shorter time than for diamagnetic samples. This approach, similar to that used in glasses,[30] should be of value in other crystalline systems where long relaxation times limit the sensitivity of the NMR method. The resonances of different species close to the paramagnetic centers could be selectively observed by varying the recycle times between pulses and saturating selectively the resonances of nuclei far from the paramagnetic ions. When this approach is used, resonances could for example be detected from ^{119}Sn nuclei in local environments with very low concentrations in the solid. This ability to observe the fast relaxing nuclei despite their low abundance, should be of particular value in cases where paramagnetic ions are incorporated only in trace concentrations within a solid.

Overall, this study has demonstrated the potential of MAS NMR in the study of paramagnetic continuous solids and suggests that incorporation of paramagnetic centers can offer a novel approach to the characterization of 3D materials by MAS NMR.

Acknowledgment. We thank the SERC for the provision of a research studentship for C.P.G. and a grant toward the purchase of the NMR equipment, A. Stoker for help with the X-ray microanalysis, and S. J. Heyes and J. M. Twyman for valuable advice concerning the NMR experiments.

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Mechanism of the Claisen Rearrangement of Allyl Vinyl Ethers

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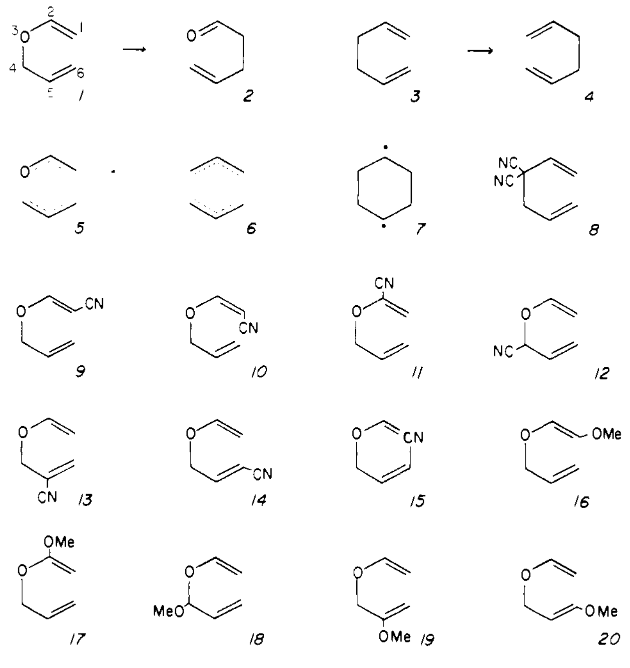
Abstract: AM1 calculations are reported for the Claisen rearrangements of allyl vinyl ether and 23 derivatives. The reactions are predicted, correctly, to take place preferentially via chair-type transition states and to lead preferentially to E isomers. While some of the reactions are predicted to take place by two alternative paths, corresponding to alternative synchronous and nonsynchronous mechanisms, involving transition states that are, respectively, aromatic and biradicaloid, the distinction here is only marginal, and most of the reactions took place by a single unique path of intermediate type.

The Claisen rearrangement (CLR) of allyl vinyl ethers to γ,δ-unsaturated carbonyl compounds (e.g. $\mathbf{1} \rightarrow \mathbf{2}$; Chart I) bears an obvious formal analogy to the Cope rearrangement (COR) of 1,5-hexadienes (e.g. **3**). Both reactions are concerted,[1] taking place via transition states (TS) with chair-type geometries,[2,3] and it was formerly assumed that both are synchronous,[1] being typical "allowed"[4] pericyclic reactions with aromatic[5] TSs (**5** and **6**). However, experimental[6] and theoretical[7] studies in these laboratories showed some years ago that the COR normally takes place by an alternative nonsynchronous mechanism first suggested by Doering et al.[8] where the symmetrical intermediate is a biradicaloid derived from the biradical (**7**) by through-bond interactions between the radical centers. This was a surprising conclusion because it had been generally assumed that "allowed" pericyclic reactions are always synchronous unless the synchronous path is inaccessible for steric reasons.

Chart I



A possible explanation of this apparent anomaly was given recently in the form of a new reaction rule,[9] that multibond reactions are not normally synchronous, a multibond reaction being one where two or more bonds are formed or broken. The rationale for this is that activation barriers for reactions are due to the need to weaken bonds that break during the reaction before new bonds can begin to form. The activation energy of a synchronous two-bond reaction should then be roughly double that of an analogous one-bond one.

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(1) A *concerted* reaction is one that takes place in a single kinetic step. A *synchronous* reaction is a concerted reaction in which all changes in bonding have taken place to comparable extents in the transition state. A *two-stage* reaction is one which is concerted but not synchronous; some changes in bonding taking place mainly before, and some mainly after, the transition state.

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Since pericyclic reactions are necessarily multibond processes, the new rule might be expected to apply to them. On the other hand, the large (aromatic) resonance energies[5] of the corresponding synchronous TSs should favor synchronicity.[9] Whether or not such reactions are synchronous has therefore become an interesting question.

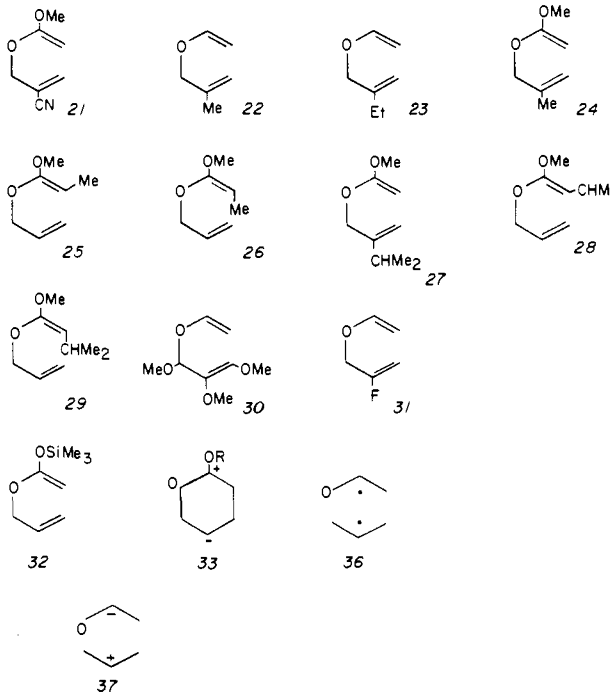
While the original work has been challenged, we have recently confirmed the biradicaloid (BR) mechanism by a detailed AM1[10] study[11] of the chair CORs of **3** and several of its derivatives. An even more recent study[12] led, however, to the surprising conclusion that the chair and boat CORs of **3** can in fact each take place by *either* path. In each case there are two distinct TSs, differing little in geometry but corresponding to mechanisms that are in principle quite different. In the biradicaloid (BR) chair TS (cf. **7**), the forming and breaking C–C bonds are short (ca. 1.64 Å), corresponding to single C–C bonds lengthened somewhat by the through-bond interaction between the radical centers. In the aromatic (ARO) TS their lengths were ca. 2.0 Å, corresponding to the lengths of analogous bonds in other ARO-type pericyclic TSs. The BR TS was predicted to be lower in energy than the corresponding aromatic (ARO) TS (cf. **7**) by 6.5 kcal/mol and lower by 10.7 kcal/mol than either boat TS, in agreement with the earlier work. However, the difference in energy between the boat BR and ARO TSs was only 2.7 kcal/mol, and this was compensated by a much less negative entropy of activation (−6.3 vs −11.0 cal/deg). The entropy of activation (−3.0 ± 3.6 cal/deg) reported[13] for the boat COR of **1** is indeed much less negative than that (−13.1 ± 1.0 cal/deg) for the chair COR, a result which had previously remained unexplained. The calculated[12] activation parameters predict the BR boat path to be favored at the temperature used in the experimental study.

