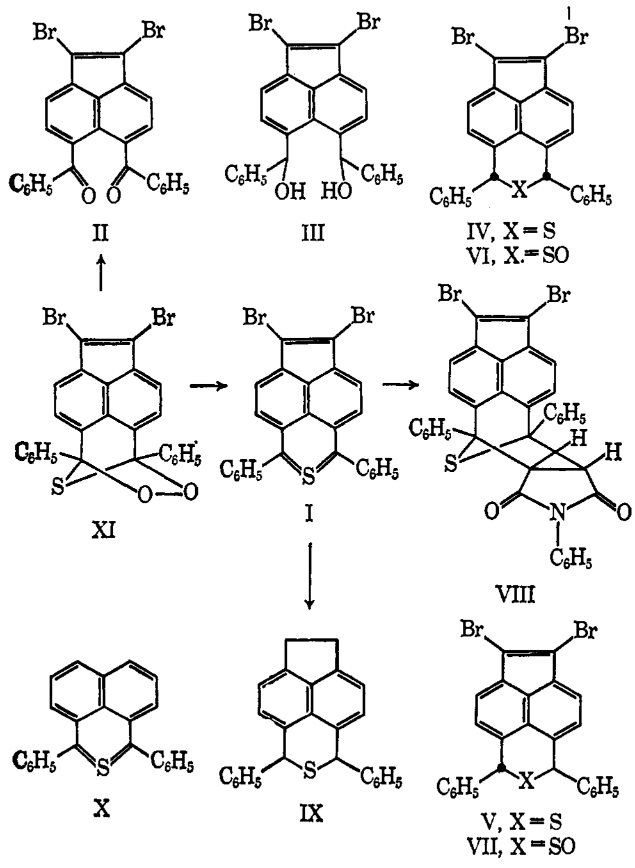
spectrum changed very little in methanol or dioxane. The nmr spectrum of I showed resonance for the phenyl protons centered at δ 7.62 and a well-defined quartet for the naphthalene protons centered at δ 7.95 and 8.35 with a coupling constant of 9 cps. The mass spectrum gave peaks at *m/e* 517.9185 (heterocycle I, 517.9164 based on $C_{26}H_{14}Br_2S$) and 485.9467 (1,2-dibromo-5,6-diphenylpyracylene, 485.9443 based on $C_{26}H_{14}Br_2$).

Reaction of I with N-phenylmaleimide in degassed benzene solution at 80° gave rise to the *exo* Diels–Alder adduct VIII as yellow needles, mp >340°, in high yield. The same adduct was obtained from the decomposition of sulfoxide VI in acetic anhydride at 120°. Adduct VIII exhibited an ultraviolet spectrum similar to the other dibromoacenaphthylene derivatives in this series. The mass spectrum of VIII showed a retro-Diels–Alder fragmentation pattern with peaks at *m/e* 517.9183 (heterocycle I) and 173 (N-phenylmaleimide) as well as the parent ion at 690.9636 (calculated 690.9671). The nmr spectrum of the adduct gave resonance for the two protons α to the imide carbonyls at δ 5.25, a position compatible with *exo* geometry.[7]

Heterocycle I did not undergo catalytic hydrogenation with palladium on carbon in methanol. Sulfide IX was obtained from I in low yield when platinum oxide was used.

The transient heterocycle 1,3-diphenyl-2-thiaphenalene (X)[1e] has been reported to undero sulfur extrusion, giving rise to 1,2-diphenylacenaphthylene. This reaction was shown to occur by ring closure of X to the corresponding episulfide. A similar conversion of I to the corresponding pyracylene has not been found thus far. Heating either melts or solutions of I above 130° results only in the formation of polymer. Degassed benzene solutions of I are completely unchanged after long irradiation with a variety of wavelengths of light.[8]



