

13 (1.0 g., 0.00382 mole) in 30 ml. of glacial acetic acid. The solution was stirred for 6 hr. at room temperature and worked up as usual. The product was

chromatographed on Woelm neutral alumina (activity III) to give 0.1 g. of recovered 13, and 0.6 g. (0.00273 mole, 73%) of 2,6-di-*t*-butyl-*p*-cresol.

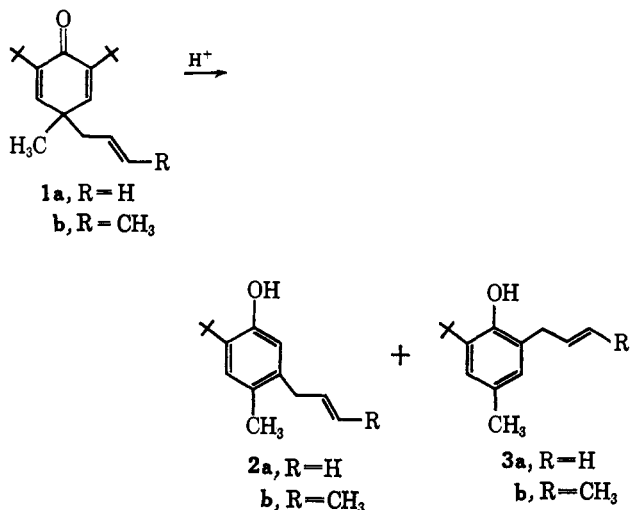
## The Mechanism of 1,3-Migrations of Allyl Groups in the Dienone-Phenol Rearrangements of 2,6-Di-*t*-butylcyclohexadienones<sup>1,2</sup>

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Contribution from the Chemical Research and Development Laboratories, Agricultural Division, American Cyanamid Company, Princeton, New Jersey. Received August 9, 1965

4-Allyl-2,6-di-*t*-butyl-4-methylcyclohexadien-1-one-3,5-*d*<sub>2</sub> was prepared and rearranged in acid. The ratio of the 1,3-rearrangement product to the 1,2-rearrangement product was much higher than in rearrangement of the undeuterated dienone. The hydrogen-deuterium kinetic isotope ratio was greater than 4. The mechanism of the 1,3-rearrangement was thus shown to involve two successive 1,2-shifts of the allyl group. The large isotope effect supports, but does not prove, the deprotonation-reprotonation mechanism for loss of a *t*-butyl group during the 1,2-rearrangement.

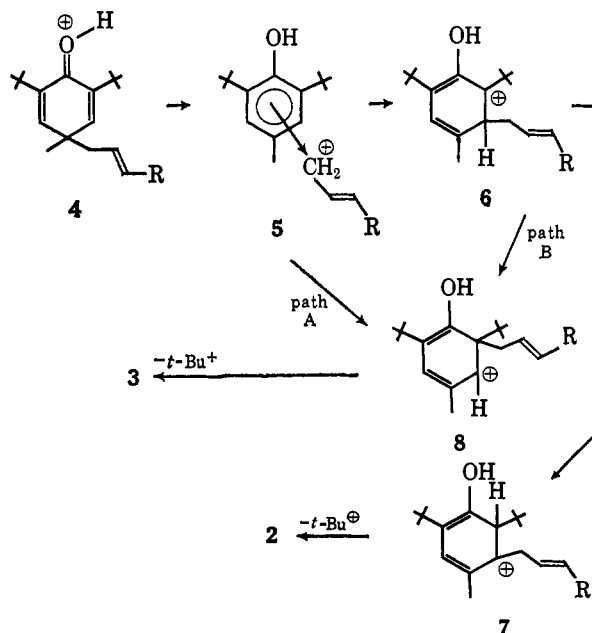
In the preceding paper,<sup>1</sup> it was reported that rearrangement of 2,6-di-*t*-butylcyclohexadienones (1) in acid gave both the products of 1,2- (2) and of 1,3-rearrangements (3), provided that an allyl or 2-butenyl group was present at the 4-position of 1. Both 1,2- and 1,3-rearrangements resulted in loss of a *t*-butyl group from 1.



