

Di-*tert*-butyl Nitroxide Quenching of the Photoaddition of Olefins to the Carbon–Nitrogen Double Bond of 3-Ethoxyisindolenone

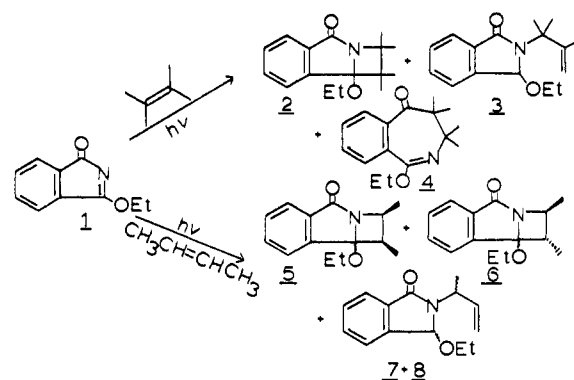
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Abstract: Quenching of the photoaddition reactions of 3-ethoxyisindolenone (**1**) to olefins by di-*tert*-butyl nitroxide (DTBN), *cis*-piperylene, and biacetyl is described. DTBN quenches product formation from photoaddition to tetramethylethylene and *cis*-2-butene differentially, whereas *cis*-piperylene and biacetyl quench formation of products from photoaddition of **1** to tetramethylethylene equally. When DTBN is employed as a quencher of the photoreactions, a portion of the DTBN is destroyed even though it is not directly excited. Products of the destruction are di-*tert*-butylhydroxylamine and di-*tert*-butylhydroxylamine ethers. The destruction appears to be unrelated to the quenching process and probably results from scavenging of radicals produced by hydrogen atom abstraction from the olefins by excited **1**. A triplet counting measurement with *cis*-piperylene as the quencher gives an intersystem crossing efficiency of 0.96 ± 0.01 and a triplet lifetime of 1.5×10^{-7} s for **1** in the absence of olefin. The quenching data are rationalized in terms of a kinetic mechanism shown in Scheme 1 which involves two nonequilibrating triplet exciplex intermediates. N- and π -type structures for the exciplexes are discussed in terms of the stereospecificity of the photoaddition reactions.

Over the past decade di-*tert*-butyl nitroxide (DTBN) has proved to be somewhat of an enigmatic quencher of electronically excited species. It and other nitroxides have been shown to quench both singlet and triplet excited states.¹⁻⁸ The mechanism of quenching is thought to be either electron exchange induced intersystem crossing or vibrational quenching where a complex deactivates directly to ground state components.^{6,7} Chapman and co-workers have reported differential quenching of the products of [2 + 2] photocycloaddition⁹ and [2 + 2] photodimerization¹⁰ of 2-cyclohexenones by DTBN. Differential quenching of photorearrangement and photoreduction of 4,4-dimethyl-2-cyclohexenone has also been observed.¹⁰ The differential quenching of these reactions has been interpreted in terms of DTBN quenching of triplet exciplex intermediates.^{10,11} Green and Singer have reported DTBN quenching of pyrene excimer fluorescence,^{12a} and Caldwell and co-workers have reported that DTBN is an efficient quencher of singlet exciplexes.^{12b} Schwerzel and Caldwell have observed that quenching of stilbene triplets by DTBN modestly favors decay to the *cis* isomer whereas azulene and other quenchers deactivate stilbene triplets to the *trans* isomer.⁷ This result has been explained in terms of electron exchange quenching of twisted stilbene triplet.^{7,12} Schuster has recently noted that DTBN is a good free-radical trapping agent and as such can quench photochemical reactions involving free-radical intermediates.¹⁴ He suggests that some of the differential quenching by DTBN observed by him and others probably results from radical scavenging rather than by deactivation of excited species.

During the past several years we have been investigating the photoaddition reactions of 3-ethoxyisindolenone (**1**) to olefins in our attempts to define structural requirements for the elusive [2 + 2]-photocycloaddition reaction of carbon–nitrogen double bonds.¹⁵ Specifically, we have reported that excited 3-ethoxyisindolenone adds to tetramethylethylene to give three products, a cycloadduct (**2**), an ene product (**3**), and an unprecedented azepinone (**4**). With *cis*- or *trans*-2-butene as the olefin, two diastereomeric cycloadducts (**5** and **6**) and two diastereomeric ene products (**7** and **8**) are formed. The cycloaddition reaction is stereorandom and the ene reaction is partially stereospecific (see Table II).¹⁵ Quenching experiments indicate that the reactions occur from a triplet state, and substituent effects in a related system suggest that cycloaddition probably occurs from a state with π, π^* configuration.¹⁶ To explain the stereochemistry for the [2 + 2]-cycloaddition



and ene reactions and the results of the quenching experiments, we proposed a 3-ethoxyisindolenone–olefin, triplet, exciplex intermediate which gives ene products with partial or complete stereospecificity and a biradical which subsequently gives ene products and [2 + 2] cycloadducts stereorandomly. We then surmised that if DTBN were able to quench the proposed triplet exciplexes in the [2 + 2]-photocycloaddition reactions of 2-cyclohexenones, it might also be able to quench the proposed triplet exciplex in our photoaddition reactions. This report describes our results with DTBN as a quencher contrasted with the diamagnetic quenchers *cis*-piperylene and biacetyl.

Results

The paramagnetic quencher, di-*tert*-butyl nitroxide, quenches product formation from photoaddition reactions of 3-ethoxyisindolenone (**1**) differentially whereas the diamagnetic quenchers, biacetyl and *cis*-piperylene, quench all products equally. As shown in Figure 1, the Stern–Volmer plots for quenching product formation from photoaddition of **1** to tetramethylethylene by DTBN are not coincident at higher DTBN concentrations, and at higher DTBN concentrations the plots for quenching ene product and azepinone are non-linear. The Stern–Volmer plots for quenching photoaddition of **1** to *cis*-2-butene (Figure 2) are linear up to 0.005 M DTBN but not coincident. The slopes of the Stern–Volmer plots for quenching cycloadduct and ene product formation from photoaddition to *cis*-2-butene are 2880 ± 35 and 3790 ± 15 L/mol, respectively (Table I). Diastereomeric cycloadducts **5** and **6** are quenched equally within experimental error, whereas the ene products **7** and **8** are quenched differentially. At 0.005 M

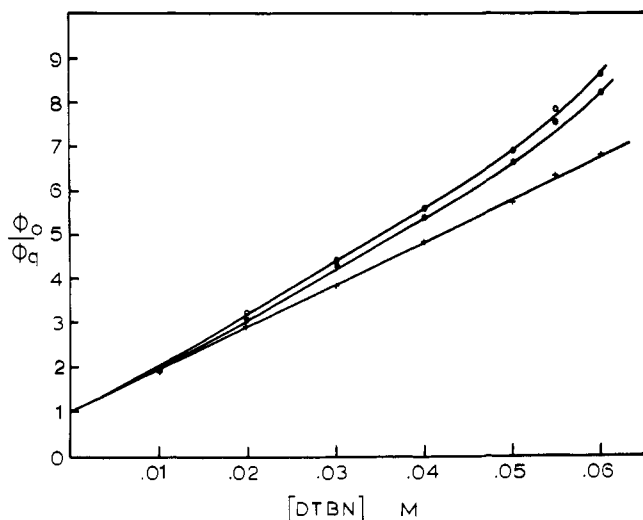


Figure 1. Stern-Volmer plot for the quenching of (+) cycloadduct **2**, (●) ene product **3**, and (○) azepinone **4** formation from photoaddition of 3-ethoxyisindolenone (**1**) to tetramethylethylene by di-*tert*-butyl nitroxide (DTBN). 3-Ethoxyisindolenone was 0.060 M and tetramethylethylene was 0.125 M in methylene chloride solvent. Solutions were irradiated with 313 nm mercury emission isolated with filters. The least-squares slope for quenching of cycloadduct **2** formation is 97.5 ± 0.5 L/mol.