Gajewski and Conrad[14] have reported studies of secondary deuterium kinetic isotope effects (SDKIE) for several CORs, which they took as evidence for a TS of variable structure, varying between the possible extremes (BR, ARO, etc.) depending on the substituents present. We were able to show[11,12] that the SDKIEs can be interpreted satisfactorily in terms of our dual mechanism, the TS having one or the other of two fixed geometries (BR, ARO). While the BR path is usually preferred in chair CORs, suitable substitution can favor the ARO mechanism, as in the case of 3,3-dicyano-1,5-hexadiene (**8**).[15] The ARO path is very strongly favored in the case of semibullvalene and bullvalene, due to the relief of ring strain in forming the corresponding TS. However, analogous pairs of BR and ARO TSs were found even in this case.[16]

Our conclusions have also been challenged by Osamura et al.[17] on the basis of MCSCF ab initio calculations, using the 3-21G basis set, which, they claimed, showed the COR of **1** to take place by the ARO mechanism. However, a detailed ab initio study by Dewar and Healy[18] has shown the 3-21G basis set to be inadequate in this connection. To obtain a satisfactory description of the COR, a much larger basis set must be used. Even the 6-31G* basis set may not be sufficient.[18]

The evidence that the COR does indeed take place by a dual mechanism, involving alternate BR and ARO paths, thus seems strong. If so, a similar dichotomy of mechanism might be expected in other pericyclic reactions, in particular the Diels–Alder (DA) reaction.[19] Indeed, Bernardi et al.[20] have recently found two distinct TSs, one aromatic and the other biradicaloid, for the DA reaction between ethylene and butadiene, the ARO one being lower in energy by 2 kcal/mol. This supports the conclusion, from AM1 calculations,[19] that DA reactions involving unsymmetrical dienes or dienophiles usually take place by the BR mechanism because conjugative substituents should selectively stabilize the biradical-like BR TS.

Chart II



Two questions therefore need to be answered in the case of the CLR: Is it a synchronous pericyclic process involving an aromatic TS? Can it take place by alternative BR and ARO mechanisms, like the COR?

A recent MNDO[21] study[22] of the CLRs of **1** and several of its derivatives seemed to imply that they take place by the BR mechanism, via biradicaloid intermediates corresponding to biradicals analogous to **7**. This conclusion was, however, weakened by the fact that the calculated activation energies were too high, by rather large amounts. Errors of this kind have been encountered in MNDO calculations for other reactions and seem to be due to the overestimation of interatomic repulsions in MNDO.[21] Since this problem has been overcome in AM1,[10] we decided to carry out a detailed AM1 study of the CLRs of **3** and a number of its derivatives.

Theoretical studies of a reaction should, if possible, refer to a number of examples where experimental data are available, because any theoretical procedure is likely to reproduce relative properties for a series of related systems better than it does absolute values for any one case. Application of this technique to the CLR has been facilitated by a recent experimental study[23] of the rearrangements of **1** and of all its monocyano derivatives, under similar conditions. Since the rates were little affected by a change in the solvent, the rates in the gas phase are likely to be similar to those in solution. This is important because our calculations refer to reactions of isolated molecules, equivalent to reactions in the gas phase.

Procedure

The procedure was that used in our study of the Cope rearrangement.[11] The calculations were carried out with AM1[10] as implemented in the AMPAC program.[24] All geometries were fully optimized. TSs were located by the reaction coordinate method[25] or by the other pro-

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(24) Available from: Quantum Chemistry Program Exchange, Program No. 506.

Table I. Heats of Formation and Activation Parameters

molecule	TS[a]	ΔH_f[b]	$\Delta H^{\ddagger}$[c] calcd	$\Delta H^{\ddagger}$[c] obsd	$\Delta S^{\ddagger}$[d] calcd	$\Delta S^{\ddagger}$[d] obsd	T[e]
1		−7.0[f]					
	BR (boat)	31.5	38.5		−8.8		
	BR	25.0 (10.2)	32.0	25.4[g]	−10.3	−15.9[g]	180
	ARO	25.7	32.7	(30.6[h])	−7.9	(−7.7)	
9		20.5					
	ARO (boat)	60.5	40.1		−6.5		
	ARO	56.1 (6.5)	35.6	27.1[g]	−7.4	−11.6[g]	150
10		21.7					
	ARO	59.1 (6.5)	37.4		−7.4		150
11		29.0					
	BR	58.4 (10.3)	29.4	22.8[g]	−9.8	−13.4[g]	90
	ARO	60.1	31.1		−7.4		
12		32.2					
	TS	61.4 (4.0)	29.2	22.3[g]	−8.6	−13.0[g]	80
13		25.2					
	TS	53.1 (8.5)	27.9	22.6[g]	−8.5	−18.0[g]	110
14		22.0					
	TS	57.7 (9.7)	35.7	28.8[g]	−9.8	−11.2[g]	150
15		22.4					
	TS	59.1 (8.6)	36.7		−10.4		150
16		−48.5					
	TS	−15.6	32.9		−10.1		80
17		−48.6					
	TS	−23.9 (6.9)	24.7		−10.8		80
18		−49.4					
	TS	−18.7	30.7	22.4[h]	−11.1	−14.7[h]	80
19		−43.5					
	TS	−13.8 (12.0)	29.7	30.9[h]	−9.6	−7.0[h]	80
20		−48.9					
	TS	−14.2	34.7	24.7[h]	−12.8[h]		80
21		−15.7					
	TS	3.2 (4.5)	19.0		−11.5		80
22		−13.7					
	TS	16.7 (11.3)	30.4		−10.5		80
23		−18.8					
	TS	11.5 (11.2)	30.3		−5.8		80
24		−55.4					
	TS	−31.8 (7.5)	23.6		−9.7		80
25		−57.8					
	TS	−28.7 (5.0)	29.1		−10.8		80
26		−57.8					
	TS	−30.4 (5.8)	27.5		−10.7		80
27		−64.0					
	TS	−40.4 (7.5)	23.6		−7.6		80
28		−68.6					
	TS	−40.3 (5.4)	28.3		−12.3		80
29		−68.7					
	TS	−38.4 (4.9)	30.3		−10.0		80
30		−122.9					
	TS	−95.0 (11.8)	27.9		−12.5		80
31		−50.9					
	TS	−22.1 (13.5)	28.8		−11.7		80

[a] For notation, see text. The first line for each entry refers to the parent allyl vinyl ether and the subsequent line, or lines to TSs. [b] Heat of formation (kcal/mol). The values in parentheses are the differences between the energies calculated for the TSs using the RHF and HE-CI version of AM1. [c] Enthalpy of activation (kcal/mol). [d] Entropy of activation (cal/deg·mol). [e] Temperature (°C) to which activation parameters refer. [f] Calculated from group additivities: −8.7. [g] Reference 23. [h] Reference 33.

cedures incorporated in AMPAC,[25] refined by minimizing the norm of the energy,[26] and characterized by calculating force constants.[26] Open-shell calculations were carried out with the "half electron"[27] version of AM1 with 3 × 3 CI (AM1-HE-CI; BIRADICAL option in AMPAC).

