(m), 1503 (s), 750 (s), 695 (s). Anal. Calcd for $C_{15}H_{17}NO$: C, 79.2; H, 7.5; N, 6.24. Found: C, 77.4; H, 7.5; N, 6.0.

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The Degenerate Side Chain Approach to the Carbon Analogue of the Claisen Rearrangement. Formation of Nine-Membered Rings by a Sterically Accelerated Ene Reaction

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Abstract: The first step of the carbon Claisen rearrangement can be examined without reference to the second step through introduction of a suitably labeled ortho allyl substituent, which would be identifiably inserted into the butenyl side chain on reversal of the first step. We have prepared substrates containing the potentially degenerate side chain, labeled alternatively with deuterium and with methyl. Interchange of the side chains does not occur up to about 350 °C, so that the activation energy of the [3,3] sigmatropic step of the carbon Claisen rearrangement must be at least 32–35 kcal mol^{-1}. These results suggest that the first step, rather than the second step as previously thought, is rate determining. The effect of oxygen vs. carbon and of aliphatic vs. aromatic can then be readily understood in terms of perturbations on the frontier molecular orbitals of the starting materials. The substrates constructed with degenerate side chains produce, as the alternative reaction at 350 °C, a high-yield ene cyclization to form nine-membered rings. This unprecedented result for simple 1,8-nonadienes is attributed to a steric acceleration arising from loss of rotational degrees of freedom on placement of the ene components in ortho-related side chains on a benzene ring.

The [3,3] sigmatropic shift is found in two classic organic rearrangements, the Claisen (eq 1) and the Cope (eq 2). Both reactions involve the migration of a σ bond between the termini of two allyl groups. In the commonest form of the Claisen rearrangement, one of the allyl double bonds is part of an aromatic ring and one allyl atom is oxygen (eq 1). The reaction

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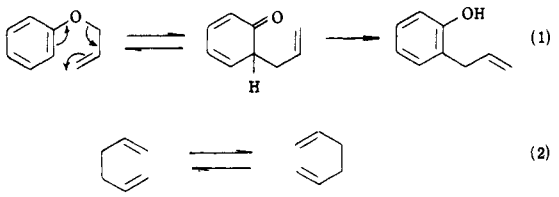
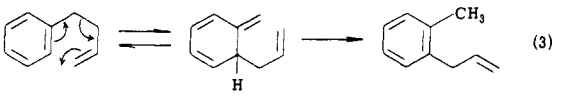


(1)

(2)

is not restricted to ethers, but also includes analogous thioethers, amines, and phosphines.[2] The Cope rearrangement (eq 2) is usually, but not always, within an all-carbon system, and both double bonds are always aliphatic. To date, the reaction that would represent the common ground between these rearrangements has not been observed without catalysis or relief of small-ring strain. This reaction would be the all-carbon version of the Claisen rearrangement, or, depending on one's perspective, the aromatic version of the Cope rearrangement (eq 3).

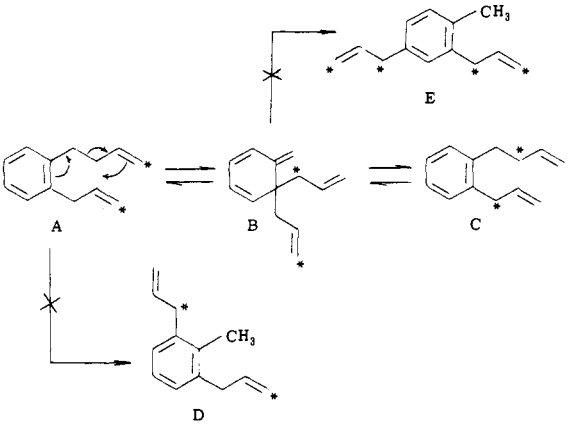


(3)

4-Phenyl-1-butene is the direct all-carbon analogue of allyl phenyl ether. Its Claisen rearrangement would involve a [3,3] sigmatropic shift to give the indicated tetraene (eq 3), followed by rearomatization via a [1,3] hydrogen shift to produce *o*-allyltoluene. Hurd et al. failed to find this rearrangement on pyrolysis of 4-phenyl-1-butene in a flow system at 400–550 °C.[3] Products included propene, benzene, toluene, naphthalene, stilbene, and isomerized phenylbutenes. Cope endeavored to encourage the reaction by placing on the allylic side chain the same electron-withdrawing groups that had been observed to promote the aliphatic (read "Cope") version of the rearrangement (eq 4, found only in the microfilm version).[4,5] Analogous substitution in the aromatic (read "Claisen") version yielded only partial decomposition (eq 5, found only in the microfilm version). A decade later, Doering and Bragoli suggested that there may be a rapid equilibrium between 4-phenyl-1-butene and the intermediate tetraene, so that the second step is rate determining.[6] They hypothesized that the tetraene cannot rearomatize to the product because of the low acidity of the doubly allylic proton, in comparison to that in the oxygen case, which is activated by a carbonyl group. These authors reported isomerization of 4-phenyl-1-butene on treatment with strong base at 350 °C to a mixture of phenylbutenes and *o*-tolylpropenes that included some *o*-allyltoluene.[6] The most recent attempts to promote the all-carbon Claisen rearrangement have placed the migrating σ bond in a cyclopropane ring. Success has been realized in two systems (eq 6 and 7, found only in the microfilm version).[7,8] The migrating bond, however, has high π character, and there is some question as to whether the reaction should be termed a sigmatropic shift (and hence related to the Claisen rearrangement) or an electrocyclic reaction (related to the ring closure of 1,3,5-hexatriene).

The effect of strong base to push the carbon Claisen rearrangement toward product[6,8] suggests that the first step, the [3,3] sigmatropic shift, occurs more readily than the second step, the [1,3] sigmatropic shift, in accord with the principles of orbital symmetry. The existence of an equilibrium in the first step can be demonstrated without the use of base catalysis by a method used by Curtin and Johnson to study the oxygen Claisen rearrangement.[9] They prepared and rearranged an allyl phenyl ether possessing allylic side chains at the ortho position with suitable labels, so that the dienone intermediate of eq 1 possesses identical geminal side chains (save for the label). Reversal of the equilibrium regenerates starting material, but with scrambling of the label.

Scheme I

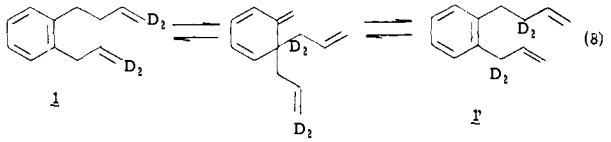


This approach, as applied to the carbon Claisen rearrangement, is illustrated in Scheme I (A ⇌ B ⇌ C). The phenylbutene (A) is constructed with an ortho allyl side chain. Migration of the other allyl group to the substituted position produces the tetraene intermediate B with degenerate side chains at the position ortho to the *exo*-methylene group. Either chain can return to the *exo*-methylene group, thereby regenerating starting material A or giving the substance C, which differs from A only in the placement of the label indicated in the scheme by an asterisk. If the label is isotopic, molecules A and C are constitutionally identical, and the action of the first step of the carbon Claisen rearrangement is to scramble the isotope. If the label is a substituent, the molecules are different and realization of the first step alone produces a rearranged product on side-chain reversal. Products D and E derive respectively from rearrangement to the unsubstituted ortho position and to the para position. These products, which require that both steps of the Claisen rearrangement occur, seem unlikely in light of the resistance of 4-phenyl-1-butene to undergo both steps. The interchange of side chains illustrated in Scheme I (A ⇌ C) requires migration of the allyl group to the more substituted ortho position. Kinetic results on oxygen Claisen systems indicate that rearrangement indeed occurs more rapidly to a substituted than to an unsubstituted position.[10]

We have employed both isotopic and substituent labeling to examine the approach of Scheme I. We report herein that, contrary to recent suggestions, the first step in the carbon Claisen rearrangement is exceedingly slow and may in fact be rate determining. The results are interpreted in terms of frontier molecular orbital theory.

