Mechanistic Studies on the Anormalous Photocycloaddition Reaction of 5-Styryl-1,3-dimethyluracil and 2,3-Dimethyl-2-butene: Formation of the "Apparent Forbidden" $[_{\pi}4_s+_{\pi}2_s]$ Cycloadduct

Eun Ju Shin*, Ho Kwon Kang†, and Sang Chul Shim‡

Department of Chemistry, Sunchon National University, Sunchon 540-100

† *Department of Agricultural Chemistry, Sunchon National University, Sunchon 540-100*

‡ *Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 130-012.*

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Irradiation of 5-styryl-1,3-dimethyluracil (5-SDU) with 2,3-dimethyl-2-butene (DMB) gives a [4+2] cycloadduct which is converted into a [2+2] cycloadduct on the prolonged irradiation. Triplet sensitization, quenching, and external heavy atom effect on the [4+2] photocycloaddition reaction demonstrate the singlet pathway and salt effect excludes a radical ion pair precursor possibility. Polar solvents increase the reaction efficiency implying a polar exciplex involvement in the [4+2] photocycloaddition reaction. Inverse temperature dependence both on the reaction and DMB fluorescence quenching of 5-SDU indicates the presence of a singlet exciplex intermediate.

Introduction

Photocycloaddition reaction of the unsaturated compounds to olefins is a reaction of considerable synthetic and theoretical interest.[1-5]

The [2+2] type is most commonly encountered photochemical cycloaddition reaction. The photochemical [2+2] cycloaddition reaction of stilbene derivatives to olefins has been thoroughly investigated[6-8] and the reaction occurs *via* a relatively nonpolar singlet exciplex intermediates formed between the electronically excited stilbene derivatives and ground state olefins, not *via* a radical ion pair.[9] Solvent[8] and temperature effects[10] on the reaction support the intermediacy of the exciplex.

The photochemical [4+2] cycloadition is also known but less frequently encountered.[11-18] The Woodward-Hoffmann rules[19] and other molecular orbital approaches[20] predict that concerted suprafacial $[_{\pi}4_s+_{\pi}2_s]$ cycloadditions are photochemically forbidden, whereas concerted suprafacial $[_{\pi}2_s+_{\pi}2_s]$ or $[_{\pi}4_s+_{\pi}4_s]$ photocycloadditions are allowed. Triplet sensitized photodimerization of conjugated diene gives [4+2] cycloadduct as a minor product along with major [2+2] cycloadducts.[21-23] This photochemically forbidden [4+2] cycloadduct is formed not concertedly but *via* a triplet biradical intermediate. For anthracene/diene systems, Yang[17,18] has proposed that formation of allowed [2+2] or [4+4] and forbidden [4+2] cycloaddition products reflects competing concerted and stepwise collapse of singlet exciplexes, with the more polar exciplexes favoring stepwise collapse leading to [4+2] cycloaddition.

In our previous study,[24] irradiation of 5-styryl-1,3-dimethyluracil(5-SDU) with 2,3-dimethyl-2-butene(DMB) produces only a [4+2] cycloadduct and, in turn, this photochemical Diels-Alder type adduct is rearranged to the [2+2] cycloadduct on the prolonged irradiation. Our interest is directed to the first step photoreaction since it is very interesting that the forbidden [4+2] cycloadduct is the only photochemical product and any allowed [2+2] cycloadduct is not observed in the first step reaction. It is likely that the presence of hetero atoms and the conjugation between the central C=C double bond and 5,6-double bond of the uracil ring in 5-SDU lead to the different photochemical behavior from other stilbene derivatives which give only the [2+2] cycloadducts.

In this paper, mechanism of this anormalous [4+2] photocycloaddition reaction of 5-SDU with DMB is investigated.

