The Photo Cycloaddition of Alkenes to s-Triazolo[4,3-b] and [2,3-b]Pyridazines (1,2).

J. S. Bradshaw (3), B. Stanovnik and M. Tišler

Department of Chemistry, University of Ljubljana, Ljubljana, Yugoslavia

s-Triazolo[4,3-b]pyridazine (I) reacted with cyclohexene under the influence of ultraviolet light to yield 4a,5,7,8,8a,9-hexahydro-9-methylene-6H-s-triazolo[1,5-a]indole (IV) and 9-cyanomethyl-4a,5,7,8,8a,9-hexahydro-6H-s-triazolo[1,5-a]indole (V). These products were formed by the addition of the alkene to the 1,8 positions of I with a concurrent cleavage of the N_4-N_5 bond. Similar additions were observed with cyclopentene and 2,3-dimethyl-1,3-butadiene. The isomeric s-triazolo[2,3-b]pyridazine (III) reacted with cyclohexene to form an isomer of IV, 4a,5,7,8,8a,9-hexahydro-9-methylene-6H-s-triazolo[4,3-a]indole (XV) and two [2 + 2] cycloadducts (XVI and XVII).

Although the photochemical addition to and reduction of N-heterocyclic aromatic compounds has been studied in some detail (4), little work has been reported for photochemical cycloadditions of alkenes to these compounds. Koch and coworkers (5) have studied the [2 + 2] photocycloaddition of alkenes to 3-ethoxyisoindolone and 2-phenyl-2-oxazolin-4-one. These reactions yielded azetidine products. Azetidine and diazetidine compounds were also observed by Tsuge and coworkers (6) for the irradiation of 2,5-diphenyl-1,3,4-oxadiazole in indene and furan. Other photocycloadditions and dimerizations of N-heterocyclic aromatics have involved carbons of the ring (7).

We have irradiated s-triazolo[4,3-b]pyridazine (I) in the presence of alkenes and have isolated unusual cycloaddition products. The alkene added to the 1,8 positions of I with a concurrent opening of the pyridazine ring. In the presence of cyclohexene, I yielded 4a,5,7,8,8a,9-hexahydro-9-methylene-6H-s-triazolo[1,5-a]indole (IV) and 9-cyanomethyl 4a,5,7,8,8a,9-hexahydro-6H-s-triazolo-[1,5-a]indole (V) (see Scheme I). With cyclopentene, I gave 4a,5,6,7,7a,8-hexahydro-8-methylenecyclopenta-[4,5]pyrrolo[1,2-b]-s-triazole (VI) and 8-cyanomethyl-4a,5,6,7,7a,8-hexahydrocyclopenta[4,5]pyrrolo[1,2-b]-s-triazole (VII). Four products were isolated when a mixture of I and 2,3-dimethyl-1,3-butadiene was irraidated. These were the 1,2 alkene adducts, 6,7-dihydro-6-isopropenyl-6-methyl-7-methylene-5H-pyrrolo[1,2-b]-s-triazole (VIII) and 7-cyanomethyl-6,7-dihydro-6-isopropenyl-6-methyl-5H-pyrrolo[1,2-b]-s-triazole (IX) and the 1,4 diene adducts, 8,9-dihydro-6,7-dimethyl-9-methylene-5H-s-triazolo[1,5-a]azepine (X) and 9-cyanomethyl-8,9-dihydro-6,7-dimethyl-5H-s-triazolo[1,5-a]azepine (XI).

When irradiated in the presence of cyclohexene, 7-methyl-s-triazolo[4,3-b]pyridazine (II) yielded trans-9-ethylidine-4a,5,7,8,8a,9-hexahydro-6H-s-triazolo[1,5-a]-indole (XII), cis-9-ethylidine-4a,5,7,8,8a,9-hexahydro-6H-s-triazolo[1,5-a]indole (XIII) and 9-(α-cyanoethyl)-4a,5,7-8,8a,9-hexahydro-s-triazolo[1,5-a]indole (XIV). The isomeric s-triazolo[2,3-b]pyridazine (III) reacted with cyclohexene to give 4a,5,7,8,8a,9-hexahydro-9-methylene-6H-s-triazolo[4,3-a]indole (XV) and 6a,6b,7,8,9,10,10a,10b-octahydrobenzo[3,4]cyclobuta[1,2-d]-s-triazolo[1,5-b]-pyridazine (XVII) and its dehydrogenated product XVI. To the best of our knowledge, most of these ring systems have not previously been reported. Specifically cyclopenta[4,5]pyrrolo[1,2-b]-s-triazole (VI and VII), 5H-pyrrolo[1,2-b]-s-triazole (VIII and IX), 5H-s-triazolo[1,5-a]azepine (X and XI), 6H-s-triazolo[4,3-a]indole (XV) and benzo[3,4]cyclobuta[1,2-d]-s-triazolo[1,5-b]pyridazine (XVI and XVII) are new.

