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Photodimerization of Indeno[2,1-*a*]indene

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Indeno[2,1-*a*]indene, a *trans*-stilbene analogue with fixed planar configuration, yielded a head-to-head and a head-to-tail C_4-cyclodimer on direct irradiation with 300 nm UV light. The fluorescence quenching and sensitization studies indicated the reaction to proceed through excited singlet state, very likely through the singlet excimer intermediate.

Twisting around the C=C bond is normally an important decay mode of electronically excited singlet as well as triplet states of olefins as shown in stilbenes. However, fluorescence is the major decay route for stilbenes where the C=C bond is incorporated into a small ring such as cyclopropene, cyclobutene, or cyclopentene so that the twisting around the C=C bond is forbidden because of the ring strain.[1-3]

The photochemistry of stilbene has been extensively studied but relatively little is known about the photochemistry of the stilbene chromophore in small ring systems. Irradiation of 1,2-diphenylcyclobutene with 335 nm light in the crystal or in hexane solution yields $2\pi+2\pi$ C_4-cyclodimer, 1,2,5,6-tetraphenyltricyclo[4,2,-0,$0^{2,5}$]octane, through a finite-lived metastable singlet excimer along with the ring splitted photoproducts, diphenylacetylene and ethylene[1] while 1,2,3-triphenylcyclopropene yields no photoproduct with quantum yield greater than 10^{-2} on direct irradiation with 313 nm light but gives $2\pi+2\pi$ C_4-cyclodimer and a noncyclic hydrogen transfer dimer on triplet sensitization with benzophenone.[3] Thus, the photochemistry of stilbene chromophore in small ring systems is dependent on the size of the ring. The structure of indeno[2,1-*a*]indene, a *trans*-stilbene analogue, is restricted to a planar configuration and the compound cannot undergo *cis*⇌*trans* photoisomerization. Saltiel and coworkers utilized the fluorescence quantum yield of unity of the compound for backing up the singlet mechanism for the direct *cis*⇌*trans* photoisomerization of stilbene.[2,4] However, nothing is known about the photochemistry of indeno[2,1-*a*]indene and photodimerization of the compound is studied in this report.

Experimental

Materials. *Indeno[2,1-*a*]indene*: Indeno[2,1-*a*]indene was synthesized by the method reported from benzyl chloride[5-7] and recrystallized from ethyl acetate and acetone. Mp 203—205 °C; NMR: δ 3.63 (s, 4H), 7.35 (m, 8H); IR: 3035, 2905, 1608, 1461, 1397, 1203, 775, 714 cm^{-1}; UV: 314 (ε_{max} 32500), 236 nm (ε_{max} 16500).

Spectra: UV spectra were recorded on a Cary 17 spectrophotometer. Infrared spectra were measured on a Perkin-Elmer Model 267 spectrophotometer in KBr pellet. Nuclear magnetic resonance spectra were measured on a Varian T-60A spectrometer against tetramethylsilane standard in chloroform-*d*. Mass spectra were determined with Hewlett Packard 5985 A GC/MS system. Fluorescence spectra were recorded on a Aminco Bowman spectrofluorometer with Aminco XY-recorder. Elemental analysis were carried out on a Coleman C, H, N analyzer.

Determination of Fluorescence Quantum Yields. Fluorescence quantum yield (Φ_F^S) of dilute solutions were calculated by Eq. 1.

$$\Phi_F^S = \Phi_F^r \times \frac{\int I_F^S(\tilde{\nu})d\tilde{\nu}}{\int I_F^r(\tilde{\nu})d\tilde{\nu}} \times \frac{O\cdot D_\lambda^r}{O\cdot D_\lambda^S} \times \frac{n_r^2}{n_s^2}, \tag{1}$$

where Φ_F^r is the fluorescence quantum yield of the reference compound. $I_F(\nu)$ and n are the corrected fluorescence intensity and refractive index respectively ($\tilde{\nu}$ in cm^{-1}). The reference compound, 2,5-diphenyloxazole (DPO) from Aldrich Chemical Co. was dissolved in benzene. Absolute quantum yield of the reference DPO in benzene is known to be 0.58. All sample compounds were dissolved in ether. The corrected fluorescence spectra were recorded on a Perkin-Elmer spectrofluorometer Model MPF-3.

Fluorescence-lifetime Measurements. The fluorescence lifetimes were measured at room temperature with an SLM-Model 480 phase-modulation spectrofluorometer utilizing continuous light that had been sinusoidally modulated.

