biradicals.[10] We have therefore studied the conversion of **1** to **2** using the latest version (MINDO/3[11]) of the MINDO semiempirical SCF MO method together with a new and very efficient procedure[12] for calculating, molecular geometries. Extensive tests[11,13] have shown that this reproduces heats of formation and activation energies with an average error of ca. 5 kcal/mol. Thus the calculated heats of formation of **1** and **2** were in error by −2.1 and 5.8 kcal/mol, respectively. Their calculated geometries[11] were also in reasonable agreement with experiment.

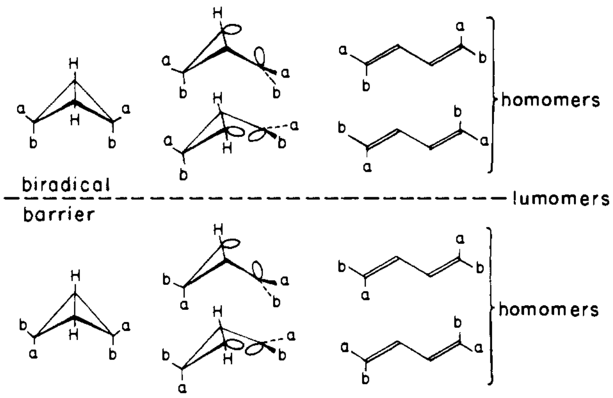
The reaction was first studied using the length of one of the breaking bonds (r_1 in **1**) as reaction coordinate, the energy of the molecule being minimized with respect to all other coordinates for each value of r_1. However, as r_1 was increased, the length of the other breaking bond (r_2 in **1**) remained unchanged as also did the angle (ϕ_2 in **1**) representing the rotational orientation of the second methylene group relative to the rest of the molecule.

We next treated the system using both r_1 and r_2 as reaction coordinates. When, however, both r_1 and r_2 were increased, the twist angles (ϕ_1 and ϕ_2 in **1**) of the methylene groups remained unchanged and the energy increased steadily. Finally we treated all four variables (ϕ_1, ϕ_2, r_1, r_2) as reaction coordinates, varying all simultaneously. In this way a symmetrical transition state was at last located, apparently analogous to that found by Wiberg[14] but corresponding to an activation energy of 90 kcal/mol. This confirmed the argument that a concerted process of this kind should have a much higher activation energy than that for an analogous one involving breaking of one bond only. The value found was indeed nearly double that (49 kcal/mol) calculated[15] for conversion of **3** to **2**.

We therefore felt confident that the reaction could not be a truly concerted pericyclic process in which both the relevant bonds in **1** break simultaneously but must take place in stages, the transition state corresponding to a situation where one bond has been almost completely broken while the other remains almost intact (cf the Diels–Alder reaction[10]). Such processes cannot be studied by procedures using single determinant wave functions; we therefore repeated the calculations including CI with the lowest doubly excited configuration.[16,17]

With CI, the reaction followed an entirely different course. Here an intermediate was formed which would be represented classically as the biradical (**4**) and which dissociated into **2** almost without activation. The rate-determining step was the formation of **4** from **1** for which we calculated an activation energy of 40.3 kcal/mol in essentially perfect agreement with experiment (40.6 kcal/mol[2,3]).

How then can we explain the stereospecificity of the reaction? As we have pointed out recently,[18] a singlet biradical is an unstable species which must undergo Jahn–Teller distortion to one or other of two more stable isomeric species. These are lumomers[19] of one another and their interconversion via the biradical is a "forbidden" process. Indeed, our calculated structure (**5**) for the intermediate shows it to be a biradicaloid,[18] derived from **4** by a direct coupling between the radical centers. This biradicaloid is a homomer of **1** and of *one* of the butadienes (**2**) that can arise from **1**. Thus **4** retains a "memory" of the structure of **1** and the subsequent conversion to **2** is stereospecific. The situation can be represented schematically as shown in Scheme I.



In order to cross from one set of homomers to the other, the reaction has to pass through a high energy biradical intermediate. However, the barrier to such a "forbidden" process is naturally less, the nearer the species is to the biradical initially. Isomerization of one of the initial biradicaloid species (**6** or **7**) to a lumomeric biradicaloid (**8** or **9**) should occur quite easily. Indeed, we calculate the barrier height to be 8 kcal/mol above **5** which itself is 35 kcal/mol above **1**. Thus the overall activation energy for conversion of **1** to "forbidden" products, violating the Woodward–Hoffmann rules, is calculated to be 43 kcal/mol, only 2.7 kcal/mol above that for the "allowed" reaction. This would correspond, at 200°, to ca. 5% of "forbidden" product. Closs and Pfeffer[4] found that the reactions were indeed stereoselective rather than stereospecific, the proportion of "forbidden" product being 4–7%.

