Communications to the Editor

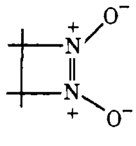
3,3,4,4-Tetramethyl-1,2-diazetine 1,2-Dioxide, a Useful Low-Energy Triplet Quencher

Sir:

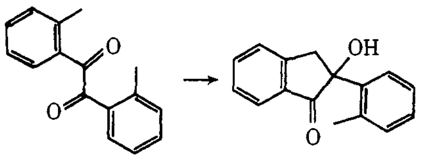
For the past decade conjugated dienes have played an important role in the study of photochemical reactions. The short-wavelength absorption (λ_{max} 224 nm) and relatively low triplet energy (E_T = 59 kcal/mol)[1] of *trans*-piperylene have made this compound especially useful as a triplet quencher. While its tendency to undergo photosensitized isomerization provides the added possibility of using it for triplet counting,[2] in most quenching experiments isomerization and dimerization of diene quenchers introduce unwanted variables. Interpretation of diene quenching data is also complicated by efficient quenching of the excited singlet states of aromatic compounds.[3] In this report we describe an alternative triplet quencher which lacks many of the disadvantages of the dienes.

We recently reported that 2,3-bis(hydroxylamino)-2,-3-dimethylbutane was readily oxidized to the 1,2-diazetine 1,2-dioxide **1**.[4,5] While this product was found to undergo efficient photodecomposition (ϕ = 0.43) to 2,3-dimethyl-2-butene and nitric oxide when irradiated with 2537-Å light, it was found to be remarkably inert to photosensitization. Despite its failure to undergo a photosensitized reaction, it has now been found that triplet energy is in fact transferred to **1** even from very low energy triplet donors. Thus, **1** was found to inhibit photopinacolization of benzophenone (E_T = 68.5 kcal/mol)[6] in isopropyl alcohol, the photocyclization[7] of 2,2′-dimethylbenzil (**2**) (benzil E_T = 54 kcal/mol),[6] and the photooxidation of anthracene (E_T = 42.4 kcal/mol)[8] and of 9,10-dimethoxyanthracene in bromobenzene.[9]

The relatively short wavelength absorption of **1** [$\lambda_{max}^{C_6H_{14}}$ 260 nm (ϵ 9200) (ϵ 112 at 310 nm); $\lambda_{max}^{CH_3OH}$ 255 nm (ϵ 10,000) (ϵ 35 at 310 nm)] coupled with the likelihood that this compound has an unusually low triplet energy suggested the possibility of using the compound as a general triplet quencher. This possibility appeared even more attractive following unsuccessful attempts to quench the fluorescence of naphthalene and anthracene derivatives with **1**. Concentrations of **1** as high as 0.1 *M* were without effect even on strongly electron-donating fluorescers such as 9,10-dimethoxyanthracene. Thus, unlike piperylene, **1** appears to be unable to quench singlets having energies below its own singlet energy. Quenching by **1** appears therefore to be diagnostic of triplet energy transfer.

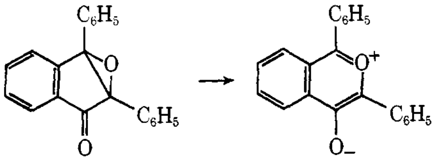


1

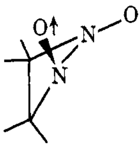


2

The triplet energy and lifetime of **1** could be estimated by the 2,3-diphenylindenone oxide (**3**) color test.[10] In this test a steady-state concentration of the colored pyrylium oxide (**4**) is established. The colored species **4** is continuously formed by direct absorption of light by **3** and is concomitantly destroyed by singlet oxygen formed by energy transfer from sensitizer triplets. Addition of substances which quench the sensitizer or destroy singlet oxygen causes inhibition of oxidation and leads to increased color. In the present case, **1** (10^{-2} *M* in benzene) produced increased color with triplet sensitizers having energies of at least 42.4 kcal/mol (anthracene).[11] Since **1** failed to inhibit the oxidation of 2-methyl-2-pentene by chemically generated singlet oxygen (hypochlorite and hydrogen peroxide),[13] the color increases are not due to singlet oxygen trapping.



3 **4**



5

These observations suggest an effective[10] triplet energy for **1** of 35.6–42.4 kcal/mol, although unfortunately singlet–triplet absorption spectra of **1** by oxygen perturbation in chloroform[8] which might have verified this energy gave no new maxima.[14] Since triplet **1** does not sensitize oxygen in the color test as efficiently as does triplet anthracene, its intrinsic lifetime must be less than that of anthracene triplet. The latter is limited by oxygen quenching and has been estimated as ~2 × 10^{-7} sec.[10] This short lifetime of triplet **1** suggests that **1** may undergo significant geometrical distortion in its triplet state, a process which might also account for the absence of observable singlet–triplet absorption. A

---

(1) R. E. Kellogg and W. T. Simpson, *J. Amer. Chem. Soc.*, **87**, 4230 (1965).

