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Photochemically Induced Single Electron Transfer Reactions of Benzils with Allylstannane. Direct Observation of Reactive Intermediates by ESR Method

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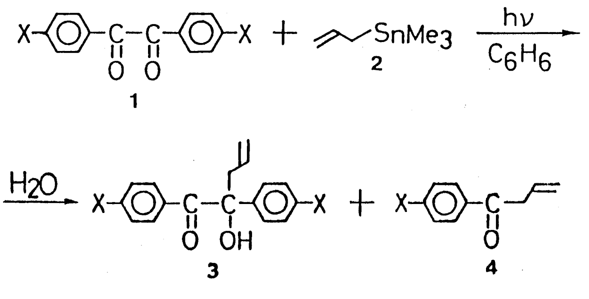
Although the photochemically induced reaction of benzil with allyltrimethylstannane in benzene afforded α-allylbenzoin as a major product, benzil did not react thermally with the same reagent. An ESR observation disclosed that the benzil anion radical ion-paired upon contact with trimethylstannyl cation (BSnMe$_3$) was generated during irradiation. Its structure was confirmed by the detection of satellite signals arising from tin isotopes. Moreover, a triplet radical pair was also observed during the photolysis of a solid solution containing benzil and allylstannane at 77 K. This reaction proceeded via a single electron transfer from allylstannane to photoexcited benzil, followed by a cleavage of the C-Sn bond of the allyltin cation radical. Ultimately, a radical pair composed of BSnMe$_3$ and the allyl radical was formed and their coupling gave α-allylbenzoin as an isolated product.

During the last decade, the chemistry of organotin compounds has received widespread investigation.[1] Among them, allylstannanes are known to be attractive reagents because of their utility in organic syntheses.[2] Recently, photochemical allylations using allylstannanes have become of great interest in connection with the field of photoinduced electron-transfer chemistry.[3–7] One of the most essential strategies probed in these systems has been fragmentation after a photoinduced single electron transfer process of cation radicals to yield radicals and cationic species. This prevents any back electron transfer to reproduce reactants in their ground states. The synthetic aspects of the photoallylations of iminium salts,[3] cyano compounds,[5] monoketones,[6] and quinones[7] using allylstannanes have been reported independently; it is proposed that the photochemical excitation of substrates causes single electron transfer from allylstannane. In these studies, allyltin cation radicals have been considered to undergo a C-Sn bond cleavage, while generating the allyl radical which recombines with anion radicals. However, there have been few attempts to clarify the mechanism by a direct observation of the reactive paramagnetic intermediates. In our recent preliminary reports on the photochemical reaction of quinones with allylstannanes,[7] we proposed a single electron transfer mechanism on the basis of both the CIDNP and the ESR diagnoses. As a further extension, we report here on the results of a photochemically induced reaction of benzils with allylstannane. Since benzil has two adjacent carbonyl groups which could give a stable anion radical and a long-lived excited triplet state,[8] it is suitable for an investigation of the reactive intermediates generated in a photochemically induced electron transfer reaction.

Results

1) Photochemically Induced Reactions between Benzils and Allylstannane. Irradiation (>400 nm) of a deaerated benzene solution (25 ml) containing benzil **1a** (1 mmol) and allyltrimethylstannane **2** (2 mmol) for 3 h under an argon atmosphere gave, after silica-gel column chromatography, α-allylbenzoin **3a** (98%)



Scheme 1.

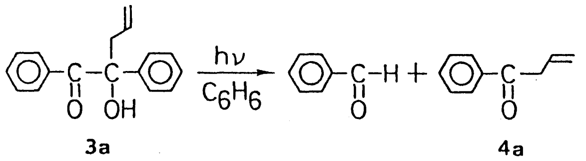
Table 1. Photochemical Reactions of Benzils **1** with Allylstannane **2**

