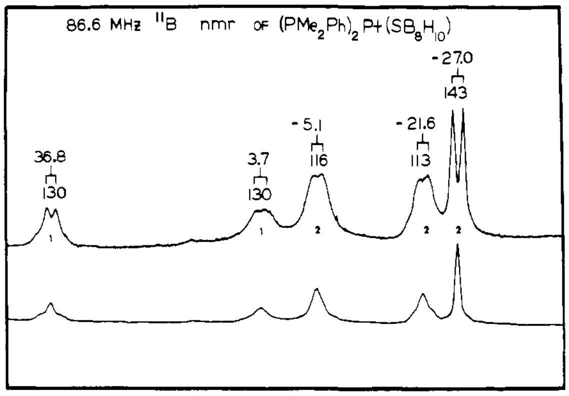

Figure 2. The 86.6-MHz ^{11}B NMR spectrum of 9,9-$(PPhMe_2)_2$-6,9-$SPtB_8H_{10}$. The lower spectrum is ^{1}H decoupled. Chemical shifts are in parts per million relative to $Et_2O{\cdot}BF_3$ with negative values to high field. The J_{BH} is given below the bracket and the relative intensity under the peak.

Pt. If the thiaborane ligand is SB_8H_8, then according to the PERC formalism[5] the complex is closo (22 e$^-$ = $2n + 2$). However, the SB_8H_{10} ligand with two "extra" hydrogens is predicted to be nido (24 e$^-$ = $2n + 4$) with an open structure. The evidence cited below clearly favors the SB_8H_{10} formulation and thus the nido structure is not "unexpected". Those studies of d^8 and d^9 metalloheteroboranes which have uncovered unexpected structures are probably correct because of the mild reaction conditions used, but it should be noted that they have not confronted directly the possibility that extra hydrogen atoms could account for the observation of a nido structure.

The x-ray structure gives some indication of bridging hydrogens on the open face between borons 7,8 and 5,10. The average B-B distance between 7,8 and 5,10 in III and IV is 1.844 (28) Å. Other boranes with bridge hydrogens in the same place show the following distances (Å): 1.88 (1) in $B_{10}H_{12}(SMe_2)_2$[9] and 1.87 (1) in 6,6-$(Et_3P)_2$-5,9-Me_2-6,5,9-$NiC_2B_7H_9$.[10] With no bridge hydrogen this distance is significantly longer: 1.973 (4) in $B_{10}H_{14}$[11] and 2.037 (7) in 5-THF-6-$(CO)_3$-6-MnB_9H_{12}.[12]

Additional evidence favoring the SB_8H_{10} ligand comes from the parent peak profiles in the mass spectra of I and II. Both spectra show excellent agreement between calculated and observed ion intensities for P through P − 7. (For II with P of 566 for $^{198}Pt^{11}B_8{}^{12}C_{12}{}^1H_{40}{}^{31}P_2{}^{34}S^+$ the calculated (observed) intensities are 0.003 (none), 0.006 (0.01), 0.07 (0.07), 0.14 (0.15), 0.31 (0.36), 0.65 (0.71), 1.00 (1.00), 0.99 (1.14).)

The ^{1}H NMR provides the best evidence for extra hydrogens. The spectra of I-IV show a broad peak at τ 11-12. In the case of III a ^{1}H-{^{11}B} spectrum was obtained and showed that the peak at τ 11.4 was due to bridge hydrogens since it was sharpened but not shifted by decoupling. The remainder of the spectrum is consistent with the phosphine ligands and unresolved terminal B-H signals.

The ^{11}B NMR spectra of I-IV are consistent with the x-ray structure, but give no evidence of bridge hydrogens; those of I-III are almost identical, and that of I is shown in Figure 2.[13] Since ^{195}Pt ($I = \frac{1}{2}$) is 34% naturally abundant, observation of a 1:4:1 triplet for the signals at +36.8 and −21.6 upon {^{1}H}-^{11}B decoupling allows them to be assigned to atoms B-4 and B-8,10, respectively ($J_{^{11}B-^{195}Pt}$ = 260 and 240 Hz), those directly bonded to Pt.

