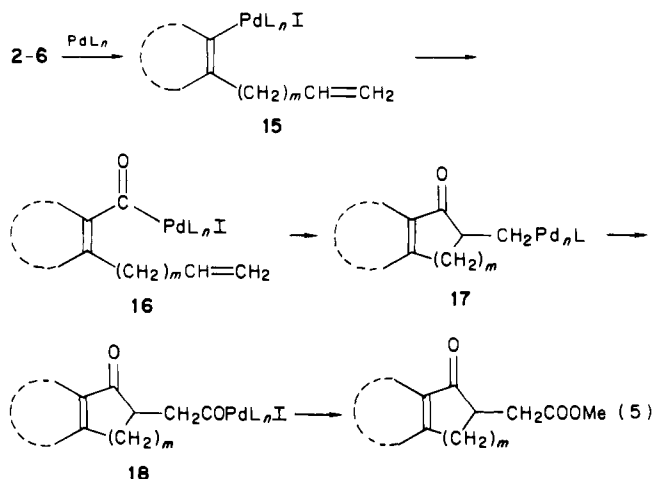
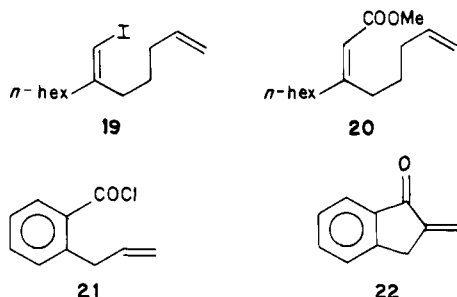


than methanolysis. The intermediate **17** must then undergo the second CO insertion to give **18** faster than dehydropalladation. Unlike **16**, the intermediate **18** evidently prefers methanolysis to intramolecular or intermolecular acylpalladation (eq 5). After



the initial oxidative addition step, each of the presumed intermediates has at least one alternate and plausible path to follow, as discussed above. And yet none of these alternate steps appears to be competitive in the reaction. Especially noteworthy is that neither carbopalladation involving aryl- and alkenylpalladium species nor dehydropalladation, two key microsteps in the Heck-type reaction, occurs in the presence of CO.

To probe the intermediacy of **16**, we prepared **19**⁸ and subjected it to the standard carbonylation conditions described above. After



24 h, the major product formed in ca. 50% yield was **20**.⁹ The results not only indicate that, in this case, methanolysis of the presumed acylpalladium intermediate is faster than its intramolecular acylpalladation reaction to produce a seven-membered ring but also support the assumption that **16** must be intermediate in the cyclization reaction.

Finally, that the intramolecular acylpalladation process is indeed feasible has been indicated by the reaction of **21** with Pd(PPh₃)₄ (1 equiv) and NEt₃ (1.5 equiv) in CH₃CN-benzene (1/1) at 55 °C for 1 h to give **22**⁹ in 50% isolated yield. Unfortunately, **21** is incompatible with MeOH so that the development of a catalytic process via methanolysis is not feasible in this case.

Further transformations of the cyclic ketone products as well as the development of asymmetric cyclization procedures are under investigation.

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Supplementary Material Available: Experimental section including experimental procedures and spectral data for products (7 pages). Ordering information is given on any current masthead page.

Nature of the Migrating Group in 1,5-Sigmatropic Hydrogen Shifts

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Sigmatropic rearrangements, in particular suprafacial 1,5-hydrogen shifts, have recently found use in synthetic methodology.² Systematized and analyzed by Woodward and Hoffmann³ these symmetry-allowed processes have been shown by numerous experimental⁴ and theoretical studies^{5,6} to occur in a concerted manner. Less well established is the nature of the migrating group or the factors which influence its character. The formal molecular orbital analysis treats the transition state for the 1,5-shift in 1,3-pentadiene in terms of interaction of a hydrogen atom and a pentadienyl free radical. On the other hand, it has been suggested that the transition state for [1,5]-sigmatropic migration in cyclopentadiene is such that the migrating hydrogen is "protonic" while the underlying carbon skeleton resembles an "aromatic" cyclopentadienyl anion.⁷

Electron density surfaces corresponding to $\psi^2 = 0.002$ electron/bohr³⁸ have been obtained from 3-21G wavefunctions^{9,10} for the transition structures for [1,5] migration in 1,3-pentadiene, cyclopentadiene, and 3-cyano-1,3-pentadiene.¹¹ Radii for the migrating hydrogens, obtained from least-squares fitting the electron density surface to nuclear-centered spheres,⁸ are provided in Table I. An example showing the relationship between the

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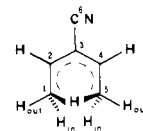
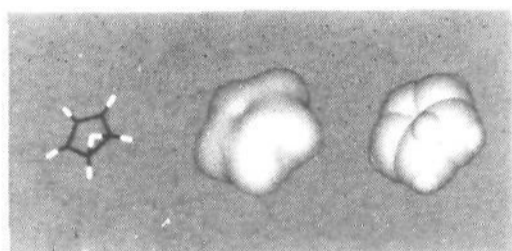