(2) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(3) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968).

(4) Prepared by treating aqueous 2,3-bis(hydroxylamino)-2,3-dimethylbutane with bromine at 25° for 1 hr, followed by extraction with chloroform and recrystallization from methanol; P. Singh, D. G. B. Boocock, and E. F. Ullman, *Tetrahedron Lett.*, 3935 (1971). The previously reported isolation of the intermediate, 1,2-dihydroxy-3,3,4,4-tetramethyl-1,2-diazetidine, with periodate as oxidant, is erroneous. This compound was confused with acetone oxime; J. F. W. Keana, D. J. Dinerstein, and D. P. Dolata, *ibid.*, 119 (1972).

(5) Small quantities are available commercially from Syva Co., Palo Alto, Calif.

(6) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(7) T. L. Burkoth and E. F. Ullman, *Tetrahedron Lett.*, 145 (1970).

(8) D. F. Evans, *J. Chem. Soc.* 1351 (1957).

(9) R. Livingstone and V. S. Rao, *J. Phys. Chem.*, **63**, 794 (1959).

(10) E. F. Ullman and W. A. Henderson, *J. Amer. Chem. Soc.*, **89**, 4390 (1967).

(11) Although perylene (E_T = 35.6 kcal/mol)[12] was not quenched by **1**, naphthacene (E_T = 29.3 kcal/mol) caused quenching possibly as a result of its photooxidation to naphthacenequinone (E_T = 55.8 kcal/mol).[6]

(12) J. B. Birks and M. A. Sliffin, *Nature (London)*, **191**, 761 (1961).

(13) C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, **90**, 6233 (1968).

(14) Weak previously unreported oxygen-induced bands at 476, 576, 628, and 767 nm due to chloroform were initially misleading and illustrate the necessity for caution in the interpretation of such spectra.

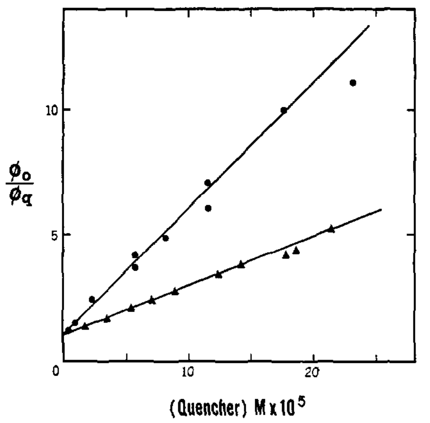


Figure 1. Effect of quencher **1** on the quantum yield of isomerization of *trans*-stilbene sensitized by benzathrone (●) and by anthracene (▲).

plausible geometry might be the twisted form **5** which would owe its stability to the same factors that stabilize nitroxide radicals.

Quenching of benzanthrone (E_T = 47 kcal/mol)[15] and anthracene triplets by **1** was studied quantitatively by observing the effect of **1** on the quantum yields of the sensitized isomerization of *trans*-stilbene. The experimental conditions employed were identical with those in flash photolysis experiments in which the sensitizer triplet lifetimes (τ_s) in the presence of *trans*-stilbene had been determined.[15] Under these conditions quenching should follow eq 1 where subscripts s and t refer to sensitizer and *trans*-stilbene, respectively.

$$\phi_0/\phi_q = (1 + k_{qs}\tau_s[Q])(1 + k_{qt}\tau_t[Q]) \qquad (1)$$

sitizer and *trans*-stilbene, respectively. Since at quencher concentrations [Q] of $\leqslant 10^{-4}$ *M* experimental plots of ϕ_0/ϕ_q were linear (Figure 1), one of the terms in eq 1 must be ~1 and can be neglected. This must be the *trans*-stilbene quenching term ($1 + k_{qt}\tau_t[Q]$) because the stilbene triplet lifetime is $<2 \times 10^{-7}$ sec[10] and the quenching rate constant k_{qt} cannot exceed diffusion control ($<7 \times 10^9$ M^{-1} sec^{-1}).[15] From the slopes (5.1×10^4 M^{-1} for benzanthrone and 2×10^4 M^{-1} for anthracene) and the respective sensitizer triplet lifetimes (τ_s = 3.6×10^{-5} and 1.7×10^{-4} sec),[15] rates of energy transfer from sensitizer to **1** (k_{qs}) of 1.4×10^9 M^{-1} sec^{-1} (benzanthrone) and 1.2×10^8 M^{-1} sec^{-1} (anthracene) are calculated. These rates are consistent with the conclusion that E_T for **1** lies near that of anthracene.[16]

Based on the above described efficiency of **1** as a triplet quencher, its short wavelength absorption, and the absence of both singlet quenching and triplet reactivity, we recommend that **1** be considered as a practical alternative to diene triplet quenchers where wavelengths above 300 nm can be employed.

