1*H*-Azirines as Intermediates in the Photolysis of 1,2,3-Triazoles

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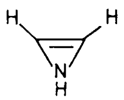
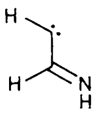
Photolytic conversion of 1-aryl-1,2,3-triazoles (**5**) and (**14**) into the 'rearranged' indoles (**4**) and (**15**), respectively provides the first evidence for antiaromatic 1*H*-azirines, *e.g.* (**8**), as reactive intermediates in a photochemical reaction.

Although molecular orbital calculations indicate that the formally antiaromatic 1*H*-azirine (**1**)† is stable relative to the isomeric imidoyl carbene (**2**),[1] little evidence has been obtained for the participation of these azirines in reactions in which carbenes of type (**2**) are generated, and none for such reactions in solution. Thus 1*H*-azirines are formed in the flash vacuum pyrolysis of various substituted 1,2,3-triazoles[3] as is 1*H*-benzazirine in the similar decomposition of isatin,[4] but azirines were not detected in the gas phase thermolysis or solution phase photolysis of 1-aryl triazoles and benzotriazoles.[5,6] We now present evidence for the intermediacy of dipole-stabilised 1*H*-azirines in the solution phase photolysis of substituted 1-aryl-1,2,3-triazoles. 1*H*-Azirines have previously been proposed as intermediates in solution, in the addition of phthalimido-nitrene to alkynes.[7]

Irradiation of an acetonitrile solution of triazoles (**3a**—**d**) at 254 nm gave, with the exception of the ethyl ester (**3a**), moderate yields of the expected benzindoles (**4a**—**d**) as the only isolable products (0, 47, 76, 48% respectively) (Scheme 1).‡§ Similarly, irradiation of the isomeric triazoles (**5a**—**d**) gave the *same* benzindoles (**4a**—**d**) together with smaller amounts of the expected benzindoles (**6a**—**d**) (see Table 1). Irradiation of benzindole (**6a**) gave none of the isomerised product (**4a**).



(**1**)



(**2**)

A mechanistic interpretation of these results is proposed in Scheme 2. Imidoyl carbene (**7**) obtained on photolysis of triazole (**5**) undergoes two modes of reaction: direct cyclisation to the naphthalene 2-position leading to benzindole (**6**) or rearrangement, *via* the 1*H*-azirine (**8**), to the isomeric carbene (**9**) which cyclises to benzindole (**4**). Generation of carbene (**9**) however results only in direct cyclisation to benzindole (**4**). No traces of indoles (**6**) were detected on photolysis of triazoles (**3**). This indicates that either cyclisation of carbene (**7**) to azirine (**8**) or ring opening of azirine (**8**) to carbene (**9**) is irreversible. Molecular orbital (MNDO) calculations[8] on model compounds indicate that azirine (**10**) is more

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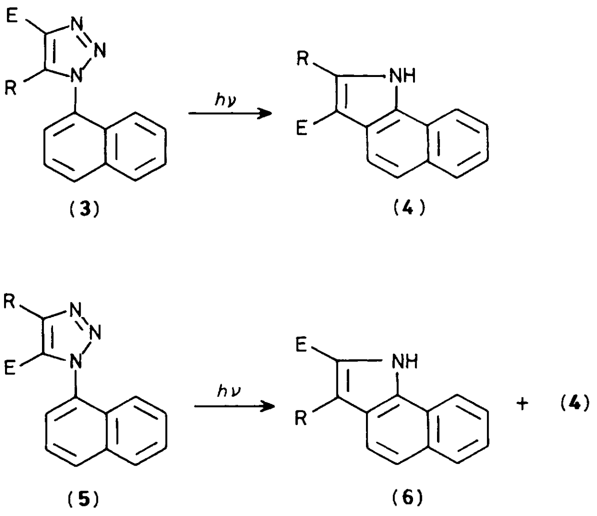
† Calculations also indicate a high barrier (35 kcal mol^{-1}) for inversion at nitrogen, and a preferred conformation with the N–H bond at an angle of 68° to the ring plane, thus reducing overlap between the nitrogen lone pair orbital and the π-system (ref. 2).

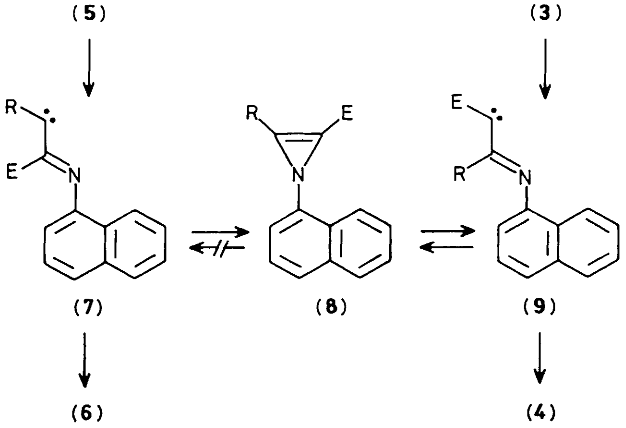
‡ The known triazoles and indoles reported here agreed with literature descriptions and all the new compounds were fully characterised.