Run	Benzil	E^{peak} (1/1$^{\cdot-}$)$^{a)}$	Conversion of 1/%	NMR yield/%$^{b)}$ 3	NMR yield/%$^{b)}$ 4	Isolated yield/%$^{b)}$ 3	Isolated yield/%$^{b)}$ 4
1	**1b**: X=Cl	−0.87 V	87	**3b**: 92,	**4b**: 8	**3b**: 75,	**4b**: 5
2	**1a**: X=H	−1.48 V	83	**3a**: 98,	**4a**: 2	**3a**: 83,	**4a**: trace
3	**1c**: X=Me	−1.55 V	66	**3c**: 99,	**4c**: trace	**3c**: 85,	**4c**: trace
4	**1d**: X=MeO	−1.59 V	65	**3d**: 99,	**4c**: trace	**3d**: 87,	**4d**: trace

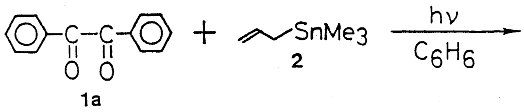
a) Obtained by cyclic voltammetry: Pt electrode, tetraethylammonium perchlorate (0.1 M) in acetonitrile solution vs Ag/0.1 M AgClO$_4$. b) Yields based on starting benzil consumed. NMR yields were estimated by ^{1}H NMR using 1,2-dichloroethane as an internal standard.

and allyl phenyl ketone **4a** (2%) as isolated products (Run 2 in Table 1 and Scheme 1). Under these conditions benzil **1a** was selectively excited; the absorption of light by allylstannane **2** was negligible. The reaction did not proceed without irradiation.9) The structures of **3a** and **4a** were identified by spectroscopic analyses. The characteristic spectral data of the major product **3a** are described below. The IR spectrum of **3a** showed absorption bands due to hydroxyl and carbonyl groups at 3470 and 1650 cm^{-1}, respectively. In its ^{1}H NMR spectrum, the diastereotopic allylic methylene protons appeared at 2.98 ppm (dd, J=7, 14 Hz) and 3.15 ppm (dd, J=7, 14 Hz). In its mass spectrum, strong fragment ion peaks appeared at m/z 147 and 105. It seems that the subsequent photochemical reaction of **3a** afforded **4a**, since the irradiation of a benzene solution of **3a** afforded **4a** under similar conditions (Scheme 2).10) The photochemical reactions of other *p*-disubstituted benzils **1b-d** with **2** proceeded similarly and gave the corresponding α-allylbenzoins as the major products. All of the results are summarized in Table 1. On the contrary, no reaction was observed for the irradiation of benzil in the presence of allylsilane, which has a lower reducing ability compared to that of allylstannane.11)

2) **ESR Investigations.** To elucidate the feature of reactive intermediates, an ESR technique was applied to the present reactions. Upon irradiating a thoroughly degassed benzene solution of benzil **1a** (3×10^{-2} M) and allyltrimethylstannane **2** (6×10^{-2} M) in an ESR cavity (1M=1 mol dm^{-3}), the spectrum due to a paramagnetic species was observed (Fig. 1). From a detailed analysis of the spectrum, the species was assigned to a benzil anion radical which was ion-paired upon contact with the trimethylstannyl cation at the two carbonyl oxygen atoms (i.e., BSnMe$_3$). Its structure was clearly confirmed by the detection of satellite signals arising from tin isotopes.12) The ESR signal due to BSnMe$_3$ was observed even after turning off the light. The lifetime of BSnMe$_3$ was about 40 s. Compared with the hyperfine coupling constants of the other ion-paired benzil anion radicals, the tightness of the interionic interaction between the benzil anion radical and the stannyl cation could be estimated approximately.13) As is well-known, the spin densities of the *o*- and *p*-carbons in the benzil anion radical become higher with any increase in the perturbation of the cation on the carbonyl oxygens. Based on the results shown in Table 2, the trimethylstannyl cation seems to interact with the benzil anion radical more strongly than does those with alkali metal cations.14) Similar paramagnetic species were detected during photochemical reactions of **1b** and **1c**



Scheme 2.



