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Role of the Charge Transfer Interactions in Photoreactions. 1. Exciplexes between Styrylnaphthalenes and Amines[1a]

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Abstract: Measurements have been made of the fluorescence quantum yields (ϕ_{FM}), lifetimes, spectra, and of the photoisomerization quantum yields (ϕ_C) of *trans*-styrylnaphthalenes (StN's) in deaerated and aerated solutions of *n*-hexane and acetonitrile, and the effect of the addition of amines on these properties has been studied. The fluorescence quenching is associated with exciplex emission, and the Stern–Volmer quenching coefficient increases with a decrease in the amine ionization potential. ϕ_C is reduced proportionately less than ϕ_{FM}, and in some cases it is increased, by the addition of the amine. Analysis of the data for β-StN + diethylaniline (DEA) in *n*-hexane provides extensive kinetic parameters which indicate that the photoisomerization occurs via the triplet state with a quantum efficiency $q_{CT} = 0.41$, increased to $q_{CT} = 0.47$ (± 0.01) in the presence of DEA or oxygen. Similar results have been obtained for α-StN and 4-Br-α-StN. A model of the S_1 potential of β-StN is proposed.

Interest in the photophysics and photochemistry of electron donor–acceptor (DA) complexes has been increasing in recent years.[2] The long term aim of our studies on charge transfer (CT) interactions in the ground[3] and excited[4] states is to investigate the role of DA complexes in the photochemical and photophysical behavior of the partners.[5,6] Substrates of particular interest are the styrylnaphthalenes (StN's) both because their study can give useful information concerning the photoreaction mechanism of stilbene-like molecules and because their relatively long fluorescence lifetime makes them particularly suitable for a quenching study.

The fluorescence and photochemistry of StN's in the absence of quenchers has recently received much attention.[7-11] The fluorescence has a high quantum efficiency q_{FM} which decreases in the presence of oxygen. The photoisomerization quantum yield ϕ_C increases with increase in concentration of StN and of dissolved oxygen. On the basis of the experimental results, all observers consider that the photoisomerization probably occurs by a triplet mechanism.

The influence of perturbers other than oxygen, acting through CT interaction, on StN photochemistry, has not been investigated previously. This paper reports the results of a study of exciplexes formed by the two isomers α-StN and β-StN in the first excited singlet state S_1 with some amine electron donors. α-StN, para-substituted with bromine in the phenyl group (4-Br-α-StN), was also studied. The quenchings of fluorescence and trans → cis photoisomerization of StN's by amines were compared to obtain information on the photoreaction mechanism.

Experimental Section

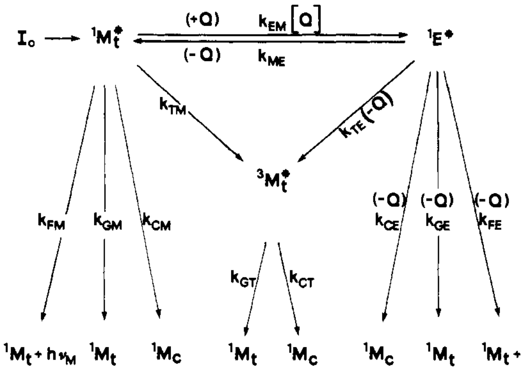
The StN's were synthesized for previous work and their preparation is described elsewhere.[7] The amine quenchers were commercial products (Fluka AG *puriss.* grade) distilled over NaOH under reduced pressure before use. The solvents were from Carlo Erba RS or RP grade, purified following conventional methods when necessary.

The fluorescence spectra and quantum yields were measured with a Perkin-Elmer MPF-3 spectrofluorimeter with an accessory for spectrum correction using rhodamine B as a quantum counter. The measurements of the emission yields were carried out in dilute solutions (absorbance ~0.05 at 350 nm), using quinine bisulfate in 1 N H_2SO_4 as standard. A CGA DC-3000/1 spectrofluorimeter was also used. The solutions were deaerated by bubbling nitrogen. The Stern–Volmer (SV) fluorescence quenching coefficient $K = k_{QM}\tau_M$ (M^{-1}) was obtained from observations of the fluorescence quantum yield ϕ_{FM} as a function of the amine concentration [Q]. The ratio of the fluorescence quantum yields was equated to the intensity ratio at the analytical wavelength. The fluorescence quenching rate parameter k_{QM} ($M^{-1}\ s^{-1}$) can be obtained, if the S_1 lifetime τ_M, at infinite dilution, is known.

The fluorescence lifetimes were measured in *n*-hexane by a sampling fluorometer with a resolution time of 1 ns.[12] The decay curves, corrected for the instrumental response time, fit an exponential decay law for the (β-StN + DEA) exciplex (studied in more detail because of its higher emission intensity) and for α-StN, but the data for β-StN cannot be expressed by a single exponent (the value of 15 ns reported below corresponds to the best fit observed).

The photoisomerization quenching was studied spectrophotometrically, using an Unicam SP500/2 spectrophotometer, under the same experimental conditions as the fluorescence studies. The trans → cis quantum yield (ϕ_C) was determined at various amine concentrations [Q] and at a fixed concentration of StN (~1.5×10^{-4} M), sufficiently high to assure a total absorption of the 350-nm incident light (the quenchers do not absorb at this irradiation wavelength).

Reaction Kinetics and Rate Parameter Notation. Exciplex Formation and Dissociation. The following kinetic scheme and notation are used to describe the behavior of the singlet excited molecule $^1M_t{}^*$ and the singlet exciplex $^1E^*$ ($= {}^1(M_t{\cdot}Q)^*$) formed by its interaction with the amine Q. The derivation of the equations is given elsewhere.[13] Subscripts t and c refer to trans and cis isomers, respectively.



(1)

At [Q] = 0, the quantum efficiency of each $^1M_t{}^*$ process is

$$q_{XM} = k_{XM}/k_M \tag{2}$$

where

$$k_M = \sum_X k_{XM} = 1/\tau_M \tag{3}$$

is the $^1M_t{}^*$ decay parameter, τ_M is the $^1M_t{}^*$ lifetime, and X = F, G, C, or T.

When [Q] is large, the quantum efficiency of each $^1E^*$ process is

$$q_{XE} = k_{XE}/k_E \tag{4}$$

where

$$k_E = \sum_X k_{XE} = 1/\tau_E \tag{5}$$

is the $^1E^*$ decay parameter, τ_E is the $^1E^*$ lifetime, and X = F, G, C, or T.

