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The Solid State Photochemistry of 2(1*H*)-Pyrazinones. Structural Revision of the Photoproduct

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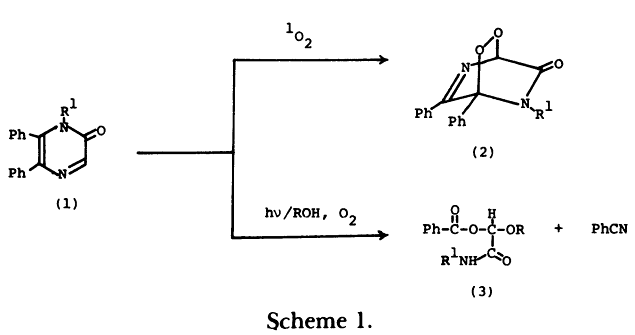
Synopsis. Irradiation of 1-methyl-5,6-diphenyl-2(1*H*)-pyrazinone (**1a**) and 1-methyl-5,6,7,8-tetrahydro-2(1*H*)-quinoxalinone (**1b**) in the solid state gave the [4+4] *syn-trans* cyclodimers (**4a—b**) in almost quantitative yields, while these pyrazinones in solution phase were inert upon irradiation. On the other hand, the 2(1*H*)-pyrazinones (**1c—e**) were inert to photolysis in both the solution and solid states.

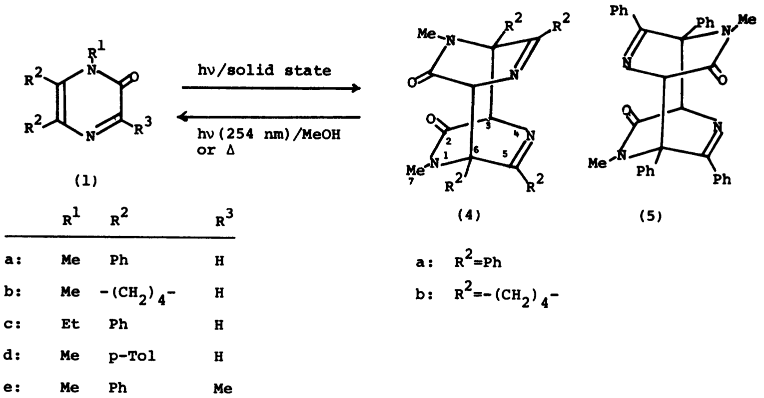
The [2+2] and [4+4] photocyclodimerization of aromatic compounds is a well-established photoreaction; examples of both inter- and intramolecular [4+4] cycloadditions of naphthalenes and anthrathenes are known.[1)] However, those of heteroaromatic compounds have received little attention. The photochemical [4+4] cyclodimerizations of 2-pyridones and 2-pyrones in the solution phase have been reported by Taylor and Kan,[2)] Paquette and Slomp,[3)] and de Mayo and Yip.[4)] A similar photochemical [4+4] cyclodimerization of 4,6-diphenyl-2-pyrone in both solution and the solid state was reported by Rieke and Copenhafer.[5)] The photocyclodimer, thus obtained, was assigned to be an *anti-trans* configuration. In a series of photochemical studies on the 2(1*H*)-pyrazinones (**1**), we have reported that the 2(1*H*)-pyrazinones (**1**) reacted with singlet oxygen to give stable *endo*-peroxides (**2**),[6,7)] and irradiation of **1** in alcohol under an oxygen atmosphere yielded amide derivatives (**3**).[7)] The solid state photochemistry of the 2(1*H*)-pyrazinones (**1**) was also studied. In a previous paper[8)] we reported the photoreaction of 2(1*H*)-pyrazinone (**1a**) in the solid state and the structure of *anti-trans* cyclodimer (**5**) was erroneously given to the photoproduct. An X-ray crystallographic analysis,[9)] which was measured by Kaftory however, clarified the photoproduct was *syn-trans* cyclodimer (**4a**). In this paper we like to revise the structure of the photoproduct.

