Tetrahedron Vol 33, pp 1247 to 1251 Pergamon Press 1977 Printed in Great Britain

1,2,4-TRIAZOLES—XXXI†

PHOTODIMERIZATION OF *s*-TRIAZOLO[4,3-a]PYRIDINES: FORMATION OF CYCLOBUTANE DIMERS[1]

K. T. POTTS,[a] E. G. BRUGEL[c] and W. C. DUNLAP[d]
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12181, U.S.A.

(*Received in the USA 29 July 1976; Received in the UK for publication 31 December 1976*)

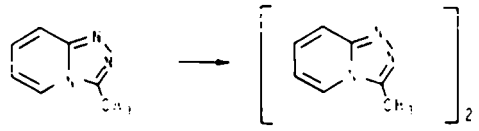
Abstract—Irradiation of several methyl substituted *s*-triazolo[4,3-a]-pyridines and 3-hydroxy-*s*-triazolo[4,3-a]pyridines with UV light gave thermally labile cyclobutane photodimers by dimerization of the 5,6-double bond in one molecule with the 7,8-double bond in another.

Heterocyclic systems, particularly those containing nitrogen, have been found to undergo varied reactions induced by UV light. These have involved isomerizations, photocycloadditions to olefins and carbonyl compounds, photoelimination reactions, and dimerizations.[2] The behavior of heteroaromatic systems with bridgehead N atoms under the influence of UV light has received little attention in the above studies. The irradiation of *v*-triazolo[1,5-a]pyridine in methanol has been reported to give α-picoline, α-picolylmethyl ether and α-picolylmethanol in poor yield,[3a] and in a study of a 6,6-fused system, both ring contraction to a substituted indolizine and ring expansion to a substituted pyrrolo[1,2-a]azepine were observed.[3b] In this communication we describe the ready photodimerization of several methyl and 3-hydroxy derivatives of the *s*-triazolo[4,3-a]pyridine ring system to cyclobutane derivatives, this present mode of dimerization being particularly interesting in view of the recent report[4] of the formation of a [4π + 4π] *anti-trans* dimer on irradiation of the isomeric *s*-triazolo[1,5-a]pyridine system at 263 nm in methylene chloride or ethanol.

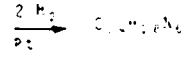
Chemical results. 3 - Methyl - *s* - triazolo[4,3-a]pyridine (**1**), in dry tetrahydrofuran, was irradiated[5] in a quartz flask with UV light: at 2537 Å the reaction was essentially complete in 12 hr; at 3600 Å (Pyrex reactor) 7 days were required for completion of the photoreaction. The product slowly separated on the walls of the irradiation vessel and was obtained as large colorless crystals, with a m.p. (192–193°) significantly higher than that of 3 - methyl - *s* - triazolo[4,3-a]pyridine (134°) to which it reverted on heating above its m.p. for a few minutes. Dimerization was indicated by the NMR spectrum which showed two slightly different Me groups, the loss of aromatic protons, and the presence of some new olefinic and methine protons. The UV spectrum with a shift to shorter wavelength suggested interruption of the chromophore present in the starting material. Tenacious retention of solvent precluded analysis of an anhydrous product but it was readily characterized as its dipicrate, clearly different from the picrate of 3 - methyl - *s* - triazolo[4,3-a]pyridine. Similarly the photoproduct derived from 3,5 - dimethyl - *s* - triazolo[4,3-a]pyridine (see below) also formed a dipicrate easily distinguishable from the picrate of the corresponding monomer.

On hydrogenation the photoproduct **2** absorbed 2 molecules of hydrogen giving hydrogenation product **3** with properties markedly different from those of its precursor. It decomposed at its m.p. (247–248°) forming non-identifiable fragments and its UV spectrum [λ_{max} 236 nm, log ε 3.58], was indicative of a simple *s*-triazole nucleus.[6] Its NMR spectrum was that of a complex, saturated hydrocarbon, and its mass spectrum was consistent with the addition of 2 molecules of hydrogen to a dimeric product of 3 - methyl - *s* - triazolo[4,3-a]-pyridine, further confirmed by additional analytical data and the ready formation of a dipicrate.