At intermediate values of [Q], the quantum yield ϕ_{XM} of each $^1M_t{}^*$ process is given by

$$\frac{q_{XM}}{\phi_{XM}} - 1 = K[Q] \tag{6}$$

where K is the SV coefficient describing the quenching of $^1M_t{}^*$ by Q. K is usually determined from measurements of ϕ_{FM} as a function of [Q]. In terms of the parameters of eq 1, 3, and 5,[13]

$$K = \frac{k_E k_{EM}}{k_M(k_E + k_{ME})} \tag{7}$$

It may also be expressed as[13]

$$K = \frac{k_{QM}}{k_M} = p\frac{k_{EM}}{k_M} \tag{8}$$

where k_{EM} is the diffusion-controlled collisional rate parameter, k_{QM} is the $^1M_t{}^*$ quenching rate parameter, and

$$p = \frac{k_E}{k_E + k_{ME}} \tag{9}$$

is the quenching reaction probability per collision between $^1M_t{}^*$ and Q.

At intermediate values of [Q], the quantum yield ϕ_{XE} of each $^1E^*$ process is

$$\frac{q_{XE}}{\phi_{XE}} - 1 = \frac{1}{K[Q]} \tag{10}$$

where X = F, G, C, or T. Observations of ϕ_{FE} as a function of [Q] thus provide an independent means of determining K.

The total singlet ($^1M_t{}^* + {}^1E^*$) quantum yield $\phi_X{}^S$ of each process is given by

$$\phi_X{}^S = \phi_{XM} + \phi_{XE} = \frac{q_{XM} + q_{XE}K[Q]}{1 + K[Q]} \tag{11}$$

with X = F, G, C, or T. Observations of $\phi_X{}^S$ as a function of [Q], and of q_{XM} and K, enable q_{XE} to be determined. For X = F or T, the total quantum yield $\phi_X = \phi_X{}^S$.

For X = C or G, there is also a contribution to ϕ_X from $^3M_t{}^*$, namely,

$$\phi_X{}^T = \phi_T{}^S q_{XT} \tag{12}$$

where $q_{XT} = k_{XT}/k_T$ and $k_T = k_{CT} + k_{GT}$.

The total quantum yield

$$\begin{aligned}\phi_X &= \phi_X{}^S + \phi_X{}^T \\ &= \frac{(q_{XM} + q_{TM}q_{XT}) + (q_{XE} + q_{TE}q_{XT})K[Q]}{1 + K[Q]} \\ &= \phi_{XM}{}' + \phi_{XE}{}'\end{aligned} \tag{13}$$

for X = C or G. The case X = C (isomerization) is the more interesting. The total photoreaction quantum yield ϕ_C at any [Q] is the sum of the two contributions, by the excited molecules which are not quenched and react in the monomeric form ($\phi_{CM}{}'$) and those which react through the complex ($\phi_{CE}{}'$).

$$\phi_C = \phi_{CM}{}' + \phi_{CE}{}' = \frac{\phi_C{}^\circ + \phi_C{}^{\lim}K[Q]}{1 + K[Q]} \tag{14}$$

where

$$\phi_C = \phi_C{}^\circ = q_{CM} + q_{TM}q_{CT} \tag{14a}$$

at [Q] = 0, and

$$\phi_C = \phi_C{}^{\lim} = q_{CE} + q_{TE}q_{CT} \tag{14b}$$

is the limiting value at high [Q]. Observations of K and of ϕ_C as a function of [Q] enable $\phi_C{}^{\lim}$ to be determined.

Oxygen Perturbation. Superscript a indicates that a solution is aerated, i.e., it is in equilibrium with the atmosphere at room temperature. An aerated solution contains a molar concentration [O_2] of oxygen, which introduces $^1M_t{}^*$ and $^1E^*$ quenching processes of rate parameters k_{OM} and k_{OE}, respectively, additional to those shown in eq 1.

When [Q] = 0

$$q_{FM}/q_{FM}{}^a = \tau_M/\tau_M{}^a = 1 + k_{OM}[O_2]/k_M = 1 + K_{OM} \tag{15}$$

When [Q] is large

$$q_{FE}/q_{FE}{}^a = \tau_E/\tau_E{}^a = 1 + k_{OE}[O_2]/k_E = 1 + K_{OE} \tag{16}$$

In general

$$q_{XY}/q_{XY}{}^a = 1 + K_{OY} \tag{17}$$

where Y = M or E, and X = F, G, or C, but *not* T.

Oxygen quenching of an excited singlet state S_1 is equivalent to catalyzed $S_1 \rightarrow T_1$ intersystem crossing (ISC),[13] so that

$$(q_{TY} + K_{OY})/q_{TY}{}^a = 1 + K_{OY} \tag{18}$$

where Y = M or E.

At intermediate [Q], K (eq 7) becomes

$$\begin{aligned}K^a &= \frac{k_{EM}(k_E + k_{OE}[O_2])}{(k_M + k_{OM}[O_2])(k_E + k_{ME} + k_{OE}[O_2])} \\ &= \frac{K(1 + K_{OE})}{(1 + K_{OM})(1 + K_{OE}{}')}\end{aligned} \tag{19}$$

where

$$K_{OE}{}' = k_{OE}[O_2]/(k_E + k_{ME}) = pK_{OE} \tag{20}$$

Results

Fluorescence and Photoisomerization of StN's. The fluorescence and photoisomerization quantum yields of the *trans*-StN's were observed in deaerated and aerated *n*-hexane and acetonitrile solutions at an excitation wavelength of λ_{ex} = 350 nm in the absence of the amine. The values of q_{FM} and $\phi_C{}^\circ$ for the deaerated solutions and of $q_{FM}{}^a$ and $\phi_C{}^{\circ a}$ for the

Table I. Fluorescence and Photoisomerization Quantum Yields of Dilute Solutions of *trans*-StN's (λ_{ex} = 350 nm)

		Deaerated			Aerated		
Solute	Solvent	q_{FM}	$\phi_C{}^\circ$	q_{CT} (eq 25)	$q_{FM}{}^a$	$\phi_C{}^{\circ a}$	$q_{CT}{}^a$ (eq 25a)
β-StN	*n*-Hexane	0.71	0.12	0.41	0.36	0.31	0.48
	Acetonitrile	0.51	0.18	0.37	0.32	0.19	0.28
α-StN	*n*-Hexane	0.64	0.14	0.39	0.51	0.20	0.41
	Acetonitrile	0.25	0.28	0.37	0.23	0.27	0.35
4-Br-α-StN	*n*-Hexane	0.47	0.23	0.43	0.40	0.23	0.38
	Acetonitrile	0.30	0.28	0.40	0.27	0.27	0.37

