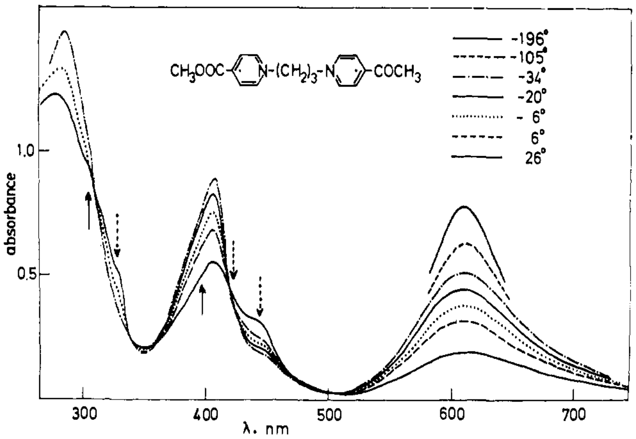

Figure 2. Temperature dependence of the spectrum of **3** in MTHF. Concentration is $0.85 \times 10^{-4}M$: ⟵ and ⇠ show absorption bands due to 4-carbomethoxy- and 4-acetylpyridinyl moieties, respectively.

spectrum of **5** is very much similar to the sum of the spectra of 1-methyl-4-carbomethoxy- and 1-methyl-4-acetylpyridinyl radicals.[7] According to the concentration independence of the spectrum of **3** at room temperature (1×10^{-3}–5×10^{-5} *M*), the absorption spectrum of **3** can be ascribed to the intramolecular interaction, and the visible absorption at 615 nm may be a charge-transfer band between two kinds of pyridinyl moieties.

The spectrum of the MTHF solution of **3** shows remarkable temperature dependence with several isosbestic points, as shown in Figure 2. The intensities of 615- and 408-nm absorption bands increased, while the absorption due to each pyridinyl moiety decreased with decreasing temperature. These temperature dependences of the absorption bands remove a possibility of the equilibrium between singlet and triplet states[8] in the closed form of **3**, and suggest the equilibrium of the open and closed forms, mentioned above. If ϵ_c is assumed to be a molar absorption coefficient of the closed form of **3**, since the molar absorption (ϵ) at 615 nm increased to approach 7800 with decreasing temperature, plots of $\log [\epsilon/(\epsilon_c - \epsilon)]$ against $1/T$ show a straight line in dilute solution, as shown in Figure 3. The enthalpy ($-\Delta H$) and entropy (ΔS) changes from the open to the closed form were evaluated to be 5.6 kcal and -10.5 eu, respectively. Deviation of the plots from the straight line in rather concentrated solution may be due to intermolecular interaction between the diradicals.

An unexpectedly low-spin concentration of **3** (~14%) was observed at room temperature.[9] However, Figure 2 suggests that the open form of **3** in MTHF amounts approximately to 70%. A similar difference between observed spin concentration and the expected one from the absorption spectrum was also observed in **4**. The effective distance for the spin dipolar interaction seems to be greater than that for the observable charge-transfer band between two radical moieties. From these considerations, it seems that the open-form diradical, in which the charge-transfer band is unob-

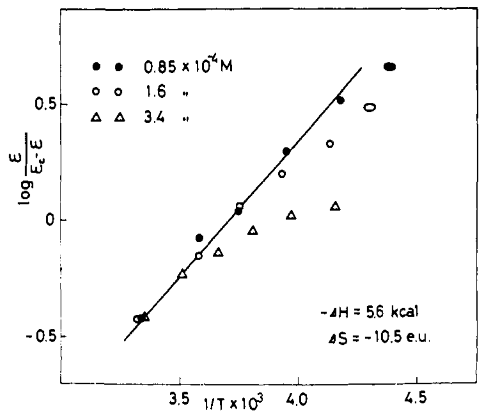

Figure 3. Plots of $\log [\epsilon/(\epsilon_c - \epsilon)]$ against $1/T$ in the hetero diradical **3**. A straight line was obtained by a least-squares fit, where the data at $-48°$ were excluded from the calculation.

served, is divided into two kinds of conformations. These open forms are a weakly *interacted* conformation of the radical moieties and a *noninteracted* one, which are energetically similar. In the former, the spin dipolar interaction of two moieties results in undetectable broad esr through motional broadening in liquid solution.

