

- is also due to an acid-catalyzed reaction of the initially formed benzvalene derivative, which can, however, be isolated in this case.⁵⁴
- (53) H. Hogeveen, W. F. J. Hurdeman, and E. P. Schudde, *Tetrahedron Lett.*, 4211 (1974).

- (54) H. Hogeveen and W. F. J. Hurdeman, submitted for publication.
- (55) The initially formed benzvalene derivative reacts faster with the solvent (dimethyl acetylenedicarboxylate) as it rearranges to its aromatic valence isomer. When chloroform is used as solvent this compound is the only product detectable in the reaction of 1 and dimethyl acetylenedicarboxylate.⁵³
- (56) In this reaction the Diels-Alder cycloadduct was formed in ~50% yield. The other products were not identified but are probably due to an acid-catalyzed rearrangement of diene 4. The rate constant given in Table I should therefore be regarded as an upper limit.
- (57) Compare R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *Tetrahedron Lett.*, 615 (1962).

The Aromatic Cope Rearrangement. Thermal Reactions of *cis*-1-Aryl-2-vinylcyclopropanes

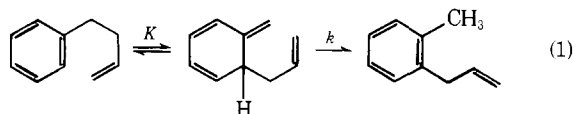
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Abstract: At 140–150 °C *cis*-1-phenyl-2-vinylcyclopropane (**1c**) undergoes *cis* ⇌ *trans* interconversion with $\Delta H^\ddagger = 32$ kcal/mol, $\Delta S^\ddagger = -5.8$ eu, and at or above 200 °C formation of 4-phenylcyclopentene occurs. Attempts to trap the Cope rearrangement product, bicyclo[5.4.0]undeca-1,4,8,10-tetraene (**3**), via Diels-Alder adducts failed. Heating **1c** with potassium *tert*-butoxide at 150 °C gave 1-phenyl-1,3-pentadiene (**4**). This product was formed only from **1c**, and in the presence of *tert*-butyl alcohol-*O-d* recovered **1c** and **1t** were devoid of deuterium. A route to **4** via formation of a tetraenide ion from **3** followed by ring opening is postulated. Treatment of *cis*-1-(*m*-methoxyphenyl)-2-vinylcyclopropane (**7c**) with ethyl mercaptide gave *cis*-1-(*m*-hydroxyphenyl)-2-vinylcyclopropane (**8c**). Heating **8c** at 120 °C gave 6,9-dihydro-5*H*-benzocyclohepten-1-ol (**10**). Treatment of *cis*-1-(*p*-methoxyphenyl)-2-vinylcyclopropane gave only *trans*-1-(*p*-hydroxyphenyl)-2-vinylcyclopropane. The relevance of these results to the aromatic Cope rearrangement is discussed.

Introduction

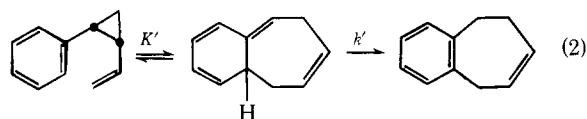
Since its discovery by Cope¹ in the early 1940s, the Cope rearrangement has become the prototype for the [3,3] sigmatropic shift. In distinct contrast to the Claisen rearrangement,² the Cope rearrangement has been most reluctant to reveal itself if one double bond of the 1,5-hexadiene system is incorporated in an aromatic ring. Thermolysis of 4-phenyl-1-butene produces no *o*-allyltoluene,³ and the presence of activating substituents on C₄ does not permit observation of the Cope rearrangement.⁴ Use of naphthalene or phenanthrene rings with activated molecules such as diethyl α -allyl- α -(2-naphthyl)malonate or diethyl α -allyl- α -(9-phenanthryl)malonate gave products of a complex rearrangement, which might result from further reaction of an initial Cope rearrangement product, though the mechanism is still unknown.⁵ The first study productive of isomers interpretable as the direct result of a Cope rearrangement was based on the very reasonable assumption that the rearrangement can indeed proceed (eq 1) but $K \ll 1$ and that observation of the rearrangement



is prevented because the prototropic step does not proceed at a reasonable rate, i.e., $k \rightarrow 0$. To activate the prototropy the 4-phenyl-1-butene was heated with potassium *tert*-butoxide, and *o*-allyltoluene along with *cis*- and *trans*-*o*-propenyltoluenes was obtained.⁶ Despite the inviting prospect revealed, the actual mechanism of formation of these products has never been securely tied to the Cope rearrangement.

One further ingredient in the recipe for the present approach to the problem was added by the observation of Doering and

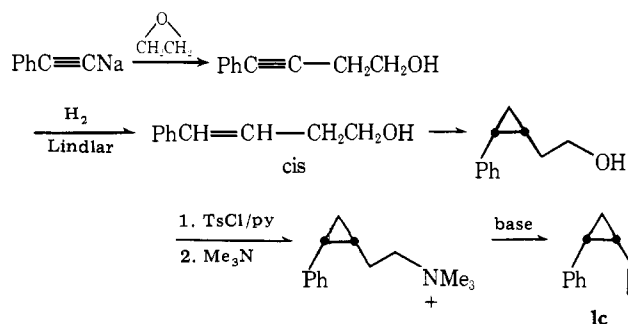
Roth⁷ that when C₃ and C₄ of the hexadiene moiety are incorporated into a cyclopropane ring with proper stereochemistry the Cope rearrangement is greatly accelerated. Applied to 4-phenyl-1-butene this principle leads to *cis*-1-phenyl-2-vinylcyclopropane, a substrate of considerable interest in the present context (eq 2). The acceleration of the rearrangement



is accompanied by the further advantage that $K' \gg K$, because the relief of strain from opening the cyclopropane will offset a large part of the loss of aromatic resonance energy. Since we expected k' to be about equal to k , we planned to attempt to trap the direct Cope product in other ways.

cis-1-Phenyl-2-vinylcyclopropane. Synthesis and Reactions

An attempt to develop a directed synthesis of *cis*-1-phenyl-2-vinylcyclopropane (**1c**) via the route of Scheme I was



abandoned because the conversion of *cis*-4-phenyl-3-buten-1-ol to *cis*-1-phenyl-2-(β -hydroxyethyl)cyclopropane could not be pushed beyond 70%, and separation of product and reactant could only be accomplished by GLC. Since isolation of a sufficient quantity to permit further synthetic steps proved extremely tedious, this route was abandoned in favor of a modified form of the procedure of Goh, Closs, and Closs.⁸ Their route uses the reaction of phenyldiazomethane with butadiene in the presence of zinc chloride. We found the *cis*/*trans* ratio in the product sensitive to the zinc halide used; the original authors obtained 2.8 with zinc chloride while we reached 4.5 with zinc iodide. The two isomers are conveniently separable by GLC and pure **1c** was readily obtained by this route.

