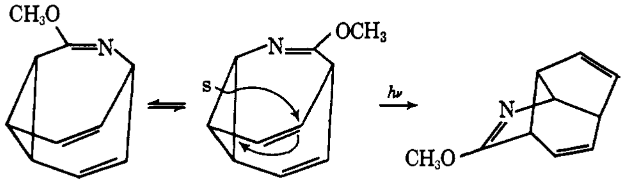
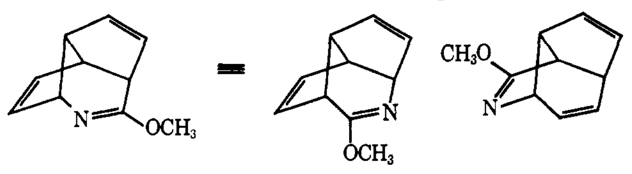
the same conditions but with acetone as both solvent and sensitizer, the reaction rate was faster than that of the unsensitized runs *but* **1** *was the sole product.* Continued irradiation of **1** in this medium resulted in no further chemical change.

These results are congruent with the existence of a photoequilibrium between **1** and **6** under the conditions of direct irradiation. Further, the data are consistent with the formation of **2**, **3**, and **5** from singlet **6**. Symmetry-allowed disrotatory cyclization of the diene component in **6** gives **2** and **3** depending upon the direction of orbital rotation, while a concerted 1,3 suprafacial shift of bond a (see **6**) affords **5**.[9] Photoproduct **4** probably arises directly from singlet **1**; the simplest pathway leading to **4** is a 1,3 shift of cyclopropyl bond s in valence tautomer **7**. In this regard, it is particularly important to note that isomeric imino ethers **8** and **9** were not produced, despite the fact that these structures can also be derived from alternative vinylcyclopropane rearrangements in **1** and **7**.



1 **7** **4**

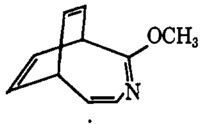


8 **9**

Finally, the significant sensitizing effect of acetone would seem to suggest that the singlet states of **1** and **6** cross to the corresponding triplet states with poor efficiency.

Acknowledgment. We wish to thank Badische Anilin and Soda Fabrik for a generous gift of cyclooctatetraene and Richard Cryberg for his assistance in obtaining the 100-MHz spectra.

(9) Here it is interesting that the formation of iv which could arise



iv

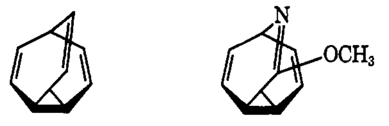
by a similar 1,3 suprafacial shift of bond b in **6** was not observed.

Leo A. Paquette, Grant R. Krow
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210
Received August 9, 1968

Benzazabullvalenes. Synthesis and Interconvertibility[1]

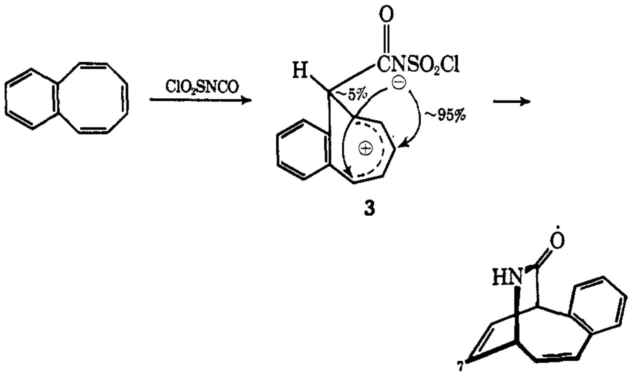
Sir:

Previously we have shown that incorporation of an imino ether function into the bullvalene molecule (**1**) drastically diminishes the number of accessible structural arrangements from 1,209,600 in **1** to only 28 in **2**.[2,3] The simplicity of the averaging process in **2** has been attributed to the strong preference of the nitrogen atom for the imino ether bond. Equally significant was the observation that the aza substituent also exhibits preferential attachment to the "bridgehead" carbon (as shown in **2**). We now report the extension of this study to benzo derivatives of **2** in the course of which an especially intriguing structural dependence on photochemical reactivity and an unprecedented thermal rearrangement have been delineated.