It was found<sup>1</sup> that both 1,2- and 1,3-rearrangements were intramolecular, and that both rearrangements occurred without allylic rearrangement of the *trans*-2-

butenyl group. The percentage of 1,3-migration appeared to depend on the ability of the migrating group to bear a positive charge, since no 1,3-migration occurred when the migrating substituent was an ethyl group, approximately equal amounts of 1,2- and 1,3-migration took place when an allyl group migrated, and only 1,3-rearrangement of the *trans*-2-butenyl (crotyl) group could be demonstrated. Rearrangement of 1b to 3b, however, was accompanied by loss of the crotyl group to give 2,6-di-*t*-butyl-4-methylphenol in approximately equal amounts.

Two general types of mechanisms, which we will call the single-migration and the double-migration mechanisms, can be written to account for the 1,3-rearrangements. In the single migration mechanism the protonated dienone 4 is converted to an intermediate  $\pi$ -complex (5), in which the migrating group is not



linked to any one carbon of the ring by a  $\sigma$ -bond. Collapse of the  $\pi$ -complex to a "classical" carbonium ion will result in formation of a  $\sigma$ -bond between the migrating group and an adjacent ring carbon.

(1) Reactions of Cyclohexadienones, XII. Preceding paper, part XI: B. Miller and H. Margulies, *J. Am. Chem. Soc.*, **87**, 5106 (1965).

(2) Part of this work has been published as a preliminary communication: B. Miller, *Tetrahedron Letters*, No. 22, 1733 (1965).

If the migrating carbonium ion is of high energy, it should attack the nearest available position, resulting in 1,2-migration to form 6. If the migrating carbonium ion is more stable, collapse of the intermediate might be deferred until the migrating group reached the *ortho* position and a more stable carbonium ion (that is, the protonated 2,4-cyclohexadienone 8) could be formed (path A). Loss of a *t*-butyl group from 8 would give 3. Carbonium ion 6, on the other hand, would have to undergo a further transformation to 7 before losing a *t*-butyl group to give 2.

Other variations of the "single migration mechanism" can be written in which formation of 6 occurs directly from 4, in a step competing with formation of the  $\pi$ -complex 5 rather than following it. It is also conceivable, although rather improbable, that 8 could arise directly from 4 *via* a single transition state, rather than *via* the intermediate 5. All of these possibilities, however, share the characteristic that the first  $\sigma$ -bond formed by the migrating group in the 1,3-rearrangement is at the carbon which will become the *ortho* position of the phenol. The movement of the migrating group to a carbon two atoms away occurs in a single step, rather than by successive 1,2-migrations.

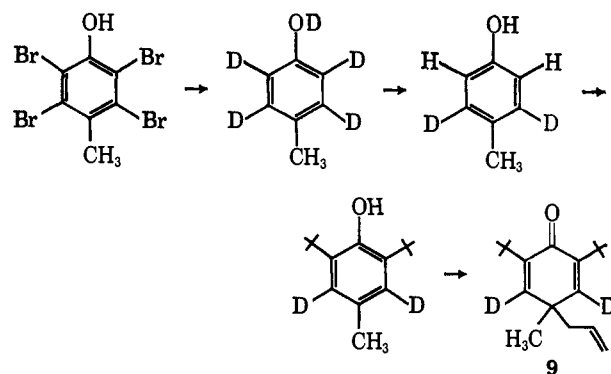
In the alternative "double migration mechanism," the initial step leading to both 1,2- and 1,3-rearrangements is migration of the rearranging group to the *meta* position to give 6. Loss or migration of a hydrogen from 6, of course, would again lead to the 1,2-rearrangement product 2. However, a second 1,2-migration of the allyl or butenyl group (path B) would again lead to 8, and thence to the 1,3-rearrangement product 3.