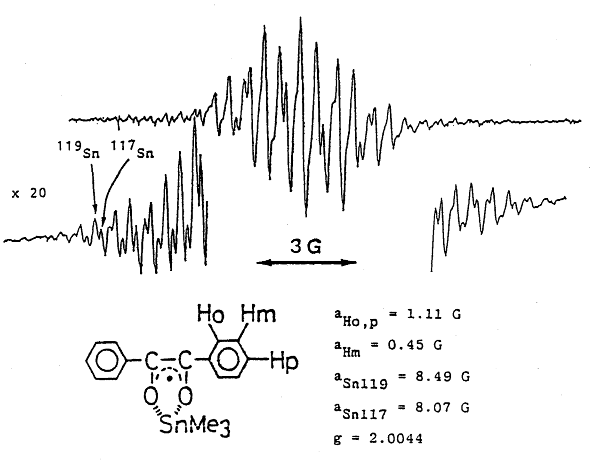
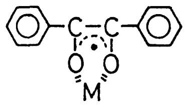


Fig. 1. ESR spectrum observed during irradiation of a benzene solution containing **1a** and **2**. The insets show resolved ^{117}Sn and ^{119}Sn splittings at high gain.

Table 2. Hyperfine Coupling Parameters of Benzil Anion Radicals

Metal	Temperature	$^{a)}H_{o,p}/G^{b)}$	$^{a)}H_m/G^{b)}$
K$^{+a)}$	R.t.	0.92	0.35
K$^{+a)}$	−20 °C	0.92	0.35
Na$^{+a)}$	R.t.	0.91	0.36
Na$^{+a)}$	−20 °C	0.94	0.36
SnMe$_3^+$	10 °C	1.11	0.45
SnBu$_3^+$	10 °C	1.10	0.46



a) See Ref. 13. b) G=10^{-4} T.

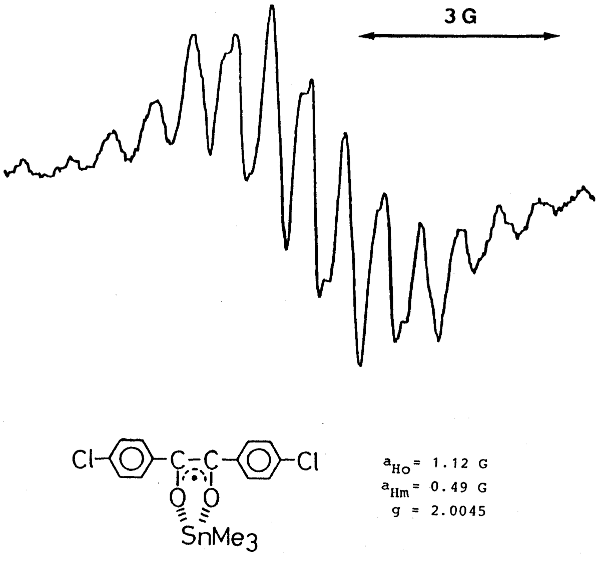


Fig. 2. ESR spectrum observed during irradiation of a benzene solution containing **1b** and **2**.

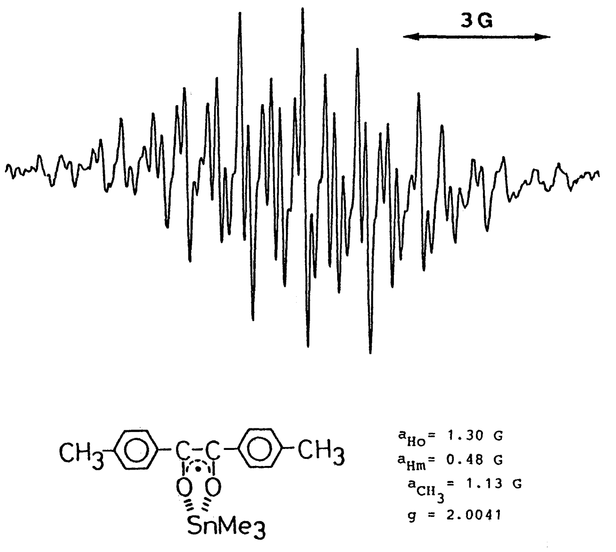


Fig. 3. ESR spectrum observed during irradiation of a benzene solution containing **1c** and **2**.

