Some Thermal and Photochemical Reactions of *cis*- and *trans*-Substituted Enedi-imines

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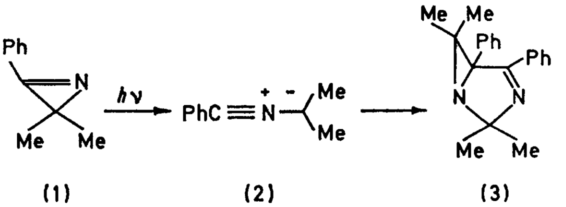
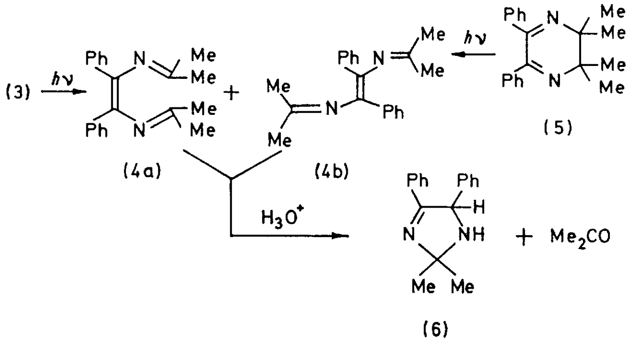
Summary The *cis* enedi-imine (**4a**) obtained from the irradiation of 1,3-diazabicyclo[3,1,0]hex-3-ene (**3**) undergoes a novel thermal cyclization to a diazacycloheptadiene; the isomeric *trans*-enedi-imine (**4b**) is photochemically converted into a diazachrysene derivative.

Arylazirines are known to undergo photodimerization to 1,3-diazabicyclo[3,1,0]hex-3-enes.[1] The formation of these dimers can be interpreted in terms of 1,3-dipolar addition[2] of an initially generated nitrile ylide (**2**) onto a ground state azirine molecule.[3] On further irradiation, the 1,3-diazabicyclohexene system undergoes photochemical ring opening to an enedi-imine intermediate.[4] The formation of imidazolines from the irradiation of dihydropyrazines has also been proposed to involve an enedi-imine intermediate.[5] Here we describe a previously unobserved photoreaction in the enedi-imine system, and call attention to the role which the methyl substituents play in its thermal behaviour.



4,5-Diphenyl-2,2,6,6-tetramethyl-1,3-diazabicyclo[3,1,0]-hex-3-ene (**3**), m.p. 71—72°, was prepared (50%) from the photolysis of a concentrated pentane solution of dimethylphenylazirine (**1**). Further irradiation of (**3**) in pentane at 25° with 2537 Å light led to a mixture of two substances. The products were separated by fractional crystallization and identified as *cis*- (**4a**) (50%) and *trans*-2,7-dimethyl-4,5-diphenyl-3,6-diazaocta-2,4,6-triene (**4b**) (40%).† These same two compounds could also be obtained from the irradiation of dihydropyrazine (**5**). Both isomers were transformed into imidazoline (**6**) and acetone when treated with methanol containing a trace of acid. This observation provides substantial support for the mechanism of imidazoline formation[5] from the irradiation of dihydropyrazines. Enedi-imines (**4a**) and (**4b**) were found to be photochemically interconverted under the reaction conditions employed.



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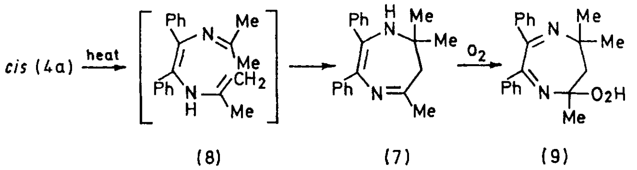
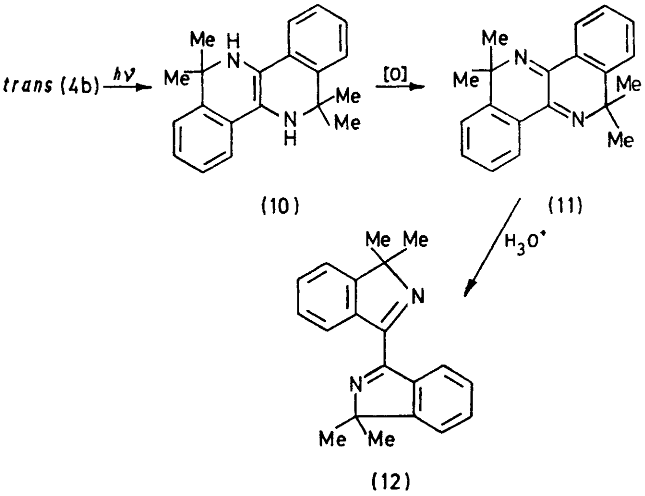
† All compounds analysed satisfactorily. Complete spectroscopic and degradative details will be given in our full manuscript.

When a solution of *cis*-enedi-imine (**4a**) in degassed CHCl$_3$ was left at room temperature, 2,3-diphenyl-5,7,7-trimethyl-1,4-diazacyclohepta-2,4-diene (**7**) (90%), m.p. 117—119° was produced. The formation of product (**7**) from *cis*- (**4a**) can be interpreted in terms of a 1,3-hydrogen shift to give (**8**) as a transient intermediate which could then lead to (**7**) by enamine addition across the neighbouring imine double bond. The passage of *cis*- (**4a**) to (**7**) is undoubtedly assisted by the driving force arising from relief of methyl group interactions.



When (**7**) was left for several hours in an aerated chloroform solution at 25°, it underwent a smooth conversion into hydroperoxide (**9**), m.p. 142—143°.† This structure was supported by the observation that (**9**) liberated iodine from an acidified potassium iodide solution. The formation of hydroperoxides from the reaction of enamines and certain Schiff bases with molecular oxygen has been reported.[6]

The *trans*-enedi-imine (**4b**) was irradiated in methanol to give the expected compounds (**6**), (**7**), and (**9**). However, the major product (53%) of the irradiation of *trans*- (**4b**) was the diazachrysene derivative (**11**), m.p. 189—190°. This compound was transformed into isoindole (**12**), m.p. 203—204°, on treatment with aqueous acid. The formation of (**11**) from (**4b**) is analogous to the photocyclization of stilbenes.[7] We have, in fact, been able to detect the presence of (**10**) as a transient intermediate in the reaction mixture. This material is subsequently oxidized to (**11**) on workup.



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[7] For a review see F. R. Stermitz in 'Organic Photochemistry,' Vol. I, ed. O. L. Chapman, Marcel Dekker, 1967, p. 247.