An essential difference between the single migration and double migration mechanisms is that the ratio of products (2/3) is determined, in the double migration mechanism, by competition between the second migration of the allyl (or crotyl) group and migration of a hydride ion (or loss of a proton) from the *meta* to the *ortho* position. The hydrogen atoms in the 3- and 5-positions of 1, on the other hand, play no part in determining the ratio of 1,2- to 1,3-rearrangement products in the single-migration mechanism. It should be possible, therefore, to distinguish between these two paths by observing the effect of deuterium substitution at the 3- and 5-positions of 1. Rearrangement by a double migration should show a marked deuterium isotope effect, while rearrangement *via* a single migration should show a negligible deuterium isotope effect.

## Results

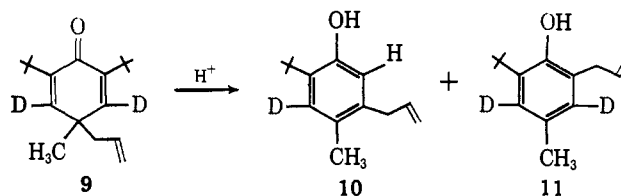
The effect of deuterium substitution upon the ratio of products from rearrangement of 4-allyl-2,6-di-*t*-butyl-4-methylcyclohexadien-1-one (1a) was examined, since a change in the normal 1:1 ratio of 1,2- to 1,3-migrations<sup>1</sup> should be quite easy to detect.

The 3,5-dideuterio analog 9 was synthesized as shown below. The rate of catalytic reduction of 2,3,5,6-tetrabromo-*p*-cresol tended to decrease markedly after absorption of 2 moles of hydrogen or deuterium, but prolonged reduction with deuterium gave *p*-cresol-2,3,5,6-*d*<sub>4</sub> in quantitative yield. In order to avoid incorporation of deuterium into the *t*-butyl groups, the deuterium was removed from the *ortho* positions of the cresol by refluxing with hydrochloric acid. Re-



action with isobutylene catalyzed by sulfuric acid gave 2,6-di-*t*-butyl-*p*-cresol-3,5-*d*<sub>2</sub>. Finally, formation of the anion using potassium *t*-butoxide in *t*-butyl alcohol and alkylation with allyl bromide gave 9. Mass spectroscopic analysis showed the presence of 27.4% monodeuterated 9 and 6.9% deuterium-free 9, indicating that 79.4% of the 3- and 5-positions were occupied by deuterium.

Rearrangement of 9 in an acetic acid solution containing 10% (by volume) of sulfuric acid gave a mixture of two products, which were isolated by v.p.c. The retention times of the two products were identical



with those of 2a and 3a. The n.m.r. spectrum of 11, the product of lower retention time, was identical with that of 3a,<sup>3</sup> except for the virtual absence of aromatic protons. The n.m.r. spectrum of 10, the product of higher retention time, was identical with that of 2a,<sup>1</sup> except for the absence of the *meta* aromatic proton peak at *ca.*  $\tau$  3.1. The *o*-hydrogen peak at  $\tau$  3.65 (in CDCl<sub>3</sub>) was present. No mechanistic significance could be attributed to this, however, since it was shown that exchange of the *ortho* protons under the conditions of rearrangement was appreciably faster than rearrangement. The *ortho* proton of 3a was replaced by deuterium by refluxing for several hours with deuterium oxide containing 3% H<sub>2</sub>SO<sub>4</sub>. Its n.m.r. spectrum showed the absence of the *ortho* proton. After standing in 10% sulfuric acid in acetic acid for 1 hr., the n.m.r. spectrum showed complete replacement of deuterium by protons.

The deuterium-free dienone 1a was rearranged in the same acid mixture used for the rearrangement of 9. The ratios of products of 1,2- and 1,3-rearrangements were determined by v.p.c. Rearrangement of 1a gave 2 and 3 in the ratio 50:50. Rearrangement of 9 gave 10 and 11 in the ratio 26:75. Analyses of products obtained from duplicate rearrangements agreed within 1%.