Results and Discussion.

Compounds I, II and III were irradiated with ultraviolet light in a mixture of the appropriate alkene and methylene chloride. After the starting material had reacted, the solvent was removed and the products were isolated on the vapor phase chromatograph (vpc). Enough material was purified by repeated isolation on the vpc for analysis by ir, nmr and high resolution mass (MS) spectrometry. Exact yields were not determined; however, the total yielded in each case was 50% or more.

The products (see Scheme I) had very distinctive nmr spectra. Compounds IV, VI, VIII and X exhibited singlet peaks at 7.8 ± 0.2 δ for H_2 and two doublets with small splitting or two singlets at 5.85 ± 0.15 δ and 5.10 ± 0.15 δ

SCHEME I
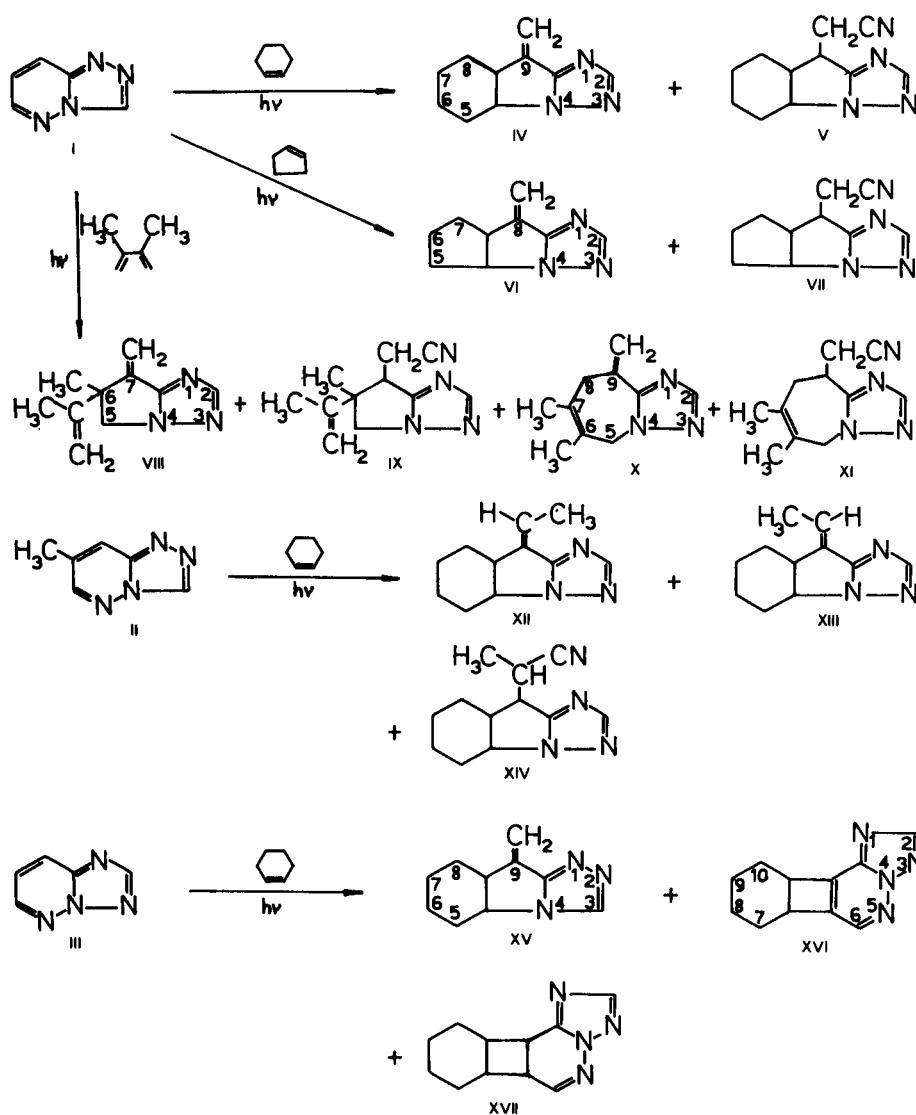
for the methylene hydrogens. Multiplets were observed at 4.4 ± 0.3 δ for H_{4a} (IV and VI) and for the two hydrogens at H_5 in VIII and at 3.1 ± 0.3 δ for H_{8a} (IV) and H_{7a} (VI). Compound X exhibited singlet peaks for two hydrogens each at 4.82 δ (H_5) and 3.22 δ (H_8). The nmr spectrum for compound XV was nearly the same as that for IV except the singlet at 7.81 δ for IV was shifted to 8.22 δ for XV. These spectral features are consistent for the assigned structures and show that IV, VI, VIII and X are 2,3-disubstituted s-triazoles and XV is 3,4-disubstituted (8).