Results and Discussion

AM1 calculations were carried out for allyl vinyl ether (**1**) and 23 derivatives (**9**–**31**; see Charts I and II). As a check on the nature of the TSs, their energies were recalculated with AM1-HE-CI. The heats of formation calculated for the reactants and TSs are shown in Table I.

The AM1 and AM1-HE-CI values for the energies of the TSs (Table I) differ by <12 kcal/mol, and most of the differences are much smaller. This implies (see ref 11) that the TSs should be regarded as closed-shell species with relatively little biradical character and that the RHF (AM1) values for their energies should be accepted. Similar conclusions were reached in the previous studies of the CLR and COR referred to above. The following discussion is therefore based on the AM1 energies and geometries.

The CLR, like the COR, can in principle take place via TSs with chair or boat geometries.[2,3] Calculations for both paths were carried out in the case of **1** and **9**. The corresponding activation parameters are shown in Table II. As expected, the enthalpy of activation ($\Delta H^{\ddagger}$) for the boat rearrangement is in each case much greater than that for the chair, in agreement with experiment.[3] Calculations for the rearrangements of the other derivatives (**10**–**24**) of **1** were therefore confined to the chair route. Indeed, the calculation for the boat rearrangement of **9** was carried out by mistake. We discovered the error through an apparent

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(26) McIver, J. W.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.
(27) See: Dewar, M. J. S.; Merz, K. M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 5146.

Table II. Geometries of Reactants and Transition States

species[a]		geometries[b]								
		C_1–C_2	C_2–O	O–C_4	C_4–C_5	C_5–C_6	C_1–C_6	C–R_1	C–R_2	C–R_3
1	REACT	1.336	1.387	1.429	1.488	1.330	5.360			
	TS BR (chair)	1.407	1.323	1.577	1.429	1.400	1.843			
	TS BR (boat)	1.405	1.315	1.591	1.425	1.399	1.886			
	ARO (chair)	1.402	1.305	1.715	1.410	1.394	1.956			
9	REACT	1.349	1.377	1.434	1.487	1.330	5.355	1.413		
	TS (chair)	1.413	1.293	1.783	1.401	1.393	2.021	1.422		
	TS (boat)	1.408	1.287	1.854	1.396	1.387	2.130	1.416		
10	REACT	1.347	1.375	1.434	1.487	1.331	5.334	1.412		
	TS	1.411	1.291	1.799	1.401	1.393	2.047	1.421		
11	REACT	1.342	1.389	1.432	1.487	1.330	4.942	1.429		
	TS	1.413	1.332	1.558	1.436	1.400	1.831	1.427		
	ARO	1.403	1.307	1.756	1.411	1.389	2.011	1.438		
12	REACT	1.336	1.391	1.437	1.500	1.329	5.806	1.464		
	TS	1.403	1.313	1.678	1.423	1.395	1.929	1.442		
13	REACT	1.334	1.377	1.425	1.500	1.339	3.576	1.424		
	TS BR	1.402	1.332	1.526	1.449	1.406	1.852	1.411		
	ARO	1.409	1.300	1.725	1.414	1.410	1.949	1.418		
14	REACT	1.336	1.390	1.426	1.488	1.339	5.457	1.418		
	TS	1.411	1.317	1.603	1.423	1.410	1.852	1.434		
15	REACT	1.336	1.389	1.427	1.488	1.338	5.318	1.418		
	TS	1.411	1.315	1.616	1.421	1.408	1.876	1.434		
16	REACT	1.346	1.390	1.430	1.488	1.330	5.419	1.376		
	TS	1.422	1.308	1.652	1.416	1.401	1.878	1.391		
17	REACT	1.336	1.380	1.436	1.487	1.330	4.689	1.381		
	TS	1.407	1.316	1.592	1.428	1.393	1.919	1.370		
18	REACT	1.336	1.386	1.425	1.498	1.329	4.010	1.416		
	TS	1.408	1.322	1.595	1.435	1.400	1.842	1.403		
19	REACT	1.336	1.389	1.429	1.497	1.341	4.842	1.388		
	TS	1.405	1.337	1.539	1.444	1.408	1.832	1.382		
20	REACT	1.337	1.387	1.429	1.484	1.342	5.346	1.384		
	TS	1.408	1.321	1.584	1.426	1.412	1.841	1.407		
21	REACT	1.336	1.381	1.431	1.500	1.339	4.179	1.381	1.424	
	TS	1.402	1.331	1.526	1.451	1.398	1.935	1.361	1.410	
22	REACT	1.337	1.387	1.430	1.497	1.336	5.051	1.482		
	TS	1.405	1.330	1.549	1.441	1.406	1.835	1.475		
23	REACT	1.336	1.386	1.431	1.498	1.336	4.683	1.491		
	TS	1.405	1.329	1.551	1.441	1.405	1.834	1.483		
24	REACT	1.337	1.380	1.435	1.496	1.336	4.529	1.380	1.482	
	TS	1.405	1.321	1.568	1.438	1.398	1.911	1.370	1.476	
25	REACT	1.342	1.381	1.435	1.487	1.330	4.739	1.472	1.380	
	TS	1.414	1.306	1.651	1.418	1.394	1.964	1.487	1.374	
26	REACT	1.342	1.379	1.436	1.487	1.330	4.822	1.472	1.381	
	TS	1.416	1.309	1.629	1.420	1.395	1.930	1.485	1.371	
27	REACT	1.337	1.380	1.436	1.497	1.337	4.238	1.381	1.499	
	TS	1.405	1.321	1.568	1.438	1.400	1.911	1.370	1.491	
28	REACT	1.341	1.381	1.436	1.487	1.330	4.758	1.487	1.380	
	TS	1.417	1.308	1.639	1.418	1.395	1.939	1.501	1.372	
29	REACT	1.341	1.379	1.435	1.487	1.330	4.865	1.487	1.382	
	TS	1.416	1.306	1.651	1.418	1.394	1.969	1.503	1.374	
30	REACT	1.336	1.387	1.435	1.506	1.353	4.839	1.411	1.377	1.380
	TS	1.408	1.329	1.553	1.453	1.419	1.822	1.405	1.378	1.405
31	REACT	1.336	1.389	1.425	1.508	1.344	4.801	1.356		
	TS	1.403	1.335	1.529	1.455	1.412	1.837	1.353		

[a] REACT implies the parent ether; for other abbreviations, see text. [b] Bond lengths (Å).

conflict between our calculated activation parameters and experiment. We therefore carefully checked the geometries of the other TSs. All had chair configurations.

The geometries of the reactants are not reported in detail because they showed no unexpected features. The lengths of the C–C and C–O bonds in them are listed in Table II. The reactions were predicted to lead preferentially to E isomers, as seems to be generally the case.

As noted above, our studies of CORs have shown[12] that such a reaction can as a rule take place by either of two distinct paths, each with a distinct TS. One TS corresponds to the "classical" aromatic (ARO) mechanism and the other to the biradicaloid (BR) mechanism suggested by Doering et al.[8] The same is true for the CLR of **1**. Table I shows the activation parameters for the two paths. While the enthalpy of activation ($\Delta H^{\ddagger}$) for the ARO mechanism is again higher than that for the BR one, the difference (0.7 kcal/mol) is much less than that (6.5 kcal/mol) in the case of **3**.