Irradiation of the Sample and Separation of Dimers. Purified benzene solution of indeno[2,1-*a*]indene (100 mg/100 ml) was degassed by bubbling nitrogen through the solution for 30 min and irradiated in a Rayonet reactor (The Southern New England Ultraviolet Company) equipped with 300 nm fluorescence lamps for 10 h. The solvent was evaporated off and compound A was isolated by extraction of the residue with ethanol and recrystallized from methanol–water mixture. Compound B was isolated from the remaining residue by recrystallization from ethanol.

Found: Compound A; C, 94.00; H, 5.59%, compound B; C, 94.13; H, 5.98%. Calcd for $C_{32}H_{24}$: C, 94.09; H, 5.91%.

Quantum Yield Measurements. A solution of 3 ml of indeno[2,1-*a*]indene (2.3×10^{-3} M†) in several purified solvents[6] 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 450 W Hanovia mercury arc lamp (Type 679 A 36). A Corning glass filter #7-54 and a solution filter of 2.5×10^{-3} M potassium chromate in 1% sodium carbonate aqueous solution were used to get a monochromatic light of 313 nm. The light intensity was measured by tris(oxalato)ferrate(III) actinometry and the amounts of photoproducts were analyzed by UV spectrophotometer at 314 nm.

Results and Discussion

Product Analysis. A benzene solution of indeno-

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† 1 M = 1 mol dm^{-3}.

[2,1-*a*]indene (4.9 mM) was irradiated for 10 h in a Rayonet reactor equipped with 300 nm fluorescent lamps. Separation of products by extraction and recrystallization gave products A and B in 2: 1 ratio. The photochemical conversion was almost complete. Both compounds were pure as shown by their Mp; compound A 183—184 °C, compound B decomposes at 290 °C before melting. The structures of compounds A and B were determined by their IR, ^{1}H NMR, mass, UV spectral data and elemental analyses.

Mass spectra of both compounds A and B show molecular ion peak at *m*/*e* 408 which is twice the molecular weight of indeno[2,1-*a*]indene. The base peak appears at *m*/*e* 204 which is exactly the molecular weight of starting material in both compounds. This indicates that compounds A and B easily undergo splitting into starting materials on electron impact suggesting compounds A and B to be C_4-cyclodimers. The elemental analyses of compounds A and B gave exactly the same data which are consistent with the dimeric structure.

The central double bond stretching of starting material at 1608 cm^{-1} are not apparent in the infrared spectra of compounds A and B and λ_{max} at 314 nm disappeared. These observations further substantiate the structure of compounds A and B to be $2\pi+2\pi$ type C_4-cyclodimers.

The ^{1}H NMR spectrum of compounds A in chloroform-*d* shows two doublets at 2.8 (d, 4H, $J=17$ Hz) and 3.2 (d, 4H, $J=17$ Hz) and two mutiplets at 6.9 (m, 8H) and 7.2 (m, 8H) ppm (δ). That of compound B also shows two doublets at 3.1 (d, 4H, $J=17$ Hz) and 3.7 (d, 4H, $J=17$ Hz) and a multiplet at 6.9 (m, 16H). The data are in agreement with the C_4-cyclodimers of indeno[2,1-*a*]indene, compound A being a head-to-tail (HT) cyclodimer and compound B being a head-to-head (HH) cyclodimer.

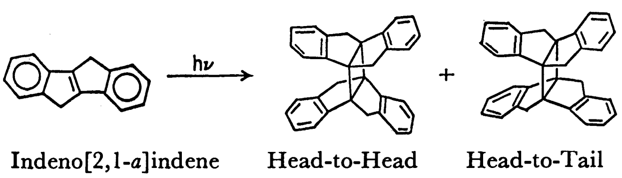

Fig. 1

In HT dimer, H_b, the outer proton of methylene bridge is deshielded by the ring current of upper benzene ring, but H_a, the inner proton of methylene group, is shielded by the same ring current. Thus H_b resonance corresponds to 3.2 ppm peaks and that of H_a corresponds to 2.7 ppm peaks. The same ring currents cause the ring protons H_c and H_d to be shielded and the protons H_e and H_f to be deshielded as two multiplets appear in the NMR spectrum of compound A.

