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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*<sub>2</sub> labels and the rates of their Cope rearrangements have been determined in perdeuterated cyclohexane at 164 °C. The measured rates in s<sup>-1</sup> × 10<sup>5</sup> 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<sup>-5</sup> s<sup>-1</sup>. 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

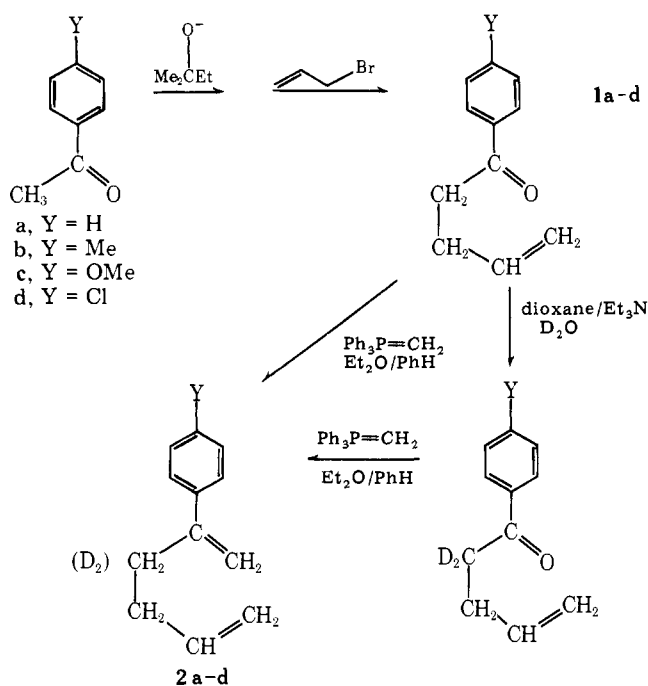
The mechanisms of the Cope and Claisen rearrangements must certainly be the most thoroughly investigated of all "concerted" thermal reactions.<sup>1</sup> Despite all of this study, the mechanism of the Cope rearrangement is once again in a fluxional state,<sup>2,3</sup> perhaps an inevitable state for 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 C<sub>2</sub> (or C<sub>5</sub>) in *cis*-hexatriene.<sup>4,5</sup> As a comparison standard we chose the Cope rearrangement, where in the transition state C<sub>2</sub> 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 permissive<sup>2</sup> and suggestive<sup>3</sup> 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,<sup>6</sup> 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 C<sub>3</sub> 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

Scheme I



necessary to choose the Wittig reaction conditions carefully, because use of the dimsyl anion in  $\text{Me}_2\text{SO}$ <sup>7</sup> resulted in significant loss of deuterium from labeled samples.

Compound **1a** is known<sup>8</sup> and the properties of our sample were in complete accord with published data. The remaining ketones **1b-d** were identified by their spectral properties, which showed only the expected changes from the spectra of **1a**. All of the dienes were completely identifiable from their NMR spectra, with deuteration producing the expected changes in each case. Thus, for example, **2a** has an NMR spectrum having a five-proton multiplet at 7.23 (phenyl), a two-proton triplet at 2.50 ( $\text{CH}_2$  at  $\text{C}_3$ ), a two-proton multiplet at 2.15 ( $\text{CH}_2$  at  $\text{C}_4$ ), a single-proton multiplet at 5.73 (CH at  $\text{C}_5$ ), and a complex set of bands centered at 5.0 ppm (4 H,  $\text{CH}_2\text{S}$  at  $\text{C}_1$  and  $\text{C}_6$ ). The spectrum of the deuterated sample of **2a** showed no absorption at 2.50 ppm and the multiplet at 2.15 ppm was collapsed to a clean doublet. The NMR analyses indicated that **2a-d** were greater than 98% doubly deuterated, i.e., no measurable absorption was found in the 2.50-ppm region in any sample used in the kinetic study.

In addition to **2a-d** we prepared and rearranged 3-methyl-2-phenyl-1,5-hexadiene (**3**). Compound **3** was prepared from propiophenone by a route analogous to that of Scheme I, no deuteration being needed in this case. The diastereotopic protons at  $\text{C}_4$  of 2-methyl-1-phenyl-4-penten-1-one showed clearly separated resonances at 2.16 and 2.51 ppm, which helps confirm the structure of that intermediate. However, in the spectrum of the diene **3** the bands resulting from the diastereotopicity of these protons were no longer separable and thus this characteristic structural feature could not be confirmed. Otherwise the spectral properties of **3** were in full agreement with the proposed structure.

