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Cis−*Trans* Isomerization and Oxidation of Radical Cations of Stilbene Derivatives

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Isomerization from *cis* stilbene derivatives (*c*-**S** (**S** = RCH=CHC$_6$H$_5$: **1**, R = C$_6$H$_5$; **2**, R = 4-CH$_3$C$_6$H$_4$; **3**, R = 4-CH$_3$OC$_6$H$_4$ (= An); **4**, R = 2,4-(CH$_3$O)$_2$C$_6$H$_3$; **5**, R = 3,4-(CH$_3$O)$_2$C$_6$H$_3$; **6**, R = 3,5-(CH$_3$O)$_2$C$_6$H$_3$; **7**, AnCH=C(CH$_3$)C$_6$H$_5$; **8**, AnCH=CHAn)) to *trans* isomers (*t*-**S**) and oxidation of **S** with O_2 were studied in γ-ray radiolyses of *c*-**S** in Ar-saturated 1,2-dichloroethane (DCE) and of **S** in O_2-saturated DCE, respectively. On the basis of product analyses, it is suggested that a smaller barrier to *c*−*t* unimolecular isomerization for *c*-**3**$^{\bullet+}$−**5**$^{\bullet+}$ and **8**$^{\bullet+}$ than for *c*-**1**$^{\bullet+}$, **2**$^{\bullet+}$, and **6**$^{\bullet+}$ due to the single bond character of the central C=C double bond for *c*-**3**$^{\bullet+}$−**5**$^{\bullet+}$ and **8**$^{\bullet+}$ with a *p*-methoxyl group but not for *c*-**1**$^{\bullet+}$, **2**$^{\bullet+}$, and **6**$^{\bullet+}$ without a *p*-methoxyl group because of the contribution of a quinoid-type structure induced by charge−spin separation. The isomerization proceeds via chain reaction mechanisms involving *c*−*t* unimolecular isomerization and endergonic hole transfer or dimerization and decomposition. The isomerization of *c*-**3**$^{\bullet+}$ to *t*-**3**$^{\bullet+}$ is catalyzed by addition of 1,4-dimethoxybenzene but terminated by triethylamine. The regioselective formation of **3d** in oxidation of **3**$^{\bullet+}$ with O_2 is explained by spin localization on the β-olefinic carbon in **3**$^{\bullet+}$. The results of product analyses are compared with the rate constants of the unimolecular isomerization and the oxidation for **S**$^{\bullet+}$ measured with pulse radiolyses.

Introduction

Numerous studies on reactions of radical cations of aromatic olefins have been reported from the synthetic and mechanistic points of view.[1−5] It is well-known that *cis*(*c*)−*trans*(*t*) isomerization and addition of a nucleophile occur in radical cations of aromatic olefins as typical reactions. The reactivities depend on the structure or substituents of the radical cations. No unimolecular *c*−*t* isomerization occurs in the stilbene radical cation (St$^{\bullet+}$),[2] although it does in the radical cations of *c*-4,4′-dibromostilbene and *c*-4,4′-dimethylstilbene.[2c] *t*-St$^{\bullet+}$ has little reactivity toward O_2,[3a,4,5] while the radical cation of (*E*)-2,3-diphenyl-2-butene has a high reactivity toward O_2.[4g] Factors which control the reactivities of the radical cations are still unclear.

We have recently reported reactions of radical cations of stilbene derivatives using pulse radiolysis in 1,2-dichloroethane,[6] unimolecular isomerization from *cis* to *trans* isomeric radical cations as well as bimolecular reactions with O_2 (oxidation). On the basis of the rate constants for the reactions, we have found that the unimolecular *c*−*t* isomerization and oxidation with O_2 of such stilbene radical cations, particularly with substitution of a *p*-methoxyl group as an electron-donating substituent in radical cations of stilbene derivatives, remarkably enhances the isomerization and oxidation at room temperature. It is concluded that separation and localization of a positive charge and an unpaired electron play the most important role in increasing the reactivities.[6] In order to confirm this conclusion, product analyses of *c*−*t* isomerization and oxidation by O_2 of radical cations of eight stilbene derivatives (**S**$^{\bullet+}$ = **1**$^{\bullet+}$−**8**$^{\bullet+}$) as shown in Scheme 1 were carried out using γ-ray radiolyses and chloranil photosensitization. We have also found that isomerization from *c*-**S**$^{\bullet+}$ to *t*-**S**$^{\bullet+}$ proceeds via

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(5) Tokumaru and his co-workers reported that *t*-**1**$^{\bullet+}$ reacts toward O_2 at a rate constant of $k_{O_2} = 1.3 \times 10^6$ M^{-1} s^{-1} in the laser flash photolysis of 9-cyanoanthracene−*t*-**1** in DMSO.[4f,g]

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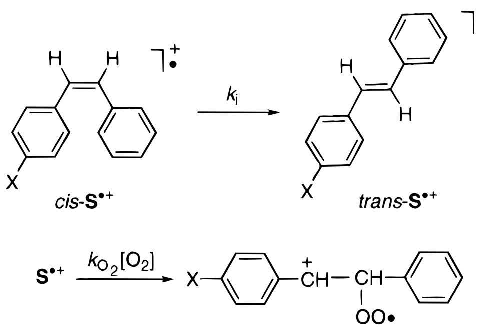
Scheme 1



$S^{\bullet+} = RCH{=}CR'R''^{\bullet+}$

	R	R'	R''
$1^{\bullet+}$	C_6H_5	H	C_6H_5
$2^{\bullet+}$	$4\text{-}CH_3C_6H_4$	H	C_6H_5
$3^{\bullet+}$	$4\text{-}CH_3OC_6H_4$	H	C_6H_5
$4^{\bullet+}$	$2,4\text{-}(CH_3O)_2C_6H_3$	H	C_6H_5
$5^{\bullet+}$	$3,4\text{-}(CH_3O)_2C_6H_3$	H	C_6H_5
$6^{\bullet+}$	$3,5\text{-}(CH_3O)_2C_6H_3$	H	C_6H_5
$7^{\bullet+}$	$4\text{-}CH_3OC_6H_4$	CH_3	C_6H_5
$8^{\bullet+}$	$4\text{-}CH_3OC_6H_4$	H	$4\text{-}CH_3OC_6H_4$

chain reaction mechanisms at a higher concentration of **S**, that the isomerization of *c*-$\mathbf{3}^{\bullet+}$ to *t*-$\mathbf{3}^{\bullet+}$ is catalyzed by addition of 1,4-dimethoxybenzene but terminated by triethylamine, and that a quinoid-type structure of $\mathbf{3}^{\bullet+}$ with a positive charge and an unpaired electron separately is responsible for regiospecific formation of an oxygenated product of a $\mathbf{3}^{\bullet+}$ with a *p*-methoxyl group.

Results

Product Analyses of Isomerization of *c*-$\mathbf{S}^{\bullet+}$. Product analyses of the γ-radiolyses of *c*-**S** (1.0×10^{-2} M) in Ar-saturated 1,2-dichloroethane (DCE) were carried out at room temperature. The main product was *t*-**S** the yields of which were almost equivalent to those of *c*-**S** consumed. Table 1 summarizes the conversions of *c*-**S**, the yield of *t*-**S** based on the conversion of *c*-**S** respectively, the *G* values for the yield of *t*-**S** with a definition of the number of *t*-**S** molecules produced per 100 eV of radiation energy absorbed by a sample solution, and $G_{\lim}$ for the *G* value when the concentration of *c*-**S** is extrapolated to infinity in the plots of inverse *G* values vs the inverse concentration of *c*-**S**. Since the *G* value of the formation of *c*-$\mathbf{S}^{\bullet+}$ is approximately 2.5 in butyl chloride at 77 K,[7] the *G* and $G_{\lim}$ values of *c*-**S** consumed and final products in unimolecular reactions of *c*-$\mathbf{S}^{\bullet+}$ are less than 2.5 at room temperature.