1 **2**

Treatment of benzocyclooctatetraene[4] with chlorosulfonyl isocyanate (CSI) at 82° for 3 hr followed by hydrolysis of the resulting N-(chlorosulfonyl)lactam with aqueous NaOH in acetone gave in 82% yield amide **4**, mp 226–227°;[5] $\nu_{max}^{CH_2Cl_2}$ 3390 and 1680 cm^{-1}; $\lambda_{max}^{CH_3CN}$ 269 mμ (ε 9700). Electrophilic attack of CSI on benzocyclooctatetraene therefore proceeds to give dipolar benzotropylium cation **3**, addition occurring in the manner expected from protonation data.[6] Collapse of the zwitterion occurs chiefly by bonding to C-5; careful nmr analysis of the unpurified amide indicated that an upper limit of 7% cyclization to C-3 could have occurred.[7]



3

4

The crystalline imino ether **5**,[5] obtained in 96% yield from **4** by treatment with trimethyloxonium fluoroborate, exhibited ultraviolet absorption (in hexane) at 273.5 mμ (ε 8500) and nmr peaks for H$_1$ and H$_6$ at δ 4.10 (doublet, J = 5.6 Hz) and 4.56 (triplet, J = 6.0 Hz), respectively. Irradiation of **5** with acetone sensitization afforded in 93% yield primarily benzazabullvalene **6** (>95%), plus benzisoazabullvalene **7** (<5%).[8] The structures of **6** [mp 113–114°;[5]

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[1] Unsaturated Heterocyclic Systems. XLVIII. For the previous paper in this series, see L. A. Paquette and G. Krow, *J. Am. Chem. Soc.*, **90**, 7149 (1968).

[2] L. A. Paquette and T. J. Barton, *J. Am. Chem. Soc.*, **89**, 5480 (1967).

[3] L. A. Paquette, T. J. Barton, and E. B. Whipple, *ibid.*, **89**, 5481 (1967).

[4] W. Merk and R. Pettit, *ibid.*, **89**, 4787 (1967).

[5] Satisfactory elemental analyses were obtained for all new compounds.

[6] W. Merk and R. Pettit, *J. Am. Chem. Soc.*, **90**, 814 (1968).

[7] The limited available quantity of this minor isomer precluded its isolation and characterization.

[8] We herein propose the name *isobullvalene* to unknown hydrocarbon i in an effort to maintain some degree of constancy in nomencla-