Results and Discussion

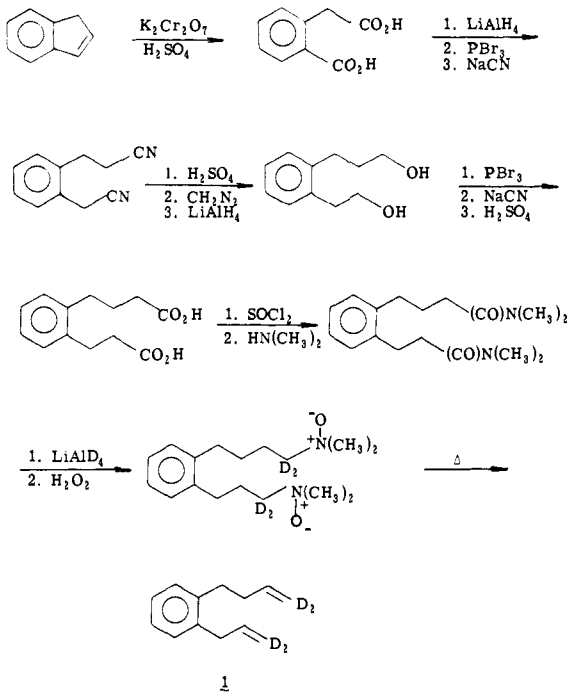
Isotopic Label. The two side chains in the tetraene intermediate B of Scheme I can be kept structurally identical by using a deuterium label, as illustrated in eq. 8. The first step



(8)

of the carbon Claisen rearrangement (**1** ⇌ **1′**) would be accompanied by loss of allylic resonances and appearance of alkenic resonances in the ^{1}H NMR spectrum. We have prepared 4-*o*-allylphenyl-1-butene (**1**), labeled with deuterium in the terminal alkene positions, in 15 steps by the procedure outlined in Scheme II. The two side chains are functionally identical and differ only in the number of methylene groups. Therefore, the two chains can be built up simultaneously and in parallel. Indene provides the ideal starting material, since it can be cleaved to give the dicarboxylic acid (homophthalic acid) in which the side chains differ by one methylene group.

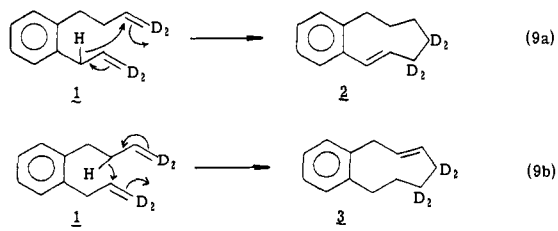
Scheme II



The side chains can be elaborated by the standard reactions listed in Scheme II. The yield was found to be higher when the two carbons in each side chain were introduced stepwise, rather than together, e.g., via oxirane addition to a Grignard reagent. The only sensitive aspect of the synthesis was the introduction of deuterium on the double bond without isotopic scrambling or double-bond isomerization. We settled on the Cope elimination, following the approach of Humski et al.,[11] since this reaction proceeds at low temperatures under neutral conditions. The structure and deuterium incorporation of the product were proved by IR, NMR, mass spectrometric, and elemental analysis methods.

Pyrolyses were carried out in the gas phase on 50–60-μL samples in a sealed pyrolysis tube of approximately 250-mL volume, at room temperature pressures of 0.1 mm. Runs were carried out at 50 °C intervals from 150 to 400 °C. No observable change occurred up to 300 °C. At 350 °C, two new major peaks appeared in the VPC trace, and above 400 °C, complete destruction of the molecule to lower boiling materials (toluene, xylene) occurred. In the range 320–380 °C, starting material and the two new components (also a minor component that we did not investigate) were present in about equal proportions and could be collected by VPC. The recovered starting material showed no scrambling of deuterium right up to the temperature of complete destruction (400 °C).

The major products of the pyrolysis of **1** were found to be the result of the two type III[12] ene reactions that give nine-membered rings, as depicted in eq 9 (**2, 3,** drawn as trans but



(9a)

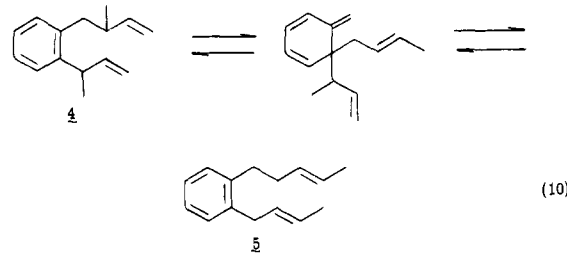
(9b)

double-bond geometry not known). We obtained spectroscopic and chemical proof of the structures from undeuterated material. Both products had a mass spectral molecular weight of 172, isomeric to starting material, and absorbed 1 mol of hydrogen to produce the known benzocyclononene.[13a] The NMR spectra of both **2** and **3** contained an alkenic resonance of integral 2. Thus four alkenic protons had been lost, with respect to starting material. This observation eliminated simple double-bond migration. The spectrum also showed no methyl resonances, so that the alternative ene products, the methylbenzocyclooctenes, can be eliminated. It only remained to place the double bond in the nine-membered ring. Of the three possible isomers, the α,β-unsaturated form is known[13b] and has similar spectral properties (including the lack of UV absorption attributed to a perpendicular orientation between the styryl double bond and the aromatic ring) to our product **2.** The γ,δ-unsaturated isomer is also known but was different from **3,** so that we concluded that **3** was the β,γ-unsaturated isomer. The proton spectra of the deuterated modifications of **2** and **3** showed loss of the appropriate resonances. The deuterium labeling also demonstrated that the carbon Claisen rearrangement had not occurred prior to the ene reaction, as the resulting products would each have had one deuterium located on the double bond of **2** and **3.** The deuterated forms showed two full alkene protons but loss of aliphatic protons.

We also used the Conroy approach to test for the Claisen intermediate in the case of the parent 4-phenyl-1-butene, by heating the molecule with maleic anhydride in various high-boiling solvents.[14] No adduct, however, was observed.

The importance of these observations to understanding the ene reaction will be addressed in a later section. Intervention of the ene reaction was surprising, because the parent 1,8-nonadiene gives a poor yield of cyclononene even at 400 °C. We therefore sought a method to avoid the ene pathway via methyl substitution on the side chains.

Methyl Substituent Label. A methyl substituent on the allylic fragment is known both to speed up the Claisen rearrangement[10] and to slow down the ene reaction.[15] The ene reaction is fastest for migration of a primary hydrogen, intermediate for a secondary hydrogen, as in **1,** and slowest for a tertiary hydrogen. Hyperconjugative electron delocalization in the transition state probably accounts for the lowering of the Claisen activation energy. Of course, placement of two methyl groups at each of the allylic positions of **1** would destroy any possibility of an ene reaction, but the resulting pair of quaternary centers may impose considerable steric hindrance to allylic migration in the Claisen rearrangement. Consequently, we decided to examine the molecule **4** with one methyl group at each of the allylic positions (eq 10).

