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PHOTOCYCLOADDITION REACTIONS OF ARYLAZIRINES WITH HETERO-MULTIPLE BONDS

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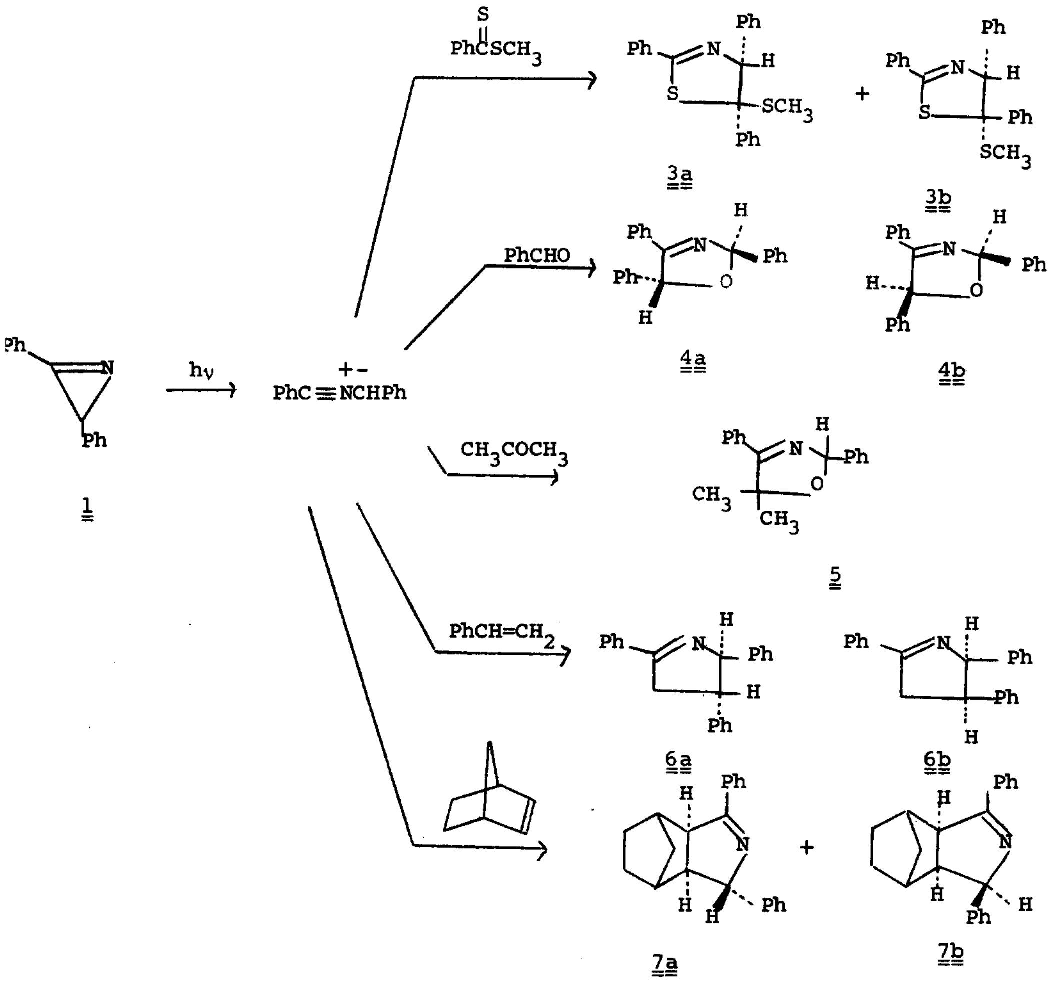
Previous studies on the photochemistry of arylazirines have shown that the electronically excited singlet state of the three membered ring opens to give a nitrile ylide intermediate.[1] This intermediate 1,3-dipole can be trapped by ground state cycloaddition reactions with suitable dipolarophiles. Trapping agents reported hitherto in this system include electron deficient carbon-carbon multiple bonds and, in their absence, the carbon-nitrogen double bond of unreacted azirine.[2,3] It was anticipated that the photoaddition of arylazirines would not be restricted to just electron deficient olefins, but would also occur with a variety of dipolarophiles. This concept was supported by the recently published work of Huisgen which showed that these reactions do occur with nitrile ylides generated by ground state reactions.[4] In this communication we report on the cycloaddition reactions of diphenylazirine with (1) the carbonyl group of aldehydes and ketones (2) the thiocarbonyl group of dithioesters (3) strained carbon-carbon double bonds, and (4) carbon-carbon bonds which are activated by a single aromatic substituent. The photocycloaddition of azirines with a wide variety of dipolarophiles provides a synthetic route into systems otherwise difficult to prepare.[5]