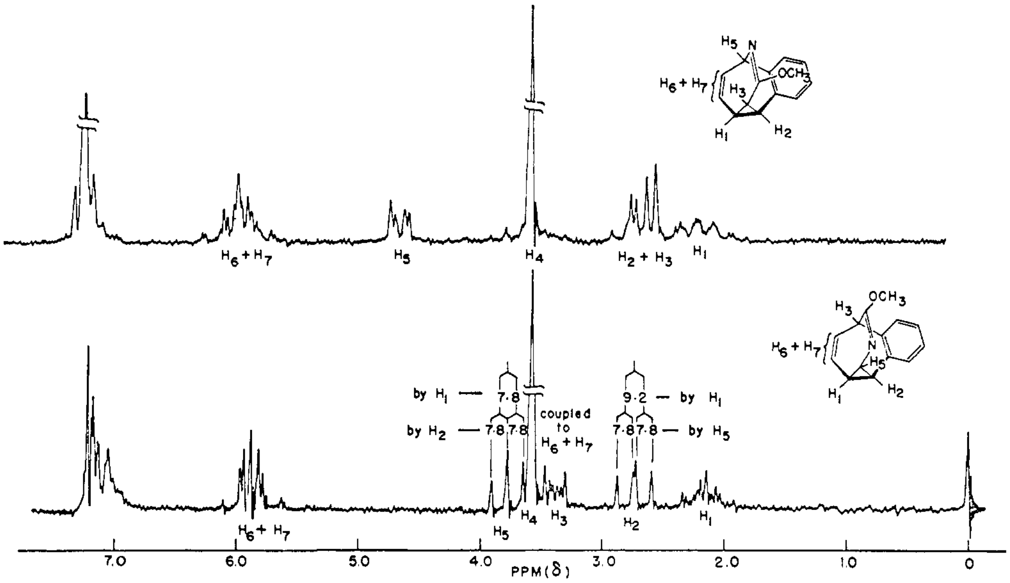
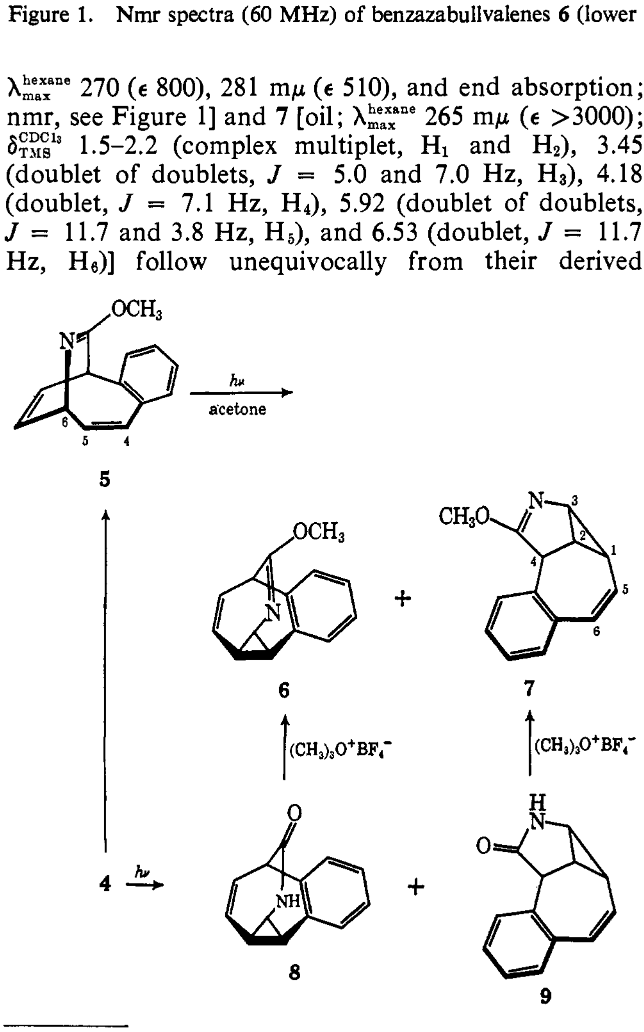


Figure 1. Nmr spectra (60 MHz) of benzazabullvalenes **6** (lower curve, $CDCl_3$) and **10** (upper curve, C_2Cl_4).

λ_{max}^{hexane} 270 (ϵ 800), 281 mμ (ϵ 510), and end absorption; nmr, see Figure 1] and **7** [oil; λ_{max}^{hexane} 265 mμ (ϵ >3000); $\delta_{TMS}^{CDCl_3}$ 1.5–2.2 (complex multiplet, H_1 and H_2), 3.45 (doublet of doublets, J = 5.0 and 7.0 Hz, H_3), 4.18 (doublet, J = 7.1 Hz, H_4), 5.92 (doublet of doublets, J = 11.7 and 3.8 Hz, H_5), and 6.53 (doublet, J = 11.7 Hz, H_6)] follow unequivocally from their derived spectral properties. Direct irradiation of **5** in ether (quartz optics) led to much polymerization; the characterizable portion of the product mixture consisted of **6** (20%) and at least 18 minor products (total yield of 10%).



In contrast, it was found that photosensitized irradiation of lactam **4** in acetone solution produced in quantitative yield a mixture of amides which without purification was treated directly with trimethyloxonium fluoroborate. Vpc analysis and preparative-scale tlc isolation of the two major imino ethers indicated that these products were **6** (17%) and **7** (50%). This provides clear evidence that lactam **9** predominates in the sensitized irradiation. Direct photolysis of **4** (THF, quartz optics) afforded **8** and **9** in yields of 21 and 33%, respectively. Amide **9** could be isolated in pure form, mp 239–243° dec;[5] $\nu_{max}^{CH_2Cl_2}$ 3390 and 1710 cm^{-1}; $\lambda_{max}^{CH_3CN}$ 264.5 mμ (ϵ 6500); nmr closely related to that of **7**.[9]

