addition presumably occurred via the isomerization of the *anti*-π-allylpalladium complex to the syn complex.

Allylic alcohols bearing either an aliphatic or an aromatic bromide chemoselectively reacted with benzaldehyde to give the corresponding homoallylic alcohols (entries 18 and 19). Under these conditions, oxidative addition of an allyl alcohol to Pd(0) proved to be faster than that of an aryl bromide.[11]

The chemoselectivity between an allylic alcohol and an allylic acetate was investigated with 4-acetoxy-2-(Z)-butenol. The result demonstrated the high reactivity of allylic alcohol (entry 20). The product (X:OAc) was the same as that found in the addition of 1,4-diacetoxy-2-(Z)-butene (61%, syn/anti = 28/72). 2-(Z)-Butene-1,4-diol also added to benzaldehyde to produce the homoallyl alcohol (X:OH, 60%, syn/anti = 35/65). The addition of these 2-(Z)-butenes exhibited anti selectivity different from that of (Z)-crotyl alcohol.[12]

We expect that this carbonyl allylation will become a method of considerable synthetic utility, complementing the known allylmetal method,[8,13] since the starting allylating agents, allylic alcohols, are easily prepared and are relatively stable.[14] Further studies clarifying the full scope, limitations, and mechanism of this new process are in progress.

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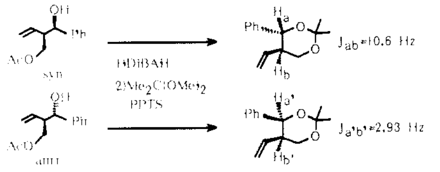
(11) This was also true for the oxidative addition of an allyl acetate. See ref 5d.

(12) The anti selectivity should be dependent on the isomerization of *anti*-π-allylpalladium complex to syn complex easily occurring by steric hindrance of bulky substituents (X). The adduct was converted to 1,3-dioxane derivative, and the configuration was determined by following the reported results: Koga, K.; Yamada, S. *Chem. Pharm. Bull.* **1972**, *20*, 526.



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Chair and Boat Transition States for the Cope Rearrangement. A CASSCF Study

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Although there is general agreement that the chair Cope rearrangement of 1,5-hexadiene passes through a species with C_{2h} symmetry,[2] the geometry and nature of this species remain controversial. Both MINDO/2[3] and MINDO/3[4] calculations found this species to be an intermediate, with bond lengths, R, between the two allyl fragments of about 1.61 Å. More recent AM1 calculations gave a geometry for the non-C_{2h} transition state that was very close to that of the C_{2h} intermediate,[5] suggesting the the Cope rearrangement might be a concerted reaction and that the C_{2h} species might be a transition state. Nevertheless, the value of R = 1.646 Å in the C_{2h} species is still indicative of a nonsynchronous reaction,[6] with bond making preceding substantial bond breaking.

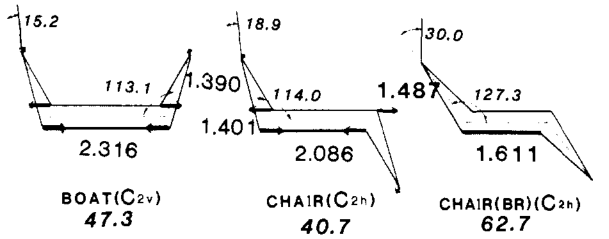

Figure 1. CAS-optimized geometries (in Å and deg) and relative energies (in kcal/mol) of boat (C_{2v}) and chair (C_{2h}) transition states and biradicaloid (BR) chair (C_{2h}) intermediate. Arrows on the transition states are the reaction coordinate.

In multi-bond reactions, it is essential to correlate properly all the electrons involved. Previously, we reported the results of ab initio 3-21G MCSCF calculations on the chair Cope rearrangement.[7] Of the 52 ^1A_g configurations that arise in C_{2h} symmetry from 6 electrons in 6 active orbitals, the 12 most important configurations were used to define MCSCF orbitals for use in CI calculations which included all 52 configurations. These calculations found the C_{2h} species to be the transition state, with a much longer interallylic bond length (R = 2.062 Å) than those obtained by the semiempirical calculations. The bond lengths in the transition state indicated that σ bond breaking is synchronous with σ bond making in the chair Cope rearrangement.

However, these ab initio calculations have been criticized[5] for their lack of full geometry optimization and incomplete vibrational analysis and for their use of an incomplete set of MCSCF configurations. Herein we report the results of MCSCF calculations on both the chair and boat Cope rearrangements that are without any of these deficiencies.

All of the calculations were performed with a complete active space (CAS) SCF wave function, consisting of all the singlet configurations that arise from the 6 electrons, which are involved in the Cope rearrangement, being distributed among 6 active orbitals. Both chair (C_{2h}) and boat (C_{2v}) geometries were fully optimized with analytical gradients,[8] using the 3-21G basis set.[9] The optimized geometries are shown in Figure 1. Each was characterized as a transition state by a full vibrational analysis with the Cartesian finite difference of gradients. The interallylic bond length of R = 2.086 Å for the chair is very similar to 2.062 Å found previously.[7] A natural orbital analysis of the CASCF wave functions showed that the number of electrons in the three "antibonding" MOs is 0.285 for the chair and 0.357 for the boat transition states. These antibonding orbital occupation numbers should be compared with 0.204 for 1,5-hexadiene. The transition states thus have 10–15% more diradical character than the reactant, but the transition states are still very much closed-shell species. This is indicative of the synchronous nature of the reaction.

