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Mechanism of the Triplet-Sensitized Photolysis of *N*-(1-Naphthylsulfonyl)-*N*-phenyl-*O*-(*p*-toluoyl)hydroxylamine

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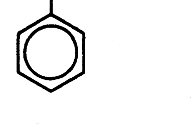
The title hydroxylamine (SO_2NT) undergoes triplet-sensitized photolysis in the presence of benzophenone (BP) or its derivative to give rearrangement and fragmentation products. Observations of the toluoyloxyl-migrated products, which are not obtained by the triplet-sensitized photolysis of *N*-(1-naphthoyl)-*N*-phenyl-*O*-(*p*-toluoyl)hydroxylamine (NT), indicate the occurrence of an efficient intersystem crossing of a triplet radical pair initially formed into a singlet radical pair. Internal heavy-atom-like effects of the partially charged sulfonyl sulfur and oxygen atoms are suggested to be responsible for this effective spin inversion. The finding that benzil, both the excited singlet and triplet states of which lie below those of SO_2NT, causes a sensitized photolysis of this hydroxylamine to afford the same rearrangement and fragmentation products establishes the fact that a reaction sensitized by BP or its derivative proceeds through a triplet-exciplex intermediate. The effects of the solvent polarity and substituents of BP on the quantum yields for the reaction are discussed.

In a previous paper[1)] we described in some detail the effects of substituents on benzophenone (BP) upon the mechanism of the triplet-sensitized photolysis of *N*-(1-naphthoyl)-*N*-phenyl-*O*-(*p*-toluoyl)hydroxylamine (NT) by substituted BP, and found that the sensitized reaction proceeds via a triplet-exciplex intermediate in which an electron or energy transfer occurs, depending on the nature of substituents on BP.

The S–O bond in a sulfonyl group has been suggested to have a somewhat large semipolar bond character,[2)] so that the sulfonyl sulfur and oxygen atoms possess greater positive and negative charges, respectively, compared with the carbonyl carbon and oxygen atoms. The relative rate of diffusional separation of a caged triplet radical pair to its spin inversion was found to play a key role in determining the product distribution of the sensitized photolysis of NT.[3)] We expect that the replacement of amide carbonyl in an NT molecule by a sulfonyl group affects this relative rate as well as the product distribution.

In order to obtain greater insight into the behavior of a triplet-exciplex intermediate and a caged triplet radical pair, we investigated the sensitized photolysis of *N*-(1-naphthylsulfonyl)-*N*-phenyl-*O*-(*p*-toluoyl)hydroxylamine (SO_2NT) with BP, 4-(dimethylamino)benzophenone (DAB), 4,4′-dimethoxybenzophenone (DMB), 3,3′-bis(trifluoromethyl)benzophenone (BFB), and benzil (BZ).



SO_2NT

1-Np = 1-naphthyl p-Tl = p-tolyl

Results

Phosphorescence Quenching of Sensitizers by SO_2NT. SO_2NT exhibits phosphorescence with an 0–0 band at 485 nm in 1,2-dichloroethane at 77 K. From this 0–0 band the first triplet excitation energy (E_{T_1}) was

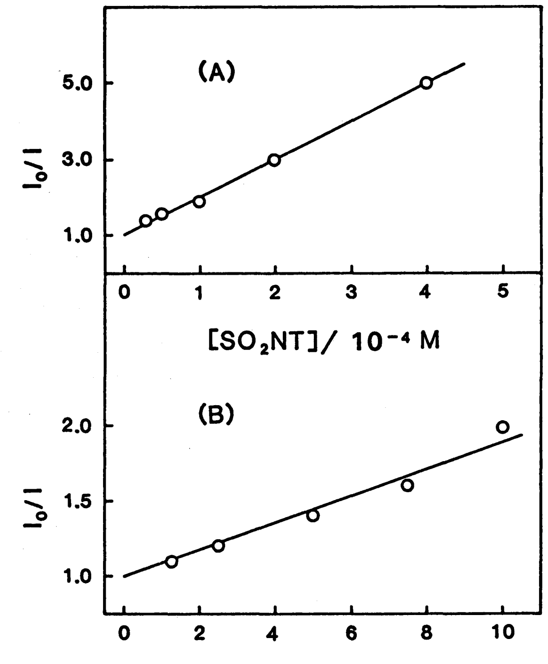


Fig. 1. Stern–Volmer plots (A) for the phosphorescence quenching of BP (0.050 M) by SO_2NT in oxygen-free 1,2-dichloroethane at room temperature and (B) for the phosphorescence quenching of BZ (0.050 M) by SO_2NT in MeOH–EtOH (1 : 1 v/v) at 77 K. I and I_0 refer to the phosphorescence intensities with and without SO_2NT, respectively. Excitation wavelength=(A), (B) 366 nm.