Products V, VII, IX, XI and XIV exhibited an ir band at 2240 ± 10 cm^{-1} indicative of the cyano group. The nmr spectra for these compounds showed the triazole hydrogen at 7.70 ± 0.10 δ as well as the hydrogen (s) on the carbon α to the triazole ring at 4.4 ± 0.5 δ. The

base peak in the MS for compounds V and VII and a major fragment of IX and XI was M-40 which corresponds to a loss of CH_2CN. The base peak for XIV was M-54 which shows the loss of $CH(CH_3)CN$. Again these spectra are consistent with the assigned structures.

Geometrical isomers XII and XIII were assigned the structures indicated in accordance with their nmr spectra. The overall spectra were similar to that of IV except one methylene hydrogen was missing and a new methyl peak was present. The geometric isomers were assigned on the basis of the similarity of the spectra to that of known compounds. First, the chemical shifts for the methylene proton in XII and XIII were almost identical to that for cis-2-(2'-cyanovinyl)imidazole (the methylene hydrogen is trans to the heterocyclic ring) and trans-2-(2'-cyano-vinyl)imidazole (methylene hydrogen is cis to the ring)

respectively (9). Second, the methyl of XII has a homo-allylic $^5J_{HH}$ coupling constant of about 2.5 Hz while the methyl in XIII does not exhibit splitting. Homoallylic coupling constants have been shown to be greater in *trans* alkene systems (10). The methyl group in XII is *trans* to carbon 8a which contains a hydrogen. These data support the assigned structures.

The nmr spectra for compounds XVI and XVII are consistent for 7,8-disubstituted-*s*-triazolo[2,3-*b*]pyrida-zines. The peaks at 7.80 ± 0.05 δ and 7.40 ± 0.03 δ can be attributed to H_2 and H_6 respectively (11). Compound XVI is definitely an aromatic compound as shown by its ir and mass spectra. It was probably derived by dehydro-genation on the hot inlet to the vpc of H_{6a} and H_{10b} of compound XVII.

The photochemical reaction probably involves an excited state of I wherein position 8 is activated towards radical reactions. Indeed, the photoalkylation of com-pound I in alcohol, which is known to be a radical reaction (4), gave mainly 8-alkyl-*s*-triazolo[4,3-*b*]pyrid-azine along with some 7-alkyl and 7,8-dihydro products (12). In the absence of a good hydrogen donor, the excited I molecule could add to the alkene to form diradical XVIII (see Scheme II). The cyclohexyl radical then would add to N_1 with a concurrent homolytic cleavage of the N_4-N_5 bond to form the vinyl nitrene intermediate XIXa. That these two processes are con-certed is suggested by the fact that compound I reacted exclusively to form the 2,3-disubstituted triazole system (IV and V) while III formed the 3,4-disubstituted triazole (XV). Had the N_4-N_5 cleavage occurred first, III probably would have formed the more stable 2,3-disub-stituted triazole system (13). The final step can be either a hydride transfer from the ring hydrogen to the electron deficient carbon in XIXb followed by·the loss of hydrogen cyanide to form IV (process a) or hydride transfer from the imino carbon to yield V (process b).