Other derivatives of this ring system also formed photoproducts. In addition to 3-methyl-, 5-methyl-, 6-methyl-, 7-methyl- and 8 - methyl - *s* - triazolo[4,3-a] -

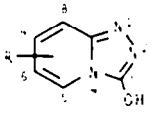


1 **2**

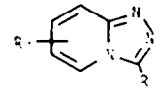


3

pyridine, 3 - hydroxy - *s* - triazolo[4,3-a]pyridine (**4**; R = H) and its 5-methyl- (**4**; R = 5-Me), 6-methyl- (**4**; R = 6-Me) and 8-methyl- (**4**; R = 8-Me) derivatives as well as 3,5 - dimethyl - *s* - triazolo[4,3-a]pyridine (**5**; R = Me; R' = 5-Me) readily gave photoproducts with properties in general similar to those described above.



4

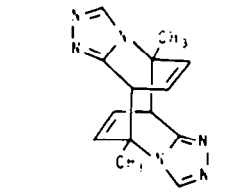


5

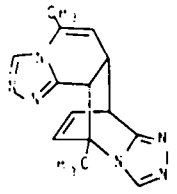
The substitution pattern in the above *s*-triazolo[4,3-a]pyridines appeared to have little effect on the ease of photodimerization but solvent choice was critical, the most effective solvents being tetrahydrofuran, dimethoxyethane and ether. When alcohol was used as solvent, decomposition of the fused-ring system occurred, as had been observed previously with *v*-triazolo[1,5-a]pyridine.[3a]

†Dedicated to Professor R. B. Woodward on the occasion of his 60th birthday.

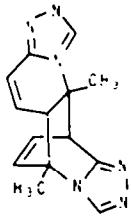
Structural and stereochemical assignments. Analysis of the NMR spectra of the photodimers of several Me-substituted derivatives of *s*-triazolo[4,3-a]-pyridine established which bonds were participating in the photoreaction, in much the same way as the structures of the 2-aminopyridine and N-methyl-2-pyridone photodimers were established.[7] In the 2-aminopyridine photodimers, a methyl group attached to an sp^3 carbon atom appeared as a singlet, while a Me group adjacent to a H atom on a double bond occurred as a slightly split doublet (J = 1.2 Hz) and analogous spectral characteristics were observed in this present case.



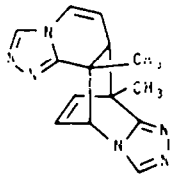
6



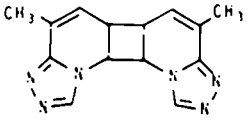
7



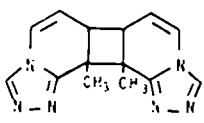
8



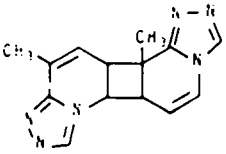
9



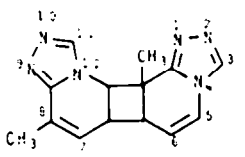
10



11



12



13

The spectral data described above show that dimerization must have involved the 6-membered ring of the fused system, with the formation of [2 + 2], [2 + 4] or [4 + 4] adducts, all of which are capable of existing in several different stereochemical modifications. A *transoid-trans* [4 + 4] adduct (**6**) (as well as the corresponding *transoid-cis*, *cisoid-trans*, and *cisoid-cis* adducts), similar to the [4 + 4] photodimer of 2-aminopyridine, was eliminated by the NMR spectrum of the photodimer from either 5 - methyl - *s* - triazolo[4,3-a]pyridine (**5**; R = H; R^1 = 5-CH_3) or the corresponding 8-Me compound (**5**; R = H; R^1 = 8-Me). Both of these spectra showed only one singlet Me resonance and one doublet Me resonance, whereas structure **6** for the photoproduct would require all the Me resonances to be singlets. Similarly the photoproduct from the corresponding 6-Me compound would require the Me resonances to be doublets.

†Experimental. A detailed analysis of the NMR data of these photoproducts and those described in the following publications will be published elsewhere.

