The IR spectrum of a solution of **1** and **2** in CH_2Cl_2 saturated with C_2H_2 is also consistent with eq 1. That spectrum contains bands at 965 ($\nu_{Mo=O}$ of **1**) and 935 cm^{-1} ($\nu_{Mo=O}$ of **2**) in approximately a 1:3 ratio and a band at 1684 cm^{-1} ($\nu_{C\equiv C}$ of bound C_2H_2 in **2**).[10] The latter is 290 cm^{-1} lower than the corresponding stretching frequency of free C_2H_2 (1974 cm^{-1}) and is indicative of significant weakening of the triple bond on coordination. The features of the IR spectrum attributable to **2** may be compared with the corresponding absorptions in the IR spectrum of $OMo(S_2CNEt_2)_2(HC\equiv CCO_2Me)(\nu_{Mo=O}$ 925 and $\nu_{C\equiv C}$ 1790 cm^{-1}).[2]

Further substantiation of the stoichiometry of the reaction between **1** and C_2H_2 in CH_2Cl_2 was provided by examining the variation in molar absorptivity at 490 nm that accompanies changing the pressure of C_2H_2 over the solution at 25 °C. The relationship between the apparent molar absorptivity (ϵ_{app}), the molar absorptivities of **1** and **2** (ϵ_1 and ϵ_2, respectively), the pressure of C_2H_2, and the equilibrium constant (K) for eq 1 is shown in eq 2. The values of ϵ_{app} were obtained at five different pressures of C_2H_2 (determined by gas chromatography) ranging from 0.04 to 0.30 atm. The plot of ϵ_{app} vs. ($\epsilon_1 - \epsilon_{app})/P_{C_2H_2}$ was linear and yielded $K = 16$ atm^{-1} and $\epsilon_2 = 46$ cm^{-1} M^{-1}.

$$\epsilon_{app} = [(\epsilon_1 - \epsilon_{app})/KP_{C_2H_2}] + \epsilon_2 \qquad (2)$$

Addition of $NaBH_4$ (0.2 mmol) to DMF (4.0 mL) solutions of **2** (0.056 mmol) containing H_2O (1.0 mL) yields ethylene (0.020 mmol), butadiene (0.006 mmol), and H_2 (0.163 mmol) after 4 h at 30 °C.[15] These products are identical with those obtained[16-17] in various ratios for the reduction of C_2H_2 by $NaBH_4$ in aqueous systems using "molybdothiol catalysts", and by these catalysts alone under extremely alkaline conditions.[16] Addition of acids (HCl, CF_3CO_2H) to DMF solutions of **2** yields no detectable ethylene or butadiene. Similar acidification of solutions of the Mo(II) complexes, Mo(CO)-$(C_2H_2)L_2$ ((L = S_2CNEt_2, $S_2P(i\text{-}Pr)_2$), gave significant amounts of C_2H_4.[11,18]

Evidence has been presented previously which suggests that the substrate-activating, molybdenum-containing site of oxidases cycles molbydenum between oxidation states VI and IV during catalysis.[19] Our observations that the oxomolybdenum(IV) core binds the nitrogenase substrate acetylene but is unaffected by ethylene adds credence to the suggestion that molybdenum-containing reductases (particularly nitrogenase) may use these same oxidation states, but in reverse.[1,6-8,19] Further, the evidence presented herein may be relevant to and support the mechanism of acetylene reduction in the "molybdothiol" systems,[6,16] where, although no intermediates have been isolated, molybdenum(IV) has been implicated in the catalytically active entity.

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On the Mechanism of the Thermal Cope Rearrangement of Allyl-Substituted Cyclopropenes

Sir:

Recently, Doering[1] and Dewar[2,3] have drawn attention to the possibility of a two-step mechanism for the Cope rearrangement, in which formation of the new C–C bond precedes rupture of the old one, so that the reaction involves a biradical intermediate. At this time we wish to report on a study dealing with the thermal Cope rearrangement of allyl-substituted cyclopropenes. Our results suggest that the Cope rearrangement of this system does not proceed via a pericyclic process but rather involves the formation of an intermediate analogous to the 1,4-cyclohexylene biradical.