### Kinetic Studies and Results

Rates of the Cope rearrangements of the deuterated **2a-d** were determined in dilute solution in perdeuterated cyclohexane using an ampule technique. A trace of diphenylamine was added to inhibit polymerization.<sup>9</sup> Rearrangement was followed by NMR using the decrease in the number of terminal olefinic protons to monitor the disappearance of *3,3-d\_2* reactant. The cleanly separated multiplet near 5.75 ppm was used as the internal reference standard. Reaction was followed to equilibrium, and in all cases the rates were accurately first

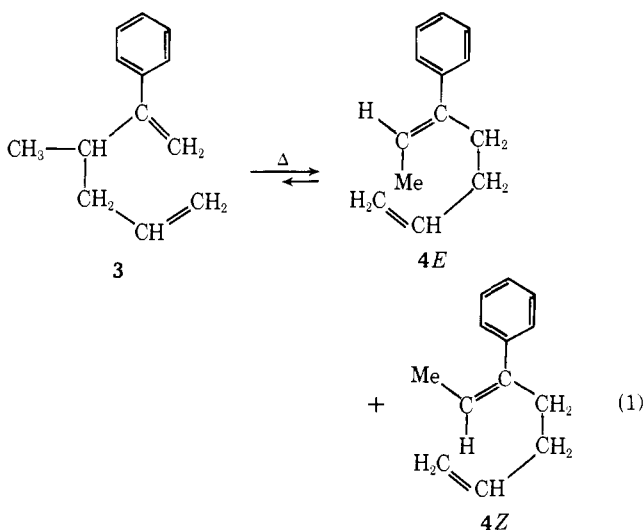
Table I. Rates of the Cope Rearrangement of 2-Aryl-1,5-hexadienes in Cyclohexane at 164 °C

Compd	$k_1 \times 10^5, \text{s}^{-1}$	Rel rate <sup>b</sup>
<b>2a</b> (H)	$5.1 \pm 0.7^a$	80
<b>2b</b> (Me)	$2.33 \pm 0.13$	38
<b>2c</b> (OMe)	$6.0^c$	90
<b>2d</b> (Cl)	$5.9 \pm 1.3$	90
<b>3</b>	$1.82 \pm 0.05$	27 (5.5) <sup>d</sup>

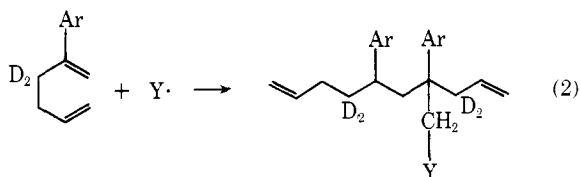
<sup>a</sup> 95% confidence limits. <sup>b</sup> Relative to 1,5-hexadiene,<sup>4</sup> but corrected for reaction in the condensed phase (see text). <sup>c</sup> All four data points agree to two significant figures; thus error analysis would be misleading. <sup>d</sup> Value in parentheses is relative to 3-methyl-1,5-hexadiene corrected to the solvent phase.

order in reactant. Following the procedure adopted by Doering<sup>2</sup> we have neglected the isotope effect in calculating the rate constants, i.e., it is assumed that  $k_{\text{obsd}} = k_1 + k_{-1}$  and  $k_1 = k_{-1}$ . During the reaction the change in number of terminal olefinic protons is close to one, that is from ca. 3.98 initially to ca. 3.05 at equilibrium. Consequently the analysis is critically dependent upon the accuracy of the integration, so analyses of each sample were made in duplicate and each spectrum was integrated three times. The results are given in Table I, and as the error limits indicate the rate constants are of moderate accuracy only. However, Dewar and Wade<sup>3</sup> have measured the rate of rearrangement of **2a** (in *o*-dichlorobenzene) and they report a value of  $k_1 = 6.6 \times 10^{-5} \text{s}^{-1}$  at 165 °C. The excellent agreement between the two values lends confidence in both results.

Owing to the expense incurred for the perdeuterated solvent, we were able to make two runs with **2a** and **2b** and only one each for **2c** and **2d**. In view of this and of the moderate accuracy achieved by the NMR analysis we decided to add a further example which would permit an alternative mode of analysis. Compound **3** was therefore prepared and its rate of rearrangement was determined with cyclohexane as solvent and using GLC as the analytical method. Rearrangement of **3** does not proceed to completion, but to equilibrium (**3**  $\rightleftharpoons$  **4**) with  $K = 4.0$ . The reaction could lead to a mixture of *4-E* and *4-Z* isomers (eq 1), and even though the GLC analysis of the



product showed only a single symmetric peak, we believe that both isomers were formed.<sup>11</sup> Originally we had been concerned about the possible problem of dimer (or oligomer) formation from the styrene double bond, which could lead to a reduction of the ratio of terminal olefinic protons to the standard (eq 2). With the NMR analysis this could lead to an overestimate of the reaction rate. While the equilibrium value of 3.05 obtained



in the NMR analyzed runs indicates that the problem did not arise, the result with 3 where such a reaction could be monitored proves again its absence and the clean nature of the Cope rearrangement under these conditions.