A solution of 2,3-diphenylazirine (1)[6] (0.3g) in 150 ml of benzene which contained an equimolar amount (0.26g) of methyldithiobenzoate[7] was irradiated under a nitrogen atmosphere with an internal water cooled mercury arc lamp (500W) through a Pyrex filter. Column chromatography and recrystallization from hexane yielded two Δ^2-thiazolines, 3a (mp 116-117°) and 3b (mp 125-126°). Nmr analysis of the crude photolysate indicated that 3b was the major adduct

(3a/3b = 1.0/1.5) by comparison of the methyl singlets at τ7.86 (3a) and 8.10 (3b).[8] The total isolated yield of 3a and 3b was 25%.



Similar irradiation of a solution of 1 (0.3g) in 150 ml of benzene which contained an excess of benzaldehyde (0.388g) proceeded to give two Δ^3-oxazolines, 4a (mp 107-108°) and 4b (obtained as an oil which eluded attempts at recrystallization). Isolation of 4a and 4b in 25% total yield was accomplished by liquid-liquid partition chromatography. The ratio of the two cycloadducts (4a/4b = 1:2) was determined by nmr analysis of the doublets associated with proton H_5 (τ3.72 (4a) and τ3.87 (4b)) in the crude photolysate.[8]

The photocycloaddition of diphenylazirine with acetone was not as facile. When a solution of 1 (0.3g) in 150 ml of benzene which contained a moderate excess of acetone (0.27g) was irradiated, no photoadduct was obtained; instead tetraphenylpyrazine was produced on extended irradiation.[2] However, when a large excess of acetone was used, a single cycloadduct was isolated in moderate yields. On the basis of its spectral data this material is assigned as 2,4-diphenyl-5,5-dimethyl-Δ^3-oxazoline (5): m/e 251 (parent), 193 (p - CH_3COCH_3); ir (neat) 6.14 (C=N), 9.5 and 9.65μ (C-O); nmr ($CDCl_3$) τ8.35 (s 6H), 3.43 (s, 1H), 2.10-3.10 (m, 10H). The low field position of proton H_2 supports this orientation of addition.[8]

The photolysis of a solution of 1 (0.5g) and excess styrene (0.5g) in 500 ml of benzene afforded Δ^1-pyrrolines 6a and 6b (combined yield 50%). The mixture of pyrrolines could be separated by liquid-liquid partition chromatography. Comparison of the signals of proton H_5, which appeared at τ4.42 (6b) and 4.71 (6a), indicated that 6a was the major component (6a/6b = 1.5/1) of the mixture.[8]

The less reactive dipolarophile norbornene also formed a mixture of two adducts with diphenylazirine. Irradiation of a solution of 1 (0.57g) and norbornene (5.8g) in 500 ml of benzene gave a 1:1 mixture of tricyclic Δ^1-pyrrolines 7a and 7b in 36% yield. Crystallization of the mixture from ether-hexane gave 7a as a crystalline solid, mp 141-143°. The nmr spectra of 7a and 7b were essentially identical to the adducts obtained from the reaction of N-(p-nitrobenzyl)benzimidoyl chloride with triethylamine and norbornene.[4b]

From the above examples it can be concluded that the photocycloaddition of arylazirines with dipolarophiles is a general reaction which may be used for the synthesis of a variety of five-membered heterocyclic rings.

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8. All spectral data obtained for the compounds in this paper are in very good agreement with those reported for similar compounds.[4]