Both isomers **1c** and **1t** (*trans*) are known compounds, but it is important here to note that not only can they be separated by GLC, but they can be separately identified by NMR, and mixtures can be quantitatively analyzed by NMR. The benzylic proton resonance in **1c** is centered at 2.4 ppm, and that of **1t** is at 1.7 ppm, in good agreement with the observation that the benzylic proton peak for *cis*-1,2-diphenylcyclopropane is at 2.45 ppm and for *trans* is at 2.13 ppm.¹² Thus the presence of small amounts of **1c** in **1t** is readily monitored in the 2.0–2.5-ppm region. Similarly the internal proton of the allyl group shows the expected multiplet between 5.3 and 5.7 ppm for **1t**, but for **1c** this multiplet is moved upfield since it must now be in the shielding cone of the phenyl group, being situated upfield from 5.2 ppm. Hence the presence of small traces of **1t** in **1c** is recognized by the presence of absorbance in the 5.2–5.7-ppm region.

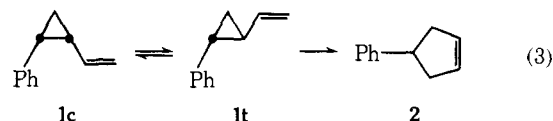
Compound **1c** is a most interesting substrate for thermal reactions. If the phenyl group participates (eq 2) **1c** acts as an analogue of *cis*-1,2-divinylcyclopropane, which undergoes a Cope rearrangement with extraordinary facility.^{7,9} Should the prototropic shift prevent consummation of this [3,3] shift, then **1c** could act as a 1,2-disubstituted cyclopropane and interconvert with **1t**.¹⁰ Finally **1c** might be expected to behave as a vinylcyclopropane and be converted to 4-phenylcyclopentene.¹¹ Not unexpectedly it proved much easier to unmask the *cis*-*trans* isomerization and 4-phenylcyclopentene formation than the desired Cope rearrangement and we shall take up these reactions first.

When heated to about 140 °C **1c** converts to **1t** sufficiently rapidly to be conveniently observable. No other reaction appears to occur at this temperature, thus permitting observation of the isomerization without interference. Isomerization was studied kinetically between 141 and 168 °C, and the activation parameters $\Delta H^\ddagger = 32 \pm 3$ kcal/mol and $\Delta S^\ddagger = -5.8 \pm 0.7$ eu were found for the *cis* \rightarrow *trans* reaction. These values are in good accord with those found for *cis*-1,2-diphenylcyclopropane, i.e., $\Delta H^\ddagger = 33$ kcal/mol and $\Delta S^\ddagger = -10$ eu.¹³ Compared with the value of $\Delta H^\ddagger = 56$ kcal/mol for *cis*-1-ethyl-2-methylcyclopropane,¹⁴ our results show that the isomerization intermediate is stabilized by ca. 24 kcal/mol. Berson¹⁵ has recently shown that if a trimethylene diradical is formed as an intermediate, simultaneous rotation of both methylene groups occurs with both 1,2-dideuteriocyclopropane and 1-phenyl-2-deuteriocyclopropane. This mechanism would, if applicable to the present case, permit only *cis* \rightarrow *cis* reaction via cleavage of the 1,2 bond. That reaction cannot be detected in our case. Two routes to avoid the dilemma without abandoning the biradical intermediate are (a) isomerization occurs only via cleavage of the 1,3 and 2,3 bonds (a possibility suggested by Berson), or (b) double methylene rotation is not exclusive and is accompanied by a lesser component of single methylene rotation.

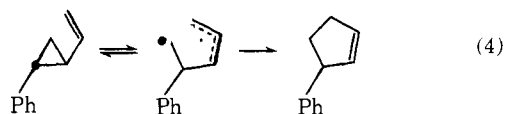
We are inclined strongly toward alternative (b). Reactions of **1c** and 1,2-diphenylcyclopropane have very similar activation parameters. If for the latter we assume that cleavage of the 1,2 bond (k_{12}) is activated to the expected extent by the

phenyl groups (ca. 25 kcal/mol), then cleavage of the 1,3 and 2,3 bonds could compete effectively only if specially activated. From the results on 1-phenyl-2-deuteriocyclopropane,¹⁵ we know that $k_{12} + k_{13} = 2 \times 10^{-5} \text{ s}^{-1}$ at 310 °C. Thus for the diphenyl case we can calculate that at 310 °C $k_{\text{obsd}} = 7 \times 10^{-2} \text{ s}^{-1} = 2(1 \times 10^{-5})F + k_{12}$ where F is the special activation factor. Also from the work of Crawford and Lynch,¹⁶ the value $k_{\alpha}/k_i = 1.5$ for optically active *trans*-1,2-diphenylcyclopropane. Since $k_{\alpha} = 2(1 \times 10^{-5})F + k_{12}$ and $k_i = 2(1 \times 10^{-5})F$ if the double methylene rotation occurs exclusively, k_{12} must equal $(1 \times 10^{-5})F$. Thus the double methylene rotation requirement leads to a necessary activation factor $F \sim 2000$, or at 310 °C $\Delta\Delta G^\ddagger \sim 8$ kcal/mol. This activation is not expected to be provided by either a remote phenyl or vinyl group, because neither the PhC-C· nor C=C-C· radicals show any particular stabilization.^{17,18} Thus we conclude that our results indicate the presence of some measure of single methylene rotation, while Crawford's study appears to require that random methylene rotation occur with the *trans*-1,2-diphenylcyclopropane, if the less substituted bond cleavage is excluded. Should conrotatory ring opening and closure be preferred,¹⁵ it is easy to see that with a *cis*-disubstituted cyclopropane like ours, the double methylene rotation would be sterically unfavorable and some measure of single rotation (or its equivalent, a disrotatory ring opening and conrotatory closure) might intervene. Unfortunately this explanation fails with *trans* isomers.

At temperatures approaching 200 °C **1c** is converted to 4-phenylcyclopentene (**2**). This reaction almost certainly proceeds via conversion first to **1t** and then it rearranges to **2** (eq 3).¹⁹ This conclusion was reached by Simpson and Rich-



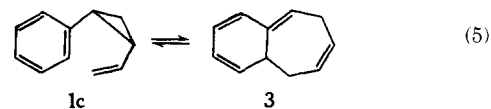
ey,¹⁹ who studied the formation of **2** from **1t** kinetically and found $\Delta H^\ddagger = 40$ kcal/mol and $\Delta S^\ddagger = -0.35$ eu for the reaction. We did not study the reaction beyond showing that the product was indeed 4-phenylcyclopentene, since it was not a limiting feature in our intended study. It is interesting to note that we did not find any 3-phenylcyclopentene in the product. This also points to the absence of cleavage of the less substituted bonds (eq 4), since fission of the less substituted bond



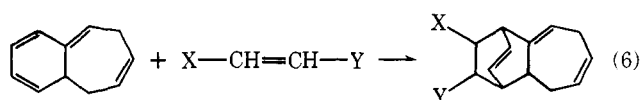
adjacent to the vinyl group would lead to 3-phenylcyclopentene.