Structures **7** and **8** represent the two possible ways of forming a [2 + 4] product from 5 - methyl - *s* - triazolo[4,3-a]pyridine (**5**; R = H; R^1 = 5-Me), for each product there being four stereoisomers. Structure **8** need not be considered further since both Me groups should appear as singlets. However, the NMR data does not exclude structure **7** whose spectrum should contain both a singlet Me resonance and a doublet Me resonance. The spectrum of the photodimer derived from 8 - methyl - *s* - triazolo[4,3-a]pyridine (**5**; R = H; R^1 = 8-Me) readily resolved this point for, if the 7,8-bond were involved in the reaction, the structure of the photoproduct would be **9**, one of the four possible stereoisomers, and its NMR spectrum would be expected to contain two singlet Me resonances.

Structures **10** and **11** represent one each of the four possible stereoisomers formed by the respective addition of the 5,6- and 7,8-bonds to themselves in 8 - methyl - *s* - triazolo[4,3-a]pyridine (**5**; R = H; R^1 = 8-Me). Cyclobutane formation involving these bonds may also be excluded on the basis of the NMR spectrum of the photoproduct derived from 8 - methyl - *s* - triazolo[4,3-*a*]pyridine (**5**; R = H; R^1 = 8-Me) as structure **10** would require two doublet Me resonances and structure **11** two singlet Me resonances. Similarly, in the photoproduct obtained from 5 - methyl - *s* - triazolo[4,3-a]pyridine (**5**; R = H; R^1 = 5-Me) the structure corresponding to **10** would require two singlet Me resonances in its NMR spectrum, whereas for the structure corresponding to **11**, the reverse situation would exist with two doublet Me resonances being required.

This exclusion process now leaves cyclobutane formation involving the 5,6-bond in one molecule and the 7,8-bond in the other molecule, one of the possible isomers formed by such an arrangement being **12**. This would require one doublet Me resonance and one singlet Me resonance for the photoproduct obtained from 8 - methyl - *s* - triazolo[4,3-a]pyridine (**5**; R = H; R^1 = 8-Me). NMR data consistent with cyclobutane formation through the 5,6- and 7,8-bonds were obtained for the photoproducts of the other *s*-triazolo[4,3-a]pyridines examined indicating that, within the substitution pattern studied, the substituent had little effect on the type of dimer formed.

The photodimer **12**, represented in the head-to-tail configuration, may also exist in a head-to-head configuration **13**. The 100 MHz NMR spectra† of the photodimers of 3 - hydroxy - 6 - methyl - *s* - triazolo[4,3-a]pyridine (**4**; R = 6-Me) (Table 1) and 3 - hydroxy - 8 - methyl - *s* - triazolo[4,3-a]pyridine (**4**; R = 8-Me) show that the photoproducts have the *cis-cisoid-cis*, head-to-head configuration **16**. In the spectrum of the former H_5 was shown to be slightly coupled to H_{6a} ($J_{5,6a}$ = 0.8 Hz) in an allylic-type coupling, since irradiation at the resonance frequency of H_{6a} resulted in a collapse of the H_5 doublet to a broad singlet. Assignment of H_8 to the lower field, more intense pair of resonances, is consistent with the effect of the 9-N atom on a "peri" H atom, shown earlier[8] to be quite appreciable in *s*-triazolo[4,3-a]pyridines.

Interrelationships between the hydrogens attached to the cyclobutane carbons (an ABC system) was clearly shown by decoupling experiments. Irradiation at δ 3.82 (H_{12b}) resulted in the collapse of the H_{12a} resonance at δ 4.73 to a broad singlet; similarly the H_{6a} resonance at δ 3.13 also gave a broad singlet. In addition, irradiation at δ 3.13 (H_{6a}) resulted in the collapse of the H_{12b} resonance to a doublet.

Table 1. NMR data for several photoproducts derived from *s*-triazolo[4,3-a]pyridine derivatives[a]

Starting *s*-Triazolo[4,3-a]pyridine Derivative	Chemical Shifts (δ)											
	H_5	C_6-CH_3	H_{6a}	C_{6b}-CH_3	H_7	H_8	H_{12a}	H_{12b}	H_6	H_{6b}	C_8-CH_3	C_{12b}-CH_3
3-OH, 6-CH_3 (4; R = 6-CH_3)	6.66	2.28	3.23	1.40	5.88	6.25	4.73	3.82				
3-OH, 8-CH_3 (4; R = 8-CH_3)	6.66		3.12				5.74		5.32	3.58	1.77	1.49