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Received September 21, 1971

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[7] M. Itoh and S. Nagakura, *J. Amer. Chem. Soc.*, **89**, 3959 (1967); *Bull. Chem. Soc. Jap.*, **39**, 369 (1966).

[8] T. Sakata and S. Nagakura, *ibid.*, **42**, 1497 (1969).

[9] Determination of relative spin concentration was done using the same procedure as described in the previous papers (ref 1).

Quenching of Excited States by Stable Free Radicals. The Effect of Di-*tert*-butyl Nitroxide on Stilbene and Naphthalene Triplets

Sir:

Several authors have recently reported the use of stable free radicals as quenchers of reactive intermediates in photochemical reactions.[1,2] Curiosity about the interactions between free radicals and excited species, and a desire to evaluate quenching by free radicals as an adjunct to existing methods for studying photochemical reactions, prompted us to undertake a systematic study of the mechanism by which di-*tert*-butyl nitroxide[3] (DTBN) quenches photoexcited triplets in solution. We have initially chosen to monitor DTBN quenching of sensitized trans → cis isomerization of *trans*-stilbene. This system has been studied extensively and seems to be well understood.[4] We present here our initial results, which indicate that DTBN quenches both benzophenone and stilbene triplets with high efficiency, and that these triplets are quenched significantly more rapidly than naphthalene triplet.

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[1] (a) L. A. Singer and G. A. Davis, *J. Amer. Chem. Soc.*, **89**, 158 (1967); (b) N. C. Yang, R. Loeschen, and D. Mitchell, *ibid.*, **89**, 5465 (1967); (c) O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *ibid.*, **90**, 1657 (1968); (d) L. A. Singer, G. A. Davis, and V. P. Muralidharan, *ibid.*, **91**, 897 (1969); (e) P. de Mayo, *Accounts Chem. Res.*, **4**, 41 (1971).

[2] L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 6497 (1969).

[3] A. K. Hoffman, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *ibid.*, **86**, 639 (1964).

[4] (a) G. S. Hammond, *et al.*, *ibid.*, **86**, 3197 (1964); (b) W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966); (c) J. Saltiel, *ibid.*, **89**, 1036 (1967); (d) J. Saltiel, *ibid.*, **90**, 6394 (1968); (e) H. A. Hammond, D. E. de Meyer, and J. L. R. Williams, *ibid.*, **91**, 5180 (1969); (f) R. A. Caldwell and R. P. Gajewski, *ibid.*, **93**, 532 (1971).

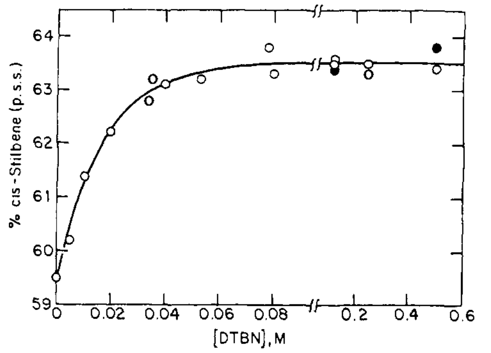

Figure 1. Variation of benzophenone-sensitized stilbene photostationary state composition with different nitroxide concentrations: ○, starting with *trans*-stilbene; ●, starting with *cis*-stilbene.