Figure 1 shows the geometries calculated for the two TSs. The BR TS resembles the TS given by the earlier MNDO calculation,[21] the breaking (C–O) bond being only a little longer than in the reactant while the C_1–C_6 bond is already very short (1.84 Å). These values are consistent with the BR mechanism.[11,19] Both bonds are longer in the ARO TS, as expected.[12] However, the difference between the TSs is much less than it was in the case of **3**, where the lengths of the C_1–C_6 and C_3–C_4 bonds in the TSs differed by 0.4 Å.

Another interesting feature of the CLR TSs (Figure 1; see ref 21) is the fact that the hydrogen atoms at C_2 and C_5 are tilted out of the C_1–C_2–O and C_4–C_5–C_6 planes. A similar distortion from local planarity was found in the COR TSs from **3**. The reason for it has already been extensively discussed.[7,8,11,19,28]

Since the geometries of the TSs for the other CLRs did not differ qualitatively from the BR or ARO TSs for **1**, they are not

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(28) Schuler, F. W.; Murphy, G. W. *J. Am. Chem. Soc.* **1950**, *72*, 3155.

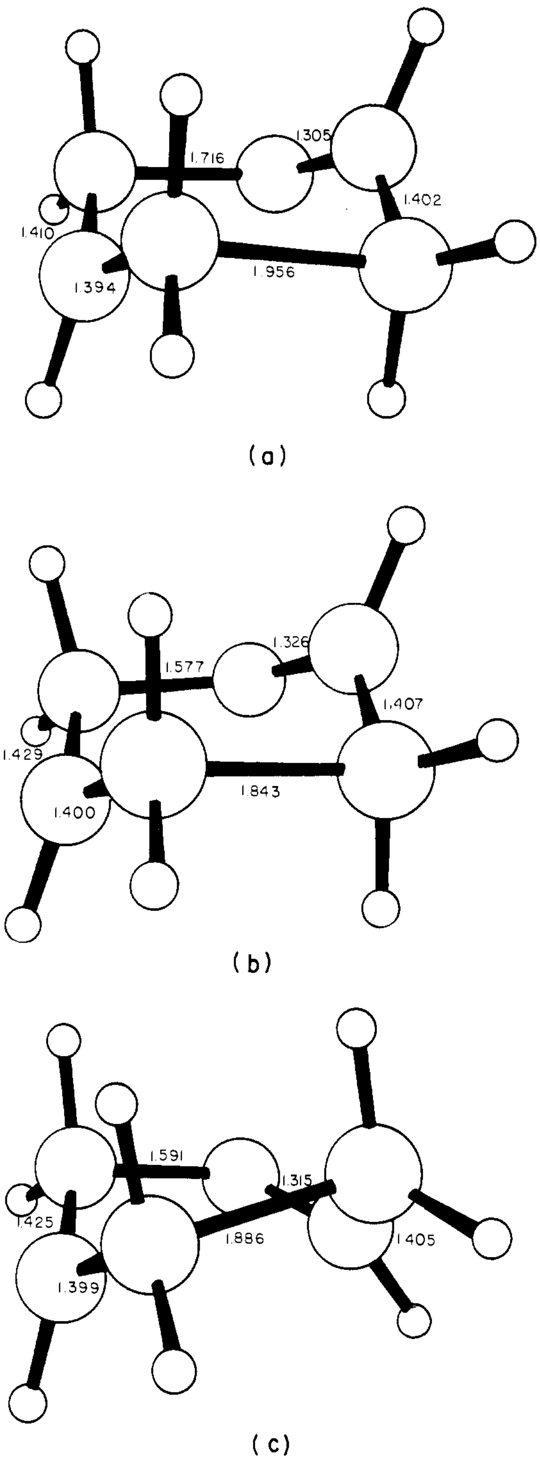

Figure 1. Geometries calculated for transition states (TS) for Claisen rearrangements of allyl vinyl ether (**1**): (a) aromatic (ARO) chair TS; (b) biradical (BR) chair TS; (c) BR boat TS.

reproduced in detail. The only significant quantities are the lengths of the C–C and C–O bonds in them, which are listed in Table II.

Pairs of distinct TSs, one ARO and the other BR, were found for several of these reactions; see Table I. The differences between the calculated enthalpies of activation were again very small. However, most of the reactions seemed to take place by only a single path, and lengths of the forming (C_4–O) and breaking (C_1–C_6) bonds in the corresponding TSs vary more or less continuously between the values calculated for the BR and ARO TSs from **1**; see Table II. Thus, the distinction between the two types of reaction paths, which was so clear-cut in the case of the COR, seems to have virtually disappeared in the CLR, the TSs showing a continuous gradation between the two extremes.

This difference is easily explained. CORs are approximately thermoneutral, being exactly so in the case of symmetrical (degenerate) rearrangements. Their TSs should therefore correspond to the symmetrical aromatic or biradicaloid intermediates or be close to them, as our calculations indeed predicted.[11] The CLR, on the other hand, is inherently quite strongly exothermic, the heat of reaction for that of **1** being ca. -20 kcal/mol. Since its TS should therefore be an "early" one, the difference in structure between the ARO and BR TSs should be less than that between the corresponding aromatic or biradical intermediates. Indeed, the difference may well disappear, the two TSs coalescing into a single TS with an intermediate geometry.

Gajewski and Conrad[14] postulated such a situation for both the COR and the CLR, on the basis of their studies of SDKIEs. Our previous studies[11,12,15,16] have shown that the COR does not follow this pattern, the reactions taking place by one or the other of two distinct mechanisms, not by a single "merged" mechanism. The CLR, however, does seem to follow the course suggested by Gajewski and Conrad, the calculated TS structures varying virtually continuously between the two extremes.

In the discussion[9] of multibond reactions, it was pointed out that such a reaction may take place in a synchronous manner if the activation energy of the synchronous process is low. Several examples were cited. The discussion here indicates that the same may be true for reactions that are very exothermic and consequently have early TSs. In an early TS, where changes in bonding have taken place only to a limited extent, the distinction between different possible reaction paths should be correspondingly attenuated.

Table III shows the dipole moments and formal charges on atoms other than hydrogen, calculated for the reactants and TSs. While the TSs are systematically more polar than the reactants, the differences are small. The changes in the charge on individual atoms on passing from the reactants to the TSs are also small. The rates of these reactions should therefore be little affected by the solvent. This indeed is the case for the CLRs of **1** and its cyano derivatives.[23]

Activation Parameters. Table I compares our activation parameters for **1**, and for its cyano derivatives (**9**–**14**), with the experimental values reported by Burrows and Carpenter.[23] The experimental values refer to reactions in dibutyl ether solution, except for **1**, for which gas-phase values have also been reported.[28]

There is a surprising difference between the two sets of experimental values for **1**, the enthalpy of activation ($\Delta H^{\ddagger}$) being greater by 5.2 kcal/mol, and the entropy of activation ($\Delta S^{\ddagger}$) less negative by 8.2 cal/deg, in the gas phase than in solution. Burrows and Carpenter point out that the value of $\Delta S^{\ddagger}$ (-15.9 eu) in solution is more in line with values found for analogous CORs, e.g. -13.0 ± 1.0 for the COR of **3**. However, it seems unlikely that the discrepancy could be due to experimental error. While the gas-phase measurements were carried out some time ago, there is no good reason to doubt their accuracy.