We have found that $L_2Pt(SB_8H_{10})$ complexes also form when $SB_{11}H_{11}$ is substituted for SB_9H_9 as a starting material. Other experiments show that thiaboranes are degraded by ethanol. It appears that our synthetic method is a degradative insertion reaction where the Pt moiety is able to form a kinetically stable coordination complex after the thiaborane has been degraded to an SB_8 framework. The range of metallothiaboranes which are susceptible to degradation by alcohol is not defined. However, since the previously reported $L_2M(SB_9H_9)$ (M = Pd, Pt) complexes[6] were recrystallized from solutions containing ethanol and display ^{11}B NMR spectra strikingly similar to those which we find for the $L_2Pt(SB_8H_{10})$ complexes (Figure 2), they should be reinvestigated.

Acknowledgment. We are indebted to Dr. William Butler for help with the x-ray crystallography. We thank Professor Don Gaines (Wisconsin) for 86.7-MHz ^{11}B NMR and Professor Sheldon Shore (Ohio State) for ^{1}H-{^{11}B} NMR. We also thank the National Science Foundation for partial support of this research (Grant MPS74-0047 A01).

Supplementary Material Available. Tables of atomic coordinates and bond distances for III (18 pages). Ordering information is given on any current masthead page.

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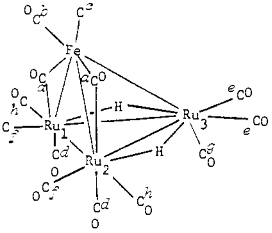
Molecular Dynamics of Mixed-Metal Clusters. Carbon-13 Nuclear Magnetic Resonance Study of $H_2FeRu_3(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$

Sir:

Metal surfaces undergo two basic types of dynamic processes: (1) The substrate (CO, H, etc.) moves on the surface, and (2) the metals themselves rearrange.[1,2] Studies of metal clusters aimed at modeling these surface dynamics have produced a variety of examples of the first type of mobility.[3,4] We present here evidence that the clusters $H_2FeRu_3(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$ undergo dynamic processes not only involving ligand mobility but also a process in which the metals themselves move.

A previous ^{13}C DNMR study of $H_2FeRu_3(CO)_{13}$ (**1**) has been published.[5] In connection with our larger study of mixed-metal clusters, we reexamined the variable-temperature



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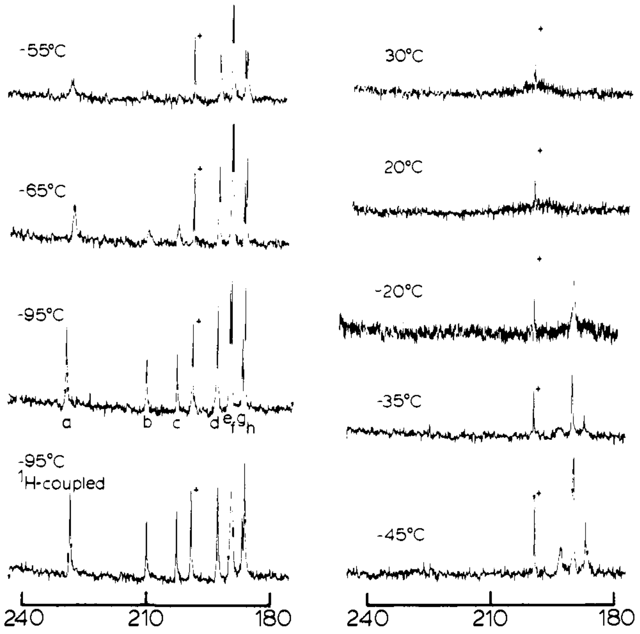


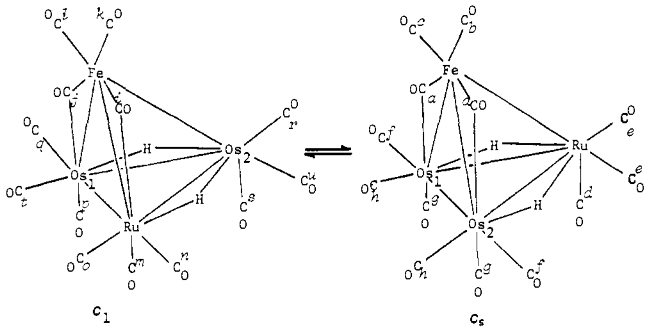
Figure 1. ^{13}C NMR spectra of $H_2FeRu_3(CO)_{13}$. Chemical shifts are relative to TMS. As the temperature is raised above 30 °C, the $H_2FeRu_3(CO)_{13}$ spectrum sharpens to a single resonance at 198 ppm. The peak at 199 ppm marked with a + is due to $Ru_3(CO)_{12}$ impurity.