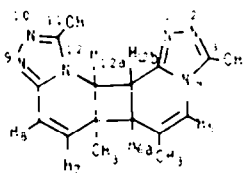
Starting *s*-Triazolo[4,3-a]pyridine Derivative	J, Coupling Constants (Hz)										
	C_6-CH_3, H_5	H_5, H_{6a}	H_{6a}, H_{6b}	H_{12a}, H_{12b}	H_{12b}, H_{6b}	C_8-CH_3, H_7	H_5, H_6	H_6, H_{6a}	H_{6a}, H_{6b}	H_{6b}, H_7	H_{6b}, H_{12a}
3-OH, 6-CH_3 (4; R = 6-CH_3)	1.3	0.8	10.1	8.0	8.6						
3-OH, 8-CH_3 (4; R = 8-CH_3)						1.3	8.0	8.0	8.0	8.0	8.0

[a]Determined in DMSO-d_6.

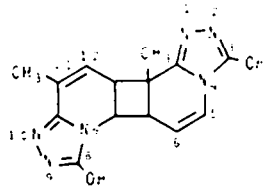
The coupling between protons 12a and 12b (8.0 Hz) establish a *cis-cisoid-cis* configuration **14** for these photodimers. Coupling constants for similar hydrogens in the carbostyril photodimer were found to be 8.0 Hz for the *cis-cisoid-cis* dimer and 2.0 Hz for the *cis-transoid-cis* dimer.[9] Attempts to apply other techniques to establishing the *cis* arrangement of the cyclobutane protons[10] were unsuccessful due to the complexity of the present ring system.

The question of head-to-head vs head-to-tail configuration for the photodimers was readily settled by the NMR spectrum of the photodimer of 3-hydroxy-8-methyl-*s*-triazolo[4,3-a]pyridine (**4**; R = 8-Me) (Table 1). The head-to-tail configuration **15** would require two doublets (H_5 and H_{12}) and four doublet of doublets (H_6, H_{6a}, H_{6b} and H_{12a}). On the other hand the head-to-head configuration **16** would require three doublets (H_5, H_7 and H_{12a}), two doublet of doublets (H_6 and H_{6a}) and one triplet of doublets (H_{6b}). The NMR spectrum represents the latter arrangement of coupling between the various protons, the various interrelationships between the protons being established by extensive decoupling experiments. The coupling constants $J_{6b,6a} = J_{6b,12a} = 8.0$ Hz indicate that these three hydrogens must be on the same side of the cyclobutane ring and is additional evidence in favor of the *cis-cisoid-cis* assignment made above. The calculated spectrum, using a LAOCOON 3 program, was in excellent agreement with the experimental spectrum.

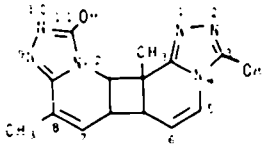
The absence of Me groups in the 6-membered rings of the photoproducts resulted in considerably more complex NMR spectra. In the NMR spectrum of the photodimer of *s*-triazolo[4,3-a]pyridine itself (**5**; R = R' = H), a complex multiplet located at δ 5.60 can be assigned to protons H_6 and H_{12a}, since the latter is located next to the bridgehead N atom at position 12. A pattern located at δ 6.29 can be assigned to H_7 and H_8 and, on scale expansion, this pattern resolved into a close AB pattern, where H_7 was further coupled to H_{6b} ($J_{7,6b} = 0.5$ Hz). A similar pattern was also observed in the 100 MHz NMR spectrum of the photodimer of *sym*-di-(3-*s*-triazolo[4,3-a]pyridyl) ethane.[11]



14



15



16

The other three cyclobutane hydrogens may be assigned with reasonable degree of certainty to the two multiplets centered at δ 4.40 and δ 4.00. The multiplet at δ 4.40 most likely corresponds to H_{6b}, since it would be a triplet of doublets and irradiation at this frequency sharpened the H_8 and H_7 into a true AB pattern.