Other things being equal, the $\Delta S^{\ddagger}$ for CLRs should be less negative than those for normal (chair) CORs because the high values for the latter refer to BR mechanisms. The $\Delta S^{\ddagger}$ for ARO boat CORs, which follow the ARO mechanism,[12] range from -3 to -6 eu. The $\Delta S^{\ddagger}$ for a merged mechanism should lie between the two extremes, as indeed is the case for the calculated $\Delta S^{\ddagger}$ in Table I. Our calculated $\Delta S^{\ddagger}$ for **1** is closer to the value observed in the gas phase than in solution.

Changes in enthalpy and entropy, due to solvation, lead to opposite changes in the free energy. Thus, even if solvation does not lead to a large change in the rate of a reaction, it may nevertheless lead to large compensating changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Indeed, the difference (1.5 kcal/mol) between the values of $\Delta G^{\ddagger}$ for the CLR of **1** in the gas phase and solution at 450 K is much less than the corresponding difference in $\Delta H^{\ddagger}$. The differences between the two sets of activation parameters could therefore be reasonably attributed to solvation.

Cyano Substituents. Table I compares our calculated activation parameters for the CLRs of the monocyano derivatives with the values reported by Burrows and Carpenter.[23] In accordance with

Table III. Dipole Moments and Formal Charges of Species Involved in Claisen Rearrangements

species		dipole moment, D	formal charge, e								
			C_1	C_2	O	C_4	C_5	C_6	R_1	R_2	R_3
1	REACT	1.79	−0.281	−0.038	−0.224	0.001	−0.203	−0.210			
	TS BR (chair)	1.77	−0.217	−0.019	−0.245	−0.006	−0.299	−0.099			
	TS BR (boat)	1.39	−0.278	0.046	−0.249	0.027	−0.365	−0.063			
	ARO (chair)	1.98	−0.242	0.013	−0.275	−0.014	−0.282	−0.097			
2	PRODUCT	2.60	−0.230	0.183	−0.287	−0.216	−0.166	−0.130			
9	REACT	4.35	−0.176	0.032	−0.211	0.000	−0.214	−0.197	−0.147		
	TS (chair)	2.66	−0.161	0.076	−0.287	−0.001	−0.282	−0.069	−0.163		
	TS (boat)	3.13	−0.224	0.128	−0.320	0.029	−0.306	−0.038	−0.165		
10	REACT	5.29	−0.175	0.030	−0.204	−0.002	−0.215	−0.197	−0.138		
	TS	4.14	−0.156	0.070	−0.281	−0.004	−0.268	−0.076	−0.154		
11	REACT	2.07	−0.192	0.088	−0.213	0.000	−0.203	−0.202	−0.143		
	TS BR	3.85	−0.153	0.060	−0.201	−0.030	−0.230	−0.132	−0.152		
	ARO	3.75	−0.204	0.129	−0.247	−0.023	−0.241	−0.112	−0.166		
12	REACT	2.34	−0.257	−0.048	−0.211	0.156	−0.166	−0.191	−0.194		
	TS	3.17	−0.223	0.004	−0.254	0.117	−0.262	−0.100	−0.170		
13	REACT	3.56	−0.332	−0.009	−0.211	0.010	−0.068	−0.149	−0.130		
	TS BR	4.53	−0.253	0.039	−0.236	0.032	−0.229	−0.052	−0.152		
	ARO	4.33	−0.261	0.063	−0.279	0.022	−0.181	−0.063	−0.146		
14	REACT	2.51	−0.266	−0.049	−0.219	−0.005	−0.138	−0.100	−0.143		
	TS	2.25	−0.211	−0.005	−0.240	−0.011	−0.273	0.027	−0.162		
15	REACT	1.99	−0.270	−0.045	−0.221	−0.010	−0.135	−0.100	−0.149		
	TS	2.07	−0.219	0.012	−0.247	−0.005	−0.282	0.029	−0.174		
16	REACT	2.48	−0.056	−0.152	−0.216	0.004	−0.201	−0.213	−0.051		
	TS	2.01	−0.022	−0.061	−0.243	−0.031	−0.264	−0.136	−0.084		
17	REACT	0.76	−0.248	0.126	−0.256	0.008	−0.194	−0.209	−0.076		
	TS	0.88	−0.243	0.185	−0.285	0.021	−0.357	−0.065	−0.050		
18	REACT	2.17	−0.279	−0.028	−0.254	0.180	−0.192	−0.184	−0.089		
	TS	0.49	−0.233	0.029	−0.290	0.166	−0.316	−0.073	−0.103		
19	REACT	1.00	−0.274	−0.042	−0.226	−0.011	−0.019	−0.247	−0.047		
	TS	1.36	−0.198	−0.057	−0.235	−0.030	−0.102	−0.121	−0.068		
20	REACT	3.36	−0.283	−0.035	−0.223	0.022	−0.267	−0.026	−0.050		
	TS	2.44	−0.211	−0.017	−0.243	−0.006	−0.322	0.075	−0.103		
21	REACT	3.33	−0.236	0.115	−0.243	0.021	−0.075	−0.138	−0.078	−0.136	
	TS	4.92	−0.279	0.230	−0.271	0.055	−0.281	−0.017	−0.014	−0.157	
22	REACT	1.61	−0.283	−0.035	−0.223	0.007	−0.143	−0.212	0.079		
	TS	1.71	−0.208	−0.036	−0.238	−0.003	−0.240	−0.103	0.068		
23	REACT	1.63	−0.282	−0.036	−0.221	0.009	−0.139	−0.207	0.072		
	TS	1.67	−0.210	−0.033	−0.238	−0.002	−0.240	−0.101	0.063		
24	REACT	0.73	−0.248	0.127	−0.254	0.014	−0.138	−0.209	−0.076	0.074	
	TS	0.83	−0.236	0.175	−0.276	0.024	−0.300	−0.069	−0.047	0.063	
25	REACT	0.42	−0.183	0.114	−0.254	0.008	−0.190	−0.215	0.081	−0.074	
	TS	0.82	−0.183	0.194	−0.296	0.015	−0.339	−0.070	0.070	−0.061	
26	REACT	0.47	−0.184	0.115	−0.252	0.008	−0.191	−0.215	0.079	−0.077	
	TS	0.94	−0.183	0.193	−0.295	0.018	−0.352	−0.065	0.060	−0.051	
27	REACT	0.75	−0.249	0.126	−0.253	0.016	−0.134	−0.203	−0.077	0.063	
	TS	0.84	−0.238	0.176	−0.276	0.025	−0.293	−0.070	−0.048	0.055	
28	REACT	0.43	−0.178	0.116	−0.254	0.008	−0.190	−0.216	0.072	−0.073	
	TS	0.80	−0.177	0.196	−0.299	0.018	−0.351	−0.066	0.053	−0.054	
29	REACT	0.47	−0.179	0.116	−0.251	0.008	−0.191	−0.216	0.071	−0.078	
	TS	0.73	−0.176	0.198	−0.297	0.016	−0.341	−0.072	0.064	−0.063	
30	REACT	3.28	−0.270	−0.035	−0.258	0.179	−0.039	−0.071	−0.079	−0.002	−0.034
	TS	0.94	−0.214	0.008	−0.276	0.157	−0.147	0.077	−0.099	−0.058	−0.093
31	REACT	2.50	−0.267	−0.045	−0.211	−0.009	0.018	−0.261	−0.104		
	TS	2.47	−0.196	−0.054	−0.227	−0.026	−0.086	−0.143	−0.108		

the arguments given above, the calculated $\Delta H^{\ddagger}$'s are systematically larger (mean $\delta(\Delta H^{\ddagger}) = 6.5$ kcal/mol), and the calculated $\Delta S^{\ddagger}$'s, systematically less negative (mean $\delta(\Delta S^{\ddagger}) = 4.8$ eu) than the experimental ones. With a corresponding correction, the calculated and observed $\Delta H^{\ddagger}$'s agree quite well; see Figure 2. AM1 thus reproduces the relative values of $\Delta H^{\ddagger}$ better than the absolute values. This supports our contention, that theoretical studies of reaction mechanisms should be based on calculations for a number of examples for which experimental data are available, rather than a single example. The results here suggest a further reason for this procedure in cases where the experimental values refer to reactions in solution. If no large changes in polarity are involved, the effects of solvation are likely to be similar for a series of analogous reactions.