^{13}C NMR spectra of $H_2FeRu_3(CO)_{13}$, and on the basis of a crucial ^1H coupling-decoupling experiment we offer a dramatically clear and different interpretation of the molecular dynamics. A comparison of the ^1H coupled and decoupled spectra at −95 °C[6] (Figure 1) clearly illustrates significant broadening of only two of the eight resonances. This broadening indicates that the carbonyls which give rise to these resonances are trans to the two hydrogens.[7] Only carbonyls *e* and *f* in **1** fit this requirement, and they are assigned accordingly, although they cannot be distinguished.[8] Bridging carbonyls appear furthest downfield in other cluster systems,[9-11] and thus the resonance at 229 ppm with relative intensity 2 can be attributed to the bridging carbonyls *a*. Since carbonyls bound to Fe are known to give resonances downfield from those bound to Ru,[12] the resonances at 203 and 211 ppm can be assigned to the nonequivalent carbonyls *b* and *c* but cannot be individually identified. Of the three remaining carbonyls, only *g* is unique and must give rise to the resonance at 187 ppm with relative intensity 1. Carbonyls *d* and *h* cannot be distinguished, although *d* is trans to the bridging carbonyl and most likely gives the downfield resonance at 193 ppm.[13]

As the temperature is raised, resonances due to carbonyls *a*, *b*, and *c* collapse, indicating the occurence of *bridge-terminal interchange localized on Fe.* Before these peaks disappear completely, a second fluxional process begins at −65 °C as the resonances due to carbonyls *d* and *h* begin to decrease in intensity. By −45 °C these two resonances have essentially collapsed. The lack of appearance of an averaged resonance in the iron-carbonyl region suggests that carbonyls *d* and *h* interchange with those on Fe. A reasonable mechanism for this interchange would average carbonyls *a*, *b*, *c*, *d*, and *h* through a cyclic movement around the $Fe-Ru_1-Ru_2$ plane. Close examination of the molecular structure of $H_2FeRu_3(CO)_{13}$, as determined by x-ray diffraction,[14] shows that carbonyls *a*, *b*, *d*, and *h* all lie approximately in this $Fe-Ru_1-Ru_2$ plane. Studies of dimers,[15] trimers,[16,17] and larger clusters[18] have shown the importance of such cyclic paths.

The final fluxional process begins at −45 °C and simultaneously averages the three remaining carbonyls *e*, *f*, and *g* with *a*, *b*, *c*, *d*, and *h*. The crystal structure of $H_2FeRu_3(CO)_{13}$ has shown it to be asymmetric, as illustrated in **1**, with the Fe atom closer to Ru_1 and Ru_2 than to Ru_3.[14] *We propose that the final exchange process occurs by a shift in the metal framework in which the Fe atom moves closer to Ru_3 and away from Ru_1 with a concomitant shift of the bridging hydrogens.*[19] This generates a structure completely identical with that of **1** but in which the $Fe-Ru_2-Ru_3$ triangle possesses the bridging carbonyls. A cyclic process, identical with that discussed above, can now occur around the $Fe-Ru_2-Ru_3$ plane. A third equivalent shift would generate a cyclic process around the $Fe-Ru_1-Ru_3$ plane. These equivalent shifts and the resultant cyclic movements will have the effect of averaging all the carbonyls in the molecule. An alternate final exchange process, consistent with the observed NMR changes, would involve localized scrambling on Ru_3 coupled with a cyclic process around the $Ru_1-Ru_2-Ru_3$ triangle. Although these two possible mechanisms cannot be distinguished for $H_2FeRu_3(CO)_{13}$, the NMR data discussed below for $H_2FeRuOs_2(CO)_{13}$ unambiguously shows that the exchange in the latter cluster occurs by the intrametallic rearrangement process.[20]

The overall similarity of the infrared, NMR, and electronic absorption spectra of $H_2FeRu_3(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$ indicates that these clusters are isostructural.[21] The infrared and ^1H NMR spectra of $H_2FeRuOs_2(CO)_{13}$ further show the existence of the two structural isomers shown and hereafter denoted by their C_1 and C_s symmetry labels.[22]