Thermolysis of 1,2-diphenyl-3-allyl-3-methylcyclopropene[4] (**1**) at 150 °C for 48 h produced an equilibrium mixture of recovered starting material (37%), 1,3-diphenyl-2-methyl-3-allylcyclopropene (**2**, 11%) and 1,2-diphenyl-6-methyltricyclo[2.2.0.0²·⁶]hexane (**3**, 53%). The same distribution of
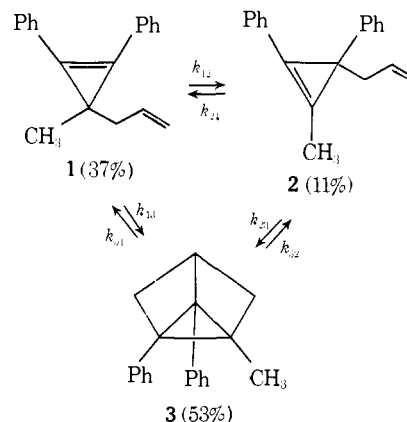
products was obtained by heating either **2** or **3** at 150 °C for 48 h. The rates and the corresponding Arrhenius parameters,

which were determined over a 20 °C temperature range, are comparable to those determined for the Cope rearrangement of 2-phenyl-3,3-dideuterio-1,5-hexadiene[2] (k_{21} = 5.25 × 10^{-5} s^{-1} at 150°; E_a = 31.9 ± 2.5 kcal/mol). It is interesting to note that the rate of rearrangement of **2** → **1** (k_{21}) is approximately three times faster than the reverse process **1** → **2** (k_{12}). This is probably due to the restoration of conjugation between the phenyl substituents. This added conjugation could also account for the fact that **2** cyclizes to tricyclohexane **3** at a faster rate than does **1** (i.e., k_{23} ~ 2.5k_{13}).

The thermal chemistry of the closely related 3-(1-methylallyl)-substituted diphenylcyclopropenes[5] **4** and **5** were also studied in order to determine the preferred transition state geometry for the rearrangement. Thermolysis of cyclopropene **4** at 140 °C for 19 h afforded 1,3-diphenyl-2-methyl-3-((E)-2-butenyl)cyclopropene (**6**) as the major product in 45% yield.
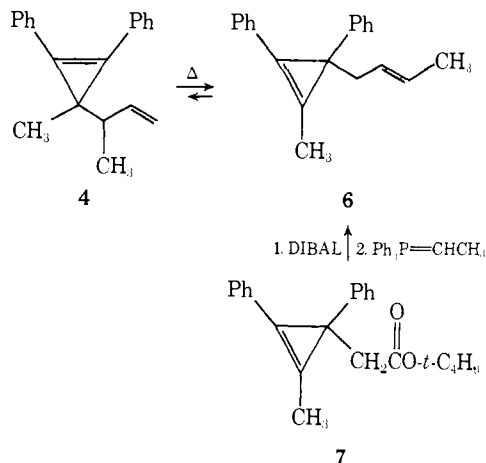

In addition to unreacted starting material (45%), small quantities of tricyclo[2.2.0.0^{2,6}]hexane (**8**) were also present in the crude reaction mixture. The identity of cyclopropene **6** was based on its spectroscopic and analytical properties and was further confirmed by comparison with an independently synthesized sample.[6] Subjection of **6** to similar thermolysis conditions afforded **4** and tricyclohexane **8**.

