트란스-1, 2-비스피라질에틸렌의 광화학적 환원

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(1977. 1. 11 접수)

Photochemical Reduction of *trans*-1, 2-Bispyrazylethylene

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(Received Jan. 11, 1977)

요 약. 질소를 방향족고리에 포함하고 있는 헤테로 화합물인 트란스-1, 2-비스피라질 에틸렌을 쿠멘, 이소프로판올, 시멘용매등에 녹여 빛을 쪼여준 결과 광화학적 환원이 일어나 1, 2-비스피라질 에탄이 됨을 알았다. 알칼리 금속염이 이 환원반응에 미치는 영향, 용매효과, 증감제와 아줄렌등의 영향으로 부터 이 환원 반응은 $(n, \pi^*)^1$ 상태로부터 일어남을 알았다.

ABSTRACT. Photochemical reduction of 1, 2-bispyrazylethylene, a stilbene like heterocompound, was studied in hydrogen donating solvents and reduction product, 1, 2-bispyrazylethane, was identified. Salt and solvent effects on the quantum yields of the reduction, sensitization and quenching studies showed that the reactive state for the photochemical reduction of the compound is $(n, \pi^*)^1$ state rather than $(\pi, \pi^*)^1$ state.

INTRODUCTION

Nitrogen containing heteroaromatic compounds can be excited to both (n, π^*) and $(\pi. \pi^*)$ states by light absorption because of nonbonding electrons on nitrogen atom. The electronic configuration of thus obtained two excited states is quite different from each other. Consequently, the reactivities of these states are also expected to be different. Recently, there are considerable research activities concerning these problems[1~4]. The photochemistry of carbonyl compounds in which both (n, π^*) and (π, π^*) excited states are possible has been studied extensively[5]. Two main routes, Norrish type I and II processes, are followed in carbonyl photochemistry originating from (n, π^*) singlet and triplet states.

Aromatic ketones can undergo photoreduction via (n, π^*) triplet states and free radical intermediates. The same type of reactions are expected for (n, π^*) states of nitrogen containing heteroaromatic. These expectations are verified in the photoreactions of 2-butylquinoline[6], acridine[7], and 1, 2-bispyridylethylene[8].

A new compound, 1, 2-bispyrazylethylene, shows no distinct $n{\rightarrow}\pi^*$ band in UV-VIS spectra despite four non-bonding electron pairs in the molecule. It was suggested[9] that $(n, \pi^*)^1$ state has about the same energy as $(\pi, \pi^*)^1$ state and consequently extensive mixing between these two states results obscuring $n{\rightarrow}\pi^*$ band. The fluorescence enhancement of this compound by alkaline salts and the low fluorescence quantum yield led to this conclusion.

The photochemical reduction of the compound is studied to understand the character of the excited states of this compound more thoroughly.

EXPERIMENTAL

Materials

1, 2-Bispyrazylethylene: *trans*-Bispyrazylethylene was synthesized by the method reported[9]—m. p 191~2 °C. Elemental analysis C 65.5 %, H 4.59 %, N 30.0 % (Calc. C 65.21 %, H 4.38 %, N 30.42 %)[9].

1, 2-Bispyrazylethane: 1, 2-Bispyrazylethane was synthesized by catalytic hydrogention of *trans*-1, 2-bispyrazylethylene. nmr 3.20 ppm (*s*, 2H) 8.43 ppm (*m*, 3H), ir same as that of 1, 2-bispyrazylethylene except the disappearance of 978 cm^{-1} band and the appearance of new 3,000~2,900 cm^{-1} band.

Cumene : Cumene was synthesized from benzene and *n*-propyl alcohol and distilled over phosphorous pentoxide. b. p 152~152.5 °C.

p-Cymene : *p*-Cymene (Aldrich Chem. Co., Inc.) was redistilled over phosphorous pentoxide. b. p 177 °C.

Isopropyl Alcohol: Isopropyl alcohol (Wako Chemical Ind., Inc.) was treated with iodine and magnesium and distilled. b. p 82.5 °C.

Benzene: Benzene (Merck, analytical grade) was treated with sulfuric acid[9]. b. p 80.0 °C.