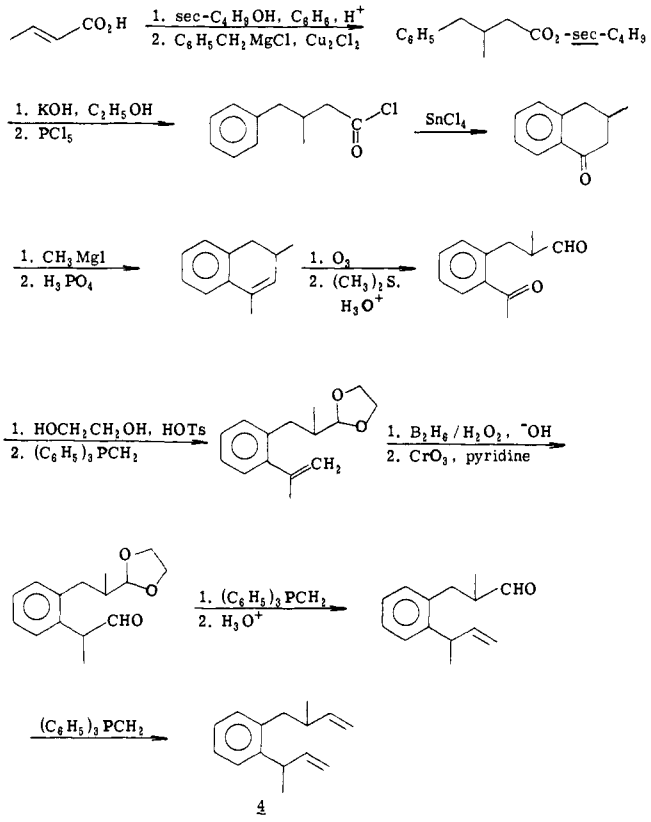


(10)

The methyl groups not only serve to facilitate the Claisen rearrangement at the expense of the ene reaction, but they also function as the label to demonstrate that the first Claisen step, the [3,3] sigmatropic shift, has occurred, without reference to the second Claisen step. Since the side chains in the tetraene intermediate of eq 10 differ in the location of the methyl groups, reversal of the reaction can produce either the starting material **4** or the new product **5.** Observation of the latter material would demonstrate the occurrence of the first Claisen step. The methyl group serves yet the fourth function of stabilizing the product **5** with a disubstituted double bond, over the starting material **4** with a monosubstituted double bond. Thus failure to observe the rearrangement could not be attributed to a thermodynamic bias for starting material.

One of our first approaches to the synthesis of **4** followed the

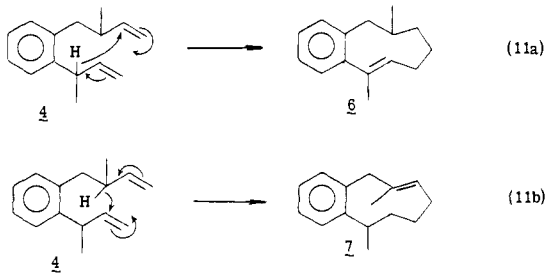
Scheme III



procedure of Scheme II, with 2,3-dimethylindene as the starting material. Many variations of the approach, however, failed, for reasons detailed elsewhere.[16] A principal problem in constructing both side chains at the same time was reaction between functionalities on the separate chains. In addition, the approach required several double nucleophilic substitutions at secondary centers (see Scheme II). Consequently, we decided to build up the side chains substantially independently and to alter the nature of the chain-lengthening steps. The successful 16-step synthesis is outlined in Scheme III.

Preparation of 1,3-dimethyl-3,4-dihydronaphthalene required modification of the literature procedures.[17] Ozonolysis in methanol followed by treatment with dimethyl sulfide unexpectedly gave the dimethyl acetal of the desired keto aldehyde, so that treatment with dilute acid was required to isolate the product. The short side chain was completed by protection of the aldehyde, Wittig reaction, hydroboration, oxidation, and a second Wittig reaction. Deprotection of the remaining aldehyde group and a third Wittig reaction produced the desired molecule **4,** contaminated by some undeprotected acetal, which could be recycled through the procedure. The diastereomeric identity of **4** (threo, erythro, or a mixture) is not known.

Pyrolyses were carried out in the same fashion as with the deuterated material **1.** A reaction began to occur at 270 °C, and by 320 °C the starting material **4** had been almost completely consumed to give two new products in an 80/20 ratio. By GC/MS, both products were found to be isomers of starting material (mol wt 200). The major product was easily isolated by preparative gas chromatography. The NMR spectrum immediately revealed that this material was not the result of the Claisen rearrangement (**5**), as there was only one alkenic proton, rather than four. Furthermore, although there were two different methyl groups, one was cleanly split into a doublet, indicative of a methyl attached to a CH fragment. An infrared band at 740 cm^{-1} was characteristic of a trisubstituted alkene. All the spectral properties were consistent with structure **6** (shown as the *E* isomer but geometry not known), the



product of the ene reaction of eq 11a. Spectral analysis definitively excluded the alternative eight-membered rings. The substantial decrease in the number of alkenic protons eliminates most other paths, such as simple double-bond isomerization. Ozonolysis of **6** gave a keto aldehyde, in agreement with the structure assignment. Compound **6** was found to be very resistant to catalytic hydrogenation, as expected for a trisubstituted and styryl double bond.

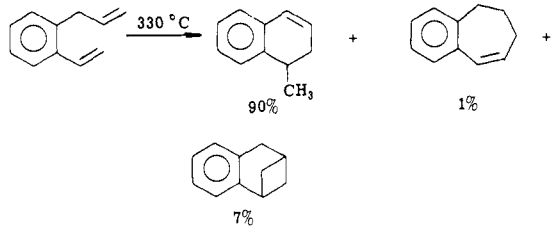
The minor product of pyrolysis could not be isolated in pure form, but only as the major component in a 60/40 mixture. Rather than carry out an additional preparative VPC pass on an already minuscule quantity, we obtained the 80-MHz ^1H NMR spectrum by difference on the CFT-20. The spectrum of **6** was subtracted from that of the minor product until its peaks were nulled. The resulting rather clean spectrum again immediately eliminated the Claisen product **5** and indeed was most consistent with the alternative nine-membered ring product of the ene reaction in eq 11b (**7,** shown as the *E* isomer but geometry not known). The characteristic portions of the spectrum included the unit alkene resonance, two methyl resonances (one a singlet, the other a doublet), and an allylic/benzylic AB quartet. In contrast to **6,** the hydrogenation of **7** proceeded smoothly to a product of mol wt 202. The higher reactivity is attributed to the separation of the double bond from the aromatic ring.

It appears that the reactivity of the dimethyl compound **4** is quite parallel to that of the unsubstituted compound **1.** Under pyrolysis conditions, both undergo a type III intramolecular ene reaction[12] to form the two possible nine-membered rings. If anything, the methyl-substituted substrate reacts unexpectedly at a slightly lower temperature. Before addressing ourselves to the implications of these results on the mechanism of the carbon Claisen rearrangement, we will briefly examine the ene reaction.

The Ene Pathway. As mentioned earlier, abstraction of a tertiary hydrogen in the ene reaction normally is slower than abstraction of a secondary hydrogen, and a primary (methyl) hydrogen migrates the most rapidly.[15] These results may be due to the steric accessibility of the proton in the less substituted systems. Thus intramolecular ene cyclization occurs most rapidly for dienes possessing a terminal methyl group.[15] Dienes, such as ours, lacking terminal methyls normally undergo the ene reaction rather reluctantly. Thus 1,6-heptadiene is unreactive to 500 °C, even though the ene product would be a six- or a seven-membered ring.[18] 1,7-Octadiene cyclizes to cyclooctene but appears to revert to starting material via a retro-ene above 320 °C.[19] 1,8-Nonadiene, which is analogous to our systems **1** and **4,** produces only a poor yield of cyclononene,[20] which does not revert to diene up to 470 °C.[21] The longer chain lengths impose an entropic bias against cyclization.