The synthetic route used to prepare cyclopropene **5** resulted in an inseparable 1:1 mixture of diastereomers. One of the diastereomers (**5a**) was found to undergo the Cope rearrangement at a slightly faster rate (i.e., twofold) than the other. By carrying out the reaction of the 1:1 mixture of diastereomers to ca. 80% conversion, it was possible to obtain a pure sample of the slower reacting diastereomer (**5b**) after column chromatography. Thermolysis of this diastereomer (**5b**) at 130 °C for 36 h afforded a mixture of 1,2-diphenyl-3-methyl-3-
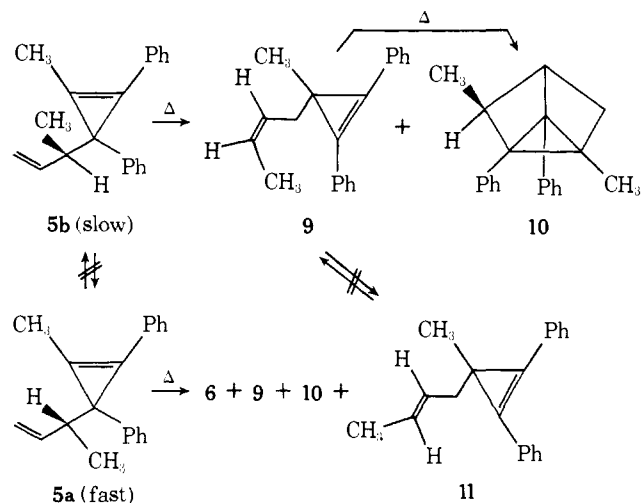
((Z)-2-butenyl)cyclopropene (**9**, 50%) and 1,2-diphenyl-3,6-dimethyltricyclo[2.2.0.0^{2,6}]hexane (**10**, 50%).[8] When the thermolysis of the 1:1 diastereomeric mixture of **5** was carried out to low conversions (ca. 25%), a mixture of **6** (2%), **9** (6%), **10** (4%), and 1,2-diphenyl-3-methyl-3-((E)-2-butenyl)cyclopropene (**11**) (12%) was obtained in quantitative yield. The distribution of the 1,2-diphenyl-substituted (E)-**11** and (Z)-**9** isomers formed in this experiment (ratio **11/9** = 2/1) corresponds exactly to the ratio of reacted starting material (i.e., **5a/5b** = 2/1) thereby establishing the complete stereospecificity of the reaction. The structures of **9** and **11** were verified by comparison with independently synthesized samples.[6] Both **9** and **11** show a reluctance to undergo the reverse Cope rearrangement, and instead they undergo internal 2 + 2 cycloaddition to give an isomeric set of tricyclohexanes.[9-11] A control experiment showed that **9** and **11** were not interconverted under the thermal conditions employed.