The *G* values for the yield of *t*-**S** were 10−20 for *c*-**1**, **2**, and **6** without a *p*-methoxyl group and approximately 100 for *c*-**3**−**5** and **8** with a *p*-methoxyl group. The *G* values increased significantly with increasing concentration of *c*-**3**−**5** and **8**, while the concentration of *c*-**1**, **2**, and **6** had less significant influence on the *G* values (Figure 1). Plots of the reciprocal of the *G* values vs the reciprocal of the concentration of *c*-**S** in the range of 5.0×10^{-3} to 5.2×10^{-2} M provided $G_{\lim}$ values over the range between 30 and more than 10^4 as shown in Table 1. The *G* value and $G_{\lim}$ for the yield of *t*-**7** were 5.4 and 20, respectively, for *c*-**7** with a *p*-methoxyl group which were significantly smaller than those for other **S**. On the other hand, *c*-**S** was not formed in γ-radiolyses of Ar-saturated DCE solutions containing *t*-**S**.

Effects of additives on the *G* value were studied in γ-radiolysis of *c*-**3** in DCE (Table 2). Both triethylamine (TEA) at 2.0×10^{-2} M and O_2 at 1.3×10^{-2} M completely terminated the isomerization, while addition of 1,4-dimethoxybenzene (DMB) at 2.0×10^{-2} M accelerated the isomerization. The oxidation potentials measured for *c*-**3**, TEA, and DMB are 0.94, 0.80, and 0.90 eV which are in the same order of the ionization potentials of 8.07, 7.50, and 7.96 eV for *c*-**3**, TEA, and DMB, respectively.

Product Analyses of Oxidation of $\mathbf{S}^{\bullet+}$. Product analyses of the γ-radiolyses of **S** (1.0×10^{-2} M) in O_2-saturated DCE ($[O_2] = 1.3 \times 10^{-2}$ M) were carried out at room temperature. Table 3 summarizes the *G* values for the yields of oxidation products (**a**−**d**). The total yields of **a**−**d** based on consumption of **S** were more than 70%; therefore, **a**−**d** were formed as the main products.[8] On the other hand, **a**−**d** were not formed in the γ-radiolyses of Ar-saturated DCE solutions containing **S**. Formation of **a**, **b**, and **c** was observed in the oxidation of all $\mathbf{S}^{\bullet+}$ with O_2. **1d**, **2d**, and benzyl 4-methylphenyl ketone, and **8d** were produced as the minor products in reactions with small **G** values (0.05−0.3) in γ-radiolyses of **1**-O_2, **2**-O_2, and **8**-O_2, respectively, while **3d** was the main product with the largest *G* values (2.6−3.0) in the γ-radiolysis of **3**-O_2. It should be emphasized that **2d** and benzyl 4-methylphenyl ketone were produced as the minor products in the oxidation of **2**, while **3d** was formed without benzyl 4-methoxyphenyl ketone in the oxidation of **3**.

Product analyses of the oxidation of *t*-$\mathbf{1}^{\bullet+}$ or *t*-$\mathbf{3}^{\bullet+}$ generated by photoinduced electron transfer from *t*-**1** or **t-3** to a chloranil triplet were also carried out on mixtures of *t*-**1** or *t*-**3** at 5.0×10^{-3} M and chloranil at 5×10^{-3} M in O_2-saturated acetonitrile using a high pressure Hg lamp. The products were found to be equivalent to those obtained in γ-radiolyses in O_2-saturated DCE (Table 3).

Laser Flash Photolysis of Chloranil-S. The chloranil triplet with an absorption maximum of $\lambda_{\max} = 510$ nm[9] was generated in the flash photolysis of mixtures of *t*-**1** or *t*-**3** and chloranil in acetonitrile at 355 nm and quenched by *t*-**1** or *t*-**3** with a second-order rate constant of $k_q = 7.8 \times 10^9$ M^{-1} s^{-1} equivalent to the diffusion-controlled rate constant. Triplet quenching was accompanied by the formation of *t*-$\mathbf{1}^{\bullet+}$ or *t*-$\mathbf{3}^{\bullet+}$ with $\lambda_{\max} =$ 480 or 500 nm, respectively, and the chloranil radical anion with $\lambda_{\max} = 450$ nm.[10] The decay rate of *t*-$\mathbf{1}^{\bullet+}$ with $\lambda_{\max} = 480$ nm did not depend on the concentration of O_2, while that of *t*-$\mathbf{3}^{\bullet+}$ with $\lambda_{\max} = 500$ nm did. The rate constant of the reaction of *t*-$\mathbf{3}^{\bullet+}$ and O_2 (k_{O_2}) was calculated to be $k_{O_2} = (0.9 - 1.4) \times 10^7$ M^{-1} s^{-1} from the dependence of the decay rate on the concentration of O_2.

Discussion

Isomerization of c-$\mathbf{S}^{\bullet+}$. It is well established that $\mathbf{S}^{\bullet+}$ is formed initially by hole transfer from the radical cation

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[7] Hamill, W. *Radical Ions*, Kaiser, E. T., Kevan, L., Eds.; New York Intersciences: New York, 1968; p 321. Klinshpont, E. R. *Organic Radiation Chemistry Handbook*; Milinchuk, V. K.; Tupikov, V. I. Eds.; Ellis Hariwood: New York, 1989; p 26.

[8] Isomerization products were also observed with small *G* values at higher conversions in prolonged γ-radiolyses of several St. For example $G = 0.29$ and 0.14 were obtained for the formation of *c*-**7** and *t*-**7** at 52−56% conversion in the γ-radiolyses of *t*-**7** and *c*-**7**, respectively. It is suggested that the isomerization occurs via complicated processes including decomposition of the main products formed initially.

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Table 1. Products from γ-Radiolyses of *c*-S (S = 1−8),[a] Rate Constant of Unimolecular Isomerization of *c*-$S^{\bullet+}$ (k_i),[b] and Oxidation Potentials of S[c]

	γ-radiolyses					oxidation potentials		
S	conv of *c*-**S**, %	yield of *t*-**S**, %	*G*-value of *t*-**S**	G_{lim}	k_i/s^{-1}	$E_{1/2}^{ox}$ of *c*-**S**, V	$E_{1/2}^{ox}$ of *t*-**S**, V	$\Delta E_{1/2}^{ox}(c-t)$, V
1	6.0	94	18.9	30	$<10^6$	1.25	1.14	0.11
2	5.4	100	18.2	200	$<10^6$	1.16	1.05	0.11
3	32.5	76	81.5	$>10^3$	4.5×10^6	0.94	0.82	0.12
4	26.0	100	105.6	$>10^4$	1.3×10^7	0.80	0.64	0.16
5	22.7	97	94.7	$>4 \times 10^3$	1.4×10^7	0.87	0.72	0.15
6	2.9	100	10.2	140	$<10^6$	1.23	1.03	0.20
7	2.0	85	5.4	20	$<10^6$	0.90	0.77	0.13
8	39.1	100	120.6	$>10^4$	5.5×10^6	0.70	0.55	0.15

[a] Dose, 2.6×10^2 Gy; concentration of substrate, 1.0×10^{-2} M in Ar-saturated DCE; room temperature; conversion of *c*-**S**, the conversion of *c*-**S**; yield(*t*-**S**), the yield of *t*-**S** based on conversion of *c*-**S**; *G* value of *t*-**S**, the yield of *t*-**S** with definition of the number of molecules per 100 eV energy; G_{lim}, the *G* value of *t*-**S** when the concentration of *c*-**S** is extrapolated to infinity in the plots of inverse *G* values of *t*-**S** vs the inverse concentration of *c*-**S**. [b] k_i, calculated from the formation of *t*-$S^{\bullet+}$ during pulse radiolyses of *c*-**S** at 5.0×10^{-3} M in Ar-saturated DCE.[6] [c] Halfwave oxidation potentials ($E_{1/2}^{ox}$(*c*-**S**) and $E_{1/2}^{ox}$(*t*-**S**)) of *c*-**S** and *t*-**S** at 1.0×10^{-2} M, reference electrode of $Ag/AgNO_3$, supporting electrolyte of 10^{-1} M tetraethylammonium tetrafluoroborate in acetonitrile; $\Delta E_{1/2}^{ox}(c-t) = E_{1/2}^{ox}(c\text{-}\mathbf{S}) - E_{1/2}^{ox}(t\text{-}\mathbf{S})$.