The reaction of vinyl nitrenes to form substituted acetonitriles (process b) is a known reaction. For example, styryl nitrene, generated by three different processes, gave phenylacetonitrile (14). Process a, on the other hand, has not been previously observed. It is possible that the neighboring triazole ring is facilitating the reaction through a base association with the departing hydrogen cyanide.

An alternate mechanism for this cycloaddition reaction, initial cleavage of the N_4-N_5 bond followed by cyclo-addition, is not operative. Photolysis of the initial cleavage product, *trans*-3-(2'-cyanovinyl)-*s*-triazole (9), in the presence of cyclohexene, did not yield cycloaddition products. Also, the irradiation of product V did not yield IV which lends support to a common intermediate such as XIXb for both products.
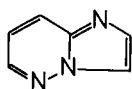
SCHEME II
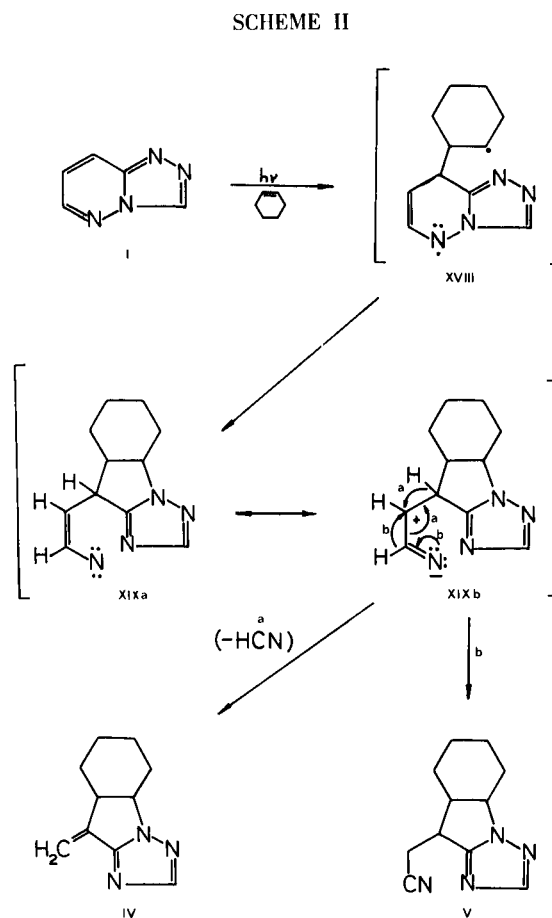
One major problem with our proposed mechanism is that compounds VIII and IX would be expected to have structures XX and XXI. Radical addition should be on
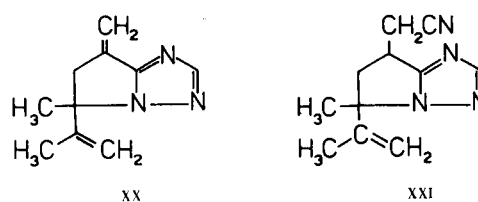

carbon 1 of the diene to give the more stable allylic radical. Addition to carbon 1 would lead to XX and XXI for the 1,2 diene reaction and the observed X and XI for 1,4 addition. The nmr spectra for VIII and IX give convincing evidence that the assigned structures (VIII and IX) and not XX and XXI are correct. Lehn and Wagner have shown that the hydrogens on the carbon α to nitro-gen in pyrrolidines with hindered rotations are not equivalent but exhibit a doublet of doublets in the nmr (15). Compounds VIII and IX have a doublet of doublets at 4.05 and 4.02 δ respecitvely. The fact that this

doublet of doublets *does not* change for compound IX gives even more compelling proof. Had those peaks been for the hydrogens at position 6 in XX, there would have been a major change in XXI due to the proton at position 7. Why radical addition is at carbon 2 of the diene is not known. It may be that the excited I molecule is so reactive that it can add either to carbon 1 or 2 of the butadiene. When the addition is at 2, products VIII and IX form. When on 1, only the 1,4 addition to form X and XI occurs.