Evidence for a Cope Rearrangement of **1c**

Direct rearrangement of **1c** without rearomatization would produce 1,4,8,10-bicyclo[5.4.0]undecatetraene (**3**) (eq 5). This



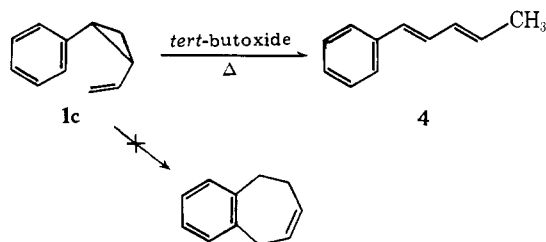
reaction was not expected to be detectable because the equilibrium constant must be exceedingly small. Using the incremental procedure of Benson,²⁰ we calculate $\Delta H^\circ = +14$ kcal/mol, which if ΔS° is ignored would lead to $K \sim 3 \times 10^{-8}$ at 400 K. Our initial attempts to detect **3** were aimed at trapping **3** via formation of a Diels-Alder adduct (eq 6) of the



cyclohexadiene moiety with some reactive dienophile. The attempts were abortive. With dimethyl acetylenedicarboxylate at 225 °C **1c** gave a series of at least ten products all in low yield. None was identified! When heated at 96 °C with maleic anhydride, **1c** gave polymer, recovered reactant, and an unidentified oil (inseparable mixture). A mixture of **1c** and *N*-phenylmaleimide heated at 100 °C gave only polymer. We did not push the matter further.

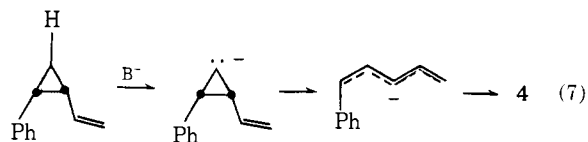
In an attempt to accelerate the prototropy we followed the lead of Doering⁶ and heated **1c** with a solution of sodium methoxide in methanol at 145 °C. No reaction was observable. However, when potassium *tert*-butoxide was used as the base at 150 °C, a new product was obtained in 42% yield. It was immediately obvious from the NMR spectrum of this product that it was not benz-1,4-cycloheptadiene. The compound was identified by its UV and NMR spectra as *trans,trans*-1-phenyl-1,3-pentadiene (**4**) (Scheme II). The UV spectrum

Scheme II

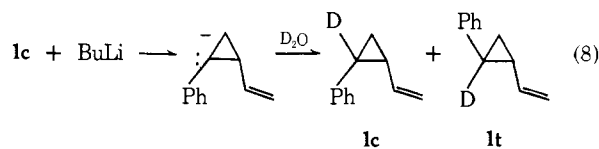


matches that given for **4**,²¹ and the NMR spectrum is in accord with expectations for this molecule including the three-proton doublet at 1.8 ppm with $J = 6$ Hz. No **4** is obtained from **1c** when **1c** is heated with *tert*-butyl alcohol at the same temperature and the same time in the absence of potassium *tert*-butoxide.

Thermal conversion of cyclopropanes to alkenes is well known,²² but the last experiment above appears to preclude this route to **4**. Ring opening of cyclopropyl anions to give allyl anions is also known,²³ but in the present case this route to **4** would require removal of an unactivated cyclopropyl proton (eq 7). To account for our results via this route, one must as-



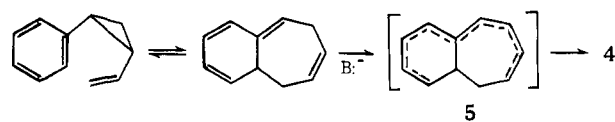
sume that the more rapid loss of the benzylic and allylic protons must be reversible, and that the stabilized anions which result do not suffer ring opening. That these requirements may be met under conditions which do not lead to formation of **4** was demonstrated by treating **1c** with butyllithium in THF and quenching with deuterium oxide. Only a mixture of **1c** and **1t** containing deuterium largely, if not exclusively, at the benzyl position was obtained (eq 8). After 4 days at 23 °C or a few



hours at 50–60 °C solutions of **1c** and butyllithium generated no **4**. However, **1c** heated at 150 °C in *tert*-butyl alcohol-*O-d* and potassium *tert*-butoxide gave **4** extensively deuterated in the side chain, but recovered **1c** and also **1t** were completely free of deuterium! These experiments appear to exclude a cyclopropyl anion as the precursor for **4**.

We propose therefore that **4** is formed via reversible generation of **3**, which loses its most acidic proton to give anion **5**, and ring opening to give the 1-phenylpentadienide ion which

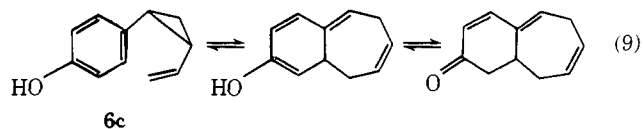
Scheme III



leads to **4** on protonation (Scheme III). Ion **5** opens to give 1-phenylpentadienide ion not only because the aromatic ring is regenerated, but also because it has been found that non-tetraenide ions do not cyclize,²⁴ thus suggesting that such anions are more stable in acyclic form. This proposal requires that **4** can be obtained only from **1c**, since **1t** will not undergo a concerted [3,3] shift. A mixture containing 80% **1c** and 20% **1t** was heated at 96 °C with *tert*-butoxide for 24 days and produced 26% of **4**, derived entirely from **1c**. Control samples heated in the absence of *tert*-butoxide showed that no thermal isomerization of **1c** → **1t** occurred under these conditions. Thus the route to **4** via **3** provides the most satisfactory rationale for all the data.

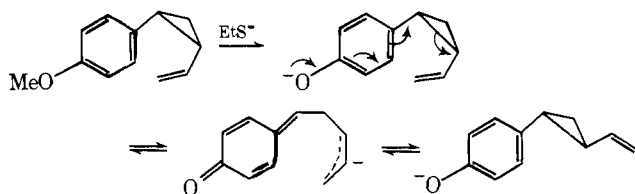
Studies with *cis*-1-(Hydroxyphenyl)-2-vinylcyclopropanes

It seemed reasonable that if **3** is indeed reversibly generated from **1c** at temperatures near 100 °C, the addition of a hydroxyl group on the phenyl might provide an internal trap by converting the Cope product into an unsaturated ketone (eq 9). The most likely candidate for this appeared to be the *p*-

