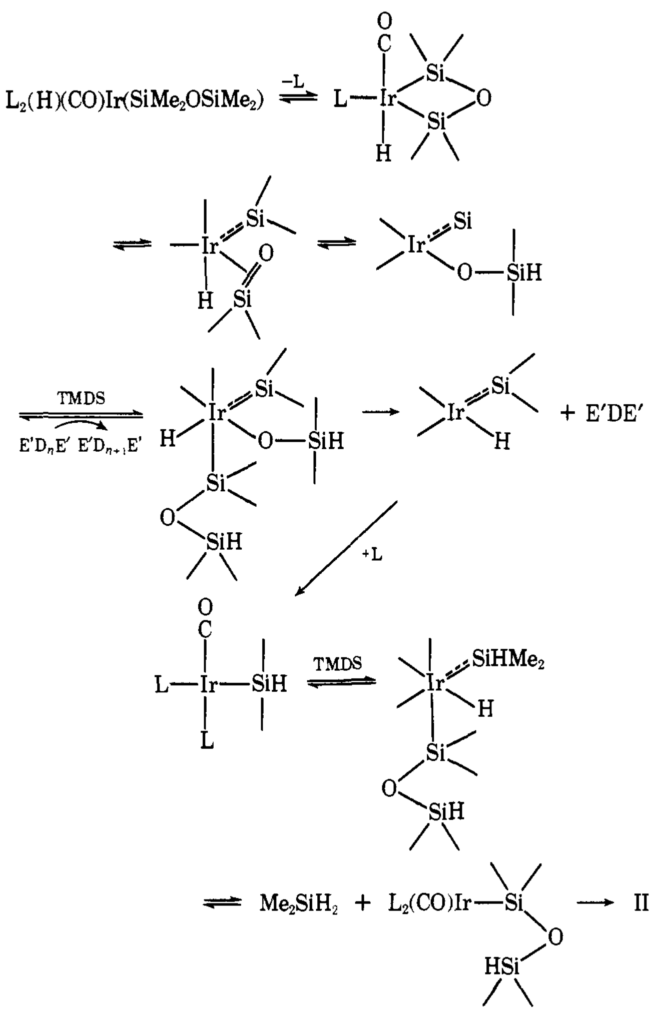
Scheme I



at room temperature, and the catalyst may be recovered as long as excess TMDS is present.

To date, all the data which we have are consistent with a mechanism in which the cyclometalladisiloxane ring cleaves to form a coordinated dimethylsilylene and a coordinated $Si{=}O$ double bond (Scheme I).[7,8] This step is analogous to the scission of metallacyclobutane intermediates in proposed mechanisms for the olefin metathesis reaction.[9] A sequence of oxidative-addition reactions of Si-H bonds and reductive-elimination of Si-O bonded species results in the initial formation of E'DE' and dimethylsilane as shown in Scheme I. As the concentration of E'DE' increases, this trimer may add to the iridium complex in place of TMDS, leading to the production of $E'D_2E'$ and dimethylsilane. The higher oligomers are then formed sequentially according to eq 2.

$$E'D_nE' + TMDS \rightarrow E'D_{n+1}E' + Me_2SiH_2 \qquad (2)$$

The implications of our observations are several and important. With proper control of rates, silicone polymers with perfectly alternating groups may be prepared. Stereochemically preferred configurations of the ring could lead to stereoregular silicone polymers in analogy with the Ziegler-Natta catalyzed polymerization of olefins. Finally, our observations represent the first demonstration that a well-defined, four-membered metallocycle can readily decompose under thermal conditions in the manner postulated for the olefin metathesis reaction.[10] Indeed, our results suggest that such a decomposition mode may be general to four-membered metallocycles and opens the prospect of using multiple bond chemistry for elements which do not form stable multiple bonds.

Acknowledgment. The authors are grateful to Dr. William Butler for his assistance in the x-ray work and to the Dow Corning Corp. for financial support.

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Orbital Symmetry and the Benzene ⇄ Benzvalene Interconversion

Sir:

A recent review of the photochemistry of benzene[1] has prompted me to try to clear up a misunderstanding regarding the application of the orbital symmetry arguments to some of the reactions. The particular case to which I will direct myself is the benzene-benzvalene interconversion. In this reaction a bicyclobutane entity is formed from two π bonds. Therefore it is of interest to consider first what can be said about this process in itself.

On pp 31 and 34 Woodward and Hoffmann[2] state that the butadiene → bicyclobutane reaction is an example of the case where there is no symmetry element of the right type to analyze the reaction. Straightforward construction of a correlation diagram "can only lead to the conclusion—often false—that a reaction is symmetry allowed". On pp 75-78 they consider the reaction again. The bicyclobutanes are formed from butadienes by irradiation and are found to be remarkably stable. The activation energy for isomerization to butadiene is 41 kcal/mol. This thermal process is interpreted as an allowed $[_{\sigma}2_s + _{\sigma}2_a]$ reaction and the observed stereochemistry tallies. Apparently this conversion for which the correlation diagram would have shown allowed character in all modes will in fact be forbidden for some of them, but allowed with high activation energy for others. This state of affairs has been recognized by Dewar and Kirschner.[3,4] They have shown that the difference in activation energy between "allowed" and "forbidden" bicyclobutane → butadiene reactions is only 2.7 kcal/mol which nicely illustrates our point. They also concluded that there are no correlation diagram arguments for an allowed or forbidden designation to either the bicyclobutane → butadiene reactions or the benzvalene → benzene transformation.

