of ^{1}DMDPA* and $^1O_2(^1\Delta_g)$,[7] we find that 102 kcal/mol is required to produce the excited hydrocarbon ^{1}DMDPA* and $^1O_2$ in the $^1\Delta_g$ state (Figure 2). The excitation light at 266 nm has an energy of 108 kcal/mol. Thus the process is energetically allowed with a maximum excess of 6 kcal/mol. To produce the $^1O_2$ in the $^1\Sigma_g^+$ state requires 9 kcal/mol more than that provided by the exciting light. We therefore conclude that in the newly observed adiabatic dissociation channel the $^1O_2$ is produced in the $^1\Delta_g$ state.

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(6) From literature values of the thermochemistry of DMDPA and related endoperoxides the minimum value for the enthalpy of dissociation is used in order to determine the maximum energy available upon photodissociation.

(7) For a theoretical and experimental discussion of $^1O_2$, its spectroscopy, and reactions, see: Wasserman, H. H.; Murray, R. W., Eds. "Singlet Oxygen"; Academic Press: New York, 1979.

Substituent Effects on the Aliphatic Claisen Rearrangement. 1. Synthesis and Rearrangement of Cyano-Substituted Allyl Vinyl Ethers

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There has recently been a renaissance of interest in the aliphatic Claisen rearrangement both as a technique for organic synthesis[1] and as an important part of the shikimate biosynthetic pathway.[2] It is therefore somewhat surprising that there has, to our knowledge, been no systematic study of substituent effects on the rate of the reaction. In this communication we report the first stage of such an investigation. Our intentions are to provide a body of empirical data that could be employed by synthetic organic chemists and also to test the various qualitative[3] and quantitative[4] theories of substituent effects on pericyclic reactions.

This stage of the investigation centers on the synthesis and rearrangement of the five cyano-substituted allyl vinyl ethers 1-5.
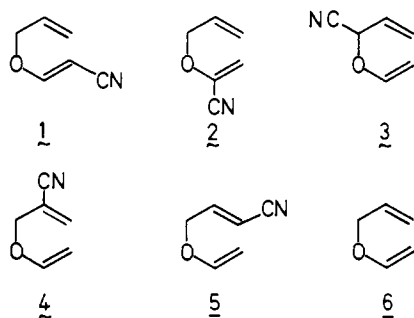
Of special interest is the comparison of the activation parameters for their [3,3]-sigmatropic rearrangement with those for the parent compound **6**. The cyano substituent was chosen as a sterically small π acceptor, although its radical stabilizing properties[5] might also be important for some theoretical interpretations.[4] The *E* configurations of compounds **1** and **5** were also selected to min-

(1) (a) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227–232. (b) Bennett, G. B. *Synthesis* **1977**, 589–606. (c) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1974**, *22*, 1–252.
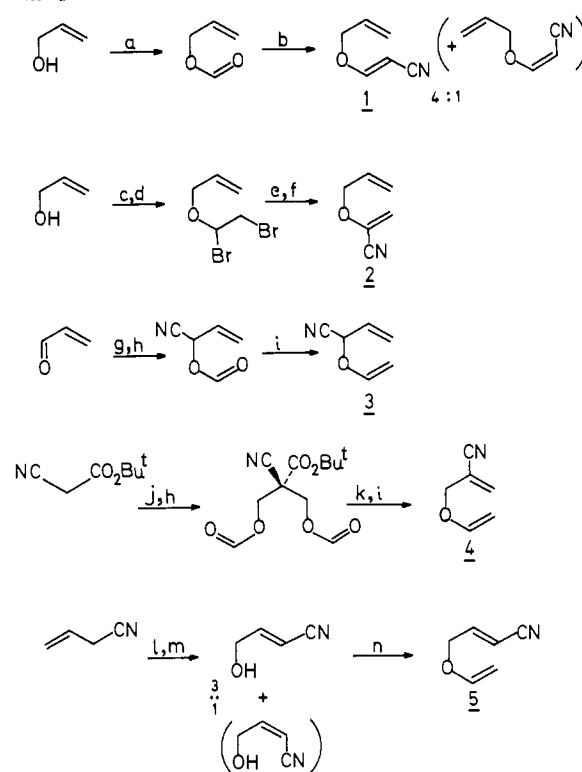
(2) Ganem, B. *Tetrahedron* **1978**, *34*, 3353–3383.