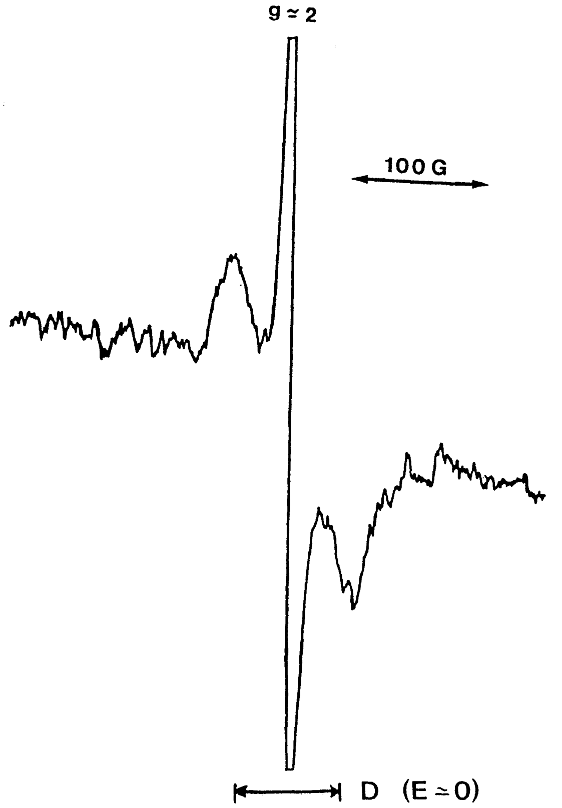


Fig. 4. ESR spectrum observed just after irradiation of a solid solution containing **1a** and **2** in toluene at 77 K.

(Fig. 2, 3).

In order to investigate the primary process in detail, the ESR method was also applied to photolysis at 77 K. Upon irradiating a toluene solution containing **1a** and **2** at 77 K, a weak, but unequivocal, axially symmetric triplet ESR signal was observed in addition to strong absorption due to the doublet state of other radicals (Fig. 4). No triplet signal was detected in the photolysis of a solid solution containing only **1a** or **2**. This shows that the presence of both benzil and allylstannane is essential to form the observed triplet species. Interestingly, the fine structure of the triplet signal altered by an elongated irradiation and the other doublet signal developed (Fig. 5). From an analysis of the zero-field splitting parameters of the triplet species, the mean distance between the two radicals formed just after photolysis was estimated to be about 7.0 Å.[15] When the sample was dissolved by warming it to room temperature, only $BSnMe_3$ was detected with or without irradiation. Furthermore, when the solution was re-cooled to 77 K (without irradiation), the triplet signal was no longer observed, though the weak doublet signal remained.

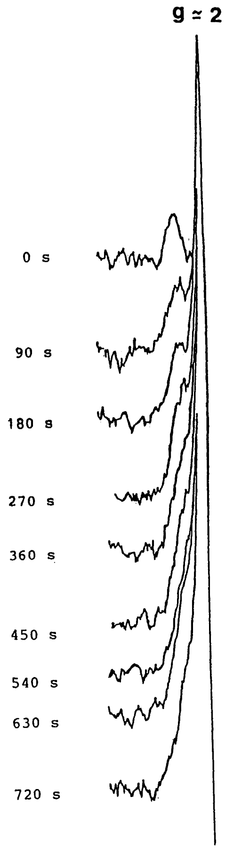


Fig. 5. ESR spectral change observed during photolysis of **1a** with **2** in a solid toluene solution at 77 K.

Discussion

ESR techniques are one of the useful tools for investigating the mechanistic aspects of electron transfer reactions.[16] The ESR observation for the photochemical reaction of benzils **1** with allylstannane **2** in the liquid state disclosed that the paramagnetic species, $BSnMe_3$, was generated as a key intermediate. This fact suggests that two processes, a photochemically induced single electron transfer from **2** to excited **1** and the cleavage of **2**$^{+\cdot}$ to yield $BSnMe_3$, are involved in the reaction. It is well-known that the tetraalkyltin cation radicals are unstable and undergo an instantaneous cleavage of the C-Sn bond.[17] In the present system in which allylstannane was employed, the fragmentation of $\mathbf{2}^{+\cdot}$ produced the trimethylstannyl cation and the allyl radical; the former paired ionically with the benzil anion radical. Thus, the radical pair composed of the allyl radical and $BSnMe_3$ was formed. Two experimental facts indirectly support this interpretation; one is the relative reactivity of benzils and the other is the regioselectivity in allylations. First, the relative reactivity of benzils is dependent upon their reduction potentials. As is widely known, the free-energy exchange in the photoinduced electron-transfer process can be estimated using the Rehm-Weller equation.[18]