Table II. StN's in *n*-Hexane and Acetonitrile Solution. Fluorescence Lifetime (τ_M, in ns) and DEA Fluorescence Quenching Coefficients (K, K^a, in M^{-1}) and Rate Parameters (k_{QM}, in $M^{-1}\ s^{-1}$)

	n-Hexane				Acetonitrile	
Compound	τ_M	K	k_{QM}	K^a	K	K^a
β-StN	15	135	9.0×10^9	76	139	93
α-StN	1.9	35	1.8×10^{10}	35	28	28
4-Br-α-StN	1.1	28	2.5×10^{10}	28	32	32

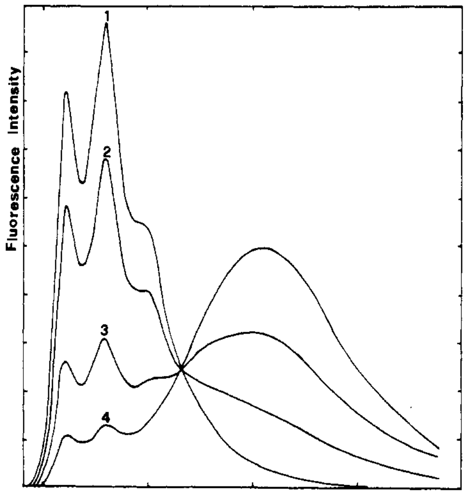


Figure 1. Emission spectra of β-StN in *n*-hexane, alone (1) and with increasing amounts of diethylaniline: [DEA] = 0.34×10^{-2} M (2), 1.5×10^{-2} M (3), 5.0×10^{-2} M (4).

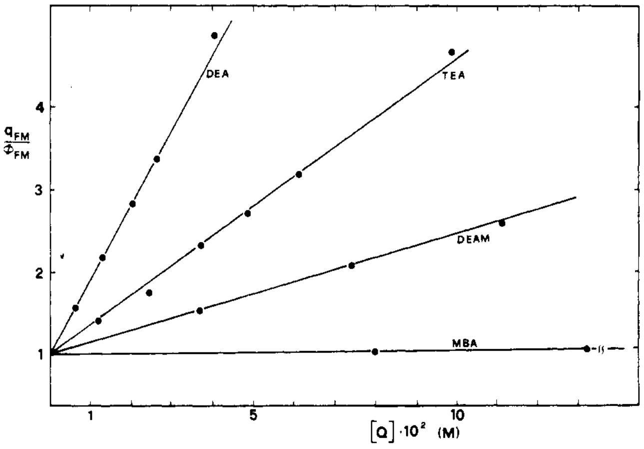


Figure 2. Stern-Volmer plots for fluorescence quenching of β-StN in acetonitrile by amines of different ionization potential (IP) (diethylaniline. DEA, IP = 6.98 eV; triethylamine, TEA, IP = 7.50 eV; diethylamine, DEAM, IP = 8.01 eV; monobutylamine, MBA, IP = 8.71 eV). Amine concentration is designated by [Q].

aerated solutions are listed in Table I. The values of τ_M for the deaerated *n*-hexane solutions are listed in Table II.

Fluorescence Quenching. The absorption and fluorescence spectra of StN's in the presence of amines are consistent with the formation of excited molecular complexes (exciplexes) by CT interaction. No changes were observed in the absorption spectra with increasing amine concentration, showing the complexes to be dissociated in the ground state. The quenching of the StN fluorescence is associated with the appearance of a structureless exciplex fluorescence band at longer wavelengths. Figure 1 shows typical emission spectra for the β-StN + diethylaniline (DEA) system.

The SV quenching coefficient K decreases with increase in the ionization potential of the amine quencher, as shown in Figure 2 for β-StN. This behavior shows that the amine acts as an electron donor, and the StN as an electron acceptor, in forming an AD exciplex.[13] Similar behavior was observed for α-StN and its 4-Br derivative.

Table II lists the SV quenching parameters K and K^a for β-StN, α-StN and its 4-Br derivative in deaerated and aerated *n*-hexane solutions, respectively. The values of k_{QM}, obtained from K, τ_M and eq 8, are also listed in Table II.

Table III lists the values of ϕ_{FM} and q_{FM}/ϕ_{FM} for deaerated solutions of the StN's, in different solvents, as a function of the DEA concentration [Q].

Photoisomerization Yields. The presence of the amine also affects the StN photoisomerization quantum yield ϕ_C. Table III lists the values of ϕ_C at different DEA concentrations [Q] for deaerated solutions of the StN's in different solvents.

SV-type plots of $\phi_C{}^\circ/\phi_C$ against [Q] show more or less strong deviations from linearity, compared with the linear SV plots of q_{FM}/ϕ_{FM} against [Q], and their gradients are always less than K, showing that amines do not reduce ϕ_{FM} and ϕ_C proportionately. Figure 3 compares the plots of $\phi_C{}^\circ/\phi_C$ and q_{FM}/ϕ_{FM} against DEA concentration [Q] for deaerated *n*-hexane solutions of β-StN and α-StN.

Table IV compares the effective SV coefficient of photoisomerization quenching K_{QC} with the SV fluorescence quenching coefficient K for β-StN in three solvents (deaerated and aerated) quenched by DEA and triethylamine (TEA). Figure 4 presents the corresponding SV-type plots for β-StN + DEA in benzene and acetonitrile, showing the strong influence of the solvent on the behavior.