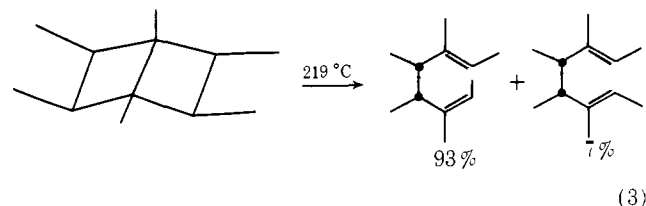
In Table I the results found in this investigation have been converted to relative rates. The careful study of the rate of 1,5-hexadiene in the gas phase by Doering, Toscano, and Beasley<sup>2</sup> was used as the comparison standard. It has generally been assumed that the rates of concerted reactions of hydrocarbons in the gas phase and in nonpolar solvents are quite comparable, but in the present case we have used the experimental result of a study of 3-phenyl-1,5-hexadiene in both solvent and gas phase<sup>3</sup> instead. Dewar and Wade found, rather unexpectedly, that 3-phenyl-1,5-hexadiene rearranges four times faster in a condensed phase (*o*-dichlorobenzene) than in the gas phase. This result removes the apparent inconsistency between the results of Doering et al.<sup>2</sup> and the earlier study of 1,5-hexadiene by Humski, Malojcic, Borcic, and Sunko.<sup>12</sup> The latter study was carried out with neat samples in sealed ampules. Since the factor of 4 between the rates in solvent and in the gas phase appears both in the direct study of Dewar and Wade and also with the Doering and Borcic-Sunko results, we have used this factor in comparing our results with those of Doering even though our solvent differs from those used in the other studies.

## Discussion

Mechanistic considerations of the Cope rearrangement have ranged from (a) cleavage of the diene into two allyl radicals followed by subsequent recombination, (b) passage through a single transition state with partial bonding between C<sub>1</sub>-C<sub>6</sub> and C<sub>3</sub>-C<sub>4</sub> of the diene skeleton and possessing either a chair or a boat conformation, to (c) the generation of a 1,4-cyclohexadiyl diradical intermediate. The mainstream view has been that the normal route ("low-temperature reaction") proceeds via alternative (b) using the chair conformation. The boat form transition state provides a competitive route only at a higher temperature ("intermediate temperature reaction"), and alternative (a) intervenes at still higher temperatures.<sup>13-15</sup> The diradical route appears to have been a casualty of neglect, and Doering in his recent careful study of the kinetics of rearrangement of 1,5-hexadiene has resurrected the diradical largely via thermochemical considerations.<sup>16</sup> Dewar and Wade<sup>3</sup> have supplied some experimental evidence which was interpreted as supporting the diradical route, at least for appropriately substituted hexadienes. Dewar has also carried out some calculations which have led to the postulation of a wider range for the diradical mechanism.<sup>10</sup>

In the present context the mechanistic problem can be simplified by considering only the chair form and ignoring the boat form, whether transition state or diradical. Then one question is: does the energy surface generated by bringing together two allyl radicals properly aligned geometrically and phasewise run smoothly downhill to the 1,4-cyclohexadiyl diradical, or is there a minimum corresponding to an intermediate geometry and the transition state? Presumably there must exist a minimum for the diradical, so the experimental problem is to ascertain whether there exists a transition state, an intermediate, or both. One test to apply depends on the possible partitioning of an intermediate among several decomposition routes. This test was applied indirectly by Roth and Martin,<sup>18</sup> who found that thermal decomposition of

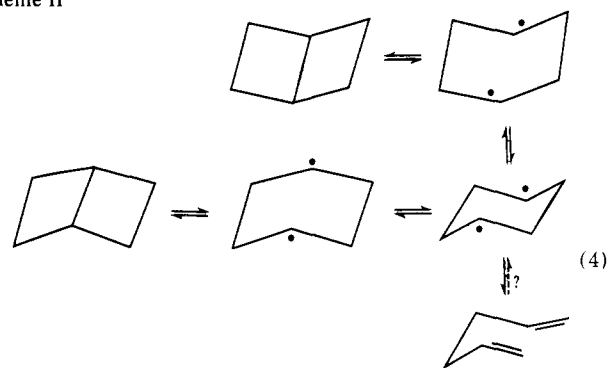
stereoisomeric 5,6-dimethyl-2,3-diaza-2-bicyclo[2.2.2]octenes, presumably via a 1,4-cyclohexadiyl diradical,<sup>19</sup> gave products not observed during the Cope rearrangement of *meso*- or *dl*-3,4-dimethyl-1,5-hexadiene.<sup>25</sup> It was considered that the diradical did partition, but the Cope rearrangement of *meso*- or *dl*-3,4-dimethyl-1,5-hexadiene.<sup>25</sup> It was considered that the diradical did partition, but the Cope rearrangement did not lead to partitioning. A recent study of *all-exo*-hexamethyl[2.2.0]hexane showed that at 219 °C decomposition gave two dienes (eq 3).<sup>21</sup> Reaction is presumed to proceed



via a 1,4-cyclohexadiyl diradical,<sup>22</sup> and once again the reaction was not stereospecific. Goldstein and Benzon<sup>23</sup> found that *all-exo*-2,3,5,6-tetradeuteriobicyclo[2.2.0]hexane decomposed completely stereospecifically between 135 and 180 °C, and that return to the bicyclic molecule was competitive with cleavage to the diene.