With this background, the high-yield cyclization of **1** and the even faster cyclization of the dimethylated **4** seem remarkable. The facilitation of the ene pathway appears to result from the peculiar arrangement of the two portions of the 1,8-nonadiene chain as ortho-related side chains on the benzene ring. Reduction in rotational degrees of freedom permits the components of the ene reaction more easily to assume the proper geometry for reaction. We have found that a similar

disposition of a 1,6-heptadiene also facilitates the ene reaction, although there may be a change in mechanism (eq 12).[22] In



(12)

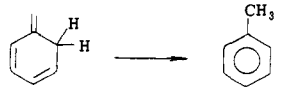
4-*o*-allylphenyl-1-butene (**1**), incorporation of the relatively unreactive 1,8-nonadiene moiety into ortho-disposed side chains reduces the ene temperature at least 100 °C and raises the yield. A similar geometric factor may be operative in *trans,trans*-1,6-cyclodecadiene (a 1,6-heptadiene), which undergoes an ene reaction as low as 250 °C.[19]

Similarly, the anomalous effect of the methyl groups in **4** in lowering the reaction temperature a further 50 °C may be the result of steric factors. There may be relief of strain associated with the methyl groups themselves. Alternatively, the methyl groups may force the migrating hydrogens into a more favorable position for the ene reaction to occur. We cannot carry the conformational analysis any further, since we do not know the diastereomeric identity of our **4** nor do we know the double-bond geometry in **6** and **7**. There is, however, a geometry for both the erythro and the threo isomers of **4** that can direct both methyl groups away from the interior of the incipient nine-membered ring, thereby reducing steric interactions and placing the hydrogen in a favorable position for migration.

The ene reaction mechanism can range from a rate-limiting abstraction of the allylic hydrogen, through a broad spectrum of concerted reactions, to rate-limiting diradical formation. Our data do not specify the mechanism. The absence of cyclobutane products argues against a diradical mechanism, and the product distribution from **4** may suggest that allylic hydrogen abstraction is kinetically important.

In summary, the intramolecular ene reaction of doubly terminal 1,8-dienes can be accelerated by placement of each vinyl group in ortho-related side chains of a benzene ring. Acceleration is observed whether the migrating allylic hydrogen is secondary or tertiary. The reaction proceeds smoothly to give a high yield of benzocyclononadienes.

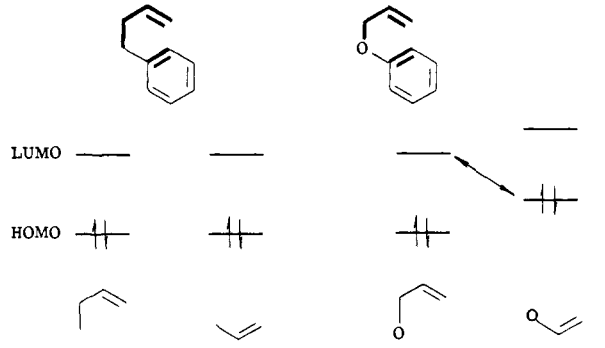
The Carbon Claisen Pathway. We have constructed a system whereby the first step of the carbon Claisen rearrangement (eq 3) could be observed without the necessity of the second. The ease of the first step and the reluctance of the second step had been suggested by earlier observations, including the effect of base and the constraints of orbital symmetry. The recent results of Marvell,[8] however, suggest that the role of base is not critical, since their reactions occurred equally well in acid, base, or neutral conditions. The role of the base had been assumed to be removal of the α proton in order to permit rearomatization,[6] since this proton is next to a carbonyl group and hence is relatively acidic in the oxygen Claisen but much less acidic in the carbon Claisen. Although these [1,3] hydrogen shifts are forbidden by orbital symmetry, there is ample literature precedent for their occurrence. Thus the ortho triene tautomer of toluene rapidly aromatizes at room temperature (eq 13). The



(13)

analogy between the isomerization of eq 13 and that in the second step of the carbon Claisen of eq 3 is rather close. These "forbidden" [1,3] sigmatropic shifts occur either stepwise or by an antarafacial stereochemistry.[23] The effect of base may

Scheme IV



be the result of entirely different considerations, which we are currently testing.

Our observations suggest that the slow step of the carbon Claisen rearrangement probably is the [3,3] sigmatropic reaction rather than the [1,3] hydrogen shift. Our experiments set a lower limit to the activation energy ($\Delta H^{\ddagger}$) of about 32–35 kcal mol^{-1} (when $\Delta S^{\ddagger}$ is about -30 eu), with a reaction temperature above 350 °C. Since the ene reaction intervenes at or below this temperature, the carbon Claisen rearrangement cannot be observed. In the parent system of eq 1, 4-phenyl-1-butene, other reaction pathways intervene at lower temperatures and prevent observation of the carbon Claisen.[24] Unless the ene reaction and all these other pathways with lower activation energies[24] can be frustrated, the carbon Claisen rearrangement cannot be manifested. Alternatively, the Claisen pathway can be accelerated electronically or sterically, as was used in the strained systems of eq 6 and 7.

If the carbon Claisen is not slow because of the lack of acidity of the allylic proton in the second step, then what are the reasons for the reluctance of the first step? Certainly the fact that the oxygen Claisen is thermodynamically more favored than the carbon Claisen contributes to the slow rate. Comparisons also can be made with the oxygen Claisen and with the Cope rearrangement in terms of frontier molecular orbital theory. The Cope and the carbon Claisen rearrangements involve the same atoms but with the obvious difference that both double bonds in the former case are aliphatic but one in the latter is aromatic. Just as benzene is a poor diene in the Diels–Alder reaction compared to butadiene, because the double bonds are tied up in the aromatic ring, 4-phenyl-1-butene is a poor substrate for six-electron rearrangement, because of loss of aromaticity. The accelerative effect of oxygen on the Claisen rearrangement can then be viewed as the result of perturbations on the frontier molecular orbitals in the first step. An arbitrary division of orbitals, following that of Fleming,[25] is given in Scheme IV. The effect of the oxygen atom as an electron donor is to raise both the HOMO and the LUMO of the two-electron portion (the ionization potential of anisole is less than that of toluene, and that of ethyl vinyl ether is less than that of 1-pentene), thereby intensifying the interaction between the four-electron LUMO and the two-electron HOMO. Electron-withdrawing substituents on the four-electron portion, e.g., cyano in eq 4 and 5, would lower the four-electron HOMO and LUMO, further intensifying the critical HOMO–LUMO interaction. Alternative choices of division into components would lead to identical conclusions.[25] Thus the ease of the oxygen Claisen rearrangement is very likely caused by the effect of oxygen on orbital interactions in the first step rather than on acidity considerations in the second.

Experimental Section

Melting points (uncorrected) were obtained on a Hirschberg apparatus. ^{1}H NMR spectra were obtained at 60 MHz with Varian T-60 and Perkin-Elmer R-20B spectrometers. Signal-averaged and dif-

ference ^1H NMR spectra were obtained at 80 MHz with a Varian CFT-20 spectrometer. All chemical shifts are reported in parts per million downfield from tetramethylsilane (Me_4Si). Infrared spectra were recorded on Beckman IR-5 and IR-10 and Perkin-Elmer 283 spectrometers. Conventional mass spectra were obtained on a CEC Model 21-104. GC/MS were obtained on a Hewlett-Packard 5700A gas chromatograph coupled to a Hewlett-Packard 5930A mass spectrometer. Data were accumulated and presented through use of the HP/Nova data computer program. Routine gas chromatography was performed on Hewlett-Packard F & M Model 900 and Varian Aerograph Series 1520 gas chromatographs with thermal conductivity detectors. Elemental analyses were obtained from Micro-Tech Laboratories, Skokie, Ill. A Welsbach T-23 laboratory ozonator was used to generate 1.5–2% O_3 in O_2 from oxygen at 1.125 psi and 110 V. Hydrogenations were performed on a standard low-pressure apparatus. Pyrolyses were done in a tube furnace of homemade design. All organometallic reactions described were performed under an atmosphere of N_2 passed through drying tubes. Tetrahydrofuran (THF) was dried by refluxing and distilling from $LiAlH_4$ under a N_2 atmosphere.

