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THE AROMATIC COPE REARRANGEMENT: ACTIVATION PARAMETERS

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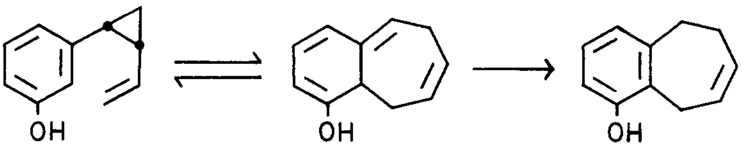
The activation parameters ($\Delta H^{\neq}$ = 26.7 ± 4.0 kcal/mol and $\Delta S^{\neq}$ = 17.5 ± 9.8 eu) have been measured for the Cope rearrangement of <u>*cis*</u>*-1-(*<u>*m*</u>*-hydroxyphenyl)-2-vinylcyclopropane.*

The Cope rearrangement, unlike the Claisen rearrangement, does not proceed normally when one of the double bonds of the 1,5-hexadiene unit is incorporated into an aromatic ring.[1] We reported recently the first clear example of an "aromatic" Cope rearrangement.[2] Potentially, there exist two possible stumbling blocks for the aromatic Cope rearrangement, loss of aromatic resonance energy in the 3,3-shift could increase the activation energy to too high a level, or the formal 1,3-hydrogen shift could be rate determining and, if concerted, thermally recalcitrant. Doering has suggested the latter explanation.[3] We report here a kinetic study of our aromatic Cope rearrangement which sheds light on these problems.[4]

In our reaction (eq. 1) reactant and product can act as weak acid catalysts for the proton transfer step. Despite this, the rearrangement of pure substrate in ethanol at 127.1° was too slow to permit accurate measurement. However, in the presence of added phenol, reaction proceeded reasonably, and increasing the phenol concentration from 2.23 x 10^{-2} to 2.41 M led to a rate increase of less than 20%. Under these conditions, the 3,3-sigmatropy becomes rate determining, and rates were measured as follows at the indicated temperatures, 121.3° k = 1.92 ± 0.15 sec.^{-1}, 127.1° k = 4.07 ± 0.38 sec.^{-1}, 133.9° k = 5.73 ± 0.38 sec.^{-1} (95% confidence limits N = 20).[5] These results give $\Delta H^{\neq}$ = 26.7 ± 4.0 kcal/mol and $\Delta S^{\neq}$ = -17.5 ± 9.8 eu for the aromatic Cope rearrangement.



(1)

The cost in enthalpy of encasing one of the double bonds in a benzene ring can be assessed directly by comparison with the $\Delta H^{\neq}$ = 19.4 kcal/mole found for cis-1,2-divinylcyclopropane.[6] This difference of 7.3 kcal/mol when added to the value of $\Delta H^{\neq}$ = 34.5 kcal/mol for 1,5-hexadiene[7] indicates that the $\Delta H^{\neq}$ for Cope rearrangement of 4-phenyl-1-butene would be near 42 kcal/mol.[8] If no severe entropic problems occur, this result shows that the rearrangement step will be very slow. Despite this, the reaction should be observable if the proton transfer step is properly catalyzed. Experiments to test this idea are in progress.

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References and Notes

1. A. C. Cope, L. Field, D. W. H. MacDowell, and M. E. Wright, J. Am. Chem. Soc., 78, 2547 (1956).
2. E. N. Marvell and C. Lin, ibid., 100, 877 (1978).
3. W. von E. Doering and R. A. Bragole, Tetrahedron, 22, 385 (1966).
4. Rearrangements were run by an ampoule technique using a 0.0713 M solution of 1-(m-hydroxphenyl)-cis-2-vinylcyclopropane in ethanol containing tetradecane as an internal standard. Analysis was by glc on a 100' capillary column of MBMA, and duplicate runs were made. Integrations were made with a Hewlett-Packard model 3373B digital integrator. All of the runs used to determine the activation parameters used solutions 0.567 M in phenol.
5. The temperature range available for this study was limited by the extremely low rate below 120° and by increasingly rapid competition by cis-trans isomerization of the substrate above 135-140°.
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7. W. von E. Doering, V. G. Toscano, and G. H. Beasley, Tetrahedron, 27, 5299 (1971).
8. This assumes that the $\Delta\Delta H^{\neq}$ between boat and chair forms remains constant for the 1,5-hexadiene and 4-phenyl-1-butene series, and that the $\Delta\Delta H^{\neq}$ found here for the boat series also applies to the chair set.

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