Pyridine: Pyridine (Wako Chemical Ind., Inc.) was treated with zinc chloride and hydrochloric acid and distilled. b. p 115.5 °C.

Acetonitrile: Acetonitrile (Wako Chemical Ind., Inc.) was treated with chlorobenzoic acid followed by potassium permanganate treatment and distilled. b. p 82 °C.

Azulene: Azulene (Aldrich Chem. Co,. Inc.) was sublimed immediately before use.

Benzophenone and Naphthalene: Both compounds were zone refined by James Hinton

Lithium Chloride: Lithium chloride (Wako

Chemical Ind., Inc.) was used as received.

Spectra: UV spectra were recorded on a Cary 17 spectrophotometer. Infrared spectra were measured on a Perkin-Elmer Model 267 spectrophotometer in carbon tetrachloride or chloroform solvents. Potassium bromide pellets were also used. Nuclear magnetic resonance spectra were measured on a Varian T-60A spectrometer against tetramethylsilane standard in deuterochloroform or in carbon tetrachloride.

Analysis of Products

Irradiated samples were analyzed by thin layer chromatogram of silica gel(Wako gel B-5, 0.25 mm thick) utilizing carbon tetrachloride-diethyl ether-ethanol (15:10:3 v/v) mixture as a developing solvent and iodine vapor as visualization agent. Vapor phase chromatography (Varian Aerograph Model 2800 Series) utilizing 10 % FFAP on Chromosorb packed column (6′ ×1/8″ copper tubing). Flame ionization detector was used with 30 m*l*/min He flow rate, 225 °C column temperature, and 250 °C injector temperature. Synthesized 1, 2-bispyrazylethane was used as a standard in both cases.

Irradiation of the Sample

Cumene or cymene solution of 1, 2-bispyrazylethylene (100 mg/70 m*l*) was degassed by bubbling through nitrogen gas into the solution and irradiated in a Rayonet Reactor (The Southern New England Ultraviolet Company) equipped with 350 nm fluorescent lamps.

Quantum Yield Measurements

A solution of 3 m*l* of 1, 2-bispyrazylethylene in hydrogen donating solvents was put into a Pyrex ampoule and degassed by three freeze-pump-thaw cycles with cooling in liquid nitrogen and then sealed. Thus prepared samples were irradiated in a "merry-go-round" unit with a 450 W Hanovia mercury arc lamp (Type 679 A 36). Corning glass filter #7-54 and #0-52 was used to isolate 366 nm monochromatic light and

a Corning glass filter #7-54 and a solution filter of $2.5 \times 10^{-3} M$ potassium dichromate in 1 % sodium carbonate aqueous solution were used to get a monochromatic light of 313.0 nm. The light intensity was measured by ferrioxalate actinometry[10] and the amounts of photoproducts were monitored by vapor phase chromatography.

RESULTS AND DISCUSSION

Identification of Photoreduction Product

Irradiated solutions of 1, 2-bispyrazylethylene in hydrogen donating solvents were analyzed by TLC and GC against 1, 2-bispyrazylethane standard synthesized by catalytic hydrogenation of 1, 2-bispyrazylethylene. The $cis \rightleftharpoons trans$ isomerization accompanied the formation of 1, 2-bispyrazylethane, an expected photoreduction product, as shown in *Fig.* 1 and 2. Some unknown products are also formed in small amounts. When 1, 2-bispyrazylethane is mixed with irradiated sample and subjected to GC

analysis, only the intensity of 1, 2-bispyrazylethane peak increased showing that the major photoreduction product is indeed 1, 2-bispyrazylethane.