Homophthalic acid was prepared by oxidation of indene by $K_2Cr_2O_7$ in aqueous sulfuric acid in 84% yield.[18,26]

Homophthalyl alcohol was obtained by reduction of homophthalic acid by $LiAlH_4$ in 77% yield.[26,27]

α-Bromo-*o*-(2-bromoethyl)toluene was prepared by treatment of homophthalyl alcohol with PBr_3 in 87% yield.[26,28]

3-[*o*-(Cyanomethyl)phenyl]propionitrile. The dibromide (5.0 g, 0.018 mol) in 10 mL of 95% ethanol was converted to the dinitrile by treatment with 2.4 g (0.049 mol) of NaCN in 4 mL of H_2O.[26] The yield of dinitrile was 2.00 g (66%): bp 180–200 °C (1 mm); IR (film) 3075 (w), 2960 (m), 2255 (s), 1498 (m), 1426 (s), 742 (s) cm^{-1}; NMR (neat) δ 2.50 (m, 4, CH_2), 3.50 (s, 2, benzylic CH_2CN), 7.00 (s, 4, phenyl).

3-[*o*-(Carboxymethyl)phenyl]propionic Acid. The dinitrile (2.00 g, 0.012 mol) was hydrolyzed to the diacid with 32 g of 50% sulfuric acid (by weight).[26] The yield of diacid was 2.30 g (95%): mp 138–140 °C; IR (KBr) 3030 (s), 2917 (s), 1705 (s), 1498 (w), 1418 (s), 748 (m) cm^{-1}; NMR (CD_3COCD_3) δ 2.80 (m, 4, CH_2), 3.65 (s, 2, CH_2CO_2H), 7.10 (s, 4, phenyl), 10.3 (br s, 2, CO_2H). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.46; H, 5.77. Found: C, 63.37; H, 6.11.

Methyl *o*-(2-carbomethoxyethyl)phenylacetate was prepared by treatment of the diacid with diazomethane generated from *N*-nitroso-*N*-methylurea.[26] The yield of diester was 9.15 g (82.5%): bp 130–140 °C (0.35 mm); IR (film) 3008 (w), 2957 (m), 1725 (s), 1500 (m), 1441 (s), 762 (s) cm^{-1}; NMR ($CDCl_3$) δ 2.85 (m, 4, CH_2), 3.45 (s, 6, OCH_3), 3.55 (s, 2, benzylic $CH_2CO_2CH_3$), 7.00 (s, 4, phenyl). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.10; H, 6.78. Found: C, 66.32; H, 6.86.

3-[*o*-(2-Hydroxyethyl)phenyl]-1-propanol was obtained by reduction of the diester with $LiAlH_4$.[26] The yield of diol was 5.25 g (73%): bp 180–200 °C (1.8 mm); IR (film) 3367 (s), 2942 (m), 2867 (m), 1498 (m), 1454 (m), 1053 (s), 754 (s) cm^{-1}; NMR ($CDCl_3$) δ 1.85 (m, 2, CH_2), 2.80 (br m, 4, benzylic CH_2), 3.70 (br m, 4, OCH_2), 4.35 (br s, 2, OH), 7.15 (s, 4, phenyl). The product was very hygroscopic, so no elemental analysis was obtained.

1-(3-Bromopropyl)-2-(2-bromoethyl)benzene was prepared by treatment of the diol with PBr_3.[26] The yield of dibromide was 6.54 g (74%): bp 147–170 °C (1 mm); IR (film) 2987 (m), 1498 (w), 1458 (m), 1439 (m), 1265 (m), 762 (s) cm^{-1}; NMR ($CDCl_3$) δ 2.15 (m, 4, CH_2), 2.65 (m, 2, benzylic CH_2), 3.35 (br m, 4, CH_2Br), 7.15 (s, 4, phenyl).

4-[*o*-(2-Cyanoethyl)phenyl]butyronitrile. The same procedure was used as for the smaller dinitrile.[26] This time, however, the dinitrile was not isolated but was hydrolyzed directly to the diacid. The product dinitrile was identified by its infrared spectrum: IR (film) 3030 (w), 2940 (m), 2250 (m), 1498 (m), 1457 (m), 760 (s), 687 (s) cm^{-1}.

4-[*o*-(2-Carboxyethyl)phenyl]butyric Acid. The hydrolysis procedure paralleled that for the earlier diacid.[26] Recrystallization of the crude product from H_2O gave 4.61 g (92%) of diacid: mp 148–150 °C; IR (KBr) 2980 (s), 1708 (s), 1464 (m), 1435 (s), 1408 (s), 737 (m), 692 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.90 (m, 2, CH_2), 2.60 (br m, 8, benzylic and α CH_2), 7.15 (s, 4, phenyl), 10.3 (br s, 2, CO_2H). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.10; H, 6.78. Found: C, 66.77; H, 6.88.

4-[*o*-(2-Chlorocarbonylethyl)phenyl]butyryl Chloride. Thionyl chloride (15 g, 0.125 mol) was added to 14 g (0.059 mol) of the diacid, and the mixture was stirred with cooling for 10 min. The mixture was allowed to warm to room temperature, then was heated to 80 °C and stirred until evolution of HCl and SO_2 ceased (2.5 h). The diacid chloride was not isolated but was converted directly to the diamide. The product was identified by its infrared spectrum: IR (film) 2942 (w), 1783 (s), 1498 (w), 1453 (w), 1236 (s), 757 (m) cm^{-1}.

4-[*o*-(2-(Dimethylcarbamyl)ethyl)phenyl]-*N,N*-dimethylbutyramide. An aqueous solution (35 g) containing 40% of dimethylamine (0.30 mol) was placed in a round-bottomed flask equipped with a stirrer and a dropping funnel. With cooling in an ice-salt bath, the diacid chloride was added dropwise. After 30 min, the cooling bath was removed, and the mixture was stirred for an additional 24 h. The H_2O was removed under vacuum, and the remaining dark solid was dissolved in ether and THF. The solution was dried ($MgSO_4$), and after evaporation of the solvent the diamide was reduced without further purification. The diamide was identified by its infrared spectrum: IR (film) 2975 (s), 2887 (m), 1647 (s), 1497 (m), 1450 (m), 760 (m) cm^{-1}.

4-[*o*-(3-*N,N*-Dimethylaminopropyl-*3,3-d*$_2$)phenyl]butyl-*1,1-d*$_2$-dimethylamine. A solution of 7.4 g (0.026 mol) of unpurified diamide in 110 mL of THF was added dropwise to a suspension of 2.2 g (0.05 mol) of $LiAlD_4$ in 150 mL of anhydrous ether. The mixture was refluxed for 24 h, and 8 mL of 5% NaOH was added to destroy excess deuteride. The lithium salts were filtered and extracted three times with refluxing THF. The combined organic layers were dried ($MgSO_4$), the ethers were evaporated, and the residue was vacuum distilled to yield the diamine: bp 100–125 °C (0.3 mm); IR (film) 2938 (s), 2853 (s), 2765 (m), 2173 (m), 2040 (m), 1492 (m), 763 (s) cm^{-1}; NMR ($CDCl_3$) δ 1.45 (br m, 6, CH_2), 2.25 (s, 12, NCH_3), 2.65 (m, 4, benzylic CH_2), 7.05 (s, 4, phenyl).