Two similar heterocyclic compounds, imidazo[1,2-*b*]-pyridazine (XXII) and tetrazolo[1,5-*b*]pyridazine (XXIII) did not undergo cycloaddition with cyclohexene. Com-

XXII   XXIII
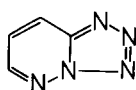
pound XXII is not as reactive to radical reactions as I (12,16) and the N_4-N_5 bond is not as readily cleaved (9). Thus, even if initial radical addition took place to the alkene, the stronger N_4-N_5 bond could prevent closure to N_1 (see Scheme II). Compound XXIII reacted but did not yield cycloaddition products. The products were probably those previously reported for the photolysis of this compound (17).

EXPERIMENTAL

All ir spectra were obtained on a Perkin-Elmer 137 spectrophotometer. JEOL JNM C60-HL and JEOL JNM PS-100 spectrometers were used to obtain the nmr spectra. A Varian model 1800 temperature programming vapor phase chromatograph (vpc) was used to isolate all reaction products. A 5' x ¼" stainless steel column packed with 10% SE-30 on 80/100 mesh chromosorb G/AW was used in all cases. The mass spectra (MS) were obtained on a CEC-20-110 C high resolution mass spectrometer. A rayonet Photochemical Reactor was used for all irradiations. Thin layer chromatography (tlc) was carried out on Kieselgel F-254 plates purchased from Merck AG.

Starting Materials.

Pure samples of *s*-triazolo[4,3-*b*]pyridazine (I) (18), 7-methyl-*s*-triazolo[4,3-*b*]pyridazine (II) (19), *s*-triazolo[2,3-*a*]pyridazine (III) (11), imidazo[1,2-*b*]pyridazine (XXIII) (20), and tetrazolo-(1,5-*b*]pyridazine (18) were prepared in this laboratory. Cyclohexene, cyclopentene, 2,3-dimethyl-1,3-butadiene and methylene chloride were used as received from Flucka AG.

Irradiation of Compound I and Cyclohexene.

Compound I (200 mg., 16.7 mmoles), 1 ml. of cyclohexene and 15 ml. of methylene chloride were irradiated in a pyrex tube by 3600 Å light. After 21 hours, no starting material was observed when the mixture was subjected to tlc analysis using a 9:1 mixture of chloroform and methanol for development. The solvent and excess cyclohexene were evaporated under vacuum. The resulting gummy mixture was isolated by vpc at 100° for 8

minutes, then programming the temperature to 220° at 10° per minute. Two peaks were isolated with a ratio of 1 to 1.5, and an estimated yield of 20 and 30%.

Peak 1 (compound (IV) exhibited the following spectral properties: nmr (δ): 7.81 (s, 1, H_2), 5.70 (d, 1, J = 3, methylene H), 5.04 (d, 1, J = 2.5, methylene H), 4.28 (m, 1, H_{4a}), 3.36 (m, 1, H_{8a}), 1.80 (m, 4, $H_{5,8}$), 1.46 (m, 4, $H_{6,7}$); MS: 175 (M^+, 100), 160 (16), 147 (20), 146 (25), 134 (45), 133 (20), 132 (23), 121 (30), 120 (17); molecular weight: Calcd. for $C_{10}H_{13}N_3$: 175.11094. Found: 175.11053.

Peak 2 (compound V) exhibited the following spectral properties: ir, 2240 cm^{-1} (CN); nmr (δ): 7.76 (s, 1, H_2), 4.22 (m, 1, H_{4a}), 3.1-2.7 (m, 4, H_{8a}, H_9, CH_2CN), 1.76 (m, 4, $H_{5,8}$), 1.48 (m, 4, $H_{6,7}$); MS: 202 (M^+, 59), 175 (10), 162 (100), 122 (20), 121 (28), 120 (13); molecular weight; Calcd. for $C_{11}H_{14}N_4$: 202.12184. Found: 202.12083.

Irradiation of Compound I and Cyclopentene.

