Tetrahedron Letters No. 9, pp 701 - 704, 1973. Pergamon Press. Printed in Great Britain.

SINGLET QUENCHING MECHANISMS III (1). SENSITIZED ISOMERIZATION OF HEXAMETHYLBICYCLO [2.2.0]HEXA-2,5-DIENE. A CHAIN REACTION.

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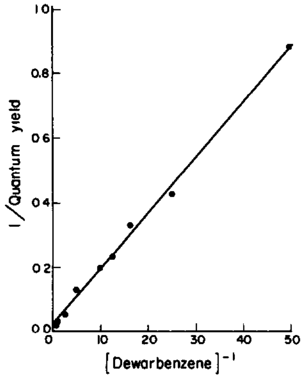
(Received in USA 30 October 1972; received in UK for publication 21 January 1973)

We have recently observed a photosensitized chain reaction of hexamethylbicyclo[2.2.0]hexa-2,5-diene (**1**) to hexamethylbenzene (**2**) (Fig. 1). Although there are a number of mechanisms which might rationalize this result, we believe that our evidence is consistent only with a chain process involving radical cation propagation. An ionic intermediate is indicated by the observations that the quantum yield decreases in going from either methanol or acetonitrile to the nonpolar solvent, benzene. In benzene the quantum yield does not exceed unity and so the isomerization is most likely not a chain process. The quantum yield is increased by adding salts, such as sodium or lithium



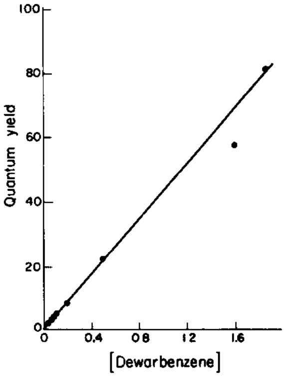


Fig. 1a. Plot of (quantum yield)$^{-1}$ vs. (hexamethylbicyclo[2.2.0]hexa-2,5-diene concentration)$^{-1}$ for the naphthalene-sensitized isomerization in methanol.

Fig. 1b. Plot of quantum yield vs. hexamethylbicyclo[2.2.0]hexa-2,5-diene concentration for the naphthalene-sensitized isomerization in methanol.

perchlorate, to the methanolic solution and is decreased by the addition of the bases sodium acetate or sodium formate. In the presence of 0.05 M sodium acetate the quantum yield decreases by a factor of 3.4-3.8, whereas 0.05 M sodium formate reduces the quantum yield by a factor of 2.4 (2,3). The ionic species responsible for chain propagation cannot be a proton since it is well established that proton addition to 1 in methanol yields products other than 2 (7). We have confirmed this under our reaction conditions and find none of these other rearrangement products in our photosensitized reactions. We find these results compatible only with the following mechanism for propagation:

1. $1^{+\cdot} \longrightarrow 2^{+\cdot}$
2. $2^{+\cdot} + 1 \longrightarrow 2 + 1^{+\cdot} \longrightarrow 2 + 2^{+\cdot}$
3. $2^{+\cdot} + X \longrightarrow Y$
4. $2^{+\cdot} + B \longrightarrow (CH_3)_5C_6\text{-}CH_2 + \overset{+}{HB}$

Where X is some adventitious chain-terminating agent, and B is added base. Electrochemical experiments indicate that step 2 would be thermoneutral or slightly exothermic since E1/2 for 1 is +1.58 V and 1.62 V for 2, both in acetonitrile vs. S.C.E.(8) Although a chain termination process, $A^{-\cdot} + 2^{+\cdot} \longrightarrow A + 2$, might be expected, no intensity dependence, over a range of 200, was observed.

The details of the initiation process are not well understood at this time. If simple singlet initiation were occurring the plots shown in Fig. 1 would be expected to be non-linear in the region where there is little fluorescence quenching. That this behavior is not observed indicates that the initiation steps may be complex and involve more than just the singlet state.(9)

However, agreement with the postulate that singlet sensitization leads to charge transfer, and in polar solvents ultimately to ion-radicals,(10) we find that the fluorescence of sensitizers is quenched in accord with their ability to accept an electron and 1 quenches the fluorescence of diphenyloxazole in accord with its ability to donate an electron (Fig. 2).