An undeuterated sample of the diamine was prepared in the same manner, but with $LiAlH_4$: bp 101–127 °C (0.5 mm); IR (film) 2938 (s), 2853 (m), 2762 (m), 1493 (m), 1463 (s), 752 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.38 (br m, 6, CH_2), 2.05 (s, 12, NCH_3), 2.40 (br t, 8, benzylic CH_2 and CH_2N), 6.98 (s, 4, phenyl). Anal. Calcd for $C_{13}H_{30}N_2$: C, 77.86; H, 11.45; N, 10.69. Found: C, 75.56; H, 11.55; N, 9.65. The analytical sample was collected by preparative VPC and could not be adequately purified.

4-(*o*-Allyl-*3,3-d*$_2$-phenyl)-1-butene-*1,1-d*$_2$. The diamine was placed in a 100-mL round-bottomed flask cooled with ice, and 5 mL of 30% H_2O_2 was added dropwise over a 30-min period. The cooling bath was removed, and the mixture was stirred overnight at room temperature. The excess peroxide was destroyed by a catalytic amount of lead oxide, and the H_2O was removed in vacuo leaving the diamine oxide as the residue. The diamine oxide was not isolated or characterized, but was immediately pyrolyzed in a 130–170 °C oil bath at 0.2-mm pressure for 1 h. The distillate was caught in a trap cooled in an acetone–dry ice bath, rinsed from the trap with ether, and washed with two 10-mL portions of 5% HCl and with two 10-mL portions of saturated $NaHCO_3$. The ether was dried ($MgSO_4$) and evaporated, and the residue was distilled to give deuterated diene **1** in good yield: bp 56–62 °C (0.9 mm); IR (CCl_4) 3030 (m), 2920 (s), 2315 (w), 2210 (w), 1608 (s), 1496 (s), 1453 (s) cm^{-1}; NMR ($CDCl_3$) δ 2.41 (m, 4, benzylic CH_2 and allylic CH_2), 3.27 (d, 2, benzylic-allylic CH_2), 5.75 (br s, 2, vinyl), 7.00 (s, 4, phenyl).

An undeuterated sample of **1** was prepared in the same manner from undeuterated diamine: bp 42–43 °C (0.5 mm); IR (film) 2935 (s), 2890 (m), 1644 (m), 1497 (m), 754 (s) cm^{-1}; NMR (CCl_4) δ 2.35 (m, 4, benzylic CH_2 and allylic CH_2), 3.17 (d, 2, benzylic-allylic CH_2), 5.30 (m, 6, vinyl), 6.90 (s, 4, phenyl). Anal. Calcd for $C_{13}H_{16}$: C, 90.70; H, 9.30. Found: C, 90.60; H, 9.49. The overall yield from diacid was about 40%.

Pyrolyses were performed by placing 50–60 μL of the diene of interest into a 250-mL ampule, which was degassed to 0.10 mm, sealed under vacuum, and placed in a tube furnace at the appropriate temperature. After 12–13 h, the ampule was partially cooled, and the products were condensed (dry ice) into the tip of the ampule. The tip was broken off, its contents were analyzed, and the components were isolated by VPC.

Pyrolysis of 4-*o*-Allylphenyl-1-butene (1). Pyrolysis of the deuterated diene yielded no reaction up to 320 °C and complete decomposition above 370 °C. Between 320 and 360 °C, three products in addition to the starting material were observed. The two major products and starting diene were present in approximately the same percentage and were isolated by preparative VPC (SE-30). The recovered starting diene (**1**) showed no rearrangement. One product was identified as 1,2-benzocyclonona-1,3-diene-*5,5,6,6-d*$_4$ (**2**): IR (film) 3030 (m),

2940 (s), 2873 (m), 2220 (w), 2118 (w), 1494 (m), 1453 (m), 758 (s), 743 (s), 731 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.72 (br s, 4, CH_2), 2.75 (m, 2, benzylic CH_2), 6.30 (m, 2, vinyl), 7.20 (s, 4, phenyl). Anal. Calcd for $C_{13}H_{12}D_4$: C, 88.64; H, D, 11.36. Found: C, 88.07; H, D, 11.39. The other product was identified as 1,2-benzocyclonona-1,4-diene-*6,6,7,7-d*$_4$ (**3**): IR (film) 3030 (m), 2955 (s), 2895 (m), 2222 (m), 2118 (w), 1495 (s), 1474 (s), 1452 (s), 763 (s), 750 (s), 743 (s), 734 (s), 652 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.65 (br t, 2, CH_2), 2.70 (br t, 2, benzylic CH_2), 3.50 (d, 2, benzylic-allylic CH_2), 5.55 (m, 2, vinyl), 7.15 (s, 4, phenyl). Anal. Calcd for $C_{13}H_{12}D_4$: C, 88.64; H, D, 11.36. Found: C, 87.83; H, D, 11.18. Pyrolysis of pure samples of **2** and **3** at 350 °C for 13 h afforded no decomposition or isomerization. The pyrolyzed samples were recovered by preparative VPC (SE-30) and their spectra were identical with those of unpyrolyzed samples. Pure samples of deuterated **2** and **3** and, separately, a mixture of **2** and **3** were hydrogenated by placing a few milligrams of 10% Pd/C into a 5-mL, round-bottomed flask and then adding a solution of 20–30 μL of the unsaturated compound in 2–3 mL of methanol. The mixture was stirred at atmospheric pressure under a H_2 atmosphere until H_2 uptake was complete (2–3 mL). The catalyst was filtered, and the solution was concentrated. The components of the residue were separated by VPC (SE-30). The only product obtained, in addition to some unreacted starting dienes, was identified as benzocyclononene-d_4: IR ($CDCl_3$) 3030 (w), 2938 (s), 2892 (m), 1498 (m), 1475 (m), 1457 (s), 897 (s), 2262 (w), 2213 (m), 2125 (w) cm^{-1}; NMR ($CDCl_3$) δ 1.50 (br d, 6, CH_2), 2.72 (m, 4, benzylic CH_2), 7.00 (s, 4, phenyl). Anal. Calcd for $C_{13}H_{14}D_4$: C, 87.64; H, D, 12.36. Found: C, 88.42; H, D, 12.50. An undeuterated mixture of **2** and **3** was also hydrogenated by the above method to give benzocyclononene, whose infrared spectrum was identical with the literature spectrum.[13a]

2,4-Dimethyl-1,2-dihydronaphthalene was prepared by the steps outlined in Scheme III according to modifications of literature procedures.[17,29] Physical and spectral properties of all materials agreed with their literature values.

3-(*o*-Acetylphenyl)-2-methylpropanal. 2,4-Dimethyl-1,2-dihydronaphthalene (4.82 g, 30.6 mmol) in 400 mL of absolute CH_3OH was cooled to −78 °C as 1.5% O_3 in O_2 was passed vigorously through the solution via a glass frit until saturation of O_3 was indicated by the solution's turning blue (20 min). The solution was flushed with N_2 until the color disappeared, followed by treatment with $(CH_3)_2S$ (38.00 g, 0.612 mol) at −50 °C. After a few minutes, the cooling bath was removed and the mixture allowed to warm to room temperature over a 2-h period. The mixture was rotary evaporated and the residue taken up in 50 mL of ether. The solution was washed with 40 mL of saturated $NaHCO_3$ and two 50-mL portions of brine, and was then dried over anhydrous Na_2SO_4. Rotary evaporation of the solvent left 4.37 g (61%) of the acetal: NMR (CCl_4) δ 0.72 (d, 3, CH_3), 2.48 (s, 3, CH_3), 2.65–3.22 (m, 3, CH and $ArCH_2$), 3.25 and 3.27 (s, 6, OCH_3), 3.97 (d, 1, OCHO), 7.08–7.29 (m, 3, ArH), 7.46–7.62 (m, 1, ArH); IR (film) 2970 (m), 2940 (m), 2880 (m), 2830 (m), 1725 (m, free CHO), 1690 (s), 1600 (w), 1570 (w), 1357 (m), 1253 (s), 1072 (s), 960 (m), 762 (s) cm^{-1}.