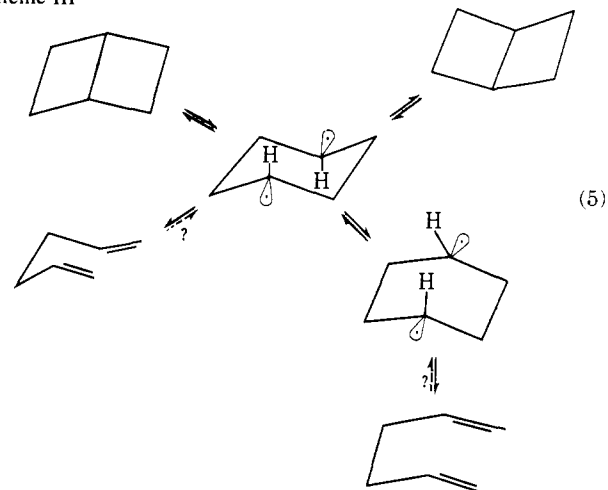
These results have been conventionally interpreted as necessitating the series of steps shown in Scheme II, but recently

Scheme II



a theoretical study<sup>24</sup> of the 1,4-cyclohexadiyl diradical suggested the revised route of Scheme III. The data of Sinnema et al.<sup>21</sup> show that for the hexamethyl derivative the free-energy difference for direct decomposition of the chair diradical to diene and indirectly via the boat diradical is only 2.5 kcal/mol. Both Doering and Roth<sup>25</sup> and Goldstein and Benzon<sup>13</sup> found

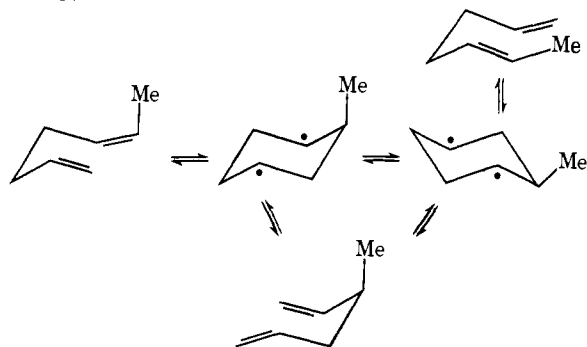
Scheme III



the free-energy difference between chair and boat routes for the Cope rearrangement to be close to 5.7 kcal/mol. If the mechanism of Scheme III is correct, the free-energy barrier

between chair and boat diradicals cannot exceed 2.5–3.0 kcal/mol.<sup>26</sup> The value seems reasonable based on the expected free-energy barrier for chair–chair interconversions of a cyclohexane with two trigonal atoms in a 1,4 orientation.<sup>27</sup> Thus if the diradical acts as an intermediate in the Cope rearrangement, the conformational interconversion of the diradical might well occur prior to decomposition to diene. Such a conformational interconversion would permit a route to *cis*–*trans* isomerization of a hexadiene without Cope rearrangement (Scheme IV). Frey and Solly<sup>30</sup> examined the thermal behavior

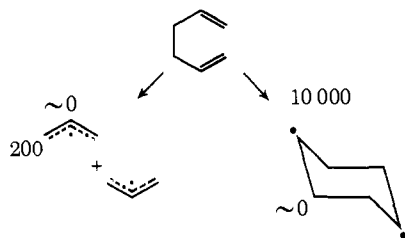
Scheme IV



of *cis*- and *trans*-1,5-heptadienes and 3-methyl-1,5-hexadiene in considerable detail, and they did not find any clearly identifiable *cis* → *trans* isomerization independent of the Cope rearrangement.<sup>31</sup> In summary it can be said that the evidence does not *establish* that the Cope rearrangement involves a transition state rather than the diradical intermediate but it is supportive of such a conclusion.