The bond lengths in the TSs of this limited series of reactions follow the pattern indicated above in that they fail to show a clear distinction between BR and ARO mechanisms. A further indication is provided by the values of $\Delta S^{\ddagger}$ for analogous BR and ARO reactions. Thus, while the difference between the ARO and BR $\Delta H^{\ddagger}$'s for the CORs of **3** is >6 cal/deg, a conclusion strongly supported by experiment,[12] and while the average of the two values is the same (ca. −9 cal/deg) for the COR of **3** and the CLR of **1**, the difference between the two values for the latter is only 2.5 cal/deg. This again indicates the tendency of the two mechanisms to coalesce in the case of the CLR.

Alkoxy Substituents. Table I shows the activation parameters calculated for the monomethoxy derivatives of **1**. The most striking feature is the very large predicted decrease in $\Delta H^{\ddagger}$ brought about by methoxy at C_2. While no kinetic data for **17** have been reported, data are available[29,30] for the corresponding (trimethylsilyl)oxy) derivative (**32**). The activation energy for its CLR is less by ca. 9 kcal/mol than that for **1**, close to our estimate of

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(29) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.

(30) Gajewski, J. J.; Emrani, J. *J. Am. Chem. Soc.* **1984**, *106*, 5733.

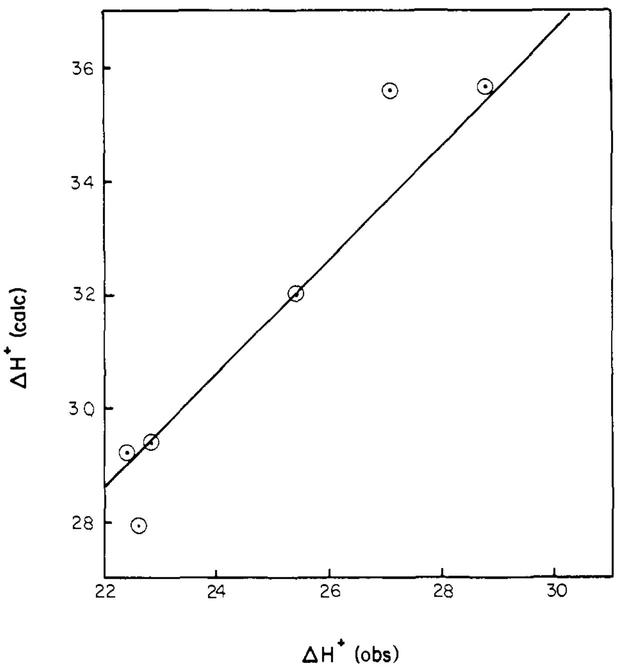

Figure 2. Plot of calculated vs observed enthalpies of activation ($\Delta H^{\ddagger}$; kcal/mol) for the Claisen rearrangements of **1** and its monocyano derivatives.

the corresponding difference between **1** and **17** (7.3 kcal/mol).

The large acceleration might be attributed to the fact that biradicals are by nature very polarizable, corresponding, in resonance terminology, to a contribution by a corresponding dipolar resonance structure, i.e. **33**. The calculated charges (Table II) seem at first sight consistent with this interpretation (cf. ref 31), the charge at C_2 in the TS being +0.185 compared with −0.019 in the TS from **1**. However, an almost equal change occurs in the parent ether, the difference between the changes at C_2 in the reactant and TS being almost the same as for **1**. The rate of rearrangement of **32** is indeed almost unaffected by a change in the solvent, the rate in acetonitrile being only 33% greater than that in carbon tetrachloride.[30]

These results can be explained quite easily in terms of simple MO theory, by an argument similar to that used to explain why NO_2 acts as a +E substituent.[32]

Consider the methoxymethyl (**34**) and dimethoxymethyl (**35**) radicals (Figure 3a). The interaction between the oxygen and carbon p AOs in **34** leads to their replacement by a pair of MOs, one bonding and the other antibonding (Figure 3b), and to a transfer of electrons from oxygen to carbon. This polarization of the π electrons is, however, unlikely to lead to any significant change in the overall electron distribution because it will be countered by polarization of the CO σ bond, cf. carbon monoxide.

Since **35** has a plane of symmetry (Figure 3a), its MOs must be symmetric, or antisymmetric, for reflection in that plane. The p AOs, ϕ_1 and ϕ_2, of the oxygen atoms can be replaced by symmetric ($\phi_1 + \phi_2$) and antisymmetric ($\phi_1 - \phi_2$) combinations, only the former interacting with the (symmetric) carbon p AO. The antisymmetric MO ($\phi_1 - \phi_2$) thus remains unchanged, its energy being the same as that of an oxygen p AO. The interaction between the symmetric MO ($\phi_1 + \phi_2$) and the carbon 2p AO is analogous to that between the oxygen and carbon p AOs in $MeOCH_2$, the only difference being that the "resonance integral" is greater, by a factor of $\sqrt{2}$. The splitting of orbital energies due to the interaction is therefore greater in **35** than in **34**, and the overall energy is correspondingly more negative; see Figure 3. The larger interaction will also lead to a correspondingly greater transfer of π electrons from oxygen to carbon. This, however, should be offset by polarization of the σ electrons, there now being *two* CO σ bonds. The extra methoxy in **35** should thus lead to stabilization without much change in polarity. This is exactly what our calculations predict and experiment indicates.

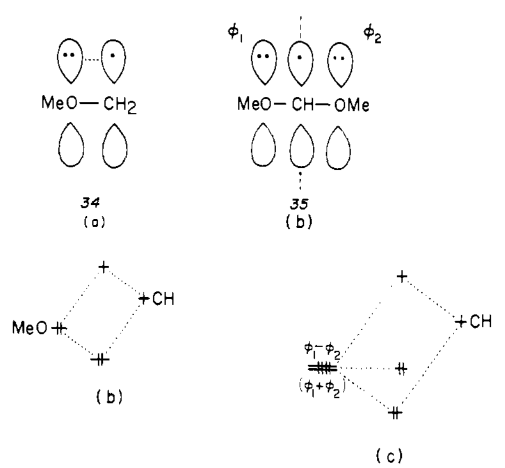

Figure 3. Interacting p AOs in methoxymethyl cation (**34**) and dimethoxymethyl cation (**35**). The dotted line in **35** denotes a plane of symmetry. Orbital interactions in **34** and **35** are indicated beneath.