EXPERIMENTAL

Optimum conditions for the dimerization were found to be irradiation of *ca* 0.05 molar solutions in THF with lamps emitting principally light of 2537 Å (or 3000 Å) wavelength in a Rayonet RPR-100 photochemical reactor. The photoproduct separated readily from soln and was removed at intervals from the reaction medium. Continuous monitoring of the photoreactions with TLC indicated that one product only was being formed in all cases.

The *s*-triazolo[4,3-a]pyridine derivatives were prepared and purified as described in the lit.[12-14] 3-Methyl-*s*-triazolo[4,3-a]pyridine picrate formed yellow micro-needles from water, m.p. 216–218°. (Found: C, 43.29; H, 2.84; N, 23.14. Calc. for $C_{11}H_{10}N_4O_7$: C, 43.10; H, 2.78; N, 23.20%).

3,5-Dimethyl-s-triazolo[4,3-a]pyridine picrate formed yellow needles from EtOH/Et_2O, m.p. 189–191°. (Found: C, 45.05; H, 3.37; N, 22.28. Calc. for $C_{14}H_{12}N_4O_7$: C, 44.68; H, 3.21; N, 22.34%).

The following illustrates the general procedure used in the photoreactions and in the characterization of the products.

cis - cisoid - cis - 3,11 - *Dimethyl* - 6a,6b,12a,12b - *tetrahydrobis* - s - *triazolo*[4,3-a: 4',3'-a']*cyclobuta*[1,2-c: 3,4-e']*dipyridine*. A soln of 3 - methyl - *s* - triazolo[4,3-a]pyridine[12] (1.33 g, 0.01 mol) in dry THF (200 ml) was filtered free of any suspended matter into a 10 in. quartz test tube and, after 5 min of irradiation (2537 Å) a solid began to form on the walls of the flask. The reaction was complete after 12 hr. Recrystallization from MeOH:ether afforded fine, colorless needles: 0.8 g (60%), m.p. 192–193° (at 3600 Å in a Pyrex vessel reaction required 72 hr for completion): $\lambda_{max}^{CH_3OH}$ 270 nm (log ε 3.33), 290 (3.00); NMR (D_2O) δ 2.28 (s, 3, C_3–CH_3), 2.40 (s, 3, C_{11}–CH_3), 3.73–4.42 (m, 3, hydrocarbon), 5.18–5.72 (m, 2, olefinic and hydrocarbon), 6.19–6.29 (m, 2, olefinic), 6.91 (d, 1, C_3–H). The dipicrate formed yellow micro-needles from water, m.p. 193–195°. (Found: C, 43.29; H, 2.86; N, 23.08. Calc. for $C_{26}H_{20}N_{12}O_{14}$: C, 43.10; H, 2.78; N, 23.20%).

When benzene was used as solvent, a 35% yield of photoproduct was obtained after 108 hr of irradiation at 3600 Å. Deoxygenation of the photolysis medium by passing through dry N_2 had no appreciable effect on the formation of the photodimer.

cis - cisoid - cis - 3,11 - *Dimethyl* - 5,6,6a,6b,7,8,12a,12b - *octahydrobis* - s - *triazolo*[4,3-a: 4',3'-a']*cyclobuta*[1,2-c: 3,4-e']*dipyridine*† *cis* - *cisoid* - *cis* - 3,11 - Dimethyl - 6a,6b,12a,12b - tetrahydrobis - *s* - triazolo[4,3-a: 4',3'-a']cyclobuta[1,2-c: 3,4-e'] - dipyridine (1.0 g, 0.004 mol) in MeOH (100 ml) and platinum oxide (20 mg) were shaken together over H_2 in a Parr apparatus (25 psi of H_2, 6 hr). Norit was added, the mixture filtered and, upon addition of ether, the product separated as fine, colorless needles: 0.9 g (90%), m.p. 237–248°; IR (KBr) 3400 (H_2O); $\lambda_{max}^{CH_3OH}$ 236 nm, log ε 3.58; NMR (CF_3CO_2H) no olefinic protons; mass spectrum (70 eV), *m/e* (rel intensity), M^+ 270 (48). (Found: C, 58.16; H, 6.96; N, 29.10. Calc. for $C_{14}H_{18}N_4 \cdot H_2O$: C, 58.28; H, 7.01; N, 29.29%).