A priori, four types of symmetry allowed, concerted, *trans,trans* ($2\sigma + 2\pi$) cycloadditions[10] are possible from the photoexcited states of **4** and **5**. Strikingly, the primary isomerization pathway is seen to be highly dependent upon the nature of the heteroatomic bridge. In **5**, "topside" migration of the nitrogen atom from C_6 to C_5 with concurrent rebonding of the "underside" p orbital at C_4 to the backside of C_6 is preferred. Rebonding of the nitrogen atom again occurs in **4**, but migration to C_7 predominates. Remarkably, shift of the carbonyl group in **4** (or of the methoxyl-bearing carbon in **5**) is not detected despite the fact that all previously recorded ($2\sigma + 2\pi$) cycloadditions are found in the area of ketone photochemistry.[11] Nor is benzo-

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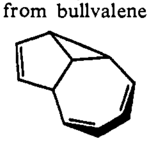
ture within this series of isomeric hydrocarbons. It may be seen that isobullvalene (i) is derived from bullvalene by a 1,3-sigmatropic shift



i

of one of the three double bonds away from the bridgehead carbon. Also, isobullvalene may be considered a vinylog of semibullvalene. The preparation of i is presently under active investigation in this laboratory.

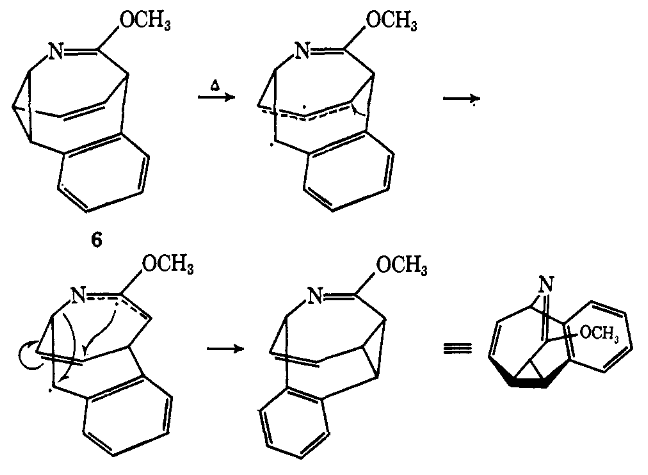
[9] Full details of these spectra, as well as spin decoupling, will be given in our complete paper.

[10] R. Hoffmann, private communication. We thank Professor Hoffmann for communicating to us his thoughts on ($2\sigma + 2\pi$) photochemical cycloadditions.

[11] See, for example: (a) L. A. Paquette, R. F. Eizember, and O. Cox, *J. Am. Chem. Soc.*, **90**, 5153 (1968); (b) J. R. Williams and H. Ziffer, *Chem. Commun.*, 194, 469 (1967); (c) B. Naun, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **48**, 1680 (1965), and earlier papers; (d) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963); (e) W. W. Kwie, B. A. Shoulders, and P. D. Gardner, *J. Am. Chem. Soc.*, **84**,

vinyl bonding observed.[12] The causative factors behind the contrasting photochemical behavior of **4** and **5** appear to be subtle and are presently the subject of further study.

Because of the benzo fusion in **6**, this molecule is not expected to exhibit a propensity for Cope rearrangement,[13] and such is the case. However, when a solution of **6** in tetrachloroethylene was heated to 125–150°, an *irreversible* reaction occurred in high yield. The rate of rearrangement could be conveniently followed by nmr; the following first-order rate constants and thermodynamic parameters were determined: $k_{125} = 1.68 \times 10^{-4}$ sec^{-1}; $k_{133} = 3.08 \times 10^{-4}$ sec^{-1}; $k_{143} = 7.52 \times 10^{-4}$ sec^{-1}; $\Delta H^{\ddagger} = 26.6$ kcal/mol; $\Delta S^{\ddagger} = -9.6$ eu. The nmr spectrum (Figure 1) of the thermal product is uniquely adaptable to benzazabullvalene formula **10**; mp 127–128.5°;[5] $\lambda_{\max}^{\text{hexane}}$ 265 (ϵ 350) and 276 mμ (ϵ 280), together with end absorption. Mechanistic passage to **10** requires a double migration; a possible reaction pathway is outlined.



6

10

The above-described thermal results would pass undetected in the case of benzobullvalene because of the obvious degeneracy of the rearrangement in this instance. At question, therefore, is whether there may be available to bullvalene and its congeners additional degenerate pathways which could compete with the Cope rearrangement at moderate to elevated temperatures.