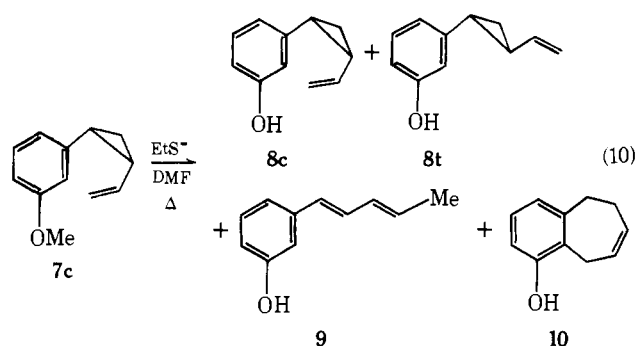


hydroxy isomer (**6c**), so we attempted to prepare this from *p*-hydroxybenzaldehyde. When the hydrazone could not be induced to form *p*-hydroxyphenyldiazomethane, the direct route was abandoned. The *cis* isomer of 1-(*p*-methoxyphenyl)-2-vinylcyclopropane was obtained by our modification of Closs' procedure. This *cis* isomer was formed in at least a 9:1 ratio over the *trans*. Treatment of the mixture with sodium thioethoxide in DMF²⁵ gave in the base-soluble fraction 17% of 1-(*p*-hydroxyphenyl)-1,3-pentadiene, 76% of *trans*-1-(*p*-hydroxyphenyl)-2-vinylcyclopropane, and none of the desired *cis* isomer. Presumably the initially formed phenoxide ion can undergo a facile, reversible cyclopropane ring opening (Scheme IV), that is, acting as a vinylogous cyclopropanol.²⁶

Scheme IV



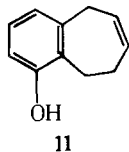
To prevent this mode of *cis* → *trans* isomerization we chose to prepare the *m*-hydroxyphenyl isomer, which is functionally incapable of reacting in this manner. The meta isomer can, of course, generate two isomeric Cope products, a complication we had hoped to avoid with the para substituent. Synthesis of 1-(*m*-methoxyphenyl)-2-vinylcyclopropane (**7c**) was accomplished by the modified Closs procedure. Demethylation with thioethoxide in DMF gave the desired 1-(*m*-hydroxyphenyl)-2-vinylcyclopropane (**8**), 70% *cis* (**8c**) and 30% *trans* (**8t**), along with two other products (eq 10). The first of these (24%) was readily identified as 1-(*m*-hydroxyphenyl)-1,3-pentadiene (**9**) because of the close relationship between its NMR spectrum and that of **4**. The second 28% was less readily assigned a structure, but was finally identified as 6,9-dihydro-5*H*-benzocyclohepten-1-ol (**10**), a compound which might be expected



to be derived from one of the Cope rearrangement products. This same compound was also obtained when **8c** was heated at 121 °C with a solution containing phenoxide ion, and also when **8c** was heated alone at 125 °C.

Since the structure of compound **10** is crucial, it was very carefully ascertained. The presence of a phenolic group was indicated by the infrared spectrum (3592, 3400, 1321, and 1281 cm^{-1}), and confirmed by the expected bathochromic shift in the ultraviolet spectrum (220, 273 nm \rightarrow 240, 294 nm) upon addition of ethanolic potassium hydroxide.²⁷ Mass spectral analysis by the peak matching technique gave the molecular weight as 160.089, which corresponds to a formula of $\text{C}_{11}\text{H}_{12}\text{O}$. cursory examination of the NMR spectrum shows three aromatic protons (trisubstituted benzene ring), two olefinic protons, three methylene groups, and no methyls. One mole of hydrogen is absorbed on catalytic hydrogenation, and since no band in the infrared near 975 cm^{-1} disappears, this must be a *cis*-disubstituted double bond. These data require the presence of one additional ring in **10**, and the basic carbon skeleton, as well as the position of the hydroxyl group, was established when the hydrogenation product was identified as 6,7,8,9-tetrahydro-5*H*-benzocyclohepten-1-ol.²⁸ Both the melting point and the NMR spectrum are in accord with the published data.

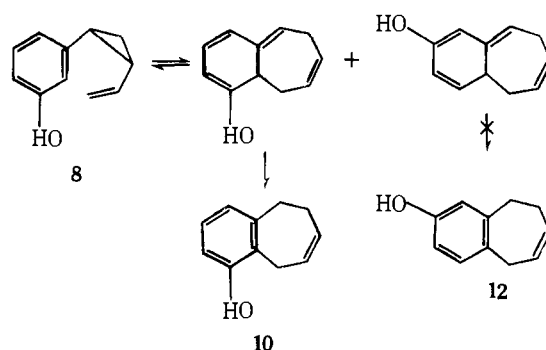
The aliphatic region of the NMR spectrum of **10** contains three separate patterns for methylene groups at 2.3, 2.97, and 3.5 ppm. Triple irradiation at 2.3 and 3.5 ppm simultaneously reduced the olefinic multiplets at 5.4–5.9 ppm to an AB pattern with $J_{\text{AB}} = 12$ Hz. Irradiation in the olefinic region reduced the multiplet at 3.5 ppm to a doublet, $J = 2$ Hz, which confirms its position between the benzene ring and the double bond. At this point only two structures are possible, **10** or **11**. Resolution



of which was correct was achieved by adding incremental portions of the shift reagent $\text{Eu}(\text{fod})_3$ and noting that of the three methylene resonances, the one which shifts to the greatest extent was at 3.5 ppm. Thus the methylene between the ring and the double bond must also be nearest the hydroxyl, permitting assignment of structure **10** as the correct one.

Exclusive formation of **10** raises the question of why it is formed and **12** is not, if the Cope rearrangement is involved. The explanation is not immediately apparent. Generally the Claisen rearrangement of a meta-substituted phenyl allyl ether is faster to the position para to the meta substituent than to the ortho position.²⁹ If this holds true for the Cope rearrangement in the present case, it implies that the reversal of the Cope rearrangement is faster than the prototropic conversion to **10** or **12** (Scheme V), and that the rate of conversion to **10** is much faster than to **12**. We have not yet prepared 1-(2-methyl-3-hydroxyphenyl)-2-vinylcyclopropane to test whether the product analogous to **12** can be formed.

Scheme V



Discussion

Prior to the work described here there existed no unequivocal evidence for participation of an aromatic double bond in the Cope rearrangement. Here we have shown that a 4-phenyl-1-butene system, albeit activated by an appropriately situated cyclopropane ring, can rearrange in mildly basic solution (**8c** in ethanol containing phenoxide ion), mildly acidic solution (**8c** in *tert*-butyl alcohol) to bond C_1 to an ortho carbon of the benzene ring, to cleave the bond between C_3 and C_4 , and to invert the double bond in the allylic portion C_1 – C_3 . Lacking only evidence for the repositioning of the double bond from the benzene ring, this fulfills all of the structural requirements for the Cope rearrangement. Is it the normal thermally activated, noncatalyzed process associated with the Cope rearrangement? Obviously eliminated by our results is acid-catalyzed electrophilic aromatic substitution. A diradical reaction is also unlikely, since reaction occurs below the temperature at which *cis*–*trans* isomerization occurs, and the diradical reaction considered by Dewar³⁰ would allow no role for the cyclopropyl group. Since reaction of **8c** can occur in the absence of base, the thermal concerted [3,3] sigmatropic shift mechanism seems most probable. Thus we suggest that the Cope rearrangement can occur, as does the Claisen, when one double bond is part of a benzene ring.