$$\Delta G = 23.06(E(\mathbf{2}^{+\cdot}/\mathbf{2}) - E(\mathbf{1}/\mathbf{1}^{-\cdot}) - e^2/\varepsilon d) - E^{\mathrm{T}}\ (\mathrm{kcal\ mol^{-1}})$$

Here, $E(\mathbf{2}^{+\cdot}/\mathbf{2})$ is the oxidation potential of **2**, $E(\mathbf{1}/\mathbf{1}^{-\cdot})$ is the reduction potential of **1**, $e^2/\varepsilon d$ is the Coulombic term (d is the distance between two ion radicals and ε is the solvent dielectric constant), and E^{T} is the triplet excitation energy of **1**.[19] Due to the limitation in the derivatives of the benzil series, we can assume that the contribution of both the Coulombic term and the triplet energy are equal. If the reaction proceeds via a photochemically induced electron-transfer process, there must be a relationship between $E(\mathbf{1}/\mathbf{1}^{-\cdot})$ and the reactivity. In fact, the higher is the reduction potential of benzil, the higher is its conversion yield (Table 1). This fact shows that the reaction may be caused by a photochemically induced single electron transfer from **2** to excited **1**.[20] Second, the regioselectivity in allylation is correlated to both the spin density and the steric hindrance of the intermediary radical. As previously reported,[7] in the photochemical reactions of *p*-quinones with allylstannane, allylation occurs at several positions with low selectivity and the *p*-semiquinone radical combined with the trimethylstannyl moiety (p-$QSnMe_3$) and the allyl radical are simultaneously observed by ESR during irradiation (Fig. 6). On the other hand, in the case of benzil, allylation occurs only at the carbonyl carbon. It is doubtless that the allyl adducts are afforded by coupling between the allyl radical and $XSnMe_3$ (X=B or *p*-Q) at the positions with high spin density. Based upon both the hyperfine coupling parameters and simple HMO calculations, the spin densities of $XSnMe_3$ were estimated. Scheme 3 shows $XSnMe_3$ represented by a linear combination of the limiting structural formulas; the spin density, calculated by simple HMO, is summarized at the bottom.[21] In the p-$QSnMe_3$, where one carbonyl oxygen is combined with trimethylstannyl moiety, moderate spin densities are distributed to the naked carbonyl oxygen, olefinic ring carbon, and carbonyl carbon, respectively. In fact, the allyl radical attacks these positions with low selectivity. While in $BSnMe_3$ where the trimethylstannyl moiety is attached to two neighboring carbonyl oxygens, the spin densities are localized only to the two carbonyl carbons. In fact, allylation occurred at the carbonyl carbon with high selectivity. Furthermore, a steric hindrance around the oxygen atoms would affect whether *O*-allylation occurs or not. In the former case, one oxygen atom of p-$QSnMe_3$ is free from the trimethylstannyl moiety, which makes possible the *O*-allylation. However, in the latter case, two neighboring oxygen atoms of $BSnMe_3$ are covered with the $SnMe_3$ moiety, making *O*-allylation disadvantageous.