Alkaline Salt Effects on the Photoreduction

The fluorescence is in general quenched by heavy atoms largely due to enhanced $S_1 \rightsquigarrow T_1$ intersystem crossing[11]. However, the fluorescence of *trans*-1, 2-bispyrazylethylene[9] and retinal[12] is enhanced by alkaline salts such as sodium acetate and potassium iodidedue to $\diagdown N : M^+$ or retinal-M^+ complex formation where M^+ is alkaline metal cation. A blue shift of the $(n, \pi^*)^1$ state as a result of this complex formation widens the gap between the lowest $(\pi, \pi^*)^1$ and imbedded $(n, \pi^*)^1$ state as shown in *Fig.* 3 or increase the (π, π^*) character in the lowest excited state enhancing the quantum yield of fluorescence originated from $(\pi, \pi^*)^1$ character. If photoreduction of *trans*-1, 2-bispyrazylethylene is occurring from the (n, π^*)
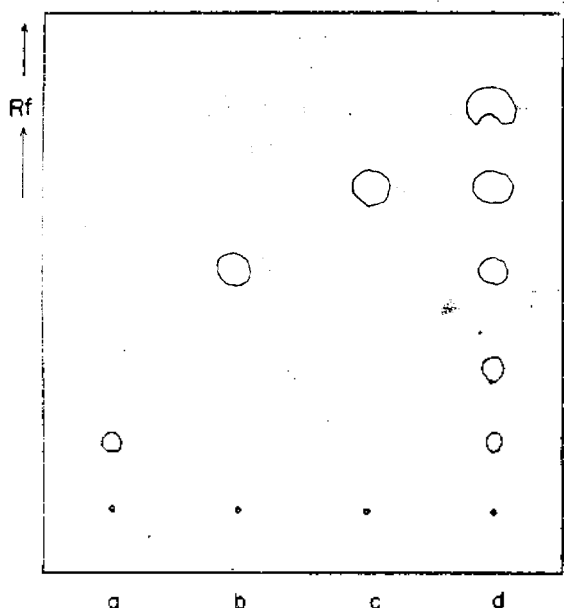

Fig. 1. Thin layer chromatogram of photoreduction products.
a: *trans*-1, 2-Bispyrazylethylene, b: *cis*-1, 2-bispyrazylethylene, c: 1, 2-bispyrazylethane, d: irradiated sample.
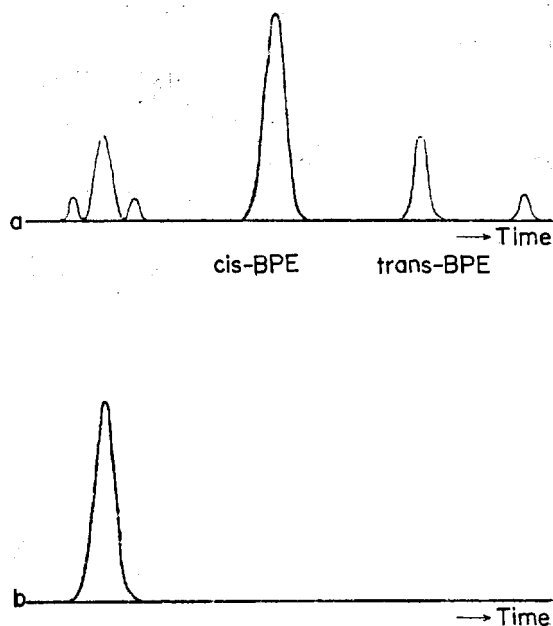

Fig. 2. GC analysis of photoreduction products.
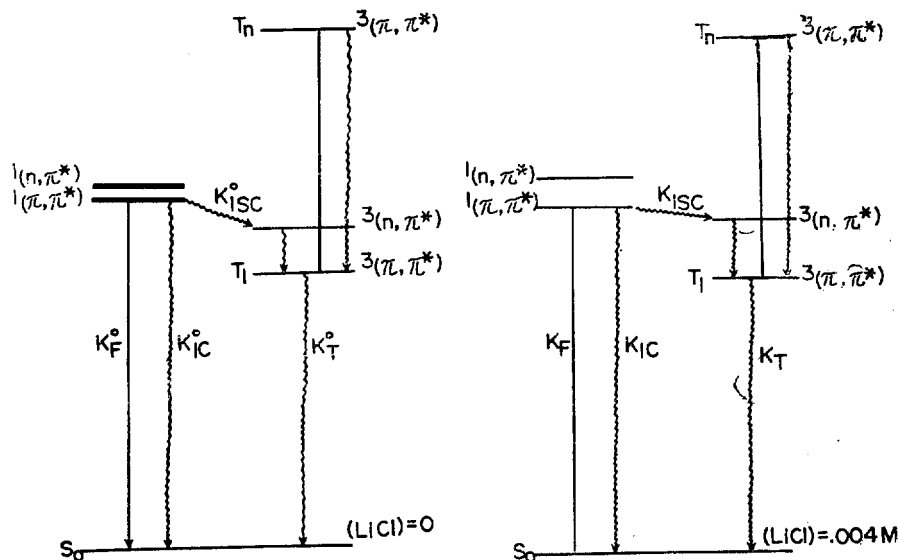a: Irradiated sample, b: 1, 2-bispyrazylethane.