(3) Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877–1884.

(4) Gajewski, J. J. *Acc. Chem. Res.* **1980**, *13*, 142–148.

(5) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

Scheme I[a]

Table I. Kinetic Data for Compounds 1-6

compd	temp range, °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol K)	k_{rel}, 100 °C
1	124–174	27.08 ± 0.09	−11.6 ± 0.2	0.90
2	66–115	22.84 ± 0.19	−13.4 ± 0.5	111
3	55–101	22.33 ± 0.20	−13.0 ± 0.6	270
4	90–140	22.58 ± 0.26	−18.0 ± 1.3	15.6
5	135–185	28.76 ± 0.54	−11.2 ± 1.2	0.11
6	113–173	25.40 ± 0.65	−15.9 ± 1.5	(1)

imize steric effects in the transition state for the rearrangement.[1a] The syntheses of **1** → **5** are summarized in Scheme I.

A few points in these syntheses require comment. The conversion of allyl formate to **1** by a Wittig reaction was inspired by the work of LeCorre[6a] and Subramanyam et al.[6b] We confirmed the observation of these investigators that unstabilized phosphorus ylides would not undergo an analogous reaction, although the reasons for this are not clear.

We were unable to convert acrolein cyanohydrin to **3** by either Hg^{2+} or Pd^{2+} catalyzed exchange with ethyl vinyl ether[7] although this procedure was successful in the synthesis of **5**. The use of the Tebbe reagent,[8] allowing preparation of **3** and **4** from the corresponding formates of the corresponding allylic alcohols, followed the precedent of Pine et al.[9]

The synthesis of compound **4** was by far the most difficult, primarily because the corresponding allylic alcohol (3-hydroxy-propene-2-carbonitrile) was extremely susceptible to polymeri-

(6) (a) LeCorre, M. *Bull. Chim. Soc. Fr.* **1974**, 2005–2008. (b) Subramanyam, V.; Silver, E. H.; Soloway, A. H. *J. Org. Chem.* **1976**, *41*, 1272–1273.

(7) Burgstahler, A. W.; Nordin, I. C. *J. Am. Chem. Soc.* **1961**, *83*, 198–206.

(8) Tebbe, F. N.; Parshall, G. W.; Reddy G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613.

(9) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270–3272.

zation and hence was not a viable synthetic intermediate.

All of the new[10] compounds **1 → 5** were characterized by NMR, IR, and mass spectrometry.[11] Compounds **1** and **5** could be distinguished from their *Z* isomers by the significantly larger vicinal coupling constants of the vinyl hydrogens for the *E* configuration in the ^{1}H NMR.

The activation parameters for Claisen rearrangement of **1-6** were determined by using dilute (typically 5×10^{-3} M) solutions in anhydrous, degassed, di-*n*-butyl ether. Analyses were performed by following the disappearance of starting material using an analytical high-pressure liquid chromatograph equipped with variable wavelength UV detector and digital integrator. In each case control experiments confirmed a complete mass balance and showed no detectable side reactions. Activation parameters were calculated from the Eyring equation by using rate constants determined at five temperatures (six temperatures for **6**). All of the compounds exhibited good first-order kinetics over several half-lives. The results are summarized in Table I.

Detailed theoretical interpretations of these results are given in the following communication, but a few points are sufficiently striking to be made here.

