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Photochemical C_4 -Cycloadduct Formation between 5(E)-Styryl-1,3-dimethyluracil and Some Olefins-Via Photochemical Diels-Alder Type [4 + 2] Adduct

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The cyclobutane forming photocycloaddition reaction of 5(E)-styryl-1,3-dimethyluracil with some olefins occurs on the 5,6-double bond of uracil ring rather than the expected central double bond via an intermediate, probably the photochemical Diels-Alder type adduct. This intermediate formed on short term irradiation of 5(E)-styryl-1,3-dimethyluracil and 2,3-dimethyl-2-butene solution is converted into the C_4 -cycloadduct on the prolonged irradiation. Quantum yield of the intermediate formation is not linear with the concentration of 2,3-dimethyl-2-butene probably due to the secondary reaction accompanied with the complex reaction kinetics. The intermediate is formed from the lowest excited singlet state.

Introduction

The photophysical and photochemical behaviors of stilbene have been extensively studied and the results have contributed prominently to the development of a mechanistic theory of photochemical reactions.¹ The mechanistic details of the photochemical E \rightleftharpoons Z isomerization² and photodehydrocyclization³ of stilbene are well established. Photocycloaddition of stilbene to numerous olefins^{4,5} has been thoroughly studied and is known to undergo via a relatively nonpolar singlet exciplex intermediates formed between the electronically excited stilbene and ground state olefins and not via a radical ion pair.⁶

Heterocyclic compounds containing both (n, π^*) and (π, π^*) excited states behave differently from stilbene because of the participation of (n, π^*) states in the decay and/or reaction processes.^{7,8} Our laboratory has been interested in the photochemical and photophysical behavior of stilbene derivatives containing hetero-atoms for some time and reported previously that both unimolecular and bimolecular reactions of 1,2-bispyrazinylethylene are very different from those of stilbene because of the high intersystem crossing efficiency.⁹⁻¹⁴

The photocycloaddition reaction of the stilbene derivatives which contain hetero-atoms or are unsymmetrically substituted has been paid little attention until now. 5(E)-Styryl-1,3-dimethyluracil, in which one phenyl ring in stilbene is replaced with a pyrimidine base,¹⁵ is unsymmetrically substituted around the central C = C bond and has both (n, π^*) and (π, π^*) excited states resulting in the different photochemical and photophysical properties from stilbene. It was previously reported that E \rightleftharpoons Z photoisomerization¹⁶ and photocyclization¹⁷ of 5(E)-styryl-1,3-dimethyluracil occur via the excited singlet state as those of stilbene. The photocyclo-

addition reaction of 5(E)-styryl-1,3-dimethyluracil with some olefins is investigated.

Experimental

Materials. 5(E)-Styryl-1,3-dimethyluracil was prepared by palladium-catalyzed reaction^{18,19} of styrene and 1,3-dimethyluracil.²⁰ 2,3-Dimethyl-2-butene (Aldrich Chemical Co., Milwaukee, USA) was purified by distillation. Dimethyl maleate, methyl crotonate, and dimethyl ethylidene-malonate (Aldrich) were used without further purification. Fumaronitrile (Aldrich) were recrystallized twice from ethanol. Azulene (Aldrich) was purified by vacuum sublimation. Benzophenone (Sigma Chemical Co., St. Louis, USA) was recrystallized from cyclohexane. Kiesel Gel 60 (70-230 mesh, Merck, D-6100 Darmstadt, F.R. Germany) and Kiesel Gel GF₂₅₄ (Merck) were used for silica gel column chromatography and thin layer chromatography, respectively.