A second approach to testing whether the Cope rearrangement involves a transition state or a diradical intermediate depends on structure–reactivity relations. The problem here is to provide clean a priori differences between the rate responses to substituents for the transition state and for the diradical. We consider that the transition state is potentially a very variable entity, having possible structures, symmetrical or unsymmetrical, with a six-membered ring nearly dissociated into two allyl radicals at one extreme and almost fully converted to a 1,4-cyclohexadiyl diradical at the other. When the allyl radicals can be experimentally identified (by cross coupling) or when an experimentally identifiable intermediate is found, we would concede that the single transition state route was no longer tenable. In our view then it is easier to set up some numerical estimates for the rate effect of a phenyl group at various positions on the extreme situations, and to consider that the transition state effects must be between these. Scheme V shows these rate effects diagrammatically (calculated at 450

Scheme V



K). The value of 200× for the terminal position was derived using a minimum stabilization energy for a cinnamyl radical of 5.0 kcal/mol more than that of an allyl radical.<sup>32</sup> Similarly the 10 000× figure for the diradical was based on the assumption that  $\frac{2}{3}$  of the benzyl radical stabilization energy of ca. 12–13 kcal/mol<sup>33</sup> would be available at the transition state leading to the diradical. Certainly we view these numbers as order of magnitude indicators rather than values to be met if the extremes are to be accepted.

We will now turn to a consideration of our results and those of Dewar and Wade.<sup>3</sup> There are four important pieces of information to be derived from our data. First, an aromatic substituent at C<sub>2</sub> produces a rather large rate increase. Second, the rates for the series of substituted phenyl substituents do not give a satisfactory Hammett plot either with  $\sigma$  or  $\sigma^+$ , and the plot of  $\log k$  vs.  $\sigma$  is curved, being concave upward. Third, the influence of the para substituents on the rate is small, the rate variation from methyl to chlorine being about 2.5. Fourth, the presence of a methyl group at C<sub>3</sub> reduces the effectiveness of a phenyl group at C<sub>2</sub> by a very significant amount. How well do these fit the pattern expected of the diradical route? We consider the magnitude of the rate acceleration of the phenyl group to be much too small, perhaps by two orders of magnitude. In the same vein we view the factor of 4 between the rates for phenyls at C<sub>2</sub> and C<sub>3</sub><sup>3</sup> to be much smaller than should be expected for the diradical. If the diradical were involved we would expect a satisfactory Hammett plot with either  $\sigma$  or  $\sigma^+$ , since radical formation by hydrogen abstraction from substituted toluenes gives satisfactory correlations.<sup>34</sup> The small effect of substituents is appropriate for radical reactions,<sup>34</sup> where  $\rho$  values of ca. –0.1 to –0.6 are common; however, the influence of substituents in our case is in the reverse direction, i.e., electron-attracting substituents increase the rate. We conclude that our results do not support the diradical route.

How well do our results fit the pattern expected of the concerted, single transition state mechanism? The question is not simple to answer, since we have no other experimental model on which to base predictions. Functionally the C<sub>2</sub> atom is the central atom of a three-atom system in which a  $\pi$  bond is moved from one side of the center atom to the other. Considered in this simple sense it is the  $\pi$  equivalent of the central carbon of an S<sub>N</sub>2 substitution where a  $\sigma$  bond is moved from one side of that atom to the other. Aromatic substitution on the S<sub>N</sub>2 central carbon accelerates the reaction by about 100 times, the Hammett plots for meta- and para-substituted phenyl substituents are not linear but are curved and indeed are concave upward, and the influence of substituents such as chlorine, methyl, methoxyl is small, being in the range of two- to threefold.<sup>35</sup> In essence the behavior of the two systems is indeed very much alike. We conclude that in both cases the phenyl group can stabilize an orbital which is partly involved in bonding to other atoms, and that in both cases the change in electron density at the central carbon is small but can vary in response to substituent effects. The observed patterns are reasonable for transition states.

A methyl substituent at C<sub>3</sub> enhances the rate of the Cope rearrangement.<sup>30</sup> However, **3** reacts three times more slowly than **2a**, or to place it in better context, the addition of a phenyl group to C<sub>2</sub> in 3-methyl-1,5-hexadiene increases the rate only about fivefold. Thus the phenyl group is now 15 times less effective than in the C<sub>3</sub>–H example. Clearly the 3-methyl group causes severe steric inhibition of conjugation of the phenyl group. This result is compatible with either mechanism.

At this time the evidence concerning the mechanism of rearrangement of 2-aryl-1,5-hexadienes seems to us to be inconclusive. The presently available data are quite reasonably interpreted by the concerted single transition state route so we see no compelling reason to adopt a new mechanism. However, we agree with Dewar and Wade that the evidence does reduce the latitude of structural possibilities for the transition state to those having more resemblance to the diradical than to two separated allyl radicals.

