

[4πs + 4πs] PHOTOCYCLOADDITIONS OF  
2-METHYL-s-TRIAZOLO[1,5-a]PYRIDINES TO PYRIDONES

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Concerted [4πs + 4πs] photocycloadditions are allowed processes according to the conservation of orbital symmetry<sup>1</sup>. While there are several examples of [4πs + 4πs] photochemical dimerizations<sup>2-11</sup>, few examples of [4πs + 4πs] cross photocycloadditions between two different molecules are reported in the literature<sup>12,13</sup>.

In the previous paper<sup>14</sup>, it was shown that 2-methyl-s-triazolo[1,5-a]pyridine (Ia) and its methyl derivatives (Ib,c) on irradiation with ultraviolet light (263nm) give rise to photodimers (IIa-c). (Reaction 1) Furthermore the chemical and spectral behaviors of I and II suggested that this dimerization reaction proceeds through the excimer state.

In the present paper, we wish to report [4πs + 4πs] cross photocycloadditions (anti-trans formation) of 2-methyl-s-triazolo[1,5-a]pyridines to pyridones (III). (Reaction 2)

A solution of 2-methyl-s-triazolo[1,5-a]pyridine<sup>15</sup> (Ia) (90mmole) and pyridone (IIIa) (30mmole) in methylene chloride or acetonitrile (100ml) was irradiated for three hours at room temperature (20°C) by a high pressure mercury lamp (160w) with a Pyrex filter. After the reaction solution was evaporated in vacuo,

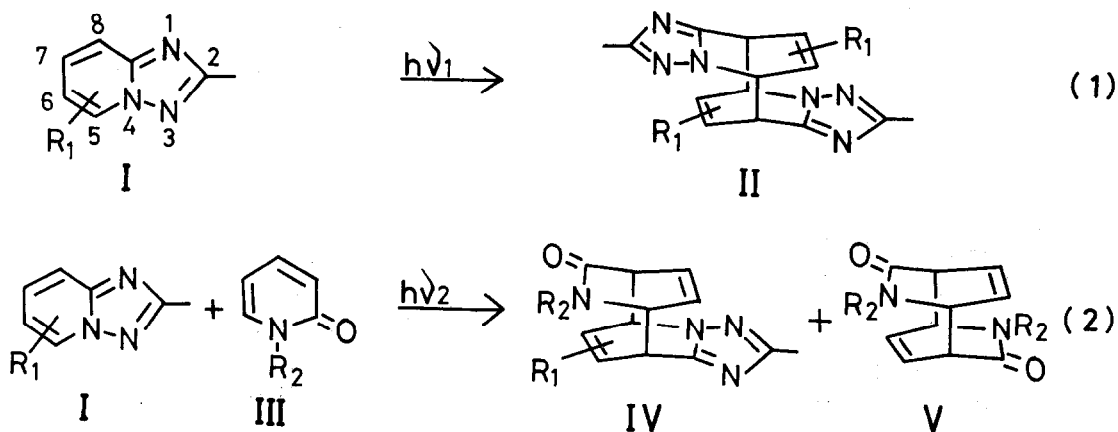


Table 1.

I		III		Yield (%) <sup>*</sup>	
R <sub>1</sub>	R <sub>2</sub>			IV	V
H (Ia) (0.9M)	H (IIIa) (0.3M)	H	(IIIa) (0.3M)	46.9 (IVa)	17.0 (Va)
H (Ia) (0.3M)	H (IIIa) (0.3M)	H	(IIIa) (0.3M)	29.2 (IVa)	31.0 (Va)
H (Ia) (0.9M)	CH <sub>3</sub> (IIIb) (0.3M)	CH <sub>3</sub>	(IIIb) (0.3M)	66.3 (IVb)	24.3 (Vb)
8-CH <sub>3</sub> (Ic) (0.9M)	H (IIIa) (0.3M)	H	(IIIa) (0.3M)	44.7 (IVc)	15.4 (Va)
5-CH <sub>3</sub> (Id) (0.9M)	H (IIIa) (0.3M)	H	(IIIa) (0.3M)	27.5 (IVd)	32.8 (Va)

\* isolated yield based on the consuming starting materials

the residue was chromatographed on alumina using methylene chloride-methanol as eluent. The product (IVa) was recrystallized from methylene chloride-methanol to give colorless powder of MP 182-2.5°(d): IR  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>: 1670(CO). NMR(CD<sub>3</sub>COOD/TMS): 2.33(3H, s, -CH<sub>3</sub>) 3.77(1H, d-d, J=6.5 and 9H<sub>Z</sub>, H<sub>3</sub>') 4.47(2H, m, H<sub>6</sub>' and H<sub>8</sub>) 5.33(1H, d-d, J=6.5 and 9H<sub>Z</sub>, H<sub>5</sub>) 5.89(1H, d-d, J=6.5 and 8H<sub>Z</sub>, H<sub>4</sub>') 6.30(1H, d-d, J=6.5 and 8H<sub>Z</sub>, H<sub>5</sub>') 6.52(1H, d-d, J=6.5 and 8H<sub>Z</sub>, H<sub>7</sub>) 6.98(1H, d-d, J=6.5 and 8H<sub>Z</sub>, H<sub>6</sub>). Anal: Calcd for C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>O: C 63.14, H 5.30, N 24.55, Found: C 62.72, H 5.25, N 24.33. Mass spectrum: m/e 133, 95. The product (Va) was recrystallized from acetic acid to give colorless needles of MP 224-7°. Its spectral data were in agreement with those of authentic sample reported earlier by E. C. Taylor<sup>9</sup>. Compound (IIa)(dimer of Ia) was not detected in the reaction mixture. Other triazolopyridines<sup>16</sup> (Ic,d) having the methyl substituent at the 5- or 8- position and N-methyl pyridone (IIIb) undergo the similar photoreaction to give the products IVb-d and Vb-d respectively. The reaction yields were shown in Table 1.