---

[15] W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

[16] A referee's suggestion that ground-state complexing might affect these rates is inconsistent with the absence of changes in the spectra of benzene solutions of anthracene and benzanthrone upon making the solutions 2×10^{-2} *M* in **1**.

Edwin F. Ullman,* Prithipal Singh
Contribution No. 45, Syva Research Institute
Palo Alto, California 94304

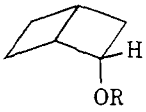
Received February 19, 1972

Strained Ring Systems. XIII.[1] Solvolysis of *endo*-Bicyclo[2.2.0]hex-2-yl 3,5-Dinitrobenzoate. A Possible Route to the Homoallylic Δ^3-Cyclohexenyl Cation

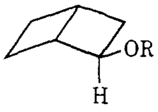
Sir:

Of the isomeric bicyclic C_6 ([2.1.0]-5-carbinyl,[2a] [3.1.0]-2-yl,[2a–d] [2.1.1]-5-yl,[2e] and [2.2.0]-2-yl[2f]) and the bicyclo[*m*.2.0]alkyl ([2.1.0]-2-yl, [2.2.0]-2-yl, [3.2.0]-6-yl, and [4.2.0]-7-yl)[3] derivatives, only the literature for the *endo*-bicyclo[2.2.0]hex-2-yl system is presently lacking. We wish to report the results of kinetic and product studies obtained in the solvolysis of *endo*-bicyclo[2.2.0]hex-2-yl 3,5-dinitrobenzoate (**1**-ODNB) in 60% (v/v) aqueous acetone.

The synthesis of **1**-ODNB utilized the previously reported inseparable mixture of **1**-OH and its exo isomer, **2**-OH,[4] which was converted in the usual manner[2e] to



1



2

the mixture of **1**-ODNB and **2**-ODNB used in this investigation. The kinetic data, determined by the conductance method,[5] and thermodynamic parameters for solvolysis of **1**-ODNB in 60% aqueous acetone are listed in Table I. Applying the factor of 6×10^3 as the difference in rate constants for a tosylate in acetic acid at 50° and a 3,5-dinitrobenzoate in 60% aqueous acetone at 100°[2c] to the acetolysis rate constant of 2-OTs,[2f] we arrive at k_{endo}/k_{exo} = 8×10^7 for the bicyclo[2.2.0]hex-2-yl system;[6] this and the rate ratios for the other isomeric bicyclic C_6 derivatives are given in Table II.

The hydrolysis products from **1**-ODBN generated in the presence of *sym*-collidine to eliminate acid-catalyzed rearrangements were most interesting. Not only was the ion-pair return product, *endo*-bicyclo[3.1.0]hex-2-yl ODNB (**3**-ODNB), obtained in substantial quantity but an excess of its alcohol **3**-OH was present when compared to the product results from the solvolysis of **3**-ODNB and its exo isomer, **4**-ODNB (Table III).[7,8]

---

[1] For paper XII in this series see R. N. McDonald and R. R. Reitz, *J. Org. Chem.*, in press.

[2] (a) K. B. Wiberg and A. J. Ashe, *J. Amer. Chem. Soc.*, **90**, 63 (1968); (b) E. C. Friedrich and M. A. Saleh, *Tetrahedron Lett.*, 1373 (1971); (c) P. R. Brook, R. M. Ellam, and A. S. Bloss, *Chem. Commun.*, 425 (1968); (d) G. H. Schmid and A. Brown, *Tetrahedron Lett.*, 4695 (1968); (e) K. B. Wiberg, R. A. Fenoglio, V. Z. Williams, and R. W. Ubersax, *J. Amer. Chem. Soc.*, **92**, 568 (1970); (f) R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1878 (1967).

[3] K. B. Wiberg, V. Z. Williams, and L. E. Friedrich, *J. Amer. Chem. Soc.*, **92**, 564 (1970). This reference contains a comparison of the rates of solvolysis of bicyclo[*m*.2.0]alkyl derivatives and the prediction of the large endo/exo rate ratio found for **1** and **2**.

[4] R. N. McDonald and G. E. Davis, *J. Org. Chem.*, **34**, 1916 (1969). A 36:64 mixture of **1**-OH and **2**-OH, respectively, was converted to the mixture of dinitrobenzoates. The solvolytic infinity titer corresponded to 23.2% reaction based on the total amount of **1**- and **2**-ODNB or 64.5% on available **1**-ODNB, assuming that the **1**-ODNB:**2**-ODNB ratio was the same as that of the starting alcohol mixture.

[5] (a) Using a M-D Mini-Cell[5b] coupled to a Beckman RC-18A conductivity bridge; (b) available through R-M Research Products, Inc., Manhattan, Kan. 66502.

[6] The magnitude k_{endo}/k_{exo} in this system readily allowed the use of the mixture of **1**- and **2**-ODNB in the rate studies.

[7] The products from similar hydrolysis of **4**-ODNB (glpc analysis) are the same as obtained from **3**-ODNB within experimental error. The product distribution from **3**-ODNB in this study differs from that