Experimental

Materials. 5-Styryl-1,3-dimethyluracil was prepared as previously reported.[24] DMB(Aldrich) was used as received. Benzophenon(Sigma) was twice recrystallized from cyclohexane and vacuum sublimed; mp. 47.6-48.3℃. Azulene(Aldrich) was recrystallized from *n*-pentane, and vacuum sublimed; mp. 98.9-99.9℃. Methyl iodide(Aldrich, 99%) was refluxed with zinc for 1 h and distilled in the dark, bp. 43-44℃. Solvents were purified following the literature procedures.[25]

Preparative Photolysis. Preparative-scale irradiations were carried out in cylindrical Pyrex reactors(50-500 m*l* capacity) equipped with a Rayonet Photochemical Reactor(Southern New England Ultraviolet Co.) Model RPR-208 with 4 RUL 3500 Å fluorescence lamps. Solutions were irradiated after bubbling with nitrogen gas through the reaction mixture and monitored by TLC. Solvent was removed by rotary evaporation at reduced pressure. Nonvolatile mixtures were separated by column chromatography on Kiesel Gel 60(70-230 mesh, Merck) and HPLC(Waters Associates Model 244 liquid chromatograph equipped with Model 660 A solvent delivery system, Model 440 UV absorbance detector fixed at 254 nm and 280 nm, and Model U 6 K universal injector) on μ-Bondapak C_{18} column(3.9 mm i.d.x 30 cm, Waters Associates Co.).

Quantum Yield Measurements. 3.0 m*l* solutions were loaded in the Pyrex tubes (13×100 mm, Corning) and degassed by four freeze-pump-thaw cycles at 10^{-6} torr with cooling in liquid nitrogen and then flame sealed. These ampules were irradiated at 366 nm using CS 0-52 and 7-37 Corning glass filters in a merry-go-round apparatus immersed in a thermostated water bath with Hanovia 450 W medium pressure mercury arc lamp(Type 697A36). Photolysis was carried

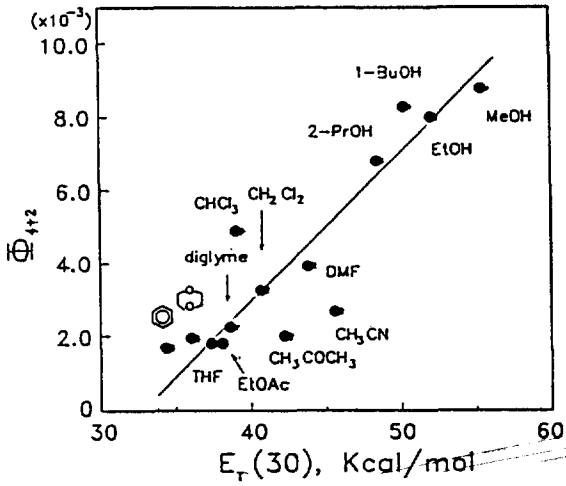

Figure 1. Solvent effect on the [4+2] cycloaddition reaction of 5-SDU(5×10^{-3} M) with DMB (0.84 M).

out to less than 5% conversion to minimize the back and parallel reactions. Light intensities were measured by ferrioxalate actinometry.[26] The quantitative analysis for the quantum yield measurements was carried out by HPLC.

Fluorescence Measurements. Aminco-Bowmann spectrophotofluorometer with an Aminco-XY recorder and 1P21 photomultiplier tube was employed in fluorescence studies. Sample temperature was controlled by passing cold nitrogen gas through the liquid nitrogen trap. Temperature was monitored with a copper-constantan thermocouple placed in a sample cell.

Results and Discussion

Solvent Effect. $[{}_{\pi}4_s+{}_{\pi}2_s]$ cycloaddition is photochemically forbidden. Yang[18] has proposed a correlation between the polarity of arene-1,3-diene exciplexes with the orientation of photocycloaddition of 1,3-dienes to arenes. The polar exciplexes undergo the "apparent forbidden" stepwise $[{}_{\pi}4_s+{}_{\pi}2_s]$ cycloaddition.

Figure 1 represents the solvent effect of the [4+2] cycloaddition reaction of 5-SDU with DMB. The reaction quantum yield increases with the solvent polarity leading to the conclusion that [4+2] cycloaddition reaction occurs from a polar charge-transfer character exciplex formed between 5-SDU and DMB. The more solvent polarity increases, the more stabilized the polar exciplex is, and the more efficient the nonconcerted [4+2] cycloaddition reaction is.

