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s-Triazolo[4,3-b]Pyridazine Photochemistry. The Stereochemistry of the Photocycloaddition of 3-Hexene.

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s-Triazolo[4,3-b]pyridazine(STP) has previously been reported to undergo an unusual [3+2] photocycloaddition with alkenes wherein the alkene adds to the 1 and 8 positions of the substrate with concommitant N_4 - N_5 bond cleavage yielding a 5,6-disubstituted-6,7-dihydro-7-methylene(and 7-cyanomethyl)-5H-pyrrolo[1,2-b]-s-triazole molecule.[1,2] We now wish to report the photochemical synthesis and spectral structural determination of the novel cis- and trans-3-hexene [3+2] cycloaddition reaction products.

When either cis- or trans-3-hexene and STP are irradiated in methylene chloride using a quartz immersion photoreactor, six products are isolated by vpc[3]: Compound I; ir(NaCl) 1668 cm^{-1}; nmr(δ): 0.96(t, 6H, CH_3),1.7(m, 4H, CH_2),3.08(m, 1H, H_6),4.13(dt, 1H, $J_{6,5}$=1.8 Hz, H_5),5.28(d, 1H, J=2 Hz, methylene H),5.92(d, 1H, J=2 Hz, methylene H), 8.0(s, 1H, H_2); Mass Spectrum: M^+=177.12632 ($C_{10}H_{15}N_3$). Compound II; ir(NaCl) 1670 cm^{-1}; nmr(δ): 0.96(t, 3H, CH_3),1.13(t, 3H, CH_3),1.78(m, 4H, CH_2),3.40(m, 1H, H_6),4.45(dt, 1H, $J_{6,5}$=6.0 Hz, H_5),5.28(d, 1H, J=2 Hz, methylene H),5.90(d, 1H, J=2 Hz, methylene H),8.00(s, 1H, H_2). Mass Spectrum: M^+=177.126591 ($C_{10}H_{15}N_3$). Compound III; ir(NaCl) 2225 cm^{-1}(CN), nmr(δ): 1.09(t, 6H, CH_3),1.9(m, 4H, CH_2),2.57(dt, 1H, $J_{7,6}$=5.75 Hz, H_6), 2.91(d, 2H, J_{7,CH_2}=7 Hz, CH_2CN),3.16(dt, 1H, $J_{6,7}$=5.75 Hz, $J_{CH_2,7}$=7 Hz, H_7), 4.03(dt, 1H, $J_{6,5}$= 5.75 Hz, H_5),7.93(s, 1H). Mass Spectrum: M^+=204.13615 ($C_{11}H_{16}N_4$). Compound IV; ir(NaCl) 2250 cm^{-1}(CN), nmr(δ): 1.08(t, 3H, CH_3),1.10(t, 3H, CH_3),1.55-2.00(m, 4H, CH_2),2.7-2.95(m, 3H, H_6, CH_2CN),3.60(m, 1H, H_7),4.18(dt, 1H, $J_{6,5}$=2.0 Hz, H_5),7.95(s, 1H, H_2). Mass Spectrum: M^+=204.13720 ($C_{11}H_{16}N_4$). Compound V; ir(NaCl) 2250 cm^{-1}(CN), nmr(δ): 0.96(t, 3H, CH_3),1.12(t, 3H, CH_3), 1.55-2.0(m, 4H, CH_2),2.75-3.0(m, 3H, H_6, CH_2CN),3.10(dt, 1H, $J_{6,7}$=2 Hz, H_7),4.45(dt, 1H, $J_{6,5}$=

5.8 Hz, H_5),7.91(s, 1H, H_2). Mass Spectrum: M^+=204.13639 ($C_{11}H_{16}N_4$). Compound VI; ir(NaCl) 2250 cm^{-1}(CN), nmr(δ): 1.1(t, 3H, CH_3),1.2(t, 3H, CH_3),1.75(m, 4H, CH_2),2.72(m, 3H, H_6, CH_2CN), 3.5(dt, 1H, $J_{6,7}$=2.0 Hz, H_7),4.31(dt, 1H, $J_{6,5}$=2.1 Hz, H_5),7.91(s, 1H, H_2).

Compounds I and II have been identified as the trans and cis isomers, respectively, of 5,6-diethyl-6,7-dihydro-7-methylene-5H-pyrrolo[1,2-b]-s-triazole. Compounds III through VI have been identified as the four geometric isomers of 7-cyanomethyl-5,6-diethyl-6,7-dihydro-5H-pyrrolo[1,2-b]-s-triazole.