In HH dimer, H_a is deshielded in contrast to that of HT dimer and 3.7 ppm peaks correspond to H_a resonance. All ring protons, H_c, H_d, H_e, and H_f of HH dimer are shielded by the ring current of upper benzene ring and only one multiplet appears in the NMR spectrum of compound B.

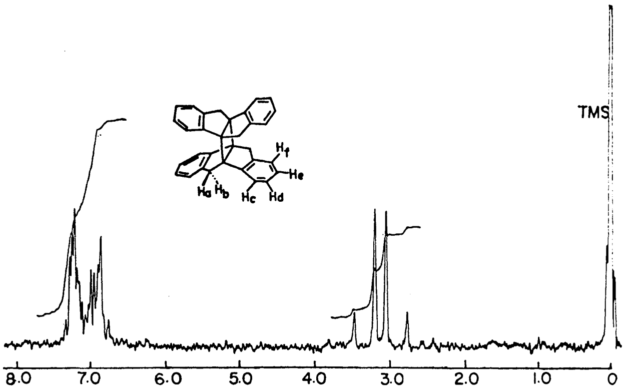

Fig. 2. ^{1}H NMR spectrum of H-T dimer of indeno[2,1-*a*]indene.

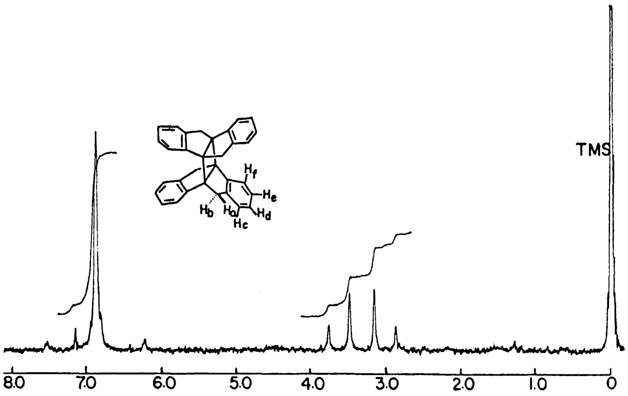

Fig. 3. ^{1}H NMR spectrum of H-H dimer of indeno[2,1-*a*]indene.

Fluorescence Studies. Indeno[2,1-*a*]indene is strongly fluorescent and the fluorescence quantum yield is reported to be unity. However, the fluorescence quantum yield of the compound in ether was determined to be 0.85 when 2,5-diphenyloxazole which has same UV absorption characteristics as indeno[2,1-*a*]indene was used as a reference compound. This implicates that there is some radiationless decay routes other than fluorescence from the excited singlet state of indeno[2,1-*a*]indene in contrast to the results reported earlier.[2)]

The fluorescence quenching of indeno[2,1-*a*]indene by electron deficient olefins, fumaronitrile and dimethyl fumarate, is very efficient while electron rich olefin, 2,3-dimethyl-2-butene (TME) does not quench fluorescence of indeno[2,1-*a*]indene.

The lifetime calculated from the slope of Stern-Volmer plot for fluorescence quenching by fumaronitrile and dimethyl fumarate is about 3.3 ns if $k_q=k_{diff}=2.25\times10^{10}$ M^{-1} s^{-1} is assumed. This value is in agreement with the value of 1.99 ns measured directly from the fluorescence.

Reaction Mechanism. If the cyclodimerization occurs *via* a singlet excimer, the following mechanistic scheme can be proposed for the reaction

$$I \longrightarrow I^*, \qquad (2)$$

$$I^* \xrightarrow{k_f} I + h\nu_f', \qquad (3)$$

$$I^* \xrightarrow{k_d} I, \qquad (4)$$

TABLE 1. SOLVENT EFFECTS AND EXTERNAL HEAVY ATOM EFFECTS ON THE PHOTOCYCLODIMERIZATION OF INDENO[2,1-*a*]INDENE

Solvent	Hexane	Acetonitrile	Benzene	Methyl iodide	Ethyl bromide
Viscosity	0.294 cP†	0.345 cP	0.564 cP	0.500 cP	0.402 cP
Quantum yield	1.80×10^{-2}	1.35×10^{-2}	0.75×10^{-2}	Undetectable	0.62×10^{-2}

† 1 P=0.1 Pa s.

$$I^* + I \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} \text{Excimer}, \tag{5}$$

$$\text{Excimer} \xrightarrow{k_{\text{dim}}} \text{Dimers}, \tag{6}$$

$$\text{Excimer} \xrightarrow{k_{\text{ed}}} 2\,I, \tag{7}$$

where I is indeno[2,1-*a*]indene.