The quantum yield of the [4+2] cycloaddition reaction decreases on the addition of benzophenone triplet sensitizer (Table 1) suggesting that the reaction proceeds through a singlet manifold. As shown in Table 2, azulene, an efficient triplet quencher, does not quench the [4+2] cycloaddition reaction of 5-SDU with DMB. Table 3 shows that the quantum yield decreases slightly on addition of external heavy atoms further supporting the participation of the singlet excited state of 5-SDU in the reaction.

$[{}_{\pi}4_s+{}_{\pi}2_s]$ cycloaddition reaction occurs stepwise, following the rule of conservation of orbital symmetry for an excited-state process. The possibility of the intermediacy of a radical ion pair formed from electron-transfer processes can be tested by investigation of the salt effect on the reaction. Addition of Bu_4NClO_4, $Mg(ClO_4)_2$, and Bu_4NI salts in the concentration of 1.2×10^{-3} to 1.0×10^{-2} M does not have any influence on the reaction indicating that radical ion pair is not involved in the [4+2] photocycloaddition reaction.

From these results, the singlet polar exciplex seems to collapse stepwise to afford the [4+2] cycloadduct.

Table 1. Benzophenone Effect on the [4+2] Cycloaddition Reaction of 5-SDU(5×10^{-3} M) with DMB(0.84 M) in Dichloromethane

$[\phi_2CO]\times10^2$, M	0	1	2	4	6	8	10
$\Phi_{4+2}\times10^3$	3.2	3.0	2.8	2.6	2.2	2.0	1.8

Table 2. Azulene Effect of the [4+2] Cycloaddition Reaction of 5-SDU(5×10^{-3} M) with DMB(0.84 M) in Dichloromethane

$[Az]\times10^4$, M	0	4	8	12	16	20	30
$\Phi_{4+2}\times10^3$	3.2	3.2	3.2	3.2	3.2	3.1	3.1

Table 3. Heavy Atom Effect on the [4+2] Cycloaddition Reaction of 5-SDU(5×10^{-3} M) with DMB(0.84 M) in Dichloromethane

$[CH_3I]\times10^2$, M	0	4	8	12	16	20
$\Phi_{4+2}\times10^3$	3.3	3.2	3.2	3.1	3.1	3.0

DMB Concentration Effect. The quantum yield of the [4+2] photocycloaddition reaction increases with DMB concentration(0.2-1.4 M). If [4+2] cycloadduct is produced *via* the singlet exciplex, the following mechanism can be written.

$$5\text{-SDU}\xrightarrow{I_a}{}^1\text{5-SDU}$$

$${}^1\text{5-SDU}\xrightarrow{k_p}{}^1p$$

$${}^1\text{5-SDU}\xrightarrow{k_f}\text{5-SDU}+h\nu_f$$

$${}^1\text{5-SDU}\xrightarrow{k_i}\text{5-SDU}$$

$${}^1\text{5-SDU}\xrightarrow{k_{isc}}{}^3\text{5-SDU}$$

$${}^1\text{5-SDU}+\text{DMB}\xrightarrow{k_r}{}^1[\text{5-SDU---DMB}]\xrightarrow{f}[4+2]\ \text{cycloadduct}$$

$${}^1p\xrightarrow{k_d}\alpha\,{}^1\text{5-SDU}+(1-\alpha)5(Z)-\text{SDU}$$

$$\frac{1}{\Phi_{4+2}}=\frac{1}{f}\left(1+\frac{1}{k_r\tau[\text{DMB}]}\right)$$

$$\tau=1/(k_p+k_f+k_i+k_{isc})$$

where, ^{1}5-SDU represents the excited singlet state of *E*-form of 5-SDU, I_a the intensity of the absorbed light, k_p, k_f, k_i, k_{isc}, k_r, and k_d the rate constant of the twisted ^{1}5-SDU formation, fluorescence, internal conversion, intersystem crossing, exciplex formation, and decay of ${}^1p$ to ground state *E*- and *Z*-SDU, f the fraction giving the [4+2] cycloadduct from

