

Acknowledgment. We thank Professor Michl of the University of Utah for helpful discussions. This work was supported in part by the Office of Naval Research and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

- (1) For leading references, see "Organic Peroxides", D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1970.
- (2) The systematic name for this compound is 1,4-diphenyl-2,3-benzodioxin. We prefer to use the trivial name that identifies **2** as containing both an *o*-xylylene moiety and a peroxide linkage.
- (3) J. Y. Koo and G. B. Schuster, *J. Am. Chem. Soc.*, **99**, 6107 (1977).
- (4) J. M. Holland and D. W. Jones, *J. Chem. Soc. C*, **530** (1970). In this paper the pyranone was reported to take up O₂ in the dark; the peroxide that results in that circumstance is probably a polymer.
- (5) The endoperoxide was characterized as follows: IR (CHCl₃) 2950, 1785, 1525, 1460, 1330 cm⁻¹; ¹H NMR (CDCl₃, internal Me₄Si) δ 6.8–7.0 (m, 2 H), 7.2–7.9 (m, 12 H); ¹³C NMR (CDCl₃, internal Me₄Si) δ 166, 136, 130.8, 130.2, 129.6, 129.3, 128.8, 128.2; mol wt (osmometry) required 330, found 328 ± 4; active oxygen contents, 87 ± 10% of theoretical. Anal. Calcd for C₂₁H₁₄O₄: C, 76.36; H, 4.24. Found: C, 76.36; H, 4.27.
- (6) These compounds were identified by comparison with authentic samples. The *o*-dibenzoylbenzene was prepared according to F. R. Jensen, *J. Org. Chem.*, **25**, 269 (1960), and the phenyl (*o*-benzoyl)benzoate according to F. F. Blicke and R. D. Swisher, *J. Am. Chem. Soc.*, **56**, 902 (1934).
- (7) This observation is consistent with formation of **2** and **5** along parallel paths from **1**.
- (8) The adduct was characterized as follows: IR (CHCl₃) 2980, 1870, 1690, 1600, 1490 cm⁻¹; ¹H NMR (CDCl₃, internal Me₄Si) δ 7.0–7.85 (m, 14 H), 4.1 (s, 2 H); mol wt (osmometry) required 384, found 381 ± 5; active oxygen content, 94.4 ± 6% of theoretical. Anal. Calcd for C₂₄H₁₆O₅: C, 74.99; H, 4.20. Found: C, 74.65; H, 4.28. The stereochemistry of **6** is not yet known.
- (9) Leading references: (a) K. L. Tseng and J. Michl, *J. Am. Chem. Soc.*, **99**, 4840 (1977); (b) W. R. Dolbier, Jr., K. Matsui, J. Michl, and D. U. Horak, *ibid.*, **99**, 3876 (1977); (c) E. Chacko, J. Bornstein, and D. J. Sardella, *Tetrahedron Lett.*, 1095 (1977); (d) R. D. Miller, J. Kolc, and J. Michl, *J. Am. Chem. Soc.*, **98**, 8510 (1976); (e) D. S. Weiss, *ibid.*, **97**, 2550 (1975).
- (10) The triplet and singlet energy of *o*-dibenzoylbenzene is above that of biacetyl: G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).
- (11) In a recent review Michl has suggested, based on theoretical considerations, that an *o*-xylylene peroxide is the key chemiluminescent intermediate in the light-forming reaction of luminol: J. Michl, *Photochem. Photobiol.*, **25**, 141 (1977), and references cited therein.
- (12) Typical conditions. [1] = 5 × 10⁻⁴ M, [perylene] = 2 × 10⁻⁴ M, [maleic anhydride] = 1 × 10⁻³ M in benzene at 92 °C. Maleic anhydride will not significantly quench perylene singlets under these conditions.
- (13) Fellow of the Alfred P. Sloan Foundation 1977–1979.

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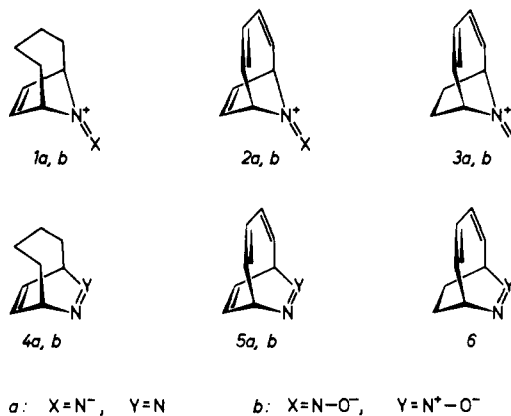
Bis-Pericyclic Reactions: Retrocycloaddition and the Importance of Avoiding Piecewise Analysis¹

Sir:

