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An Unusual 1 - 3 Photo Cycloaddition of Alkenes to s-Triazolo/4,3-b/Pyridazine

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Although the photochemical alkylation of N-heterocyclic aromatic compounds by alcohols, ethers and amines[2,3] has been studied in some detail, the photochemical cycloaddition reactions of alkenes to N-heterocyclic aromatic compounds has been little studied. Koch and coworkers[4] and Tsuge and coworkers[5] have recently shown that certain alkenes add to activated imino groups to yield substituted azetidine compounds. We now report that the photochemical cycloaddition of alkenes to s-triazolo/4,3-b/pyridazine (I)[6] does not give azetidine products but rather an unusual 1 - 3 addition to the 1,8 positions of I with a concurrent opening of the pyridazine ring occurs.

A solution of 200 mg of I, 1 ml of cyclohexene and 15 ml of methylene chloride was irradiated with 3600 Å light in a Rayonet Photochemical Reactor. After 21 hours, the solvent was removed and the products were isolated on a vapor phase chromatograph yielding 9-methylene-5,6,7,8-tetrahydro-9H-s-triazolo /1,5-a/indole (II, 26 %) and 9-cyanomethyl-5,6,7,8-tetrahydro-9H-s-triazolo /1,5-a/indole (III, 39 %)(see scheme I).In the presence of 2,3-dimethyl-1,3-butadiene, I yielded four products: 5,6-dihydro-6-isopropenyl-6-methyl-7-methylene-9H-pyrrolo/1,5-a/-s-triazole (IV), 7-cyanomethyl-5,6-dihydro-6-isopropenyl-6-methyl-9H-pyrrolo/1,5-a/-s-triazole (V), 5,8-dihydro-6,7-dimethyl-9-methylene-9H-s-triazolo/1,5-a/azepine (VI) and 9-cyanomethyl-5,8-dihydro-6,7-dimethyl-9H-s-triazolo/1,5-a/azepine (VII).

The nuclear magnetic resonance (nmr) spectra together with the mass spectra (MS) (Table I) show that the products result from an addition of the alkene to the 1,8 positions of I with a concurrent opening of the pyridazine ring between nitrogen atoms 4 and 5. In the case of the diene, 1,4 addition of the diene also occurs. Compound II is a result of a loss of HCN from the initial addition intermediate. This occurs during the reaction as shown by the fact, that the irradiation of III did not give II. The nmr peak at 7.81 δ for II is indicative of an s-triazolo compound substituted in the 2,3-positions[7]. The mass spectra of compounds III, V and VII have base peaks at M-40. These are a result of the loss of CH_2CN from the parent compound.