Given that the Cope rearrangement involving an aromatic ring is indeed a reality, why has it been so difficult to uncover an authentic case? Clearly the suggestion put forward by Doering⁶ that the prototropic step is nowhere near as facile in the Cope case as it is in the Claisen is very important, since even in what should be relatively favorable cases, we have been unable to identify any products derivable from the Cope rearrangement in the absence of some process for expediting the prototropic step. It is also possible that there is an increase in ΔH^\ddagger for the Cope rearrangement when one of the double bonds is replaced by a benzene ring. Surprisingly this replacement causes no observable increase in ΔH^\ddagger for the Claisen rearrangement as long as it is the enol ether bond which is replaced. Thus ΔH^\ddagger for allyl phenyl ether is 30.7 kcal/mol,³¹ while for allyl vinyl ether ΔH^\ddagger is 29.7 kcal/mol.³² At the moment we can give no quantitative answer to the question of whether the Cope rearrangement follows the Claisen pattern, but some rough approximations can be made.

The Cope rearrangement of 1,5-hexadiene has ΔH^\ddagger equal to 34.5 kcal/mol,³³ and it rearranges via a chair form transition state.³⁴ Rearrangement of *cis*-1,2-divinylcyclopropane was found to require a ΔH^\ddagger of 20 kcal/mol,⁹ and this molecule must necessarily react via a boat form transition state. Recently Goldstein³⁵ has reported that the Cope rearrangement of 1,5-hexadiene via the boat form transition state has ΔH^\ddagger equal to 44.7 kcal/mol, i.e., 10 kcal/mol above the chair form. From this one concludes that the presence of the cyclopropane ring reduces ΔH^\ddagger by ca. 25 kcal/mol, which indicates that the cyclopropane ring is virtually completely opened at the tran-

sition state. In this study we have shown that the Cope rearrangement can occur faster than the *cis*-*trans* isomerization, which for **1c** had ΔH^\ddagger equal to 32 kcal/mol. We have not as yet studied the kinetics of the rearrangement process, but a crude experiment suggested that the rearrangement is about five times faster at 96 °C, presuming that the prototropy (in *tert*-butoxide) is not rate determining. We propose therefore that ΔH^\ddagger for the Cope rearrangement of **1c** is of the same order of magnitude as for the isomerization, and estimate therefore $\Delta H^\ddagger \approx 30$ kcal/mol.

Given this ΔH^\ddagger of 30 kcal/mol for **1c** we can estimate ΔH^\ddagger for the Cope arrangement of 4-phenyl-1-butene (**13**). Lacking the cyclopropane ring **13** must have ΔH^\ddagger 25 kcal/mol above **1c**, but since **13** can react via the chair transition state ΔH^\ddagger is reduced by 10 kcal/mol. The final estimate for **13** is then 45 kcal/mol. That value gives $\Delta\Delta H^\ddagger \approx 10$ kcal/mol for the replacement of a double bond by a phenyl ring in the Cope rearrangement. That the estimate may perhaps be on the high side is suggested by the 1,5-H shift of 5-methyl-1,2,4-hexatriene ($\Delta H^\ddagger = 23.9$ kcal/mol)³⁶ and of 1-(*o*-tolyl)allene ($\Delta H^\ddagger = 28.8$ kcal/mol).³⁷ However, if the $\Delta\Delta H^\ddagger$ above is too high by even a factor of 2 the combination of the increase, in ΔH^\ddagger for the Cope step, and the recalcitrant prototropy makes it very clear why the "aromatic Cope rearrangement" has evaded detection for so long.

Experimental Section

***cis*-1-Phenyl-2-vinylcyclopropane (1c).** An ether solution of phenyldiazomethane was prepared from 6 g (0.05 mol) of benzalhydrazone according to the procedure of Staudinger and Gaule.³⁸ The solution obtained contains about 0.035 mol of phenyldiazomethane.³⁹ About 50 mL of hexadiene was condensed in a flask and 4 mL of a 0.3 M solution of zinc iodide in ether was added in one portion, followed by dropwise addition of the phenyldiazomethane solution. Additional zinc iodide solution was introduced via a syringe when the color of the phenyldiazomethane persisted. After the addition had been completed, the solution was stirred for 0.5 h, and the solvent and excess butadiene were evaporated under reduced pressure. The residue was washed with water, then extracted with pentane, and the pentane solution was dried (MgSO₄). The crude product was isolated by distillation, bp 56–80 °C (25 mm) [lit.⁴⁰ bp 74 °C (6 mm) for **1c** and 84 °C (7 mm) for **1t**]; GLC analysis showed **1c**:**1t** = 5:1. The isomers were separated on a 5% DEGS column at 100 °C with **1c** being eluted first. Pure **1c**: UV max (cyclohexane) 290 nm (ϵ 49), 274 (174), 265 (299), 260 (317), 255 (334), 248 (371); IR (CCl₄) 1637, 1603, 1493, 1031, 990, and 899 cm⁻¹; NMR (CCl₄) δ 0.8–1.4 (m, 2 H), 1.6–2.0 (m, 1 H), 2.0–2.5 (m, 1 H), 4.6–5.16 (m, 3 H), 7.12 (broad s, 5 H). The spectral data match the published values.⁸ Samples of **1t** was also obtained, UV max (cyclohexane) 276 nm (ϵ 535), 268 (ϵ 670), 262 (ϵ 664); NMR (CCl₄) δ 0.8–1.3 (m, 2 H), 1.4–2.1 (m, 2 H), 4.7–5.7 (m, 3 H), 6.8–7.3 (m, 5 H). The spectral data are in full agreement with published results.⁴⁰

***Cis-Trans* Isomerization of 1c.** Isomerization was carried out in cyclohexane solution in sealed tubes. The tubes were carefully cleaned and dried before use and the cyclohexane solution was degassed under nitrogen by the freeze-thaw cycle procedure. Analysis of the product was made by GLC using a 20% SE-30 on Chromosorb G AW DMCS column (1/8 in. \times 5 ft) at 100 °C. The **1c** used was analytically pure and was obtained by preparative GLC. For kinetic studies capillary ampules containing 40 μ L of solution were used, and a constant-temperature bath (± 0.01 °C) was used. For the analysis *n*-butylbenzene was used as an internal standard and peak areas were determined with a Hewlett-Packard digital integrator. Analyses were run in triplicate, and the kinetic studies were carried out at 141, 150, 161, and 168 °C. First-order rate constants k_{obsd} were obtained from the equation

$$k_{\text{obsd}} = 1/t \ln(A_0 - A_e) / \ln(A - A_e)$$

where the A values are ratios of the peak integration of **1c** and the standard. The equilibrium value, A_e , was determined from the point at which the concentration of **1c** remained constant. Individual rate constants k_1 (**1c** \rightarrow **1t**) and k_{-1} were determined from the equations $k_{\text{obsd}} = k_1 + k_{-1}$ and $K_e = k_1/k_{-1}$. Activation parameters were ob-

Table I. Rate Constants for Thermal Isomerization of **1c**

Temp, °C	$k_{\text{obsd}} \times 10^6$	$k_1 \times 10^6$	$k_{-1} \times 10^6$	K_e
141	6.06 \pm 0.50	4.86 \pm 0.38	1.20 \pm 0.15	4.04 \pm 0.38
150	10.0 \pm 0.36	8.72 \pm 0.34	1.28 \pm 0.18	6.80 \pm 0.91
161	37.5 \pm 2.2	32.4 \pm 2.0	5.05 \pm 0.72	6.41 \pm 0.82
168	57.9 \pm 2.4	50.4 \pm 2.3	7.66 \pm 1.0	6.58 \pm 0.86

tained from the least-squares best straight line of a plot of $\log k_1$ vs. $1/T$ (K). The results are given in Table I.

