Photocyclodimerization of Arylazirenes to 1,3-Diazabicyclo[3,1,0]hex-3-enes

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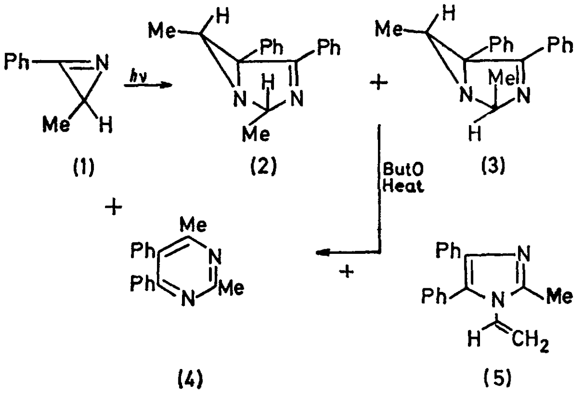
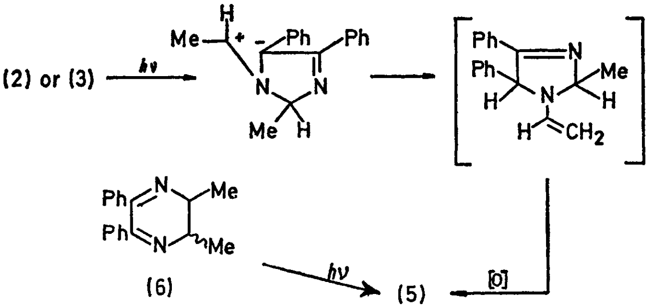
Summary Irradiation of arylazirenes gives 1,3-diazabicyclo[3,1,0]hex-3-enes *via* 1,3-dipolar addition of an initially generated nitrile ylide on to a ground state arylazirene molecule.



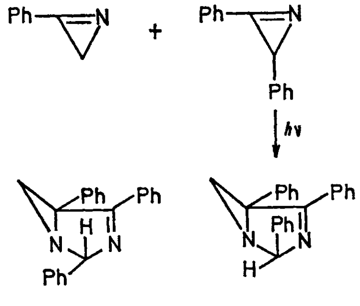
Irradiation of diphenylazirene in cyclohexane has been shown to give *endo*- and *exo*-2,4,5,6-tetraphenyl-1,3-diazabicylo[3,1,0]hex-3-enes and tetraphenylpyrazine in comparable amounts.[1] The formation of these products has been interpreted in terms of 1,3-dipolar addition of the initially generated nitrile ylide[2] on to diphenylazirene. We have found that the photodimerization of arylazirenes is a very general phenomenon.

Irradiation of the Δ^1-azirene[3] (**1**) in cyclohexane at room temperature gave a 3:1 mixture of diazabicyclohexenes (**2**) and (**3**) (45%). The structures are based on spectroscopic and chemical evidence.[4]† Chemical confirmation was obtained by treating (**2**) and/or (**3**) with KOBu^t in toluene under reflux to give the pyrimidine (**4**) (85%), m.p. 105—106°.

In addition to dimers (**2**) and (**3**), pyrimidine (**4**) (8%), and the imidazole† (**5**) (12%), m.p. 83—84° were also isolated from the irradiation of (**1**). Imidazole (**5**) was independently synthesized by irradiation of the pyrazine (**6**) in cyclohexane by the procedure of Beak and Miesel.[4] These workers have shown that 2,3-dihydropyrazines rearrange to imidazoles upon photolysis.

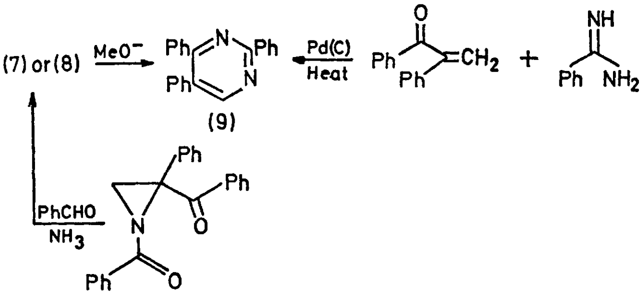


That compounds (**4**) and (**5**) are secondary photoproducts was confirmed by the finding that the photolysis of (**2**) [and/or (**3**)] in cyclohexane afforded (**4**) and (**5**). The photoconversion of (**2**) [and/or (**3**)] into (**5**) may proceed *via* an azomethine ylide, formed by cleavage of the aziridine C–C bond.[5,6] Proton transfer followed by oxidation of the transient *N*-vinylimidazoline readily accounts for the formation of (**5**). The isolation of (**4**) from the photolysis of (**2**) [and/or (**3**)] can be attributed to cleavage of the aziridine C–N bond followed by loss of hydrogen.

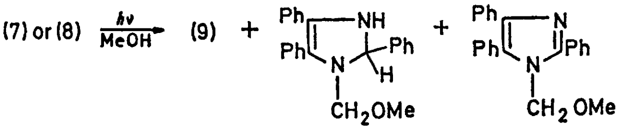


(7) (8)

Evidence for the mechanism of the photodimerization of arylazirenes was derived by irradiation of an equimolar mixture of 2-phenyl- and 2,3-diphenyl-azirene. At 3130 Å the extinction coefficient for diphenylazirene is *ca.* 20 times that of phenylazirene, so that *ca.* 95% of the light is absorbed by diphenylazirene in the above experiment. Under these conditions a mixture of two 1:1 adducts were isolated in *ca.* 50% yield. These were purified by liquid–liquid partition chromatography (l.l.p.c.) and identified as *endo*- and *exo*-2,4,5-triphenyl-1,3-diazabicyclo[3,1,0]hex-3-ene (**7**)



and (**8**) on the basis of the following evidence. The component of shortest l.l.p.c. retention time, (**7**) (20% of the 1:1 adducts), had m.p. 176—177°, and the second component (**8**) (80%) had m.p. 85—87°. Upon treatment with sodium methoxide in methanol, (**7**) and/or (**8**) afforded 2,4,5-triphenylpyrimidine (**9**), m.p. 110—111°, also prepared independently by reaction of α-phenylacrylophenone with benzamidine followed by oxidation (Pd–C). The above structural assignments were further confirmed by independent synthesis of (**7**) and (**8**) from 1,2-dibenzoyl-2-phenylaziridine, benzaldehyde, and ammonia. The formation of (**7**) and (**8**) is best rationalized in terms of 1,3-dipolar addition of the initially generated nitrile ylide on to phenylazirene.



(10) (11)

On further irradiation (in cyclohexane) (**7**) and (**8**) are converted into triphenylpyrimidine in low yield. Irradiation of (**7**) [or (**8**)] in methanol gave two new compounds in addition to (**9**) (5%), which were assigned structures (**10**)† (8%), m.p. 148—149°, and (**11**)[4] (15%), m.p. 112—113°. Treatment of (**11**) with aqueous acid afforded triphenylimidazole. The latter products, (**10**) and (**11**) can be attributed to the addition of methanol to the azomethine ylide formed on irradiation of (**7**) [or (**8**)].

We thank the National Institutes of Health and the Alfred P. Sloan Foundation for financial support.

(*Received*, 21*st January* 1972; *Com.* 089.)

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† All compounds gave satisfactory analyses. Complete spectroscopic and degradative details will be given later.

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