## Discussion

The large effect of deuterium substitution in the 3- and 5-positions shows that 1,3-migration of the allyl group proceeds through an intermediate in which

(3) B. Miller, *J. Org. Chem.*, 30, 1964 (1965).

breaking a carbon-hydrogen bond can compete with allyl migration. The effect cannot be attributed simply to a reduction in the rate of 1,2-allyl migration by the adjacent deuterium atom. The effect of  $\beta$ -deuterium substitution on solvolysis of alkyl halides and tosylates (which is probably the best model available for the breaking of a C-C bond) is small in all cases.<sup>4</sup> Since the vinyl proton is essentially orthogonal to the bond being broken, its retarding effect on the rate would be abnormally small, and it might even show a small accelerating effect.<sup>4</sup> Whatever effect it has, furthermore, should be approximately the same for the 1,2- and 1,3-rearrangements, since both must involve breaking of the C-C bond. It appears that any effect of the  $\beta$ -deuterium on the initial bond-breaking step can safely be ignored.

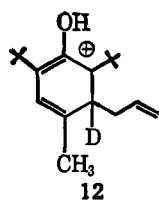
Similarly, Melander<sup>5</sup> has shown that the rate of attack by positive ions at aromatic rings is not affected by substitution of tritium for hydrogen at the position being attacked. Insofar as migration of an allyl carbonium ion to the 3-position can be equated with attack by an external reagent, the effect of deuterium substitution on the migration would similarly be negligible.

Since the effect of deuterium substitution on the initial 1,2-migration of the allyl group can be neglected, migration to either 3-position of a monodeuterated dienone will be equally probable. The hydrogen isotope effect,  $k_H/k_D$ , therefore, will be solely determined by the relative rates of allyl migration and of deuterium or hydrogen loss in carbonium ion **6**. When  $k_{\text{allyl}}$  is the rate of migration of an allyl group from the 3- to the 2-position of **6**

$$\frac{k_H}{k_D} = \frac{k_{\text{allyl}}}{k_D} \times \frac{k_H}{k_{\text{allyl}}} = \frac{\% \mathbf{11}}{\% \mathbf{10}} \times \frac{\% \mathbf{2}}{\% \mathbf{3}}$$

provided that **10** and **11** are derived solely from **9**, rather than monodeuterated or deuterium-free dienone.

Of the 27.4% of **9** which is monodeuterated, one-half will react to give products derived from migration of the allyl group towards the deuterium-free 3-position. Since this fraction, as well as the 6.9% which is deuterium free, will give equal amounts of 1,2- and 1,3-migration products, the yield (in per cent) of **10** which is derived from carbonium ion **12** is  $26 - \frac{1}{2}(\frac{1}{2}(27.4) + 6.9) = 15.7$ . Similarly, the yield of **11** derived from



**12** is  $75 - \frac{1}{2}(\frac{1}{2}(27.4) + 6.9) = 64.7\%$ . Substitution of these values in the equation above gives  $k_H/k_D = 4.1$ . It should be noted that this value of  $k_H/k_D$  was calculated on the implicit assumption that  $k_{\text{allyl}}$  was the same for both **6** and **12**. It seems probable that, in fact,  $k_{\text{allyl}}$  will be affected by the presence of a deuterium atom on the  $\alpha$ -carbon. Substitution of a deuterium atom on the  $\alpha$ -carbon reduces the rate of solvolysis of alkyl halides and sulfonates by 10–20%.<sup>6</sup>

(4) E. A. Halevi in "Progress in Physical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1963, pp. 189–200.

(5) L. Melander, *Arkiv Kemi*, **2**, 211 (1950).

(6) Ref. 4, pp. 171–173.

If a similar rate factor applied to migration of the allyl group,  $k_H/k_D$  would be somewhere between 4.5 and 5.0. About the best that can be said, however, is that  $k_H/k_D$  should be greater than 4.1.