Table I. Stern-Volmer Slopes for Quenching Photoaddition of **1** to Olefins^a

Olefin	Quencher (concn range, M)	Products	Slope M ⁻¹
Tetramethylethylene ^b	Tetramethyldiazetane dioxide (0-0.01)	2, 3, 4	88 ± 5^d
Tetramethylethylene ^b	Biacetyl (0-0.05)	2, 3, 4	76 ± 2
Tetramethylethylene ^b	<i>cis</i> -Piperylene (0-0.05)	2, 3, 4	132 ± 2
Tetramethylethylene ^b	Di- <i>tert</i> -butyl nitroxide (0-0.05)	2	97.5 ± 0.5
<i>cis</i> -2-Butene ^c	Di- <i>tert</i> -butyl nitroxide (0-0.005)	5, 6	2880 ± 35
<i>cis</i> -2-Butene ^c	Di- <i>tert</i> -butyl nitroxide (0-0.005)	7 + 8^e	3790 ± 15

^a Samples of 0.060 M **1** in spectrograde methylene chloride were used for all measurements. Irradiations were performed with 313-nm light isolated with solution filters (see Experimental Section). ^b The concentration of tetramethylethylene was 0.125 M. ^c The concentration of *cis*-2-butene was 0.125 M. ^d This slope was taken from ref 15. ^e Ene products **7** and **8** could not be separated by GLC and were analyzed together.

DTBN the diastereomeric ene product ratio is 2.4 compared with an ene product ratio of 3.1 in the absence of the quencher¹⁵ (see Table II). Less than 1% of the *cis*-2-butene was isomerized to *trans*-2-butene during the course of the reaction in the presence or absence of DTBN. The slopes of the Stern-Volmer plots for quenching photoaddition to *cis*-2-butene are substantially higher than the slope of the linear Stern-Volmer plot (97.5 ± 0.5 L/mol) for quenching [2 + 2] photocycloaddition to tetramethylethylene by DTBN (Table I). With the diamagnetic quenchers, biacetyl and *cis*-piperylene, the photoproducts from addition of **1** to tetramethylethylene are quenched equally, and the Stern-Volmer plots are linear up to 0.05 M quencher with slopes of 76 ± 2 and 132 ± 2 L/mol, respectively (Table I). All quantum yield experiments were designed to ensure that the photoproducts and DTBN received no light. Also the ene products have been shown to be photostable.

A triplet counting plot¹⁷ of the reciprocal of the quantum yield for *cis*-*trans* isomerization of *cis*-piperylene vs. reciprocal

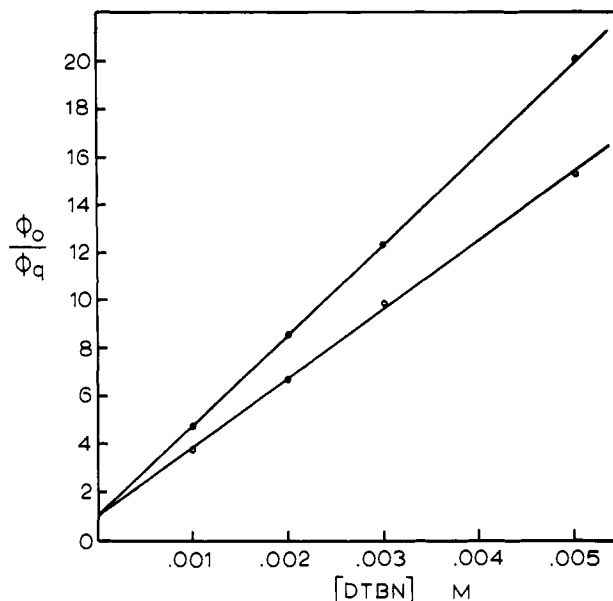


Figure 2. Stern-Volmer plot for quenching of (○) cycloadduct **5, 6** and (●) ene product **7 + 8** formation from photoaddition of 3-ethoxyisindolenone (**1**) to *cis*-2-butene by di-*tert*-butyl nitroxide (DTBN). 3-Ethoxyisindolenone was 0.060 M and *cis*-2-butene was 0.125 M in methylene chloride solvent. Solutions were irradiated with 313 nm mercury emission isolated with filters. The least-squares slopes for quenching cycloadduct **5, 6** formation and ene product **7 + 8** formation are 2880 ± 35 and 3790 ± 15 L/mol, respectively.

Table II. The Effect of Olefin Stereochemistry and DTBN on Product Ratios

Olefin ^a	Concn of DTBN, mol/L	5/6 ^b	7/8 ^c	(5 + 6) ^b / (7 + 8)
<i>cis</i> -2-Butene ^d	0	2.0 ± 0.1	3.1 ± 0.1	0.72 ± 0.01
<i>trans</i> -2-Butene ^d	0	2.1 ± 0.1	0.69 ± 0.04	1.7 ± 0.1
<i>cis</i> -2-Butene	0.005	2.0 ± 0.1	2.4 ± 0.1	1.1 ± 0.1

^a Less than 1% of the *cis*-2-butene was isomerized to *trans*-2-butene during the course of the irradiations. ^b Cycloadduct ratios and cycloadduct to ene product ratios were measured by GLC. ^c Ene product ratios were measured by NMR. ^d These data were taken from ref 15.

of *cis*-piperylene concentration is linear with a slope of 0.0016 ± 0.0004 mol/L and an intercept of 1.89 ± 0.02 . The triplet counting experiment was performed over the range 0.0167–0.100 M *cis*-piperylene at 0.060 M 3-ethoxyisindolenone. No tetramethylethylene was used because it interfered with the GLC analysis of the *cis*-*trans* isomerization of piperylene.

When di-*tert*-butyl nitroxide was employed as a quencher of photoaddition of **1** to tetramethylethylene and *cis*-2-butene, some of the DTBN was destroyed. Irradiation of an argon degassed 3.0-mL sample of 0.060 M 3-ethoxyisindolenone, 0.125 M tetramethylethylene, and 0.050 M di-*tert*-butyl nitroxide with 16.6×10^{19} quanta at 313 nm destroyed 13% of the DTBN as measured by visible spectroscopy at 448 nm. In this experiment all of the incident quanta were absorbed by 3-ethoxyisindolenone (**1**) and no more than 15% of **1** was destroyed. Oxygen purging of the irradiated sample restored 47% of the destroyed DTBN. Regeneration of di-*tert*-butyl nitroxide with oxygen suggests that a product of the photo-reaction is di-*tert*-butylhydroxylamine.¹⁸⁻²⁰ A preparative irradiation of **1** plus tetramethylethylene and DTBN yielded

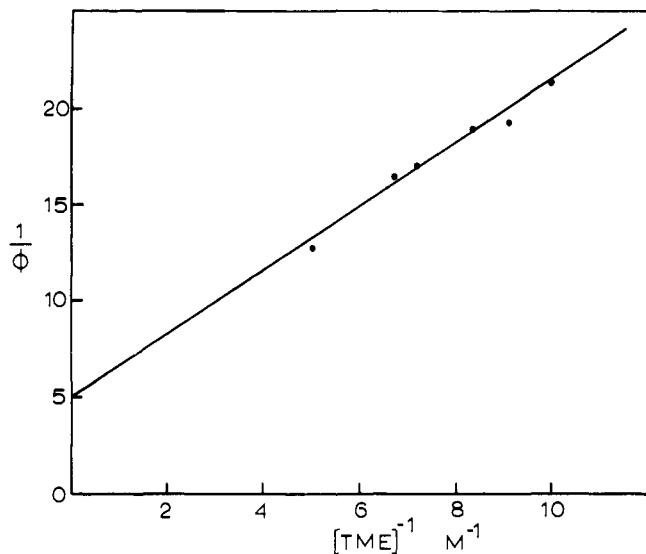
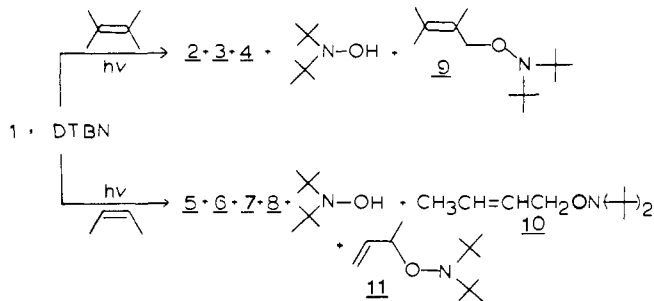


Figure 3. Plot of reciprocal of the quantum yield of di-*tert*-butyl nitroxide (DTBN) destruction vs. reciprocal of tetramethylethylene concentration. Solutions were 0.060 M 3-ethoxyisindolenone and 0.050 M DTBN in methylene chloride solvent and were irradiated with the 313 nm mercury emission isolated with a monochromator. The least-squares slope and intercept are 1.65 ± 0.13 mol/L and 5.0 ± 1.0 , respectively.