The ^{13}C NMR spectra[23] of $H_2FeRuOs_2(CO)_{13}$ (Figure 2) shows resonances arising from both isomers. At −60 °C the C_s isomer is predominant,[22] and it must give rise to the eight larger peaks. The bridging carbonyls *a* appear furthest downfield at 217 ppm. Carbonyls *b* and *c*, terminally bound to Fe, appear at 211 and 204 ppm but cannot be distinguished. In both isomers, the carbonyls bound to Ru and Os are grouped separately with the Ru carbonyls appearing from 184–189 ppm, while the Os carbonyls appear from 168–177 ppm. This compares well with $H_2FeRu_3(CO)_{13}$ which shows all of its Ru carbonyl resonances between 187 and 193 ppm. The larger Ru carbonyl resonance at 185 ppm corresponds to the two equivalent carbonyls *e*, while the smaller resonance at 188 ppm of relative intensity 1 must be due to *d*. This fully agrees with the ^1H-coupled spectrum in which only *e* shows coupling to the two hydrogens. The Os carbonyls can also be assigned with the aid of the ^1H-coupled spectrum, since only the resonance due to *h* collapses to a broad peak. The remaining peaks at 174.5 and 174.9 ppm are assigned to *f* and *g* but cannot be separately identified.

The C_1 isomer gives rise to 13 peaks, 10 of which are clearly observed. The three remaining resonances are accidentally equivalent to other resonances but can be located by intensity comparisons. In C_1, the two bridging carbonyls *i* and *j* are no longer equivalent. The resonance due to *i* occurs at 229 ppm and compares well to the 229-ppm bridging CO resonance in $H_2FeRu_3(CO)_{13}$. Carbonyl *j* presumably is located upfield at 211 ppm, beneath the resonance due to *b*. The two terminal Fe carbonyls *k* and *l* show resonances at 210 and 201 ppm, but they cannot be separately assigned. In the Ru carbonyl region