A solution of compound I, cyclopentene and methylene chloride was irradiated as above yielding two products in a ratio of 42 to 58. Product 1 (compound VI) exhibited the following spectral properties: nmr (δ): 7.81 (s, 1, H_2), 5.77 (d, 1, J = 3, methylene H), 5.21 (d, 1, J = 2.5, methylene H), 4.75 (m, 1, H_{4a}), 3.88 (m, 1, H_{7a}), 2.2-1.5 (m, 6, $H_{5,6,7}$); MS: 161 (M^+, 100), 160 (32), 146 (10), 133 (47), 132 (25), 120 (10), 119 (14), 78 (10); molecular weight: Calcd. for $C_9H_{11}N_3$: 161.09529. Found: 161.09430.

Product 2 (compound VII) exhibited the following spectra: ir: 2230 cm^{-1} (CN); nmr (δ): 7.85 (s, 1, H_2), 4.80 (m, 1, H_{4a}), 3.15 (m, 2, $H_{7a,8}$), 2.82 (d, 2, J = 4, CH_2CN), 2.2-1.7 (m, 6, $H_{5,6,7}$); MS: 188 (M^+, 21), 148 (100), 120 (8); molecular weight: Calcd. for $C_{10}H_{12}N_4$: 188.10620. Found: 188.10937.

Irradiation of Compound I and 2,3-Dimethyl-1,3-butadiene.

A solution of compound I, 2,3-dimethyl-1,3-butadiene and methylene chloride was irradiated as above yielding four products at a ratio of 25:50:17:8. Product 1 (compound VIII) exhibited the following spectra: nmr (δ): 7.85 (s, 1, H_2), 5.85 (s, 1, methylene H), 5.07 (s, 1, methylene H), 5.01 (s, 1, methylene H), 4.92 (s, 1, methylene H), 4.05 (dd, 2, J = 11, H_5), 1.70 (s, 3, CH_3), 1.53 (s, 3, CH_3); MS: 175 (M^+, 23), 174 (23), 161 (12), 160 (100), 121 (14), 120 (13), 109 (10); molecular weight: Calcd. for $C_{10}H_{13}N_3$: 175.11094. Found: 175.11063.

Product 2 (compound X) exhibited the following spectral properties: nmr (δ): 7.60 (s, 1, H_2), 6.00 (s, 1, methylene H), 5.18 (d, 1, J = 2.5, methylene H), 4.82 (s, 2, H_5), 3.22 (s, 2, H_8), 1.88 (s, 6, CH_3); MS: 175 (M^+, 100), 174 (22), 160 (72), 145 (14), 134 (15), 120 (19); molecular weight: Calcd. for $C_{10}H_{13}N_3$: 175.11094. Found: 175.11105.

Product 3 (compound IX) exhibited the following spectral properties; ir: 2240 cm^{-1} (CN); nmr (δ): 7.78 (s, 1, H_2), 4.95 (m, 2, methylene H), 4.02 (dd, 2, J = 11, H_5), 3.52 (t, 1, J = 7, H_7), 2.75 (m, 2, CH_2CN), 1.86 (s, 3, CH_3), 1.40 (s, 3, CH_3); MS: 202 (M^+, 100), 201 (11), 187 (50), 162 (69), 160 (19), 135 (31), 134 (19), 121 (12), 120 (16); molecular weight: Calcd. for $C_{11}H_{14}N_4$: 202.12184. Found: 202.12184.

Product 4 (compound XI) exhibited the following spectra: ir: 2235 cm^{-1} (CN); nmr: 7.58 (s, 1, H_2), 4.68 (d, 2, J = 8, H_5), 3.20 (m, 1, H_9), 2.80 (m, 4, H_8, CH_2CN), 1.84 (s, 6, CH_3); MS: 202 (M^+, 100), 201 (13), 187 (50), 162 (71), 135 (32), 134 (16); molecular weight: Calcd. for $C_{11}H_{14}N_4$: 202.12184. Found: 202.12184.

Irradiation of Compound II and Cyclohexene.

Compound II was irradiated in the presence of cyclohexene as above yielding three products at a ratio of 26:30:44.