14% of 1-(2,3-dimethyl-2-butenyl)-*N,N*-di-*tert*-butylhydroxylamine ether (**9**) characterized by the spectroscopic and



analytical data described in the Experimental Section. A similar preparative irradiation of **1** in the presence of *cis*-2-butene and DTBN yielded two *cis*-2-butene di-*tert*-butyl nitroxide adducts. 1-(2-Butenyl)-*N,N*-di-*tert*-butylhydroxylamine ether (**10**) was isolated in 1% yield, and 3-(1-butenyl)-*N,N*-di-*tert*-butylhydroxylamine ether (**11**), in 2.4% yield. These products were separated by medium-pressure silica gel liquid chromatography and characterized from spectroscopic and analytical data. The stereochemistry of **10** could not be unambiguously assigned from the NMR spectrum. Formation of the di-*tert*-butylhydroxylamine ethers suggests that allyl radicals are formed and trapped by DTBN during the irradiations. Scavenging of radicals by nitroxides to give hydroxylamine ethers is well documented.²¹

The quantum yield of destruction of DTBN was measured as a function of tetramethylethylene concentration. A plot of the reciprocal of the quantum yield of DTBN destruction vs. reciprocal of tetramethylethylene concentration (Figure 3) is linear with a slope of 1.65 ± 0.13 mol/L and an intercept of 5.0 ± 1.0 .

In contrast with DTBN, piperylene and biacetyl were not destroyed when employed as quenchers of the photoaddition of **1** to tetramethylethylene. Furthermore, piperylene was not destroyed when used in the triplet counting experiment.

The quantum yields for product formation from photoaddition of 3-ethoxyisindolenone to tetramethylethylene have been remeasured with improved control of wavelength and improved analytical technique and are reported in Table III.

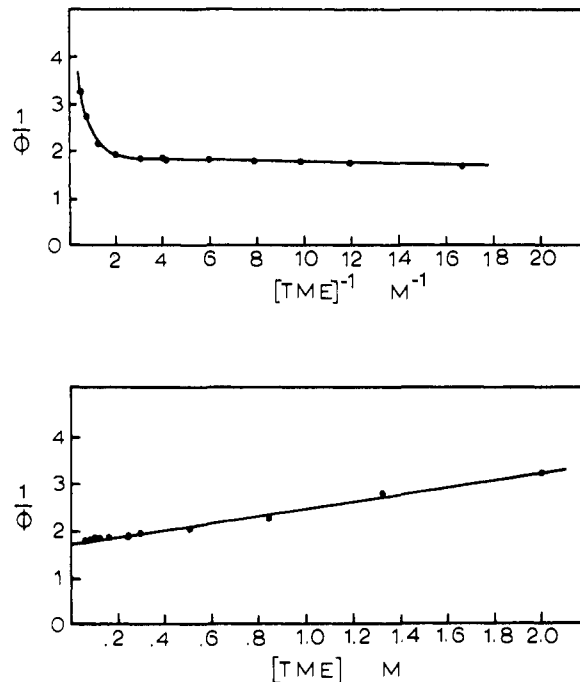


Figure 4. Plots of reciprocal of total quantum yield of product formation (**2** + **3** + **4**) vs. tetramethylethylene concentration and reciprocal of tetramethylethylene concentration. Solutions were 0.060 M 3-ethoxyisindolenone in methylene chloride solvent and were irradiated with the 313 nm mercury emission isolated with filters. The least-squares slope and intercept for the linear plot are 0.80 ± 0.03 L/mol and 1.63 ± 0.02 , respectively.

Table III. Quantum Yield of Photoaddition of 3-Ethoxyisindolenone to Tetramethylethylene as a Function of Tetramethylethylene Concentration^a

[Tetramethylethylene], mol/L	ϕ cyclo-adduct 2	ϕ aze-pinone 4	ϕ ene product 3
0.064	0.23	0.13	0.23
0.085	0.23	0.13	0.22
0.102	0.23	0.13	0.21
0.127	0.23	0.13	0.21
0.169	0.23	0.13	0.20
0.250	0.23	0.12	0.20
0.254	0.22	0.13	0.20
0.330	0.22	0.12	0.19
0.508	0.21	0.12	0.18
0.847	0.19	0.10	0.16
1.33	0.14	0.082	0.14
2.00	0.12	0.071	0.11

^a Solutions were 0.060 M 3-ethoxyisindolenone in methylene chloride solvent and were irradiated with 313-nm mercury emission isolated with filters.

Product ratios are still independent of olefin concentration, and at the higher olefin concentrations olefin still appears to quench photoaddition. Plots of reciprocal of total quantum yield of product formation vs. tetramethylethylene concentration and reciprocal of tetramethylethylene concentration are shown in Figure 4. The previously reported quantum yields for photoaddition of **1** to 1,1-dimethoxyethene,¹⁵ which yields a single product, 3,4-benzo-6,6-dimethoxy-5-ethoxyazabicyclo-[3.2.0]hept-3-en-2-one, were similarly corrected. The slopes and intercepts of the linear plots of reciprocal of quantum yield vs. olefin concentration are summarized in Table IV. With these corrections the two plots of reciprocal of quantum yield vs. olefin concentration no longer have identical intercepts as reported earlier.¹⁵

In the Experimental Section we report an improved technique for the preparation of 3-ethoxyisindolenone via O-

Table IV. Slopes and Intercepts of Plots of Reciprocal of Quantum Yield vs. Olefin Concentration^a

Olefin	Concn range, mol/L	Slope, L/mol	Intercept
Tetramethylethylene	0.064–2.00	0.80 ± 0.03	1.63 ± 0.02
1,1-Dimethoxyethene	0.060–2.00	0.32 ± 0.03	1.36 ± 0.03

^a Samples 0.060 M in **1** in spectrograde methylene chloride were used for all measurements.

alkylation of the silver salt of phthalimide. With the experimental modifications the isolated yield of **1** has been increased from 59% to 84%.

Discussion

A suitable mechanism for photoaddition of 3-ethoxyisoindolenone to olefins must account for (1) quenching by the olefins (Figure 4, Table IV), (2) the stereochemistry of the additions (Table II), (3) quenching by diamagnetic quenchers (Table I), (4) the triplet counting experiment, (5) quenching by DTBN (Figures 1 and 2, Table I), and (6) destruction of DTBN (Figure 3).

The corrected quantum yields for photoaddition as a function of olefin concentration are still consistent with olefin quenching of the singlet state and addition to the triplet state of **1**.¹⁵ As discussed in our earlier report, the fact that plots of reciprocal of quantum yield of addition vs. olefin concentration are linear suggests that all triplets are captured by olefin in the olefin concentration range examined in competition with unimolecular decay.¹⁵ Inefficiency in reaction of 3-ethoxyisoindolenone triplets with olefin would impart upward curvature to the plot of ϕ^{-1} vs. tetramethylethylene concentrations in the low olefin concentration region (see Figure 4). The intercepts of these linear plots with tetramethylethylene and 1,1-dimethoxyethene as the olefins are not equal (Table IV) and are larger than the reciprocal of the intersystem crossing efficiency ($\phi_{isc}^{-1} = 1.04$, vide infra). These observations, together with the observation that the maximum quantum yield for all reactions observed with tetramethylethylene is significantly less than the intersystem crossing efficiency, suggests that there is one or more energy-wasting process after interception of the triplet state of **1** by tetramethylethylene.