Qualitative applications of orbital symmetry conservation rules often focus on the number of electrons delocalized about a monocyclic atomic array in the transition state of a concerted reaction. Thus a thermal transformation is designated "allowed", if the total number of (4q + 2)_s and (4r)_a components is odd.² Equivalently this requirement is met for (4M + 2) and (4N) electron transition states, if an arbitrary set of atomic orbital constituents is isoelectronic with the appropriate "Hückel"/"aromatic" or "Möbius"/"aromatic" arrangements, respectively.^{3,4} Within this conceptual framework it is natural to speculate on the consequences for bis-, tris-, or polykis-pericyclic reactions arising formally by incorporating cycles with opposing electronic effects. Thus a bis-pericyclic, face-to-face cycloaddition which couples a (4N)-forbidden and a (4M + 2)-allowed fragment might conceivably experience a kinetic barrier relative to the same reaction lacking the (4N) moiety.

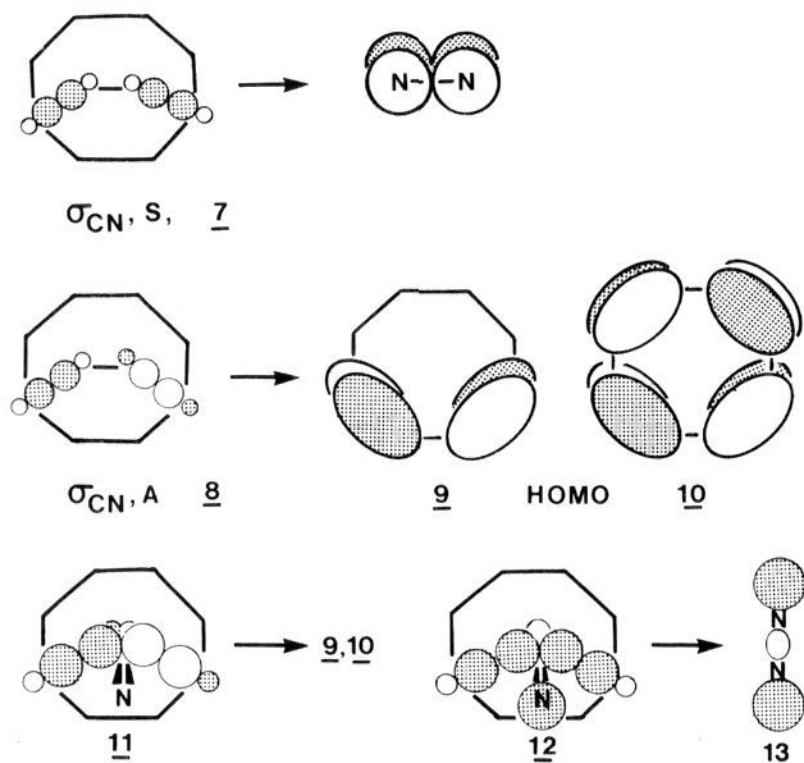
Anastassiou and Yamamoto have recently concluded that

the rate of nitrogen extrusion for diazenes **1a–3a** falls in the order **1a** > **2a** > **3a**.⁵ The "less efficient" fragmentation for **2a** relative to **1a** was interpreted as caused by the presence of the butadiene bridge in the former. Namely, the corresponding bis-pericyclic transition state is destabilized by a suprafacial (4N) = 8-electron component. Experiments we have conducted with the analogous azoalkanes **4a**, **5a**, and **6** do not sustain this supposition. Furthermore we show that evaluation of the bicyclic transition states piecewise⁶ leads to illusory predictions which can be sidestepped by a straightforward MO analysis.



It has been shown that treatment of azo *N*-oxides with hexachlorodisilane at 25 °C leads to azoalkanes, if the carbon skeleton is saturated,⁸ and to cyclic dienes derived from them, if it is unsaturated.⁹ The desired *N*-oxide precursors, **4b** (mp 113–114 °C) and **5b** (mp 82–83 °C), were prepared by basic peroxide, hydrolytic oxidation^{9,10} of the corresponding urazole adducts obtained in turn from the cycloaddition of *N*-methyltriazolinedione (MTAD) and cyclooctadiene¹⁰ (COD) and cyclooctatetraene¹¹ (COT), respectively.¹² Each was dissolved in CDCl₃, cooled to -40 °C, and treated with an excess of the silane reagent. The reactions were monitored by NMR between -30 to -40 °C. Over a period of hours the bicycles were converted quantitatively to COD and COT as determined by integration against an internal standard. No signals for an intermediate azoalkane were observed. Clearly nitrogen extrusion is much faster than deoxygenation. At -30 °C no discrimination between the presence or absence of the butadiene bridge is evident. With the exception of a single case,¹³ all 1,2-diazacyclohexa-1,4-dienes likewise have gone unobserved at temperatures below -30 °C.¹⁴ Within the experimental limits, the results suggest that the bis-pericyclic process occurs unretarded relative to the simple pericyclic reaction. Complementing the lability of **4a** and **5a** is the behavior of azodiene **6** which can be isolated but decomposes quantitatively at 50 °C to 1,3,5-cyclooctatriene and nitro-¹⁵