determined to be 59 kcal mol^{-1} (1 kcal=4.184 kJ). The first singlet excitation energy (E_{S_1}) was estimated to be 88 kcal mol^{-1} based on its UV and fluorescence spectral data in 1,2-dichloroethane at room temperature. As shown in Fig. 1A, the room-temperature phosphorescence of BP (E_{S_1}=75; E_{T_1}=69 kcal mol^{-1})[4] in oxygen-free 1,2-dichloroethane was efficiently quenched by SO_2NT according to the Stern–Volmer relationship with a slope (quenching constant) of 1.0×10^4 M^{-1} (1 M=1 mol dm^{-3}), making the participation of triplet BP in the sensitized reaction highly probable. Because the room-temperature phosphorescence of DAB (E_{S_1}<88; E_{T_1}=62 kcal mol^{-1}),[1] DMB (E_{S_1}=77; E_{T_1}=71 kcal mol^{-1}),[4] and BFB (E_{S_1}<88; E_{T_1}=69 kcal mol^{-1})[1] were too weak or overlapped with their very weak fluorescence, phosphorescence quenching experiments were conducted at low temperature. The phosphorescence of these sensitizers (0.050 M) were found to be quenched by SO_2NT (0.010 M) to a considerable extent in 1,2-dichloroethane at 77 K. A comparison of the E_{S_1} of SO_2NT with that of each sensitizer makes a singlet-singlet energy transfer from any sensitizer (quantum yield of intersystem crossing, $\Phi_{isc} \approx 1$)[1] to SO_2NT very unlikely.

An observation of BZ-phosphorescence quenching by SO_2NT in an alcohol glass at 77 K (Fig. 1B) suggests the involvement of a triplet-exciplex intermediate in this quenching process, since both singlet-singlet and triplet-triplet energy transfers from BZ (E_{S_1}=59; E_{T_1}=53 kcal mol^{-1})[4] to SO_2NT are endothermic and, hence, seem to make only a minor contribution to the emission quenching of BZ. In addition, SO_2NT (0.010 M) quenched the BZ (Φ_{isc}=0.92)[4] fluorescence to a slight extent (about 5%) in 1,2-dichloroethane at room temperature, implying the minor contribution of, if any, a singlet exciplex to the overall emission quenching of BZ.

Triplet-Sensitized Photolysis. Irradiation of an oxygen-free 1,2-dichloroethane solution of SO_2NT (**1**, 1.3—10.0×10^{-3} M) containing each sensitizer (0.050 M) with 366-nm light resulted in the appearance of rearrangement products **2** and **3**, which were not observed in the BP-sensitized photolysis of NT,[3] in addition to fragmentation products **4**—**6**, as shown in Scheme 1. These products were identified by comparing the retention times of their HPLC peaks with those of independently prepared authentic or commercially available samples. Control experiments reveal that the decomposition of SO_2NT takes place to a negligible extent without the sensitizer, and that the obtained products do not undergo sensitized photolysis under the same irradiation conditions.