The lack of stereospecificity in the cycloaddition reaction and the partial stereospecificity in the ene reaction (Table II) indicate that at least a portion of the ene reaction occurs via a different reaction pathway than the pathway leading to cycloadducts. A probable intermediate in the pathway to cycloadducts is a long-lived biradical which randomizes olefin stereochemistry. The long-lived biradical may also be an intermediate in the stereorandom component of the ene reaction.

Quenching of the photoaddition of 3-ethoxyisoindolenone to tetramethylethylene by biacetyl and *cis*-piperylene most likely occurs by triplet energy transfer from the triplet state of **1**. The slopes of the Stern–Volmer plots (Table I) with these quenchers compare favorably with the previously reported slope for quenching by 3,3,4,4-tetramethyl-1,2-diazetane 1,2-dioxide,¹⁵ and no differential quenching of products is observed. Diazetane dioxide is reported by Ullman and Singh not to be an effective singlet quencher.²²

The intercept of the triplet counting plot, with *cis*-piperylene as the quencher and 3-ethoxyisoindolenone as the sensitizer, gives an intersystem crossing efficiency for **1** of 0.96 ± 0.01 in the absence of olefin. The triplet lifetime for **1** times the rate constant for triplet quenching ($\tau_{T1}k_{qt}$) calculated from the triplet counting data is 1200 L/mol. Assuming that the rate

Table V. Lifetimes of Intermediates

Intermediate and conditions	Data used	Lifetime, s
Singlet state (τ_S) ^a	Olefin quenching plot Figure 4, Table IV	2×10^{-10}
Triplet state (τ_{T1}) ^b absence of olefin	Triplet counting data	1.5×10^{-7}
Triplet state (τ_{T2}) ^b presence of 0.125 M TME	Stern–Volmer plot with <i>cis</i> -piperylene, Table I	1.6×10^{-8}
Exciplex 1 with <i>cis</i> -2-butene ^c (τ_{c1})	Stern–Volmer plot with DTBN, Figure 2, Table I	$>3.6 \times 10^{-7}$
Exciplex 2 with <i>cis</i> -2-butene ^b (τ_{c2})	Stern–Volmer plot with DTBN, Figure 2, Table I	3.6×10^{-7}

^a The singlet lifetime was calculated using a rate of $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for k_{sq} . The rate of olefin singlet quenching was estimated from the rate of 1,1-dimethoxyethylene quenching of the singlets of diphenylvinylene carbonate³¹ and the fact that the rate constant for quenching singlets of **1** by tetramethylethylene is twice as large as the rate constant for quenching singlets of **1** by 1,1-dimethoxyethylene (calculated from the slopes and intercepts in Table IV). ^b Rates of triplet and exciplex quenching were assumed to be equal to the rate of diffusion at 20 °C in methylene chloride.²³ ^c Because of the complexity of the kinetics, the lifetime of E₁ could not be calculated; however, it is longer than the lifetime of E₂.

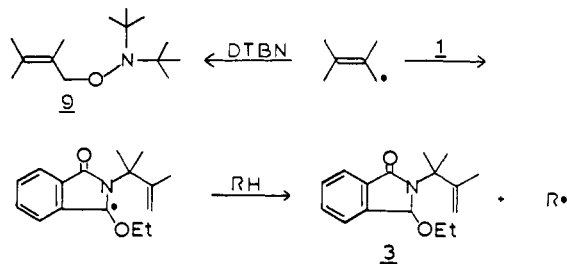
of triplet energy transfer to *cis*-piperylene is diffusion controlled in methylene chloride solvent at 20 °C ($8 \times 10^9 \text{ L/mol s}^{23}$), the lifetime (τ_{T1}) of the triplet state of **1** is $1.5 \times 10^{-7} \text{ s}$ in the absence of olefin. The slope of the Stern–Volmer plot for quenching photoaddition to tetramethylethylene by *cis*-piperylene (Table I) gives a τ_{T2} of $1.6 \times 10^{-8} \text{ s}$ in the presence of 0.125 M tetramethylethylene (see Table V for a summary of the lifetimes of various intermediates). The effect of tetramethylethylene on the triplet lifetime of **1** confirms the conclusion made earlier that tetramethylethylene efficiently captures the triplet state of **1** in competition with unimolecular decay.

Differential quenching by di-*tert*-butyl nitroxide is consistent with quenching of intermediates of different lifetimes or at different rates. The Stern–Volmer plots (Figure 1) for DTBN quenching of the photoaddition of **1** to tetramethylethylene suggest that DTBN is quenching the triplet state of **1** as well as a subsequent intermediate leading to the ene product (**3**) and the azepinone (**4**) but not to the cycloadduct (**2**). The triplet state is implicated as one of the intermediates quenched, from the similarity of the slopes of the Stern–Volmer plots with diamagnetic quenchers (Table I). Although DTBN is known to quench singlet states very efficiently,⁸ quenching of the singlet state of **1** is probably not competitive with intersystem crossing. The intersystem crossing rate constant is estimated at $5 \times 10^9 \text{ s}^{-1}$ from the estimated singlet lifetime (Table V). The rate of diffusion²³ in methylene chloride at 20 °C times the highest concentration of DTBN employed is only $5 \times 10^8 \text{ s}^{-1}$.

The Stern–Volmer plot for DTBN quenching of photoaddition to *cis*-2-butene (Figure 2) is consistent with the quenching of longer lived parallel intermediates, not the triplet state of **1**, leading to ene products and cycloadducts, respectively. Quenching of a common intermediate such as the triplet state of **1**, alone or together with one or more additional intermediates, would not give the linear, noncoincident Stern–Volmer plots (Figure 2).

The observation that DTBN is partially destroyed with formation of di-*tert*-butylhydroxylamine and di-*tert*-butylhydroxylamine ethers when employed as a quencher of the photoaddition reactions of **1** implicates DTBN as a free-

radical scavenger as noted by Schuster.¹⁴ Free-radical scavenging could result in differential quenching of product formation and unusual Stern-Volmer behavior. DTBN could scavenge an allyl radical which might be an intermediate in formation of the ene type products. However, this possibility does not seem likely in at least two respects. The regiochemistry of the free-radical addition reaction required to generate **3**



appears to be kinetically and thermodynamically unfavorable and is contrary to the regiochemistry of radical scavenging by DTBN. The efficiency of quenching by DTBN is not related to the efficiency of its destruction. DTBN quenches photoaddition of **1** to *cis*-2-butene approximately 30 times more efficiently than addition of **1** to tetramethylethylene; however, four times more DTBN is destroyed with tetramethylethylene as the olefin than with *cis*-2-butene as the olefin. In fact with *cis*-2-butene as the olefin, the destruction of DTBN is insignificant. This observation suggests that the destruction of DTBN occurs in parallel with the quenching by DTBN and is not related to the quenching.

The di-*tert*-butylhydroxylamine and di-*tert*-butylhydroxylamine ethers probably result from DTBN scavenging of radicals produced by hydrogen atom abstraction from the olefins by excited 3-ethoxyisindolenone (**1**). The observed destruction of DTBN as a function of olefin structure is consistent with this mechanism. Based upon allyl radical stability and the statistical factor, excited 3-ethoxyisindolenone should abstract hydrogen atoms more rapidly from tetramethylethylene than from *cis*-2-butene.