Exciplex Fluorescence. The wavenumber $\nu_{FE}{}^{max}$ of the exciplex fluorescence maximum is markedly solvent dependent, and it shifts to lower energies with increase in solvent polarity. Table V lists observations of $\nu_{FE}{}^{max}$ for the exciplexes of β-StN, α-StN, and 4-Br-α-StN with DEA in ten solvents at room temperature. The exciplex dipole moment was estimated by comparison of the effect of solvent polarizability on $\nu_{FE}{}^{max}$ for the exciplexes of the StN's and anthracene with the same donor DEA.[14] Assuming the exciplexes to have the same volume, dipole moments of about 10 D are obtained for both (α-StN + DEA) and (β-StN + DEA). Similar values have been re-

Table III. Quantum Yields of Fluorescence (ϕ_{FM}) and Photoisomerization (ϕ_C) of Deaerated Solutions of StN's as a Function of DEA Concentration ([Q], in 10^{-2} M)

Solute	Solvent	[Q]	ϕ_{FM}	q_{FM}/ϕ_{FM}	ϕ_C	ϕ_{CM}'	ϕ_{CE}'
β-StN	*n*-Hexane	0	0.71	1.00	0.12	0.12	0
		0.865	0.33	2.17	0.12	0.055	0.065
		1.72	0.21	3.32	0.12	0.036	0.083
		3.45	0.13	5.65	0.13	0.022	0.099
		6.90	0.069	10.3	0.13	0.011	0.110
	Benzene	0		1.00	0.125	0.125	0
		1.78		2.55	0.163	0.049	0.14
		3.56		4.10	0.19	0.031	0.185
		5.16		5.48	0.235	0.023	0.200
		7.12		7.18	0.235	0.017	0.210
	Acetonitrile	0	0.51	1.00	0.18	0.18	0
		0.65	0.27	1.90	0.116	0.095	0.015
		1.99	0.135	3.77	0.080	0.048	0.024
		2.99	0.10	5.15	0.060	0.035	0.027
		3.99	0.078	6.55	0.050	0.027	0.028
α-StN	*n*-Hexane	0	0.64	1.00	0.14	0.14	0
		1.95	0.38	1.68	0.20	0.083	0.094
		3.90	0.27	2.36	0.19	0.060	0.138
		7.80	0.17	3.73	0.19	0.037	0.170
	Acetonitrile	0	0.25	1.00	0.28	0.28	0
		1.53	0.175	1.43	0.215	0.195	0.021
		4.54	0.11	2.30	0.17	0.122	0.037
		7.65	0.08	3.12	0.125	0.090	0.044
4-Br-α-StN	*n*-Hexane	0	0.47	1.00	0.23	0.23	0
		2.00	0.30	1.56	0.24	0.148	0.088
		3.82	0.23	2.07	0.245	0.111	0.13
		5.00	0.196	2.40	0.24	0.096	0.148
		7.64	0.15	3.14	0.25	0.073	0.173
	Acetonitrile	0	0.30	1.00	0.28	0.28	0
		3.83	0.135	2.22	0.205	0.126	0.058
		5.75	0.105	2.84	0.170	0.099	0.072
		9.58	0.074	4.06	0.143	0.069	0.080

Table IV. Quenching of β-StN by Amines. Photoisomerization Quenching Coefficient K_{QC} (M^{-1}), from Gradient of SV Plot of $\phi_C{}^{\circ}/\phi_C$ against Amine Concentration ([Q]), Compared with SV Fluorescence Quenching Coefficient K (M^{-1})[a]

	Quencher					
	DEA		DEA[a]		TEA[a]	
Solvent	K_{QC}	K	$K_{QC}{}^a$	K^a	$K_{QC}{}^a$	K^a
n-Hexane	<0	135	6.4	76	4.5	23
Benzene	<0	87	1.4	53	3	21
Acetonitrile	65	139	65	93	16	36

[a] Superscript a = aerated solution.

ported for (anthracene + DEA),[14] (naphthalene + TEA),[15] and (fluorene + TEA)[4] exciplexes.

The exciplex fluorescence quantum yield ϕ_{FE} was observed as a function of [Q] for the (β-StN + DEA) exciplex in deaerated *n*-hexane solution. Figure 5 plots $1/\phi_{FE}$ against $1/[Q]$ for this system. A linear plot, consistent with eq 10, is obtained, apart from a slight deviation from linearity at high [Q] (this is explained below). The intercept/gradient ratio gives $K = 150\ M^{-1}$ in satisfactory agreement with the value of $K = 135\ M^{-1}$ obtained from the SV β-StN fluorescence (ϕ_{FM}) quenching data.

Linear extrapolation of the $1/\phi_{FE}$ vs. $1/[Q]$ plot (Figure 5) to $1/[Q] = 0$ gives $q_{FE} = 0.72$. The exciplex fluorescence lifetime at high [Q] is $\tau_E = 29$ ns and $\tau_E{}^a = 18$ ns in deaerated and aerated *n*-hexane solutions, respectively.

Analysis. β-StN in *n*-Hexane. Table VI collects the observed photophysical parameters for the (β-StN + DEA) system in deaerated and aerated *n*-hexane solutions. It also lists the values of the other parameters derived therefrom, using the observed parameters and the reaction kinetic relations indicated in Table VI.

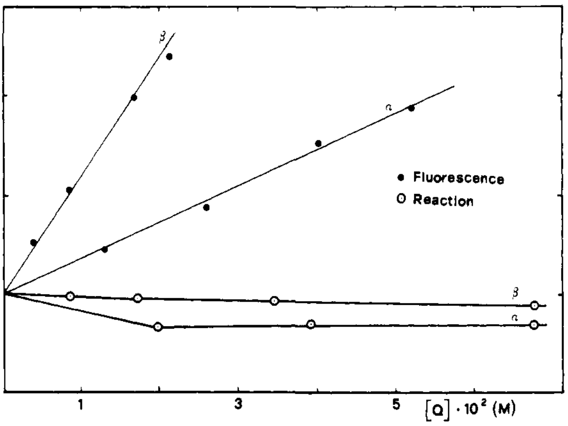


Figure 3. Stern-Volmer-type plots for fluorescence (q_{FM}/ϕ_{FM}) and photoreaction ($\phi_C{}^{\circ}/\phi_C$) quenching of *trans*-α- and β-StN's by DEA (concentration = [Q]) in deaerated *n*-hexane solutions.

At [Q] = 0 in deaerated solution, the isomerization quantum yield is

$$\phi_C{}^{\circ} = q_{CM} + q_{TM}q_{CT} \tag{14a}$$

and in aerated solution it is

$$\phi_C{}^{\circ a} = q_{CM}{}^a + q_{TM}{}^a q_{CT}{}^a \tag{14c}$$

Table V. Solvent Effect on the Wavenumber ν_{FE}^{max} of the Exciplex Fluorescence Peak of Styrylnaphthalenes + DEA at ~20 °C

Solvent	Dielectric constant (20 °C)[a]	ν_{FE}^{max} (10^4 cm^{-1}) β-StN	α-StN	4-Br-α-StN
n-Hexane	1.89	2.22	2.09	2.11
n-Heptane	1.92	2.22	2.10	2.09
Cyclohexane	2.02	2.20	2.12	2.09
Methylcyclohexane	2.02	2.15	2.10	2.07
Benzene	2.28	2.08	2.00	1.97
Toluene	2.39	2.06	2.00	1.97
Diethyl ether	4.34	2.04	1.98	1.95
Chlorobenzene	5.71	2.03	1.94	1.92
Ethyl acetate	6.09	1.94	1.88	1.87
Dichloroethane	10.65	1.92	1.85	1.82

[a] Taken from "Table of Dielectric Constants of Pure Liquids", N.B.S. Circular 514, August 1951, Washington, D.C.