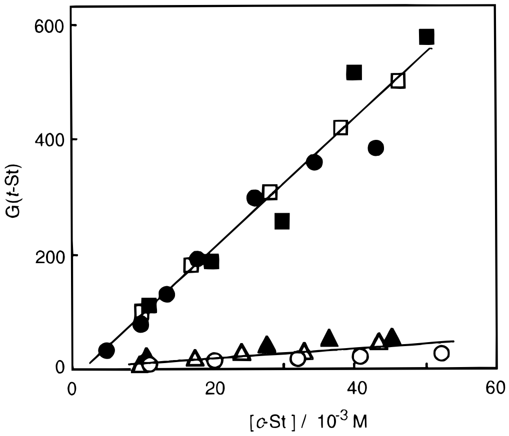

Figure 1. Plots of the *G* values of the yield of *t*-**1**−**6** vs concentration of *c*-**1**−**6** in γ-radiolyses of *c*-**1** (○), *c*-**2** (▲), *c*-**3** (●), *c*-**4** (□), *c*-**5** (■), *c*-**6** (△), respectively (1.0×10^{-2} M), in an Ar-saturated DCE at room temperature.

Table 2. Effects of Additives on Isomerization of *c*-3 to *t*-3 in γ-Radiolysis of *c*-3[a]

additives	concentration, M	$E_{1/2}^{ox}$, V	*G* value
none	–	0.94[b]	67
oxygen	1.3×10^{-2}	–	0
triethylamine	2×10^{-2}	0.80	0
1,4-dimethoxybenzene	2×10^{-2}	0.90	154

[a] Dose, 2.4×10^2 Gy; Ar-saturated DCE solution containing *c*-**3** at a concentration of 1×10^{-2} M and the additive at the concentration mentioned at room temperature; $E_{1/2}^{ox}$, halfwave oxidation potential of the additive; *G* value of *t*-**3** formed. [b] Value of *c*-**3**.

of DCE ($DCE^{\bullet+}$) as shown in the following initiation processes where e_s^- denotes a solvated electron and is stabilized by dissociative attachment to DCE during γ-radiolyses of **S** in DCE (Scheme 2).[7,11−13] Formation of *c*-$S^{\bullet+}$ must be responsible for the isomerization of *c*-**S** to *t*-**S** in the γ-radiolyses of *c*-**S** in Ar-saturated DCE. The yields of *t*-**S** indicate that *c*-**S** isomerizes stoichiometrically to *t*-**S** (Table 1). The *G* values for *c*-**3**−**5** and **8** with a *p*-methoxyl group are much larger than those for *c*-**1**, **2**, and **6** without a *p*-methoxyl group and for *c*-**7** with a *p*-methoxyl group. The large difference is consistent with the rate constant of unimolecular *c*−*t* isomerization (k_i listed in Table 1) and suggests a difference in the reaction mechanism. The difference may be explained by a smaller barrier to isomerization for *c*-$\mathbf{3}^{\bullet+}$−$\mathbf{5}^{\bullet+}$ and $\mathbf{8}^{\bullet+}$ than for *c*-$\mathbf{1}^{\bullet+}$, $\mathbf{2}^{\bullet+}$, and $\mathbf{6}^{\bullet+}$ due to the single bond character of the central C=C double bond for *c*-$\mathbf{3}^{\bullet+}$−$\mathbf{5}^{\bullet+}$ and $\mathbf{8}^{\bullet+}$ but not for *c*-$\mathbf{1}^{\bullet+}$, $\mathbf{2}^{\bullet+}$, and $\mathbf{6}^{\bullet+}$ because of the contribution of a quinoid-type structure, B, with separation and localization of the positive charge on the oxygen of the *p*-methoxyl group and an unpaired electron on the β-olefinic carbon (Scheme 3). The contribution of B is decreased by the electron-donating methyl group on the olefinic carbon; therefore, it is suggested that the single bond character of the C=C double bond is lower in *c*-$\mathbf{7}^{\bullet+}$ than in *c*-$\mathbf{3}^{\bullet+}$ and that the barrier to the twisting of the C=C double bond is higher in *c*-$\mathbf{7}^{\bullet+}$ than in *c*-$\mathbf{3}^{\bullet+}$.

The *G* value for the isomerization increased with increasing concentration of *c*-**S** (**S** = **1**−**8**) in the range of 10^{-2}−10^{-1} M (Figure 1). G_{lim} was calculated from the extrapolation of linear plots of the reciprocal of the *G* values vs the reciprocal of the concentration of *c*-**S** (Table 1). Because the *G* and G_{lim} values are expected to be less than 2.5 for the yield of the DCE radical cation initially produced by γ-radiolysis at room temperature, the large G_{lim} values indicate that the isomerization of *c*-**S** to *t*-**S** proceeds via a chain reaction mechanism.

Chain Mechanism Involving Unimolecular Isomerization of *c*-$S^{\bullet+}$ (S = 3−5 and 8). The unimolecular isomerization of *c*-$\mathbf{3}^{\bullet+}$−$\mathbf{5}^{\bullet+}$ and *c*-$\mathbf{8}^{\bullet+}$ to *t*-$\mathbf{3}^{\bullet+}$−$\mathbf{5}^{\bullet+}$ and *t*-$\mathbf{8}^{\bullet+}$, respectively, occurs predominantly with a rate constant of $k_i = 4.5 \times 10^6$ to 1.4×10^7 s^{-1}. Since dimerization of *c*-$\mathbf{3}^{\bullet+}$ with *c*-**3** preferably occurs at the rate constant of $k_d = 2.0 \times 10^8$ M^{-1} s^{-1} particularly at a high concentration of 5.0×10^{-2} M, the bimolecular isomerization of *c*-$\mathbf{3}^{\bullet+}$ to *t*-$\mathbf{3}^{\bullet+}$ might be considered. However, in contrast to the dimer of *c*-$\mathbf{1}^{\bullet+}$ (*c*-$\mathbf{1}_2^{\bullet+}$), *c*-$\mathbf{3}_2^{\bullet+}$ decomposes slowly into *t*-$\mathbf{3}^{\bullet+}$ and *t*-**3** because there is no effect of the concentration of *c*-**3** on the formation of the absorption of *t*-$\mathbf{3}^{\bullet+}$. Therefore, the bimolecular isomerization of *c*-$\mathbf{3}^{\bullet+}$ to *t*-$\mathbf{3}^{\bullet+}$ through *c*-$\mathbf{3}_2^{\bullet+}$ is not important. The significant increase in the *G* values of the isomerization of *c*-$\mathbf{3}^{\bullet+}$−$\mathbf{5}^{\bullet+}$ and *c*-$\mathbf{8}^{\bullet+}$ must correspond to the unimolecular isomerization of *c*-$\mathbf{3}^{\bullet+}$−$\mathbf{5}^{\bullet+}$ and *c*-$\mathbf{8}^{\bullet+}$ involving another chain reaction mechanism in the γ-radiolysis. The chain reaction mechanism involving the unimolecular *c*−*t* isomerization and the hole transfer from *t*-$S^{\bullet+}$ formed into *c*-**S** is considered to reproduce *c*-$S^{\bullet+}$ and *t*-**S**, where *c*-$S^{\bullet+}$ denotes *c*-$\mathbf{3}^{\bullet+}$−$\mathbf{5}^{\bullet+}$ and *c*-$\mathbf{8}^{\bullet+}$. For example, Scheme 4 is

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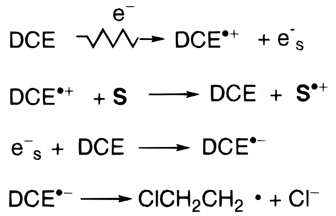
Table 3. Products from γ-Radiolyses of S (S = 1−8) in the Presence of O_2[a] or Chloranil-Photosensitized Oxidations of *t*-1 and *t*-3,[b] and Rate Constant of Oxidation of $S^{\bullet+}$ (k_{O_2})[c]