The di-picrate formed yellow micro-leafs from water, m.p. 237–238°. (Found: C, 43.12; H, 3.38; N, 23.00. Calc. for $C_{26}H_{24}N_{12}O_{14}$: C, 42.86; H, 3.32; N, 23.07%).

cis - cisoid - cis - 3,5,11,12a - *Tetramethyl* - 6a,6b,12a,12b - *tetrahydrobis* - s - *triazolo* - [4,3-a: 4',3'-a']*cyclobuta*[1,2-c: 3,4-e']*dipyridine*. 3,5 - Dimethyl - *s* - triazolo[4,3-a]pyridine[13] (1.0 g, 0.007 mol) was photolyzed at 3600 Å in THF as described above. The product crystallized from MeOH:ether or EtOH:toluene as fine, colorless needles: 0.6 g (60%), m.p. 220° dec; $\lambda_{max}^{CH_3OH}$ 240 nm (log ε 4.14), 290 (3.61); NMR (D_2O) δ 2.2 (s, 3, C_{12a}–CH_3), 2.23 (d, 3, C_3–CH_3), 3.14 (s, 3, C_3–CH_3), 3.62 (s, 3, C_{11}–CH_3), 3.90 (m, 1, C_{12b}–H), 4.06 (m, 1, C_{6a}–H), 4.50 (m, 1, C_{6a}–H), 5.51 (m, 1, C_6–H), 6.54 (q, 1, C_7–H), 6.78 (d, 1, C_8–H). (Found: C, 65.40; H, 6.27; N, 28.41. Calc. for $C_{14}H_{18}N_4$: C, 65.28; H, 6.16; N, 28.55%).

The di-picrate formed yellow needles from methanol:ether, m.p. 211–213°. (Found: C, 44.86; H, 3.39; N, 22.43. Calc. for $C_{28}H_{24}N_{12}O_{14}$: C, 44.68; H, 3.21; N, 22.34%).

cis - cisoid - cis - 3,5,11,12a - *Tetramethyl* - 5,6,6a,6b,7,8,12a,12b - *octahydrobis* - s - *triazolo*[4,3-a: 4', 3'-a']*cyclobuta*[1,2-c: 3,4-e']*dipyridine*. *cis* - *cisoid* - *cis* - 3,5 - 11,12a - Tetramethyl - 6a,6b,12a,12b - tetrahydrobis - *s* - triazolo[4,3-a: 4',3'-a']cyclobuta[1,2-c: 3,4-e']dipyridine (1.0 g, 0.003 mol) was hydrogenated as above. The product separated from MeOH:ether as fine, colorless needles: 0.6 g (59%), m.p. 273–275°; $\lambda_{max}^{CH_3OH}$ 250 nm, log ε 3.72; NMR (CH_3COOH) no olefinic or aromatic protons. (Found: C, 64.58; H, 7.53; N, 27.93. Calc. for $C_{14}H_{22}N_4$: C, 64.40; H, 7.43; N, 28.14%).

The di-picrate separated as yellow irregular flakes from water, m.p. 265–266° (Found: C, 44.28; H, 3.80; N, 22.36. Calc. for $C_{28}H_{28}N_{12}O_{14}$: C, 44.45; H, 3.73; N, 22.22%).

cis - cisoid - cis - 3,11 - *Dihydroxy* - 6a,6b,12a,12b - *tetrahydrobis* - s - *triazolo*[4,3-a: 4',3'-a']*cyclobuta*[1,2-c: 3,4-e']*dipyridine*. 3 - Hydroxy - *s* - triazolo[4,3-a]pyridine[14] (1.0 g, 0.007 mol) was irradiated at 3600 Å as described above. After 72 hr the solid was collected and purified by crystallization from MeOH:ether: 0.5 g (50%), m.p. 230° dec; IR (KBr) 3200, 3100, 2900, 1720, 1590 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 270 nm, log ε 3.86; NMR (DMSO-d_6) δ 3.49–4.00 (m, 3, hydrocarbon), 4.82–5.41 (m, 2, olefinic and hydrocarbon), 6.1 (m, 2, olefinic), 6.63 (d, 1, olefinic). (Found: C, 53.43; H, 3.78; N, 31.11. Calc. for $C_{12}H_{10}N_4O_2$: C, 53.33; H, 3.73; N, 31.10%).

