 1275 (1971).

[11] *F. P. Woerner, H. Reimlinger & D. R. Arnold,* Angew. Chem. *80,* 119 (1968).

[12] *J. H. Bowie & B. Nussey,* Chem. Commun. *1970,* 1565.

[13] *C. S. Angadiyavar, K. B. Sukumaran & M. V. George,* Tetrahedron Letters *1971,* 633.

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80. Zur Photodimerisierung von 3-Phenyl-2*H*-azirinen[1]

Vorläufige Mitteilung[2]

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Summary. Irradiation of 3-phenyl-2*H*-azirine (**2**) in benzene solution with a high-pressure mercury lamp yields 4,5-diphenyl-1,3-diazabicyclo[3,1,0]hex-3-ene (**4**) and not 3-phenylimino-4-phenyl-1-azabicyclo[2,1,0]pentane (**1**), as had been reported previously by others [2]. 2-Methyl-3-phenyl-2*H*-azirine (**3**) yields on irradiation a 2:1 mixture of 2-*exo*, 6-*exo*- and 2-*endo*, 6-*exo*-dimethyl-4,5-diphenyl-1,3-diazabicyclo[3,1,0]hex-3-ene (2-*exo*, 6-*exo*- and 2-*endo*, 6-*exo*-**5**). Irradiation of 2,3-diphenyl-2*H*-azirine (**8**) leads to the formation of 2,4,5-triphenyl-imidazole (**9**) and tetraphenylpyrazine (**10**). The suggested reaction path for the generation of **9** and **10** is shown in Scheme 2.

Kürzlich wurde mitgeteilt [2], dass bei der Bestrahlung von α-Azidostyrol in benzolischer Lösung mit einer Quecksilber-Hochdrucklampe neben 3-Phenyl-2*H*-azirin (**2**) (vgl. auch [3]) in 10% Ausbeute ein weiteres, kristallines Photoprodukt (Smp. 137–140°) isoliert werden konnte, dem auf Grund seiner spektralen Daten (NMR.-,

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[1] 18. Mitteilung über Photoreaktionen; 17. Mitteilung: siehe [1].

[2] Eine ausführliche Mitteilung soll in dieser Zeitschrift erscheinen.