## Experimental Section

**1-Phenyl-4-penten-1-one (1a).** All of the arylpentenones were prepared by the procedure of Vavon and Conia,<sup>36</sup> and the general process is described below for **1a**. A 1.8 N solution (275 mL) of sodium *tert*-

amylate was added dropwise to a mixture of 60.0 g (0.5 mol) of acetophenone and 66 g (0.55 mol) of allyl bromide in 200 mL of toluene. The reaction mixture was cooled in an ice bath during the addition and afterwards was heated to reflux for 2 h. The reaction mixture was washed thoroughly with water and the organic materials were taken up in ether. The ether extracts were dried (CaCl<sub>2</sub>) and the solvents were removed in vacuo. The residue was fractionated with a 45-cm spinning band column giving 37.8 g (35%) of **1a**: bp 108.2–108.8 °C (5 mm) [lit.<sup>6</sup> bp 140 °C (9 mm)]; IR (neat) 1680, 1640, 912, 745, 690 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) δ 7.82 (m, 2 H), 7.32 (m, 3 H), 5.78 (m, 1 H), 4.92 (m, 2 H), 2.90 (t, 2 H, *J* = 7 Hz), 2.42 (m, 2 H).

**1-(*p*-Tolyl)-4-penten-1-one (1b)**. Preparation as above on a 0.5 molar scale gave 15% of **1b**: bp 62.5 °C (0.02 mm); UV max (95% EtOH) 242 nm (ε 9580); IR (neat) 1680, 1640, 912, 825, 806, 780 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) δ 2.36 (s, 3 H), 2.42 (m, 2 H), 2.92 (t, 2 H, *J* = 7 Hz), 4.98 (m, 2 H), 5.82 (m, 1 H), 7.16 (d, 2 H, *J* = 8 Hz), 7.76 (d, 2 H, *J* = 8 Hz). Anal. Calcd for C<sub>12</sub>H<sub>14</sub>O: C, 82.72; H, 8.10. Found: C, 82.89; H, 8.46.

**1-(*p*-Anisyl)-4-penten-1-one (1c)**. Run on a 0.5-molar scale this preparation gave 30% of **1c**: bp 106 °C (0.5 mm); UV max (95% EtOH) 272 nm (ε 16 200); IR (neat) 1675, 1640, 1258, 1210, 1030, 912, 838 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) δ 2.40 (m, 2 H), 2.88 (t, 2 H, *J* = 7 Hz), 3.80 (s, 3 H), 4.98 (m, 2 H), 5.78 (m, 1 H), 6.80 (d, 2 H, *J* = 8 Hz), 7.80 (d, 2 H, *J* = 8 Hz). Anal. Calcd for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>: C, 75.76; H, 7.42. Found: C, 76.07; H, 7.41.

**1-(*p*-Chlorophenyl)-4-penten-1-one (1d)**. Preparation gave 30% of **1d**: bp 80–82 °C (0.07 mm); UV max (95% EtOH) 250 nm (ε 19 900); IR (neat) 1680, 1640, 912, 838, 795, 760, 733 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) δ 2.43 (m, 2 H), 2.94 (t, 2 H, *J* = 7 Hz), 4.98 (m, 2 H), 5.83 (m, 1 H), 7.34 (d, 2 H, *J* = 8 Hz), 7.82 (d, 2 H, *J* = 8 Hz). Anal. Calcd for C<sub>11</sub>H<sub>11</sub>Cl: C, 67.87; H, 5.69. Found: C, 67.97; H, 5.69.

**2-Methyl-1-phenyl-4-penten-1-one**. Reaction of 67 g (0.50 mol) of propiophenone with allyl bromide as described above gave 79% of 2-methyl-1-phenyl-4-penten-1-one: bp 73–74 °C (0.15 mm); UV max (95% EtOH) 242 nm (ε 9860); IR (neat) 1680, 1640, 914, 792, 703 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) δ 1.16 (d, 3 H, *J* = 6 Hz), 2.16 (m, 1 H), 2.51 (m, 1 H), 3.41 (m, 1 H), 4.98 (m, 2 H), 5.72 (m, 1 H), 7.40 (m, 3 H), 7.86 (m, 2 H). Anal. Calcd for C<sub>12</sub>H<sub>14</sub>O: C, 82.72; H, 8.10. Found: C, 82.68; H, 8.00.

**Deuteration**. Ketones **1a–d** were deuterated by the procedure of Shiner, Buddenbaum, Murr, and Lamaty.<sup>37</sup> Two grams of ketone, 0.6 g of anhydrous triethylamine, and 2.0 g of deuterium oxide (99.8% D) in 20 mL of anhydrous dioxane was heated to reflux for 17 h, after which the water was removed slowly as the dioxane azeotrope, bp 87–88 °C. The ketone was isolated and the above process was repeated twice more, or until the NMR spectrum showed that the CH<sub>2</sub> triplet near 2.90 ppm had disappeared and the multiplet near 2.42 ppm was replaced by a clean doublet, *J* ≈ 6 Hz.