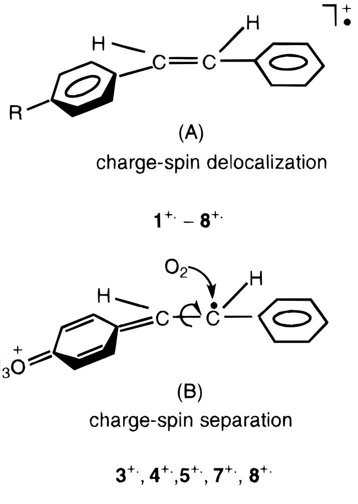
	RCH=CR′Ph				*G* value or yield				
					PhCHO	RCHO	RCH[O]CHPh[f]	$RCH_2C(=O)Ph$[g]	
S	R	R′	method[d]	conversion,[e] %	**a**	**b**	**c**	**d**	k_{O_2}, M^{-1} s^{-1}
c-**1**	Ph	H	γ	nd	1.7	–	0.9	0.1	$<10^6$
t-**1**	Ph	H	γ	nd	1.6	–	1.1	0.3	$<10^6$
t-**2**	4-$CH_3C_6H_4$	H	γ	nd	1.1	1.3	0.7	0.05[h]	$<10^6$
c-**3**	4-$CH_3OC_6H_4$	H	γ	nd	1.0	1.6	1.2	3.0	nd
t-**3**	4-$CH_3OC_6H_4$	H	γ	nd	0.9	1.4	1.4	2.6	4.5×10^7
t-**4**	2,4-$(CH_3O)_2C_6H_3$	H	γ	nd	1.3	1.5	nd	nd	4.0×10^7
t-**5**	3,4-$(CH_3O)_2C_6H_3$	H	γ	nd	1.3	2.3	nd	nd	1.2×10^7
t-**6**	3,5-$(CH_3O)_2C_6H_3$	H	γ	nd	1.0	0.9	nd	nd	$<10^6$
t-**7**	4-$CH_3OC_6H_4$	CH_3	γ	52	3.8[i]	1.7[j]	nd	0	2.8×10^7
c-**7**	4-$CH_3OC_6H_4$	CH_3	γ	56	3.5[i]	1.7[j]	nd	0	2.5×10^7
t-**8**	$(4\text{-}CH_3OC_6H_4)_2$[k]	–	γ	nd	–	1.0[j]	0.8[l]	0.2[m]	$<10^6$
t-**1**	Ph	H	*hν*	64	50	–	19	0	$<10^6$
t-**3**	4-$CH_3OC_6H_4$	H	*hν*	68	17	29	12	15	$(0.9-1.4) \times 10^7$

[a] Dose, 4.9×10^4 Gy; concentration of substrate, 1.0×10^{-2} M in O_2-saturated DCE; *G* value, the yield of oxidation products. Isomerization products were also observed with small *G* values at higher conversions in prolonged γ-radiolyses.[8] nd denotes that the values were not measured. [b] Photoirradiation of O_2-saturated acetonitrile solution containing *t*-**S** at 5.0×10^{-3} M and chloranil at 5.0×10^{-3} M using a high pressure Hg lamp at 405 nm. Product yields in % based on the consumption of *t*-**1** and *t*-**3**. [c] k_{O_2}, obtained from the dependence of the decay of $\mathbf{S}^{\bullet+}$ on the concentration of O_2 during pulse radiolyses of **S** (5.0×10^{-3} M) in the presence of O_2 in DCE,[6] or flash photolyses of **S**-chloranil (5.0×10^{-3} M each) at 355 nm in the presence of O_2 in acetonitrile. [d] Method for oxidation: γ, γ-radiolysis in the presence of O_2; *hν*, chloranil-photosensitized oxidation. [e] Conversion of *t*-**S**; yield, the yield of oxidation produced based on consumption of *t*-**S**. [f] 1-Aryl-2-phenyl-1,2-epoxyethane (aryl = R). [g] Arylmethyl phenyl ketone (aryl = R). [h] Total *G* value of **2d** and benzyl 4-methylphenyl ketone. [i] Acetophenone. [j] 4-Methoxybenzaldehyde (= **3b**). [k] **8** = $(4\text{-}CH_3OC_6H_4)CH{=}CH(4\text{-}CH_3OC_6H_4)$. [l] 4,4′-Dimethoxystilbene oxide. [m] Desoxyanisoin.

Scheme 2

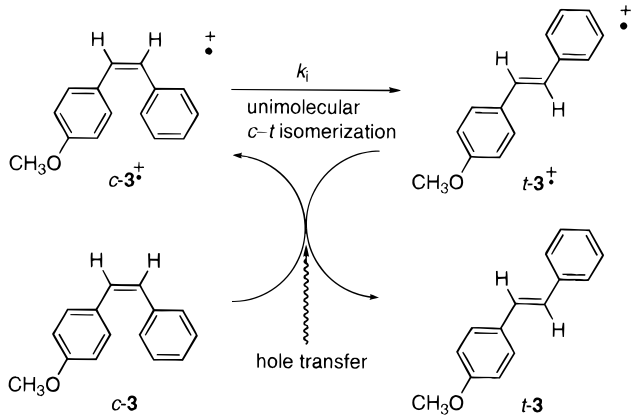


Scheme 3



proposed for the isomerization of *c*-**3** to *t*-**3**. If the hole transfer would proceed at a diffusion controlled rate (k_{diff} = 7.8×10^9 M^{-1} s^{-1}), the apparent rate constants of the hole transfer are calculated to be 3.9×10^7 to 3.9×10^8 s^{-1} at concentrations of 5.0×10^{-3} to 5.0×10^{-2} M. These rates show that the unimolecular isomerization process of *c*-$\mathbf{3}^{\bullet+}$−$\mathbf{5}^{\bullet+}$ and *c*-$\mathbf{8}^{\bullet+}$ with k_i = 4.6×10^6 to 1.4×10^7 s^{-1} is the rate-determining process. Because the hole transfer process is slightly endergonic with 0.11−0.2 V (Table 1), it probably proceeds slower than the diffusion-controlled rate. If the rate constant would be one order smaller than k_{diff} = 7.8×10^9 M^{-1} s^{-1}, the apparent rate constants of the hole transfer would be calculated to be

Scheme 4



3.9×10^6 to 3.9×10^7 s^{-1} at concentration of 5.0×10^{-3} to 5.0×10^{-2} M and could compete with the unimolecular isomerization. It is concluded that the hole transfer mechanism is reasonably suggested for the isomerization with the large G_{lim} values.

It is reasonably explained that TEA terminates the isomerization via hole transfer quenching of *c*-$\mathbf{3}^{\bullet+}$ because of the lower oxidation potential (0.80 V) than that of *c*-**3** (0.94 V) (Table 2). The isomerization of *c*-$\mathbf{3}^{\bullet+}$ was also terminated by O_2 because of the reaction of *c*-$\mathbf{3}^{\bullet+}$ with O_2. $DMB^{\bullet+}$ catalyzed the isomerization of *c*-**3** to *t*-**3** (Table 2); therefore, the catalytic *c*−*t* isomerization is similarly proposed for catalytic reactions such as the *c*−*t* isomerization of olefins, the cycloreversion of cyclobutane compounds, and the anti-Markovnikov addition of methanol to olefins by aromatic hydrocarbon radical cations.[14]

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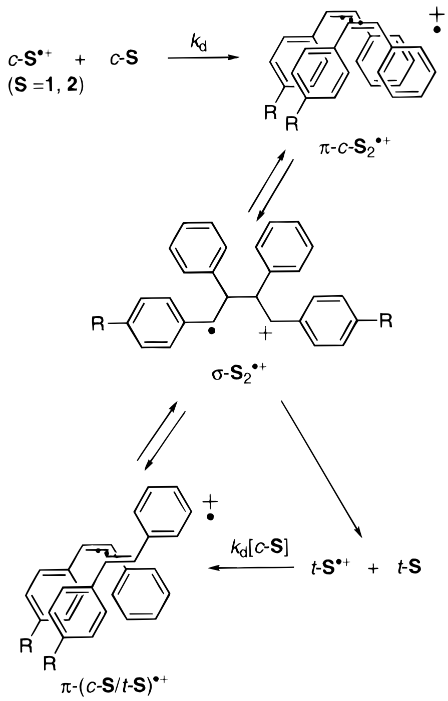
Scheme 5



Formation of a π-complex between DMB$^{•+}$ and *c*-**3** as the intermediate may be involved. When *c*-**3** encounters DMB$^{•+}$ to form a π-complex (*c*-**3**/DMB)$^{•+}$, a positive charge is partly developed on *c*-**3** and the C—C single bond character appears on the C═C double bond because of the *p*-methoxyl group. The unimolecular isomerization via the twisting around the C═C double bond then proceeds to yield *t*-**3**.