Heterocycle X was found also to undergo reaction with oxygen to give 1,8-dibenzoylnaphthalene.[1e] It was suggested that this reaction might occur by initial formation of a peroxide adduct followed by loss of sulfur to give the diketone. Dark blue benzene solutions of I saturated with oxygen rapidly faded to orange when irradiated with light of wavelengths greater than 360 mμ. Initial thin layer chromatographic examination of the reaction mixture showed the presence of two orange components, one of which was identified as the diketone II. On further irradiation or standing in the dark, the second component was observed to decompose to the diketone. Thick layer chromatography of the reaction mixture gave II in good yield. Oxygen-enriched solutions of I have been found to be stable in the dark. These results suggest that I in the excited state sensitizes the formation of singlet oxygen which then undergoes Diels–Alder reaction with ground-state heterocycle to give the peroxide adduct XI.[9] We have made no attempt to isolate XI although it seems reasonable to assume that it is the second component of the photolysis mixture. It is not possible at this time to conclude that heterocycle X reacts with oxygen in the same manner.

Heterocycle I contains $4n + 2$ peripheral π electrons which may be delocalized in a number of resonance forms. This favorable electronic configuration together with the heavy-atom influence of bromine may account for the stability of I. It is hoped that further effort, including an X-ray study of I, will make possible a more definitive description of these interesting systems.

Acknowledgments. This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation and by the Petroleum Research Fund (Grant No. 756-G). We wish to thank Mr. A. Struck of the Perkin-Elmer Company for determining the mass spectra. I. S. P. wishes to acknowledge the Shell Foundation for a Research Assistantship.

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[7] For a more detailed discussion, see ref 1c and 1e.

[8] A Hanovia 450-W medium-pressure mercury arc lamp fitted either with interference or color filters was used.

[9] For an excellent review of the role of singlet oxygen in photosensitized oxygenations, see C. S. Foote, *Accounts Chem. Res.*, 1, 104 (1968).

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Control of Photochemical Reaction Pathways by Excited-State Multiplicity. Mechanistic and Exploratory Organic Photochemistry. XXXIV[1]

Sir:

The number of intramolecular photochemical reactions in which the pathway chosen by the triplet excited state differs from that of the singlet is exceedingly limited. We presently wish to report an especially

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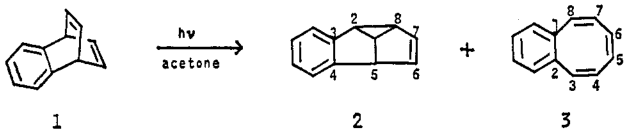
[1] For paper XXXIII see H. E. Zimmerman, K. G. Hancock, and G. L. Licke, *J. Am. Chem. Soc.*, in press.

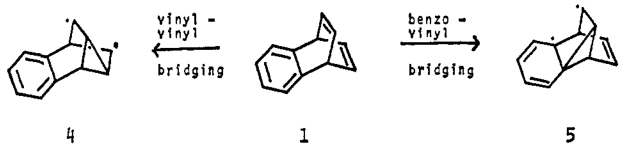
intriguing example of such behavior where the structural details of the alternative processes have been delineated and depend subtly on multiplicity.

Irradiation of benzobarrelene (**1**)[2] with acetone sensitization affords primarily (48%, 90% based on unrecovered reactant) benzosemibullvalene (**2**)[3] plus (5%, 10% based on unrecovered reactant) benzocyclooctatetraene (**3**).[4] This is analogous to our previously



reported[5] transformation of barrelene to semibullvalene and some cyclooctatetraene and is another example of the divinylmethane or di-π-methane transformation we proposed as general.[6]

