

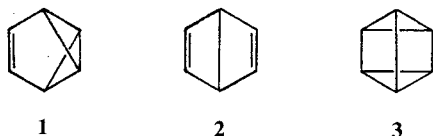
# ENERGY STORAGE AND RELEASE. DIRECT AND SENSITIZED PHOTOREACTIONS OF DEWAR BENZENE AND PRISMANE

Nicholas J. Turro, V. Ramamurthy, and Thomas J. Katz

Department of Chemistry, Columbia University,  
New York, N. Y. 10027. Received May 31, 1977.

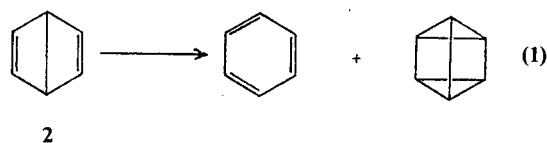
**ABSTRACT.** — The direct and triplet photosensitized excitation of Dewar benzene (2) and prismane (3) have been investigated. Direct excitation of 2 produces (in contrast to a literature report) prismane (15%), although benzene is the major product. Triplet photosensitization ( $E_T > 66$  kcal/mole) yields benzene as the exclusive product. The latter reaction involves an adiabatic ring opening of Dewar benzene triplet and a quantum chain reaction. No evidence was found for an adiabatic ring opening of 2 as a result of direct photoexcitation. Direct photoexcitation of 3 yields benzene (~90 %) and Dewar-benzene (~10 %), but triplet photosensitization ( $E_T$  as low as 50 kcal/mole) yields 2 as the major product. No evidence could be found for adiabatic formation of benzene excited states from direct excitation of 3.

The valence isomers of benzene possess the remarkable ability to store enormous quantities of potential energy in their highly strained aromatizable structure. Recently it was found that the energy rich benzvalene structure (1), even after it is excited by direct and sensitized excitation with light, survives and does not release the enormous excess energy possessed by the system<sup>1</sup>. As a continuation of our studies directed at the identification of features controlling the storage and release of chemical energy in simple, prototype organic structures<sup>2</sup>, we have investigated the direct and triplet sensitized photochemistry of Dewar benzene (2) and prismane (3).



Direct photoexcitation (254 nm) of Dewar benzene has been reported to yield benzene as the exclusive product<sup>3</sup>.

We find that although benzene is invariably the major product, when the initial concentration of 2 is less than  $10^{-2}$  M, prismane is formed in significant amounts [equation (1)]<sup>4</sup>.



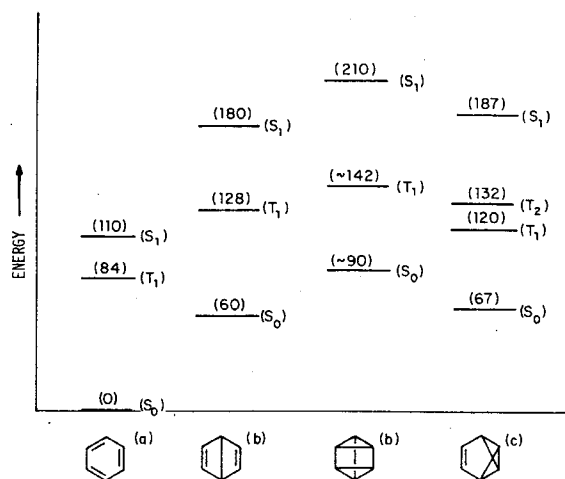
Direct	85%	15%
<sup>3</sup> sens ( $E_T > 66$ )	100%	0%
<sup>3</sup> sens ( $E_T < 66$ )	— no reaction —	—

We propose that the origin of this concentration dependence is due to a secondary *benzene triplet photosensitized* excitation of 2 which causes rearrangement to benzene. Indeed, we find that "high energy" triplet sensitizers ( $E_T > 66$  kcal/mole) effect rearrangement of 2 to benzene [equation (1) and Table 1]. Thus, benzene, produced from photolysis of 2, begins to competitively absorb, benzene triplets ( $E_T \sim 82$  kcal/mole)

