Photocycloaddition Reactions of a Bis-2*H*-azirine

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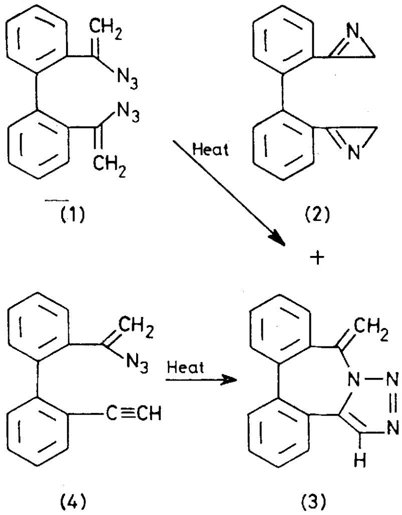
Summary Irradiation of 3,3′-(2,2′-biphenylene)bis-(2H)-azirine with electron-deficient dipolarophiles gives cycloadducts derived from a transient azabicyclo[3.1.0]hexene intermediate.

THE photocycloaddition of arylazirines with a variety of unsaturated molecules provides a convenient route for the synthesis of five-membered heterocyclic rings.[1,2] The formation of the cycloadducts has been interpreted as proceeding by way of irreversible ring opening of the azirine ring to form a nitrile ylide intermediate which is subsequently trapped by a dipolarophile.[1] Arylazirines are also known to undergo photodimerization to 1,3-diazabicyclo[3.1.0]hex-3-enes.[3,4] The formation of these dimers was rationalized in terms of 1,3-dipolar addition of the initially generated nitrile ylide on to a ground-state azirine molecule. Conditions must be carefully chosen, since the 1,3-diazabicyclohexenes are themselves photochemically labile.[5] In view of our recent interest in the photoreactions of bis-2*H*-azirines we now report some unusual features associated with the photocycloaddition of compound (**2**).

Treatment of 2,2′-divinylbiphenyl with excess of iodine azide followed by elimination of hydrogen iodide according to the general method of Hassner and his co-workers[6] afforded an excellent yield of the diazide (**1**),† m.p. 72—73 °C. Thermolysis of (**1**) in benzene for 24 h produced a mixture of the 2*H*-azirine (**2**), m.p. 84—85 °C (61%) and the triazoloazepine (**3**), m.p. 165—166 °C (17%). Structure (**3**) was verified by an independent synthesis which involved the thermolysis of the ethynylbiphenyl (**4**). The formation of (**3**) from (**1**) is best explained as proceeding *via* an intramolecular dipolar cycloaddition of one azide functionality across the neighbouring double bond of the adjacent vinyl azide followed by loss of HN_3.



Irradiation of the bis-azirine (**2**) in benzene through Pyrex resulted in the formation of a complex mixture of products. However, irradiation of (**2**) in the presence of dimethyl acetylenedicarboxylate gave a good yield of a 1 : 1 cycloadduct [*i.e.* (**5**)]. The structure of (**5**), m.p. 169—170 °C, is based on its characteristic analytical and spectral data;† n.m.r. ($CDCl_3$, 60 MHz) τ 6·88 (s, 3H), 6·50 (s, 3H), 6·02 (d, 1H, *J* 17·0 Hz), 5·57 (d, 1H, *J* 17·0 Hz), 5·28 (d, 1H, *J* 14·0 Hz), 4·37 (d, 1H, *J* 14·0 Hz), and 2·1—2·8 (m, 8H).

Irradiation of (**2**) with dimethyl fumarate in benzene took an entirely different course and produced the cycloadduct (**6**), m.p. 132—133 °C, as the only detectable photoproduct; n.m.r. τ 7·45 (d, 2H, *J* 6·0 Hz), 6·30—6·60 (m, 1H), 6·40 (s, 3H), 6·35 (s, 3H), 5·30 (dd, 1H, *J* 15·0 and 8·0 Hz),