Lewis et al. reported that the quantum yield of *t*-isomer formation for dicyanoanthracene-sensitized *c*—*t* isomerization of the *c*-4-cyanostilbene radical cation ($\phi = 13.0$) is much larger than those of **1**, **2**, and **3** ($\phi = 0.32$, 0.14, and 0.12, respectively).[2b] Tokumaru and co-workers reported that the rotational barriers assumed to be the energy differences between the C_1 90°-twisted structure and $c^{•+}$ were calculated to be 7—11 kcal mol^{-1} by the open-shell RHF method as a function of the twist angle of the central C═C double bond.[15] Because the barriers of **2**—**4** are lower than that of **1** by 1—4 kcal mol^{-1}, they suggested that the isomerization of the *c*-4-cyanostilbene radical cation may not proceed by the rotation around the C—C bond. In a manner similar to the isomerization via **3**$^{•+}$—**5**$^{•+}$ described above, the chain reaction mechanism involving hole transfer (Scheme 4) or catalytic isomerization involving a π-complex would be suggested in the isomerization of the *c*-4 cyanostilbene radical cation.

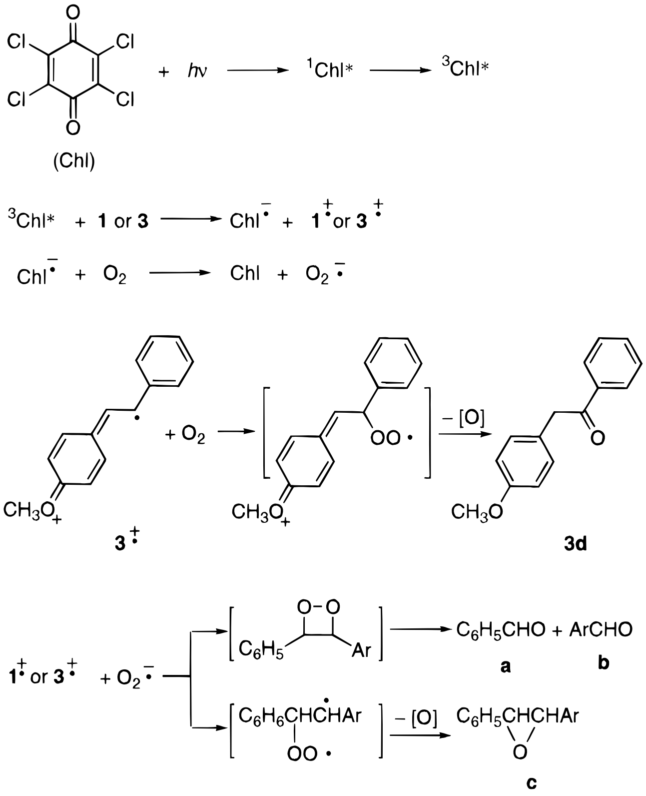
Chain Mechanism Involving Bimolecular Isomerization of *c*-S$^{•+}$ (S = 1, 2, 6, and 7). The unimolecular isomerization was not observed for *c*-**S**$^{•+}$ (**S** = **1**, **2**, **6**, and **7**) ($k_i < 10^6$ s^{-1}, Table 1), while the bimolecular isomerizations of *c*-**1**$^{•+}$ and *c*-**2**$^{•+}$ to *t*-**1**$^{•+}$ and *t*-**2**$^{•+}$ were observed in the time scale of 100—300 ns with the concentration of (5—10) × 10^{-3} M during pulse radiolyses of *c*-**1** and *c*-**2**, respectively, in DCE at room temperature.[3c,d] The bimolecular isomerization of *c*-**1**$^{•+}$ to *t*-**1**$^{•+}$ is proposed to occur through π- and σ-$\mathbf{1}_2^{•+}$ formed by dimerization of *c*-**1**$^{•+}$ with *c*-**1** at $k_d = 3.9 \times 10^8$ M^{-1} s^{-1}) (Scheme 5).[3c,d] Thermally unstable σ-$\mathbf{1}_2^{•+}$ decomposes rapidly into the thermodynamically more stable *t*-**1**$^{•+}$ and *t*-**1**.[3c,d] Since dimerization of *c*-**2**$^{•+}$ with *c*-**2** occurs at $k_d = 3.4 \times 10^8$ M^{-1} s^{-1}, the bimolecular isomerization of *c*-**2**$^{•+}$ to *t*-**2**$^{•+}$ is proposed by analogy to σ-$\mathbf{2}_2^{•+}$. A chain mechanism is possibly considered to involve the bimolecular isomerization of *c*-**1**$^{•+}$ and *c*-**2**$^{•+}$ into *t*-**1**$^{•+}$ and *t*-**1** and *t*-**2**$^{•+}$ and *t*-**2**, respectively, via π- and σ-$\mathbf{1}_2^{•+}$ and $\mathbf{2}_2^{•+}$, and the reproduction of π- and σ-$\mathbf{1}_2^{•+}$ and $\mathbf{2}_2^{•+}$ by reactions of *t*-**1**$^{•+}$ and *c*-**1** and *t*-**2**$^{•+}$ and *c*-**2**, respectively (Scheme 5).

Neither unimolecular nor bimolecular isomerization of *c*-**6**$^{•+}$ and *c*-**7**$^{•+}$ to *t*-**6**$^{•+}$ and *t*-**7**$^{•+}$ was observed in the time scale of microseconds (Table 1). However, the isomerization of *c*-**6** and *c*-**7** to *t*-**6** and *t*-**7**, respectively, were observed with the large G and G_{lim} values. This indicates that the isomerization proceeds via a chain reaction mechanism in the time scale of minutes. The chain reaction mechanism involving slow unimolecular isomerization at $k_i < 10^6$ s^{-1} and the exergonic hole transfer could be operative (Scheme 4), while another mechanism involving slow dimerization to form π- and σ-$\mathbf{S}_2^{•+}$ at $k_d < 10^6$ M^{-1} s^{-1} could be alternatively proposed (Scheme 5).

Oxidation of S$^{•+}$ with O$_2$. The reactivity of **S**$^{•+}$ toward O_2 is enhanced by charge—spin separation induced by the *p*-methoxyl group as shown from the bimolecular rate constant of **S**$^{•+}$ with O_2 (k_{O_2} listed in Table 3).[6] However, **a**—**c** were produced in similar range of G values (0.7—3.8) from oxidation of all **S**$^{•+}$ with O_2 in the γ-radiolyses of **S** in DCE (Table 3). Products **a**—**c** would be produced not directly from **S**$^{•+}$ but from complicated reactions of peroxy radicals from DCE with **S**. Because radicals such as 2-chloroethyl radical are formed from dissociative electron attachment to DCE in the initiation processes of the γ-radiolysis, the radicals would react with O_2 to yield peroxy radicals which would react toward **S** to yield oxidation products such as **a**—**c**. Products **1d**, **2d** and benzyl 4-methylphenyl ketone, and **8d** were produced with a small number of the G value in the γ-radiolyses of **1**, **2**, and **8**. The reactivities of **1**$^{•+}$, **2**$^{•+}$, and **8**$^{•+}$ toward O_2 are low as shown in $k_{O_2} < 10^6$ M^{-1} s^{-1} (Table 3). Therefore, **1d**, **2d** and benzyl 4-methylphenyl ketone, and **8d** may be formed from the secondary reaction of **1c**, **2c**, and **8c**, respectively, during a prolonged γ-irradiation. However, the G value of **3d** in the γ-radiolysis of **3d** is significantly large, compared with that for **1d** and **2d** and benzyl 4-methylphenyl ketone. Selective formation of **3d** without benzyl 4-methoxyphenyl ketone suggests the regioselective oxidation of **3**$^{•+}$ with O_2. The regioselective oxidation may be explained by the addition of O_2 to the β-olefinic carbon of **3**$^{•+}$, because of the contribution of B with separation and localization of the positive charge on the oxygen of the *p*-methoxyl group and an unpaired electron on the β-olefinic carbon (Scheme 3). It has been suggested that the density of an unpaired electron on the olefinic carbon in *t*-**8**$^{•+}$ is lower than that in *t*-**3**$^{•+}$, because an unpaired electron appears on both olefinic carbons in **8**$^{•+}$ with two symmetrical *p*-methoxyl groups.[6] The regioselective formation of **3d** can be also explained through a consideration of the relative stabilities of the two possible carbocations that could be formed from the addition of O_2 to **3**$^{•+}$.

