Table VI

H_2SO_4–H_2O	
Wt % H_2SO_4	δCH_3 (TMAC)
0–20	3.20
25–60	3.18
65	3.17
70	3.16
75	3.14
80	3.12
90–100	3.10

dilute acid to δ 3.10 in 90–100 wt % H_2SO_4 (see Table VI). TMAC in all superacid media sssumed δ = 3.10.

Low-Temperature Protonations. It is advantageous to protonate labile (*e.g.*, $CH_2BrCOCH_3$, CH_3CHO) carbonyl compounds below room temperature in order to minimize decomposition and side reactions. In these cases the base is added to the acid medium just below the freezing point of the acid. The nmr tube is then removed from the cold bath (dewar) and mixed thoroughly as the ketone and/or acid melt. Before the nmr tube warms completely it is placed in the spectrometer probe. A spectrum can be taken in 3–5 min.

Evaluation of Unknown Acid Systems. Simple measurement of a ketone chemical shift gives only an approximate acidity value in the typical experiment. In cases where the acid to be evaluated is not closely related to a calibrating acid system, individual nmr chemical shifts can be misleading. Thus, for most accurate measurements it is necessary to get more than one point on the protonation curve for the acid system to be evaluated. This can be done by (1) adding small amounts (2–3 drops) of a stronger acid or (2) adding small amounts of a strong base. In this way the chemical-shift dependence of the ketone indicator in a given acid system can be best visualized. Thus, addition of small amounts of a sufficiently strong acid will give a substituent chemical shift corresponding to "full protonation" in that acid medium. Likewise, addition of strong base will allow measurement of the unprotonated carbonyl substituent chemical shift.

For example, in evaluation of CH_3SO_3H–CH_3NO_2 solutions (CD_3NO_2 is used for nmr purposes) OH^- or H_2O may serve as the base and FSO_3H, CF_3SO_3H, or 100% H_2SO_4 act as strong acids. The best choices are OH^- and FSO_3H since these will cause the largest changes in medium acidity.

Acknowledgment. The authors wish to thank Professor R. J. Gillespie for making available unpublished acidity data on H_2SO_4–FSO_3H and FSO_3H–SbF_5 media.

Acid-Catalyzed Sigmatropic Shifts of Allyl Groups in Cyclohexa-2,4-dien-1-ones. The Possibility of Differing Reactions from n- and π-Protonated Ketones[1]

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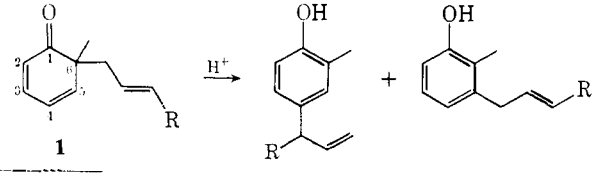
Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002. *Received January 14, 1970*

Abstract: Acid-catalyzed rearrangements of allyl-substituted cyclohexa-2,4-dien-1-ones can result in five different types of migrations. These are (starting with structure **1**) [1,2] migration of the allyl group to C-5, [3,3] migration to C-4, [3,3] migration to oxygen, [1,5] migration to C-2, and [3,5] migration to C-2. No one dienone exhibits all of these types of migrations, the occurrence of which depends on the substitution pattern on the ring. The large number of migration types observed can be reconciled with the requirements of the conservation of orbital symmetry if the assumption is made that the rearrangements proceed through both n- and π-protonated ketones.

Acid-catalyzed rearrangements of linearly conjugated dienones, such as **1**, have been reported to result principally in migration of the allyl group to C-4 of the dienone.[2-4] In earlier work[2] we have shown that these migrations proceed *via* [3,3] sigmatropic shifts[5] involving inversion of the allyl group. In one instance, a "normal" [1,2] shift of the allyl group to C-5 was reported to occur along with the migration to C-4.[3]



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We have now found that when the cyclohexadienone molecule is so substituted as to inhibit effectively either of the above migrations, acid-catalyzed reverse-Claisen migration to oxygen and [1,5][6] shifts of the allyl group to C-2 can become major rearrangement paths. Finally, an apparent [3,5][6] shift of the allyl group to C-2 with inversion has been observed, but it cannot yet be determined whether this migration proceeds in a single step or by a sequence of other migrations.

The occurrence of such a large number of migration types does not seem consistent with predictions from the Woodward–Hoffmann rules.[5] A possible way of reconciling these rules with our observations will be offered in the discussion section.

(1) (a) Reactions of Cyclohexadienones. XXIV. Part XXIII: B. Miller, *J. Amer. Chem. Soc.*, **92**, 432 (1970). (b) A preliminary account of part of this work has been published: *ibid.*, **91**, 2170 (1969).

(2) B. Miller, *ibid.*, **87**, 5115 (1965).

(3) P. Fahrni, A. Habich, and H. Schmid, *Helv. Chim. Acta*, **43**, 448 (1960).