A geometry optimization, starting from the UHF triplet geometry for the chair, coverged to a second C_{2h} stationary point, which is shown as chair (BR) in Figure 1. A calculation with one interallylic CC bond stretched and the other shortened gives a higher energy, confirming that this is a local minimum, i.e., an intermediate. This species has a very short interallylic bond length, R, of 1.611 Å and a high "antibonding" natural MO occupation of 0.582, both of which are indicative of its biradical character. However, the energy of the biradicaloid is 22.7 kcal/mol higher than that of the R = 2.086 Å chair transition state and exceeds

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(1) (a) Institute for Molecular Science. (b) University of Washington. (c) Visiting Scientist, Institute for Molecular Science, 1985.

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Table I. CASSCF Energetics Relative to *trans*-1,5-Hexadiene at 523 K (kcal/mol)

transition state	ΔE	ΔH^a	$\Delta S^{a,b}$	ΔG^a
chair	40.7	37.7	−9.0	42.0
boat	47.3	43.6	−6.2	46.8

[a] See ref 12. [b] In cal/(mol·deg).

even that of two allyl radicals by 8.6 kcal/mol. Therefore, passage of molecules through the C_{2h} biradicaloid geometry does not contribute to the Cope rearrangement.

The present results indicate that both the chair and boat Cope rearrangements are not only concerted (proceeding without formation of an intermediate) but also synchronous (with bond forming and breaking occurring simultaneously in the transition states of lower energy). Our results contrast with those from a recent AM1 study,[10] which found a biradicaloid transition state with small R (1.66 Å) to be lower in energy than an "aromatic" transition state with larger R (1.98–1.99 Å). Our results also disagree with the inference, drawn from recent ab initio calculations,[11] that "There is every reason to believe that the biradicaloid structure is in fact lower in energy" than an aromatic transition state with a large R.

As shown in Table I, the energy of the chair transition state is 40.7 kcal/mol, above the CAS-optimized C_i geometry for 1,5-hexadiene. After correction for vibrational energy differences, an enthalpy of activation of 37.7 kcal/mol is obtained,[12] which is in reasonable agreement with the experimental value of 33.5 kcal/mol.[13] Although the calculated enthalpy of activation for the chair Cope is a little too high, the calculated difference of 5.9 kcal/mol between the enthalpies of the two transition states is nearly 50% too low, compared to the difference of 11.1 kcal/mol that has been obtained experimentally.[14,15]

The value of R (2.316 Å) in the boat is 0.23 Å longer than that in the chair, and the pyramidalization angles at C2 and C5 are smaller in the boat. Electron correlation enhances the larger value of R in the boat, since Hartree–Fock (HF) optimization of the two transition states gives a diference in R that is only half as large as that found by CASSCF. AM1 calculations give virtually no difference in R between the two transition states.[6]

A "looser" transition state for the boat Cope rearrangement implies lower frequency vibrations, which is consistent with the experimental fact that the entropy of the boat transition state is considerably larger than that of the chair.[14,15] However, the CASSCF second derivatives give the vibrational entropy of the boat at 523 K as only 2.6 eu larger than that of the chair. The 0.2 eu rotational entropy difference brings the total difference in calculated entropies to 2.8 eu. This is considerably smaller than the experimental difference of 11 eu between the two transition states, but the calculated entropy of activation for the chair[12] is in reasonable agreement with the experimental value of −13.8 eu.[13]

The differences between both the enthalpies and the entropies of the two transition states appear to be underestimated by our CASSCF calculations. A possible explanation is that the variational transition state that maximizes the *free* energy of activation for the boat Cope rearrangement occurs at a looser geometry, which has a higher enthalpy and entropy than the saddle point that we have located on the CASSCF *potential* energy surface.[16,17] A similar proposal has recently been made by Dewar and Jie[10] based on their AM1 calculations.

Acknowledgment. Numerical calculations were carried out at the Computer Center of the Institute for Molecular Science. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for partial support of this research.

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Anti-Cram Selective Reduction of Acyclic Ketones via Electron-Transfer-Initiated Processes

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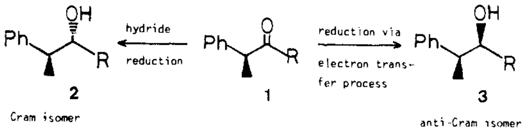
It is well-recognized that hydride reduction (e.g., $LiAlH_4$) of acyclic ketones (**1**) produces the Cram isomer (**2**) predominantly.[1] We report that the reduction via electron-transfer-initiated processes gives the anti-Cram isomer (**3**) preferentially (eq 1). This surprising finding provides a conceptual advance in the area of stereocontrol of acyclic systems.[2] The results are summarized in Table I.



(1)

Birch reduction (entries 3, 4, 9, 10, 19), Bouvault–Blanc reduction (entries 5, 11, 13, 16, 20), and samarium iodide reduction[3] (entries 6, 14, 17) always produced the anti-Cram isomers predominantly, though the selectivity itself was variable and remained at a low level. Needless to say, $LiAlH_4$ reduction gave the Cram isomers preferentially (entries 1, 7, 12, 15, 18). L-Selectride produced the Cram isomers exclusively (entries 2, 8). It was confirmed that epimerization of the product alcohols did not take place during Birch conditions and work-up procedures.

There has been a controversy on the mechanism of metal–ammonia reductions of cyclic aliphatic ketones:[4] Barton's dianion mechanism,[5] House's mechanism,[6] Rautenstrauch's mechanism[7a]

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