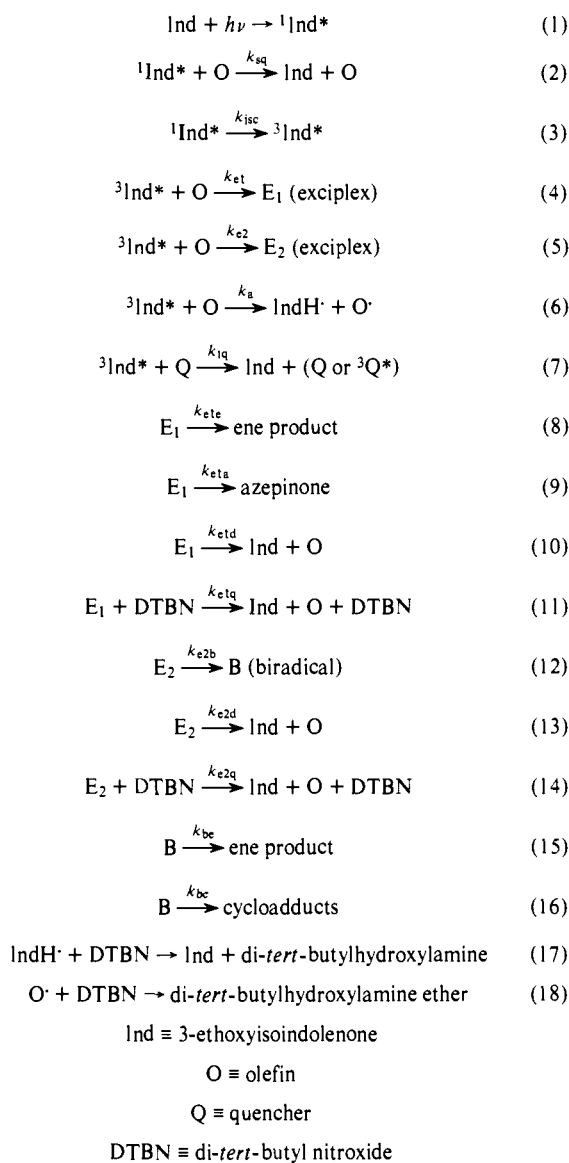
An alternate mechanism for generation of the appropriate radicals would be direct hydrogen atom abstraction by excited DTBN followed by radical scavenging. Electronically excited nitroxides, other than DTBN, have been reported to abstract hydrogen atoms intramolecularly and intermolecularly.^{19,24} Presumably, DTBN is not excited by energy transfer from excited **1**,^{6,7} although the process would be exothermic. The first excited doublet state of DTBN lies only 53 kcal/mol above the ground state.¹ A control experiment, however, in which a 3.0-mL sample of 0.050 M DTBN was irradiated at 448 nm with 16.6×10^{19} quanta in the presence of 0.125 M tetramethylethylene in methylene chloride solvent resulted in no destruction of DTBN.

Another possibility for an intermediate, quenchable by DTBN, is a biradical. Long-lived 1,4 biradicals are likely intermediates for the stereorandom cycloaddition reaction and the stereorandom portion of the ene reaction. Triplet 1,4 biradicals from Norrish type II reactions of ketones have been trapped with alkyl thiols,²⁵ hydrogen bromide,²⁶ methyl methacrylate,²⁷ and di-*tert*-butyl selenoketone²⁸ and have lifetimes in the range of 10^{-5} to 10^{-7} s.^{26,28,29} DTBN quenching of the 1,4-biradical intermediate, however, seems unlikely for several reasons. If DTBN significantly quenches the biradical intermediate, cycloaddition should be quenched in preference to ene type addition since at least a portion of the ene reaction does not occur via a long-lived biradical. In fact the opposite result is observed. The ene type addition is quenched in preference to cycloaddition (see Figures 1 and 2). DTBN quenching of the biradical intermediate should increase the stereospecificity of the ene reaction rather than decrease it (see Table II). DTBN quenching of the biradical interme-

diates to starting materials should result in some isomerization of *cis*-2-butene to *trans*-2-butene. The rate of quenching by DTBN at 0.005 M concentration if diffusion controlled is only 4×10^7 s⁻¹ which should be slow relative to the rate of bond rotation.³⁰ As stated earlier, less than 1% of the *cis*-2-butene was isomerized to *trans*-2-butene during irradiations in the presence of 0.005 M DTBN.

Since the intermediacy of the singlet state of **1**, the triplet state of **1**, allyl radicals, and 1,4 biradicals appears to be insufficient to explain the data, we propose two DTBN-quenchable nonequilibrating triplet exciplexes as additional intermediates. A kinetic mechanism employing two discrete triplet exciplexes, one leading to ene products with at least partial stereospecificity and to azepinone, and the other leading to a biradical which subsequently gives cycloadducts and ene products stereorandomly, is shown in Scheme I. Quenching

Scheme I



of the isindolenone triplet state (step 7) is significant with biacetyl, *cis*-piperylene, and DTBN as quenchers of photoaddition to tetramethylethylene. Quenching of E_1 by DTBN (step 11) occurs during the photoaddition to tetramethylethylene at higher DTBN concentrations and during the photoaddition to *cis*-2-butene in the presence of DTBN. Quenching of E_2 by DTBN (step 14) only occurs during the photoaddition to *cis*-2-butene. Steps 6, 17, and 18, involved in the destruction of DTBN, are only significant in the pho-

rereaction of **1** with tetramethylethylene. This mechanism then differs from our previously proposed mechanism for photoaddition by the intermediacy of a second triplet exciplex.¹⁵

Kinetic expressions for quantum yields are shown in Chart I. Although some of the kinetic expressions are complex, they

Chart I. Quantum Yield Expressions

- (a) $\phi_{isc} = \frac{k_{isc}}{k_{isc} + k_{sq}[O]}$ intersystem crossing efficiency
 (b) ϕ (cycloadduct from addition to tetramethylethylene) = $\frac{\phi_{isc}\tau_{T2}k_{e2}[O]\tau_{e2}k_{e2b}(1-\alpha)}{1 + \tau_{T2}k_{iq}[Q]}$
 (c) ϕ_0/ϕ_q (cycloadduct from addition to tetramethylethylene) = $\frac{\phi_{isc}\tau_{T2}k_{e1}[O]\tau_{e1}k_{e1a}}{(1 + \tau_{T2}k_{iq}[Q])(1 + \tau_{e1}k_{e1q}[Q])}$ Q \equiv DTBN
 (d) ϕ (azepinone from addition to tetramethylethylene) = $\frac{\phi_{isc}\tau_{T2}k_{e1}[O]\tau_{e1}k_{e1a}}{(1 + \tau_{T2}k_{iq}[Q])(1 + \tau_{e1}k_{e1q}[Q])}$
 (e) ϕ_0/ϕ_q (azepinone from addition to tetramethylethylene) = $\frac{\phi_{isc}\tau_{T2}k_{e1}[O]\tau_{e1}k_{e1a}}{(1 + \tau_{T2}k_{iq}[Q])(1 + \tau_{e1}k_{e1q}[Q])}$ Q \equiv DTBN
 (f) ϕ (ene product from addition to tetramethylethylene) = $\frac{\phi_{isc}(\tau_{T2}k_{e1}[O]\tau_{e1}k_{e1e} + \tau_{T2}k_{e2}[O]\tau_{e2}k_{e2b}\alpha)}{(1 + \tau_{T2}k_{iq}[Q])(1 + \tau_{e1}k_{e1q}[Q])}$
 (g) ϕ_0/ϕ_q (ene product from addition to tetramethylethylene) = $\frac{\phi_{isc}(\tau_{T2}k_{e1}[O]\tau_{e1}k_{e1e} + \tau_{T2}k_{e2}[O]\tau_{e2}k_{e2b}\alpha)}{(1 + \tau_{T2}k_{iq}[Q])(1 + \tau_{e1}k_{e1q}[Q])}$ \times

$$\left(\frac{k_{e1}k_{e1e}(k_{e2b} + k_{e2d}) + k_{e2}k_{e2b}\alpha(k_{e1e} + k_{e1a} + k_{e1d})}{k_{e1}k_{e1e}(k_{e2b} + k_{e2d}) + k_{e2}k_{e2b}\alpha(k_{e1e} + k_{e1a} + k_{e1d} + k_{e1q}[Q])} \right)$$

Q \equiv DTBN

- (h) ϕ^{-1} (destruction of DTBN) = $\frac{1}{2} \left(\frac{k_{e1} + k_{e2} + k_a}{k_a} + \frac{k_{iq}[Q]}{k_a[O]} + \frac{(k_{e1} + k_{e2} + k_a)k_{sq}[O]}{k_a k_{isc}} + \frac{k_{sq}k_{iq}[Q]}{k_a k_{isc}} \right)$

if $k_{isc} \gg k_{sq}[O]$

$$= \frac{1}{2} \left(\frac{k_{e1} + k_{e2} + k_a}{k_a} + \frac{k_{sq}k_{iq}[Q]}{k_a k_{isc}} + \frac{k_{iq}[Q]}{k_a[O]} \right)$$