Product **7d** was formed in the oxidation of **7**$^{•+}$ in spite of the contribution of B induced by charge—spin separation. It can be explained that migration of the methyl group does not occur in the benzylic peroxy radical generated by the addition of O_2 to the benzylic position of **7**$^{•+}$.

Scheme 6



(**1**, Ar= Ph; **3**, Ar= *p*-CH$_3$OC$_6$H$_4$)

It is well-known that O$_2$ hardly reacts with radical cations of aromatic olefins[4] but reacts with triplets[16,17] as well as radicals.[18] No triplet formation was observed during pulse radiolyses and γ-radiolyses of aromatic hydrocarbons as well as **S** in alkyl halide solutions. Formation of a superoxide anion ($O_2^{\bullet-}$) during the pulse radiolyses and γ-radiolyses in O$_2$-saturated DCE cannot be considered because of the smaller electron affinity of O$_2$ (11 kcal mol^{-1}) than that of DCE (40 kcal mol^{-1}). Therefore, intermediacy of $O_2^{\bullet-}$ as a reactive species can be safely ruled out of the reaction mechanism. It is shown that charge−spin separation in **3**$^{\bullet+}$ with a *p*-methoxyl group is responsible for the regioselective oxidation of **3**$^{\bullet+}$ with O$_2$ to give **3d**.

Oxidation of *t*-**1**$^{\bullet+}$ or *t*-**3**$^{\bullet+}$ generated by chloranil photosensitization was also studied in the photoirradiation of a mixture of *t*-**1** or *t*-**3**, and chloranil in O$_2$-saturated acetonitrile using a Hg lamp. The products were equivalent to those obtained in the γ-radiolysis of *t*-**1** or *t*-**3** in O$_2$-saturated DCE. The chloranil triplet (^{3}Chl*)[19] generated through a fast intersystem crossing of the singlet excited state (^{1}Chl*) by photoexcitation is quenched by *t*-**1** or *t*-**3** at a diffusion controlled rate constant of $k_{\mathrm{diff}} = 7.8 \times 10^9$ M^{-1} s^{-1} to give the chloranil radical anion (Chl$^{\bullet-}$) and *t*-**1**$^{\bullet+}$ or *t*-**3**$^{\bullet+}$ via electron transfer (Scheme 6). The rate constant of $k_{O_2} = (0.9-1.4) \times 10^7$ M^{-1} s^{-1} was obtained on the basis of the same O$_2$ concentration in O$_2$-saturated acetonitrile as in O$_2$-saturated DCE by the flash photolysis of *t*-**3**−chloranil mixtures in the presence of O$_2$ in acetonitrile. The k_{O_2} value parallels that ($k_{O_2} = 4.5 \times 10^7$ M^{-1} s^{-1}) determined during the pulse radiolysis of *t*-**3** in the presence of O$_2$ in DCE. Alternatively the difference between two k_{O_2} values is attributable to the different reactivities of *t*-**3**$^{\bullet+}$ and/or the different O$_2$ concentrations in two solvents. These results show the regioselective oxidation of **3**$^{\bullet+}$ with O$_2$ because of the charge−spin separation with *p*-methoxyl substitution.

In the chloranil-photosensitized oxidation, triplet energy transfer from ^{3}Chl* to O$_2$ occurs to give chloranil and singlet oxygen (^{1}O$_2$*). However, ^{1}O$_2$* is not reactive toward stilbene derivatives.[4a] Formation of **a**−**c** from *t*-**1** or *t*-**3** suggests that the electron transfer from Chl$^{\bullet-}$ to O$_2$ occurs slowly to produce a superoxide molecule ($O_2^{\bullet-}$) which reacts with *t*-**1**$^{\bullet+}$ and *t*-**3**$^{\bullet+}$ to give the corresponding **a**, **b**, and **c** as final products, since it has been reported that *t*-**1**$^{\bullet+}$ reacts with $O_2^{\bullet-}$ to give two **1a** products via a dioxetane intermediate (Scheme 6).[4a] However, the electron transfer from Chl$^{\bullet-}$ to O$_2$ must be slow on the ns time scale because of the endergonic character. It is suggested that products **a**−**c** are produced not directly from *t*-**1**$^{\bullet+}$ and *t*-**3**$^{\bullet+}$ but from complicated reactions of peroxy radicals generated from DCE with *t*-**1** and *t*-**3** (Scheme 6). Consequently, the formation of **3d** is attributed to regioselective oxidation of **3**$^{\bullet+}$ with O$_2$ because of the structure, B, with charge−spin separation and localization of an unpaired electron on the β-olefinic carbon (Scheme 3).

Conclusions

Isomerization from *c*-**S** (**S** = **1**−**8**) to *t*-**S** was found to occur stoichiometrically with large *G* values (5−121) and G_{lim} (20−>10000) in γ-ray radiolyses of *c*-**S** in Ar-saturated DCE at room temperature. The larger *G* values for the yield of *t*-**3**−**5** and *t*-**8** in γ-ray radiolyses of *c*-**3**−**5** and *c*-**8**, respectively, with a *p*-methoxyl group than those in those of *c*-**1**, **2**, and **6** without a *p*-methoxyl group suggest a smaller barrier to *c*−*t* isomerization for *c*-**3**$^{\bullet+}$−**5**$^{\bullet+}$ and *c*-**8**$^{\bullet+}$ than for *c*-**1**$^{\bullet+}$, **2**$^{\bullet+}$, and **6**$^{\bullet+}$ due to the greater single bond character of the former central C=C double bond for *c*-**3**$^{\bullet+}$−**5**$^{\bullet+}$ and **8**$^{\bullet+}$ relative to *c*-**1**$^{\bullet+}$, **2**$^{\bullet+}$, and **6**$^{\bullet+}$ because of the contribution of a quinoid-type structure, B, with separation and localization of the positive charge on the oxygen of the *p*-methoxyl group and an unpaired electron on the β-olefinic carbon. The isomerization of *c*-**3**−**5** and *c*-**8** proceeds via a chain reaction mechanism involving *c*−*t* unimolecular isomerization and endergonic hole transfer from *t*-**S**$^{\bullet+}$ to *c*-**S**. On the other hand, the isomerization of *c*-**1** and **2** proceeds via a chain reaction mechanism involving dimerization and decomposition into *t*-**S**$^{\bullet+}$ and *t*-**S**. Formation of **a**−**c** in a range of *G* values (0.7−3.8) in the γ-radiolyses of **S** in O$_2$-saturated DCE suggests that **a**−**c** would be produced from complicated reactions of peroxy radicals from DCE with **S**. On the other hand, the regioselective formation of **3d** with large *G* values (2.6−3.0) in oxidation of **3**$^{\bullet+}$ with O$_2$ is explained by spin localization on the β-olefinic carbon because of the contribution of B in **3**$^{\bullet+}$. The results of products analyses are essentially identical with predictions based on k_{i} and k_{O_2} for **S**$^{\bullet+}$ measured with pulses radiolyses. It should be emphasized that the reactivities of *c*−*t* unimolecular

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isomerization and reaction of $\mathbf{S}^{\bullet +}$ with O_2 can be understood in terms of charge−spin separation induced by *p*-methoxyl substitution.

Experimental Section

General. γ-Radiolysis of DCE solutions containing **S** was carried out in a Pyrex tube with an inner diameter of 1.0 cm at room temperature using a ^{60}Co γ source (dose, 2.6×10^2 Gy).[3d] Continuous photoirradiation experiments were done in Pyrex cells using a 500-W high-pressure mercury lamp. The **S**-containing solutions were saturated by bubbling with Ar or O_2 for 20 min. Oxygen concentrations were varied by bubbling with a mixture gas of N_2 and O_2 premixed in a high-pressure cylinder at several ratios. After γ-radiation and photoirradiation, the reaction mixtures were directly analyzed by GC and GC-MS and compared with authentic samples with respect of the retention times and MS fragment patterns as described below. The product yields (**a**, **b**, **1c**−**3c**, **1d**−**3d**, and **8d**) were determined by calibrations of the peaks with those of authentic samples. GC and GC-MS analyses were carried out using 2% silicon OV-17 on Uniport HP (80−100 mesh) as a column packing. The *G* values were calculated from the products yields and the absorbed dose measured by the ferrous sulfate dosimeter (Fricke dosimeter).[20]

Laser flash photolysis was carried out in Ar- or O_2-saturated solutions containing *t*-**1** or *t*-**3** (5.0×10^{-3} to 7.0×10^{-2} M) and chloranil (5.0×10^{-3} M) in acetonitrile at room temperature. A flash at 355 nm (5 ns duration, 20 mJ pulse^{-1}, diameter of 0.4 cm) was obtained by the third-harmonic oscillation from a Nd:YAG laser (Quantel Model Brilliant). The probe beam was obtained from a 450 W Xe-lamp (Osram, XBO-450) synchronized with the laser flash. The probe beam was sent into the sample solution and focused to a computer-controlled monochromator (CVI Laser, Digikrom-240). The output of the monochromator was monitored by a PMT (photomultiplier tube; Hamamatsu Photonics, R1417 or R2497). The signal from the PMT was recorded on a transient digitizer (Tektronix, 7912AD with plug-ins, 7A19 and 7B92A). The signals were converted to transient optical densities.