The acetal was dissolved in 250 mL of distilled THF and stirred with 80 mL of 0.3 M HCl for 24 h. The mixture was quenched with Na_2CO_3 and diluted with 100 mL of H_2O. Ether was added, the layers were separated, and the aqueous phase was back-extracted with 100 mL of ether. The combined organic portions were washed twice with 100 mL of brine and dried over anhydrous Na_2SO_4. Rotary evaporation of the solvent yielded 3.61 g (100%) of the keto aldehyde: NMR (CCl_4) δ 1.20 (d, 3, CH_3), 2.56 (s, 3, CH_3), 2.57–3.46 (m, 3, CH and $ArCH_2$), 7.10–7.28 (m, 3, ArH), 7.61–7.70 (m, 1, ArH), 9.61 (s, 1, CHO); IR (film) 2975 (m), 2938 (m), 2878 (w), 2820 (w), 2720 (w), 1720 (s), 1680 (s), 1600 (m), 1570 (m), 1358 (m), 1255 (s), 960 (m), 762 (s) cm^{-1}; MS (70 eV) molecular ion at *m/e* 190.

***o*-(3,3-Ethylenedioxy-2-methylpropyl)acetophenone.** The keto aldehyde (4.24 g, 22.3 mmol), 1.56 g (25.2 mmol) of ethylene glycol, and a few crystals of *p*-toluenesulfonic acid monohydrate were dissolved in 100 mL of benzene and refluxed for 13 h through a Dean-Stark trap. The mixture was cooled, treated with Na_2CO_3, and mixed vigorously with 30 mL of H_2O. The layers were separated. The aqueous phase was saturated with NaCl and extracted twice with 30 mL of ether. The organic portions were combined, washed with brine, dried over anhydrous Na_2SO_4, and rotary evaporated to yield 4.73 g (91%) of a brown oil: NMR (CCl_4) δ 0.79 (d, 3, CH_3), 2.48 (s, 3, CH_3), 2.58–2.73 (m, 3, CH and $ArCH_2$), 3.80 (m, 4, OCH_2CH_2O), 4.61 (d, 1, OCHO), 7.08–7.29 (m, 3, ArH), 7.48–7.55 (m, 1, ArH); IR (film) 2970 (s), 2940 (s), 2880 (s), 1687 (vs), 1600 (m), 1570 (m), 1357 (m), 1252 (s), 955 (s), 762 (s), 683 (s) cm^{-1}; MS (70 eV) molecular ion at *m/e* 234. The analytical sample was isolated by column chromatography. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 72.47, H, 7.78.

2-[*o*-(3,3-Ethylenedioxy-2-methylpropyl)phenyl-1-propene. Methyltriphenylphosphonium bromide (8.46 g, 23.7 mmol) was slurried in 250 mL of freshly dried THF and cooled in a methanol–ice bath. *n*-Butyllithium (10.7 mL, 23.4 mmol) in hexane was added at such a rate to maintain the temperature below 0 °C. The yellow-orange mixture was allowed to warm and then was stirred at room temperature for 3 h. The orange solution was cooled in the methanol–ice bath before the ketone acetal (4.21 g, 18.2 mmol) in 40 mL of dry THF was added dropwise. The resulting yellow slurry was stirred for 3.25 h at room temperature, refluxed for 3 h, stirred at room temperature overnight, and refluxed for an additional 1 h before cooling and subsequent quenching with 50 mL each of H_2O and ether. The layers were separated, and the aqueous phase was saturated with NaCl and extracted with ether. The ether portions were combined, washed with brine until the washings were neutral, dried over anhydrous Na_2SO_4, and rotary evaporated to yield a red oil. The oil was placed onto 161 g of Alcoa F-20 alumina on a 4 × 24.5 cm column and eluted with pentane. Fractions 6–23 (100 mL of pentane) yielded 2.28 g (55%) of very pure product: NMR (CCl_4) δ 0.87 (d, 3, CH_3), 2.02 (s, 3, CH_3), 2.19–3.04 (m, 3, CH and $ArCH_2$), 3.82 (m, 4, OCH_2CH_2O), 4.59 (d, 1, OCHO), 4.82 (br s, 1, alkene), 5.14 (br s, 1, alkene), 7.04 (t, 4, ArH); IR (film) 3080 (m), 3020 (m), 2970 (s), 2940 (s), 2920 (s), 2885 (s), 1642 (m), 1600 (w), 1490 (m), 1465 (m), 1400 (m), 1375 (m), 1160 (s), 1110 (s), 1086 (s), 1060 (s), 1040 (w), 905 (s), 770 (s), 755 (s) cm^{-1}; MS (70 eV) molecular ion at *m/e* 232. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.50; H, 8.75. Further elution with pentane yielded 0.139 of additional, impure product. Elution with ten 250-mL fractions of 10% ether in pentane yielded 0.61 g of the starting material contaminated with the diketal.

2-[*o*-(3,3-Ethylenedioxy-2-methylpropyl)phenyl]-1-propanol. The alkene acetal (2.47 g, 10.7 mmol) in 50 mL of dry THF was stirred at room temperature as 4.50 mL (4.5 mmol) of BH_3·THF (Aldrich) was added dropwise from a syringe over an 8-min period. The resulting solution was allowed to stir at room temperature for 75 min. It was then cooled to 6 °C and quenched with 1 mL of H_2O, 3.4 mL of 10% NaOH, and 1.6 mL of 30% H_2O_2. The mixture was stirred a few minutes in the ice bath, then warmed to room temperature, and stirred for 15 min. The mixture was poured into 100 mL of H_2O, and ether was added. After mixing, the layers were separated. The aqueous phase was saturated with NaCl and extracted again with ether. The combined ether portions were washed with brine, dried over anhydrous Na_2SO_4, and rotary evaporated to yield 2.75 g (97%) of the alcohol acetal: NMR (CCl_4) δ 0.90 (d, 3, CH_3), 1.21 (d, 3, CH_3), 1.72–3.50 (m, 5, CH, ArCH, $ArCH_2$, OH), 3.61 (d, 2, hydroxy CH_2), 3.86 (m, 4, OCH_2CH_2O), 4.66 (d, 1, OCHO), 7.10 (s, 4, ArH); IR (film) 3430 (br, s), 2975 (s), 2940 (s), 2880 (s), 1490 (s), 1467 (s), 1400 (s), 1157 (s), 1110 (s), 1080 (s), 1060 (s), 1040 (s), 1010 (s), 948 (s), 762 (s) cm^{-1}; MS (10 eV) molecular ion at *m/e* 250.