The rapid loss of nitrogen from **4a** and **5a** is readily apprehended by considering the fate of the electrons in the bonds to be made and broken in the pericyclic transition state. For both azocycles, the symmetric combination of the C–N bonds (**7**) may be transformed across the potential energy surface for retrocycloaddition into the second π bond of N₂. The antisymmetric union **8** likewise correlates smoothly with the highest lying π_A levels of the cycloalkenes COD (**9**) and COT (**10**). These qualitative and symmetry-sufficient orbital correlations have been confirmed by a complete MO calculation of the decomposition of azotriene **5** to cyclooctatetraene and N₂. The geometry of **5** was obtained by CNDO/B¹⁶ optimization; deazetation, followed numerically by CNDO/B, CNDO/S,¹⁷ and PRDDO.¹⁸ All of the latter produce the result that MO's **7** and **8** in **5** are strongly mixed with fragment orbitals of the same symmetry as expected for a molecule



containing upward of ten framework atoms.¹⁹ Nonetheless correlation diagrams constructed from each of the MO schemes reveal a uniform transformation of " $\sigma_{\text{CN}}(\text{S})$ " \rightarrow π_{N_2} and " $\sigma_{\text{CN}}(\text{A})$ " \rightarrow $\pi(\underline{10})$. Furthermore none of the potential energy surfaces sustain a frontier orbital crossing.

The perspective rendered by the MO correlation predicts the reaction to be "allowed" in the generally accepted sense² and circumvents entirely the ambiguous choice between competing (4N) and (4M + 2) pericycles. The parallel orbital correlation for linear diazene decomposition of **1a** and **2a** is completely analogous as depicted by **11**–**13**.²⁰ Interpretations of both the retrocycloadditions and the cheletropic extrusions by means of frontier-orbital theory²¹ is equally satisfying and supports the notion that no energy raising factors arise from the primary orbital interactions.

We conclude that, for bis-pericyclic processes of this type, a fragment-by-fragment analysis⁶ can be misleading and in general should be avoided in favor of symmetry arguments which accommodate simultaneously all the important orbital components.

Finally we note that the proposed 1,1-diazenes **1a** and **2a** are reported to decompose much less cleanly (71 and 28% COD and COT, respectively) and at higher temperatures (54 vs. -30 °C)⁵ than do the 1,2-diazenes **4a** and **5a**. Similarly the ratio of yields for diazene **3a** and azodiene **6** is 0:100% (50–55 °C).^{5,15} It is conceivable that 1,1-diazenes **1a**–**3a** are bypassed in the reduction of precursors **1b**–**3b**, they dimerize in part to tetrazines, or they fragment by a nonpericyclic process.²² The consequences for drawing conclusions about linear vs. non-linear cheletropic reactions⁵ are obvious.

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- (22) Taken at face value the yield and temperature comparisons for **1a**–**3a** and **4a**, **5a**, and **6** appear to reflect an exception to the evidently general observation that isomeric 1,1- and 1,2-diazenes extrude nitrogen under similar conditions to give identical products and product ratios, the latter usually requiring higher temperatures.²³ The product variation most likely implies competing decomposition pathways for the 1,1-diazenes, whereas the relatively high temperature employed for generation of **1a**–**3a** reflects the energy requirement for nitroso reduction.
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Organoselenium-Induced Ring Closures. Sulfur-Containing Prostacyclins. Stereoselective Synthesis of Cyclic α,β -Unsaturated Sulfoxides, Sulfones, and Sulfides and Synthesis of 6,9-Sulfoxo-5(*E*)- and -5(*Z*)-prostacyclin, 6,9-Sulfo-5(*E*)- and -5(*Z*)-prostacyclin, 6,9-Sulfo-6 α - and -6 β -4(*E*)-isoprostacyclin, and 6,9-Thiaprostacyclin

Sir:

The elegant work of Reich¹ and Sharpless² in the early 1970s demonstrated clearly the high potential of organoselenium reagents to organic synthesis. The selenium-based methodology developed since then by the aforementioned authors^{3,4} and other workers⁵ has already found profound applications to organic synthesis and the construction of complex molecules.⁶ As an extension to our previous work on selenium-induced ring closures^{7–9} and owing to the increasing importance of sulfur heterocycles in the β -lactam antibiotic¹⁰ and prostacyclin¹¹ fields, we investigated the reactions of organoselenium reagents with unsaturated sulfur-containing compounds. In this communication we wish to report new, selenium-based methodology leading to the stereoselective synthesis of cyclic α,β -unsaturated sulfoxides and sulfones and its application to the synthesis of a number of novel prostacyclin analogues.