Experimental studies have recently been reported by Coates et al.[33] for the CLRs of the 4-, 5-, and 6-methoxy derivatives (**18–20**) of **1**. Their activation parameters are listed in Table I. Allowing for the systematic error (+6.5 kcal/mol) in the AM1 $\Delta H^{\ddagger}$, the value that we calculated for **18** (24.2 kcal/mol) agrees well with theirs (22.4 kcal/mol). The discrepancy for **20** (3.5 kcal/mol) is, however, nearly double that for any of the cyano derivatives (**9–14**) while the discrepancy for **19** (7.7 kcal/mol) is twice as large again. Furthermore, while AM1 predicts **19** to rearrange much more rapidly, and **20** much less rapidly, than **1**, the rate reported by Coates et al. for **19** is far less than that for **1** while the rate for **20** is somewhat greater.

Gajewski et al.,[14,30] and Kahn and Hehre,[34] have suggested that the Claisen TS may correspond to a weakly bound radical pair; see **36**. Our calculations seem, however, to rule out such a mechanism in the gas phase. If it could operate, the corresponding biradical-like structure (**36**) should correspond to a TS on the AM1-HE-CI potential energy surface. This was not the case.

If this interpretation were correct, the energies of the TSs should run parallel to the heats of reaction (ΔH) for dissociation of the parent diene to the radical pair. The AM1 values ($\delta(\Delta H)$) of ΔH for **18–20**, relative to that for **1**, are

18, −15.3; **19**, −6.1; **20**, −9.7 kcal/mol (1)

While these results reproduce the reported order of rates (**18** > **20** > **19**), they also show that all three compounds should rearrange faster than **1**. It is therefore impossible to explain the low reactivity of **19** in this way.

The course of the reaction might, however, be influenced by solvation. Our calculations (Table III) indicate no significant difference in polarity between **1** and the corresponding TS, and the ratio of the rates of rearrangement is, as expected, correspondingly small (1.7).[33] The calculated electron distributions in Table III imply that the same should be true for all the other compounds studied, including **18–20**. However, while the corresponding rate ratio was also small (1.7) for **19**, it was large (18) for **18** and larger still (68) for **20**. This suggests that the reactions of **18** and **20** are different in solution and in the gas phase.

Biradicals are highly polarizable, a situation represented in resonance theory by writing them as hybrids of biradical and zwitterionic structures; e.g. **36** and **37**. The energy of a zwitterion is much greater than that of the corresponding biradical, because of the separation of charge in it. This limits the contribution of the zwitterion to the resonance hybrid. Solvation will decrease

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(32) Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum: New York, 1975.

(33) Coates, R. M.; Rogers, B. D.; Hobbs, S. J.; Peck, D. R.; Curran, D. *J. Am. Chem. Soc.* **1987**, *109*, 1160.

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Table IV. Kinetic Isotope Effects

	k_H/k_D for replacement of H					
	C_4			C_6		
compd	calcd(BR)	calcd(ARO)	obsd	calcd(BR)	calcd(ARO)	obsd
1	1.007	1.038	1.09[a]	0.891	0.904	0.976[a]
17	1.030[b]			0.813[b]		
32			1.48 (0.04)[c]			0.92 (0.03)[c]

[a] Reference 14. Standard deviation, 0.005. [b] TS of intermediate type; see text. [c] Reference 29. Standard deviations in parentheses.

the effect of charge separation, thus making the biradical more zwitterionic. The zwitterion will also be stabilized relative to the biradical by $-E$ (electron-releasing conjugative) substituents at suitable positions; e.g. 4 and 6 in **37**. Thus, while our calculations indicate that a 4- or 6-methoxy substituent in **1** is not sufficient to make the biradicaloid/zwitterionoid TS (**36** ↔ **37**) lower in energy than **7** in the gas phase, substitution and solvation together might make it so. This would account for the reported results.

This interpretation, however, also fails to account for the large discrepancy in the case of **19**. In view of the good agreement with experiment given by AM1 for cyano derivatives (Figure 2) and other methoxy derivatives of **1** (Table II), and for a number of CORs,[11] it seems unlikely that the discrepancy can be primarily due to errors in the AM1 results. Repetition of the kinetic measurements, preferably in the gas phase, would clearly be of interest.

Other Derivatives of Allyl Vinyl Ether. Calculations were also carried out for a number of other derivatives of **1**, for various reasons. The results are indicated in Tables I–III. Those for **21** are particularly interesting.

As noted above, the fact that alkoxy groups at C_2 greatly accelerate the CLR of **1** could be explained in terms of polarization of the TS by the substituent; cf. **33**. However, as we have already seen, this interpretation is contradicted both by our results for **17** and by the fact that the rate of the CLR of **32** is no more sensitive to changes in polarity of the solvent than that of **1**.

The zwitterionic structure (**33**) should also be stabilized by $+E$ substituents at C_5. Our calculations predict quantitatively the large decrease in $\Delta H^{\ddagger}$ in the case of **13** while failing to predict any significant change in the relative polarity of the TS. The rate of rearrangement is also insensitive to changes in the solvent. Thus, the substituent is again predicted to stabilize the TS without significantly polarizing it.

Since each of these substituents greatly reduces $\Delta H^{\ddagger}$, a dramatic decrease should occur in **21** where both are present simultaneously. Furthermore, their tendencies to polarize the TS should synergise one another. Our calculations indeed predict a very large decrease in $\Delta H^{\ddagger}$, the value for **21** (19.0 kcal/mol), implying that it should rearrange rapidly at room temperature. The predicted decrease is, however, almost exactly equal to a sum of those predicted for **13** and **17**, implying no synergism between the substituents, and the calculated charges (Table II) also fail to predict any increase in polarity of the TS.

These results emphasize again the distinction between biradicals and biradicaloids. While true biradicals should be highly polarizable, a biradicaloid need not be any more so than other kinds of closed-shell molecules. An experimental study of **21**, in particular a comparison of the rates in different solvents, would clearly be of much interest.

The effects of alkyl substituents at C_1 or C_5 were also studied. Comparison (Table I) of the activation parameters for **22** or **23** with those for **1**, and of those for **24** or **27** with **17**, implies that alkyl groups at C_5 should have an accelerating effect. On the other hand, similar comparisons of **17** with **25**, **26**, **28**, or **29** imply that alkyl groups at C_1 retard the CLR. However, since the latter compounds all contain a methoxy group at C_2, steric effects may have been involved.

A further interesting conclusion concerns the rates of rearrangement of ethers with *cis*- and *trans*-alkyl substituents at C_1 in **17**. Thus, while the *E* isomer (**25**) is predicted to be the more reactive in the case of methyl substitution, the reverse is true for isopropyl.

One last result of interest is the effect of fluorine substitution. As **31** shows, fluorine at C_5 in **1** is predicted to have a large accelerating effect.

Kinetic Isotope Effects. Gajewski et al.[14] have reported studies of secondary deuterium kinetic isotope effects (SDKIE) for the CLR of **1**. Their results are compared with our calculated (AM1) values for **1** and **17** in Table IV. The agreement is comparable with that obtained for several CORs,[11] suggesting that the calculated rate ratios can be in error by 4–5%. The rate ratios are much closer to unity than they were in the CORs studied earlier,[11] supporting the expectation, and our prediction, that the TS for the CLR of **1** is an early one.