§ Yields are based on triazole consumed. Starting triazoles were recovered from incomplete reactions, but in no case was the isomeric triazole detected (t.l.c.), nor could any be isolated, though they are well separated on t.l.c. and in column chromatography. Thus alternative mechanisms involving initial rearrangement of the triazoles were discounted.

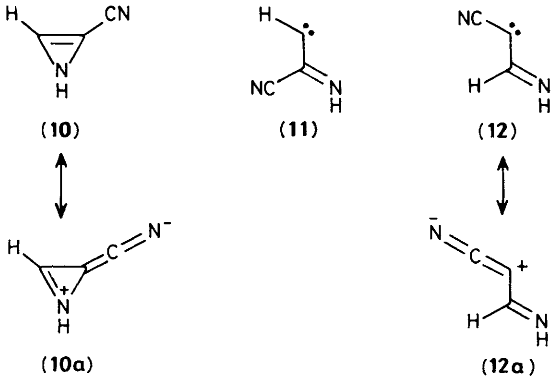


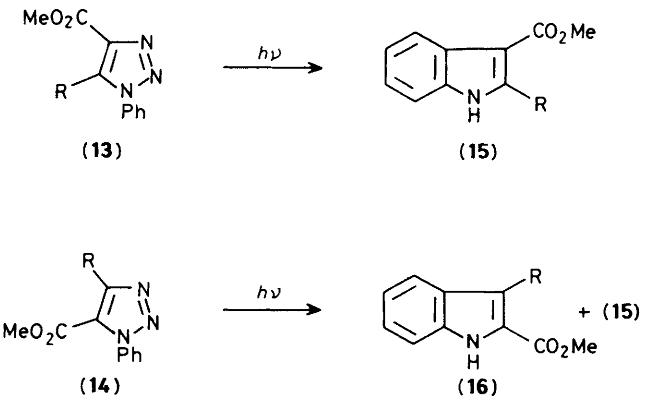
a; E = CO_2Et, R = H
b; E = CO_2Me, R = Me
c; E = CN, R = H
d; E = CN, R = Me
e; E = CO_2Me, R = H

Scheme 1



Scheme 2





a; R = H
b; R = Me

Scheme 3

Table 1. Yields of benzindoles (**4**) and (**6**) from the photolysis of triazoles (**5**).

	% Yield	
Triazole (**5**)	Indole (**4**)	Indole (**6**)
a	19	11
b	36	15
c	39	14
d	37	27

stable than carbenes (**11**) and (**12**). However the difference in energy between azirine (**10**) and carbene (**11**) (12.7 kcal mol^{-1}; 1 cal = 4.184 J) is calculated to be much greater than between (**10**) and carbene (**12**) (1.5 kcal mol^{-1}), and this is attributed to stabilisation of carbene (**12**) by the dipolar structure (**12a**). 1*H*-Azirine itself is calculated to be 8.1 kcal mol^{-1} more stable than carbene (**2**) (*cf. ca.* 20 kcal mol^{-1} given by the less refined earlier method[1]). The larger energy difference between azirine (**10**) and carbene (**11**) than between azirine (**1**) and carbene (**2**) is attributed partly to a small destabilising effect of the cyano group on carbene (**11**) but more to stabilisation of the azirine (**10**) by the non-antiaromatic dipolar structure (**10a**).

On the basis of these calculations, assuming that carbene (**9**) can undergo reversible ring closure to azirine (**8**), the failure of triazole (**3**) to afford benzindole (**6**) indicates that cyclisation of carbene (**7**) to (**8**) is irreversible, and that once formed the azirine (**8**) opens exclusively to the dipole-stabilised carbene (**9**). Furthermore, the fact that carbene (**7**) undergoes preferential rearrangement to (**9**) prior to cyclisation onto the naphthalene ring provides experimental evidence that the energy difference between these two species is substantial.

The failure of triazole ethyl ester (**3a**) to give any detectable amount of the benzindole (**4a**) is noteworthy; no clean products could be isolated from this photolysis. The reason for this is presumably associated with the presence of the ethyl group (which could, for example, be lost as ethylene from the intermediate singlet or triplet carbene) since the corresponding methyl ester (**3e**) does give the expected benzindole (**4e**) (38%) on photolysis. The fact that the isomeric triazole ethyl ester (**5a**) also gives the rearranged benzindole (**4a**) suggests that the intermediate carbene (**9**) formed directly by photolysis of triazole (**3a**) is in a different electronic state from that produced by rearrangement of carbene (**7**) *via* 1*H*-azirine (**8**).

In view of the rearrangement which accompanies photolysis of triazoles (**5**), we investigated the similar decomposition of the *N*-phenyltriazoles (**13a**,**b**) and their isomers (**14a**,**b**) (Scheme 3). In line with the above results, irradiation of (**13a**,**b**) gave solely the unrearranged indoles (**15a**,**b**) in 20 and 55% yield respectively, whilst irradiation of (**14a**,**b**) gave the rearranged products (**15a**,**b**) (5 and 42% respectively) together with the unrearranged products (**16a**,**b**) (25 and 21% respectively).§ Thus, although no similar rearrangement was observed in the photolysis of 1,4- and 1,5-diphenyl-1,2,3-triazoles,[5] stabilisation of the intermediates by electron withdrawing groups may give rise to a fairly general rearrangement of imidoyl carbenes *via* the formally antiaromatic, isomeric 1*H*-azirines.

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