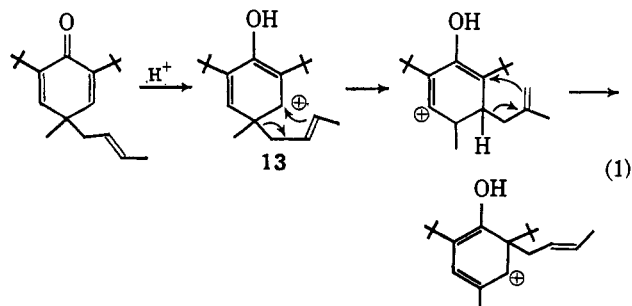
Reactions in which a proton is lost in the rate-determining step normally have deuterium isotope effects greater than 4.<sup>7</sup> The isotope effect for hydride migration in acid rearrangement of triphenylethylene glycol varies between 2.7 and 3.3 in a variety of conditions.<sup>8</sup> The isotope effect for hydride migration in 3-methyl-2-butyl-*p*-toluenesulfonate appears to be below 3.<sup>9</sup> Intermolecular hydride ion transfers also appear to have kinetic isotope effects well below 3.<sup>10</sup> If it is generally true that hydride ion shifts have low deuterium isotope effects, the observed value of  $>4$  for the isotope effect on the rearrangement of **1a** would provide strong evidence that loss of the *t*-butyl group in formation of **2** proceeds by loss of a proton and reprotonation at the *ortho* position, rather than hydride ion migration. Collins and his co-workers<sup>8</sup> have suggested that hydride-ion migrations generally do have isotope effects below 3, but the references they cite appear to be irrelevant.<sup>10a</sup> At present, therefore, we may say that the isotope effect is consistent with the deprotonation-reprotonation mechanism previously favored,<sup>1</sup> but that many more examples of isotope effects on hydride ion migration will be required before a definite conclusion can be drawn.

It may be noted that the large isotope effect observed provides clear proof of the positions of the methyl and allyl groups in **2a**, which were not definitely established in the previous paper.<sup>1</sup> There is no way in which the substitution of deuterium for the hydrogen atoms in the 3- and 5-positions of **1a** could affect the percentages of allyl and methyl migration.

As was stated above, the observed isotope effect is consistent only with a reaction mechanism involving two successive migrations of the allyl group.

Two possible routes can account for a double migration of an allyl group, and also for the observation that the crotyl group migrates without allylic rearrangement.

The migrating group may shift twice without rearrangement, or may undergo allylic rearrangement at each step (eq. 1) to give the unrearranged product.



There seems little doubt, however, that both steps in the

(7) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(8) C. J. Collins, W. T. Rainey, W. B. Smith, and I. A. Kaye, *J. Am. Chem. Soc.*, **81**, 460 (1959).

(9) S. Winstein and J. Takahashi, *Tetrahedron*, **2**, 316 (1958).

(10) P. D. Bartlett and J. D. McCollum, *J. Am. Chem. Soc.*, **78**, 1441 (1956).

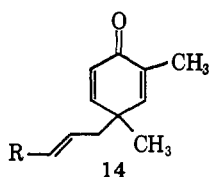
(10a) NOTE ADDED IN PROOF. Dr. Collins has informed us that his suggestion was in error, and that insufficient evidence exists to draw a conclusion as to the magnitude of hydrogen isotope effects for hydride migrations.

migration of **1b** occur without rearrangement. The observation that **1b** rearranges far faster than **1a**<sup>1</sup> strongly suggests that the positive charge at the 3-position does not attack the end of the double bond of the crotyl group, since steric interference between the terminal methyl group and the adjacent *t*-butyl group should be quite marked in a transition state such as **13**. The adverse steric effects would not be significantly countered by the polar effect of the methyl group.<sup>11</sup>

While the crotyl group of **1b**, therefore, almost certainly rearranges without any inversions, it is still conceivable that the allyl group of **1a**, which is not subject to similar steric effects, migrates by one or more cyclic transition states. Only the results of isotopic labeling experiments could conclusively rule out that possibility. In the absence of evidence to the contrary, however, there seems to be no need to assume different reaction paths for the rearrangements of such similar compounds as **1a** and **1b**.