Instruments. Ultraviolet-visible spectra were recorded on Cary 17 spectrophotometer. Infrared spectra were measured on a Perkin Elmer 267 spectrophotometer using potassium bromide pellet or sodium chloride cell. Nuclear magnetic resonance spectra were measured on Varian T-60A, Varian FT-80A at 79.542 MHz, and Bruker AM-200-SY spectrometers. Mass spectra were determined with a Hewlett Packard 5985 A GC/MS system by electron impact method. Elemental analysis was carried out on a F&M Scientific Cooperation C.H.N. Analyzer Model 180. High performance liquid chromatography was performed on a Waters Associates Model 244 liquid chromatograph equipped with Model 600A solvent delivery system, Model 440 UV absorbance detector fixed at 254 nm and 280 nm, Model U 6K universal injector. μ -Bondapak CN, Radialpak C₈, and Lichrosorb Si 60 columns were used for purpose of analysis and separation. Fluores-

cence spectra were measured on an Aminco-Bowman spectrofluorometer with an Aminco-XY recorder at room temperature.

Photoreaction of 5(E)-Styryl-1,3-dimethyluracil with Olefins. Preparative photolysis was carried out in dichloromethane solution of 5(E)-styryl-1,3-dimethyluracil (10⁻² M) and olefins (1 M). Samples were degassed by bubbling nitrogen gas and irradiated in a Rayonet Photochemical Reactor Model RPR 208 (The Southern New England Ultraviolet Co.) equipped with four RUL 3500 Å fluorescent lamps for 30-50 hours. The progress of the reactions was monitored by TLC. The solvent was evaporated in vacuo. The major photoproducts were isolated by preparative TLC or silica gel column chromatography using n-hexane-ethyl ether (1:3, v/v) as the eluting solvent or HPLC using n-hexane-ethyl ether (1:2, v/v) or water-methanol (4:6, v/v) as the eluent. Quantitative analyses of the photoproducts were carried out by HPLC.

Short irradiation of a dichloromethane solution of 5(E)-SDU and 2,3-dimethyl-2-butene produces a new material, an intermediate of C₄-photocycloadduct formation. ¹H NMR δ 1.05(s, 3H, CH₃) 1.15(s, 3H, CH₃) 1.20(s, 6H, 2CH₃) 3.20(s, 3H, N-CH₃) 3.30(s, 3H, N-CH₃) 3.8(s, 1H) 6.43(s, 2H) 7.2-7.5 (m, 5H, aromatic) ppm. Mass spectrum shows no molecular ion peak but the base peak at m/e 242(5(E)-SDU) and the fragment peak at m/e 84(DB). Calcd for C₂₀H₂₆N₂O₂: C, 73.59; H 8.03; N, 8.58%. Found: C, 73.0; H, 8.06; N, 8.39%.

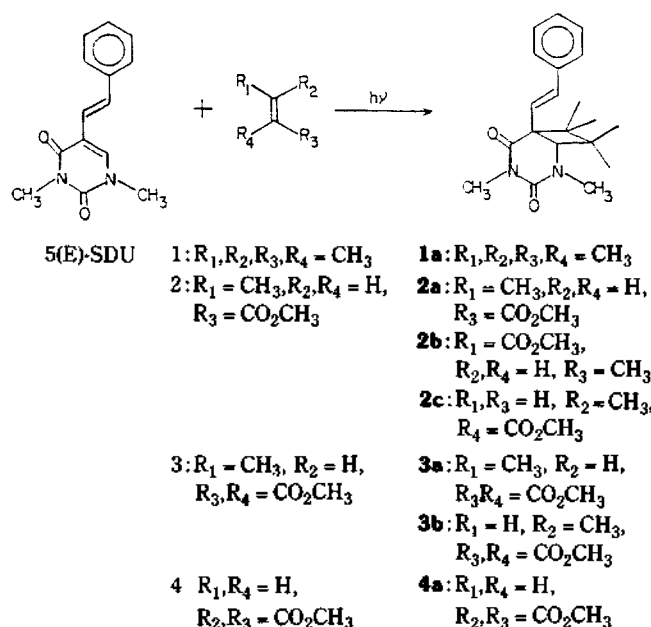
Hydrogenation product was obtained by stirring of the methanol solution of the intermediate with 5% Pd/C catalyst for 20 min. at room temperature. ¹H NMR δ 1.04(s, 3H, CH₃) 1.11(s, 3H, CH₃) 1.21(s, 3H, CH₃) 1.24(s, 3H, CH₃) 1.8-2.8(m, 4H) 3.00(s, 3H, N-CH₃) 3.34(s, 1H) 3.38(s, 3H, N-CH₃) 7.1-7.4 (m, 5H, aromatic) ppm.