The ESR observation in the solid state established the primary process of the reaction. Based upon the results described above, the observed triplet species

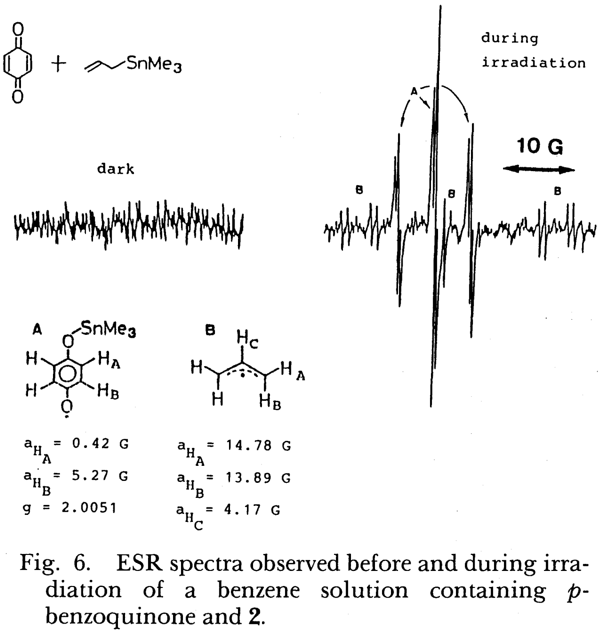
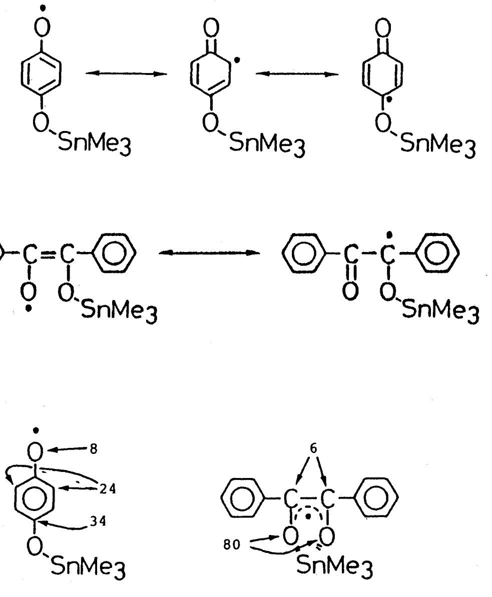
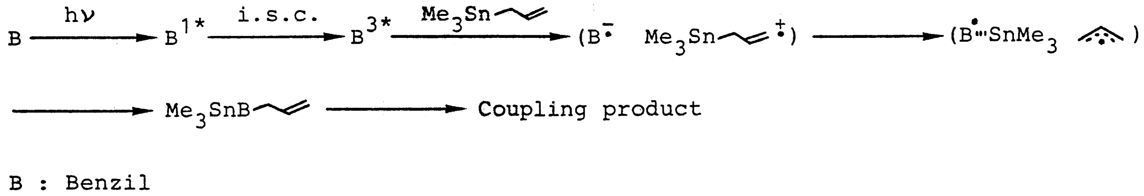


Fig. 6. ESR spectra observed before and during irradiation of a benzene solution containing *p*-benzoquinone and **2**.



Scheme 3.



Scheme 4.

might be the radical pair initially formed by a single electron transfer from **2** to photoexcited **1**. Considering the fact that the distance between two free spins was evaluated to be about 7 Å, it is reasonable to assume that the free spin of cation radical is mostly localized in the allyl moiety.[16] Confirmation of this interpretation has come from a nice experiment by Emori, Weri, and Wan.[22] They observed analogous radical pairs by using an ESR method in the photolysis of quinones with organotin compounds. Interestingly, the fine structure of the triplet species altered upon irradiation, and was at last covered with an increased signal of the doublet species. This observation may be interpreted as representing the gradual cleaving process of the radical pair into free radicals. The lifetime of $BSnMe_3$ is relatively long, whereas that of the allyl radical is too short to be detected at room temperature. Thus, only $BSnMe_3$ can be observed in a warmed liquid sample.

On the basis of these findings, we propose the photoinduced electron transfer mechanism shown in Scheme 4. This is analogous to the well-established mechanism reported in previous studies.[3–7] At first, a single electron transfer from allylstannane **2** to the photoexcited triplet benzil **1** produced a radical ion pair ($\mathbf{1}^{\bar{\cdot}}$ $\mathbf{2}^{\dot{+}}$).[23] Because of the unstable $\mathbf{2}^{\dot{+}}$ and the relatively stable allyl radical, instantaneous bond cleavage between allylic carbon and tin would result to form a radical pair composed of $BSnMe_3$ and the allyl radical. The isolated product, α-allylbenzoin, is produced by an attack of the allyl radical toward $BSnMe_3$. In our ESR experiments, $BSnMe_3$ escaped from the solvent cage would be detected in the liquid state, and the radical pair generated in the initial stage would be observed in the solid state.