The demonstration that allyl migration proceeds solely by an initial 1,2-migration of the allyl group shows that the relative rearrangement rates of **1a** and its analog with an ethyl group in the 4-position<sup>1</sup> provide good measures of the relative "migratory aptitudes" of the allyl and ethyl groups. Except for the complication introduced by elimination of the crotyl group from **1b** (which would speed the disappearance of **1b** by a factor of no more than 2), the relative reaction rates of **1a** and **1b** also mirror the migratory aptitudes of the allyl and crotyl groups. No precise values for the migratory aptitudes can be derived from the very limited data presented in the previous paper,<sup>1</sup> but it can be seen that **1b** disappears at least 100 times as fast as **1a**, which is more than 100 times as reactive as its ethyl analog. These reactivities parallel those observed for other reactions involving ethyl, allyl, and crotyl carbonium ions.<sup>12</sup>

The demonstration that a second migration of an allyl or crotyl group from the 3- to the 2-position does not occur in the rearrangement of **14**<sup>13</sup> shows that the presence of the *t*-butyl group on an adjacent carbon is



necessary for the occurrence of the second migration. Formation of a phenol from **6** by loss of a proton would force the *t*-butyl group into the same plane as the adjacent hydroxyl and allyl groups. This process is thus retarded sufficiently to allow the second migration of the allyl group to occur.

#### Experimental Section<sup>14</sup>

*p*-Cresol-2,3,5,6-*d*<sub>4</sub>. 2,3,5,6-Tetrabromo-*p*-cresol (28.0 g., 0.066 mole) was dissolved in a solution of sodium methoxide (20.0 g., 0.37 mole) in 300 ml. of

(11) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1339 (1965); see also P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965).

(12) S. Oae and C. A. Vander Werf, *ibid.*, **75**, 2724 (1953); C. A. Vernon, *J. Chem. Soc.*, 423 (1954).

(13) B. Miller, *J. Am. Chem. Soc.*, **87**, 5115 (1965).

(14) All melting points are corrected. All boiling points are uncorrected.

D<sub>2</sub>O. The mixture was reduced as usual with deuterium, using 2.0 g. of 10% palladium-on-charcoal catalyst. Deuterium (2 equiv.) was absorbed in 2 hr., after which no further immediate reaction could be observed. The reaction was allowed to stand without stirring overnight. When shaking of the mixture was resumed, a slow absorption of deuterium occurred. A further 1.8 equiv. of deuterium was absorbed in the succeeding 6 hr. The mixture was then filtered free of catalyst, acidified with dilute aqueous hydrochloric acid, and extracted three times with methylene chloride. The methylene chloride layer was dried over magnesium sulfate and evaporated to give 7.3 g. (0.0652 mole, 99%) of crude *p*-cresol-2,3,5,6-*d*<sub>4</sub> as a yellow oil. Its infrared spectrum showed the acidic proton to be a mixture of hydrogen and deuterium. It had the following moderate and strong peaks in its infrared spectrum: 3.0 (s), 3.45 (m), 4.05 (s), 4.45 (m), 5.90 (m), 6.33 (s), 6.98 (s), 7.15 (m), 7.65 (m), 8.25 (s), 8.90 (s), 11.19 (m), 12.55 (s), 14.12 (s), and 14.4 (s)  $\mu$ .

*p*-Cresol-3,5-*d*<sub>2</sub>. Crude *p*-cresol-2,3,5,6-*d*<sub>4</sub> (7.0 g., 0.0625 mole) was added to 60 ml. of 2 *N* aqueous hydrochloric acid. The mixture was refluxed for 3 hr., cooled, and the product was extracted in the usual manner to give 6.8 g. of yellow oil. Distillation at 0.3 mm. gave 5.3 g. (0.0483 mole, 77%) of *p*-cresol-3,5-*d*<sub>2</sub>, b.p. 48–50°. Its infrared spectrum had peaks at 3.0 (s), 3.45 (m), 4.45 (m), 6.25 (s), 6.32 (s), 6.70 (m), 6.80 (s), 7.05 (s), 7.55 (m), 8.16 (s), 8.37 (s), 9.53 (m), 10.10 (m), 11.17 (m), 11.38 (s), 12.21 (m), 13.62 (s), and 13.95 (m-s)  $\mu$ .