The most significant finding here is that the Cope rearrangement of **5a** and **5b** proceeds through the four-center, chairlike, conformation under conditions where a substantial amount of tricyclohexane is being formed simultaneously. A mechanism which accounts for the stereochemical results and which is consonant with all of the available data is outlined below. This process involves the initial formation of a biradical intermediate in a conformation (e.g., **13a** or **13c**) which is analogous to the chair conformation of cyclohexane. Subsequent fragmentation of this species affords the Cope rearrangement product. Ring inversion of the initially formed chair
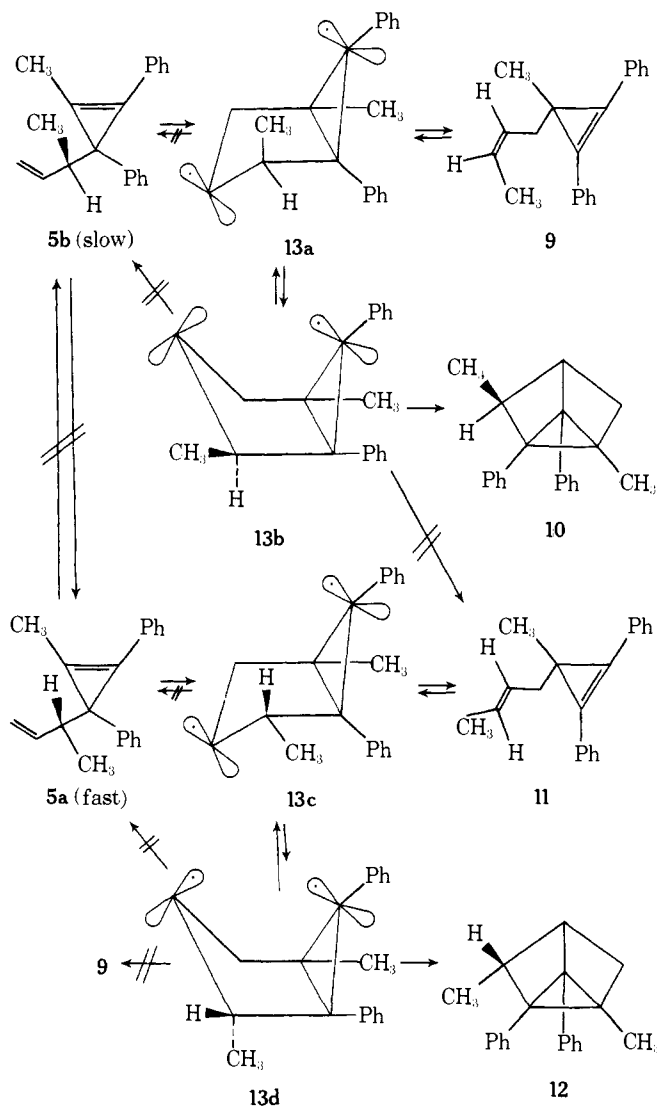
intermediate generates the boat biradical (e.g., **13b** and **13d**) which cyclizes to the tricyclo[2.2.0.0²,⁶]hexane ring system at a faster rate than bond fragmentation. This contention is substantiated by the fact that cyclopropenes **9** and **11** are not isomerized under conditions where substantial quantities of tricyclohexanes **10** and **12** are formed.

It is interesting to note that the thermolysis of diastereomer **5b** results in a significantly larger quantity of the tricyclohexane ring system than is obtained from the thermolysis of **5a**. This can be attributed to the fact that the initially formed biradical intermediate (**13a**, axial methyl) undergoes ring inversion to **13b** (equatorial methyl) at a rate which is competitive with bond fragmentation. Thus, **5b** reacts about equally from each of the conformers **13a** and **13b**. However, **5a** gives mainly cyclopropene **11**, a result indicating preferential reaction from conformer **13c** (equatorial methyl). It should also be pointed out that in the case of cyclopropene **5**, there is a distinct preference for that product arising from bonding between the terminal olefinic carbon and the cyclopropene carbon bearing the methyl group. This is undoubtedly related to the fact that π–π bridging will give the most stable biradical and thus lead to the preferential formation of cyclopropenes **9** and **11** rather than to cyclopropene **6**. Finally, the reluctance of cyclopropenes **9** and **11** to undergo the reverse Cope reaction can be attributed to thermodynamic differences of the allyl substituted cyclopropenes.

In conclusion, the above data are most consistent with the interpretation that the Cope rearrangements of these allyl substituted cyclopropenes are not pericyclic reactions but involve derivatives of 1,4-cyclohexylene as intermediates.