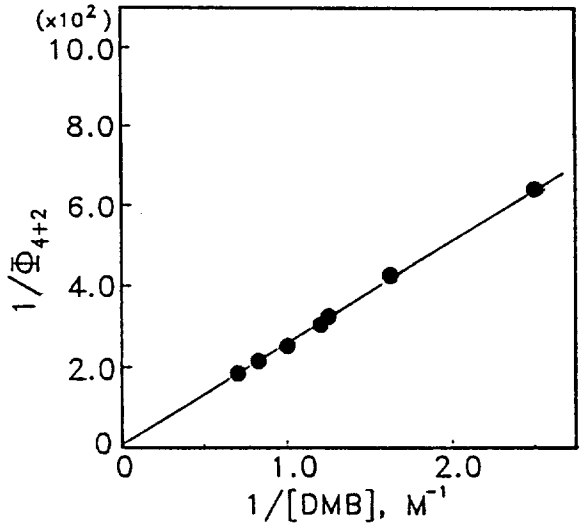

Figure 2. Plot of Φ_{4+2}^{-1} *vs* $[DMB]^{-1}$ for the [4+2] cycloaddition reaction of 5-SDU(5×10^{-3} M) with DMB(0.2-1.4 M) in dichloromethane.

Table 4. Kinetic Parameters from Φ_{4+2}^{-1} *vs* $[DMB]^{-1}$ Plot for the [4+2] Cycloaddition Reaction of 5-SDU(1.5×10^{-3} M) with DMB(0.3-1.4 M) in Ethanol

i, ℃	Slope, M	τ ns	$k_r\times10^{-8}$, $M^{-1}sec^{-1}$	Intercept	*f*
44	154	0.28	1.15	5	0.2
30	98	0.33	1.53	5	0.2
14	62	0.40	2.00	5	0.2

the singlet exciplex, ^{1}[5-SDU---DMB] the singlet exciplex formed between 5-SDU and DMB, 5(*Z*)-SDU *Z*-form of 5-SDU, and τ the singlet lifetime of 5-SDU, respectively.

As shown in Figure 2, the plot of Φ_{4+2}^{-1} *vs* $[DMB]^{-1}$ in dichloromethane is linear and its slope and intercept are 255 M and 12.5, respectively and the values of $f=0.08$ and $k_r=3.3\times10^8$ are obtained using $\tau=147$ ps(in *n*-hexane).[27] This very small *f* value may imply that the singlet exciplex has other decay processes than the formation of the [4+2] cycloadduct. A relatively nonpolar solvent, dichloromethane, is not polar enough to stabilize the polar exciplex and the exciplex favors decay to the ground state 5-SDU and DMB rather than collapsing to [4+2] cycloadduct. In ethanol, a more polar solvent, *f* value increases up to 0.2(Table 4) and the [4+2] cycloaddition through the polar exciplex becomes more efficient.

Temperature Effect. Generally, the reaction rate constant increases with increasing temperature. However, apparent rate in reversible reaction depends inversely on the temperature in the case of exthothermic reaction. If reversible exciplex formation is necessary for the [4+2] cycloaddition reaction, the negative temperature dependence of k_f, should be observed.

Temperature dependence on the plot of Φ_{4+2}^{-1} *vs* $[DMB]^{-1}$ is shown in Figure 3. As temperature increases, Φ_{4+2} decreases and slope of the plot of Φ_{4+2}^{-1} *vs* $[DMB]^{-1}$ increases. Temperature dependence of slope does not represent