2,6-Di-*t*-butyl-4-methylphenol-3,5-*d*<sub>2</sub>. A mixture of *p*-cresol-3,5-*d*<sub>2</sub> (5.0 g., 0.0455 mole) and concentrated sulfuric acid (0.3 ml.) was stirred rapidly in a three-necked flask kept in a water bath at 60–65°. A rapid stream of isobutylene was bubbled into the reaction until the hydroxyl peak at 3.0  $\mu$  in the infrared had disappeared and been replaced by a peak at 2.7  $\mu$  (ca. 5 min.). The mixture was diluted with methylene chloride, washed first with sodium bicarbonate solution and then with water, dried over magnesium sulfate, and filtered, and the solvent was evaporated to give 9.0 g. (0.0405 mole, 89%) of pale yellow fluid, which crystallized on standing. One recrystallization from methanol gave 7.0 g. of white cubes, m.p. 70.5–71.0°.

Its infrared spectrum (Nujol mull) had peaks at 2.70 (m), 3.5 (Nujol), 4.40 (w), 6.97 (s), 7.03 (m), 7.10 (s), 7.18 (s), 7.25 (w), 7.72 (m), 8.20 (s), 8.34 (m), 8.56 (s), 8.78 (s), 9.70 (w), 10.65 (w), 11.30 (m), 13.11 (w), 13.50 (m), 14.00 (w), and 14.30 (m)  $\mu$ .

4-Allyl-2,6-di-*t*-butyl-4-methylcyclohexadien-1-one-3,5-*d*<sub>2</sub>. The reaction between 2,6-di-*t*-butyl-4-methylphenol-3,5-*d*<sub>2</sub> (6.0 g., 0.0270 mole) and allyl bromide in *t*-butyl alcohol, catalyzed by potassium *t*-butoxide, was carried out as previously described.<sup>15</sup> Chromatography on 300 g. of basic alumina (activity I) yielded 3.3 g. (0.0126 mole, 47%) of the pure dienone, *n*<sub>D</sub><sup>25</sup> 1.4815. The infrared spectrum had peaks at 3.45 (s), 4.55 (w), 4.65 (w), 6.07 (s), 6.13 (s), 6.75 (m), 6.90 (m), 7.00 (m), 7.35 (m-s), 7.80 (m), 8.18 (w), 8.32 (w), 8.60 (w), 8.85 (w), 8.95 (w), 9.20 (w), 9.50 (w), 9.80 (w), 10.09 (m), 10.90 (m-s), 11.3 (shoulder), 12.20 (w), 12.95 (w), and 13.70 (w)  $\mu$ .

(15) B. Miller and H. Margulies, *J. Org. Chem.*, **30**, 3895 (1965).

*Rearrangement of 4-Allyl-2,6-di-*t*-butyl-4-methylcyclohexadien-1-one-3,5-*d*<sub>2</sub>.* 4-Allyl-2,6-di-*t*-butyl-4-methylcyclohexadien-1-one-3,5-*d*<sub>2</sub> (0.30 g.) was dissolved in 5.0 ml. of a mixture of glacial acetic (45.0 ml.) and concentrated sulfuric acid (5.0 ml.). After standing for 5.0 hr., the mixture was worked up as usual<sup>1</sup> to give 0.22 g. of dark yellow oil. V.p.c. analysis on a 6-ft., 2% XE60 on Gas Chrom Z column at 160° showed the presence of two components, with retention times of 2.9 and 7.6 min. The relative areas were in the ratio of 75:25. A second run on the deuterated ketone had area ratios of 74:26. The nondeuterated ketone was twice treated in the same

way to give area ratios of 50:51 and 51:49. The two products of reaction of 9 were isolated by v.p.c. The n.m.r. spectrum of the material with the lower retention time was identical with that of 2-allyl-6-*t*-butyl-4-methylphenol<sup>16</sup> except for the virtual absence of peaks in the aromatic hydrogen region. The n.m.r. spectrum of the product with the higher retention time was identical with that of 3-allyl-6-*t*-butyl-4-methylphenol,<sup>1</sup> except for the absence of the peak at  $\tau$  3.1.

*Acknowledgments.* The author wishes to thank Mr. R. Wayne for assistance with the n.m.r. spectra, and Dr. A. S. Kende for valuable discussions.