Table VI. Photophysical Parameters of β-StN + DEA in *n*-Hexane at Room Temperature

Deaerated solutions			Aerated solutions		
Parameter	Value	Derivation[a]	Parameter	Value	Derivation[a]
q_{FM}	0.71	Expt	q_{FM}^a	0.36	Expt
τ_M	15 ns	Expt	τ_M^a	7.6 ns	q_{FM}, q_{FM}^a, τ_M
q_{FE}	0.72	Expt	q_{FE}^a	0.45	q_{FE}, τ_E, τ_E^a
τ_E	29 ns	Expt	τ_E^A	18 ns	Expt
K	135	Expt	K^a	76 M^{-1}	Expt
ϕ_C°	0.12	Expt	$\phi_C^{\circ\,a}$	0.31	Expt
ϕ_C^{lim}	0.12	Expt	K_{OM}	0.97	q_{FM}, q_{FM}^a (15)
k_M	6.7×10^7 s^{-1}	τ_M (3)	$k_{OM}[O_2]$	6.5×10^7 s^{-1}	K_{OM}, k_M (15)
k_{FM}	4.7×10^7 s^{-1}	q_{FM}, k_M (2)	K_{OE}	0.61	τ_E, τ_E^a (16)
k_{IM} (= $k_{TM} + k_{CM} + k_{GM}$)	2.0×10^7 s^{-1}	k_M, k_{FM} (2)	K_{OE}'	0.45	K, K^a, K_{OM} K_{OE} (19)
k_E	3.45×10^7 s^{-1}	τ_M (5)			
k_{FE}	2.5×10^7 s^{-1}	q_{FE}, k_E (4)			
k_{IE} (= $k_{TE} + k_{CE} + k_{GE}$)	9.7×10^6 s^{-1}	k_E, k_{FE} (4)			
k_{QM}	9×10^9 M^{-1} s^{-1}	K, k_M (8)			
p	0.74	K_{OE}, K_{OE}' (20)			
k_{EM}	1.22×10^{10} M^{-1} s^{-1}	k_{QM}, p (8)			
k_{ME}	1.07×10^7 s^{-1}	k_E, p (9)			

[a] Numbers in parentheses refer to equations in text.

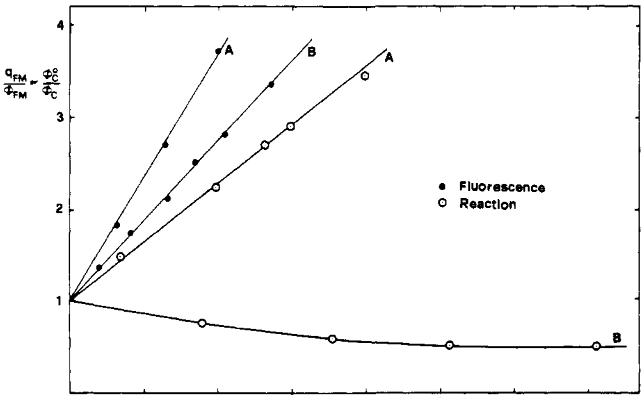


Figure 4. Stern–Volmer-type plots for fluorescence and photoisomerization quenching of *trans*-β-StN by DEA in deaerated benzene (B) and acetonitrile (A).

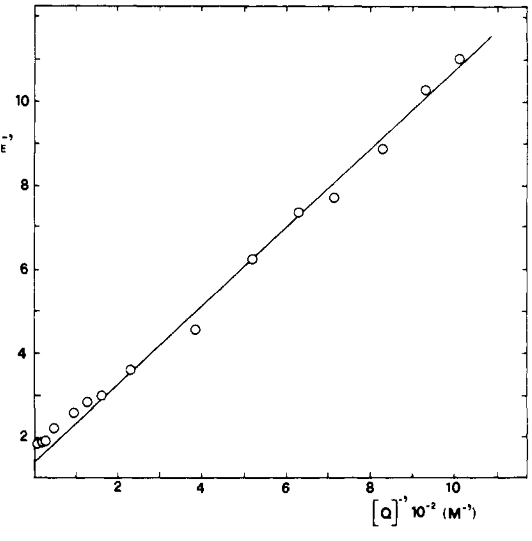


Figure 5. Dependence of the fluorescence yield for the (β-StN + DEA) exciplex on quencher concentration in deaerated *n*-hexane following eq 10.

If k_{GM} is small compared with k_{FM} and k_{TM}, as in most aromatic hydrocarbons, because of the large S_1–S_0 energy gap,[13] then

$$q_{TM} = 1 - q_{FM} - q_{CM} \tag{21}$$

$$q_{TM}^a = 1 - q_{FM}^a - q_{CM}^a \tag{21a}$$

Let us assume, as a first approximation, that oxygen has a negligible effect on q_{CT}, so that $q_{CT} = q_{CT}^a$. Elimination of q_{CM}, q_{CM}^a, q_{CT}, and q_{CT}^a from the above four equations gives

$$\frac{q_{TM}}{q_{TM}^a} = \frac{1 - q_{FM} - \phi_C^\circ}{1 - q_{FM}^a - \phi_C^{\circ a}} \tag{22}$$

Substitution of the experimental values of q_{FM}, ϕ_C°, q_{FM}^a, and $\phi_C^{\circ a}$ (Table VI) in eq 22 and of K_{OM} in eq 18 gives the following parameters: $q_{TM} = 0.33$; $q_{TM}^a = 0.66$. Comparison

Table VII. Limiting Values ($[Q] \rightarrow \infty$) of Photoisomerization Yield Induced by the Complex ($\phi_C^{\lim}$) for StN's + DEA Systems in Different Solvents

Compound	Solvent *n*-Hexane	 Acetonitrile	 Benzene
β-StN	0.12	0.03_3	0.24_5
α-StN	0.24	0.06_5	
4-Br-α-StN	0.25_5	0.106	

with $q_{FM} = 0.71$ and $q_{FM}{}^a = 0.36$ (Table VI) shows that

$$q_{FM} + q_{TM} = 1 \tag{23}$$

$$q_{FM}{}^a + q_{TM}{}^a = 1 \tag{23a}$$

within the experimental error.