We now turn to the six-electron case. The correlation diagram to which the later literature invariably refers has been given by Haller.[5] This diagram shows a correlation between an excited state of benzene and the ground state of benzvalene. However, as we have remarked earlier,[6] the diagram is in error. The π orbitals of benzvalene have the wrong symmetry labels (C_2 axis) and the correct labels would give a correlation between the ground state of benzene and that of benzvalene. The analogy with butadiene → bicyclobutane is notable. Bryce Smith[1] states on p 1312 "Note that disregarding the electronic symmetry properties of the intermediate would have produced the misleading conclusion that the thermal rearomatization of benzvalene is a symmetry allowed process". This statement clearly shows the problem that is manifest in these reactions: the rules have been stretched beyond their limits. The mere fact that the thermal rearomatization of benzvalene does not occur spontaneously does not make this process forbidden. The words forbidden and allowed are really useful only in those cases where we have a choice between two stereochemically different modes of a reaction. The fact that the rules are not directly applicable in cases where we do not have this choice in no way diminishes their value. The proof of the rules[6,11] only allows for the distinction between two pathways, one having a higher activation energy than the other.

Continuing the argument, Bryce Smith describes the reaction as proceeding from S_2 benzene via "a species formally resembling *cis-,cis-,trans*-cyclohexatriene, the so-called 'Möbius-benzene' ".[7,8] Now benzvalene has the correct symmetry labeling of the orbitals. The "intermediate" can only correlate with excited states of benzene as well as benzvalene. Benzvalene is produced from S_1 benzene as well as from S_2 benzene. In the former process there is evidence for thermal (vibrational) activation, in the latter this phenomenon is absent. Whereas the "Möbius-benzene" is invoked in the S_2 reaction, it is the "prefulvene" meta-bonded intermediate in the S_1 process.

A relation between S_1 benzene and "Möbius-benzene" was first put forward by Farenhorst[9] who showed that the two systems would be equienergetic in the Hückel approximation. This fact was—erroneously—repudiated by Bryce Smith.[10] Careful consideration shows that Farenhorst did take into account the difference in β between the normal and the Möbius ring. E_{S_1} benzene $= 6.00\,\beta$; $E_{\text{Möbius-benzene}} = 4\sqrt{3}\,\beta'$ with $\beta' = \beta \cos \pi/6 = \sqrt{3}/2\,\beta$; so $E_{\text{Möbius-benzene}} = 6.00\,\beta$. This point would not be mentioned were it not that it is exactly the antiaromatic S_1 state of benzene which would have the tendency to adopt an out-of-phase overlap to give the Möbius ring.[11] Therefore in our opinion the "Möbius-benzene intermediate" should correspond to a maximum in the ground-state potential energy surface and to a minimum on the surface of the first excited (S_1) state. Conceivably this minimum can be reached directly from S_2 benzene, but starting from S_1 the favorable out-of-phase overlap can only come into play after an energy requiring deformation of the six-membered ring.

In conclusion the following two statements seem appropriate: (i) the use of correlation diagrams, which offer the opportunity to approximate potential energy curves or surfaces, should be distinguished from the application of the Woodward–Hoffmann rules, which were developed to deduce stereochemistry; (ii) intended correlation of ground state of reactant with excited state of product or vice versa does not per se predict a high activation energy, nor does a low activation energy necessarily follow from a ground state to ground-state correlation.

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Received August 20, 1976

On the Size of the Singlet–Triplet Energy Gap in Trimethylenemethanes[1]

Sir:

Some of the organic biradical reactive intermediates, notably carbenes[2-7] and trimethylenemethanes,[8] can be intercepted in two electronic states of differing multiplicity. Although electron spin resonance (ESR) spectroscopy of immobilized samples is capable of determining the singlet or triplet nature of the molecular ground state from the temperature dependence of the signal intensity,[9,10a] in many cases this method is inapplicable to the determination of ΔE ($= E_S - E_T$) when ΔE is more positive than ~0.2 kcal/mol (triplet ground state) or more negative than ~2 kcal/mol (singlet ground state). Hence, the estimation of the singlet–triplet energy gap remains as one of the stubbornly difficult problems of biradical chemistry. By demonstrating that it is possible to trap singlet **1** (**1**-S) from a spin-equilibrated triplet-singlet mixture of **1**-T and **1**-S, the present work determines an upper limit of 3.5 kcal/mol for ΔE of a trimethylenemethane derivative, 2-isopropylidenecyclopentane-1,3-diyl.

A spin-equilibrated **1**-S-**1**-T diyl mixture can be prepared by irradiation of the diazene **2** in a rigid glassy or polycrystalline matrix containing an olefinic trapping agent, M. Warming the matrix permits diffusion and reaction according to Scheme I. The ratio of products from singlet and triplet diyls, X_s/X_t, is given by eq 1.

$$X_S/X_T = K(k_4 + k_4')/(k_3 + k_3') \qquad (1)$$

where

$$K = [\mathbf{1}\text{-S}]_{eq}/[\mathbf{1}\text{-T}]_{eq} = (\tfrac{1}{3}) \exp(-\Delta E/RT) \qquad (2)$$

Since **1** has a triplet ground state,[10a] products of capture of the singlet will be formed in detectable amounts under these conditions only if the ratio $(k_4 + k_4')/(k_3 + k_3')$ of the singlet and triplet trapping rates is large. When M = $CH_2{=}CHCN$ or $CH_2{=}CHCO_2Me$, this requirement is not satisfied, and products are formed in the typical triplet distribution.[10b] We now find, however, that such molten matrix experiments with dimethyl fumarate and dimethyl maleate give substantial quantities of singlet products.

The recognition of the singlet products is based upon criteria justified previously:[8,10b] regiospecificity favoring a high fused-to-bridged ratio (F/B), stereospecificity for cis addition, and effect of added oxygen in increasing both forms of specificity (Table I).[11]