cis - cisoid - cis - 3,11 - *Dihydroxy* - 5,6,6a,6b,7,8,12a,12b - *octahydrobis* - s - *triazolo*[4,3-a: 4',3'-a']*cyclobuta*[1,2-c: 3,4-e']*dipyridine*. *cis* - *cisoid* - *cis* - 3,11 - Dihydroxy - 6a,6b,12a,12b - tetrahydrobis - *s* - triazolo[4,3-a: 4',3' - a']cyclobuta[1,2-c: 3,4-e']dipyridine (1.0 g, 0.004 mol) was hydrogenated under the above conditions. The product separated from MeOH:ether as fine colorless needles: 0.8 g (80%), m.p. 352–354°; IR (KBr) 3300, 3200, 2000, 2900, 1710, 1680, 1610, 1540 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 250 nm, log ε 3.65; NMR (CF_3CO_2H) no olefinic or aromatic protons. (Found: C, 51.87; H, 5.26; N, 29.66. Calc. for $C_{12}H_{14}N_4O_2 \cdot 1/4H_2O$: C, 51.99; H, 5.22; N, 30.10%).

cis - cisoid - cis - 3,11 - *Dihydroxy* - 5,12a - *dimethyl* - 6a,6b,12a,12b - *tetrahydrobis* - s - *triazolo*[4,3-a: 4'-3'-a']*cyclobuta*[1,2-c: 3,4-e']*dipyridine*. 3 - Hydroxy - 5 - methyl - *s* - triazolo[4,3-a]pyridine[15] (1.0 g, 0.008 mol) was photolyzed at 3600 Å in THF as described above After 36 hr the solid was collected and purified by crystallization from MeOH:ether. 0.6 g (60%), m.p. 250° dec; IR (KBr) 3200, 3100, 2900, 1720, 1590 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 248 nm (log ε 4.14), 200 (4.03). (Found: C, 55.11; H, 4.91; N, 27.43. Calc. for $C_{14}H_{14}N_4O_2 \cdot 1/2H_2O$: C, 54.77; H, 4.91; N, 29.38%).

cis - cisoid - cis - 3,11 - *Dihydroxy* - 5,12a - *dimethyl* - 5,6,6a,6b,7,8,12a,12b - *octahydrobis* - s - *triazolo*[4,3-a: 4',3'-a']*cyclobuta*[1,2-c: 3,4-e']*dipyridine*. *cis* - *cisoid* - *cis* - 3,11 - Dihydroxy - 5,12a - dimethyl - 6a,6b,12a,12b - tetrahydrobis - *s* - triazolo[4,3-a: 4',3'-a']cyclobuta[1,2-c: 3,4-e']dipyridine (1.0 g, 0.004 mol) was hydrogenated under the above conditions. The product separated from MeOH:ether as fine colorless needles: 0.8 g (75%), m.p. 320–321°; IR (KBr) 3300, 3200, 3100, 3000, 2850, 1710, 1680, 1600 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 200 nm, log ε 4.16; NMR (CF_3COOH) no olefinic or aromatic protons; mass spectrum (70 eV), *m/e* (rel intensity), M^+ 302 (13). (Found: C, 55.43; H, 6.00; N, 27.75. Calc. for $C_{14}H_{18}N_4O_2$: C, 55.61; H, 6.00; N, 27.80%).

cis - cisoid - cis - 3,11 - *Dihydroxy* - 6,6b - *dimethyl* - 6a,6b,12a,12b - *tetrahydrobis* - s - *triazolo*[4,3-a: 4',3'-a']*cyclobuta*[1,2-c: 3,4-e']*dipyridine*. 3 - Hydroxy - 6 - methyl - *s* - triazolo[4,3-a]pyridine[15] (2.0 g, 0.014 mol) was irradiated at 3600 Å in tetrahydrofuran as described above. After 36 hr the solid was collected and purified by crystallization from EtOH:ether forming short, colorless needles: 1.6 g (80%), m.p. 200°; IR (KBr) 3200, 3000, 1720, 1580 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 255 nm (log ε 4.58), 310 (3.00).