It was observed that the methylene chloride solution of IVa reproduced Ia and IIIa on the irradiation at the wavelength below 220nm. The photodimer of III (V) was also found to be dissociated into the components (III) on the same reaction conditions.

The stereochemical structure of Vb presumed as anti-trans configuration by

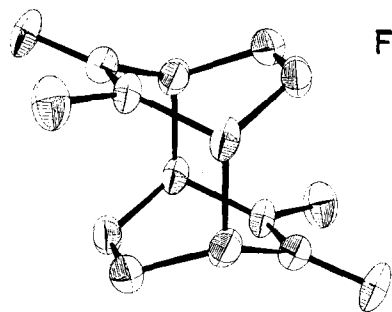


Figure 1

Vb

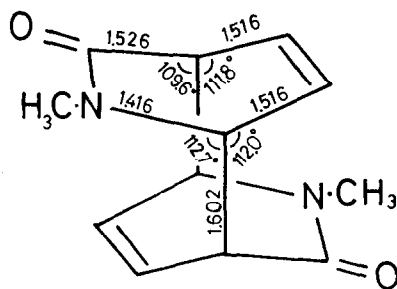


Figure 2

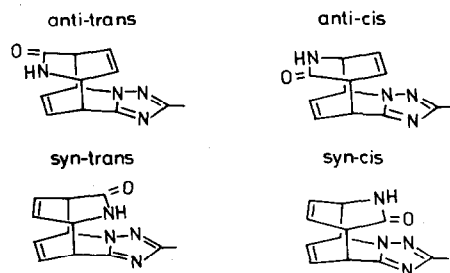
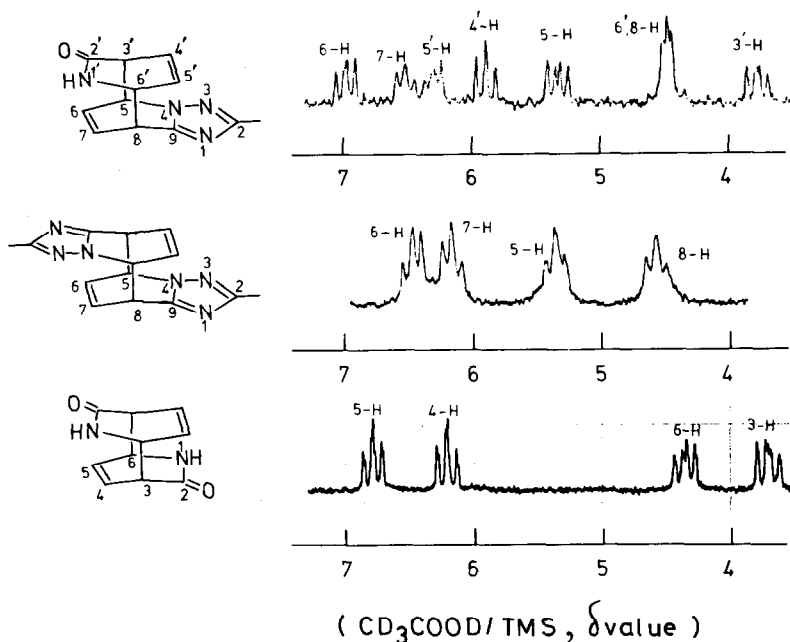


Figure 3



E. C. Taylor et al.<sup>9</sup> was established by our X-ray structure analysis. (Figure 1) It is worth noting that the distance (1.602 Å) between C(3) and C(6') is approximately 0.08-0.1Å longer than the ordinary C-C single bond distance. This may be due to the repulsion of the two pyridone components of dimer Vb.

The stereochemical assignment of IVa was made on the basis of its n.m.r. spectrum, while each of 4 types of stereochemical structures, namely, anti-trans, anti-cis, syn-trans and syn-cis could be presumed as the possible structure of IVa in the [4πs + 4πs] type reaction. (Figure 2)

The upfield shift of the 4' and 5'-protons, and the downfield shift of the 6 and 7-protons of IVa were observed by comparing its n.m.r. spectrum with those of the corresponding protons of IIa and Va as shown in Figure 3, which may be due to the diamagnetic anisotropic effects of triazolo ring.

Furthermore an irradiation of the 3'-proton of IVa affected both the 5-proton and the 4'-proton.

Here we propose the structure of the cross photocycloadduct IVa to be anti-trans as shown in Figure 2.

A reaction mechanism involving an exciplex and an excimer as intermediates may be suggested by spectroscopic results of Ia and IIIa and by application of the Pariser-Parr-Pople type semiempirical LCAO-SCF-MO-CI calculation to the electron donor-acceptor interaction in Ia and IIIa system. The stereochemical structure of IV or V may be controlled both by the configuration of the two components in the exciplex or the excimer intermediate and by steric hindrance of triazolo ring and amide.

Details will be published in a separate paper.

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