Quantum Yield Measurements. 3ml samples in Pyrex ampoules were degassed by freeze-pump-thaw method with cooling in liquid nitrogen and then sealed. These samples were irradiated in a merry-go-round apparatus with Hanovia 450 W medium pressure mercury arc lamp (Type 697A36). To isolate the mercury emission line of 366 nm, CS 0-52 and 7-37 Corning glass filters were used. Light intensities were measured by ferrioxalate actinometry²¹ and the quantitative analysis for the quantum yield measurements was carried out by HPLC techniques to less than 5% conversion to avoid competition of the back reaction.

Results and Discussion

5(E)-Styryl-1,3-dimethyluracil(5(E)-SDU) undergoes photocycloaddition reaction to olefins with different electron affinities such as 2,3-dimethyl-2-butene (DB), methyl crotonate, dimethyl ethylidenemalonate, and dimethyl maleate as in the case of stilbene. The reaction, however, yields unexpected C₄-cycloadducts between olefins and the 5,6-double bond of uracil ring rather than the expected central double bond²² (Scheme 1). Strong electron acceptors, e.g. fumaronitrile, yield no cycloadduct with 5(E)-SDU.

Preparative photolysis of 5(E)-SDU and DB(1) in dichloromethane gives a 1:1 cycloadduct **1a**, colorless oil in 14.6% yield. Mass spectrum shows the peaks at m/e 326(M⁺), 242(5(E)-SDU), and 84(DB). One of the carbonyl stretching bands (ν_{C=O} = 1680 and 1710 cm⁻¹) is blue-shifted compared to one of those in 5(E)-SDU(ν_{C=O} = 1650 and 1710 cm⁻¹), pro-



Scheme 1. Photocycloaddition reaction of 5(E)-SDU with various olefins.

bably due to the saturation of C = C double bond adjacent to the carbonyl group. UV spectrum in methanol shows two bands at 227 and 310nm with disappearance of 318 nm band of 5(E)-SDU. ¹H NMR spectrum supports the formation of a C₄-cycloadduct between uracil moiety and DB, especially from the large shift of 1-N-methyl protons(2.48 ppm) relative to those of 5(E)-SDU(3.5 ppm) and remainder of olefinic protons in styrene moiety(two doublet at 6.12 and 7.01 ppm, J = 11.9 Hz) even though these are shifted upfield compared with those of 5(E)-SDU(two doublet at 7.4 and 6.8 ppm, J = 16 Hz). ¹³C NMR spectrum shows 18 peaks in agreement with the cycloadduct.

Irradiation of a dichloromethane solution of 5(E)-SDU in the presence of excess methyl crotonate(**2**) gives three isomeric cycloadducts **2a**, **2b**, and **2c** in a ratio of 64:8:1 in total yield of 23.5%. Photolysis of 5(E)-SDU with dimethyl ethylidenemalonate(**3**) in dichloromethane affords two isomeric cycloadducts **3a** and **3b** in a ratio of 3:2. Photoreaction of 5(E)-SDU with dimethyl maleate **4** leads to the formation of a cycloadduct **4a**. The stereochemistry of the cycloadducts was determined on the basis of both the chemical shift and proton-proton coupling pattern in ¹H-NMR and ¹³C-NMR spectra. Spectral data of the C₄-photocycloadducts are summarized in Table 1-3.