The BZ-sensitized decomposition of SO_2NT with 366-nm light in N_2-purged 1,2-dichloroethane afforded the same products as those formed by a reaction sensitized with BP or its derivative. In addition to this finding, the previous observation[1] that the sensitized photolysis

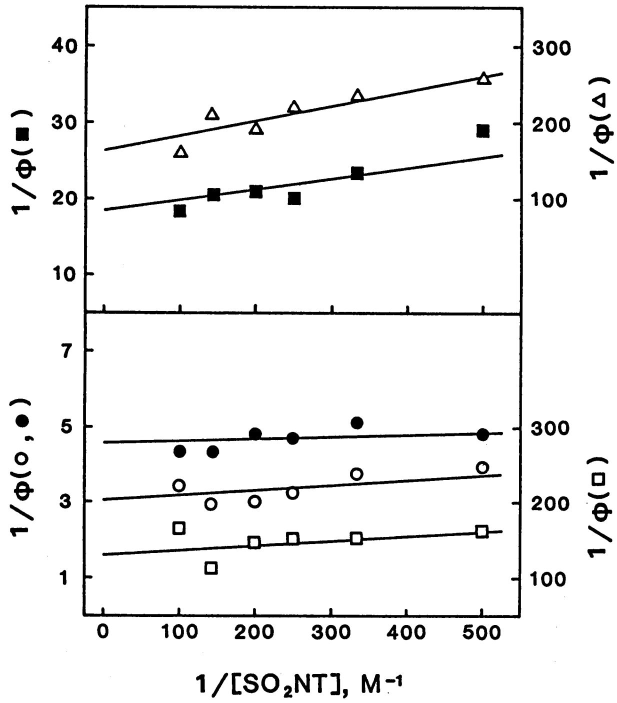
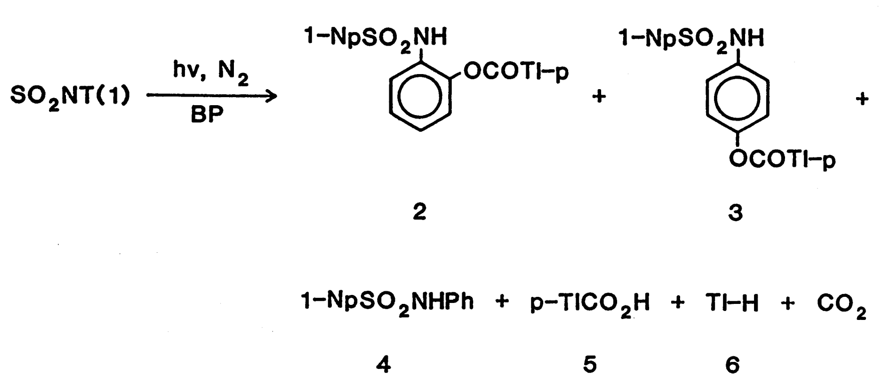


Fig. 2. Stern–Volmer plots of $1/\Phi_{-SO_2NT}$ (○), $1/\Phi_2$ (■), $1/\Phi_3$ (△), $1/\Phi_4$ (□), and $1/\Phi_5$ (●) versus 1/[SO_2NT] for the BP(0.050 M)-sensitized photolysis of SO_2NT with 366-nm light in N_2-purged 1,2-dichloroethane. Φ_{-SO_2NT}, Φ_2, Φ_3, Φ_4, and Φ_5 represent the quantum yields for the disappearance of SO_2NT and for the appearance of **2**—**5**, respectively.



Scheme 1.

of NT with substituted BP occurs by way of a triplet-exciplex intermediate strongly suggests that the sensitized reaction of SO_2NT proceeds by a mechanism similar to that proposed for NT photolysis. As typically shown in Figs. 2 and 3, a relationship between the reciprocal of the quantum yield for the reaction ($1/\Phi$) and the reciprocal of the SO_2NT concentration ($1/[SO_2NT]$) can be approximated as being linear. Similar linear plots were obtained with other sensitizers and in other solvents. Table 1 lists the limiting quantum yields (Φ_{lim}), i.e., the quantum yields extrapolated to the infinite concentration of SO_2NT, for sensitized photolysis.