Irradiation of degassed benzene solutions of 0.025 *M* *trans*- (or *cis*-) stilbene and 0.050 *M* benzophenone containing varying concentrations of DTBN at 3660 Å, for up to 60 hr, led to photostationary states whose composition varied, as shown in Figure 1, from 59.5% cis at [DTBN] = 0 to 63.5% cis at [DTBN] > 0.08 *M*. The analyses by vpc were reproducible typically to better than ±0.3% in the comparison of the mean value of replicate samples and to ±0.5% for the average deviation from the mean of replicate injections of the same sample; the modest changes we observe are thus unquestionably real. Since it is known[4a,4b] that more cis isomer is formed with sensitizers of triplet energy lower than benzophenone (E_T = 69 kcal/mol[5]), one interpretation of these results might have been that energy transfer to stilbene is occurring from an exciplex of DTBN and benzophenone triplet, having a lower effective energy than benzophenone triplet alone. An E_T for the exciplex of *ca.* 61 kcal/mol could be inferred[4b] from our photostationary states. That this is not the case was shown by experiments in which *trans*-β-methylstyrene (*trans*-β-MS) was substituted for the stilbene. Other work in this laboratory[6] has shown that the sensitized photostationary states of β-MS rapidly become cis rich as the sensitizer triplet energy is decreased below ~70 kcal/mol; thus, exciplex formation should result in a large increase in the cis component of the β-MS photostationary state. For E_T = 61 kcal/mol, >80% cis would be predicted.[6] In fact, no change at all was observed. A photostationary state consisting of 62.2% *cis*-β-MS was obtained both with no DTBN and with 0.08 *M* DTBN.

Since no evidence for ground-state complexing between DTBN and stilbene or DTBN and benzophenone could be found by uv, ir, or nmr spectroscopy, the observed variation in the stilbene photostationary states must mean that *DTBN quenches stilbene triplets in such a way as to favor decay to cis-stilbene.* This behavior is in marked contrast to the quenching of stilbene triplets by compounds having low triplet energies, such as azulene;[4a,4d] such compounds produce highly trans rich photostationary states. In fact, the "azulene effect" was completely eliminated in competitive quenching experiments when large concentrations of DTBN were used. Irradiation of ampoules having the same concentrations of *trans*-stilbene and benzophenone as above, and containing 0.010 *M* azulene, gave photostationary states consisting of 36.8% *cis*-stilbene when no DTBN was present, but 63.1% *cis*-stilbene in the presence of 0.200 *M* DTBN.

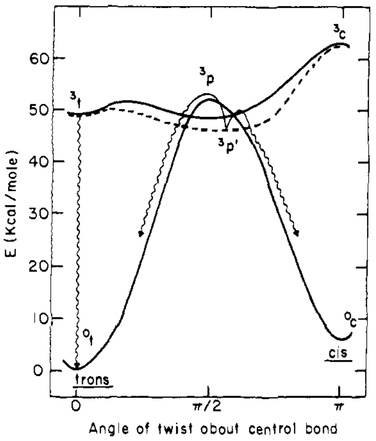

Figure 2. Schematic potential energy diagram for the lowest triplet state of stilbene (upper solid line) showing possible effect of di-*tert*-butyl nitroxide (broken line).

The apparent absence of an effect of DTBN on β-MS triplet decay may be due either to a short lifetime for the β-MS triplet or to a fortuitous identity of the spontaneous decay ratio with the DTBN-induced decay ratio. Not all olefin triplets may be quenched; thus, α-methylstilbene triplet is not affected by azulene.[4a]

An estimate of the efficiency of the quenching by DTBN may be obtained as follows. We express the fraction of cis isomer at photostationary state as

$$f_c = \frac{k_{sc} + k_{ic}[\mathrm{DTBN}]}{k_{st} + k_{sc} + (k_{it} + k_{ic})[\mathrm{DTBN}]} \qquad (1)$$

where k_{st} and k_{sc} are overall rate constants for the spontaneous decay of stilbene triplets to *trans*- or *cis*-stilbene, and k_{it} and k_{ic} are overall rate constants for the DTBN-induced decay to *trans*- or *cis*-stilbene, respectively. Analysis of Figure 1 in terms of eq 1 and the limiting values for f_c leads to $k_{it}/k_{st} = 100 \pm 20\ M^{-1}$. Saltiel[4d] has shown that the corresponding ratio of rate constants for azulene quenching gives a value of approximately 120 M^{-1}; since both azulene and DTBN thus lead to essentially the same increase in the rate of decay of stilbene triplets, and since azulene is expected to quench stilbene triplets at a diffusion-controlled rate,[4d] we conclude that the quenching by DTBN is also diffusion controlled.