Product 1 (compound XII) exhibited the following spectra: nmr (δ): 7.88 (s, 1, H_2), 5.68 (d, 1, J = 12, vinyl H), 4.37 (m, 1, H_{4a}), 3.38 (m, 1, H_{8a}), 2.18 (dd, 3, $J_{CH-CH_3} = 12$, $J_{H8a-CH_3} = 2.5$, CH_3), 1.80 (m, 4, $H_{5,8}$), 1.50 (m, 4, $H_{6,7}$); MS: 189 (M^+, 67), 160 (20), 147 (15), 146 (100), 133 (26), 79 (15), 53 (11), 52 (11), 51 (11), 41 (19), 39 (19); molecular weight: Calcd. for $C_{11}H_{15}N_3$: 189.12659. Found: 189.12677.

Product 2 (compound XIII) exhibited the following spectra: nmr (δ): 7.85 (s, 1, H_2), 6.30 (dd, 1, $J_{CH_3-CH} = 12$, $J_{H8a-CH} = 2$, vinyl H), 4.32 (m, 1, H_{4a}), 3.40 (m, 1, H_{8a}), 1.87 (d, 3, J = 11, CH_3), 1.75 (m, 4, $H_{5,8}$), 1.50 (m, 4, $H_{6,7}$); MS: 189 (M^+, 69), 188 (10), 186 (18), 163 (25), 162 (30), 160 (23), 147 (15), 146 (100), 134 (15), 133 (21), 120 (30), 81 (13), 79 (15), 53 (15), 52 (13), 51 (13), 41 (21), 39 (23); molecular weight: Calcd. for $C_{11}H_{15}N_3$: 189.12659. Found: 189.12696.

Product 3 (compound XIV) exhibited the following spectra: ir: 2245 cm^{-1} (CN); nmr (δ); 7.90 (s, 1, H_2), 4.45 (m, 1, H_{4a}), 3.05 (m, 3, $H_{8a,9}$, CHCN), 1.82 (m, 4, $H_{5,6}$), 1.65 (d, 3, J = 10, CH_3), 1.50 (m, 4, $H_{6,7}$); MS: 216 (M^+ 23), 163 (21), 162 (100), 120 (10); molecular weight: Calcd. for $C_{12}H_{16}N_4$: 216.13749. Found: 216.13695.

Irradiation of Compound III and Cyclohexene.

A mixture of compound III, cyclohexene and methylene chloride was irradiated as above. Three products at a ratio of 32:15:53 were isolated when 3000 Å light was used. Product 1 (compound XVI) exhibited the following spectra: ir (cm^{-1}); 668, 686, 766, 782, 810, 824, 856, 905, 918, 1005, 1020, 1085, 1130, 1150, 1160, 1180, 1240, 1275, 1295, 1360, 1450, 1535, 1590, 1790, 2830, 2920, 3070; nmr (δ): 7.85 (s, 1, H_2), 7.43 (d, 1, J = 6, H_6), 3.82 (t, 1, J = 12, H_{6b} or H_{10a}), 3.10 (m, 1, H_{6b} or H_{10a}), 1.1-2.0 (m, 8, $H_{7,8,9,10}$); MS: 202 (10), 200 (M^+, 30), 122 (16), 121 (100), 82 (38), 81 (18), 67 (40), 54 (22), 41 (15), 39 (15); molecular weight: Calcd. for $C_{11}H_{12}N_4$: 200.10619. Found: 200.10667.

Product 2 (compound XVII) exhibited the following spectra: ir (cm^{-1}): 880, 1145, 1180, 1260, 1360, 1450, 1520, 1605, 2830, 2910; nmr (δ) 7.77 (s, 1, H_2), 7.37 (d, 1, J = 5, H_6), 3.60 (t, 1, J = 12, H_{10b}), 2.85 (m, 1, H_{6a}), 1.2-2.1 (m, 10, $H_{6b,7,8,9,10,10a}$); MS: 202 (M^+, 16) 121 (100), 82 (42), 67 (42), 54 (20), 41 (10), 39 (10); molecular weight: Calcd. for $C_{11}H_{14}N_4$: 202.12184. Found: 202.12184.