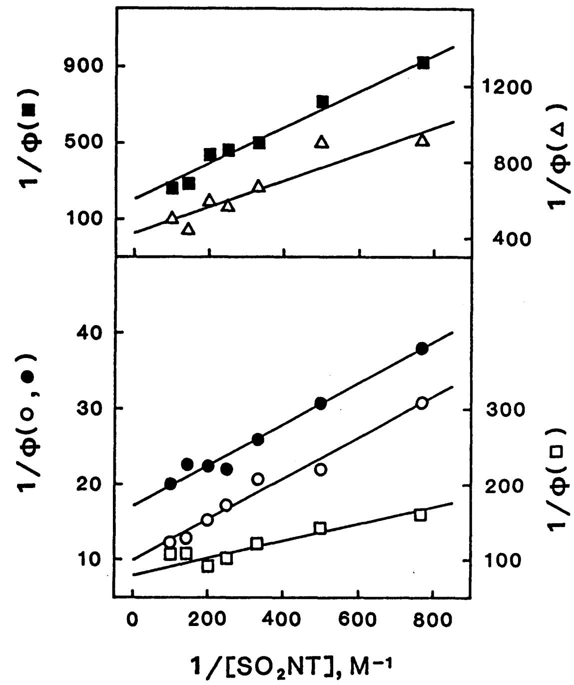


Fig. 3. Stern-Volmer plots of $1/\Phi_{\text{-}SO_2NT}$ (○), $1/\Phi_2$ (■), $1/\Phi_3$ (△), $1/\Phi_4$ (□), and $1/\Phi_5$ (●) versus $1/[SO_2NT]$ for the BZ (0.050 M)-sensitized photolysis of SO_2NT with 366-nm light in N_2-purged 1,2-dichloroethane.

Direct Photolysis. The direct photolysis of SO_2NT ($2.0—10.0\times10^{-3}$ M) with 313-nm light in N_2-saturated 1,2-dichloroethane at room temperature gave the same products as those generated by triplet-sensitized photolysis, though there was a somewhat large difference in the magnitude of Φ for each product between the direct and sensitized photolyses (Table 1). Both $\Phi_{\text{-}SO_2NT}$ and $\Phi_{2\text{-}5}$ exhibited almost a negligible concentration dependence in the $2.0—10.0\times10^{-3}$ M range.

On the other hand, 1,3-cyclohexadiene (0.050 M; $E_{S_1}=97$, $E_{T_1}=52$ kcal mol^{-1})4) decreased the phosphorescence intensity of SO_2NT (5.0×10^{-3} M) by a factor of about 2 in butyronitrile at 77 K, whereas this triplet quencher did not affect the SO_2NT-fluorescence intensity or the quantum yields for the reaction. This result suggests that direct photolysis takes place preferentially from the first singlet excited state.

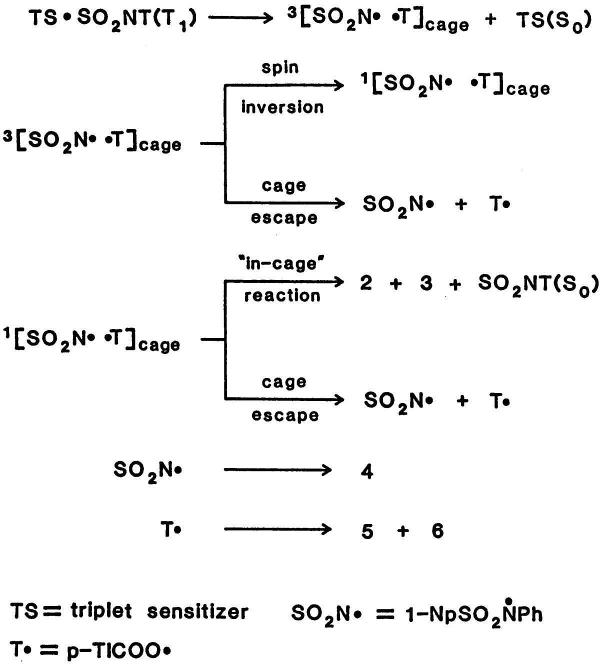
Discussion

The formation of rearrangement products **2** and **3** along with fragmentation products **4**—**6** in the triplet-sensitized photolysis of SO_2NT indicates the occurrence of a spin inversion of a triplet radical pair into a singlet one in competition with diffusive separation of a caged triplet radical pair, as illustrated in Scheme 2. We previously found that the rate of spin inversion of the triplet radical pair arising from triplet NT is much slower than that of an escape out of the cage.3) Since the sulfonyl sulfur and oxygen atoms in SO_2NT have larger charges than do the amide carbonyl carbon and oxygen atoms in NT,2) the sulfonyl group in a spin-correlated sulfonamidyl radical may exert heavy-atom-like effects to enable an efficient triplet→singlet spin inversion in a caged radical pair.5) This enhanced intersystem crossing of $^3[SO_2N\cdot\cdot T]_{\mathrm{cage}}\rightarrow{}^1[SO_2N\cdot\cdot T]_{\mathrm{cage}}$