Scheme I

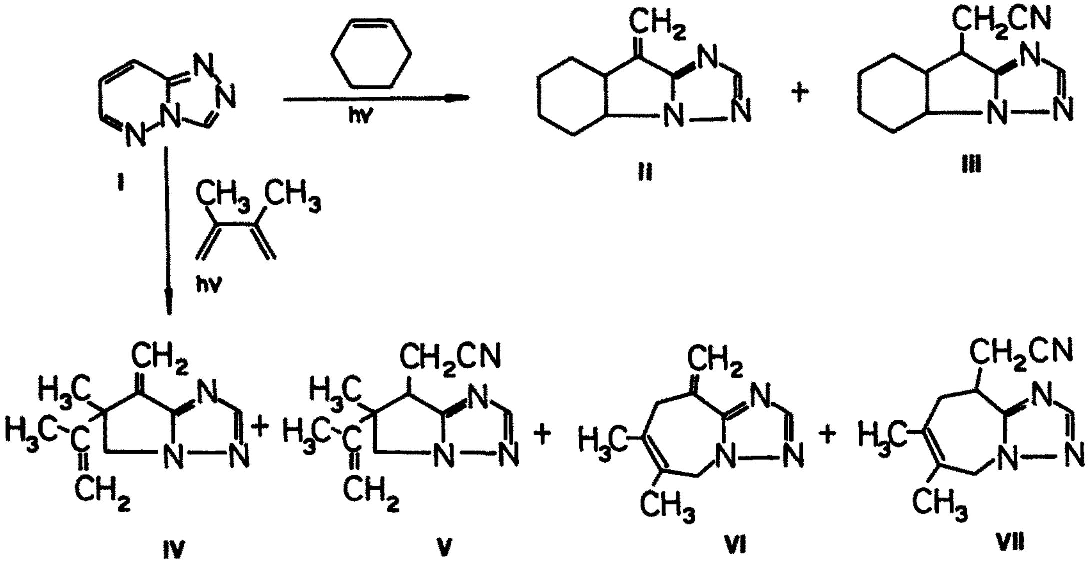


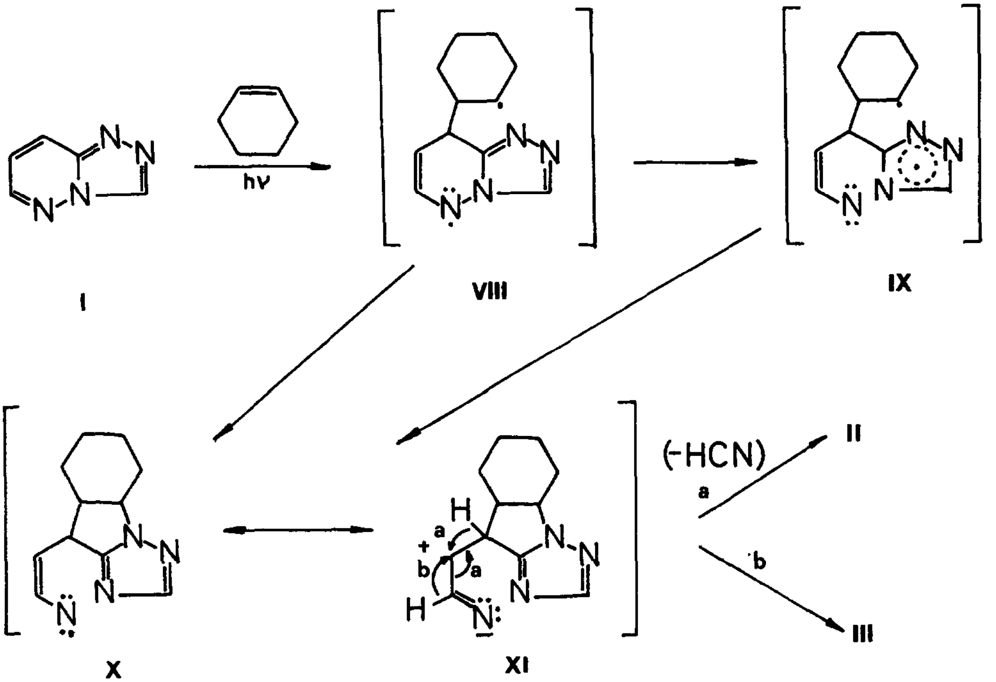
Table I

Physical Properties of Products

	NMR (δ)	Formula	Mass Spectra Calcd.	Found
II	7.81(s,1),5.70(d,1,J=3),5.04 (d,1,J=2.5),4.28(q,1),3.36(m,1), 1.80(m,4),1.46(m,4)	$C_{10}H_{13}N_3$	175.11094	175.11053
III	7.76(s,1),4.22(m,1),3.1-2.7(m,4), 1.76(m,4),1.48(m,4)	$C_{11}H_{14}N_4$	202.12184	202.12083
IV	7.85(s,1),5.85(s,1),5.07(s,1), 4.97(d,2,J=10),4.15(d,1,J=11),3.85 (d,1,J=12),1.70(s,3),1.53(s,3)	$C_{10}H_{13}N_3$	175.11094	175.11063
V	7.78(s,1),4.95(m,2),4.15(d,1,J=12), 3.85(d,1,J=10),3.52(t,1,J=7),2.75 (m,2),1.86(s,3),1.40(s,3)	$C_{11}H_{14}N_4$	202.12184	202.12184
VI	7.60(s,1),6.00(s,1),5.18(d,1,J=2.5), 4.82(s,2),3.22(s,2),1.88(s,6)	M/e 175		
VII	7.58(s,1),4.68(d,2),3.20(m,1) 2.80(m,4),1.84(s,6)	$C_{11}H_{14}N_4$	202.12184	202.12184.

The reaction is thought to be a radical addition of the excited heterocyclic compound at position 8 to the alkene (Scheme II). Position 8 is activated to both radical addition in the ground state[6] and to photochemical alkylation[8]. The resulting diradical (resonance form VIII) could undergo a homolytic cleavage of the nitrogen - nitrogen bond to form IX which would rapidly close to form the vinyl nitrene X. More likely, ring closure and nitrogen - nitrogen cleavage occurs in a conserted process. The final step can be either a hydride transfer to the electron deficient carbon in resonance form XI followed by cleavage of hydrogen cyanide (process a) to yield II or a hydride transfer from the imino carbon (process b) to yield III. The reaction does not proceed by way of an initial cleavage of the N_4 - N_5 bond since the product of such a cleavage[9], *trans*-3-(2′-cyanovinyl)-s-triazole, does not form products II and III when irradiated in the presence of cyclohexene. Process b seems reasonable since styryl nitrene, generated by three different processes, gave phenylacetonitrile[10].

Scheme II



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References

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