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(6) Cyclopropene **7** was prepared from the reaction of diphenylmethylcyclopropenyl cation with lithio-*tert*-butyl acetate⁷ followed by chromatographic separation of the isomeric acetates. The 1,2-diphenyl-substituted isomer was used to prepare cyclopropenes **9** and **11**.
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(9) It should be noted that the thermolysis of **11** produced a tricyclohexane whose structure has been assigned as *endo*-3-methyl-1,2-diphenyl-6-methyltricyclo[2.2.0.0²,⁶]hexane (**12**). Also noteworthy is the fact that the tricyclohexanes obtained from **9** and **11** differ from the tricyclohexane (**8**) obtained from the thermolysis of either **4** or **6**.
(10) Doering has recently shown that 2,5-diphenyl-1,5-heptadiene undergoes internal 2 + 2 thermal cycloaddition thereby providing reasonable analogy for the formation of the tricyclo[2.2.0.0²,⁶]hexane ring system: see ref 3b, footnote 43.
(11) The formation of tricyclohexane **10** from cyclopropene **9** occurs at a much slower rate than the formation of **10** from **5b**, thereby eliminating the sequential process **5b** → **9** → **10**. This observation indicates that the tricyclic products are not formed by a separate path but rather are produced in competition with the Cope products.

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Laser-Induced Chemiluminescence: Variation of Reaction Rates with Reagent Approach Geometry

Sir:

A basic premise in chemistry is that reactivity in bimolecular processes depends upon reagent orientation. Indirect confirmation of the stereochemical control of a reaction mechanism through the subsequent analysis of the products is common, but direct confirmation of the role of reagent orientation during a reactive encounter is exceedingly rare.¹ We describe a new technique for preparing aligned or oriented reagents using optical pumping. This technique is applied to the atom + diatom exchange reaction

$$M + I_2{}^* \rightarrow MI^* + I, \ M = In, Tl$$
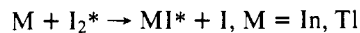
carried out in a single-collision environment. For both In and Tl we find a marked preference for collinear vs. perpendicular approach to the I–I bond in those collisions yielding excited-state products.

The metal beam enters a vacuum chamber filled with I_2 at a pressure of $\sim 5 \times 10^{-5}$ Torr. The 514.5-nm output of an argon ion laser intersects the metal beam at right angles and pumps I_2 in the intersection volume to the $v' = 43$, $J' = 12, 16$ levels of the $B^3\Pi$ (0^+u) state.² The resulting chemiluminescence is viewed by a 1-m spectrometer through a port in the vacuum chamber. The viewing direction is perpendicular to the plane formed by the metal beam and the laser beam. A polarization scrambler (wedge) is placed in front of the entrance slit so that the spectrometer response is independent of the polarization of the emission.

The laser beam is linearly polarized; the polarization vector
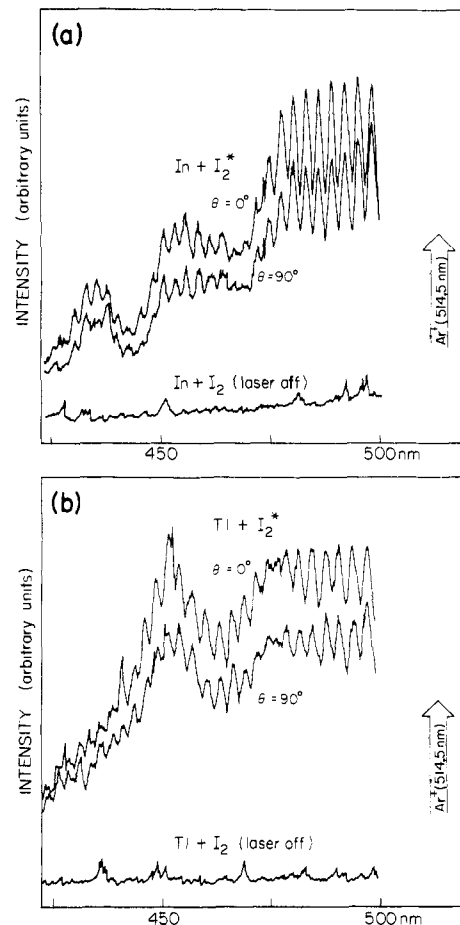
Figure 1. Laser-induced chemiluminescence spectra: (a) In + I_2*; and (b) Tl + I_2*. The angle θ is measured from the metal beam direction to the polarization vector of the plane polarized light.