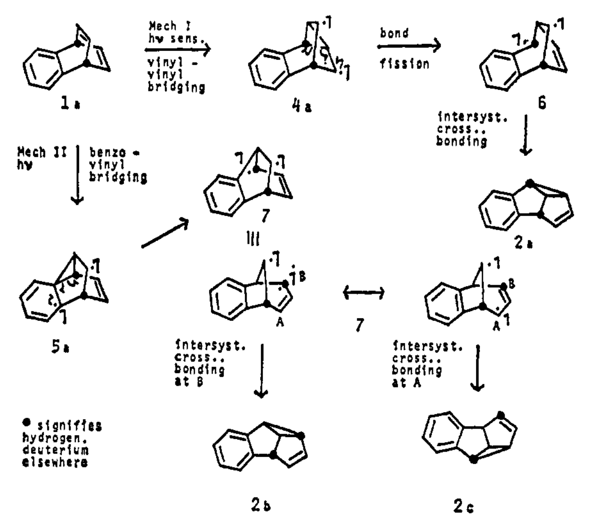
A priori, two types of bonding are possible as initial excited-state processes, vinyl–vinyl and benzo–vinyl bridging, if one assumes the same mechanism elucidated for the barrelene example. Strikingly, the path preferred has been found to depend on the excited-state benzobarrelene multiplicity, with each type of bridging leading to a different product.



It appeared that an understanding of the rearrangements required labeled benzobarrelene (**1a**); this was prepared by lithium N-deuteriocyclohexylamide in N,N-dideuteriocyclohexylamine following the general procedure used in labeling barrelene.[6] It was found that the bridgehead hydrogen atoms were located in benzosemibullvalene product (**2**) at C-2 and C-5 (*i.e.*, structure **2a** in Chart I).[3d] Inspection of Chart I reveals that this labeling is consistent with mechanism I, involving initial vinyl–vinyl bridging, but not mechanism II, proceeding with benzo–vinyl bonding.

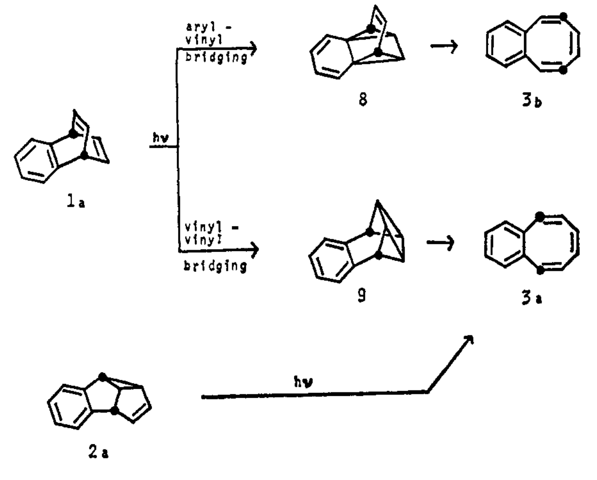
In contrast to the photosensitized irradiation, direct photolysis[3c] afforded only benzocycloctatetraene (**3**). This provides clear evidence that benzosemibullvalene (**2**) obtained on sensitization derives from the triplet, secondly that benzocyclooctatetraene arises from rearrangement of the singlet of benzobarrelene, and finally that intersystem crossing of the benzobarrelene singlet to triplet must be slow since no benzosemibullvalene could be detected in the direct irradiation.[7]

Chart I. Benzobarrelene to Benzosemibullvalene Rearrangement: Vinyl–Vinyl Bridging (Mechanism I) *vs.* Benzo–Vinyl Bridging (Mechanism II)



Remarkably, the route to give benzocyclooctatetraene on direct irradiation did not proceed *via* benzosemibullvalene despite the fact that benzosemibullvalene on irradiation also gives benzocyclooctatetraene. This conclusion derives from the differing hydrogen distributions in the benzocyclooctatetraene produced in direct irradiation of labeled benzobarrelene and from irradiation of the labeled benzosemibullvalene produced from sensitized runs (note Chart II).[3d] The label in the direct irradiation was found mainly at C-4 and C-7 (*i.e.*, **3b**), with 6% at C-3 and C-8. In the product from labeled benzosemibullvalene the hydrogen was at C-3 and C-8 (*i.e.*, **3a**), with an experimental error of ~15%.

Chart II



• signifies Hydrogen, Deuterium elsewhere

The direct irradiation labeling pattern clearly suggests quadricyclene-like intermediates **8** (major) and **9** (minor), one involving four-center vinyl-benzo cycloaddition[8] and the other deriving from vinyl-vinyl cycli-

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[2] K. Kitahonoki and Y. Takano, *Tetrahedron Letters*, 1597 (1963).