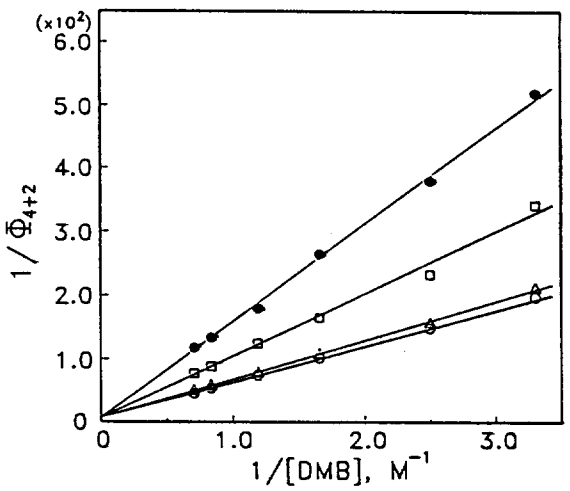

Figure 3. Temperature dependence on the [4+2] cycloaddition reaction of 5-SDU(1.5×10^{-3} M) with DMB(0.3-1.4 M) in ethanol: 44℃; ●, 30℃; □, 14℃; △, 4℃; ○.

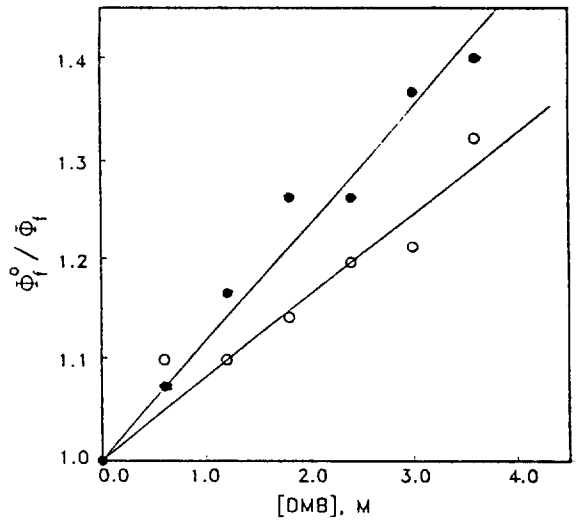

Figure 4. Temperature dependence on the fluorescence quenching of 5-SDU by DMB(0.6-3.6 M) in ethanol: 0℃; ●, 17℃; ○.

directly the temperature dependence of k_r since temperature effect on τ cannot be ignored. Before determining the temperature dependence of k_r, it is necessary to take into account variation in the singlet lifetime of 5-SDU with temperature.

We previously investigated that temperature dependence on the fluorescence of 5-SDU in methylcyclohexane-isopentane=1:1 (v/v) follows the equation:[28]

$$\ln(I_f^\circ/I_f-1)=5.86-1376/T$$

where I_f° is the limiting fluorescence intensity of 5-SDU in low temperature. The results show that an activated process leading to *E-Z* isomerization through the twisted singlet 5-SDU competes with fluorescence.

If I_f°/I_f is approximated as τ_f°/τ_f, the temperature dependence of fluorescence lifetime can be estimated roughly using the equation and fluorescence lifetime in H_2O at 20℃ (375 ps)[27] and the results are summarized in Table 4. Now, it is possible to determine k_r at various temperature from

Table 5. Kinetic Parameters for the Fluorescence Quenching of 5-SDU by DMB(0.6-3.6 M) in Ethanol

t, ℃	$k_r\tau_f$	τ, ns	k_r
0	0.13_0	0.48_2	2.69×10^8
17	0.08_1	0.38_9	2.09×10^8

slope/intercept $=(k_r\tau)^{-1}$ of Φ_{4+2}^{-1} *vs* $[DMB]^{-1}$ plot. If the temperature dependence on the lifetime of 5-SDU were the only temperature effect on the cycloaddition, k_r should be constant. It is clear that k_r given in Table 4 has a negative temperature dependence.

Temperatures dependence on fluorescence quenching of 5-SDU by DMB is shown in Figure 4. The slope, Stern-Volmer constant, of the Φ_f°/Φ_f *vs* [DMB] plot is given by $k_r\tau_f$. The slope is 0.081 at 17℃ and this gives an independent value for k_r of 2.09×10^8(Table 5). It shows good agreement with the value obtained from the Φ_{4+2}^{-1} *vs* $[DMB]^{-1}$ plot in comparison with k_r of 2.0×10^8 at 14℃. The observed negative temperature dependence of k_r may imply the intermediacy of exciplex. The reversible exciplex formation seems to be followed by subsequent stepwise collapse to form [4+2] cycloadduct.

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