Gajewski and Emrani[30] have reported analogous measurements for **32**, the KIEs differing significantly from those for **1**; see Table IV. They conclude that bond breaking must have taken place to a much greater extent in the TS than in the TS from **1** and attribute this to contribution by a resonance structure corresponding to a pair of radicals (**36**). Our calculated KIEs for **17** (Table IV) show no such effect, even though our calculated rate enhancement in **17**, due to the methoxy substituent, is similar to that brought about by the (trimethylsilyl)oxy group in **32**. A possible explanation of the discrepancy was given above, i.e. that the mechanism may be solvent dependent, solvation favoring a TS that can be written as a hybrid of **6**, **36**, and **37**. Alternatively, the TS from **32** may be strongly perturbed by a coordination of silicon to the ether oxygen (O_3). An analogous experimental study of KIEs for **17** in the gas phase would clearly be of interest.

BR and ARO Mechanisms in Pericyclic Reactions. Theoretical considerations[9] have indicated that multibond reactions are nonsynchronous in the absence of factors that specifically favor synchronicity. The aromaticity of synchronous TSs for allowed pericyclic reactions is one such factor.[9] However, our studies[11,12,15,16] of the Cope rearrangement (COR) have shown that this is not sufficient in itself, the majority of CORs taking place by a BR mechanism, and Diels–Alder reactions of unsymmetrically substituted dienes and dienophiles also seem to be nonsynchronous.[19]

Our work[12,15,16] has moreover shown that most CORs can take place by *either* route, the BR and ARO mechanisms corresponding to discrete TSs, and Bernardi et al.[20] have recently found the same to be true for the Diels–Alder reaction between ethylene and butadiene. In both cases, however, the differences in energy between the pairs of TSs were small, showing that the balance between the two possible routes is close. The aromaticity of the TSs in these allowed reactions evidently just about compensates for the disadvantage of carrying out a multibond reaction in a synchronous manner.

The "biradical" intermediates in BR reactions are not of course real biradicals. Coupling between the radical centers, usually due to through-bond interactions, leads to a closed-shell structure, which, however, cannot be represented by a conventional valence formula. Such *biradicaloids* are therefore usually formulated as biradicals, an unfortunate misrepresentation, which has caused much confusion. Since the electrons in a biradicaloid are all paired, resonance between the ARO and BR structures for a TS is possible. This admittedly is an unusual application of resonance theory because neither species corresponds to a minimum on the potential energy surface. We are considering here a one-dimensional space corresponding to the ridge separating the reactants from the products. All the points on it represent species with an imaginary vibration perpendicular to the ridge, corresponding to conversion to the reactant or product. Minima on the ridge correspond to saddle points on the potential surface, i.e. to possible TSs.

In such situations, where a molecule is depicted as a hybrid of two different structures, the effect of the resonance between them depends on the difference in geometry and the magnitude of the corresponding interaction ("resonance integral").

If the difference in geometry is large or the interaction small, the ARO and BR structures will correspond to separate stationary points on the potential surface. This seems to be the situation in the case of the Diels–Alder reaction between ethylene and butadiene and in most of the Cope rearrangements. Exceptions are expected only in cases where the two TSs differ greatly in energy. The TS of higher energy may then cease to be a stationary point.

If the difference in geometry is small and the interaction large, the two structures will merge into a single hybrid whose geometry will depend on the relative contributions of the ARO and BR wave functions. This is the situation envisaged by Gajewski where the TS can have structures varying between the BR and ARO extremes. According to our calculations, the Claisen rearrangement is an example. While pairs of TSs were found for some of the reactions we studied, the differences between them were essentially negligible, being indeed well within the uncertainties of AM1. The merging of mechanisms in the CLR is due to its large exothermicity. The TSs consequently have structures intermediate between the reactants and the aromatic or biradicaloid intermediates. The structures of the TSs are consequently much more alike than those of the intermediates.

Synchronous multibond mechanisms are expected[9] to be favored in reactions involving migration of hydrogen,[9] due to the propensity of hydrogen to form three-center bonds.[9] An allowed pericyclic reaction involving migration of hydrogen is therefore likely to be synchronous. Sigmatropic rearrangements involving migration of hydrogen, and ene reactions, are obvious examples.

Pericyclic reactions with small heats of reaction are likely to proceed by alternative BR and ARO paths. If a TS is located for such a reaction, it cannot be assumed to be the "true" TS unless and until the other TS has been located or shown not to exist. It is also necessary to use procedures able to distinguish reliably between the two mechanisms. Reasonably reliable conclusions can be derived from calculations on their own only if a very high level ab initio procedure is used. Such calculations can usually be carried out only for the simplest example of a reaction, an unfortunate limitation since the simplest example of *any* reaction is often untypical. The alternative is to combine calculations with experiment for a number of examples of a reaction where experimental data are available. Here, a less accurate treatment can suffice because it is much easier to predict relative activation parameters, etc., for a series of related reactions than their absolute values. AM1 is the obvious choice in this connection, particularly in cases where the usual RHF version can be used. The conclusions reached in this way are usually reliable. Problems arise in the case of BR mechanisms where the intermediates are truly biradical-like, due to the weaknesses of current open-shell versions of AM1.

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A Theoretical Investigation of the Intramolecular Reactions of Cyclopropylmethylene

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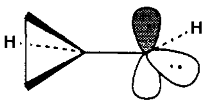
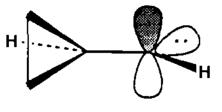
Abstract: An ab initio investigation of the energetics of the intramolecular reactions of cyclopropylmethylene (**1**) has been carried out. Geometries were fully optimized at the HF/3-21G levels, and single point calculations were made at the MP2/6-31G* and MP4SDQ/6-31G levels and combined in order to approximate relative energies at the MP4SDQ/6-31G* level. Carbene **1** exists in two conformers in which the empty p orbital overlaps the antisymmetric Walsh orbital on the three-membered ring. The conformer with the carbene and cyclopropyl hydrogens cis, **1a**, is calculated to be more stable than the trans conformer, **1b**, by 1.8 kcal/mol and separated from it by a barrier of 14.9 kcal/mol. The most favorable reaction of **1a** is the ring expansion to give cyclobutene (**2**: $\Delta H^{\ddagger} = 5.0$ kcal/mol). Ring expansion of conformer **1b** is less favorable ($\Delta H^{\ddagger} = 20.4$ kcal/mol) and the most rapid reaction of **1b** should be fragmentation to ethylene and acetylene. The fragmentation of **1** may involve a nonsynchronous pathway with an estimated barrier of 8.0 kcal/mol (from **1b**). Ring expansion may predominate in **1a** while fragmentation is favored in **1b**. The triplet carbene is calculated to lie slightly below the singlet in energy and should undergo facile cleavage to a triplet biradical. This triplet carbene may be involved in the gas-phase chemistry of **1** at high pressures.

The cyclopropyl carbene **1** occupies a unique position in the chemistry of divalent carbon intermediates. This carbene exists in two conformers, **1a** and **1b**, in which there is an expected and calculated barrier to interconversion.[1,2] It is one of the few carbenes to prefer to rearrange via a C–C insertion, to give cyclobutene (**2**) to the exclusion of the more common insertion into a β C–H bond which could yield methylenecyclopropane (**3**).[3] This ring expansion is interesting in that the least substituted bond migrates,[4] leading to stereospecific cyclobutene formation,[5,6] thus



1a



1b

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