Table I. Best Sphere Fit Radii for Migrating Hydrogen in Suprafacial [1,5]-Sigmatropic Rearrangements^a

reaction	radius of migrating hydrogen, Å	Mulliken charge on migrating hydrogen, electrons
	1.385	0.22
	1.374	0.23
	1.283	0.31

^a 3-21G//3-21G. See ref 8 for discussion of numerical methods.^b Data for 1,3-pentadiene and cyclopentadiene from ref 6b.**Figure 1.** Skeletal representation (left), total electron density surface (middle), and sphere fit to electron density surface (right) for transition state for [1,5]-sigmatropic migration in cyclopentadiene (3-21G//3-21G).

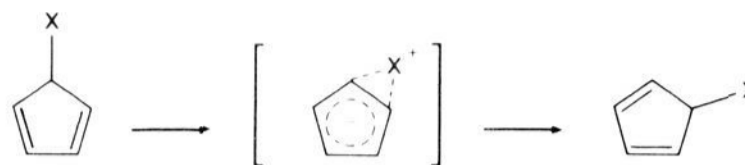
electron density surface and the sphere fit representation for the transition state for [1,5] migration in cyclopentadiene is shown in Figure 1.

The data indicate that as the underlying skeleton becomes better able to support negative charge, the size of the migrating group decreases, i.e., the hydrogen becomes increasingly more protonic. The migrating hydrogen in cyclopentadiene is somewhat smaller than a neutral hydrogen atom (1.332 Å), suggestive of a partial positive charge. Nevertheless, it is still larger than a methylene hydrogen (the methylene hydrogen radius in cyclopentadiene is 1.185 Å), suggesting that the migrating hydrogen in the transition structure is more negatively charged than that in cyclopentadiene itself. The radius of the migrating hydrogen in 1,3-pentadiene, while somewhat larger than that for hydrogen atom, is much smaller than that found in the free hydride anion (1.574 Å). This suggests that it is slightly negatively charged. The hydrogen in the transition state for sigmatropic rearrangement in 3-cyano-1,3-pentadiene is slightly smaller than the corresponding atom in 1,3-pentadiene but is still larger than free hydrogen atom. In both of the acyclic systems, the migrating hydrogens are characterized by radii similar to those in typical "hydridic" molecules, e.g., 1.351 Å in borane and 1.363 Å in silane. Given the relative insensitivity of atomic sizes of hydrogen bonded to carbon,⁸ the span of 0.1 Å noted for the systems here is significant and indicative of a marked change in the charge on the migrating species.

Mulliken charges¹² for the migrating hydrogens in 1,3-pentadiene, 3-cyano-1,3-pentadiene, and cyclopentadiene are also provided in Table I. While the migrating atoms in all three systems are indicated to be positive (consistent with the known tendency of Mulliken analysis to allocate insufficient electron population to hydrogen^{12b}) the ordering of hydrogen charges, 1,3-pentadiene \approx 3-cyano-1,3-pentadiene < cyclopentadiene (the latter the most positive), is consistent with the assignments based on atomic sizes.

The migratory aptitude of a group should be related to its inherent ability to stabilize charge. For example, groups that are able to accommodate positive charge, e.g., trimethylsilyl (Me₃Si),

should migrate more readily in cyclopentadiene than in 1,3-pentadiene, while those able to bear negative charge, e.g., methyl, should show the opposite behavior. The available experimental data are in accord. The known migratory abilities for substituents on cyclopentadiene (Me₃Si \gg H > Me^{13,14}) are consistent with a limiting representation of the transition state as incorporating an aromatic cyclopentadienyl anion; i.e.,



In contrast, hydrogen migration in cycloheptatriene is more rapid than migration of a trimethylsilyl group.¹⁵ As illustrated below,



the transition state here may be viewed in terms of migration of an "anion" across a positively charged skeleton (in the limit, the aromatic tropylium cation).

In summary, we have found that [1,5]-sigmatropic hydrogen rearrangements, while concerted, exhibit subtle differences in their transition structures, depending on the substrate. [1,5]shifts on cyclopentadiene are characterized by a relatively "cationic" migrating group, while rearrangements on 1,3-pentadiene reflect the (relatively) anionic composition of the group that migrates. Rational substitution onto the substrate skeleton should permit fine control both of migratory aptitude and stereochemistry.¹⁶

Registry No. 1,3-Pentadiene, 504-60-9; 3-cyano-1,3-pentadiene, 98875-36-6; cyclopentadiene, 542-92-7; cycloheptatriene, 544-25-2.

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X-ray Crystal Structure and Hydrocarbon Solution Dynamics of Tetrameric 1-(Dimethylamino)-3-lithiopropane

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So far precise determination of the structures of Lewis base adducts^{1,2} of alkyllithium tetramers has been impossible. Solutions of alkyllithiums containing Lewis base do not normally yield crystals³ and loosely bound Lewis base is given off again upon

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