

79. Photoinduced Reactions of Aryl-2*H*-azirines with Carbonyl Compounds¹⁾

Preliminary Communication²⁾

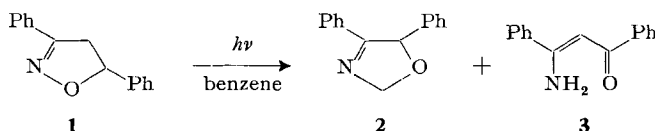
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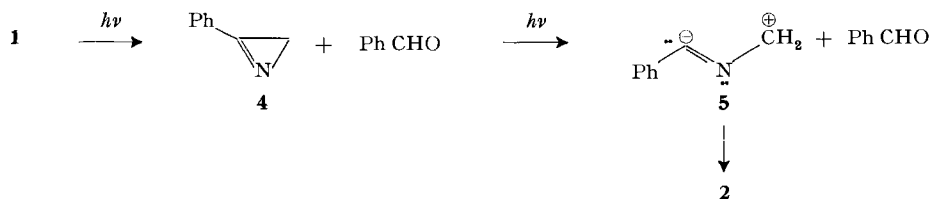
(7. V. 71)

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 [¹⁴C]-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].

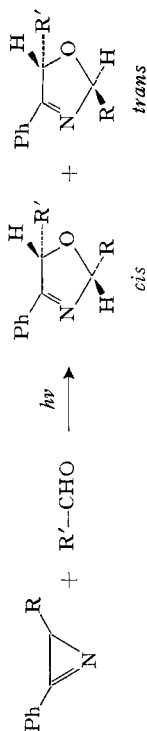


In fact, the irradiation of 3-phenyl-2*H*-azirine (**4**) [4] in benzene solution ($c = 0,046$ M, mercury high pressure lamp, argon, quartz vessel, 6 h) in the presence of equimolar

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' = <i>p</i> -CH ₃ -C ₆ H ₄ (4.24)	6 A	6 R = H, R' = <i>p</i> -CH ₃ -C ₆ H ₄	54	85,3-85,7°
4 R = H (3.62)	R' = <i>n</i> -C ₉ H ₇	9 A	7 R = H, R' = <i>n</i> -C ₉ H 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°
10 R = Ph (1.48) [4]	R' = Ph (13.4)	1 B ^{b)}	cis-11 R = R' = Ph	9	80-81°
10 R = Ph (1.48)	R' = <i>p</i> -Cl-C ₆ H ₄ (13.4)	1 B	cis-12 R = Ph R' = <i>p</i> -Cl-C ₆ H ₄	27	30°
10 R = Ph (1.48)	R' = C ₂ H ₅ (13.4)	1 B	cis-13 R = Ph R' = C ₂ H ₅	8	107-109°
10 R = Ph (1.48)	R' = <i>i</i> -C ₃ H ₇ (13.4)	1 B	cis-14 R = Ph R' = <i>i</i> -C ₃ H ₇	19	110-111°
			trans-9 R = CH ₃ R' = Ph	7	139-141°
			trans-11 R = R' = Ph	32	oil
			trans-12 R = Ph R' = <i>p</i> -Cl-C ₆ H ₄	13	oil
			trans-13 R = Ph R' = C ₂ H ₅	35	oil
			trans-14 R = Ph R' = <i>i</i> -C ₃ H ₇	9	oil

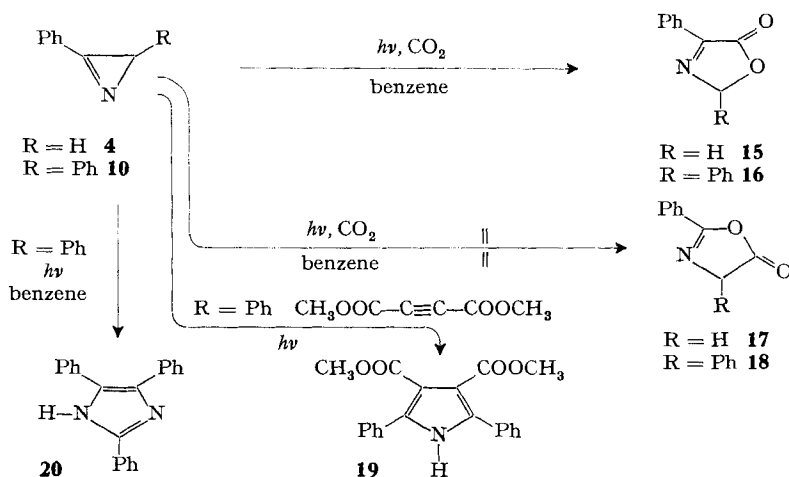
a) All new substances showed correct elemental analysis, NMR., IR., UV., and mass spectra. The assignment of the *cis*- and *trans*-configuration of the 3-oxazolines is based on chemical shifts and coupling constants: $J_{3,5}$ is in the range of 4.1 Hz for the *cis*-compounds and 5.3 Hz for the *trans*-compounds [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 2*N* 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 Table³). 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-dimethoxycarbonylpyrrole (**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

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-diarylsydnonones [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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80. Zur Photodimerisierung von 3-Phenyl-2*H*-azirinen¹⁾

Vorläufige Mitteilung²⁾

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(13. IX. 71)

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.-,

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

²⁾ Eine ausführliche Mitteilung soll in dieser Zeitschrift erscheinen.