T_n —— $^3(\pi, \pi^*)$

$^1(n, \pi^*)$
$^1(\pi, \pi^*)$ K^o_{ISC} $^3(n, \pi^*)$
T_1 —— $^3(\pi, \pi^*)$

K^o_F | K^o_{IC} | K^o_T

S_0 (LICl)=0

T_n —— $^3(\pi, \pi^*)$

$^1(n, \pi^*)$
$^1(\pi, \pi^*)$ K_{ISC} $^3(n, \pi^*)$
T_1 —— $^3(\pi, \pi^*)$

K_F | K_{IC} | K_T

S_0 (LICl)=.004M

Fig. 3. The Jablonski diagram for *trans*-1, 2-bispyrazylethylene in ethanol at 77°K.

Table 1. Alkaline salt effects on photoreduction of BPE.

[*t*-BPE]	(LiCi)	Quantum yields of photoreduction	ϕ/ϕ_0
$2\times10^{-3}\,M$	0	4.02×10^{-3}	1.00
$2\times10^{-3}\,M$	$1.0\times10^{-3}M$	3.12×10^{-3}	0.78
$2\times10^{-3}\,M$	$2.0\times10^{-3}\,M$	1.14×10^{-3}	0.28
$2\times10^{-3}\,M$	$4.0\times10^{-3}\,M$	0.97×10^{-3}	0.24
$2\times10^{-3}\,M$	Saturated	0.86×10^{-3}	0.21

ϕ, ϕ_0: Quantum yields in the presence and absence of salts respectively.

character of the lowest excited singlet state, the quantum yield of the photoreduction will be decreased as the concentration of alkaline salts increase. The effect of the alkaline salts on the photoreduction is shown in *Table* 1. The quantum yield of photoreduction decreases markedly as the concentration of lithium chloride increases and the reactive state for photoreduction is thus determined to be $(n, \pi^*)^1$ state or (n, π^*) character of the lowest excited singlet state.

Solvent Effects

As the polarity of the solvents increases, a blue shift in the $n\rightarrow\pi^*$ transition and a red

shift in the $\pi\rightarrow\pi^*$ transition are observed in general because of solvent stabilization of charge separation through H-bonding and other types of interactions.[13] This shift may cause the order of energy levels of $(n, \pi^*)^1$ and $(\pi, \pi^*)^1$ state reversed when the polarity of solvents is varied[14]. This kind of energy level inversion is also observed by varying the substituents in aromatic ketones and photochemical reactivities for reduction is drastically affected in consequence of the inversion.[15] Since $(n, \pi^*)^1$ and $(\pi, \pi^*)^1$ states of 1, 2-bispyrazylethylene are mixed strongly in the lowest excited state, this kind of solvent effect will be prominent for the compound. As

shown in *Table* 2, the quantum yield of photo-reduction of *trans*-1, 2-bispyrazylethylene decreases sharply as the polarity of solvent increases as expected. The $n \rightarrow \pi^*$ transition of 1, 2-bispyrazylethylene is blue shifted in polar solvents and $\pi \rightarrow \pi^*$ transitionis red shifted a little and (n, π^*) character of the lowest excited singlet state is consequently diminished causing the photoreduction inefficient. In acetonitrile solvent, the intersystem crossing from singlet to triplet state is perhaps enhanced as in the case of pyrimidine bases[16] and this enhanced intersystem crossing rather than solvent polarity decreases the photoreduction yield from $(n, \pi^*)^1$ state of 1, 2-bispyrazylethylene.