Molecular framework models[4] show that the ethyl substituents of compounds I and II would be in almost identical magnetic environments if they were trans to each other, but would be in dissimilar environments if cis. In the nmr spectrum of compound I, we found two methyl triplets almost superimposed, differing by less than 0.03 delta units. Compound II showed two sets of methyl triplets separated by 0.17 delta units. On the basis of this, we made a tentative assignment that compound I was trans and II cis. In further support for our assignment, a search of the literature[5] showed that Anet and Muchowski[6] reported that in five-member rings which cannot deviate appreciably from planarity (our products would be one such example), the J_{cis} of the ring protons was always appreciably larger than the corresponding J_{trans}. When decoupling measurements were made on compounds I and II the $J_{6,5}$ values were found to be quite dissimilar, compound I having a $J_{6,5}$=1.8 Hz while compound II had $J_{6,5}$=6.0 Hz. Compound II must therefore be the cis isomer[6] (see Table I).

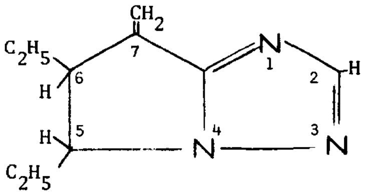
In compounds III through VI it follows that the -CH_2CN is either cis or trans to its neighboring ethyl group resulting in four possible cyanomethyl isomers. The assignment of the cyanomethyl configuration was made on the basis of decoupling measurements between protons 6 and 7. Again the larger $J_{7,6}$($J_{6,7}$) values were assigned cis configurations while the smaller $J_{7,6}$($J_{6,7}$) values were assigned trans orientations (see Table 1).

Running these reactions a higher temperature and irradiation through quartz resulted in markedly different product distributions and percentage yields (see Table II). There was no product interconversion when a mixture of compounds I-VI was subjected to heat or ultraviolet light through quartz under the conditions employed in these experiments. To the best of our knowledge, this is the first reported instance that temperature and irradiation wavelength have affected product formation and yield in a heterocyclic photochemical reaction.

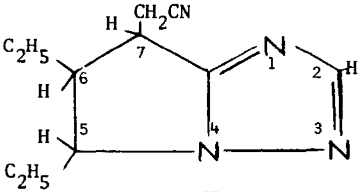
The fact that this photocycloaddition reaction is not stereospecific indicates that addition is in two steps as we previously postulated. Either a higher temperature or higher irradiation

TABLE I

Coupling Constants[a] and Configurations for Compounds I-VI.



I, II



III-VI

Comp.	$J_{6,5}$	Diethyl. Configur.	$J_{6,7}$	$J_{7,6}$	Ethyl-Cyanomethyl Configuration
I	1.8	trans	---	---	---
II	6.0	cis	---	---	---
III	5.75	cis	5.75	5.75	cis
IV	2.0	trans	---	---	cis[b]
V	5.8	cis	2.0	---	trans
VI	2.1	trans	---	2.0	trans

a. Decoupling experiments were run on a Varian XL-100.

b. Sufficient amounts of IV could not be obtained for cyanomethyl decoupling experiments. The cis assignment was made by a process of elimination.

TABLE II

Reaction Products from *cis*-3-Hexene[a]

Filter	Temp, °C	Product Yield, (%)[b]					
		I	II	III	IV	V	VI
Pyrex	24	23.3	25.6	14.5	0	31.8	5.5
Pyrex	87	27.75	28.19	12.92	7.63	15.26	8.24
Quartz	30	3.55	4.3	13.99	23.33	21.05	33.43

a. All reactions were run in evacuated, sealed tubes except for the quartz immersion reaction where nitrogen was sparged through the solution. A three-fold excess of alkene to substrate was used and in all instances CH_2Cl_2 was the solvent. Reactions were irradiated until the *s*-triazolo[4,3-b]pyridazine was no longer visible on tlc. A Hanovia high pressure mercury vapour lamp was employed in all reactions.

b. Yields are relative percentage and were calculated from the vpc data as a function of individual peak area divided by total peak area and expressed as %.

energy causes more isomerization to take place before the second or ring closing step. Higher energy also reduces the amount of hydrogen cyanide elimination from the excited intermediate.

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3. The same vpc parameters were used as in ref. 2 except that the column was packed with 5% FFAP on 80/100 mesh chromasorb G/AW.
4. Molecular Framework Models is a registered trademark of Prentice-Hall Inc., Englewood Cliffs, N. J.
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