As shown in Figure 1, irradiation of a dichloromethane solution of 5(E)-SDU and DB for a short periods of time produces a new compound which is converted into C₄-cycloadduct on the prolonged irradiation until the reactant is completely exhausted. The C₄-cycloadduct which is produced quantitatively from the photolysis of the isolated intermediate is not produced on short term irradiation of 5(E)-SDU with DB. When the dichloromethane solution of the intermediate and DB is irradiated, the formation of the C₄-cycloadduct becomes inefficient even though no other product is detected. The results indicate that the C₄-cycloadduct formation proceeds via an intramolecular reaction of the intermediate formed during irradiation.

Table 1. ^1H NMR Absorptions for C_4 -Cycloadducts in CDCl_3 (δ , ppm)

	C_1	C_3	C_6	C_9	C_{10}	C_{11-14}	R_1	R_2	R_3	R_4
<i>1a</i>	2.48	3.52	3.37	6.12	7.01	7.29-7.60	1.07	1.19	1.32	1.41
	s	s	s	d,11.9Hz	d,11.9Hz	m	s	s	s	s
<i>2a</i>	2.43	3.42	3.87	6.03	7.03	7.23-7.51	1.42	3.30	3.78	2.93
	s	s	d,9Hz	d,12Hz	d,12Hz	m	d,7.4Hz	dq,4.4Hz, 7.4Hz	s	dd,4.4Hz, 9Hz
<i>2b</i>	2.62	3.34	3.70	6.05	6.88	7.21-7.49	3.67	2.66-2.69	1.35	2.66-2.69
	s	s	d,8Hz	d,11.6Hz	d,11.6Hz	m	s	m	d,6.2Hz	m
<i>2c</i>	2.48	3.45	3.33	5.88	6.95	7.26-7.56	2.91	1.11	3.94	3.94
	s	s	d,3.4Hz	d,11.6Hz	d,11.6Hz	m	dq,3.5Hz, 7.6Hz	d,7.6Hz	dd,3.4Hz, 3.5Hz	s
<i>3a</i>	2.41	3.34	4.39	5.96	7.04	7.25-7.54	1.29	3.79	3.89	3.61
	s	s	s	d,12Hz	d,12Hz	m	d,7.6Hz	q,7.6Hz	s	s
<i>3b</i>	2.54	3.39	4.03	6.05	6.67	7.23-7.56	2.94	1.50	3.93	3.60
	s	s	s	d,11.6Hz	d,11.6Hz	m	q,7.3Hz	d,7.3Hz	s	s
<i>4a</i>	2.65	3.40	4.33	5.84	6.96	7.29-7.54	3.98	3.82	3.90	3.30
	s	s	d,9.1Hz	d,12Hz	d,12Hz	m	d,9.6Hz	s	s	dd,9.1&9.6Hz
SDU	3.50	3.53	7.25-7.60	6.80	7.40	7.25-7.60	—	—	—	—
	s	s	m	d,16Hz	d,16Hz	m	—	—	—	—

Table 2. ^{13}C NMR Absorption for Cycloadducts in CDCl_3 (δ , ppm)