- (i) ϕ_0/ϕ_q (cycloadduct from addition to *cis*-2-butene) = $\frac{1 + \tau_{e2}k_{e2q}[Q]}{1 + \tau_{e2}k_{e2q}[Q]}$ Q \equiv DTBN
 (j) ϕ_0/ϕ_q (ene product from addition to *cis*-2-butene) = $\frac{(k_{e1q}k_{e1e}k_{e1e}\tau_{e1}(k_{e2b} + k_{e2d} + k_{e2q}[Q]) + k_{e2q}k_{e2e}k_{e2b}\alpha\tau_{e2}(k_{e1e} + k_{e1d} + k_{e1q}[Q]))[Q]}{k_{e1}k_{e1e}(k_{e2b} + k_{e2d} + k_{e2q}[Q]) + k_{e2}k_{e2b}\alpha(k_{e1e} + k_{e1d} + k_{e1q}[Q])}$

if $k_{e1q}[Q] \gg k_{e1e} + k_{e1d}$ and $k_{e2q}[Q] \gg k_{e2b} + k_{e2d}$

$$= 1 + \frac{k_{e1}k_{e1e}\tau_{e1} + k_{e2}k_{e2b}\alpha\tau_{e2}}{k_{e1}k_{e1e}k_{e2q} + k_{e2}k_{e2b}\alpha k_{e1q}} k_{e1q}k_{e2q}[Q]$$

Q \equiv DTBN

- (k) ϕ (total adduct formation from addition to tetramethylethylene) = $\left(\frac{k_{isc}}{k_{isc} + k_{sq}[O]} \right) \left\{ \left(\frac{k_{e1}}{k_{e1} + k_{e2} + k_a} \right) \left(\frac{k_{e1e} + k_{e1a}}{k_{e1e} + k_{e1a} + k_{e1d}} \right) + \left(\frac{k_{e2}}{k_{e1} + k_{e2} + k_a} \right) \left(\frac{k_{e2b}}{k_{e2b} + k_{e2d}} \right) \right\}$

$$\alpha = \frac{k_{bc}}{k_{be} + k_{bc}} \quad \tau_{T2} = \text{triplet lifetime in the presence of olefin}$$

$$\tau_{e1} = \text{lifetime of } E_1 \quad \tau_{e2} = \text{lifetime of } E_2$$

fit the data remarkably well. In two cases (h and j) appropriate simplifying assumptions are made based upon the experimental conditions. Expressions e and g are consistent with the non-linear, noncoincident, Stern-Volmer plots shown in Figure 1 for quenching of ene product (**3**) and azepinone (**4**) formation by DTBN. Furthermore, the expressions predict, as observed, that azepinone formation should be quenched more efficiently than ene product formation because expression e differs from expression g by a factor less than 1. The expression h for the reciprocal of the quantum yield of destruction of DTBN simplifies to an equation linear in reciprocal of olefin concentration (Figure 3) with the assumption that k_{isc} is significantly larger than $k_{sq}[O]$. This assumption is valid in the olefin concentration region examined (see Table III and Figure 4). The simplified expression h indicates that the slope over the intercept of the plot of reciprocal of quantum yield of DTBN

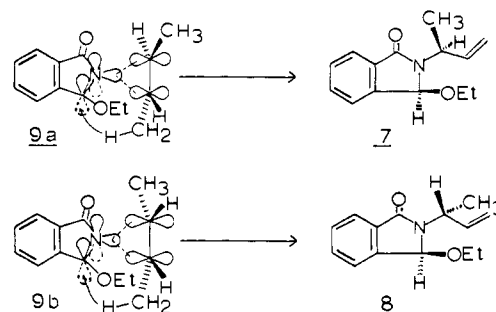
destruction vs. reciprocal of olefin concentration at constant DTBN concentration equals $(k_{e1} + k_{e2} + k_a)/k_{iq}[Q] + (k_{sq}/k_{isc})$. This expression can be evaluated from the slope of the Stern-Volmer plot for quenching formation of photocycloadduct (**2**) by DTBN (expression c) and from the slope over the intercept of the plot of reciprocal of total quantum yield for adduct formation vs. tetramethylethylene concentration (expression k). The calculated value for the expression $(k_{e1} + k_{e2} + k_a)/(k_{iq}[Q] + (k_{sq}/k_{isc}))$ is 2.25 ± 0.02 L/mol which agrees quite well with the slope over the intercept of the plot of reciprocal of quantum yield of DTBN destruction vs. reciprocal of olefin concentration (3.0 ± 0.7 L/mol). This analysis shows that three separate quantum yield measurements are internally consistent with the proposed mechanism. The Stern-Volmer expression (j) for quenching of the formation of ene products from addition to *cis*-2-butene by DTBN is complex in DTBN concentration. However, assuming that the major event, in the concentration region of DTBN examined, is exciplex quenching results in an expression linear in DTBN concentration. This assumption can be made because of the very large Stern-Volmer slopes.

The observation that DTBN reduced the stereospecificity of the ene reaction is also explicable in terms of the kinetic mechanism and the slopes of the Stern-Volmer plots. DTBN quenches E_1 , the exciplex leading to ene products with stereospecificity, more efficiently than E_2 , the exciplex leading to ene products stereorandomly.

From the quantum yield data and the kinetic expressions in Chart I, the lifetimes of some of the intermediates can be estimated and are shown in Table V. The lifetimes of the triplet state and the lifetimes of the exciplexes were calculated with the assumption that quenching occurs at a diffusion controlled rate. If this assumption is not correct, these lifetimes represent lower limits.

It is interesting to speculate on possible structures for two nonequilibrating, triplet, exciplex intermediates. The possibility of *n*- and π -type exciplexes is attractive.³² An *n*-type exciplex utilizing the nitrogen nonbonding orbital could react stereospecifically in an ene reaction. The degree of stereospecificity would depend upon the reactivity of the exciplex as a function of conformation. If the exciplex reacted exclusively when the olefin π system was coplanar with the σ framework of **1** as shown in Scheme 11, *trans*-2-butene would give **7** and *cis*-2-

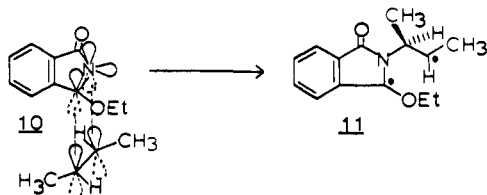
Scheme 11. A Stereospecific Ene Reaction from an *n*-Type Exciplex with the Olefin π Structure Coplanar with the σ Framework of 3-Ethoxyisindolenone



butene would give **8**. Analogous reactivity of an *n*-type exciplex from a conformation in which the olefin π system was orthogonal to the σ framework of **1** would give the opposite stereochemistry. If both conformations were reactive, but unequally, partial stereospecificity would be observed. The point of intersystem crossing of an *n*-type triplet exciplex would also be critical to the stereospecificity of the ene reaction, and only a short-lived biradical would be a possible additional intermediate. Complete stereospecificity in a triplet rearrange-

ment has been reported by Coffin, Givens, and Carlson.³³ The azepinone product (**4**) observed only with tetramethylethylene as the alkene could also arise from the *n*-type exciplex by participation of the carbonyl-carbon nitrogen σ bond. The steric effect of four methyl groups might enhance the reaction of the exciplex leading to azepinone relative to the reaction leading to ene product.

The second exciplex (E_2) might be a π -type exciplex such as **10** which could collapse to a long-lived biradical (**11**) ul-



imately giving cycloadducts and ene products stereorandomly.