It is concluded that (i) $q_{CM} = q_{CM}{}^a = 0$, i.e., the isomerization quantum yield by the singlet mechanism is insignificant; (ii) $k_{TM} = k_{IM} = 2.0 \times 10^7\ \mathrm{s}^{-1}$ (Table VI); (iii) $q_{CT} = 0.37$, from $\phi_C{}^\circ$, q_{TM}, q_{CM}, and eq 14a; (iv) $q_{CT}{}^a = 0.47$, from $\phi_C{}^{\circ a}$, q_{TM}, $q_{CM}{}^a$, and eq 14c. The finding that $q_{CT}{}^a > q_{CT}$ differs from the original assumption that these parameters were equal. Reiteration of the analysis, omitting this assumption, gives slightly modified values of $q_{CT} = 0.41$ and $q_{CT}{}^a = 0.48$.

At high [Q] the isomerization quantum yield is

$$\phi_C{}^{\lim} = q_{CE} + q_{TE}q_{CT} \tag{14b}$$

If we assume, by analogy with eq 23, that

$$q_{FE} + q_{TE} = 1 \tag{24}$$

then the following parameters are obtained.

$$q_{TE} = 0.28, \quad q_{CE} = 0$$

$$k_{TE} = k_{IE} = 9.7 \times 10^6\ \mathrm{s}^{-1}\ \text{(Table VI)}$$

$$q_{CT} = 0.46, \quad \text{from } \phi_C{}^{\lim}, q_{TE}, q_{CE}, \text{ and eq 14b}$$

This value of q_{CT} is larger than that of $q_{CT} = 0.41$ obtained for dilute solutions, but it is similar to that of $q_{CT}{}^a = 0.48$ obtained for the aerated solutions. This result indicates that CT interaction with either DEA or oxygen enhances q_{CT} from 0.41 to 0.47 (±0.01).

Triplet Isomerization Quantum Efficiencies. For β-StN in *n*-hexane solution, we obtain from eq 14a, 23, 14c, and 23a

$$q_{CT} = \phi_C{}^\circ/(1 - q_{FM}) \tag{25}$$

$$q_{CT}{}^a = \phi_C{}^{\circ a}/(1 - q_{FM}{}^a) \tag{25a}$$

These relations have been used to analyze the data for the other solutions.

The values of q_{CT} and $q_{CT}{}^a$, obtained from $\phi_C{}^\circ$, q_{FM}, $\phi_C{}^{\circ a}$, and $q_{FM}{}^a$ using eq 25 and 25a, for the other solutions are listed in Table I.

The values of $q_{CT} = 0.41$ (±0.02) for the three StN's in deaerated *n*-hexane solution agree closely, as do the values of $q_{CT} = 0.38$ (±0.02) in acetonitrile solution. This indicates that eq 23 and 25 are valid for the three StN's in these two solvents.

In *n*-hexane solution, the presence of oxygen may increase q_{CT}, as in β-StN and α-StN, or reduce q_{CT}, as in 4-Br-α-StN. In acetonitrile solution, $q_{CT}{}^a < q_{CT}$ in all three StN's.

Isomerization Quantum Yields. At intermediate [Q] from eq 13

$$\frac{\phi_C{}^\circ}{\phi_C} = \frac{1 + K[Q]}{1 + K(\phi_C{}^{\lim}/\phi_C{}^\circ)[Q]} \tag{26}$$

This relation explains why the plots of $\phi_C{}^\circ/\phi_C$ against [Q] (Figures 3 and 4) are nonlinear, and have a gradient of less than K. A more useful parameter to plot against [Q] is ($\phi_C q_{FM}/\phi_C{}^\circ\phi_{FM}$), since from eq 26

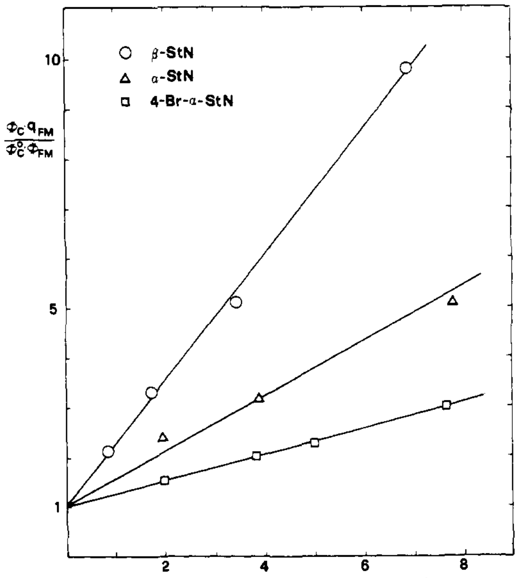


Figure 6. Linear plots for StN's in *n*-hexane following eq 27.

$$\frac{\phi_C q_{FM}}{\phi_C{}^\circ\phi_{FM}} = 1 + K(\phi_C{}^{\lim}/\phi_C{}^\circ)[Q] \tag{27}$$

which has a gradient of $K(\phi_C{}^{\lim}/\phi_C{}^\circ)$. Figure 6 shows such plots for typical systems, and Table VII lists the values of $\phi_C{}^{\lim}$ thus obtained. The values of $\phi_{CM}{}'$ and $\phi_{CE}{}'$ derived from $\phi_C{}^\circ$, $\phi_C{}^{\lim}$, K, and eq 14 are listed in Table III for the different solutions.

Discussion

There is some disagreement between the quantum yields listed in Table I and those reported in the literature.[7-9,11] This may be due to a dependence of the quantum yields on excitation wavelength, resulting from the presence of different conformers in solution.[9] The present measurements were made at a fixed excitation wavelength of 350 nm and appear to be self-consistent.

There is a marked decrease in q_{FM} in going from a nonpolar solvent (*n*-hexane) to a polar solvent (acetonitrile) (Table I). Such a solvent effect is unusual for an aromatic hydrocarbon.[13] It might be due to a specific (e.g., CT) interaction of the olefin with the polar solvent, leading to enhanced intersystem crossing (ISC). However, similar solvent effects on q_{FM} observed in solutions of *all-trans*-1,6-diphenylhexatriene (DPH) and higher diphenyl and retinol polyenes have been shown to originate in a different manner,[16] and a similar model may be applicable to the StN's, as discussed later.