**Table.** — Photochemical reactions of Dewar benzene and prismane.

Sensitizer	Triplet energy	$\Phi$ 2 → benzene	$\Phi$ 3 → 2 + benzene	$k_{q_2}$ <sup>c</sup>	$\Phi$ <sup>d</sup>
Acetone	78-81	0.4	—	$1.4 \times 10^{10}$	—
Acetophenone	74	0.4	~ 10	~ $10^{10}$	0.20
Xanthone	74	0.45	~ 10	—	0.20
<i>p</i> -methoxy acetophenone	72	0.35	~ 6	—	—
Benzophenone	69	0.16	~ 6	$2.5 \times 10^9$	0.10
4-bromo biphenyl	66	0.15	—	< $10^7$	0.12
Michler's ketone	62	—	—	—	0.08
1,4-dibromo naphthalene	60	< 0.01	—	< $10^7$	0.08
2-acetonaphthone	59	< 0.01	—	—	—
Fluorenone	53	< 0.01	—	—	0.06
Benzil	53	—	—	—	—

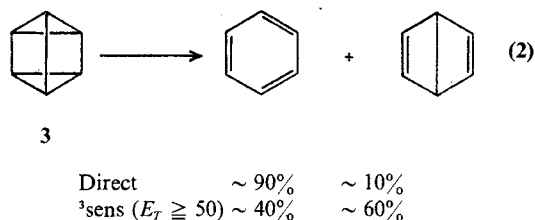
<sup>a</sup>,  $\Phi$  for benzene formation at 0.05 M Dewar benzene; <sup>b</sup>,  $\Phi$  for benzene formation at  $\infty$  M Dewar benzene, extrapolated value; <sup>c</sup>, phosphorescence quenching constant; <sup>d</sup>,  $\Phi$  for Dewar benzene and benzene formation at 0.06 M prismane.



Energy diagram for benzene isomers. Energy in kcal/mole. (a) Handbook of Photochemistry, S. Murov, Marcel Dekker, Inc. (1973). (b) Strain energy based on hexamethyl Dewar benzene, J. F. M. Oth, *Angew. Chem. Int. Ed. Engl.*, **7**, 646 (1968); J. F. M. Oth, *Rec. Trav. Chim. Pays Bas*, **87**, 1185 (1968); W. Adam, and J. C. Chang, *Int. J. Chem. Kinetics*, **1**, 487 (1969). (c) N. J. Turro, C. A. Renner, T. J. Katz, K. B. Wilberg, and H. A. Connon, *Tetrahedron Letters*, 4133 (1976); C. A. Renner, T. J. Katz, J. Pouliquen, N. J. Turro, and W. H. Waddell, *J. Amer. Chem. Soc.*, **97**, 2567 (1975).

(Fig.) are formed and cause sensitized rearrangement of 2 to benzene. Furthermore, quantum yield measurements for photosensitized rearrangement of 2 to benzene (acetophenone, xanthone and benzophenone) as a function of concentration of 2 indicate that a quantum chain is operating ( $\Phi_{\text{lim}} \sim 10$ )<sup>5</sup>. From this we conclude that triplet Dewar benzene rearranges to benzene triplet in an *adiabatic photo-reaction*. The benzene triplet produced can attack a ground state Dewar benzene molecule to produce triplet benzene and propagate the quantum chain. In the case of *direct* photoexcitation of 2 no evidence could be found for adiabatic formation of benzene singlet (absence of benzene fluorescence) or benzene triplet (lack of quantum chain). The sensitization experiments suggest that the energy of the triplet of 2 is in the range of  $\sim 68$  kcal/mole. This value is consistent with that of other strained olefins (i. e. norbornene,  $\sim 74$  kcal/mole and norbornadiene,  $\sim 67$  kcal/mole)<sup>6</sup>.