Participation of an *n*-type exciplex such as **9a** or **9b** in the photochemistry of **1** implicates a partially vacant nonbonding orbital on nitrogen in the reaction excited state. At present we have no evidence toward a configurational assignment for the reactive triplet state. Substituent effects on the photoreactivity of a structurally related molecule, 2-phenyl-2-oxazolin-4-one, implicate a π, π^* configuration for the reactive state in [2 + 2] photocycloaddition to its carbon-nitrogen double bond.¹⁶ We suspect that the reactive triplet state of **1** results from a vibronic coupling of n, π^* and π, π^* states of similar energy.³⁴ Alternatively equilibrating n, π^* and π, π^* states could be involved.

Because of the complexity of the data and the mechanism in Scheme I, we can only argue that the proposed mechanism is consistent with the data and that some reasonable alternatives are inconsistent or improbable. We note that triplet exciplexes have been implicated in the Paterno-Büchi reaction^{32a,35} and in [2 + 2] photocycloaddition to α, β -unsaturated ketones.³⁶ Furthermore, differential quenching by DTBN of [2 + 2] photocycloaddition of 1,1-dimethoxyethene to 2-cyclohexenones has similarly been interpreted in terms of exciplex quenching.^{9,11}

In summary we have observed that the paramagnetic quencher, di-*tert*-butyl nitroxide, differentially quenches product formation from photoaddition of 3-ethoxyisoindolenone (**1**) to tetramethylethylene and *cis*-2-butene. The diamagnetic quenchers biacetyl and *cis*-piperylene quench all products from photoaddition of **1** to tetramethylethylene equally, and a triplet counting plot with *cis*-piperylene gives an intersystem crossing efficiency for **1** close to unity. DTBN is partially destroyed when used to quench the photoaddition of **1** to tetramethylethylene. The destruction appears to involve scavenging of free radicals resulting from hydrogen atom abstraction from tetramethylethylene by excited **1** and does not appear to be involved in the differential quenching process. Differential quenching by DTBN is interpreted in terms of quenching of two nonequilibrating triplet exciplexes. We propose that differential quenching and/or nonlinear quenching by di-*tert*-butyl nitroxide and possibly other paramagnetic species may be an additional indirect technique for implicating the elusive triplet exciplex.^{37,38}

Experimental Section

NMR spectra were recorded using Varian Associates A-60A and HA-100 spectrometers and a JEOL PS-100 spectrometer and chemical shifts are reported in parts per million on the δ scale from internal Me₄Si. Mass spectral data were obtained at 70 eV using a Varian MAT CH-5 mass spectrometer; IR data, using a Perkin-Elmer 337 infrared spectrophotometer; and UV-visible absorption data, using a Varian Techtron 650 UV-visible spectrophotometer. Mi-

croanalyses were performed by Atlantic Microlab, Inc., Atlanta, Ga.

Improved Synthesis of 3-Ethoxyisoindolenone (1). A solution of silver nitrate (49.6 g, 0.292 mol) in 200 mL of Me₂SO was added to a stirred suspension of phthalimide (42.9 g, 0.292 mol) in 1200 mL of absolute ethanol. To this mixture was added dropwise with vigorous stirring 718 mL (0.292 mol) of standardized 0.406 N ethanolic sodium hydroxide over a period of 2 h. The off-white precipitate was isolated by suction filtration on filter paper and thoroughly washed with absolute ethanol. The solid was suspended in water, stirred vigorously for a few minutes, filtered, and washed again with ethanol. This process was repeated with acetone, and at room temperature the solid was dried in vacuo at 5×10^{-3} mm for 48 h to yield 69.7 g (94%) of silver phthalimide. During the preparation and reaction of silver phthalimide precautions were taken to exclude light. Silver phthalimide (69.7 g, 0.274 mol), ethyl iodide (46.8 g, 0.30 mol), and 1200 mL of benzene distilled from sodium were combined and refluxed for 24 h. The silver iodide was removed by suction filtration through Celite, and the solvent was removed by rotary evaporation. The off-white residue was sublimed at 5×10^{-3} mm and 120 °C to yield 42.5 g (89%) of 3-ethoxyisoindolenone as white needles (mp 131–135 °C). The 3-ethoxyisoindolenone was fractionally sublimed in a Kugelrohr oven at 5×10^{-3} mm and 115 °C prior to use to remove small quantities of phthalimide resulting from hydrolysis by atmospheric moisture.

Isolation and Characterization of Tetramethylethylene-Di-*tert*-butyl Nitroxide By-Product. A solution containing 3-ethoxyisoindolenone (2.1 g, 0.012 mol), tetramethylethylene (2.1 g, 0.025 mol), di-*tert*-butyl nitroxide (1.44 g, 0.010 mol), and 100 mL of benzene grade methylene chloride distilled from calcium hydride was degassed with nitrogen and irradiated with a Hanovia 450-W mercury lamp in a Pyrex water-cooled immersion well for 65 min. Complete destruction of 3-ethoxyisoindolenone was indicated by the disappearance of the IR signal at 6.46 μ . Silica gel TLC analysis eluting with 25% benzene in Skellysolve B showed that a new product was formed, not observed when the irradiation was conducted in the absence of di-*tert*-butyl nitroxide. The solvent was removed by rotary evaporation and the resulting liquid filtered to remove polymeric material. The new product was isolated by medium pressure liquid chromatography using a 0.5 by 20 in. column of Woelm 32–63 μ silica gel eluting with Skellysolve B at 9 mL/min. Rotary evaporation of the solvent yielded 0.395 g (14.5% relative to 3-ethoxyisoindolenone) of a clear liquid product. The product was identified as 1-(2,3-dimethyl-2-butenyl)-*N,N*-di-*tert*-butylhydroxylamine ether (**9**) from the following spectral and analytical data: IR (neat) 6.0 μ (weak); NMR (benzene-*d*₆) δ 1.30 (s, 18 H), 1.56 (s, 3 H), 1.70 (s, 3 H), 1.82 (s, 3 H), and 4.43 ppm (s, 2 H); mass spectrum (ambient temperature) *m/e* (rel intensity) 145 (19), 89 (37), 74 (25), 57 (base), and 41 (20).

Anal. Calcd for C₁₄H₂₉NO: C, 73.95; H, 12.85; N, 6.16. Found: C, 74.04; H, 12.82; N, 6.23.

To test for possible rearrangement of the hydroxylamine ether (**9**) during silica gel workup, the irradiation was repeated and the product mixture, after rotary evaporation of the solvent, was trap to trap distilled at 2×10^{-6} mm and ambient temperature. The isolated product gave NMR and IR spectra identical with those of **9**.

Isolation and Characterization of *cis*-2-Butene Di-*tert*-butyl Nitroxide By-Products. A solution containing 3-ethoxyisoindolenone (2.1 g, 0.012 mol), di-*tert*-butyl nitroxide (1.44 g, 0.010 mol), and 85 mL of spectral grade methylene chloride distilled from calcium hydride was degassed with nitrogen and cooled to –20 °C in a Pyrex immersion well. *cis*-2-Butene was bubbled into the cooled solution until approximately 15 mL had condensed. The solution was irradiated with a 450-W mercury lamp for 180 min under a nitrogen atmosphere. Two *cis*-2-butene di-*tert*-butyl nitroxide adducts were then isolated by silica gel medium pressure liquid chromatography as described for the isolation of **9**.

The first product eluted from the column was isolated in 2.4% yield (0.058 g) and characterized as 3-(1-butenyl)-*N,N*-di-*tert*-butylhydroxylamine ether (**11**) from the following spectral absorptions and elemental analysis: IR (neat) 6.08 μ (weak); NMR (DCCl₃) δ 1.23 (s, 18 H), 1.23 (d, *J* = 6.5 Hz, 3 H), 4.30 (p, *J* = 6.5 Hz, 1 H), 4.85–4.97 (m, 1 H), 5.05–5.25 (m, 1 H), and 5.7–6.3 ppm (m, 1 H); mass spectrum (ambient temperature) *m/e* (rel intensity) 199 (<1), 145 (4), 144 (8), 88 (17), 84 (12), 57 (base), and 41 (29).

Anal. Calcd for C₁₂H₂₅NO: C, 72.30; H, 12.64; N, 7.03. Found: C, 72.17; H, 12.67; N, 6.98.