Acknowledgment. We thank Professor R. Pettit for the generous gift of a 1-g sample of benzocyclooctatetraene which permitted this work to be accomplished readily. The authors acknowledge also the financial support of the Alfred P. Sloan Foundation and the National Science Foundation.

2268 (1962); (f) D. H. R. Barton, J. McGhie, and M. Rosenberger, *J. Chem. Soc.*, 1215 (1961), and earlier papers.

[12] After the completion of our study, H. E. Zimmerman, R. S. Givens, and R. M. Pagni [*J. Am. Chem. Soc.*, **90**, 4191 (1968)] reported that benzo–vinyl bonding was also not the mechanism followed in the sensitized irradiation of benzobarrelene.

[13] The preclusion of degenerate Cope rearrangements upon introduction of a fused benzene ring in bullvalene [G. Schröder and J. F. M. Oth, *Angew. Chem. Intern. Ed. Engl.*, **6**, 414 (1967)] and semibullvalene derivatives [J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 5081 (1967)] has already been noted.

Leo A. Paquette, John R. Malpass
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received August 9, 1968

A Criterion for Catalytically Active Intermediates

Sir:

Chemically or physically generated reactive intermediates have played a major role in speculations concerning mechanisms of enzyme action.[1] This communication outlines a general condition which an unstable intermediate must meet to lie on the principal path of a chemical reaction. Although a simple corollary of the principle of detailed balance, this condition's relevance to models for enzyme mechanisms has been overlooked, and its generality, as well as its pertinence to the work outlined in the accompanying communication,[1c] prompts its discussion here.

In its simplest form the problem can be formulated as shown below. A conversion of A to C can occur directly, by a path described by forward and reverse rate constants k_1 and k_{-1}, or indirectly, *via* B, an unstable, reactive isomer of A. One can envisage a catalytic device which attempts to exploit the heightened reactivity of B by facilitating the interconversion of A and B. One can then ask: under what further conditions will B lie on the major path linking A and C?

$$\begin{tikzcd} & B \arrow[dr, shift left, "k_2"] \arrow[dl, shift left] & \\ A \arrow[ur, shift left, "K_E"] \arrow[rr, shift left, "k_1"] & & C \arrow[ll, shift left, "k_{-1}"] \arrow[ul, shift left, "k_{-2}"] \end{tikzcd}$$

$$K_1 = \frac{k_1}{k_{-1}}$$

$$K_2 = \frac{k_2}{k_{-2}}$$

$$K_E < 1$$

$$\gamma \equiv \frac{\log (k_1/k_2)}{\log (K_1/K_2)} = \frac{\log (k_1/k_2)}{\log K_E} \qquad (1)$$

$$\frac{\text{reaction A} \rightarrow \text{B} \rightarrow \text{C}}{\text{reaction A} \rightarrow \text{C}} = \frac{k_2[\text{B}]}{k_1[\text{A}]} = K_E^{-\gamma}K_E = K_E^{1-\gamma} \qquad (2)$$

With the uncatalyzed conversion A → C as a standard, eq 2 may be derived which indicates that B can be a catalytically effective intermediate only if the parameter, γ, defined analogously to a Brønsted coefficient, can be made to exceed unity. The possible situations are illustrated in Figure 1 by reaction coordinate–energy diagrams. For $\gamma < 1$, both forward and reverse rate constants for the B–C interconversion show the expected effect of the instability of B: B is converted more rapidly than A to C, and C, more rapidly to A than B. This behavior must characterize all B species whose conversions to C bear a direct mechanistic correspondence to the conversion of A to C, quantitative differences between the two processes being assignable to rationalizable factors such as basicity. In this sense, noncatalytic high-energy intermediates are *normal* intermediates, for which heightened reactivity fails to compensate inferior concentration.[2]

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[1] W. P. Jencks, *Ann. Rev. Biochem.*, **32**, 639 (1963); M. Eigen and G. Hammes, *Advan. Enzymol.*, **25**, 1 (1963); D. Koshland, *ibid.*, **22**, 45 (1960); (c) D. S. Kemp and T. D. Thibault, *J. Amer. Chem. Soc.*, **90**, 7154 (1968).

[2] Breslow[3] has applied this principle in a less formal way to elimination reactions.

[3] R. Breslow, *Tetrahedron Lett.*, **8**, 399 (1964).