	<i>1a</i>	<i>2a</i>	<i>2b</i>	<i>2c</i>	<i>3a</i>	<i>3b</i>	<i>4a</i>	5(E)-SDU
C_1	27.68	28.65	28.75	28.94	28.56	28.32	29.19	27.60
C_2	152.17	152.72	152.48	152.74	152.38	152.94	151.78	150.60
C_3	35.04	34.52	35.17	34.72	34.72	34.47	35.01	36.70
C_4	171.11	172.85	173.04	172.93	172.40	171.34	171.11	162.00
C_5	52.31	50.06	50.70	50.33	48.67	48.79	50.43	111.10
C_6	61.73	55.27	57.33	56.09	57.73	59.78	57.35	139.50
C_7	45.56	49.44	41.97	52.74	61.74	60.96	49.14	—
C_8	43.74	38.63	51.22	34.72	41.20	45.28	45.98	—
C_9	130.96	129.79	128.95	129.20	129.11	131.63	127.35	120.10
C_{10}	131.36	133.49	132.09	133.61	134.21	133.94	134.69	129.00
C_{11}	137.06	137.15	133.40	136.91	136.97	136.73	136.69	137.40
C_{12}	128.30	129.04	128.95	128.96	128.97	129.02	129.09	128.50
C_{13}	128.02	128.62	128.62	128.71	128.56	128.66	128.71	127.50
C_{14}	127.19	128.19	128.20	128.15	128.19	128.31	128.30	126.30
C_{15}	19.31	17.22	170.06	172.24	12.99	12.12	170.74	—
C_{16}	21.06	172.15	52.87	52.93	169.02	167.89	52.71	—
C_{17}	23.42	52.71	17.05	14.45	53.19	53.19	170.74	—
C_{18}	24.41	—	—	—	169.11	169.30	52.90	—
C_{19}	—	—	—	—	53.65	53.19	—	—

Table 3. IR and UV Spectral Data of the Photocycloadducts

Compound	IR(cm^{-1})	UV(λ_{max} , nm) in CH_3OH
5(E)-SDU	3060, 2920, 1710, 1650, 1460, 1375, 960	318 (ϵ 24500)
Intermediate	3050, 2980, 1710, 1675, 1490, 1380	260
Hydrogenation of intermediate	3050, 2980, 1710, 1680, 1490, 1385	228, 310
<i>1a</i>	3080, 2980, 1710, 1680, 1490, 1385	227, 310 (ϵ 8170) (ϵ 30)
<i>2a-c</i>	3040, 2980, 1745, 1720, 1680, 1380	225, 300
<i>3a, b</i>	3040, 2970, 1745, 1720, 1680, 1390	227, 310
<i>4a</i>	3020, 2970, 1750, 1720, 1680, 1380	237, 300

The intermediate shows the absorption maxima around 260 nm. The carbonyl stretching bands of the intermediate (1675 and 1710 cm^{-1}) are blue-shifted with respect to those of

5(E)-SDU (1650 and 1710 cm^{-1}) indicating the saturation of 5,6-double bond of uracil ring. ^1H NMR spectrum indicates the formation of the adduct between 5-SDU and DB from

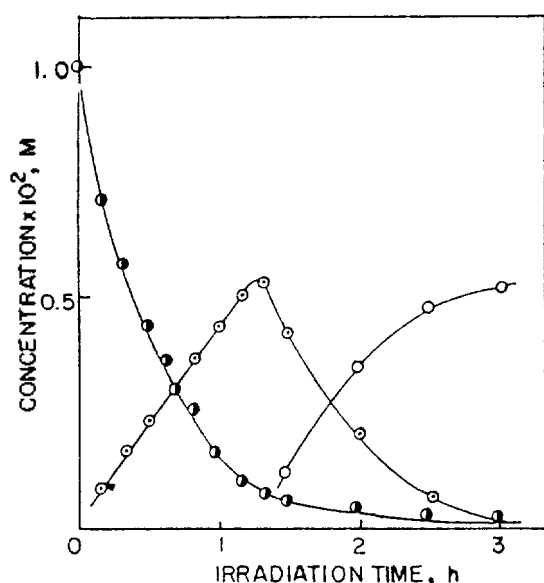


Figure 1. Time-dependence of the photoreaction of 5(E)-SDU with DB in dichloromethane. ●, 5(E)-SDU; ○, intermediate; □, [2 + 2] cycloadduct.