Sensitization and Quenching Studies

Normally the photoreduction of carbonyl compounds in the presence of hydrogen donors occurs via the (n, π^*) triplet state[17]. However, nitrogen containing heteroaromatic compounds such as acridine[7], stilbazole[8], and 1, 2-bispyridylethylene[8] are known to be photoreduced via the (n, π^*) singlet excited state. The triplet sensitization and triplet quenching studies are carried out to determine the multiplicity of the reactive state for the 1, 2-bispyrazylethylene

photoreduction.

When naphthalene$(E_T \simeq 61 \text{ kcal/mole})$is added as a photosensitizer, the quantum yield of the photoreduction decreases as shown in *Table* 3. This indicates the reactive state of the photoreduction to be (n, π^*) singlet state rather than the triplet state. Naphthalene and 1, 2-bispyrazylethylene are absorbing about the same amount of light and the photoreduction is still occurring from the 1, 2-bispyrazylethylene molecules excited directly.

When benzophenone $(E_T = 68.5 \text{ kcal/mole})$ is used as a photosensitizer, the quantum yield of photoreduction increases drastically. This is not because of triplet energy transfer from benzophenone to 1, 2-bispyrazylethylene but because of free radical formation by benzophenone triplet state in the hydrogen donating solvents and this free radical in trun attacks the 1, 2-bispyrazylethylene molecules. This explanation is backed by the triplet quenching studies as shown in *Table* 4. When azulene is added as a triplet quencher, no change is observed in the quantum yield of the photoreduction. Thus it is concluded that the photoreduction of 1, 2-bispyrazylethylene occurs via the (n, π^*) singlet

Table 2. Solvent effects on photoreduction of *trans*-1, 2-Bispyrazylethylene.

Solvent	Concentration of *trans*-1, 2-bispyrazylethylene	Quantum yields of photoreduction
Benzene +Isopropanol	$2.00 \times 10^{-3} M$	9.8×10^{-4}
Pyridine +Isporopanol	$2.00 \times 10^{-3} M$	4.0×10^{-4}
Acetonitrile+Isopropanol	$2.00 \times 10^{-3} M$	3.6×10^{-4}

Table 3. The triplet sensitization of 1, 2-bispyrazylethylene photoreduction.

Sensitizer	Concentration of the sensitizer (M)	Concentration of 1, 2-bispyrazylethylene (M)	Φ/Φ_0
Benzophenone	4.0×10^{-3}	2.00×10^{-3}	4.56
Naphthalene	2.0×10^{-2}	2.00×10^{-3}	0.47

Φ_0, Φ: Quantum yields of photoreduction in the absence and presence of sensitizers respectively.

Table 4. The triplet quenching of 1, 2-bispyrazylethy-lene photoreduction.

Concentration of azulene (M)	Concentration of 1, 2-bispyrazylethylene (M)	Φ_0/Φ
1.00×10^{-3}	2.00×10^{-3}	1.01
2.00×10^{-3}	2.00×10^{-3}	1.04
4.00×10^{-3}	2.00×10^{-3}	1.06

Φ_0, Φ: Quantum yields of photoreduction in the absence and presence of quenchers respectively.

state rather than (n, π^*) triplet state in contrast to the aromatic ketones.

The benzophenone experiment also suggests that the photoreduction occurs via the free radical intermediate and the following mechanism is proposed for the reaction.
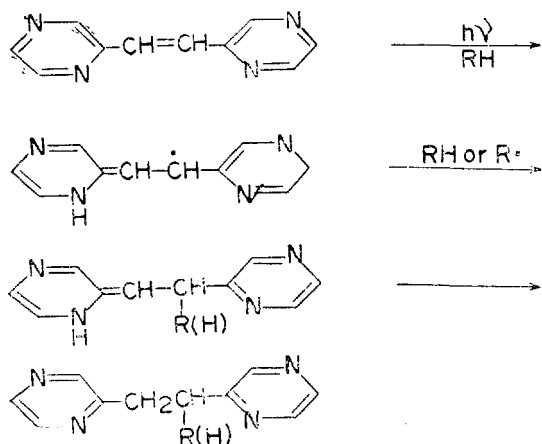
CONCLUSION

From the results of alkaline salt effects, solvent effects, sensitization and quenching studies, it is concluded that the (n, π^*) singlet state or (n, π^*) character of the lowest excited singlet state of 1, 2-bispyrazylethylene is responsible for the photoreduction of the compound.

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