The second product eluted from the column was isolated in 1% yield

(0.023 g) and characterized as 1-(2-butenyl)-*N,N*-di-*tert*-butylhydroxylamine ether (**10**) from the following spectral absorptions and elemental analysis: IR (neat) 6.03 μ (weak); NMR (DCCl₃) δ 1.25 (s, 18 H), 1.64 (d, $J = 4.9$ Hz, 3 H), 4.33 (d, $J = 4.4$ Hz, 2 H), and 5.56 ppm (m, 2 H); mass spectrum (ambient temperature) *m/e* (rel intensity) 144 (8), 88 (20), 86 (44), 84 (72), 57 (base), 49 (36), and 41 (28).

Anal. Calcd for C₁₂H₂₅NO: C, 72.30; H, 12.64; N, 7.03. Found: C, 72.12; H, 12.62; N, 7.13.

Measurement of the Ene Product Diastereoisomer Ratio from Irradiation of 3-Ethoxyisoindolenone and *cis*-2-Butene in the Presence of Di-*tert*-butyl Nitroxide. A solution containing 1.05 g of 3-ethoxyisoindolenone (0.0060 mol), 0.072 g of di-*tert*-butyl nitroxide (0.00050 mol), and 85 mL of spectral grade methylene chloride distilled from calcium hydride was degassed with nitrogen and cooled to -20 °C in a Pyrex immersion well. *cis*-2-Butene was bubbled into the solution until approximately 15 mL had condensed. The solution was irradiated with a 450-W mercury lamp for 18 min resulting in greater than 95% destruction of 3-ethoxyisoindolenone. The solution was analyzed for *cis*-*trans* isomerization of 2-butene by GLC using a 14 ft by 0.25 in., 25% β,β -oxydipropionitrile on 80-100 mesh Chromosorb P column at ambient temperature (He 60 mL/min). There was no detectable peak for *trans*-2-butene when the *cis*-2-butene peak was full scale. The solvent was removed by rotary evaporation and the ene products (**7** and **8**) were isolated together by preparative GLC as previously described.¹⁵ The ratio of diastereoisomeric ene products was measured by integration of the respective peaks in the 100-MHz NMR spectrum in the region of δ 1.53 ppm. The ratio was found to be 2.4:1.0. The diastereomer ratio was independent of the irradiation time and was not affected by overirradiation.

Reagents Used for Quantum Yield Measurements. Spectrograde methylene chloride (Fisher) was distilled from calcium hydride prior to use. 3-Ethoxyisoindolenone was fractionally sublimed in a Kugelrohr oven at 5×10^{-3} mm and 115 °C prior to use. Tetramethylethylene (Aldrich, gold label) and *cis*-2-butene (Matheson) were used without further purification. Di-*tert*-butyl nitroxide was prepared by the method of Hoffmann and co-workers²⁰ and distilled through an annular spinning band column at 55 °C (11 mm). Butane-2,3-dione was distilled at 88-88.5 °C (630 mm), and *cis*-1,3-pentadiene (Chemical Samples) was distilled at 39.5-40 °C (630 mm).

Quantum Yield Measurements. Measurement of the quantum yields of 3-ethoxyisoindolenone-olefin adduct formation and *cis*-*trans* isomerization of *cis*-1,3-pentadiene were performed with a rotating photochemical apparatus as described by Moses and co-workers.³⁹ The light source was a 550-W Hanovia mercury lamp in a water-cooled Pyrex jacket. The voltage of the electrical power to the lamp was stabilized with a Sola 2000 VA constant voltage transformer. The 313-nm mercury band was isolated using a two-compartment cylindrical quartz solution cell. The solution filter was modeled after that described by Hunt and Davis.⁴⁰ The inside cell compartment with a path length of 1.25 ± 0.05 cm contained a 1.58 M cobaltous sulfate solution, and the outside compartment with a path length of 1.65 ± 0.05 cm contained a 6.07×10^{-4} M potassium chromate solution stabilized with 0.1% sodium hydroxide. The solution filter was stable to irradiation from the 550-W mercury lamp over a period of 100 h. The entire quantum yield apparatus was immersed in a 15-gal water bath maintained at 20 ± 0.5 °C.

The quantum yield of destruction of di-*tert*-butyl nitroxide was measured with a linear type quantum yield apparatus consisting of a Bausch and Lomb 250 mm monochromator equipped with a UV-visible grating blazed at 300 nm, a 200-W Bausch and Lomb superpressure mercury light source, and a thermostated cell compartment maintained at 20 ± 0.5 °C. The monochromator was adjusted for irradiation at 313 nm with a band pass of 20 nm.

Samples (3.0 mL) of the appropriate concentrations of 3-ethoxyisoindolenone, tetramethylethylene, *cis*-2-butene, di-*tert*-butyl nitroxide, biacetyl, and *cis*-piperylene in methylene chloride solvent were placed in 13-mm Pyrex test tubes (rotating apparatus) or 10 mm i.d. square Truebore Pyrex cells (linear apparatus), degassed by four freeze (liquid nitrogen)-pump (10^{-5} mm)-thaw cycles, and sealed. Solutions containing *cis*-2-butene were prepared volumetrically at -15 °C in a cold room. The concentration of 3-ethoxyisoindolenone (**1**) was 0.060 M and greater than 99% of the incident, 313 nm light was absorbed by **1**. During the irradiation, the lamp intensity was monitored with potassium ferrioxalate actinometry.⁴¹ The light intensity averaged 1.3×10^{15} quanta/s for the rotating apparatus and

2×10^{16} quanta/s for the linear apparatus. Analyses of product formation from irradiation of 3-ethoxyisoindolenone with tetramethylethylene were obtained by GLC with a 10.5 ft by 0.25 in. column of 5% LAC 446 on 60-80 mesh acid-washed HMDS-treated Chromosorb W at 180 °C (He 60 mL/min) with benzophenone as an internal standard. 3-Ethoxyisoindolenone *cis*-2-butene photoadduct formation was measured by GLC using the same LAC 446 column at 180 °C (He 100 mL/min) with fluorenone as an internal standard. *Cis*-*trans* isomerization of 1,3-pentadiene was measured by GLC with a 12 ft by 0.25 in. column of 25% β,β -oxydipropionitrile on 80-100 mesh Chromosorb P at ambient temperature (He 60 mL/min). Gas chromatographic data were corrected for differences in detector response. Destruction of di-*tert*-butyl nitroxide was measured by visible absorption at eight wavelengths in the region 430-500 nm. The measurement was performed directly with the sealed square quantum yield cells before and after irradiation. Quantum yield irradiation times were adjusted such that no more than 20% of the starting material was destroyed during the irradiation.

Qualitative Measurement of the Photochemical Destruction of Di-*tert*-butyl Nitroxide. A methylene chloride solution (3.0 mL) containing 3-ethoxyisoindolenone (0.060 M), tetramethylethylene (0.125 M), and di-*tert*-butyl nitroxide (0.05 M) was placed in a quartz cuvette with a tight-fitting Teflon stopper and degassed with argon. The solution was irradiated at 313 nm with 16.6×10^{19} quanta using the linear quantum yield apparatus (vide supra). Di-*tert*-butyl nitroxide (13%) was destroyed during the irradiation as measured by visible spectroscopy at 448 nm. Oxygen was bubbled through the solution for 1 min, and the concentration of di-*tert*-butyl nitroxide remeasured. The oxygen regenerated 47% of the destroyed di-*tert*-butyl nitroxide. 1-(2,3-Dimethyl-1-butenyl)-*N,N*-di-*tert*-butylhydroxylamine ether was formed as shown by silica gel TLC eluting with 25% benzene in Skellysolve B. A similar experiment in which a solution 0.050 M in di-*tert*-butyl nitroxide and 0.125 M in tetramethylethylene in spectrograde methylene chloride was irradiated at 448 nm with 16.6×10^{19} quanta resulted in no destruction of the nitroxide.

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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 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 $q_{CT} = 0.47 (\pm 0.01)$ 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 ground³ and excited⁴ 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* \rightarrow *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* \rightarrow *cis*