**2-Phenyl-1,5-hexadiene-3,3-*d*<sub>2</sub> (2a)**. To a solution containing 0.0125 mol of phenyllithium in a mixture of 50 mL of benzene and 30 mL of ether was added 4.46 g (0.0125 mol) of methyltriphenylphosphonium bromide, and the mixture was stirred for 5 h. A solution containing 2.0 g (0.0125 mol) of **1a** (3,3-*d*<sub>2</sub>) in 10 mL of benzene was added dropwise and the mixture was heated under reflux for 12 h. A little deuterium oxide (0.5 g) and 100 mL of pentane were added, and the organic layer was separated and dried (MgSO<sub>4</sub>). The solvent was removed and the product was purified by GLC on a 15 ft × 1/4 in. column of 5% FFAP on Chromosorb G: UV max (95% EtOH) 238 nm (lit.<sup>8</sup> 238 nm); IR (neat) 695, 763, 910, 1000, 1625, 2110, 2210 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) δ 2.15 (d, 2 H, *J* = 6 Hz), 4.99 (m, 4 H), 5.73 (m, 1 H), 7.23 (m, 5 H).

**2-(*p*-Tolyl)-1,5-hexadiene (2b)**. This compound was prepared in both protiated and deuterated form by the procedure described above. The protiated form was prepared in 72% yield: UV max (95% EtOH) 243 nm (ε 11 000); IR (neat) 822, 914, 1680 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) δ 2.29 (s, 3 H), 2.20 (m, 2 H), 2.49 (t, 2 H, *J* = 7 Hz), 4.93 (m, 4 H), 5.70 (m, 1 H), 6.99 (d, 2 H, *J* = 8 Hz), 7.17 (d, 2 H, *J* = 8 Hz). Anal. Calcd for C<sub>13</sub>H<sub>16</sub>: C, 90.64; H, 9.36. Found: C, 90.79; H, 9.30.

The deuterated form 3,3-*d*<sub>2</sub> was prepared similarly from **1b**-3,3-*d*<sub>2</sub> and except for disappearance of the triplet at 2.49 ppm and conversion of the multiplet at 2.20 ppm to a clean doublet, *J* = 6 Hz, the physical properties were identical with those noted above.

**2-(*p*-Anisyl)-1,5-hexadiene (2c)**. This diene was prepared as above in 65% yield from **1c**: UV max (95% EtOH) 272 nm (ε 16 200); IR (neat) 832, 910, 1248, 1640 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) δ 2.15 (m, 2 H), 2.49 (t, 2 H, *J* = 7 Hz), 3.73 (s, 3 H), 4.93 (m, 4 H), 5.75 (m, 1 H), 6.71

(d, 2 H, *J* = 8 Hz), 7.21 (d, 2 H, *J* = 8 Hz). Anal. Calcd for C<sub>13</sub>H<sub>16</sub>O: C, 82.94; H, 8.27. Found: C, 82.89; H, 8.46.

Prepared in similar manner **2c**-3,3-*d*<sub>2</sub> had identical properties except that the triplet at 2.49 ppm was missing from the NMR spectrum and a doublet, *J* = 6 Hz, appeared at 2.15 ppm.

**2-(*p*-Chlorophenyl)-1,5-hexadiene (2d)**. Prepared from **1d** by the Wittig procedure above, **2d** was obtained in 68% yield: UV max (95% EtOH) 246 nm (ε 10 400); IR (CCl<sub>4</sub>) 892, 910, 1640 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) δ 2.15 (m, 2 H), 2.51 (t, 2 H, *J* = 7 Hz), 5.01 (m, 4 H), 5.73 (m, 1 H), 6.97 (s, 4 H). Anal. Calcd for C<sub>12</sub>H<sub>13</sub>Cl: C, 74.80; H, 6.80. Found: C, 74.63; H, 6.85.

A sample of **2d**-3,3-*d*<sub>2</sub> had an NMR spectrum missing the triplet at 2.51 ppm and a doublet, *J* = 6 Hz, at 2.15 ppm.

**3-Methyl-2-phenyl-1,5-hexadiene (3)**. Reaction of 2-methyl-1-phenyl-4-penten-1-one with methylenetriphenylphosphorane as described above gave **3** in 76% yield: UV max (95% EtOH) 233 nm (ε 10 000); IR (CCl<sub>4</sub>) 890, 910, 1640 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) δ 1.10 (d, 3 H, *J* = 6 Hz), 2.12 (m, 2 H), 2.71 (m, 1 H), 4.98 (m, 4 H), 5.69 (m, 1 H), 7.18 (s, 5 H). Anal. Calcd for C<sub>13</sub>H<sub>16</sub>: C, 90.64; H, 9.36. Found: C, 90.45; H, 9.20.

**3-Phenyl-2,6-heptadiene**. A 98-mg sample of **3** was dissolved in 3 mL of cyclohexane, and the solution was heated in a sealed tube for 40 h at 190 °C. The product was collected from the GLC (5% DEGS column at 125 °C): UV max (EtOH) 240 nm (ε 10 700); IR (CCl<sub>4</sub>) 910, 1640 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>) δ 1.80 (d, 3 H, *J* = 6 Hz), 2.06 (m, 2 H), 2.56 (t, 2 H, *J* = 7 Hz), 4.92 (m, 2 H), 5.74 (q with overlapping m, 2 H, *J* = 7 Hz), 7.20 (s, 5 H). Anal. Calcd for C<sub>13</sub>H<sub>16</sub>: C, 90.64; H, 9.36. Found: C, 90.52; H, 9.35.