4-Phenylcyclopentene. A solution containing 77 mg of **1c** in 4.0 mL of methylcyclohexane was heated at 224 °C in a sealed tube for 24 h. GLC analysis showed that the product contained 67% of 4-phenylcyclopentene and 33% of **1t**. Similarly a solution containing 97 mg of **1t** in 1.5 mL of methylcyclohexane was heated at 233 °C for 44 h, giving an 84% yield of 4-phenylcyclopentene: UV max (cyclohexane) 308 nm (ϵ 54), 284 (164), 268 (403), 262 (517), 258 (517), 255 (256), 248 (500); IR (neat) 1600, 1493, 753, 697, 673 cm⁻¹; NMR (CCl₄) δ 2.2–3.0 (m, 4 H), 3.42 (quintet, 1 H, $J \approx 7.5$ Hz), 5.72 (s, 2 H), 7.14 (s, 5 H). Anal. Calcd for C₁₁H₁₂: C, 91.61; H, 8.39. Found: C, 91.91; H, 8.68.

Phenylcyclopentane. Hydrogenation of 4-phenylcyclopentene, 14 mg (0.1), over platinum oxide required 1 equiv of hydrogen. The product had the following spectral properties: UV max (cyclohexane) 268, 259, 254, 249 nm (lit.⁴¹ UV max 268, 261, 254, 248 nm); NMR (CCl₄) δ 1.4–2.2 (m, 8 H), 2.94 (m, 1 H), 7.08 (m, 5 H).

Attempts to Trap 3. A. Dimethyl Acetylenedicarboxylate. A solution containing 26 mg (0.18 mmol) of **1c** and 0.21 g (1.5 mmol) of dimethyl acetylenedicarboxylate in 3 mL of methylcyclohexane was heated to 225 °C for 5 h. A clear yellow solution and an insoluble red-brown amorphous material were produced. Analysis by TLC using silica gel PF₂₅₃ and 3% ethyl ether in benzene as eluent showed at least ten compounds in the product, none of which was isolated in sufficient quantity to identify.

B. Maleic Anhydride. A solution containing 58 mg (0.40 mmol) of **1c** and 80 mg (0.82 mmol) of maleic anhydride in 3 mL of methylcyclohexane was heated at 96 °C for 24 h. A colorless solution, a yellow oil, and a white solid were obtained. GLC analysis of the solution showed only **1c** and **1t** (trace) to be present. The white solid did not melt below 300 °C. The yellow oil was treated with methanolic potassium hydroxide at reflux for 3 h. After neutralization with hydrochloric acid, the mixture was evaporated to dryness, and the residue triturated with ether. The ether solution was treated with diazomethane and the product was analyzed by GLC. Only dimethyl maleate (71%) could be identified.

C. *N*-Phenylmaleimide. A solution containing 250 mg (1.7 mmol) of **1c** and 0.80 g (4.6 mmol) of *N*-phenylmaleimide in 3 mL of methylcyclohexane was heated at 100 °C for 9 days. GLC analysis using 4-methylcyclohexanone as a standard indicated that only ca. 30% of **1c** reacted. Only *N*-phenylmaleimide and an orange, glassy solid (mp >250 °C dec) were obtained.

Reaction of 1c with *tert*-Butoxide. A solution containing 23 mg (0.16 mmol) of **1c** and 170 mg (1.5 mmol) of potassium *tert*-butoxide in 3 mL of *tert*-butyl alcohol was heated at 135 °C for 35 h. The mixture was diluted with pentane, and this solution was washed with water and dried (MgSO₄). GLC analysis showed that the product consisted of 21% **1c**, 24% of **1t**, 13% unidentified compounds, and 42% of 1-phenyl-1,3-pentadiene: UV max (EtOH) 308 nm (ϵ 10 400), 286 (28 200), 279 (27 400), 235 (9350), 227 (12 300), 221 (12 400), and 210 (16 400) [lit.²¹ UV max 282 nm (ϵ 28 800), 235 (8320)]; NMR (CCl₄) δ 1.81 (d, 3 H; $J = 6$ Hz), 5.5–6.9 (m, 4 H), 7.1–7.4 (m, 5 H); mass spectrum m/e 144.

When 3 mL of a solution 0.16 M in **1c** and 0.48 M in potassium *tert*-butoxide in *tert*-butyl alcohol-*d* (Stohler Isotopes, 98% D) was heated at 150 °C for 15 h, the product contained 9% **1c**, 11% **1t**, and 72% of **4**: NMR (CCl₄) δ 1.8 (m, 0.3 H), 5.72 (s, 1 H), 6.63 (s, 1 H), 7.0–7.4 (m, 5 H). The NMR spectra of the recovered **1c** and **1t** matched in all respects those of authentic nondeuterated samples.

Six samples, three containing a mixture of **1c** and **1t** plus *n*-butylbenzene (GLC standard) and 0.21 M potassium *tert*-butoxide solution in *tert*-butyl alcohol and three containing an identical solution except for the potassium *tert*-butoxide, were heated at 96 °C in sealed tubes for 24 days. The samples were diluted with pentane and worked up as above. Products were analyzed by GLC using an electronic digital integrator. The base-free samples showed **1c**/**1t** = 3.83 before heating

and **1c**/**1t** = 3.56 after heating, and no **4** was present after heating. The samples containing *tert*-butoxide had an initial **1c**/**1t** = 3.97 and a final value of 2.13. The values for **1c**/standard = 1.03 (initial) and 0.72 (final), for **1t**/standard = 0.26 (initial) and 0.34 (final) in those samples containing *tert*-butoxide, and the remaining product was **4**.