Direct photoexcitation of prismane (254 nm) results in formation of benzene as the major product along with minor amounts of Dewar benzene [equation (2)]. The products derived from triplet photosensitized excitation of 3 are energy dependent. "High" energy sensitizers ( $E_T > 66$  kcal/mole) lead exclusively to benzene, whereas



"low" energy sensitizers ( $E_T < 66$  kcal/mole) lead to 2 as the major product (2). The dependence of products on sensitizer energy is (like the initial failure to observe 3 from direct excitation of 2) an artifact of secondary processes. High energy sensitizers are found to produce both 2 and benzene at low conversions. Sensitized excitation of 2 (followed by its rearrangement to benzene) soon becomes competitive with sensitized excitation of 3, and the steady state concentration of 2 decreases. Low energy sensitizers, however, do not affect the rearrangement of 2 to benzene. No evidence for adiabatic formation of benzene excited states from direct excitation of 3 was obtained.

The results reported here allow a summary of the photo-reactions of benzene valence isomers to be made. In the case of direct photoexcitation aromatization to benzene occurs in competition with the regeneration of 1, 2 or 3. In the case of benzvalene, the isomerization is a degenerate reaction, revealed only by labelling. Dewar benzene yields prismane, whereas prismane yields Dewar benzene. In no case could evidence for adiabatic ring opening to excited benzene be obtained.

In the case of sensitized triplet excitation, aromatization to benzene occurs in all cases, but in the case of 1 and 2 the aromatization process proceeds via adiabatic rearrangement to benzene triplet. In the case of triplet 2, aromatization ( ${}^32 \rightarrow {}^3\text{benzene}$ ) is the exclusive process, whereas for 1 and 3 rearrangements ( ${}^31 \rightarrow 1$ , and  ${}^33 \rightarrow 2$ ) compete formation of benzene.

These results are relevant to any theory which attempts to reveal the factors which control massive energy storage and release in simple organic structures. Of particular importance is the observation that in every case investigated the electronically excited structures \*1, \*2, \*3 (both singlet and triplet) explore reaction pathways that *preserve* massive amounts of energy (i. e., adiabatic photoreactions or rearrangement to 1, 2 or 3 in competition with energy release by rearrangement to benzene ground state).

These results are also pertinent to previous reports of adiabatic photoreactions of valence isomers of naphthalene and anthracene. In particular, the *failure* of singlet Dewar benzene to undergo adiabatic rearrangement to benzene contrasts with reports that Dewar naphthalene<sup>7</sup> and Dewar anthracene<sup>8</sup> both undergo adiabatic ring opening reactions. In fact, consideration of energy surfaces leads to the initial expectation that the Dewar benzene to benzene rearrangements *should not* be an adiabatic process. In the case of the adiabatic rearrangement of Dewar naphthalene singlet to naphthalene singlet, an *ad hoc* proposal concerning the tilt of the potential surface (caused by strain energy) was proposed to rationalize the failure of radiationless deactivation from the excited surface to compete with adiabatic rearrangement. Much remains to be done to add to our theoretical understanding of energy storage and energy release by small organic molecules. The information reported here should be useful in calibrating and restricting theoretical efforts in this regard.

Finally, the triplet-sensitized formation of 2 from 3 is worthy of note since it represents an example of a rare class of "sigma bond" sensitizations. Of particular interest is the observation that sensitizers whose triplet energies are as low as  $\sim 50$  kcal/mole are capable of sensitizing this reaction. But, it is not clear whether the sensitization is by collisional energy transfer to the low lying triplet state of prismane or by exciplex formation or by Schenck type mechanism.

**Acknowledgement**

The authors at Columbia University wish to thank the Air Force Office of Scientific Research (Grant AFOSR-74-2589E), the National Science Foundation (Grants NSF-CHE76-18590 and NSF-CHE73-04672) and the National Institutes of Health (Grant GM-19173) for their generous support of this research. We also thank Dr Carl Renner for his assistance and discussions during the initial stages of this research.

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