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5-PHENYLTETRAZOLIDE ANION AS A PHOTOSENSITIZER

Peter Scheiner
Mobil Research and Development Corporation
P.O. Box 1025, Princeton, New Jersey 08540 USA

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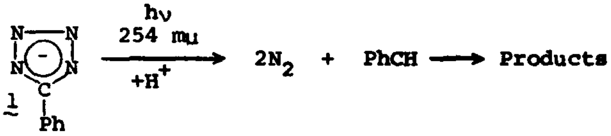
A previous report[1] described the photodecomposition of 5-phenyltetrazolide anion (1) to phenylcarbene.



It was noted that photolysis (N_2 evolution) was inhibited by dissolved oxygen. Further investigation has revealed the origin of this phenomenon and has shown that 1 can function as a "self-indicating" photosensitizer.

Conjugated dienes effectively quenched nitrogen evolution. In deoxygenated ethanol solutions, tetrabutylammonium 5-phenyltetrazolide (1, 0.026 M) failed to photolyze when irradiated[2] in the presence of 1,3-pentadiene, 2,4-hexadiene or 1,3-cyclohexadiene (each ca. 0.20 M). Since these compounds, as well as oxygen, are efficient acceptors of triplet energy,[3] it appeared probable that photolysis of 1 occurs from a relatively long-lived (quenchable) triplet state. Triplet energy transfer from 1 to 1,3-cyclohexadiene (E_T = 54 Kcal/mole) was confirmed by isolating the characteristic dimers derived from the triplet state of the diene.[4] The dimers were identical to those obtained by benzophenone photosensitization.

In cyclohexane, photolysis of 1 gives benzylcyclohexane by phenylcarbene CH insertion.[1] Quenching of the formation of this product by cis-2-trans-4-hexadiene followed a Stern-Volmer kinetic relationship (Fig. 1). That Fig. 1 represents quenching of an excited state, and not chemical interception of the phenylcarbene intermediate, is indicated by the lack of effect observed with 1-hexene.

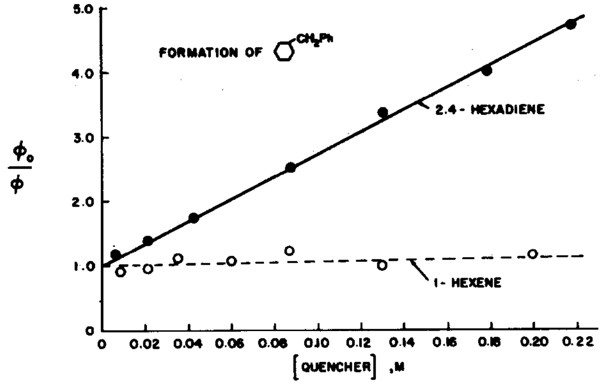


Fig. 1. Quenching of Product Formation. Photolysis of 1 in Cyclohexane.

Two examples of photosensitization by phenyltetrazolide anion were examined. Under conditions where 1 absorbed 93% of the incident radiation, trans-stilbene quenched N_2 evolution. In the process, however, stilbene underwent photosensitized isomerization. cis-Stilbene behaved in a similar manner. The photostationary state attained with tetrazolide anion (Fig. 2) lies close to that reported for other high energy sensitizers (E_T > 65 Kcal/mole).[3,5] Irradiation of the stilbenes in the absence of 1 produced a different isomer mixture.[5] Similarly, the conversion of norbornadiene to quadricyclene[6] was

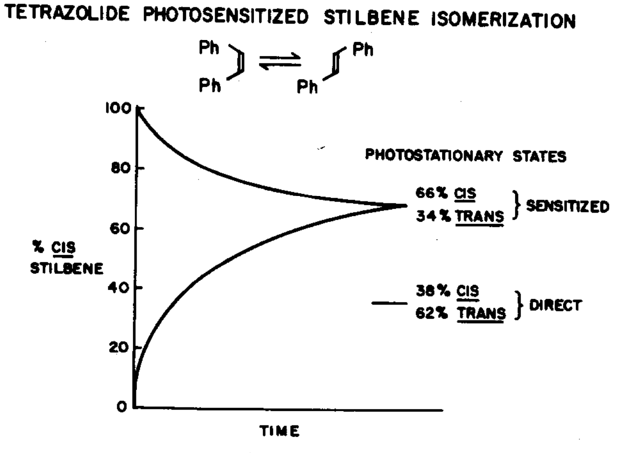


Fig. 2.

photosensitized by 5-phenyltetrazolide.

Attempts to transfer triplet energy to **1** from benzophenone (E_T = 69 Kcal/mole) and propiophenone (75 Kcal/mole) were unsuccessful, i.e., no nitrogen evolution. Thus the first triplet state of **1** appeared to possess a triplet energy greater than 75 Kcal/mole. The emission spectrum (Fig. 3) confirmed this supposition. As with benzophenone, all emission occurred from the triplet state (phosphorescence).

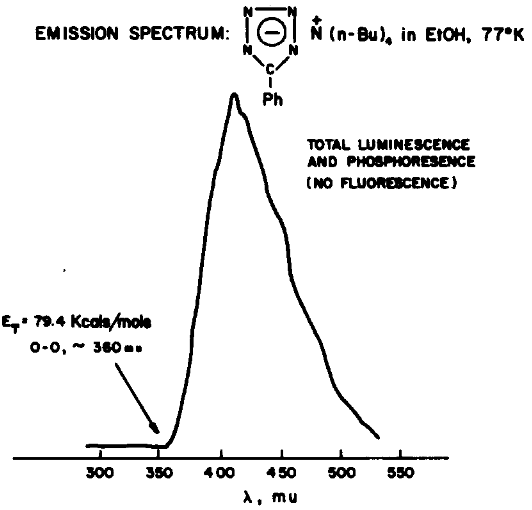


Fig. 3.

The onset of emission (360 mu) corresponds to a triplet energy of 79.4 Kcal/mole.

The triplet counting method[7] was employed to evaluate the intersystem crossing yield (the quantum yield for the production of triplets). The value was found to be 0.41.[8]

The foregoing results indicate that photoexcitation of 5-phenyltetrazolide (**1**) leads to a long-lived triplet state (E_T = 79 Kcal/mole) capable of donating its energy to suitable acceptors. A notable feature of the reagent is its indicating property. When **1** functions as photosensitizer, nitrogen evolution is quenched; with no energy transfer, photolysis occurs and nitrogen evolution is observed. This unique property of **1** might prove useful in exploratory work in energy transfer, and in assigning triplet energies to various substrates.

REFERENCES

1. P. Scheiner, J. Org. Chem., 34, 199 (1969).
2. Irradiations conducted in quartz tubes at 254 mμ in a Rayonet chamber reactor. The absorption spectrum of 1 shows λ_{max} 240 mμ ($\epsilon \sim 1.3 \times 10^4$).
3. L. M. Stephenson and G. S. Hammond, Angew. Chem. Int. Ed., 8, 261 (1969).
4. D. Valentine, N. J. Turro, and G. S. Hammond, J. Amer. Chem. Soc., 86, 5202 (1964).
5. G. S. Hammond, et al., J. Amer. Chem. Soc., 86, 3197 (1964).
6. G. S. Hammond, N. J. Turro, and A. Fisher, J. Amer. Chem. Soc., 83, 4674 (1961). G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, ibid., 86, 2532 (1964).
7. A. A. Lamola and G. S. Hammond, J. Chem. Phys., 43, 2129 (1965).
8. Piperylene isomerization in ethanol with naphthalene as the reference sensitizer. Measurements made by the Southern New England Ultraviolet Co.