Tetrahedron Letters No. 44, pp 3815 - 3818, 1975. Pergamon Press. Printed in Great Britain.

REVERSIBLE PHOTODIMERIZATION OF 2-METHYL-s-TRIAZOLO[1,5-a]PYRIDINES

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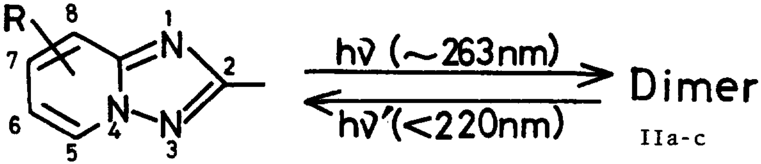
(Received in Japan 8 September 1975; received in UK for publication 22 September 1975)

It is well known that naphthalene,[1,2] anthracene[3,4] and their derivatives on irradiation with ultraviolet light give rise to photodimers. P. de Mayo and others reported the photodimerization reactions of heterocyclic compounds such as 2-pyridone,[5-8] and 2-amino-pyridine[9,10] etc. On the other hand, most aromatic hydrocarbons exhibit the fluorescence of the excimer formed by an encounter collision between the excited and the ground state molecules. Then, the excimer formation in the photodimerization reactions of these heterocyclic compounds mentioned above would be expected. However, few investigations of excimer fluorescence were reported in the photodimerization reaction of nitrogen hetero aromatics except for the observation of the excimer fluorescence in the photodimerization of thymine.

In the course of investigations on reactions of bicycloheterocyclic compounds their photoreactivities were examined under a variety of reaction conditions. In the present paper we wish to report the photodimerization reaction (anti-trans dimer formation) of methyl substituted triazolo[1,5-a]pyridines (I), which is suggested to be through an excimer state by observing the excimer fluorescence of I. A dilute solution of 2-methyl-s-triazolo[1,5-a]pyridine[11] (Ia) (1.33gr) in methylene chloride or ethanol (170ml) was irradiated for three hours at room temperature (20°c) by a low pressure mercury lamp (200w) without a Pyrex filter. After the reaction solution was evaporated in vacuo, the residue was recrystallized from methanol to give a photodimer (IIa) as colorless needles (Yield; 23%). The yield was independent on the reaction condition under nitrogen atmosphere. When a light source was substituted by a high pressure mercury lamp (400w), no photoreaction occurred. Furthermore, it was observed that Ia was reproduced from the methylenechloride solution of IIa by the irradiation at the wavelength below 220nm.

Other triazolopyridines[12] (Ib,c) having the methyl substituent at the 7- or 8- position of Ia exhibit the similar photoreaction to that of Ia. The reaction yields and the nmr spectroscopic data of Ia-c and IIa-c are shown in Table 1.

Fig.1



Ia-c a;R=H, b;R=7-CH$_3$, c;R=8-CH$_3$ IIa-c

Table 1. The chemical shifts of nmr spectra of Ia-c, IIa-c and yields of photodimerization reactions shown in Fig. 1.

Monomer	2-CH$_3$	5-H	6-H	7-H or CH$_3$	8-H or CH$_3$	Dimer※	2-CH$_3$	5-H	6-H	7-H or CH$_3$	8-H or CH$_3$	yield
Ia	7.42s	1.53d	3.09t	2.42t	2.60d	IIa	7.62s	4.61t	3.52t	3.82t	5.40t	23%
Ib	7.42s	1.63d	3.20d	7.55s	2.60s	IIb	7.62s	4.89t	4.07d	8.23s	6.00d	18%
Ic	7.42s	1.74d	3.24t	2.86d	7.42s	IIc	7.62s	5.37d•	3.71t	4.20d	8.15s	15%

※ coupling constants; J_{5-6}=6.5, J_{6-7}=8, J_{7-8}=6.5, J_{5-8}'=8.5cps, τppm

Determination of the molecular weight of IIa (measured with Hitachi Type 115 Molecular Weight Measurement Apparatus) demonstrated that IIa was undoubtedly the dimer of Ia. The stereochemical assignment of photodimer (IIa) was made on the basis of its nmr 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 structures of IIa in the [π4s + π4s] type reaction. The upfield shift of the 6-proton (τ3.52, triplet) and the 7-proton (τ3.82, triplet) of IIa and that of the 6- and 7-protons (τ8.40, multiplet) of IV were observed compared with the corresponding protons (τ3.10, triplet; τ3.65, triplet) of III and the 6- and 7-protons (τ8.00, multiplet) of V, respectively, as shown in Fig. 2, which may be due to the diamagnetic anisotropic effects of triazole ring. Furthermore an irradiation of the 8-proton (τ5.40, triplet) of IIa affected both the 5'-proton (τ4.61, triplet) and the 7-proton (τ3.82, triplet). Here we propose the structure of the photodimer IIa to be anti-trans, as shown in Fig. 3.