As is to be expected, the effects of oxygen on q_{FM} and $\phi_C{}^\circ$ decrease with decrease in the fluorescence lifetime τ_M (Tables I and II). The oxygen solubility [O$_2$] increases by a factor of 2 in going from acetonitrile to *n*-hexane solutions, thus explaining the larger oxygen effects observed in the latter solutions (Table I).

The effect of DEA addition on the isomerization yield ϕ_C depends on the solvent (Table III). In *n*-hexane solutions there is a small increase in ϕ_C. For β-StN in benzene there is a marked increase in ϕ_C. In acetonitrile solutions there is a marked decrease in ϕ_C.

From eq 14b, taking $\phi_{CE} = 0$, we obtain

$$q_{TE} = \phi_C{}^{\lim}/q_{CT} \tag{28}$$

which may be used to estimate q_{TE} from $\phi_C{}^{\lim}$ (Table VII) assuming $q_{CT} = 0.46$ as for β-StN in *n*-hexane at high [Q]. The estimated q_{TE} values are 0.28 (β-StN), 0.52 (α-StN), and 0.57 (4-Br-α-StN) in *n*-hexane solution, and 0.09 (β-StN), 0.13 (α-StN) and 0.22 (4-Br-α-StN) in acetonitrile solution. The reduced exciplex triplet yields q_{TE} and the negligible exciplex fluorescence yields q_{FE} in the polar solutions show the presence of an efficient competitive process. This is attributed to the formation of solvent-shared ion pairs which dissociate into solvated molecular ions or decay directly to the ground state without necessarily populating the reactive triplet state.[17] It is possible that the olefin negative ion radicals participate in the isomerization mechanism, in which case the estimated q_{TE} values for the acetonitrile solutions will be too high, since they assume that the isomerization occurs only via the triplet state. This aspect will be explored further in this laboratory using laser flash photolysis.

The induction of isomerization of the StN's by exciplex formation with amines in nonpolar solvents is a good indication of the ISC path in excited CT systems.[2,18] Similar behavior has been observed in a study of the quenching of excited styrylpyridines by inorganic anions. With the best electron donor used, the iodide anion, which also had the highest atomic number, the fluorescence was strongly quenched, while the photoreaction yield remained practically constant even at high quencher concentration.[6,19]

The departure from linearity of the plot of $1/\phi_{FE}$, against $1/[Q]$ at high [Q] (Figure 5), might be due to the formation of ternary exciplexes. However, comparison with previous observations of such behavior[20] indicates that [Q] is not sufficiently high for this to be likely. The exciplex fluorescence spectra at high [Q] do not show any evidence of the formation of ternary exciplexes with a second amine molecule, but they do show a slight red shift of the fluorescence peak. A similar shift has been observed at high [Q] in the (anthracene + DEA) system,[21] and it has been shown to be due to the increasing solvent polarity on adding a polar quencher (DEA) to a nonpolar solvent. This shift accounts satisfactorily for the slight deviation from linearity of the $1/\phi_{FE}$ vs. $1/[Q]$ plot of Figure 5, since the present measurements were made at a fixed wavelength, assuming $I_{FE} \propto \phi_{FE}$.

The *trans*-StN's have been shown to isomerize via a triplet mechanism, in contrast with *trans*-stilbene which isomerizes via a singlet mechanism.[22-24] The singlet mechanism involves thermally activated S_1 internal rotation from the trans (t) to the perp (p) configuration, where efficient internal conversion (IC) occurs to the ground state S_0, leading to cis (c) isomerization.[23] This process competes efficiently with the $t(S_1)$ fluorescence ($k_{FM} = 6 \times 10^8\ s^{-1}$), reducing q_{FM} to 0.08 at room temperature (it would be even lower but for the reverse $p \rightarrow t$ internal rotation[23]), and inhibiting any $t(S_1) \rightarrow t(T_1)$ ISC. In contrast, the $S_1\ t \rightarrow p$ internal rotation appears to be negligible in t-β-StN, which isomerizes via a triplet mechanism which involves $t(S_1) \rightarrow t(T_1)$ ISC ($k_{TM} = 2 \times 10^7\ s^{-1}$) in competition with $t(S_1) \rightarrow t(S_0)$ fluorescence ($k_{FM} = 4.7 \times 10^7\ s^{-1}$), giving $q_{FM} = 0.71$. $t \rightarrow p$ internal rotation in T_1 results in $p(T_1) \rightarrow p(S_0)$ ISC, leading to $p(S_0) \rightarrow c(S_0)$ internal rotation and isomerization.[24,25]

Two main factors explain the difference in the behavior of t-stilbene and t-β-StN: (i) the large difference (by a factor of 13) in the values of k_{FM}; and (ii) the rapid $S_1\ t \rightarrow p$ internal rotation in *trans*-stilbene, and its absence in β-StN.

Due to i and ii q_{TM} for t-stilbene is negligible ($q_{TM} = 0.002$, if $k_{TM} = 2 \times 10^7\ s^{-1}$ as in β-StN), so that the triplet isomerization mechanism is insignificant, while the singlet mechanism resulting from ii is dominant.[23] In β-StN the absence of any rapid $S_1\ t \rightarrow p$ internal rotation means that ISC is the only significant process competing with the fluorescence. The low value of k_{FM} results in a relatively high value of $q_{TM} = 0.29$.

The β-StN value of $q_{CT} = 0.41 < 0.5$ indicates an asymmetry in the Franck-Condon overlap integrals of the T_1 and S_0 potentials on the t and c sides of the p (S_0) maximum. CT interaction with DEA or oxygen increases q_{CT} to 0.47 ($\pm$0.01), probably due to a reduction of the potential asymmetry. The equivalent parameter in t-stilbene[23] is $q_{CM} = 0.54$.

There are striking similarities between the fluorescence properties of β-StN and DPH. In deaerated *n*-hexane solution at room temperature, they have the following properties.

	τ_M (ns)	q_{FM}	k_{FM} ($10^7\ s^{-1}$)
β-StN	15	0.71	4.7
DPH[26]	15.7	0.64	4.1

Both compounds show a marked decrease in q_{FM} on increase of the solvent polarity.