Both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for **6** are somewhat lower than the values found in an earlier investigation.[12] Part of the discrepancy can be attributed to the difference in reaction media (di-*n*-butyl ether solution vs. gas phase) although we note that the new value for $\Delta S^{\ddagger}$ (-15.9 ± 1.5 cal/(mol K)) is more in line with the activation entropies for other [3,3]-sigmatropic migrations (from -9 to -20 cal/(mol K))[1a,13,14] than was the previous value (-7.7 cal/(mol K)).[12]

The effect of the nitrile substituent, which we assume to be primarily electronic in origin, is quite substantial, covering a range of nearly 2500 in k_{rel} at 100 °C (between **5** and **3**). It is particularly interesting that an acceptor substituent at the α position of the vinyl ether function (compound **2**) causes a rate enhancement since a donor substituent at that location apparently has a similar effect.[1a,15] This unusual (non-Hammett) behavior is in accord with our qualitative model for substituent effects on pericyclic reactions.[3]

Experiments to determine the effect of a methoxy substituent on the rate of the aliphatic Claisen rearrangement are in progress. The qualitative results of these experiments are predicted in the following communication.

Supplementary Material Available: Details of the kinetics for rearrangement of compounds **1-6** (13 pages). Ordering information is given on any current masthead page.

(10) Syntheses of both **1** and **2** have been claimed (Movsum-Zade, E. M.; Mamedov, M. G.; Shikhiev, I. A. *Zh. Org. Khim.* **1976**, *12*, 1687-1689). No proofs of structure except elemental analyses were given. Curiously, an incorrect elemental composition was both calculated and observed for **2**.

(11) **1**: ^{1}H NMR (CDCl$_3$) δ 7.23 (d, *J* = 13 Hz, 1 H), 5.8-6.2 (m, 1 H), 5.2-5.5 (m, 2 H), 4.70 (d, *J* = 13 Hz, 1 H), 4.44 (m, 2 H); IR 2240, 1620 cm^{-1}; CI-MS, *m/e* (M + 1) 110. **2**: ^{1}H NMR (CDCl$_3$) δ 5.75-6.15 (m, 1 H), 5.22-5.48 (m, 2 H), 5.01 (d, *J* = 3 Hz, 1 H), 4.88 (d, *J* = 3 Hz, 1 H), 4.34 (m, 2 H); IR 2240, 1620 cm^{-1}; CI-MS, *m/e* (M + 1) 110. **3**: ^{1}H NMR (CDCl$_3$) δ 6.50 (dd, *J* = 7, 14 Hz, 1 H), 5.8-6.25 (m, 1 H), 5.5-5.95 (m, 2 H), 5.15 (m, 1 H), 4.64 (dd, *J* = 3, 14 Hz, 1 H), 4.44 (dd, *J* = 3, 7 Hz, 1 H); IR 1625 cm^{-1}; CI-MS, *m/e* (M + 1) 110. **4**: ^{1}H NMR (CDCl$_3$) δ 6.38 (dd, *J* = 7, 14 Hz, 1 H), 6.00 (m, 2 H), 4.30 (m, 2 H), 4.22 (dd, *J* = 2.5, 14 Hz, 1 H), 4.15 (dd, *J* = 2.5, 7 Hz, 1 H); *m/e* (M + 1) 110. **5**: ^{1}H NMR (CDCl$_3$) δ 6.77 (dt, *J* = 3.5, 16 Hz, 1 H), 6.54 (dd, *J* = 7, 14 Hz, 1 H), 5.67 (dt, *J* = 2.5, 16 Hz, 1 H), 4.36 (dd, *J* = 2.5, 3.5 Hz, 2 H), 4.25 (dd, *J* = 2.5, 14 Hz, 1 H), 4.15 (dd, *J* = 2.5, 7 Hz, 1 H); IR 2225, 1620 cm^{-1}; CI-MS, *m/e* (M + 1) 110.

(12) Schuler, F. W.; Murphy, G. W. *J. Am. Chem. Soc.* **1950**, *72*, 3155-3159.