The wavelength of the optical irradiation producing IIa and also reproducing Ia in ethanol solutions was examined by the aid of a grating monochrometer (Japan Spectroscopic CO., LTD, CRM-FA-Spectro Irradiator). The dimerization reaction was monitored by an intensity of the absorption spectrum (263nm) of Ia after an optical irradiation for 1/2 hour. The results shown in Fig. 4 demonstrate that the dimerization of Ia may be attributable to the excitation of Ia. In the meantime, the reaction yield of the monomerization from IIa to Ia was examined by the similar procedure to that mentioned above. The irradiation at the shorter wavelength region showed the higher reaction yield of Ia from IIa.

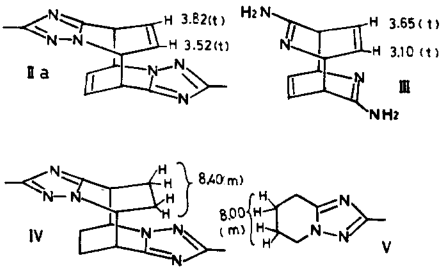


Fig.2 Compound IV and V can be prepared by catalytic reduction of IIa with Pd-C and of Ia with Raney Ni respectively.

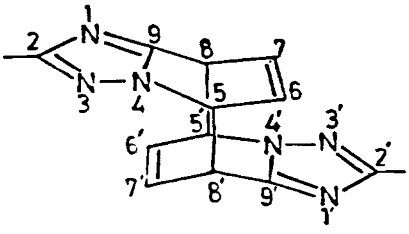


Fig.3
The anti-trans structure of IIa.

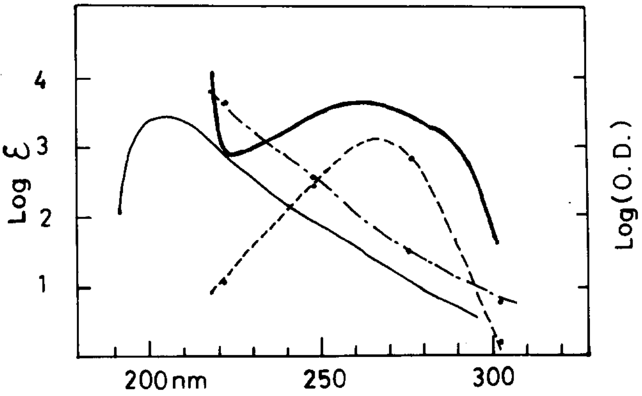


Fig.4 Absorption spectra of monomer (Ia) (▬) and dimer (IIa) (—). The dimerization reaction from Ia to IIa (----) and the monomerization reaction from IIa to Ia (·—·—), monitored by intensity decreasing (Ia → IIa) and increasing (IIa → Ia) of the absorption spectrum (263-nm band of Ia) of the reaction solution after an optical irradiation (221,248,275 and 302nm)

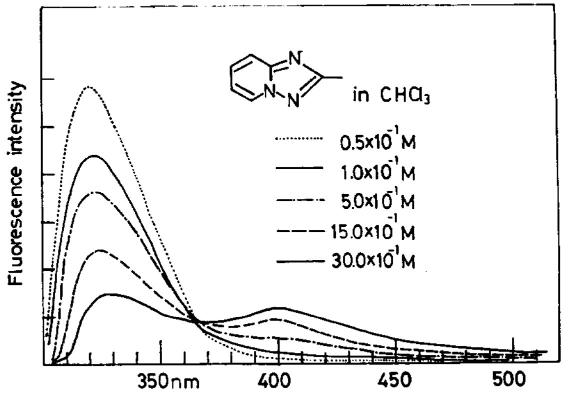


Fig.5
Concentration dependence of fluorescence spectra of Ia in $CHCl_3$. Excitation wavelength; 260nm.

It seems that the reproduction of Ia is also attributed to the excitation of IIa, though it was impossible to observe an accurate intensity change of the absorption spectrum of IIa by irradiation with <220nm because of absorption of the irradiation light source by the solvent.

The fluorescence spectrum of the chloroform solution of Ia is shown in Fig. 5 with concentration dependence of Ia. The fluorescence of Ia (λmax = 328nm) was markedly quenched and another fluorescence of the longer wavelength region was observed at the high concentration (30.0x10^{-1}M). The concentration dependence of the fluorescence of Ia in chloroform solution may suggest the excimer formation of Ia. On the other hand, the U.V. absorption spectra were observed to be independent on the concentration of Ia. (concentration; 1x10^{-2}- 1x10^{-4}M). The result shows no complex formation (dimer) in the ground state. Recent investigations[13] of the photochemical cycloadditions suggested that the exciplexes (the excimers) were intermediates of the photochemical reactions. The chemical and spectral behaviors of I and II described in this paper suggest that the dimerization reaction proceeds through the excimer state as shown in the following schema.

schema

$$\begin{tikzcd}
M \arrow[r, "h\nu"] & \left.\begin{matrix} M \\ M^* \end{matrix}\right) \arrow[r] \arrow[d] & (M\cdots M)^* \arrow[r] \arrow[d, "\text{Excimer}"] & \begin{matrix} M_2 \\ \text{(II)} \end{matrix} \\
 & M + h\nu_1 & 2M + h\nu_2 &
\end{tikzcd}$$

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