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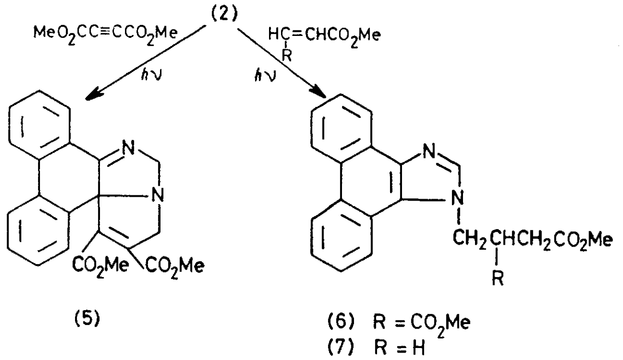
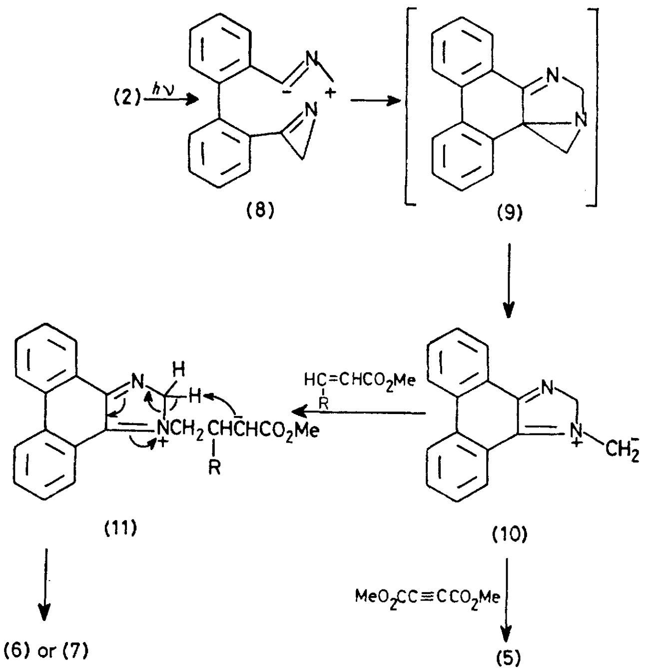
† All compounds gave satisfactory analyses. Complete spectroscopic and degradative details will be given elsewhere.

5·10 (dd, 1H, *J* 15·0 and 8·0 Hz), 2·2—2·4 (m, 5H), 2·15 (s, 1H), 1·75 (m, 1H), and 1·0—1·2 (m, 2H). In an analogous manner, photoaddition of (**2**) with methyl acrylate gave the imidazole (**7**), m.p. 76—77 °C, in high yield.





The formation of the cycloadduct (**5**) can be rationalized by the assumption that the initially generated nitrile ylide (**8**) undergoes rapid cycloaddition across the C=N double bond of the adjacent azirine ring to give a transient diazabicyclohexene (**9**). The high degree of order already present in the transition state undoubtedly enhances the rate of the intramolecular reaction relative to bimolecular cycloaddition with the added dipolarophile. The initially generated azabicyclohexene (**9**) undergoes subsequent ring opening to give the azomethine ylide (**10**) which is ultimately trapped with dimethyl acetylenedicarboxylate. Reactions involving the photochemical cleavage of bicycloaziridines to azomethine ylides[5] and their subsequent 1,3-dipolar additions to reactive multiple bonds are well known and provide good chemical analogy for the above suggestion.

The isolation of the cycloadduct (**6**) (or **7**) from the addition of dimethyl fumarate (or methyl acrylate) to the azomethine ylide (**10**) seemingly requires the formation of a discrete intermediate (**11**) in which transfer of a hydrogen from the ring to the side chain can occur. The results do not seem to be consistent with a process involving 1,3-cycloaddition of (**10**) with dimethyl fumarate followed by ring opening of the initially formed cycloadduct to give (**6**), since there is no reason why the cycloadduct derived from methyl acrylate would be expected to give (**7**) under the reaction conditions used. The formation of the cycloadducts (**6**) or (**7**) in the reaction of (**2**) with electron-deficient olefins has some interesting implications in relation to the classical 1,3-dipolar cycloaddition. Current opinion favours a concerted mechanism for dipolar cycloaddition[7] although an alternative proposal involving a spin-paired diradical intermediate has been advanced by Firestone.[8] The above data appear to provide the first example of an ene-type reaction from a 1,3-dipole. The possibility that other ene reactions can occur from 1,3-dipoles now merits serious consideration.

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