cis - cisoid - cis - 3,11 - *Dihydroxy* - 8,12b - *dimethyl* - 6a,6b,12a,12b - *tetrahydrobis* - s - *triazolo*[4,3-a: 4',3'-a']*cyclobuta*[1,2-c: 3,4-e']*dipyridine*. 3 - Hydroxy - 8 - methyl - *s* - triazolo[4,3-a]pyridine[15] (2.0 g, 0.014 mol) was photolyzed at 3600 Å as described above. After 36 hr the solid was collected and purified by crystallization from MeOH:ether: 1.4 g (70%), m.p. 200° dec; IR (KBr) 3200, 3100, 1720, 1580 cm^{-1}; λ_{max}^{MeOH} 240 nm (log ε 4.16), 315 (3.56).

†All evaporations were done under reduced pressure using a rotatory evaporator. Spectral data were obtained on the following instrumentation: IR, Perkin-Elmer Model 337 IR spectrophotometer; UV, Cary Model 14 spectrophotometer; mass spectra, Hitachi-Perkin Elmer RMU-6E mass spectrometer at 70 eV using the direct insertion probe; NMR, Varian A-60 and HA-100 spectrometers, Mps were taken in capillaries and microanalyses were by Instranal Laboratories, Inc., Rensselaer, N.Y.; IR data are reported only for the unambiguously assignable bands of structural importance.

Acknowledgements—We would like to express our appreciation to Dr. R. Kuhlnig, Sterling-Winthrop Research Institute, for his assistance in determining the 100 MHz NMR spectra and for many stimulating discussions of this problem, and also to Dr. K. Loening, Chemical Abstracts Service, for his help in deriving the systematic names for these photoproducts.

REFERENCES

[*]Support of this work by U.S. Public Health Service Research Grant CA 08495, National Cancer Institute is gratefully acknowledged; [*]Abstracted from the Ph.D. dissertations of E. B. (1970) and W. D. (1975) presented to the Graduate School,

Rensselaer Polytechnic Institute; [c]NSF Trainee 1968–70; [d]Corning Glass Foundation Fellow, 1974–75; [e]First presented at the XXIII *International Congress of Pure and Applied Chemistry*. Boston (1971).

[2]For reviews on these topics see: P. Beak and W. R. Messer, *Organic Photochemistry*, (Edited by O. L. Chapman). Vol. 2. pp. 117–167. Marcel Dekker, New York (1969). *Photochemistry*, Chemical Society Specialist Periodical Reports, Vols. 1–5. The Chemical Society, London (1970–1974).

[3a]J. H. Boyer and R. Selvarajan, *J. Heterocycl. Chem.* **6**, 503 (1969); R. M. Acheson and J. K. Stubbs, *J. Chem. Soc.* (C), 2316 (1969); A. O. Plunkett, *Chem. Commun.* 1044 (1969).

[3b]T. Nagano, M. Hirobe, M. Ioth and T. Okamoto, *Tetrahedron Letters* 3815 (1975).

[4]A. Rayonet RPR-100 photochemical reactor was used.

[5a]K. T. Potts, *Chem. Revs.* **61**, 87 (1961).

[5b]E. C. Taylor and R. O. Kan, *J. Am. Chem. Soc.* **85**, 776 (1963).

[5c]K. T. Potts, H. R. Burton, T. H. Crawford and S. W. Thomas, *J. Org. Chem.* **31**, 3522 (1966).

[5d]L. A. Paquette and G. Slomp, *J. Am. Chem. Soc.* **85**, 765 (1963).

[5e]See, e.g. H. Ziffer and I. W. Levin, *J. Org. Chem.* **34**, 4056 (1969); H. Bouas-Laurent, A. Castellan, J. P. Desvergne, G. Dumartin, C. Courseille, J. Gaultier and C. Hauw, *J. Chem. Soc.* Chem. Comm., 1267 (1972).

[5f]K. T. Potts, E. Brugel and W. Dunlap, *Tetrahedron* **33**, 1253 (1977).

[6]J. D. Bower, *J. Chem. Soc.* 4510 (1957).

[7]K. T. Potts and H. R. Burton, *J. Org. Chem.* **31**, 251 (1966).

[8]J. B. Bicking, *U.S. Pat.* 2,917,511 (15 Dec. 1959); *Chem. Abstr.* **54**, 8854e (1960).