The 2(1*H*)-pyrazinones (**1a—e**) were photochemically inert in the solution phase under an argon atmosphere.[10)] Meanwhile, the irradiation of 1-methyl-5,6-diphenyl-2(1*H*)-pyrazinone (**1a**) in the solid state with a high-pressure mercury lamp at room temperature for 20 min gave the [4+4] *syn-trans* cyclodimer (**4a**) in a quantitative yield. The structure of **4a** was confirmed on the basis of spectroscopic properties, elemental analysis, and furthermore, X-ray crystallographic analysis.[9)] The usual analytical and mass spectral data (*m/z* 524, M^+: $C_{34}H_{28}N_4O_2$, field desorption mass) of **4a** indicate the photoproduct to be dimer. The IR spectrum of **4a** showed a carbonyl stretching at $1660\,cm^{-1}$, versus $1640\,cm^{-1}$ for **1a**. The ^{1}H-NMR specrum of **4a** showed two singlets at δ 2.58 and 6.35, and a multiplet at δ 6.85—7.35 in the ratio of 3:1:10 assignable to methyl, methine, and aromatic protons, respectively, while that of **1a** showed two singlets at δ 3.31 (3H) and 8.30 (1H), and the multiplet at δ 7.1—7.45 (10H) assignable to methyl, olefinic, and aromatic protons, respectively. The singlet absorption at δ 6.35, which was assigned to methine protons at the 3 and 3′ positions, was shifted further downfield than the expected value of δ (about 4.5).[11)] A molecular model of **4a** showed that these hydrogens can be affected by a strong anisotropic deshielding effect from the four phenyl groups in the 5-, 5′-, 6-, and 6′-positions. Furthermore, ^{13}C-NMR spectrum of **4a** displayed peaks at 31.9 (q), 70.1 (d) 76.7 (s), 169.8 (s), and 178.5 ppm (s) due to carbons at 7-, 3-, 6-, 5-positions, and carbonyl carbon, respectively, in addition to aromatic carbon signals. One of four possible structures such as *syn-trans, syn-cis, anti-trans,* and *anti-cis* cyclodimers might be adopted for the photocyclodimer (**4a**).



Scheme 1.

The structure of **4a** was finally clarified to be *syn-trans* configuration by an X-ray crystallographic analysis.[9)] Similar irradiation of the 2(1*H*)-pyrazinone (**1a**) in the solid state at 254 nm for 4 h through a quartz filter also gave the [4+4] *syn-trans* cyclodimer (**4a**) in 86% yield. The [4+4] *syn-trans* dimer (**4a**) thus obtained was stable at room temperature, however, heating of **4a** to reflux in benzene or to its melting point (148—150 °C) regenerated the starting 2(1*H*)-pyrazinone (**1a**) quantitatively. Furthermore, irradiation of a solution of [4+4] *syn-trans* dimer (**4a**) in methanol through a quartz tube at 254 nm for 30 min causes reversion to the starting 2(1*H*)-pyrazinone (**1a**) in almost quantitative yield. The [4+4] *syn-trans* dimer (**4b**) was also obtained in quantitative yield when 1-methyl-5,6,7,8-tetrahydro-2(1*H*)-quinoxalinone (**1b**) was irradiated in the solid state under the same conditions as described above. On the other hand, irradiation of 1-ethyl-5,6-diphenyl-(**1c**), 1-methyl-5,6-di-*p*-tolyl-(**1d**), and 1,3-dimethyl-5,6-diphenyl-2(1*H*)-pyrazin-one (**1e**) in the solid state did not give the corresponding cyclodimers and the starting 2(1*H*)-pyrazinones (**1c—e**) were recovered quantitatively. These results suggest that the ability of the molecules to react is highly dependent on the mutual orientation and close proximity of possible reacting centers[9)] and these conditions seem to be provided by the crystal lattice and are not achieved in the solution phase.



	R^1	R^2	R^3
a:	Me	Ph	H
b:	Me	$-(CH_2)_4-$	H
c:	Et	Ph	H
d:	Me	p-Tol	H
e:	Me	Ph	Me

a: R^2=Ph

b: R^2=$-(CH_2)_4-$

Scheme 2.

Experimental

Melting points are uncorrected and were measured with a Yanaco micro-melting apparatus (MP-J3). UV spectra were determined with a JASCO UVIDEC-505 spectrometer and IR spectra were recorded on a Hitachi 260-30 spectrometer. NMR spectra were run on a JEOL FX 100 spectrometer (100 MHz).

Starting Materials. The 2(1*H*)-pyrazinones (**1a** and **1c—d**) were prepared according to the method previously described.[7] The 2(1*H*)-pyrazinones (**1b** and **1e**) were prepared by modification of this method.