References and Notes

(1) This work was supported by The Air Force Office of Scientific Research (Contract No. F44620-71-C-0119) and by the Robert A. Welch Foundation (Grant No. F-126). The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center.
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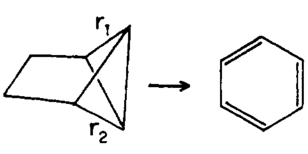
The Conversion of Benzvalene to Benzene[1]

Sir:

The conversion of benzvalene (**1**) to benzene (**2**) on heating raises several interesting problems. In particular, is this an "allowed"[2-4] process? To the best of our knowledge neither Woodward nor Hoffmann has expressed any definite opinion while Dewar[3] described it as "forbidden" on the



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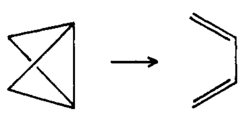

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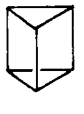

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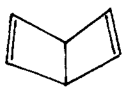

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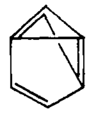

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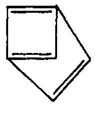

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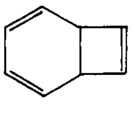

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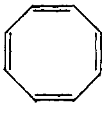

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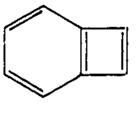

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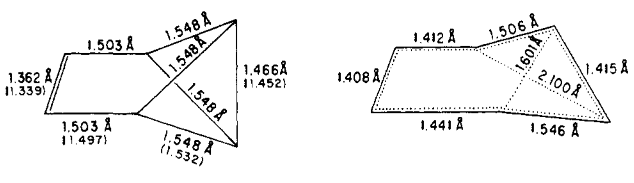
grounds that it requires a disrotatory-disrotatory opening of the bicyclobutane moiety. However, as we will see presently, the extra double bond does not play a purely passive role.

We have shown[5] that MINDO/3[6] gives a good account of the course of a variety of pericyclic reactions, both "allowed" and "forbidden", the calculated activation energies usually agreeing with experiment to within ±5 kcal/mol. We have therefore used it to study the conversion of **1** to **2**.

The reaction was followed by taking the length (r_1 in **1**) of one of the breaking bonds as a reaction coordinate, the energy being minimized with respect to all other goemetrical variables for successive increments in r_1. It soon became apparent that the reaction involves a very unsymmetrical transition state, like that in the corresponding conversion of bicyclobutane (**3**) to 1,3-butadiene (**4**).[8] In treating such biradicaloid[9] species by MINDO, it is necessary to include configuration interaction (CI) with the lowest doubly excited configuration.[10] The calculations were therefore carried out including such CI. Figure 1 shows the geometry calculated for **1** and for the transition state for conversion to **2**; it will be seen that one of the breaking bonds remains almost intact in the transition state (r_2 = 1.60 Å; see **1**) while the other is greatly weakened (r_1 = 2.10 Å).

The reaction is predicted to be extremely exothermic (ΔH, −85 kcal/mol) and the calculated activation energy is low (21.5 kcal/mol). These results certainly account well for the tendency of **1** to detonate.[11] The reaction showed none of the characteristics[4] of "forbidden" reactions, the calculated energy being a smooth function of the reaction coordinate r_1 throughout and no HOMO-LUMO crossing taking place.[5] We therefore conclude that the conversion of **1** to **2** is an "allowed" process in spite of the fact that the analogous disrotatory-disrotatory conversion of **3** to **4** is "forbidden". We had indeed been unable to establish that **1** is a lumomer[4] of **2** although it is easily seen[4] that this is the case for the other benzene isomers, prismane (**5**) and Dewar benzene (**6**).

The fact that **1** → **2** is "allowed" whereas **3** → **4** (disrotatory-disrotatory) is "forbidden" cannot be explained in terms of orbital correlations between reactants and products because the molecules do not possess enough symmetry. It can, however, be easily interpreted in terms of Evans' principle.[3] The transition state for disrotatory-disrotatory **3** → **4** is isoconjugate[3] with Hückel bicyclobutadiene and so unconditionally antiaromatic. The transition state for **1** → **2** on the other hand is isoconjugate with a hydrocarbon that can be written either as benzene with two meta bridges (**7**) or as cyclobutadiene with two meta bridges (**8**). The situation is analogous to that in the disrotatory conversion of bicyclo[4.2.0]octatriene (**9**) to cyclooctatetraene (**10**) where the transition state is isoconjugate with Hückel benzocyclobutadiene (**11**). Now the aromaticity or antiaromaticity of a ring is reduced by bond alternation,[12] so in cases such as this an appropriate alternation in the lengths of the bonds in the antiaromatic moiety will make the system on balance aromatic. Thus the lengths of the bonds in the four-membered ring of **11** undoubtedly alternate strongly whereas those in the benzene ring are presumably similar in length. In an analogously mixed transition state, similar distortions should likewise favor the contributions of the aromatic moiety. Reactions such as **1** → **2** or **9** → **10** should therefore be "allowed" and MINDO/3 calculations indicate that neither involves a HOMO-LUMO crossing.[13]



(a) (b)

Figure 1. Calculated geometry for (a) benzvalene (**1**) and (b) the transition state for the conversion of benzvalene (**1**) to benzene (**2**).

References and Notes

(1) This work was supported by the Air Force Office of Scientific Research (Contract No. F44620-71-C-0119) and by the Robert A. Welch Foundation (Grant No. F-126). The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center.

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MINDO/3 Study of Cyclobutadiene

Sir:

While the century-old problem concerning the aromaticity of cyclobutadiene (**1**) was solved 10 years ago by Pettit et al.[1] who synthesized **1** and showed it to be antiaromatic as had been predicted by simple MO theory,[2] a second re-