Table 1. Quantum Yields for the Triplet-Sensitized Photolysis of SO_2NT ($1.3—10.0\times10^{-3}$ M) with 366-nm Light at 24±3 °C

Sensitizer (0.050 M)	Solvent	Φ_{lim} a)					Φ_6 b)	R c)
		$\Phi_{\text{-}SO_2NT}$	Φ_2	Φ_3	Φ_4	Φ_5		
BP	CH_2ClCH_2Cl	0.32	0.05	0.01	0.01	0.22	0.02	0.73
BFB	CH_2ClCH_2Cl	0.31	0.06	— d)	0.01	0.19	0.03	0.66
DAB	CH_2ClCH_2Cl	0.16	0.04	0.01	0.03	0.14	<0.01	0.70—0.74
DMB	Benzene	0.51	0.08	0.01	— e)	0.28	0.01	0.74
DMB	CH_2ClCH_2Cl	0.36	0.05	0.01	— e)	0.21	0.02	0.72
DMB	CH_3CN	0.53	0.06	0.01	— e)	0.36	0.01	0.82
BZ	CH_2ClCH_2Cl	0.10	0.01	<0.01	0.01	0.06	0.01	0.67—0.75
— f)	CH_2ClCH_2Cl	0.10	0.03	0.03	0.01	0.05	<0.01	

a) $\Phi_{\text{-}SO_2NT,\mathrm{lim}}$, $\Phi_{2,\mathrm{lim}}$, $\Phi_{3,\mathrm{lim}}$, $\Phi_{4,\mathrm{lim}}$, and $\Phi_{5,\mathrm{lim}}$ are the limiting quantum yields for the disappearance of SO_2NT and for the appearance of **2**—**5**, obtained from the intercepts of linear Stern-Volmer plots of $1/\Phi$ versus $1/[SO_2NT]$, respectively. b) Quantum yield for the formation of **6** determined at $[SO_2NT]=0.010$ M. c) $R=\Phi_{5,\mathrm{lim}}/(\Phi_{2,\mathrm{lim}}+\Phi_{3,\mathrm{lim}}+\Phi_{5,\mathrm{lim}}+\Phi_6)$. d) Could not be determined because of overlapping with the HPLC peak of BFB. We assumed $\Phi_{3,\mathrm{lim}}=0.01$ to estimate the R value. e) Could not be determined because of overlapping with the HPLC peak of DMB. f) Direct photolysis with 313-nm light.



Scheme 2.

should be responsible for the formation of rearranged products. The direct photolysis of SO_2NT occurs preferentially from the singlet excited state to afford both rearrangement and fragmentation products in comparable quantum yields. The fact that **2** and **3** come from the singlet-state reaction, i.e., the geminate recombination of a singlet radical pair,[3] supports the idea that an effective triplet→singlet spin inversion in the triplet cage $^3[SO_2N\cdot\ \cdot T]_{cage}$ occurs in competition with a diffusive escape of the radicals $SO_2N\cdot$ and $T\cdot$ from this cage (Scheme 2).

As shown in Table 1, the BP-sensitized photolysis of SO_2NT gives the rearrangement products in lower quantum yields ($\Phi_{2,\text{lim}}+\Phi_{3,\text{lim}}=0.06$) than those of the fragmentation products ($\Phi_{5,\text{lim}}+\Phi_6=0.24$). Since undesirable side reactions of the sulfonamidyl radical occur, even in 1,2-dichloroethane, we used $\Phi_{5,\text{lim}}+\Phi_6$ rather than $\Phi_{4,\text{lim}}$ as a measure of the extent of the "out-of-cage" reaction. If an exothermic triplet-triplet energy transfer between BP and SO_2NT takes place in preference to an electron transfer, toluene (**6**) should be formed with substantial quantum yield, as in the case of the BP-sensitized decomposition of NT under the same irradiation conditions.[1,3] The obtained result is not consistent with this expectation. The fact that an SO_2NT anion radical generated by an electron transfer from the excited states of *N,N,N′,N′*-tetramethylbenzidine (TMB) affords **4** and **5** exclusively,[6] suggests that both the energy- and electron-transfer pathways operate in the BP-sensitized reaction of SO_2NT. However, the free-energy change (ΔG) of 12 kcal mol^{-1} for this system[10] indicates that an electron transfer from BP to SO_2NT in the triplet exciplex is improbable.