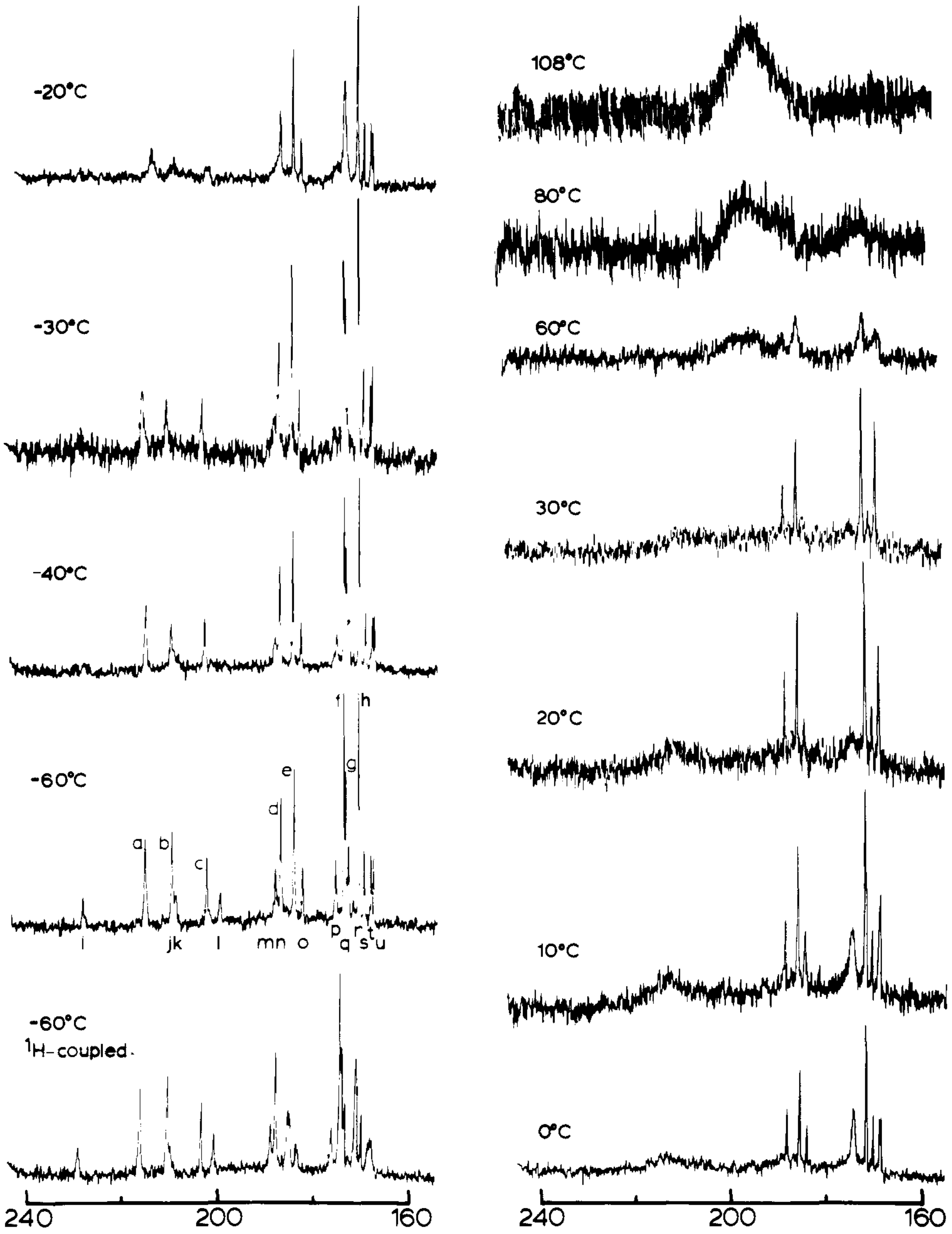


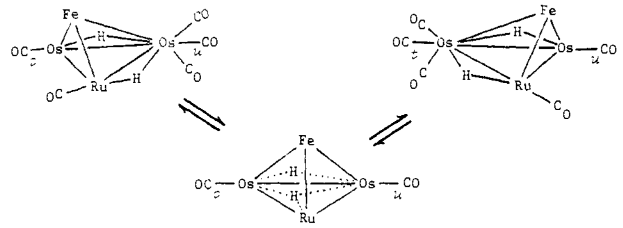
Figure 2. ^{13}C NMR spectra of $H_2FeRuOs_2(CO)_{13}$. Chemical shifts are relative to TMS.

only the resonance at 184 ppm shows coupling to the hydrogens and is therefore assigned to *o*. Carbonyls *m* and *n* appear at 188 (under *d*) and 189 ppm but cannot be individually identified. In the Os carbonyl region only the resonances at 168 and 169 ppm show ^1H coupling. These are accordingly assigned to carbonyls *t* and *u* which are trans to the hydrogens. The resonance due to carbonyl *r*, which is also trans to hydrogen and should show strong ^1H coupling, presumably lies under *h*. This accidental equivalence is consistent with the similar trans environment of *r* in C_1 and *h* in C_s. Carbonyl *p* is located trans to the bridging carbonyl and is assigned to the furthest downfield Os carbonyl resonance at 177 ppm.[13] Carbonyl *q* occurs at 174 ppm, similar to *h* and *r* which are also trans to Ru, but with *h* and *r* further upfield because they are also trans to hydrogen.[24] Finally, *s* is assigned to the peak at 170 ppm.

As the temperature is raised, three basic processes of carbonyl exchange appear. As in $H_2FeRu_3(CO)_{13}$, the bridging and terminal Fe carbonyls exchange in the lowest temperature process. These Fe carbonyl resonances are fully broadened by −40 °C in C_1, while those in C_s are not broadened until −20 °C. The second process, exactly analogous to that in $H_2FeRu_3(CO)_{13}$, averages carbonyls *i–m*, *p*, *q*, and presumably *n* of C_1 and carbonyls *a–c*, *f*, and *g* of C_s through a cyclic movement of the carbonyls around the plane that originally contained the bridging carbonyls. Again, C_1 begins this process ~40 °C before C_s.

The third fluxional process can be rationalized as a shift in the metal framework similar to that discussed above for $H_2FeRu_3(CO)_{13}$. In C_1 this process begins at 10 °C at which point the resonances due to carbonyls *o*, *s*, and presumably *r* begin to average. The resonances of carbonyls *t* and *u* do not collapse, but importantly they do *become equivalent*. We propose that this occurs by a rearrangement of the metal framework and associated ligands in which the Fe moves closer to Os_2 and away from Os_1. This in effect generates the enantiomer of the first structure, and now the Fe-Ru-Os_2 triangle possesses the bridging carbonyls. A cyclic process around this triangle averages *o*, s, and *r* with *i*, *j*, *k*, and *l*. Coupling of the intrametallic rearrangement with the cyclic processes has the net effect of averaging carbonyls *i–s*. Carbonyls *t* and *u*, however, do not enter into this exchange. As illustrated in Scheme I, this rearrangement has the effect of showing an

Scheme I



average environment to *t* and *u*, and the observation that *t* and *u* become equivalent provides strong support for this mechanism.