All chemical shifts (δ) are reported in parts per million and J values are in hertz. Halfwave oxidation potentials ($E_{p/2}^{ox}$) of 1.0×10^{-2} M samples were measured by cyclic voltametry using a potentiostat and a function generator having a scan rate of 100 mV s^{-1}, a reference electrode of Ag/AgNO$_3$, a working electrode of a platinum disk, a platinum wire auxiliary electrode, and a supporting electrolyte of 10^{-1} M tetraethylammonium tetrafluoroborate in acetonitrile.

Materials. *c*-**1** (97%) and *t*-**1** (>99.5%) were purchased from Aldrich and Tokyo Kasei and purified by means of distillation and recrystallization from ethanol, respectively, before use. The other stilbenes (**2**−**8**) were synthesized by the Wittig reaction of the corresponding substituted benzaldehyde and benzyltriphenylphosphonium chloride with sodium ethoxide in absolute ethanol at room temperature, according to literature procedures,[21] and purified by means of distillation, column chromatography on silica gel and/or recrystallization from ethanol, respectively, before use. *c*-(1-(4-Methylphenyl)-2-phenylethylene (*c*-**2**): 2.8 g (10% yield); bp 127 °C/1 mmHg; MS *m/z* 194 (M$^+$, 100), 179 (86), 165 (20), 115 (17), 96 (11). Anal. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: 92.72; H, 7.28. *t*-**2**: 4.6 g (18%); mp 120−121 °C (lit.[22] 119.5−120 °C); MS *m/z* 194 (M$^+$, 100), 179 (75), 165 (25), 115 (16), 96 (8). *c*-(1-(4-Methoxyphenyl)-2-phenylethylene (*c*-**3**): 4.3 g (15%); bp 105 °C/1 mmHg (lit.[23] 141−143 °C/3 mmHg); ^{1}H NMR (270 MHz) (CDCl$_3$) δ 7.27−7.12 (m, 7H), 6.74−6.70 (m, 2H), 6.49 (d, 1H, $J = 1.4$ Hz), 6.48 (d, 1H, $J = 1.4$ Hz), 3.72 (s, 3H); MS *m/z* 210 (M$^+$, 100), 195 (21), 179 (10), 165 (27), 152 (17), 105 (8), 89 (6). Anal. Calcd for $C_{15}H_{14}O$: C, 86.39; H, 6.71. Found: C, 86.36; H, 6.77. *t*-**3**: 7.1 g (25%); mp 137−138 °C (lit.[24] 136−137 °C); ^{1}H NMR δ 7.35−7.21 (m, 7H), 6.83−6.80 (m, 2H), 6.98 (d, 1H, $J = 4.1$ Hz), 6.97 (d, 1H, $J = 4.1$ Hz), 3.73 (s, 3H); MS *m/z* 210 (M$^+$, 100), 195 (28), 179 (12), 165 (33), 152 (18), 105 (9), 89 (5). *c*-(1-(2,4-Dimethoxyphenyl)-2-phenylethylene (*c*-**4**): 2.1 g (7.5%); bp 110 °C/0.5 mmHg; MS *m/z* 240 (M$^+$, 100), 197 (12), 165 (20), 153 (8). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.95; H, 6.78. *t*-**4**: 3.6 g (13%); mp 66−67 °C (lit.[25] 62−63 °C); MS *m/z* 240 (M$^+$, 100), 197 (12), 165 (16), 120 (6). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.94; H, 6.74. *c*-(1-(3,4-Dimethoxyphenyl)-2-phenylethylene (*c*-**5**): 2.6 g (8.9%); bp 107 °C/0.6 mmHg; MS *m/z* 240 (M$^+$, 100), 225 (34), 178 (9), 165 (18), 152 (11), 120 (6). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.98; H, 6.75. *t*-**5**: 4.8 g (16%); mp 108−109 °C (lit.[26] 111 °C); MS *m/z* 240 (M$^+$, 100), 225 (32), 178 (8), 165 (18), 152 (10), 120 (7). *c*-(1-(3,5-Dimethoxyphenyl)-2-phenylethylene (*c*-**6**): 3.3 g (11%); bp 153 °C/0.2 mmHg (lit.[27] 150 °C/0.2 mmHg); MS *m/z* 240 (M$^+$, 100), 225 (8), 209 (15), 194 (7), 178 (6), 165 (5), 152 (6). *t*-**6**: 2.9 g (9.4%); mp 56 °C (lit.[28] 56.5 °C); MS *m/z* 240 (M$^+$, 100), 225 (7), 209 (15), 194 (6), 178 (9), 165 (5), 152 (8). *c*-1-(4-Methoxyphenyl)-2-phenylpropene (*c*-**7**): 0.95 g (4.2%); mp 44−45 °C; MS *m/z* 224 (M$^+$, 100), 209 (178), 194 (11), 178 (8), 165, (6) 121 (7), 115 (5). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.65; H, 7.23. *t*-**7**: 2.5 g (11%); mp 83−84 °C; MS *m/z* 224 (M$^+$, 100), 209 (20), 194 (13), 178 (10), 165 (8), 121 (6), 115 (5). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.66; H, 7.26. *c*-1,2-Bis(4-methoxyphenyl)ethylene (*c*-**8**): 6.4 g (6.1%); mp 35−36 °C (lit.[29] 37 °C); ^{1}H NMR δ 7.20−7.16 (m, 4H), 6.76−6.73 (m, 4H), 6.43 (s, 2H), 3.76 (s, 6H); MS *m/z* 240 (M$^+$, 100), 225 (35), 209 (17), 195 (20), 182 (15), 178 (8), 165 (7), 152 (5), 135 (6). *t*-**8**: 23.0 g (39%); mp 215−216 °C (lit.[24] 214.5−215 °C); ^{1}H NMR δ 7.30−7.20 (m, 4H), 6.85−6.82 (m, 4H), 6.95 (s, 2H), 3.78 (s, 6H); MS *m/z* 240 (M$^+$, 100), 225 (30), 209 (18), 195 (19), 182 (13), 178 (10), 165 (9), 152 (7), 135 (5).