2-[*o*-(3,3-Ethylenedioxy-2-methylpropyl)phenyl]propanol. Desiccated CrO_3 (6.44 g, 64.4 mmol) was added in portions to an ice-cooled, mechanically stirred solution of dry pyridine (11.13 g, 141 mmol) in 300 mL of dry CH_2Cl_2. The resulting red mixture was allowed to warm to room temperature over a 45-min period. The alcohol (2.54 g, 10.3 mmol) in 60 mL of dry CH_2Cl_2 was added rapidly over a 10-min period. The resulting brown mixture was stirred for 15 min, treated with 100 mL of ether, and stirred for another 15 min. The entire reaction mixture and generous ether rinses of the reaction flask were filtered through Celite. The Celite pad was repeatedly rinsed with ether. The combined filtrates and rinses were filtered into a large separatory funnel. The brown solution was partially decolorized by three 100-mL washes of 10% NaOH solution and then treated with 100 mL of 5% aqueous HCl. The resulting emulsion was destroyed by addition of 100 mL each of 5% HCl and ether. The organic portion was further washed with 100 mL of H_2O, 100 mL of saturated $NaHCO_3$ solution, and two 100-mL portions of brine. The solution was dried ($MgSO_4$) and the solvent was removed by rotary evaporation to give 2.37 g (94%) of the aldehyde acetal: NMR (CCl_4) δ 0.90 (d, 3, CH_3), 1.34 (d, 3, CH_3), 1.7–3.8 (m, 3, CH and $ArCH_2$), 3.86 (m, 5, OCH_2CH_2O and ArCH), 4.65 (d, 1, OCHO), 7.11 (m, 4, ArH), 9.55 (s, 1, CHO); IR (film) 2980 (s), 2942 (s), 2890 (s), 2720

(w), 1725 (vs), 1492 (m), 1467 (m), 1400 (m), 1160 (m), 1110 (s), 1087 (s), 1062 (s), 950 (m), 764 (s) cm^{-1}; MS (70 eV) molecular ion at *m/e* 248.

3-[*o*-(3,3-Ethylenedioxy-2-methylpropyl)phenyl]-1-butene. A Wittig procedure similar to that given above was used with the temperature kept below ambient.[29] The crude product was loaded onto 70 g of alumina (Alcoa F-20) in a 1.7 × 50 cm column. The first four 50-mL pentane fractions yielded hydrocarbon byproducts, but fractions 5–21 (125 mL of pentane) yielded 1.45 g (63%) of the new alkene acetal: NMR (CCl_4) δ 0.87 (d, 3, CH_3), 1.32 (d, 3, CH_3), 1.75–3.25 (m, 3, CH and $ArCH_2$), 3.87 (m, 5, OCH_2CH_2O and ArCH), 4.65 (d, 1, OCHO), 4.78–5.55 (m, 2, $=CH_2$), 5.70–6.30 (m, 1, =CHR), 7.05 (s, 4, ArH); IR (film) 2965 (s), 2930 (m), 2875 (s), 1635 (m), 1488 (m), 1462 (m), 1396 (m), 1370 (m), 1156 (m), 1108 (s), 1085 (s), 1060 (m), 915 (m), 755 (m) cm^{-1}; MS (10 eV) molecular ion at *m/e* 246. The analytical sample was prepared by preparative VPC (¼ in. × 6 ft 5% Dow Corning High Vacuum Grease on Chromosorb G AW-DMCS at 200 °C). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.79; H, 8.95.

3-Methyl-4-[*o*-(1-methylallyl)phenyl]-1-butene (4). The aldehyde acetal (0.93 g, 3.7 mmol) was stirred with 1.43 mL of concentrated HCl in 34 mL of acetone under a N_2 atmosphere for 3 h. An equal volume of H_2O was added, and the mixture was then neutralized with $NaHCO_3$. The mixture was extracted once with 25 mL of ether. The aqueous phase was saturated with NaCl and the resulting organic layer removed. The procedure was repeated once more before the aqueous phase was extracted twice with 25 mL of ether. The combined organic phases were washed twice with 20 mL of brine, dried over anhydrous $MgSO_4$, and rotary evaporated to yield 0.83 g of a mixture of starting material and product. It was found to be most effective to carry out the Wittig reaction on the mixture.

The Wittig procedure was similar to that given above, with the temperature kept below ambient.[29] The residue recovered from evaporation of the solvent was placed onto 70 g of alumina (Alcoa F-20) in a 1.7 × 50 cm column. Fractions 3–6 (50 mL of pentane) yielded 231.8 mg (29%) of the product: NMR (CCl_4) δ 0.98 (d, 3, CH_3), 1.27 (d, 3, CH_3), 2.22–2.80 (m, 3, CH and ArCH), 3.68 (m, 1, ArCH), 4.71–5.07 (m, 4, $=CH_2$), 5.51–6.26 (m, 2, =CHR), 7.03 (t, 4, ArH); IR (film) 3080 (m), 3030 (m), 2980 (s), 2940 (m), 2880 (m), 1640 (m), 1493 (m), 1455 (m), 1420 (m), 1375 (m), 900 (m), 865 (s), 760 (m) cm^{-1}; MS (70 eV) molecular ion at *m/e* 200. The GC/MS revealed that the diene probably was a pair of diastereomers. The 70-eV MS of the smaller component differed only in the relative intensities of a few peaks. Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.66; H, 10.22. Further elution with 7% ether in pentane yielded 401.6 mg of still protected aldehyde acetal. Yield of the diene based on unprotected material was 49%.

Pyrolysis of 4. Initial pyrolyses were performed on 5 μL of **4** in a 20-mL tube evacuated to 0.03 mm, which was freeze–thawed twice before being sealed at −78 °C. The tubes were heated to 270, 310, and 360 °C in a tube furnace. The contents were studied by VPC (⅛ in. × 6 ft 10% SE-30 on Chromosorb W 80/100 at 175 °C with 20 mL/min He flow). At 270 °C, a new component in nearly equal abundance with **4** appeared. At 310 °C, there was an 80:20 mixture of two new products. A small amount of decomposition was observed at 360 °C, but the main products were the same two components in an 83:17 ratio.

Preparative scale pyrolyses were prepared in the same manner with approximately 40 μL of **4**. Four such runs were made at 320 °C. Product separation was done by preparative VPC (¼ in. × 6 ft 4.8% Apiezon L on Chromosorb G AW-DMCS 60/70 at 205 °C with 21 mL/min He flow). The major pyrolysis product was easily isolated and assigned structure **6**: NMR (CCl_4) δ 1.05 (d, 3, CH_3), 1.2–1.9 (br m, 7, CH and CH_2), 1.97 (s, 3, CH_3), 2.54 (d, 2, $ArCH_2$), 5.64 (m, 1, alkene), 7.25 (m, 4, ArH); IR (film) 3060 (m), 3010 (m), 2950 (s), 2920 (s), 2865 (m), 2845 (s), 1485 (m), 1445 (s), 1370 (m), 830 (w), 755 (s), 740 (s) cm^{-1}; MS (70 eV) molecular ion at *m/e* 200. The minor pyrolysis product was obtained as the major component of a 60:40 mixture with **6**. The NMR spectrum was obtained by proportionate substraction of the spectrum of **6**. The minor component was assigned structure **7**: NMR (CCl_4) δ 1.45 (d, 3, CH_3), 1.5–2.0 (m, 4, CH_2), 1.86 (s, 3, CH_3), 2.61 (m, 2, allylic), 2.78 (A of AB quartet, 1, allyl-benzyl CH_2), 3.36 (m, 1, benzyl), 4.12 (B of AB quartet, 1, allyl-benzyl CH_2), 4.53 (t, 1, alkene), 7.20 (s, 4, ArH); MS (70 eV) molecular ion at *m/e* 200. Hydrogenation of **6** (5.2 mg in 200 μL of ethanol with 0.5 mg of 10% Pd/C) for 2 h at room temperature or for 2 h at 56–58 °C yielded unreacted starting material. Hydrogenation of **6** with PtO_2 also gave no reaction. Hydrogenation of **7** (10% Pd/C) gave the expected dimethylbenzocyclononene (molecular ion at *m/e* 202). Ozonolysis[29] of **6**, followed by treatment with $(CH_3)_2S$, gave a keto aldehyde (molecular ion at *m/e* 232, aldehydic proton resonance).

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Supplementary Material Available: Equations 4–7, showing examples of aliphatic and aromatic rearrangements and all-carbon Claisen rearrangement (1 page). Ordering information is given on any current masthead page.

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