The second effect of the intrametallic rearrangement in C_1 occurs when the Fe atom moves away from Ru and generates the Fe-Os_1-Os_2 triangle with the bridging COs. This movement results in isomerization to the C_s isomer and is the final averaging process. It begins at 40 °C, and results in the averaging of all carbonyls on both isomers. It is important to note that the variable-temperature ^1H NMR spectra[22] indicate that the $C_s \rightleftharpoons C_1$ isomerization occurs in the same temperature range as shown by the ^{13}C NMR spectra. Studies are currently in progress employing $H_2FeRu_2Os(CO)_{13}$, $H_2Ru_4(CO)_{13}$, and phosphine derivatives of $H_2FeRu_3(CO)_{13}$ to elucidate further the nature of these fluxional processes.

Acknowledgment. We thank A. Freyer for assistance in obtaining NMR spectra and L. M. Jackman for helpful discussions. This research was supported by the Office of Naval Research.

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(19) In the actual rearrangement the iron itself moves very little. The Ru_1–Ru_2–Ru_3 triangle, however, undergoes substantial reorganization.
(20) In the previous NMR study[5] of $H_2FeRu_3(CO)_{13}$, the spectral changes corresponding to the second and third scrambling processes were attributed first to localized scrambling of the Ru carbonyls followed by a final process involving opening of the bonds between the bridging carbonyls and Fe.
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(23) Spectra for the sample enriched to 40% with ^{13}CO were recorded using 3:1 $CHFCl_2/CDCl_3$, $CDCl_3$, and toluene-d^8 solvents for the appropriate temperature ranges. In each case spectra were recorded at the same temperature in different solvents and were identical except for very small chemical shift changes.
(24) The assignment of the upfield resonance to carbonyl *r* trans to hydrogen is internally consistent with our earlier assignment derived from the ^1H coupled–decoupled spectra. These clearly showed that the carbonyls trans to hydrogen give the most upfield resonances.

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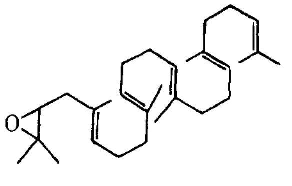
Cyclization Studies with Nor- and Homosqualene 2,3-Oxide

Sir:

In order to learn more about the critical initial phase in the bioorganic polycyclization of squalene 2,3-oxide and related terpenoid epoxides,[1] syntheses and reactivity studies of 4-norsqualene 2,3-oxide (**1**) and homosqualene 2,3-oxide (**2**)



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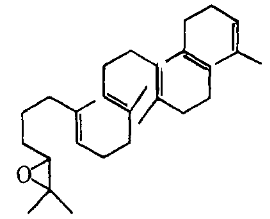

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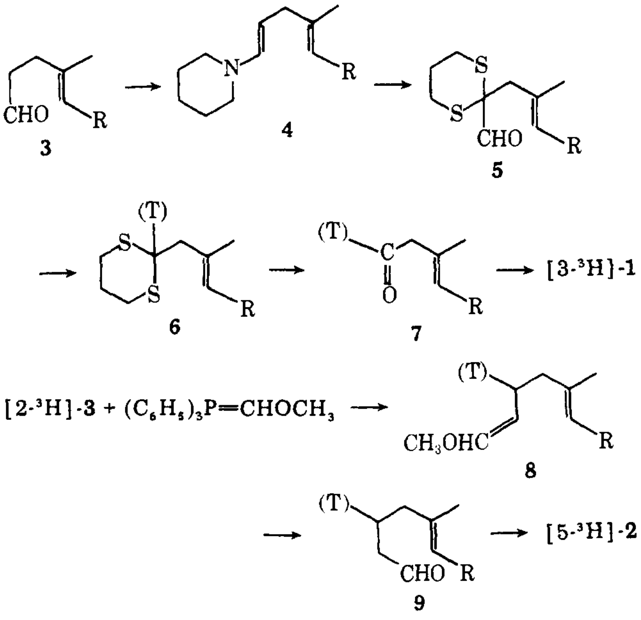
were carried out. The behavior of these two analogues under biological and abiological conditions not only bears on the physical organic mechanism of A-ring formation,[1] but also suggests that a comparatively high degree of enzyme control is exercised to achieve the oxide/neighboring π-bond juxtaposition necessary for initiating cyclization of the normal substrate.

In connection with the favored synthetic approach to oxide **1**, we faced the need for a selective method of degrading a given aldehyde to the noraldehyde, applicable even where the product is the sensitive β,γ-unsaturated type. Toward this end the enamine **4** of aldehyde **3**,[2] on treatment with trimethylene di-



$R = (CH_2)_2C(CH_3){=}CH(CH_2)_2CH{=}C(CH_3)(CH_2)_2CH{=}C(CH_3)(CH_2)_2CH{=}C(CH_3)_2$