[3] (a) All new compounds gave acceptable analyses. (b) The structural assignment was based on nmr [τ 2.67–3.20 m (4 H, aromatic), 4.43–4.62 q (1 H, H_6), 4.83–5.00 q (1 H, H_7), 6.10–6.28 q (1 H, H_5), 6.74–6.98 q (1 H, H_1), 7.02–7.25 t (1 H, H_2), 7.25–7.55 d (1 H, H_8); $J_{12} = J_{18} = J_{28} = 6.5$ cps, $J_{15} = 6.0$ cps, $J_{56} = J_{78} = 2.0$ cps, $J_{67} = 5.0$ cps] and degradation. (c) Full details of photolysis conditions, synthetic and degradative aspects, and spin decoupling are given in our full paper. Photolysis was in isopentane in sealed, degassed Vycor tubes strapped to a water-cooled well of a 450-W medium-pressure lamp. (d) Assay of labeled compounds is detailed in our full paper.

[4] L. Friedman, *J. Am. Chem. Soc.*, **89**, 3071 (1967).

[5] H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966).

[6] H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967).

[7] After the qualitative aspects of our study were complete the related photochemical study of tetrafluorobenzobarrelene was reported by J. P. N. Brewer and H. Heany, *Chem. Commun.*, 811 (1967). These workers found our barrelene to semibullvalene route to be followed and noted a multiplicity effect qualitatively similar to that presently found except that some tetrafluorobenzosemibullvalene product was found on direct irradiation in contrast to the present study.

[8] Most recently G. R. Ziegler and G. S. Hammond, *J. Am. Chem. Soc.*, 90, 513 (1968), reported the first case of such benzo–vinyl addition and concluded it came from the singlet since the reaction could not be sensitized.

zation. Therefore the major singlet process involves benzo-vinyl interaction in contrast to the preferred vinyl-vinyl interaction in the triplet.

The preferred triplet vinyl-vinyl bonding seems to derive from the lower energy of the triplet species engendered in an endwise overlap. Vinyl-vinyl overlap gives a species approximating the electronics of triplet cisoid butadiene (E_T = 53.5 kcal/mole[9a]) while vinyl-benzo overlap leads to a styrene-like triplet (E_T = 61.8 kcal/mole[9b,c]).

Finally, it should be noted that the excited singlet vinyl-vinyl and vinyl-benzo cycloadditions are symmetry allowed.[10]

Acknowledgment. Support of this research by predoctoral National Institutes of Health fellowships to R. S. G. and R. M. P., by National Institutes of Health Grant GM 07487, and by the National Science Foundation is gratefully acknowledged.

(9) (a) D. F. Evans, *J. Chem. Soc.*, 1735 (1960), for cyclohexadiene; (b) D. F. Evans, *ibid.*, 1351 (1957); (c) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965), for *trans*-β-methylstyrene (59.8 kcal/mole).

(10) (a) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965); (b) H. E. Zimmerman, *ibid.*, **88**, 1564 (1966); (c) H. E. Zimmerman, *Science*, **153**, 837 (1966).

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The Lithium Salt Catalyzed Epoxide–Carbonyl Rearrangement

Sir:

We wish to report that epoxides undergo facile lithium salt catalyzed rearrangement to carbonyl compounds in benzene solution. A dual mechanism is proposed which accounts for the strong anion dependence of both product distribution and reaction rate.

Lithium bromide is effectively insoluble in benzene, but the addition of 1 mole of tri-*n*-butylphosphine oxide/mole of salt leads to a soluble complex which may be used to effect epoxide rearrangement.[1] The electrophilic aspect of this reaction is evident from the marked rate depression observed on addition of a small amount of THF or the use of monoglyme in place of benzene as solvent. However, cyclohexene oxide reacts more rapidly than its 1-methyl or 1,2-dimethyl analog, as shown by the data in Table I. Product yields were excellent in all instances.[3] Rate constants were obtained by following loss of epoxide (vpc).