We use the ratio (R) of $\Phi_{5,\text{lim}}$ to ($\Phi_{2,\text{lim}}+\Phi_{3,\text{lim}}+\Phi_{5,\text{lim}}+\Phi_6$) in order to estimate the contribution of the electron-transfer pathway to the overall reaction, since an electron transfer in the exciplex intermediate $TS\cdot SO_2NT(T_1)$ (Scheme 2) is thermodynamically possible for DAB ($\Delta G=-3$ kcal mol^{-1}). An increase in the solvent polarity or electron-donating ability of sensitizer is predicted to increase the contribution of this pathway, giving the increased R value[7d,11,12] As evident in Table 1, the R value is subject to solvent polarity and substituent effects to only a small extent. Even for the DAB–SO_2NT system, almost the same R value was obtained. This observation cannot be explained in terms of an electron- or energy-transfer mechanism in the triplet exciplex proposed for the sensitized photolysis of NT.[1] Furthermore, the R value for the BZ-sensitized reaction is in reasonable agreement with that for BP or its derivative, thus demonstrating that the SO_2NT-derived triplet exciplexes have similar properties to each other, but differ from the NT-derived ones regarding structure and reactivity. The appreciable charge transfer-type interaction between the sulfonyl sulfur atom in SO_2NT and the sensitizer's carbonyl oxygen atom within the exciplex intermediate $TS\cdot SO_2NT(T_1)$ may affect the course of the decomposition of this intermediate so as to yield preferentially fragmentation products **4** and **5**, originating from the electron-transfer pathway.

Experimental

General Methods. ^{1}H NMR spectra were recorded on a JEOL FX-200 spectrometer. Tetramethylsilane was used as an internal standard. Other general methods were the same as those described in a previous paper.[1]

Materials and Solvents. *N*-(1-Naphthylsulfonyl)-*N*-phenyl-*O*-(*p*-toluoyl)hydroxylamine (SO_2NT, **1**), *N*-[*o*-(*p*-toluoyloxy)phenyl]-1-naphthalenesulfonamide (**2**), *N*-[*p*-(*p*-toluoyloxy)phenyl]-1-naphthalenesulfonamide (**3**), and 1-naphthalenesulfonanilide (**4**) were prepared according to the previously described procedures.[3] The physical properties of these compounds are as follows:

SO_2NT: Mp 145.5—146.5 °C (twice from EtOH); IR (KBr) 1760, 1330, and 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=2.37$ (3H, s), 7.16—8.14 (15H, m), and 8.70 (1H, d, $J=9$ Hz). Found: C, 68.88; H, 4.47; N, 3.37%. Calcd for $C_{24}H_{19}NO_4S$: C, 69.05; H, 4.59; N, 3.36%.

2: Mp 142.5—143.5 °C (twice from EtOAc–hexane); IR (KBr) 3550, 3490, 3420, 3300, 1740, 1335, and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=2.46$ (3H, s), 6.92—8.12 (15H, m), and 8.50 (1H, d, $J=9$ Hz). Found: C, 68.86; H, 4.32; N, 3.43%. Calcd for $C_{24}H_{19}NO_4S$: C, 69.05; H, 4.59; N, 3.36%.

3: Mp 167—169 °C (twice from EtOAc); IR (KBr) 3570, 3500, 3430, 3280, 1740, 1330, and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=2.42$ (3H, s), 6.94—8.21 (15H, m), and 8.74 (1H, d, $J=9$ Hz). Found: C, 68.82; H, 4.29; N, 3.43%. Calcd for $C_{24}H_{19}NO_4S$: C, 69.05; H, 4.59; N, 3.36%.