*1-Methyl-5,6,7,8-tetrahydro-2(1*H*)-quinoxalinone (**1b**);* mp 126.5—128 °C; UV (EtOH) (ε) 231 (8300) and 340 nm (6900); IR (KBr) 1645 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ=1.7—1.9 (4H, m, methylene), 2.5—2.8 (4H, m, methylene), 3.48 (3H, s, NCH$_3$), and 8.01 (1H, s, 3-H); ^{13}C-NMR (CDCl$_3$) δ=21.7 (t), 21.8 (t), 26.1 (t), 29.6 (t), 29.5 (q, NCH$_3$), 131.4 (s, C-5 or C-6), 135.0 (s, C-6 or C-5), 144.2 (d, C-3), and 156.3 (s, C=O). Found: C, 65.58; H, 7.34; N, 16.96%. Calcd for $C_{19}H_{12}N_2O$: C, 65.83; H, 7.36; N, 17.06%.

*1,3-Dimethyl-5,6-diphenyl-2(1*H*)-pyrazinone (**1e**);* mp 169—170 °C; UV (EtOH) (ε) 268 (11300) and 338 nm (8700); IR (KBr) 1645 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ=2.58 (3H, s, CH$_3$), 3.29 (3H, s, NCH$_3$), and 7.1—7.4 (10H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ=21.1 (q, CH$_3$), 33.9 (q, NCH$_3$), 126.8 (d), 127.7 (d), 128.2 (d), 128.9 (d), 129.3 (d), 130.1 (d), 132.3 (s), 132.6 (s), 136.5 (s, C-5 or C-6), 137.9 (s, C-6 or C-5), 155.2 (s, C-3), and 155.9 (s, C=O). Found: C, 78.24; H, 5.78; N, 10.12%. Calcd for $C_{18}H_{16}N_2O$: C, 78.23; H, 5.83; N, 10.13%.

*Photochemical Reactions of the 2(1*H*)-Pyrazinones (**1a—e**) in the Solid State.* The recrystallized 2(1*H*)-pyrazinone (**1**) (100 mg) was sandwiched between a pair of Pyrex plates or quartz plates (thickness 2 mm) and this solid sample was irradiated with a high-pressure (300 W) or low-pressure mercury lamp (20 W) for 20 min—4 h at a distance *ca.* 5 cm at room temperature. After irradiation, the reaction product was purified by recrystallization from chloroform-hexane to afford the [4+4] *syn-trans* cyclodimer (**4**).

The [4+4] syn-trans *cyclodimer (**4a**);* mp 148—150 °C; UV (EtOH) (ε) 261 (3600) and 351 nm (450); IR (KBr) 1660 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ=2.58 (6H, s, NCH$_3$), 6.35 (2H, s, 3-H), and 6.85—7.35 (20H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ=31.9 (q, NCH$_3$), 70.1 (d, C-3), 76.7 (s, C-6), 127.1 (d), 127.4 (d), 128.4 (d), 128.6 (d), 136.5 (s), 138.4 (s), 169.8 (s, C-5), and 178.5 (s, C=O); *m/z* (Field desorption mass) 524 (M$^+$). Found: C, 77.84; H, 5.37; N, 10.67%. Calcd for $C_{34}H_{28}N_4O_2$: C, 77.86; H, 5.25; N, 10.62%.

The [4+4] syn-trans *cyclodimer (**4b**);* mp 138.5—140 °C; IR (KBr) 1660 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ=1.53—2.18 (10H, m, methylene), 2.2—2.36 (2H, m, methylene), 2.38—2.8 (4H, m, methylene), 2.75 (6H, s, NCH$_3$), and 4.48 (2H, s, 3-H); ^{13}C-NMR (CDCl$_3$) δ=18.6 (t), 22.1 (t), 32.4 (t), 36.2 (t), 30.5 (NCH$_3$), 67.3 (s, C-6), 72.2 (d, C-3), 172.0 (s, C-5), and 177.9 (s, C=O); *m/z* (Chemical ionization mass) 329 (QM$^+$). Found: C, 65.59; H, 7.32; N, 16.79%. Calcd for $C_{18}H_{24}N_4O_2$: C, 65.83; H, 7.36; N, 17.06%.

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