Experimental

Materials. Benzene and toluene were distilled from sodium wire under a nitrogen atmosphere. Benzils **1a**—**d** were synthesized according to the reported methods and recrystallized from benzene.[24] Allylstannane **2** was synthesized according to the reported method and purified by distillation.[25]

General Procedures. The photochemical reaction of benzil with allylstannane in a benzene solution was carried out as follows. A deaerated benzene solution (25 ml in a Pyrex tube) containing **1** (1 mmol) and **2** (2 mmol) was irradiated through a glass filter (Toshiba VY-42) for 3 h at room temperature with a high-pressure mercury lamp (500 W). After irradiation, the reaction mixture was quenched with water, concentrated in vacuo and separated by column chromatography on silica gel (Merck Keisel gel 60H), eluting with hexane-ether. For a determination of the NMR yield, 1,2-dichloroethane was used as an internal standard.

ESR Measurements. ESR measurements were carried out using the reaction vessel described in our previous report.[7c] The sample was sealed off under high vacuum. The ESR spectra were observed by a JEOL JES-FE1XG X-band ESR spectrometer system. A Mn^{2+} marker and 2,2-diphenyl-1-picrylhydrazyl were used for a determination of the zero-field splitting constant, the hyperfine splitting constants, and *g*-values. A typical ESR measurement in the liquid state was as follows. A benzene solution of benzil **1** was mixed with allylstannane **2** just before the measurement. Irradiation was carried out with the light of a 500-W high-pressure mercury lamp through a glass filter (Toshiba VY-42). ESR observations were made before, during, and after irradiation. The solid-state measurement was carried out as follows. After mixing of **1** with **2** in a toluene solution, an ESR quartz cell containing the toluene solution was placed in the tip of a quartz Dewar filled with liquid nitrogen, and the Dewar was inserted into the cavity. The irradiation and observation were undertaken in a similar manner as described above.

Physical Properties of the Products. 1,2-Diphenyl-2-hydroxy-4-penten-1-one (3a): Pale yellow needles from hexane-ether; mp 90—92 °C. MS; *m/z* 105, 147, 235. Found: C, 80.85; H, 6.36%. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39%. IR (KBr); 3470 (OH), 1650 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$); δ=2.98 (1H, dd, *J*=7, 14 Hz), 3.15 (1H, dd, *J*=7, 14 Hz), 4.23 (1H, s), 4.9—5.2 (2H, m), 5.6—5.9(1H, m), 7.2—7.8 (10H, m).

1,2-Bis(4-chlorophenyl)-2-hydroxy-4-penten-1-one (3b): Yellow needles from hexane-chloroform; mp 72—74 °C. MS; *m/z* 139, 141, 251, 253. Found: C, 63.30; H, 4.33; Cl, 21.97%. Calcd for $C_{17}H_{14}Cl_2O_2$: C, 63.57; H, 4.39; Cl, 22.07%. IR (KBr); 3420 (OH), 1660 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$); δ=2.83 (1H, dd, *J*=7, 14 Hz), 3.08 (1H, dd, *J*=7, 14 Hz), 3.91 (1H, s), 5.0—5.3 (2H, m), 5.6—5.8 (1H, m), 7.26 (2H, d, *J*=9 Hz), 7.33 (2H, d, *J*=9 Hz), 7.42 (2H, d, *J*=9 Hz), 7.74 (2H, d, *J*=9 Hz).