By steady state approximation,

$$\Phi_{\text{dim}}^{-1} = \frac{(k_f+k_d)(k_{-e}+k_{\text{dim}}+k_{\text{ed}})}{k_{\text{dim}}\,k_e}[I]^{-1} + \frac{k_{\text{dim}}+k_{\text{ed}}}{k_{\text{dim}}}. \tag{8}$$

The linear relationship between Φ_{dim}^{-1} and $[I]^{-1}$ is expected if the mechanism is valid.

When Φ^{-1} is plotted against $[I]^{-1}$ for the [I] of 5×10^{-3}—2×10^{-2} M in benzene solution at 21 °C, a good linear relationship (correlation coefficient: 0.999) is obtained as shown in Fig. 4.

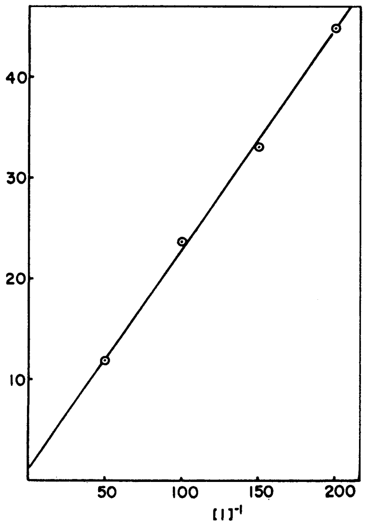

Fig. 4. Plot of the reciprocal of the quantum yield for photodimerization *vs.* the reciprocal of the indeno[2,1-*a*]indene concentration in benzene solution at 21 °C.

The intercept, $(k_{\text{dim}}+k_{\text{ed}})/k_{\text{dim}}$, is 1.20 and the slope which is given by $(k_f+k_d)(k_{-e}+k_{\text{dim}}+k_{\text{ed}})/k_{\text{dim}}k_e$ is 0.22. From these results and $\tau=1/(k_f+k_d)=1.99$ ns in dilute solution,

$$k_e\times\frac{k_{\text{dim}}}{k_{-e}+k_{\text{dim}}+k_{\text{ed}}} = k_e\frac{1}{\dfrac{k_{-e}}{k_{\text{dim}}}+\dfrac{(k_{\text{dim}}+k_{\text{ed}})}{k_{\text{dim}}}}$$
$$= 2.3\times10^{9}\ \text{M}^{-1}\,\text{s}^{-1}.$$

Thus the minimum value for k_e which is the rate constant for singlet excimer formation is 2.76×10^{9} $\text{M}^{-1}\,\text{s}^{-1}$ and the maximum value for that will be diffusion controlled rate constant of 2.25×10^{10} $\text{M}^{-1}\,\text{s}^{-1}$, the value obtained by the simplified Debye expression, $k_{\text{diff}}=8RT/3000\eta$, taking the viscosity of hexane as 0.294 cP at 25 °C.8)

The ratio of A/B monitored by NMR is about two and is independent on indeno[2,1-*a*]indene concentration indicating that the two dimers are formed through a common intermediate.

From these results, it is suggested that two dimers, HH and HT, are formed through a singlet excimer. The direct evidence for this mechanism will be obtained through the investigation of the temperature effect9,10) on the

$$k_e\times\frac{k_{\text{dim}}}{k_{-e}+k_{\text{dim}}+k_{\text{ed}}},$$

and this work is in progress.

The quantum yield of cyclodimerization in various solvents are shown in Table 1. The higher quantum yields are obtained in less viscous solvents indicating that the photocyclodimerization is dependent on the diffusion and association of solute molecules. External heavy atom effect as shown in methyl iodide decreases cyclodimerization quantum yield drastically indicating unequivocally that the excited singlet state is the reactive state for cyclodimerization. This mechanism was strongly substantiated by the triplet sensitization studies. No dimerization was observed when the benzene solution of indeno[2,1-*a*]indene was irradiated for 20 h with 366 nm UV light in the presence of benzophenone as a triplet sensitizer (E_T=68.3 kcal/mol). In acetonitrile solvent, the intersystem crossing from singlet to triplet state is perhaps enhanced as in the case of pyrimidine bases11) and this enhanced intersystem crossing along with the slower diffusion of singlet excited molecules decreases the photocyclodimerization yield.

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