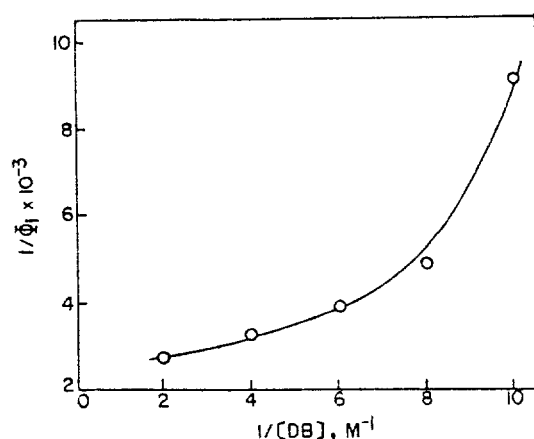
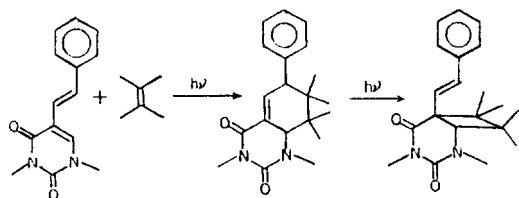


Figure 2. DB concentration effect on the photoreaction of 5(E)-SDU with DB to form the intermediate in dichloromethane with excitation wavelength of 366 nm.



Scheme 2. Photocycloaddition reaction of 5(E)-SDU with DB proceeding through an intermediate.

four methyl peak and the presence of trisubstituted C=C double bond probably substituted at 5-position of uracil ring from a singlet peak at 6.43 ppm. On the basis of these data, the structure of the intermediate is assigned to photochemical Diels-Alder type [4 + 2] cycloadduct.

Comparison of spectral data between the intermediate and its hydrogenation product further supports the structure of the intermediate. UV absorption maxima of hydrogenation product of the intermediate are blue-shifted due to the satu-

Table 4. Azulene Quenching of Photoreaction of 5(E)-SDU and DB in Dichloromethane.^a

[Azulene], M	Φ_i	Φ_i^0/Φ_i^b
0	3.7×10^{-4}	1.00
2×10^{-3}	3.5×10^{-4}	1.06
3×10^{-3}	3.5×10^{-4}	1.06
4×10^{-3}	3.5×10^{-4}	1.06
5×10^{-3}	3.5×10^{-4}	1.06

^a Concentrations of 5(E)-SDU and DB are 3×10^{-3} and 0.5 M, respectively. ^b Φ_i^0 and Φ_i are quantum yields in the absence and presence of azulene, respectively.

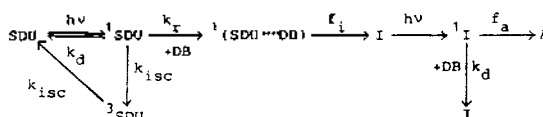
Table 5. Sensitization of Photoreaction of 5(E)-SDU and DB in Dichloromethane^a

[Benzophenone], M	(1- α) ^b	Φ_i	Φ_i^0/Φ_i^c
0	0	3.7×10^{-4}	0
0.06	0.31	3.7×10^{-4}	1.1×10^{-4}
0.08	0.41	4.2×10^{-4}	2.0×10^{-4}
0.10	0.44	5.0×10^{-4}	2.9×10^{-4}
0.12	0.49	5.3×10^{-4}	3.5×10^{-4}
0.14	0.52	5.7×10^{-4}	3.9×10^{-4}

^a Concentration of 5(E)-SDU and DB are 3×10^{-3} and 0.5 M, respectively. ^b 1- α is the fraction of the exciting light absorbed by benzophenone. ^c Φ_i and Φ_i^0 are quantum yields in the presence and absence of benzophenone, respectively.

ration of double bond supporting the presence of a conjugated double bond in the intermediate. IR spectrum shows the carbonyl stretching bands (1680 and 1710 cm⁻¹) at the same positions as those of C₄-cycloadduct. A singlet peak at 6.43 ppm in ¹H NMR spectrum of the intermediate disappears and multiplet at 1.8-2.8 ppm appears confirming the assignment of a peak at 6.43 ppm to a vinyl proton.