In DPH the weak $S_1 \rightarrow S_0$ fluorescence is induced by coupling to the strong $S_2 \rightarrow S_0$ transition through the $S_2 - S_1$ energy gap ΔE.[16,27] A change in solvent polarity or temperature modifies ΔE and, hence, changes k_{FM} and q_{FM}. Extensive experimental data on DPH fluorescence in ten solvents[26] have been analyzed and shown to be quantitatively consistent with this model.[27]

In β-StN the absorption spectrum shows the $S_1 \leftarrow S_0$ transition to be weak, and the $S_2 \leftarrow S_0$ transition to be strong. By analogy to DPH, it is proposed that the $S_1 \rightarrow S_0$ fluorescence is induced by coupling to the $S_2 \rightarrow S_0$ transition through the $S_2 - S_1$ energy gap ΔE, so that k_{FM} and q_{FM} depend on the solvent polarity and temperature. This model is consistent with the available data, and further experiments are being undertaken to confirm, modify, or extend it.

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References and Notes

(1) (a) Presented in part at the Tenth National Congress of the Associazione Italiana di Chimica Fisica, Padova, October 1975; (b) on leave of absence from The Schuster Laboratory, University of Manchester, Manchester, U.K.

(2) See, e.g., R. S. Davidson in "Molecular Association", Vol. I, R. Foster, Ed., Academic Press, London, 1975, pp 215–334, and references therein.

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Photochemical Transformations. 19. Photosensitized Reactions of β-Methylallyl Chloride[1]

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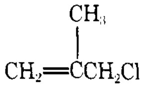
Abstract: Photochemical reactions and reactivities of β-methylallyl chloride, sensitized by acetone and by benzene, have been studied. The principal products were an isomer, 1-chloro-1-methylcyclopropane, and a dimer, 5-chloro-4-chloromethyl-2,4-dimethyl-1-pentene. Smaller amounts of other C_8 products were also found. The ratio of isomerization to dimerization was markedly dependent upon sensitizer and upon the concentration of methylallyl chloride. In acetonitrile solvent, with either sensitizer, the quantum yield of the chlorocyclopropane reached a limiting value as the concentration of allylic chloride was increased, while that of the dimer increased linearly with concentration of substrate. The results are discussed mechanistically.

The direct irradiation of allyl chloride as a neat liquid or as a solid has been shown to lead to products that can be rationalized as resulting from initial homolytic cleavage of the allylic carbon–chlorine bond.[2] Sensitized irradiation of allyl chloride and of a wide variety of substituted allylic chlorides in solution, on the other hand, has been reported to induce a 1,2-chlorine migration–cyclization reaction to yield cyclopropyl chloride or substituted cyclopropyl chlorides.[3]

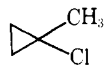
We now report an example of sensitized irradiations of an allylic chloride where the photocyclization is accompanied by products resulting from homolytic cleavage of the carbon–chlorine bond, and a study of some of the factors affecting the distribution of the several products.

Earlier work in this laboratory[3] has shown that the acetone-photosensitized rearrangement of β-methylallyl chloride (**1**) in acetonitrile gives 1-chloro-1-methylcyclopropane (**2**) in good yield. While we were working out synthetic procedures for this and for other 1-chloro-1-alkylcyclopropanes,[4] we observed a curious inverse relationship between the chemical yield of **2** and the initial concentration of **1**; this led to the study described herein.



$CH_2{=}C(CH_3)CH_2Cl$

1



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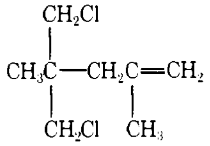
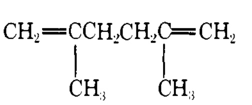


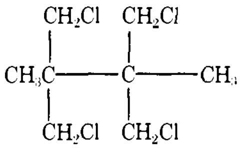
$CH_3C(CH_2Cl)_2{-}CH_2C(CH_3){=}CH_2$

3



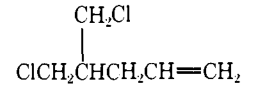
$CH_2{=}C(CH_3)CH_2CH_2C(CH_3){=}CH_2$

4



$CH_3C(CH_2Cl)_2{-}C(CH_2Cl)_2{-}CH_3$

5



$ClCH_2CH(CH_2Cl)CH_2CH{=}CH_2$

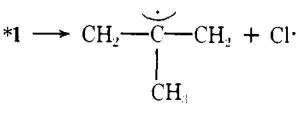
6

When moderately concentrated solutions of **1** dissolved in 20% acetone in acetonitrile (sensitizer/solvent) were irradiated, three products, in addition to **2**, were produced. They were readily separated by gas chromatography. The most abundant of these was identified by ^1H NMR and mass spectra as 5-chloro-4-chloromethyl-2,4-dimethyl-1-pentene (**3**), the known[5] dimer of **1**. Found in substantially lesser amounts than **3** were two other C_8 compounds, 2,5-dimethyl-1,5-hexadiene (**4**) and 1,4-dichloro-2,3-bis(chloromethyl)-2,3-dimethylbutane (**5**). The latter two compounds represented about 4% of the total of C_8 compounds. **4** was identified by spectral comparisons with a sample prepared by magnesium-induced coupling of **1**. **5** was identified by its mass and ^1H NMR spectra.

It seems obvious that these dimeric products are the result of radical processes involving homolysis of the carbon–chlorine bond in **1**, and their production may be interpreted (in part, at least) in a fashion similar to that for the direct irradiation of liquid and of solid allyl chloride with 254-nm light.[2] Volman and Phillips observed that, in the pure liquid, allyl chloride gave the dimer **6** in 0.13 quantum yield and 1,5-hexadiene in 0.04 quantum yield, along with a large number of other products. Thus in the simplest sense one may write the reactions in Scheme I as leading to **3**, **4**, and **5** from **1**.

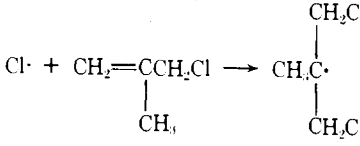
Scheme I

$$1 + {}^3S \longrightarrow {}^*1 + {}^0S \tag{1}$$



$$^*1 \longrightarrow CH_2{-}\dot{C}(CH_3){-}CH_2 + Cl\cdot \tag{2}$$

7



$$Cl\cdot + CH_2{=}C(CH_3)CH_2Cl \longrightarrow CH_3\dot{C}(CH_2Cl)_2 \tag{3}$$

8

$$7 + 7 \longrightarrow 4 \tag{4}$$

$$7 + 8 \longrightarrow 3 \tag{5}$$

$$8 + 8 \longrightarrow 5 \tag{6}$$