Reaction of 1c with Butyllithium. A solution (5 mL) of **1c** (81%) and **1t** (19%), 140 mg (1.0 mmol), in THF was mixed under nitrogen with 6 mL of 0.90 M butyllithium in *n*-hexane, and the red-brown solution was stirred for 60 h at 23 °C. The solution was then light yellow. More butyllithium was added and the solution was stirred for 48 h longer. Again butyllithium was added and the solution was heated to 60 °C for 1.5 h. Aliquots (0.5 mL) were withdrawn periodically and analyzed by GLC. No **4** was formed in any case, and only conversion of **1c** to **1t** was noted, the final solution containing 87% **1t**. When a similar reaction mixture was quenched with deuterium oxide after 5 h at 0 °C, the NMR spectrum of **1c** showed the band at 2.3 ppm to integrate for 0.57 H, and for **1t** the region between 1.5 and 2.0 ppm showed 1.75 H.

cis-1-(*p*-Methoxyphenyl)-2-vinylcyclopropane. A solution of *p*-methoxyphenyldiazomethane in anhydrous ether was prepared from 9.5 g (70 mmol) of *p*-methoxybenzaldehyde by the method of Closs and Moss.⁴² Approximately 50 mL of 1,3-butadiene was condensed in a three-necked flask and about 4 mL of ca. 0.3 M zinc iodide in ether was added. To this solution was added dropwise the solution of *p*-methoxyphenyldiazomethane. When the red color persisted additional zinc iodide solution was added as needed (ca. 3 mmol was required generally). The solution was stirred for 30 min after the final addition, and the solvent and excess butadiene were removed under reduced pressure. The residue was mixed with pentane and the mixture was washed with water and then dried (MgSO₄). Distillation gave 1.31 g (10.8%) of *cis*-1-(*p*-methoxyphenyl)-2-vinylcyclopropane: bp 93–95 °C (1.5 mm); NMR (CCl₄) δ 0.6–1.3 (m, 2 H, CH₂ of cyclopropane), 1.4–1.9 (m, 1 H, CHC=), 2.20 (m, 1 H, ArCH), 3.68 (s, 3 H, OMe), 4.7–5.1 (m, 3 H, CH=CH₂), 6.68 (d, 2 H, *J* = 8 Hz, Ph), 7.02 (d, 2 H, *J* = 8 Hz, Ph) (matches reported spectrum⁸). Analysis by GLC on a 6 ft × 1/4 in. 5% DEGS on Chromosorb G column at 120 °C showed contamination by ca. 10% of the *trans* isomer.

trans-1-(*p*-Hydroxyphenyl)-2-vinylcyclopropane. The above ether was demethylated according to the procedure of Feutrill and Merrill.²⁵ A solution of sodium eththiooxide in anhydrous DMF was prepared from 58 mg (1.4 mmol) of sodium hydride and 88 mg (1.4 mmol) of ethanethiol in 4 mL of DMF. A sample (104 mg, 0.60 mmol) of the above ether was added and the solution was heated to 120 °C under nitrogen for 14 h. Aliquots analyzed by GLC on a 5 ft × 1/4 in. 20% SE-30 on Chromosorb G at 160 °C showed the reaction to be ca. 50% complete, and that further heating caused decomposition of the product. The reaction mixture was cooled in an ice bath and was acidified with 3 N hydrochloric acid. The product was taken up in ether and the solution was washed with water and then 5% sodium hydroxide solution. The ether layer was dried (MgSO₄) and preparative GLC gave 80% *cis*-1-(*p*-methoxyphenyl)-2-vinylcyclopropane, 14% of an unidentified product, and 5% of 1-(*p*-methoxyphenyl)-1,3-pentadiene: mp 57–60 °C; UV max 217, 291 nm; NMR (CDCl₃) δ 1.79 (d, 3 H, *J* = 5 Hz, CH₃C=), 3.80 (s, 3 H, MeO), 5.6–7.0 (m, 6 H, 4=CH and 2 Ph), 7.3 (2 H, Ph) (lit.⁴³ mp 58–60 °C, UV max 217, 290 nm).

The sodium hydroxide extract was acidified and was extracted with ether. The ether extract was washed with water and dried (MgSO₄). Preparative GLC gave 17% of 1-(*p*-hydroxyphenyl)-1,3-pentadiene [NMR (CCl₄) δ 1.74 (d, 3 H, *J* = 6 Hz, CH₃C=), 4.74 (broad s, 1 H, OH), 5.4–7.0 (m, 6 H, 4=CH and 2 Ph), 7.17 (d, 2 H, *J* = 8 Hz, Ph)] and 76% of *trans*-1-(*p*-hydroxyphenyl)-2-vinylcyclopropane [IR (CHCl₃) 3415 (broad), 3096, 3049, 3030, 1689, 1603, and 1575 cm⁻¹; NMR (CCl₄) δ 0.8–1.3 (m, 2 H, CH₂ cyclopropane), 1.4–1.9 (two m, CHC=, CHAr), 4.8–5.8 (m, 4 H, CH=CH₂ and OH), 6.62 (d, 2 H, *J* = 8 Hz, Ph), 6.87 (d, 2 H, *J* = 8 Hz, Ph); mol wt (mass spectrum peak match) 160.088 (calcd for C₁₁H₁₂O, 160.089)].

cis-1-(*m*-Methoxyphenyl)-2-vinylcyclopropane (7c). This compound was prepared from 9.5 g of *m*-methoxybenzaldehyde according to the procedure described for *cis*-1-(*p*-methoxyphenyl)-2-vinylcyclopropane. The crude product, 1.8 g (12%), was collected at 85–87 °C (1.3 mm) and GLC analysis on a 20% SE-30 column at 160 °C showed that this product contained 97% of a mixture of **7c** and **7t** (not separable on this column); NMR integration indicated 80% **7c** and 20% **7t** (see below). The spectral properties of the mixture follow: IR (neat)

1633, 1600, 1583, 1490, 1258, 997, 903, 788 cm⁻¹; NMR (CCl₄) δ 0.8–1.3 (m, 2.1 H), 1.5–1.9 (m, 1.21 H), 2.1–2.4 (m, 0.79 H, PhCH of **7c**), 3.72 (s, 3.0 H, used as reference standard), 4.7–5.2 (m, 2.76 H), 5.2–5.8 (m, 0.18 H, 1 H of vinyl group of **7t**), 6.5–6.7 (m, 3 H), 6.9–7.2 (m, 1 H). Anal. Calcd for C₁₂H₁₄O: C, 82.72; H, 8.10. Found: C, 82.79; H, 8.23.

cis-1-(*m*-Hydroxyphenyl)-2-vinylcyclopropane (8c). A solution of sodium thioethoxide in DMF was generated in situ from 1.08 g (25.6 mmol) of sodium hydride and 1.67 g (26.8 mmol) of ethanethiol in 22 mL of DMF. To this was added 1.21 g (6.95 mmol) of **7c** (80%) + **7t** (20%), and the solution was heated under nitrogen at 124 °C for 10 h. The mixture was cooled to 0 °C, was acidified with 3 N hydrochloric acid, and was extracted then with ether. The ether solution was washed with water and extracted with 5% sodium hydroxide solution. The alkaline extract was acidified and this solution was extracted with ether. This ether solution was washed with water, dried (MgSO₄), and analyzed by GLC on a 20% SE-30 column at 160 °C. Analysis showed the presence of 43% of a mixture of **8c** (70%) and **8t** (30%), 28% of **10**, 24% of 1-(*m*-hydroxyphenyl)1,3-pentadiene (**9**), and 5% of unidentified material. The materials could be separated preparatively via GLC on the SE-30 column.