Benzaldehyde (**1a**−**6a**), acetophenone (**7a**), substituted benzaldehyde (**3d**−**6b**), stilbene oxide (**1c**), deoxybenzoin (**1d**), and desoxyanisoin (**8d**) were purchased from Aldrich or Tokyo Kasei, while substituted stilbene oxides (**2c**, **3c**) and substituted phenylmethyl phenyl ketones (**2d**, **3d**) were prepared from oxidation of the corresponding stilbenes (**2**, **3**) using 3-chloroperoxybenzoic acid and from Friedel−Crafts acylation of benzene using (4-methylphenyl)acetyl chlorides and (4-methoxyphenyl)acetyl chlorides, respectively. Benzyl 4-methylphenyl ketone and benzyl 4-methoxyphenyl ketone were also prepared as authentic samples in GC analyses from Friedel−Crafts acylation of anisole and toluene using phenylacetyl chloride, respectively. The prepared compounds were purified by column chromatograph on silica gel and identified by ^{1}H NMR and GC-MS. *c*-4-Methylstilbene oxide (*c*-**2c**): ^{1}H NMR δ 7.37−7.28 (m, 9H), 4.35 (d, 1H, $J = 1.0$ Hz), 4.34 (d, 1H, $J = 1.0$ Hz), 2.28 (s, 3H); MS *m/z* 210 (M$^+$, 10), 194 (22), 181 (100), 165 (30), 149 (8), 140 (23), 107 (85), 105 (60), 89 (20), 79 (14), 77 (31). *t*-**2c**: ^{1}H NMR δ 7.35−7.26 (m, 9H), 3.86 (d, 1H, $J = 2.9$ Hz), 3.84 (d, 1H, $J = 2.9$ Hz), 2.28 (s, 3H); MS *m/z* 210 (M$^+$, 12), 194 (30), 181 (100), 165 (23), 149 (12), 140 (29), 107 (77), 105 (57), 89 (15), 79 (17), 77 (35). *c*-4-Methoxystilbene oxide (*c*-**3c**): ^{1}H NMR δ 7.81−7.28 (m, 9H), 4.40 (d, 1H, $J = 1.2$ Hz), 4.39 (d, 1H, $J = 1.2$ Hz), 3.72 (s, 3H); MS *m/z* 226 (M$^+$, 8), 2.11 (26), 197 (100), 165 (20), 153 (14), 135 (36), 105 (10), 77 (15), 65 (3), 51 (6). *t*-**3c**: ^{1}H NMR δ 7.81−7.28 (m, 9H), 3.90 (d, 1H, $J = 3.2$ Hz), 3.88 (d, 1H, $J = 3.2$ Hz), 3.74 (s, 3H); MS *m/z* 226 (M$^+$, 9), 211 (29), 197 (100), 165 (18), 153 (15), 135 (42), 105 (14), 77 (16), 65 (7), 51 (9). (4-Methylphenyl)methyl phenyl ketone (**2d**): ^{1}H NMR δ 7.82−7.70 (m, 2H), 7.27−7.05 (m, 7H), 4.16 (s, 2H), 2.27 (s, 3H); MS *m/z* 210 (M$^+$, 14), 149 (15), 121 (5), 105 (M$^+$ − 4-CH$_3$C$_6$H$_4$CH$_2$,

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100), 77 (16). (4-Methoxyphenyl)methyl phenyl ketone (**3d**): ^{1}H NMR δ 7.88−7.76 (m, 2H), 7.57−6.63 (m, 7H), 4.14 (s, 2H), 3.76 (s, 3H); MS *m*/*z* 226 (M^+, 20), 121 ($M^+ - 4\text{-}CH_3OC_6H_4$, 100), 105 (93), 91 (5), 77 (34), 65 (2), 51 (9). Benzyl 4-methylphenyl ketone: ^{1}H NMR δ 7.74 (m, 2H), 7.25−7.16 (m, 5H), 7.07 (m, 2H), 4.18 (s, 2H), 2.34 (s, 3H); MS *m*/*z* 210 (M^+, 3), 119 ($M^+ - C_6H_5CH_2$, 100), 105 (16), 91 (22). Benzyl 4-methoxyphenyl ketone: ^{1}H NMR δ 7.87 (m, 2H), 7.29−7.15 (m, 5H), 6.86 (m, 2H), 4.18 (s, 2H), 3.70 (s, 3H); MS *m*/*z* 226 (M^+, 1), 135 ($M^+ - C_6H_5CH_2$, 100), 107 (10), 92 (10), 77 (15), 64 (4), 51 (8).

Other chemicals including triethylamine, 1,4-dimethoxybenzene, and chloranil were purchased from Tokyo Kasei and purified by distillation or recrystallization prior to use.

1,2-Dichloroethane (DCE) used as a solvent was distilled over calcium hydride. Acetonitrile (Tokyo Kasei) was used without further purification.

Characterizations of Oxygenated Products a−d. Oxygenated products **a**, **b**, **1c**−**3c**, **1d**−**3d**, and **8d** of **S** (**S** = *c*- and *t*-**1**−**8**) were analyzed by GC and GC-MS using authentic samples, while assignment of **4c**−**8c** and **4d**−**6d** was carried out on the basis of the MS fragment patterns observed after the γ-irradiation of **S** in O_2-saturated DCE and after photoirradiation of chloranil-**S** mixture in O_2-saturated acetonitrile (Table 3). The *m*/*z* number of peaks and the relative intensity in parentheses are described below.

1. Benzaldehyde (**1a**): 106 (M^+, 100), 105 (100), 94 (12), 77 (98), 51 (34); stilbene oxide (**1c**): 196 (M^+, 20), 178 (5), 167 (100), 152 (17), 105 (32), 91 (20), 77 (13); deoxybenzoin (**1d**): 196 (M^+, 3), 105 ($M^+ - C_6H_5CH_2$, 100), 91 (5), 77 (32), 51 (6).

2. **1a**; 4-methylbenzaldehyde (**2b**): 120 (M^+, 100), 119 (100), 108 (10), 105 (63), 91 (97); **2c**: 210 (M^+, 16), 194 (18), 181 (100), 165 (32), 149 (16), 140 (20), 107 (88), 105 (55), 89 (20), 79 (23), 77 (23); **2d**: 210 (M^+, 10), 149 (13), 121 (7), 105 ($M^+ - 4\text{-}CH_3C_6H_4CH_2$, 100), 77 (22); benzyl 4-methylphenyl ketone: 210 (M^+, 2), 119 ($M^+ - C_6H_5CH_2$, 100), 105 (11), 91 (24).

3. **1a**; 4-methoxybenzaldehyde (**3b**): 136 (M^+, 72), 135 (100), 107 (17), 92 (13), 77 (28), 64, 51, 39; **3c**: 226 (M^+, 6), 211 (25), 197 (100), 182, 165 (12), 153 (12), 135 (40), 105 (9), 77 (13); **3d**: 226 (M^+, 18), 121 ($M^+ - 4\text{-}CH_3OC_6H_4$, 100), 105 (87), 91 (5), 77 (30), 65 (2), 51 (8). The regioselective formation of **3d** was clearly indicated by the retention time and fragment pattern which are different from those of benzyl 4-methoxyphenyl ketone in GC and GC-MS analyses.

4. **1a**; 2,4-dimethoxybenzaldehyde (**4b**): 166 (M^+, 100), 165 (91), 149 (13), 135 (22), 122 (18), 106 (14), 77, 63; 2,4-dimethoxystilbene oxide (**4c**): 256 (M^+, 7), 227 (100), 165, 152, 91 (51); 2,4-dimethoxybenzyl phenyl ketone (**4d**): 256 (M^+, 18), 240 (70), 197 (8), 151 ($M^+ - 2,4\text{-}(CH_3O)_2C_6H_3$, 100), 121 (26), 105 (7), 77 (7).

5. **1a**; 3,4-dimethoxybenzaldehyde (**5b**): 166 (M^+, 100), 165 (56), 151 (14), 95 (12), 77 (8); 3,4-dimethoxystilbene oxide (**5c**): 256 (M^+, 15), 227 (100), 196 (10), 181 (8), 165 (6); 3,4-dimethoxybenzyl phenyl ketone (**5d**): 256 (M^+, 8), 240 (20), 195 (71), 167 (24), 151 ($M^+ - 3,4\text{-}(CH_3O)_2C_6H_3$, 100), 139 (28), 105 (11).

6. **1a**; 3,5-dimethoxybenzaldehyde (**6b**): 166 (M^+, 100), 165 (35), 135 (15), 109 (8); 3,5-dimethoxystilbene oxide (**6c**): 256 (M^+, 44), 227 (100), 212 (24), 196 (28), 181 (9), 152 (8), 107 (88), 105 (55), 89 (20), 79 (23), 77 (23); 3,5-dimethoxybenzyl phenyl ketone (**6d**): 256 (M^+, 19), 165 (45), 151 ($M^+ - 3,5\text{-}(CH_3O)_2C_6H_3$, 100), 137 (16), 122 (8), 105 (86), 77 (17).

7. Acetophenone (**7a**): 120 (M^+, 55), 105 (100), 77 (54), 51 (11); **7b** (= **3b**); 4-methoxy-α-methylstilbene oxide (**7c**): 240 (M^+, 16), 225 (20), 211 (100), 195 (30), 179 (13), 170 (18), 149 (36), 105 (41), 77 (23), 51 (9).

8. **8b** (= **3b**); 4,4′-dimethoxystilbene oxide (**8c**): 256 (M^+, 4), 227 (100), 212 (8), 114 (6); desoxyanisoin (**8d**): 256 (M^+, 5), 135 ($M^+ - 4\text{-}CH_3OC_6H_4$, 100), 121 (9), 107 (6), 77.

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