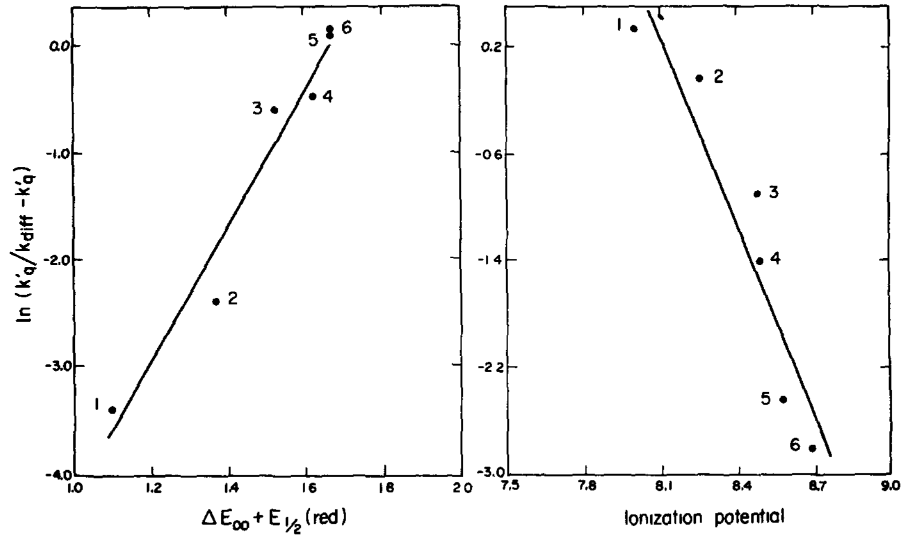


Fig. 2a: Correlation of electron-accepting ability of fluorescers with rate constants for quenching with hexamethylbicyclo[2.2.0]hexa-2,5-diene. The fluorescers are: (1) diphenylfuran; (2) 1,4-bis[2-(4-methyl-5-phenoxazolyl)]benzene; (3) 1,4-bis-2-(5-phenyloxazolyl)benzene; (4) 2-(1-naphthyl)-5-phenyloxazole; (5) 2,5-bis(5-*tert*-butylbenzoxazolyl)-2-thiophene; and (6) 2,5-diphenyloxazole.

2b: Correlation of electron donation ability of quenchers with rate constants for quenching 2,5-diphenyloxazole fluorescence.

The quenchers are: (1) Hexamethylbicyclo-[2.2.0]hexa-2,5-diene; (2) cyclohexa-1,3-diene; (3) *cis*, *cis*-2,4-hexadiene; (4) *cis*, *trans*-2,4-hexadiene; (5) tetrahydrothiophene; (6) *cis*-1,3-pentadiene.

Acknowledgment: We are indebted to Dr. G. Popp for performing the electrochemical experiments and to Dr. G. N. Taylor, of Bell Telephone Laboratories, for valuable discussions.

References

1. T. R. Evans, R. W. Wake, and M. M. Sifain, *Mol. Photochem.*, **3**, 275 (1971).
2. The sensitizer was naphthalene and the concentration of **1** was 0.05 *M*. All quantum yields reported were measured using the ferrioxalate actinometer (4), but other actinometers, benzophenonepiperylene (5) and benzophenone-ethyl alcohol (6), gave results which were in agreement with

those obtained with the ferrioxalate measurements. **1** was purchased from Aldrich Chemical Company, Inc., and usually used as received. Repeated distillations, under high vacuum, and/or chromatography on silica gel only served to increase the amount of hexamethylbenzene in starting material. Experiments with "purified" **1** gave, within experimental error, the same results as those using unpurified material. Direct irradiation of **1**, 1.6 *M* in methanol, with a Southern New England Ultraviolet Photoreactor, at ∼300 nm yielded **2** with a quantum yield of 0.14. We conclude from these results that chain reaction observed here is not due to impurities. The sensitizers were all recrystallized before use and the solvents were passed through a column of Al_2O_3, silica gel and activated charcoal, then distilled.

3. Neither sodium acetate nor sodium perchlorate had any measureable effect on the fluorescence quenching of naphthalene by **1**.
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8. A chain process is also initiated electrochemically. When a 3 x 10^{-3} molar sample of **1** is electrolyzed, in acetonitrile containing lithium perchlorate, to 10% completion all of the starting material has been converted to **2**. Therefore the chain length under these conditions is >10. Under these conditions no products other than **2** are observed. At longer electrolyzing times oxidation products of **2** are formed.
9. We have found that both acetophenone and benzophenone initiate a chain process in polar solvents, which can be quenched by base (either sodium acetate or tributyl amine) and enhanced by the addition of sodium perchlorate In these cases the quantum yield limits at a value of 2-4 rather than increasing in proportion to the concentration of **1**.
10. This has been shown to be the case for singlet pyrene quenched by dimethylaniline, N. Orbach, R. Potashnik, and M. Ottolenghi, *J. Phys. Chem.*, **76**, 1133 (1972), and Y. Taniguchi, Y. Nishina, and N. Mataga, *Bull. Chem. Soc. (Japan)*, **45**, 764 (1972).