4: Mp 158.5—159 °C (twice from EtOH–H_2O); IR (KBr) 3240, 1320, and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=6.94$—8.26 (12H, m) and 8.76 (1H, d, $J=9$ Hz). Found: C, 67.72; H, 4.39; N, 4.96%. Calcd for $C_{16}H_{13}NO_2S$: C, 67.82; H, 4.62; N, 4.94%.

In addition to *p*-toluic acid and toluene, 4-(dimethylamino)benzophenone (DAB), 4,4′-dimethoxybenzophenone (DMB), benzophenone (BP), 3,3′-bis(trifluoromethyl)benzophenone (BFB), benzil (BZ), and *N,N,N′,N′*-tetramethylbenzidine (TMB) were purified by the same methods as those used in our previous studies.[1,3] 1,3-Cyclohexadiene was fractionally distilled and stored in a refrigerator. Benzene and 1,2-dichloroethane were of spectroscopic grade and used without further purification. Methanol, ethanol, acetonitrile, and butyronitrile were purified according to the standard methods.[13]

Quantum Yields and Redox Potentials. The same procedure and filter combination as those described in a previous paper[1] were applied for determining the quantum yields for the sensitized photolysis of SO_2NT with DAB (conversions of SO_2NT=5—18%), DMB (11—51%), BP (13—59%), BFB (8—40%), and BZ (3—8%). Irradiation of SO_2NT in a given solvent containing TMB with light of wavelengths longer than 330 nm was accomplished in a similar manner to the case of *N*-(1-naphthoyl)-*N*-phenyl-*O*-(*p*-toluoyl)hydroxylamine.[1] The 313-nm light for the direct photolysis of SO_2NT was isolated by the use of potassium chromate (2.0×10^{-3} M) in a 1 wt% aqueous solution of potassium carbonate and Corning 7-54 filters. The quantum yields for direct photolysis (conversions of SO_2NT=3—13%) were similarly determined as in a previous case.[3] All of the quantum yields are averages of more than five determinations. The half-wave reduction potential of SO_2NT was measured under the same conditions as those described in a previous paper.[1]

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6) For examining products derived from an SO_2NT anion radical, SO_2NT (5.0×10^{-3} M) was photolyzed with light of wavelengths longer than 330 nm under N_2 in the presence of TMB [0.010 M; E_{S_1}=83, E_{T_1}=63 kcal mol^{-1}; oxidation potential, $E_{\text{ox}}^{\text{TMB}}$=0.32 V vs. saturated calomel electrode (SCE) in CH_3CN][7] in benzene, 1,2-dichloroethane, and acetonitrile at room temperature. Based on the simplified Weller equation, $\Delta G(\text{kcal mol}^{-1})=23.06(E_{\text{ox}}^{\text{TMB}}-E_{\text{red}}^{SO_2NT})-E_{S_1}^{\text{TMB}}$(or $E_{T_1}^{\text{TMB}}$),[8] free-energy changes (ΔG) for electron transfer from the TMB excited states to SO_2NT (reduction potential $E_{\text{red}}^{SO_2NT}=-1.62$ V vs. SCE in CH_3CN) were calculated to be -38 kcal mol^{-1} for the S_1 state and -18 kcal mol^{-1} for the T_1 state in acetonitrile. Thus, the electron transfer from both excited states of TMB is thermodynamically very favorable process. HPLC and GLC analyses of the photolyzates established the negligible formation of rearrangement products **2** and **3** and one of the fragmentation products, toluene (**6**), whereas fragmentation products **4** (30—40%) and **5** (>90%) were detected as main products. Decreased yield of **4** must be due to side reactions of the sulfonamidyl radical $1\text{-NpSO}_2\dot{\text{N}}\text{Ph}$, which arise in competition with hydrogen abstraction giving **4**.[9]

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10) The simplified Weller equation[8] allows us to calculate ΔG values for electron transfer from the triplet-state sensitizer (S) to the ground-state SO_2NT in acetonitrile: ΔG (kcal mol^{-1})=>14 (S=BFB, $E_{\text{ox}}^{\text{S}}>2$ V vs. SCE), 12 (BP, 1.90 V), 8 (DMB, 1.82 V), and -3 (DAB, 0.97 V).[1]

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