**Kinetic Studies**. Rates of the degenerate Cope rearrangements of **2a–d** were followed by the decrease in the number of vinyl protons and increase in the number of methylene protons in the NMR spectra. All integrations were performed in triplicate and were averaged. Runs were made using 5% solutions of substrate in cyclohexane-*d*<sub>12</sub> (99.5% D) containing a trace of diphenylamine. Solutions were placed in cleaned and dried Pyrex ampules, degassed by freeze-thaw cycles, and sealed under vacuum. Ampules were heated in a thermostated bath at 164.0 ± 0.1 °C. *A*<sub>0</sub> values were obtained on the original solutions and *A*<sub>∞</sub> values were derived from samples heated for 12–14 h. During the study of **2c** two samples gave erratic results when integration of the olefinic protons was used, but the integrations of the methylene protons gave consistent results and these were used in place of the olefinic integrations.

Rate of rearrangement of **3** was determined using solutions in cyclohexane containing 10% biphenyl as internal standard and a trace of diphenylamine. Solutions were sealed in ampules and heated as above, and analysis was performed on a 5% DEGS column on Chromosorb G at 150 °C. Rearrangement on the column was shown to be negligible, and areas were determined with a Disc integrator.

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- We are indebted to Professor Dewar for preprints of the full paper by Dewar and Wade and a second paper on some theoretical studies of the Cope rearrangement by MINDO/3.
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## Absolute Rate Constants for Reactions of Phenyl Radicals<sup>1</sup>

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**Abstract:** The absolute rate constant for the addition of *p*-carboxyphenyl radical to *p*-bromobenzoate anion in aqueous solution has been determined by optical pulse radiolysis and time-resolved ESR experiments to be  $7.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  (corrected to zero ionic strength). The rate constants for addition of phenyl radicals to typical aromatic systems should be of this same magnitude. Addition of *p*-carboxyphenyl radical to benzene occurs with a similar rate constant and results in the formation of a substituted cyclohexadienyl radical that can be quantitatively oxidized to biphenyl-4-carboxylic acid. Abstraction from hydrogen donors results in the quantitative formation of benzoic acid. By reference to the absolute rate for addition to *p*-bromobenzoate the rate constant for H abstraction from isopropyl alcohol has been determined from competitive measurements of benzoic acid formation to be  $5.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . Measurements by optical pulse radiolysis and time-resolved ESR methods give comparable values. H atom abstraction from other alcohols is found to be only modestly slower. It is clear from these measurements that the lifetime of phenyl radicals in the presence of most organic materials will usually be very low so that reactions second order in phenyl radicals will not normally be important.

### Introduction

In spite of the considerable importance of the reactions of phenyl radicals in organic chemistry,<sup>2</sup> there have been only a few sporadic attempts to determine the absolute rate constants for these reactions. Cercek and Kongshaug,<sup>3</sup> in pulse radiolysis studies on aqueous solutions of iodobenzene and *p*-bromophenol, attributed increases in the optical absorption at 270 nm to the addition of phenyl and *p*-hydroxyphenyl radicals to the starting materials. In the latter case they estimated a rate constant of  $7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . Bhatia and Schuler<sup>4</sup> used this value as a reference and from relative rate measurements determined a rate constant of  $3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  for abstraction of hydrogen from isopropyl alcohol by the *p*-hydroxyphenyl radical. Packer et al.<sup>5</sup> found that the radiolysis of toluenediazonium cation in aqueous solutions containing methanol induced a chain reaction with the methanol and from an assumed chain length estimated a rate constant  $>10^5$  for

abstraction of H from the methanol by the *p*-methylphenyl radical. Janzen and co-workers using spin trapping methods have estimated the rate constant for addition of phenyl to benzene to be  $10^5 \text{ M}^{-1} \text{ s}^{-1}$  and have determined the relative rates for abstraction of hydrogen from the simple alcohols.<sup>6</sup> Very recently Lorand and coworkers<sup>7</sup> have compared the reactions of phenyl radicals with diffusion limited reactions and have estimated  $3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  for the rate constant for H abstraction from secondary alcohols and  $\sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for addition to benzene. Although it is clear that the rate constants for the reactions of phenyl radicals are considerably greater than those for similar reactions of  $\pi$  radicals, there is at the present time a considerable uncertainty in the literature as to the exact magnitude of the rate constants. Knowledge of the absolute values of these rate constants is important so that one can properly take into account various competing processes and define the limiting phenyl radical concentration attainable in a given experimental situation.