(13) Wehrli, R.; Schmid, H.; Belluš, D.; Hansen, H.-J. *Helv. Chim. Acta* **1977**, *60*, 1325-1356.

(14) Willcott, M. R.; Cargill, R. L.; Sears, A. B. *Prog. Phys. Org. Chem.* **1972**, *9*, 25-98.

(15) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868-2877.

## Substituent Effects on the Aliphatic Claisen Rearrangement. 2. Theoretical Analysis

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We have recently described a simple theoretical model that gives a good qualitative description of substituent effects on most thermal pericyclic reactions.[1] Our approach has been to focus on the π electrons of the various species involved and then to use simple Hückel molecular orbital (HMO) theory to evaluate the effect of a substituent on the transition state and the reactant(s). Transition states are modeled by the π-isoconjugate ground-state structure[1-3] while, at the zeroth level of approximation, π-donor substituents are represented by a carbanion and π-acceptors by a carbonium ion.[1] The difference in HMO π-electron energy between the transition state and reactant models (ΔE_{π}) is then compared for the reaction of interest and its unsubstituted analogue. This procedure yields the parameter $\Delta\Delta E_{\pi}$ whose sign and (in the case of neutral hydrocarbons) magnitude represent the predicted effect of the substituent on the activation enthalpy of the reaction. Thus if $\Delta\Delta E_{\pi}$ is negative (in absolute β units), the substituent is predicted to decrease $\Delta H^{\ddagger}$ with respect to that for the unsubstituted analogue whereas a positive $\Delta\Delta E_{\pi}$ means that the substituent should increase $\Delta H^{\ddagger}$. Surprisingly, given the crudeness of the model, there is a quantitative correlation between the calculated $\Delta\Delta E_{\pi}$ and the experimental $\Delta\Delta H^{\ddagger}$ for pericyclic, radical, and biradical reactions of unsaturated hydrocarbons.[3] This quantitative agreement presumably means that the basic approach is valid and, we assume, suitable for making qualitative predictions in heteroatomic pericyclic reactions.

In an analysis of the aliphatic Claisen rearrangement one begins by replacing the π-donor oxygen of the allyl vinyl ether by a carbanion. Such an approximation will, of course, quantitatively overestimate the importance of the oxygen lone pair but can be expected to give qualititatively correct results.[1] The π electrons of the unsubstituted reactant are therefore represented by an allyl anion and an isolated ethylene. The model for the transition state depends upon the geometry of the real activated complex. If the reaction proceeds through a chair conformation (A), then the oxygen lone pair that was in conjugation in the reactant will become almost orthogonal to the pericyclic array of orbitals in the transition state. On the other hand, the conjugation can be maintained if the transition state adopts a half-chair conformation (B) similar to that of cyclohexene. The orbital connectivity of A can be modeled by a phenyl anion whereas B is better modeled by a heptatrienyl anion because the orthogonality of orbitals on oxygen prevents completion of a cycle.[4]

A

B
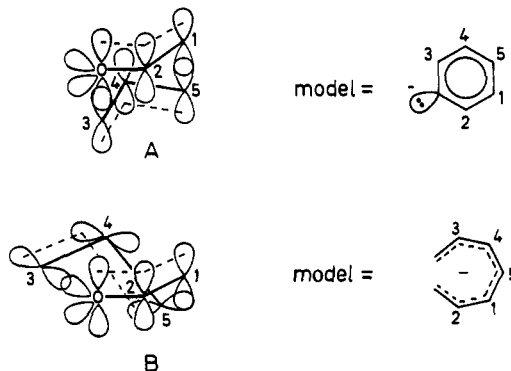
(1) Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877-1884.

(2) Wilcox, C. F., Jr.; Carpenter, B. K.; Dolbier, W. R., Jr. *Tetrahedron* **1979**, *35*, 707-711.

(3) Wilcox, C. F., Jr.; Carpenter, B. K. *J. Am. Chem. Soc.* **1979**, *101*, 3897-3905.