1.2-Bis(4-methylphenyl)-2-hydroxy-4-penten-1-one (3c): Colorless oil. MS; *m/z* 119, 161, 263. High resolution MS; Found: 282.1644. Calcd for $C_{19}H_{22}O_2$: 282.1616. IR (NaCl); 3440 (OH), 1670 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$); δ=2.31 (3H, s), 2.32 (3H, s), 2.98 (1H, dd, *J*=7, 14 Hz), 3.10 (1H, dd, *J*=7, 14 Hz), 4.30 (1H, s), 4.9—5.2 (2H, m), 5.6—5.8 (1H, m), 7.08 (2H, d, *J*=8 Hz), 7.17 (2H, d, *J*=8 Hz), 7.35 (2H, d, *J*=8 Hz), 7.65 (2H, d, *J*=8 Hz).

1,2-Bis(4-methoxyphenyl)-2-hydroxy-4-penten-1-one (3d): Colorless oil. MS; *m/z* 135, 177, 295. Found: C, 72.54; H, 6.46%. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45%. IR (NaCl);

3420 (OH), 1660 (C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$); δ=3.00 (1H, dd, J=7, 14 Hz), 3.08 (1H, dd, J=7, 14 Hz), 3.78 (6H, s), 4.46 (1H, s), 4.9—5.2 (2H, m), 5.6—5.8 (1H, m), 6.76 (2H, d, J=9 Hz), 6.88 (2H, d, J=9 Hz), 7.37 (2H, d, J=9 Hz), 7.76 (2H, d, J=9 Hz).

1-Phenyl-3-buten-1-one (4a): Colorless oil. ^{1}H NMR (CDCl$_3$); δ=3.75 (2H, d, J=7 Hz), 5.1—5.3 (2H, m), 6.0—6.1 (1H, m), 7.4—7.7 (6H, m), 7.9—8.0 (4H, m).

1-(4-Chlorophenyl)-3-buten-1-one (4b): Colorless oil. ^{1}H NMR (CDCl$_3$); δ=3.71 (2H, d, J=7 Hz), 5.1—5.3 (2H, m), 6.0—6.1 (1H, m), 7.42 (2H, d, J=9 Hz), 7.88 (2H, d, J=9 Hz).

1-(4-Methylphenyl)-3-buten-1-one (4c): Colorless oil. ^{1}H NMR (CDCl$_3$); δ=2.37 (3H, s), 3.73 (2H, d, J=7 Hz), 5.1—5.3 (2H, m), 6.0—6.1 (1H, m), 7.16 (2H, d, J=9 Hz), 7.78 (2H, d, J=9 Hz).

1-(4-Methoxyphenyl)-3-buten-1-one (4d): Colorless oil. ^{1}H NMR (CDCl$_3$); δ=3.70 (3H, d, J=7 Hz), 3.86 (2H, s), 5.1—5.3 (2H, m), 6.0—6.1 (1H, m), 6.93 (2H, d, J=9 Hz), 7.94 (2H, d, J=9 Hz).

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9) When a benzene solution containing **1a** and **2** was allowed to stand for a week, the starting reactants were recovered.

10) In this reaction, trace amount of benzaldehyde was generated, which could be detected by ^{1}H NMR.

11) The oxidation potential of allyltrimethylstannane was 0.98 V, and that of allyltrimethylsilane was 1.58 V.

12) The simulated spectrum agreed with the observed one. (Parameters shown in Fig. 1 were used.)

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20) If Coulombic term is completely neglected, ΔG values are positive in the cases of **2b—d**. Perhaps Coulomb interaction is essential to this system and attributable to this exothermic photoinduced electron transfer reaction.

21) In the HMO calculation, we assumed that stannyl cation perturbed only at carbonyl groups, and the magnitude of perturbation was estimated as $-e^2/r$ where r is the distance between two ions. The ionic character of the tin-oxygen bond and the distance r are assumed to be 30% and 3.5 Å, respectively. The dihedral angle between phenyl ring and carbonyl group was estimated to be 50°. For the case of **1a**, each parameters are as follows; α(O)=2.02, β(CO)=0.52, β(C<phenyl> C<carbonyl>)=0.64, and other β(CC)=1.00.

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23) No fluorescence spectrum of **1a** and no CT absorption between **1a** and **2** in a benzene solution could be observed. Because of the high efficiency of intersystem crossing ($S_1 \rightarrow T_1$) in the excited state of benzil, we can assume that this reaction proceeds via excited triplet state.

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