Lithium perchlorate is also insoluble in benzene, but again can be solubilized by tri-*n*-butylphosphine oxide. Interestingly, both the rates and the products obtained with this reagent (Table II) differ greatly from those obtained with LiBr. Thus the rate of rearrangement of the secondary,secondary epoxide 1 falls off sharply, while both **2** and **3**, containing tertiary centers, react more rapidly. Increasing the proportion of phosphine oxide to $LiClO_4$ causes a large rate decrease, and, in fact, the fastest reactions observed to date are those of **2** and **3** with "insoluble" $LiClO_4$ alone.[4] The product ratios under these conditions remain as shown in Table II.

Table I. Rearrangement by $LiBr \cdot Bu_3P{\rightarrow}O$ (0.71 *M*) in Benzene at 80°

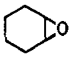
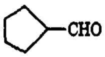
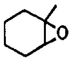
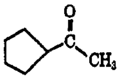
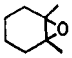
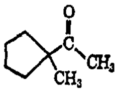
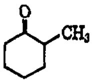
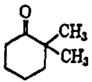
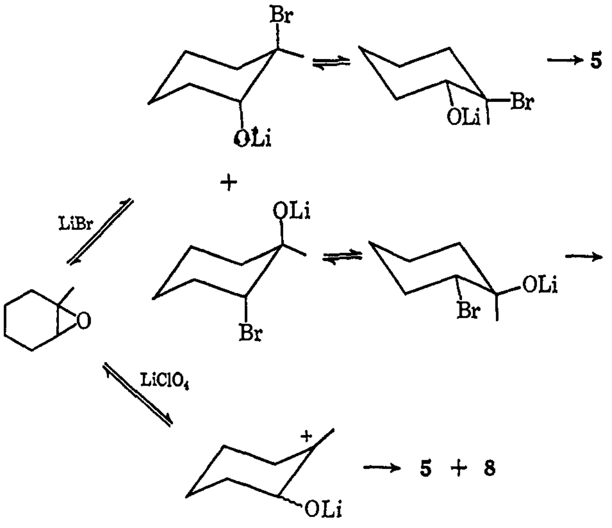
Reactant	10^4k, sec^{-1}	Products
 **1**	2.85	 **4**
 **2**	1.0	 **5**,70% +  **6**,30%
 **3**	0.05	 **7**

Table II. Rearrangement by $LiClO_4 \cdot Bu_3P{\rightarrow}O$ (0.71 *M*) in Benzene at 80°

Reactant	10^4k, sec^{-1}	Products
1	0.01	**4** (low yield)
2	Too fast (> 30)	**5**,20% +  **8**,80%
3	8.8	**7**,90% +  **9**,10%

We suggest that the lithium halide catalyzed reaction occurs through the intermediacy of the halohydrin salt,[5] while the lithium perchlorate catalyst serves to



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(1) Other dipolar materials also exert this solubilizing influence, *e.g.*, hexamethylphosphoramide and the ylide tri-*n*-butylcarboethoxymethylenephosphorane. The mechanism described here is responsible for the ylide–epoxide reaction we have recently reported;[2] details will be presented in the full paper.

(2) R. M. Gerkin and B. Rickborn, *J. Am. Chem. Soc.*, **89**, 5850 (1967).

(3) The aldehyde **4** is partially lost in the course of reaction, possibly *via* aldol condensation (**5** is stable). When run in the presence of ylide,[1] the unsaturated ester[2] is obtained in ~90% yield.

(4) Quite clearly the epoxides exert a considerable solubilizing influence on this salt; when epoxide is added to a refluxing mixture of benzene and $LiClO_4$ (on the bottom of the flask), a ring of the salt appears almost immediately at the surface of the boiling liquid. Under these conditions, the reactions of **2** and **3** are complete in less than 5 min.

(5) A similar intermediate has been proposed for the reaction of **1** with methyllithium in the presence of lithium iodide (in ether).[6] Lithium bromide apparently does not compete well with the methyllithium