(16) B. Miller, *J. Org. Chem.*, 30, 1964 (1965).

## Dienone-Phenol Rearrangements of 6-Allylcyclohexa-2,4-dienones and 4-Allylcyclohexa-2,5-dienones. Acid Catalysis of Cope Rearrangements<sup>1</sup>

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Received August 9, 1965*

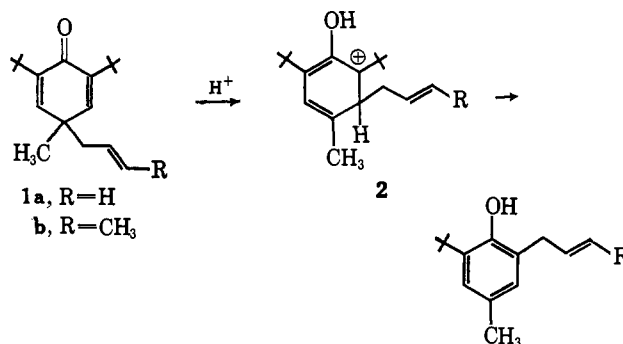
*Formation of phenols by acid-catalyzed rearrangement of cyclohexa-2,4-dienones and cyclohexa-2,5-dienones results in both 1,2- and 1,3-migration of allyl and crotyl groups. While the 1,2-migrations proceed without allylic rearrangement of crotyl groups, 1,3-rearrangements result in complete allylic inversion of crotyl groups. Both 1,2- and 1,3-migrations appear to be intramolecular. The percentage of 1,3-migration is higher when a crotyl group migrates than when an allyl group migrates. The 1,3-migrations appear to resemble Cope rearrangements in which the migrating allyl group bears appreciable positive charge in the transition state. Substitution of methyl groups at C-1 of cyclohexa-2,5-dienones directs the migrating group in the 1,2-migration entirely to C-5, rather than C-2. This is ascribed to a steric effect. 4-Allylcyclohexa-2,5-dienones are conveniently prepared by careful thermal rearrangement of 6-allylcyclohexa-2,4-dienones.*

Cyclic rearrangements of allylic compounds, such as the Cope and Claisen rearrangements, normally differ in several respects from acid-catalyzed carbonium ion rearrangements. The cyclic processes are normally thermally initiated and are "relatively insensitive to external catalytic influence."<sup>2,3</sup> The migrating groups in reactions closely related to carbonium ion rear-

rangements migrate without internal rearrangement, and indeed, with retention of configuration.<sup>4</sup> The migrating allylic groups in Cope and Claisen rearrangements, on the other hand, invariably undergo at least one allylic inversion.<sup>2</sup> Finally, Cope and Claisen rearrangements proceed by direct 1,3-migrations of the allylic groups,<sup>2</sup> while carbonium ion migrations normally proceed by sequences of 1,2 shifts.<sup>5,6</sup>

In this paper, we wish to report on a group of rearrangements which combine characteristics of cyclic rearrangements and of carbonium ion reactions.

We recently reported that the apparent 1,3-migration of the allylic group in the acid-catalyzed rearrangement of dienone 1a<sup>7</sup> actually proceeds by a sequence of two 1,2-shifts.<sup>1</sup> This reaction was the first example



(1) Reactions of Cyclohexadienones, XIII. Preceding paper, *J. Am. Chem. Soc.*, 87, 5111 (1965).

(2) S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 655-706.

(3) The Claisen rearrangement, however, has recently been found to be catalyzed by boron trihalides: (a) P. Fahrni, A. Habich, and H. Schmid, *Helv. Chim. Acta*, 43, 448 (1960); (b) A. Habich, R. Barner, R. M. Roberts, and H. Schmid, *ibid.*, 45, 1942 (1962).

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 500-503.

(5) (a) Y. Pocker in ref. 2, pp. 1-26; (b) J. A. Benson, ref. 2, pp. 111-232.

(6) For a possible exception, see W. A. Mosher and J. C. Cox, Jr., *J. Am. Chem. Soc.*, 72, 3701 (1950).

(7) B. Miller and H. Margulies, *ibid.*, 87, 5106 (1965).