The quantum yield of photoreaction of 5(E)-SDU with DB forming the intermediate (Φ_i) is about 4×10^{-4} in dichloromethane at [5(E)-SDU] = 3×10^{-4} M and [DB] = 0.5 M. Φ_i increases with increasing the concentration of DB. Inefficient intersystem crossing ($\Phi_{isc} = 0.052$ in ethanol)²³ and moderate fluorescence quenching by DB of 5(E)-SDU ($k_q = 1.1 \times 10^9$ M⁻¹sec⁻¹) imply low reactivity of excited triplet state. If the excited singlet state of 5(E)-SDU only is involved in the photoreaction of 5(E)-SDU and DB, the following kinetic scheme can be written, where SDU = 5(E)-SDU, I = intermediate, and A = C₄-cycloadduct; f_i is the fraction that the intermediate is formed from ¹(SDU...DB) complex; f_a is the fraction that the C₄-cycloadduct is formed from ¹I.



Intermediate formed initially by the photoreaction of 5(E)-SDU with DB undergoes the subsequent secondary photoreaction to form C₄-cycloadduct and, in turn, the excited singlet intermediate is quenched by remaining DB. This complex reaction kinetics results in the upward-curvature in the plot of Φ_i^{-1} vs. [DB]⁻¹ as shown in Figure 2.

Φ_i is nearly unquenched by azulene, an efficient triplet quencher (Table 4), indicating that the reaction yielding the

intermediate occurs in the lowest excited singlet state of 5(E)-SDU. This is consistent with very small quantum yield of intersystem crossing of 5(E)-SDU.

As shown in Table 5, Φ_i increases slightly with increasing the concentration of benzophenone suggesting that the excited triplet state of 5(E)-SDU can undergo the same type of reaction, even though with low efficiency. The quantum yield of pure triplet photoreaction(Φ_t) of 1.03×10^{-3} is estimated from extrapolation of the quantum yield to the point where only the benzophenone absorbs the exciting radiation (i.e., $1 - \alpha = 1$). Total quantum yield(Φ) is expressed by the following:

$$\Phi_t = \Phi_s + \Phi_{isc} \times \Phi_i$$

where Φ_s and Φ_t represent the quantum yields of photoreaction occurring via the excited singlet state and triplet state, respectively, and $\Phi_{isc} \times \Phi_i$ is the quantum yield of triplet state photoreaction on direct irradiation. Φ_s of 3.5×10^{-4} is obtained from $\Phi(4 \times 10^{-4})$, $\Phi_{isc}(0.052)$, and $\Phi(1.03 \times 10^{-3})$. Photoreaction to form the intermediate, therefore, occurs mainly via the excited singlet state with small participation of triplet state reaction.

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Reaction of Methylenethioxanthene with Thiyl Radical: Formation of A Vinyl Sulfide

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Reactions of methylenethioxanthene (**3**) with n-propanethiol in the presence of di-t-butyl peroxide(DTBP) afforded preferentially propyl 9-thioxanthenyldenemethyl sulfide(**8**) rather than propyl 9-thioxanthenyldenemethyl sulfide(**9**) regardless of the concentration of n-propanethiol. On the other hand reactions of **3** with a low concentration of n-propanethiol in the presence of dibenzoyl peroxide(DBPO) gave **8**, 1,2-bisthioxanthenyldiene ethane(**11**), and thioxanthenyldenemethyl benzoate(**12**) but only **8** was formed at high concentration of the thiol. The formations of these products were rationalized by an electron transfer mechanism.

Introduction

The reaction of thioxanthylum ion (**1**) with diphenyl- and dibenzylmercury under nitrogen atmosphere afforded 9-phenyl- and 9-benzylthioxanthene, respectively. However, bis-

9,9^l-thioxanthenyldimethane (**2**) was obtained from the analogous reaction with dimethylmercury instead of 9-methylthioxanthene.¹ The formation of **2** suggests inevitably the involvement of methylenethioxanthene (**3**) as key intermediate. Therefore, it was assumed that **2** would be formed via a