The mixture of **8c** and **8t** was not separated on this column and was obtained as a liquid which was analyzed by NMR. Properties of the mixture follow: IR 3600, 1640, 1610, 1590, 1498, 998, 910 cm⁻¹; NMR (CDCl₃) δ 0.8–1.4 (m, 2.1 H), 1.6–2.0 (m, 1.48 H), 2.1–2.5 (m, 0.76 H, benzyl proton of **7c**), 4.8–5.2 (m, 3.55 H), 5.3–5.8 (m, 0.28 H, one vinyl proton of **7t**), 6.5–6.9 (m, 2.86 H), 7.0–7.2 (m, 0.8 H). Anal. Calcd for C₁₁H₁₂O: C, 82.46; H, 7.55. Found: C, 82.55; H, 7.54.

1-(*m*-Hydroxyphenyl)-1,3-pentadiene (9). Separation of **9** and **10** from the mixture obtained above was difficult and a pure sample of **9** was not obtained. The following spectral data were derived from a sample containing about 62% of **9** and 38% of **10** with the spectral pattern for **10** removed by subtraction: IR (CHCl₃) 3600, 3420 (broad), 1602, 1585, 1490 cm⁻¹; NMR (CDCl₃) δ 1.79 (d, 3 H, *J* = 6 Hz), 4.7 (s, OH), 5.5–7.2 (m, 8 H, not clearly separable from bands due to **10**).

6,9-Dihydro-5H-benzocyclohepten-1-ol (10). This compound was obtained as a by-product in the demethylation reaction described above. It was also obtained from **8c** as described below.

A. A sample, 15.5 mg (0.097 mmol), of 75% **8c** (25% **8t**) and 4.9 mg (0.052 mmol) of potassium phenoxide in 0.5 mL of ethanol was sealed in a Pyrex ampule and heated at 121 °C for 20 h. The solution was acidified with 2% hydrochloric acid, and then was extracted with ether. The ether extract was dried and concentrated, then the residual material was analyzed by GLC, SE-30 column at 160 °C. The product consisted of 34% of a mixture of 50% **8c** and 50% **8t**, 45% of **10**, and 18% of a material having the same retention time as **9**.

B. A second sample of the mixture containing 75% **8c** and 25% **8t**, 2 mg in 0.3 mL of ethanol, was heated at 121 °C for 20 h. The product contained 74% of the mixture of **8c** and **8t** plus 26% of **10**.

A pure sample of **10** was dimorphic: mp 79–81 °C (large prisms), 87–90 °C (needles); UV max (EtOH) (273 nm (ε 2240), 220 sh, in presence of added potassium hydroxide, 294 (2740), 240 (8350)); IR (CHCl₃) 3592, 2400 (broad) 1611, 1591, 1280 cm⁻¹; NMR (CDCl₃) δ 2.2–2.5 (m, 2 H), 2.97 (t, 2 H, *J* = 6 Hz), 3.4–3.6 (m, 2 H), 4.73 (s, OH), 5.4–5.9 (m, 2 H), 6.58 (d, 1 H, *J* = 7 Hz), 6.76 (d, 1 H, *J* = 7 Hz), 6.97 (t, 1 H, *J* = 7 Hz); mol wt (mass spectrum peak match) 160.089 (calcd for C₁₁H₁₂O, 160.090).

6,7,8,9-Tetrahydro-5H-benzocyclohepten-1-ol. Hydrogenation of 6.098 mg (3.81 × 10⁻⁵ mol) of **10** in 2 mL of ethanol over 10.2 mg of platinum oxide in a commercial model of the microhydrogenation apparatus of Clauson-Kaas and Limborg⁴⁴ used 3.26 × 10⁻⁵ mol (86%) of hydrogen. Normal workup and isolation by preparative GLC (SE-30 column at 160 °C) gave 6,7,8,9-tetrahydro-5H-benzocyclohepten-1-ol: mp 113–115 °C (lit.²⁸ mp 111–112 °C); NMR (CDCl₃) δ 1.4–1.9 (m, 6 H), 2.7–2.9 (m, 4 H), 4.6 (s, OH), 6.5–7.1 (m, 3 H), in agreement with recorded NMR spectrum.²⁷

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Rates of the Cope Rearrangement of Some 2-Aryl-1,5-hexadienes

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Abstract: A series of 2-*p*-X-phenyl-1,5-hexadienes (**2a**, X = H; **2b**, X = Me; **2c**, X = OMe; and **2d**, X = Cl) have been prepared with 3,3-*d*₂ labels and the rates of their Cope rearrangements have been determined in perdeuterated cyclohexane at 164 °C. The measured rates in s⁻¹ × 10⁵ follow: **2a**, 5.1; **2b**, 2.3; **2c**, 6.0; **2d**, 5.9. A sample of 2-phenyl-3-methyl-1,5-hexadiene (**3**) was also prepared and its rate of rearrangement was 1.8 × 10⁻⁵ s⁻¹. The rate data do not give a linear Hammett plot. The relation between these results and the mechanism of the Cope rearrangement is discussed.

Introduction

The mechanisms of the Cope and Claisen rearrangements must certainly be the most thoroughly investigated of all "concerted" thermal reactions.¹ Despite all of this study, the mechanism of the Cope rearrangement is once again in a fluxional state,^{2,3} perhaps an inevitable state for all mechanisms. The long series of careful studies of the mechanism during the 1950s and 1960s culminated in the general acceptance of a six-membered ring transition state of chairlike conformation as the single state, aside from reactant and product, needing specification to delineate the reaction surface. Several years ago we needed a relatively fixed mechanistic system to provide a sort of comparison standard against which to judge some related mechanistic information, and we seized on the Cope rearrangement as a stable choice. Briefly the problem was this. The calculated geometry for the transition state of the hexatriene electrocyclization led us to expect some special rate influence of radical stabilizing substituents at C₂ (or C₅) in *cis*-hexatriene.^{4,5} As a comparison standard we chose the Cope rearrangement, where in the transition state C₂ was presumed to be acting as a sort of electronic pivot permitting transmission of the π bond from one side to the other of that

atom in fully symmetric fashion. As our study was being completed, evidence both permissive² and suggestive³ was presented for the possible intervention of a 1,4-cyclohexadiyl diradical intermediate in the Cope rearrangement. A posteriori we have found the results of our work with a series of 2-aryl-1,5-hexadienes quite pertinent to this question and would like to present here some arguments in favor of retaining the single transition state mechanism.

Synthesis of Substrates

The Cope rearrangement of 2-aryl-1,5-hexadienes is a degenerate process, and to follow the rate of reaction requires an isotopic label. Thus while 2-phenyl-1,5-hexadiene is well known,⁶ the normal synthetic route from α-bromomethylstyrene cannot be conveniently adapted to preparation of the labeled molecule. The route chosen (Scheme I) was devised to permit simple and economical labeling at C₃ and also to permit preparation of a series of substrates with substituents in the para position of the phenyl ring. No major problems were encountered in execution of the synthesis, although the predictable diallylation, a side reaction in the first step, was responsible for some irritatingly low yields. We also found it