Product 3 (compound XV) exhibited the following spectra: nmr (δ): 8.22 (s, 1, H_3), 6.05 (d, 1, J = 2.0, methylene H), 5.30 (d, 1, J = 2.0, methylene H), 4.38 (m, 1, H_{4a}), 3.50 (m, 1, H_{8a}), 1.80 (m, 4, $H_{5,8}$), 1.47 (m, 4, $H_{6,7}$); MS: 175 (M^+, 100), 174 (33), 147 (33), 146 (93), 134 (40), 133 (33), 120 (40), 77 (47), 41 (47), 39 (53); molecular weight: Calcd. for $C_{10}H_{13}N_3$: 175.11094. Found: 175.11105.

No cyanomethyl product (similar to V) was found in this reaction. This product could have formed in such minor amounts that made isolation impossible.

Miscellaneous Irradiations.

Compound XXIII was irradiated in the presence of cyclohexene at 3600, 3000 and 2537 Å. No reaction took place. trans-3-(2'-Cyanovinyl)-s-triazole was irradiated in the presence of cyclohexene and gave no reaction. Compound XXIV did not react when irradiated in the presence of cyclohexene with 3600 Å light. With 3000 Å light, XXIV reacted but no cycloaddition

products were observed. Product V was irradiated in the presence of cyclohexene with 3600 Å light. No IV was observed after 24 hours.

REFERENCES

(1) Presented at the Fourth International Congress of Heterocyclic Chemistry, Salt Lake City, Utah, July 8-13, 1973.

(2) For a preliminary account of this work, see J. S. Bradshaw, B. Stanovnik and M. Tišler, Tetrahedron Letters, 2199 (1973).

(3) U.S. National Academy of Sciences Exchange Professor 1972-1973, on leave from the Brigham Young University, Provo, Utah.

(4) See D. G. Whitten and Y. J. Lee, J. Am. Chem. Soc., 94, 9142 (1972) for pertinent references.

(5) T. H. Koch and K. H. Howard, Tetrahedron Letters, 4035 (1972); T. H. Koch and R. M. Rodehorst, ibid., 4039 (1972).

(6) O. Tsuge, M. Tashiro and K. Oe, ibid., 3971 (1968); O. Tsuge, K. Oe and M. Tashiro, Tetrahedron, 29, 41 (1973).

(7) For reviews, see P. Beak and W. R. Messer in "Organic Photochemistry," Vol. II, O. L. Chapman, Ed., Marcel Decker, New York, N.Y., 1969, p. 117 and S. T. Reid, "Advances in Heterocyclic Chemistry," Vol. II, A. R. Katritzky and A. J. Boulton, Eds., Academic Press, New York, N.Y., 1970, p. 1.

(8) See T. Hirata, L. M. Twanmoh, H. B. Wood, A. Goldin and J. S. Driscoll, J. Heterocyclic Chem., 9, 99 (1972); and B. Stanovnik and M. Tišler, Croatia Chem. Acta, 44, 415 (1972).

(9) A. Pollak, S. Polanc, B. Stanovnik and M. Tišler, Monatsh. Chem., 103, 1591 (1972).

(10) See G. J. Martin and M. L. Martin in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. 8, Part 3, J. W. Emsley, J. Feeney and L. H. Sutcliffe, Ed., Pergamon Press, Oxford, England, 1972, p. 163.

(11) S. Polanc, B. Vercek, B. Stanovnik and M. Tišler, Tetrahedron Letters, 1677 (1973).

(12) J. S. Bradshaw, M. Tišler and B. Stanovnik, unpublished observations.

(13) P. Guerret, R. Jacquier and G. Maury, J. Heterocyclic Chem., 8, 643 (1971).

(14) J. H. Boyer, W. E. Krueger and G. J. Mikol, J. Am. Chem. Soc., 89, 5504 (1967).

(15) J. M. Lehn and J. Wagner, Tetrahedron, 26, 4227 (1970).

(16) A. Pollak, B. Stanovnik and M. Tišler, ibid., 24, 2623 (1968).

(17) T. Tsuchiya, H. Arai and H. Igeta, J. Chem. Soc. Chem. Commun., 1059 (1972).

(18) N. Takahayashi, J. Pharm. Soc. Japan, 76, 765 (1956).

(19) M. Japelj, B. Stanovnik and M. Tišler, Monatsh. Chem., 100, 671 (1969).

(20) J. Kobe, B. Stanovnik and M. Tišler, Tetrahedron, 24, 239 (1968).