It is tempting to speculate that DTBN functions as a selective, nonvertical quencher for twisted ("phantom") stilbene triplets (^{3}p),[4a,4c] and that azulene functions as a selective, vertical quencher of trans triplets (^{3}t)[4d] (Figure 2). If the limiting value of 63.5% cis obtained at high concentrations of DTBN represents the "pure" decay ratio of ^{3}p, then we estimate that in spontaneous decay this is "contaminated" with about 6% vertical decay from ^{3}t. Saltiel, however, has concluded[4d] from isotopic studies that spontaneous decay from ^{3}t is insignificant. Alternatively, our data are consistent with the interpretation that interaction with DTBN

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[5] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 132.

[6] (a) G. W. Sovocool, Ph.D. Thesis, Cornell University, 1971; (b) R. A. Caldwell, G. W. Sovocool, and R. J. Peresie, *J. Amer. Chem. Soc.*, 93, 779 (1971).

forces ^{3}p into a somewhat different range of twist from normal; this is illustrated schematically by the broken line in Figure 2. This distorted phantom triplet (represented by ^{3}p′), if it were actually a complex between DTBN and ^{3}p, might well prefer a slightly cisoid conformation to reduce steric repulsion between the phenyl and *tert*-butyl groups.

Theoretical explanation for the rapid quenching is provided by the work of Hoytink[7] and Murrell.[8] In particular, Hoytink[7] has predicted that the rate of free-radical quenching of aromatic hydrocarbons should vary inversely with the E_T of the hydrocarbon, and that the quenching process involves essentially a vibronic relaxation of the triplet, which is made spin allowed by electron exchange with the radical. Since the ground-state potential energy curve for stilbene overlaps the triplet-state curve near ^{3}p,[4d] the condition for rapid quenching by this mechanism is met admirably.

Finally, we wish to point out that preliminary quenching studies with various sensitizers, corrected for the changes in the stilbene decay ratio at different nitroxide concentrations, give linear Stern–Volmer plots from which reproducible quenching rate constants may be calculated. Assuming a diffusion-controlled rate constant of $5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ for energy transfer to stilbene in benzene, we find that DTBN quenches benzophenone triplets with $k_q = 3 \times 10^9\ M^{-1}\ \text{sec}^{-1}$, while naphthalene triplets (sensitized by benzophenone)[9] are quenched with $k_q = 6 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. For perdeuterionaphthalene,[10] the observed value of $k_q = 3.7 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ confirms the predictable[7] isotope effect on the quenching process and indicates that *DTBN quenching can be substantially slower than diffusion controlled* for triplets having relatively long nonradiative lifetimes.

Acknowledgment. We wish to thank the National Science Foundation (Grant No. GP-14796) for support of this research.

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(7) (a) G. J. Hoytink, *Mol. Phys.*, **3**, 67 (1960); (b) G. J. Hoytink, *Discuss. Faraday Soc.*, **45**, 14 (1968); (c) G. J. Hoytink, *Accounts Chem. Res.*, **2**, 114 (1969).

(8) J. N. Murrell, *Mol. Phys.*, **3**, 319 (1960).

(9) Full experimental and kinetic details will be published in the full paper.

(10) Obtained from Diaprep, Inc., in purity satisfactory for direct use.

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Received September 17, 1971

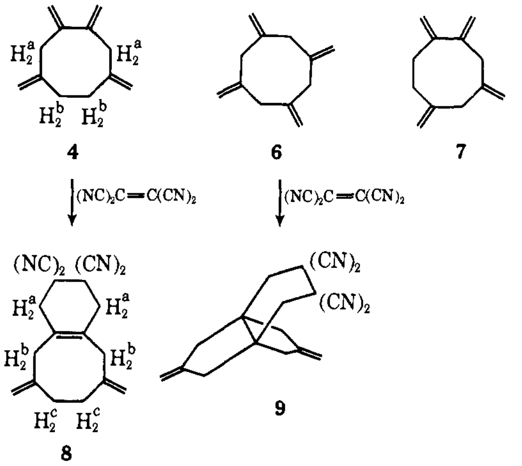
Selective Cyclooligomerization of Allene and Bis-π-allylnickel(0) Intermediates

Sir:

Nickel(0)-catalyzed oligomerization of allene leading to 1,2,4,6,9-pentamethylenecyclodecane (**1**)[1] is certainly a nonconcerted process as demonstrated by isolation of a linear allene trimer complex $Ni(C_9H_{12})$ (**2**) and its phosphine adduct $Ni(C_9H_{12})(PPh_3)$ (**3**).[2] Recently catalytic cyclotrimerization of allene with bis(tri-2-biphenylyl phosphite)nickel was briefly reported.[3] These results suggest the possibility of setting up an appropriate potential barrier controlling the growth reaction to particular oligoallenes. In fact this has been achieved. We wish to describe herein (1) a remarkable controlling effect of the phosphorus ligand in a nickel(0) complex catalyst, (2) a reexamination of the tetramer structure which previously has been erroneously assigned,[4] and (3) an allene tetramer nickel(0) complex which is related to the catalysis leading to the tetramer **4** and the pentamer **1**.

In the presence of $Ni(C_8H_{12})_2$ (C_8H_{12} = 1,5-cyclooctadiene) combined with 1–4 mol of *tert*-alkyl- or -arylphosphine as catalyst, allene produces a mixture of oligoallenes containing **4** as a main product, whereas with that containing triaryl phosphite, such as triphenyl, tri-2-tolyl, or tri-2-biphenylyl phosphite, one composed mainly of the trimer 1,2,4-trimethylenecyclohexane (**5**) is obtained regardless of the steric requirements of the ligand.[5] Higher phosphine–Ni ratios (>2) or higher catalyst concentrations (1.0–2.5 mol %) prefer formation of the tetramer **4** rather than the pentamer **1**. Similar tendency for the selectivity of oligomer formation was observed also with the Ni(0) triaryl phosphite system.[6]

The tetramer **4**, bp 40° (5 mm), *m/e* 160, shows ir and ^{1}H nmr spectra which are essentially identical with those of a sample prepared according to Lindsey's prescription[4] using $Ni(CO)_2[P(OPh)_3]_2$ as a catalyst: ir (neat) 3080 (=C—H), 2960, 2920 (C—H), 1645 (C=C), 1628 (C(=CH$_2$)C(=CH$_2$)), and 885 (=CH$_2$) cm^{-1}; ^{1}H nmr (100 MHz, CCl$_4$) δ 4.90 (d, *J* = 2.5 Hz, 2 H, =CH$_2$), 4.75 (s, 6 H, =CH$_2$), 3.00 (s, 4 H, H^a), and 2.28 (sharp s, 4 H, H^b). The ^{13}C nmr enables us to assign it unambiguously as 1,2,4,7-tetramethylenecyclooctane **4**: δ (ppm from CS$_2$) 43.2 (2 C,-*C*(=C)-), 44.5 (2 C,-*C*-(=C)-), 80.1 (2 C, =*C*H$_2$), 80.5 (2 C, =*C*H$_2$), 114.8 (2 C, =*C*CH$_2$C=), and 155.6 (2 C, -*C*H$_2$*C*H$_2$-).[7]



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(1) (a) S. Otsuka, A. Nakamura, K. Tani, and S. Ueda, *Tetrahedron Lett.*, 297 (1969); (b) S. Otsuka, A. Nakamura, S. Ueda, and H. Minamida, *Kogyo Kagaku Zasshi*, **72**, 1809 (1969).

(2) S. Otsuka, A. Nakamura, S. Ueda, and K. Tani, *Chem. Commun.*, 863 (1971).

(3) M. Englert, P. W. Jolly, and G. Wilke, *Angew. Chem.*, **83**, 84 (1971).

(4) R E. Benson and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **81** 4247 (1959).

(5) C. A. Tolman, *ibid.*, **92**, 2956 (1970).

(6) A typical experiment carried out at 70° for 20 hr using 2.1 g of allene in 10 ml of benzene gave the following results: (a) the $Ni(C_8H_{12})_2$ (2.5 mol % based on allene)–4PPh$_3$ system (conversion, 93%, selectivity: **5**, 28%; **4**, 66%; **1**, 6%); (b) $Ni[P(OPh)_3]_4$ (1.2 mol %) catalyst (conversion, 81%; selectivity: **5**, 72%; **4**, 25%; **1**, 3%).

(7) The same conclusion concerning the structure of **4** was also obtained by G. S. Reddy and R. V. Lindsey, Jr., through ^{13}C nmr study (private communication from Dr. R. V. Lindsey, Jr.).