(4) J. Leitich, *Monatsh.*, **92**, 1167 (1961).

(5) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965); *Accounts Chem. Res.*, **1**, 17 (1968).

(6) The proper designations for sigmatropic shifts in cyclic systems of π orbitals seems somewhat ambiguous. Although a shift of a group from C-6 to C-2 of a dienone could be designated as a [1,3] shift, we have chosen to count along the system of double bonds, rather than through the carbonyl group, in order to have the allowed and forbidden migrations be consistent with those in the acyclic examples.

Table I. Nmr Spectra of Cyclohexadienones (Positions in Units of τ)

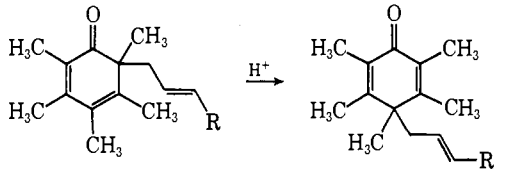
Compd	Substituent at[c] C_2	C_3	C_4	C_5	C_6	$-CH_2CH=C-$	$-CH=C(H)-CH_3$
2	Ms, 8.17	Ms, 8.02	Ms, 8.17	Ms, 8.17	Ms, 8.93	m, 7.3–7.8	
3	M, 8.16–8.21[a]	Ms, 8.00	M, 8.16–8.21[a]	M, 8.16–8.21[a]	Ms, 8.93	m, 7.2–7.8	d, 8.53 (J = 5.5)
4	Ms, 8.11	Ms, 8.05	Ms, 8.77	Ms, 8.05	Ms, 8.11	d, 7.50 (J = 5.0)	
5	Ms, 8.16	Ms, 8.09	Ms, 8.81	Ms, 8.09	Ms, 8.16	d, 7.60 (J = 6.2)	d, 8.48 (J = 6.0)
9	Hd, 4.13 (J = *ca.* 10)	Hdd, 3.06 (J = 9.8, 2.1)	Ms, 8.03	H, 4.05[b]	Ms, 8.90	m, 7.3–7.9	d, 8.43 (J = 5.5)
12	Hd, 4.18 (J = 10.0)	Hdd, 3.03 (J = 10.0, 2.3)	Bs, 8.97	Hd, 4.23 (J = 2.3)	Ms, 9.03	m, 7.4–8.0	d, 8.55 (J = 5.8)

[a] Apparently three overlapping singlets. [b] Partially covered by peak from C-2 hydrogen. [c] Substituents: B = *t*-butyl, H = hydrogen, M = methyl; splitting: d = doublet, s = singlet.

Results

The cyclohexadienones employed in this work were all prepared in the normal manner by Claisen alkylation of the sodium salts of the appropriate phenols with allyl or crotyl bromide in benzene suspension. All of the dienones were stable indefinitely in methanol or other neutral solvents at room temperature, although they all rearranged rapidly at temperatures of 100–150°.[2] Examination of the infrared spectra of the products from acid treatment of the dienones showed that rearrangement was complete in all cases before vpc analysis of the products was carried out.

We first examined the rearrangements of the pentamethylcyclohexadienones **2** and **3**, in which the usual aromatization of the products to phenols cannot occur.

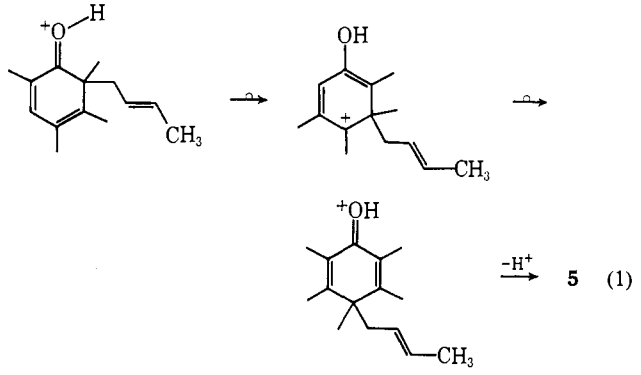


2, R = H
3, R = CH_3

4, R = H
5, R = CH_3

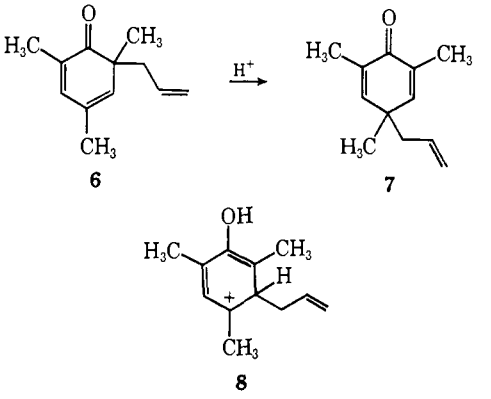
Rearrangement of **2** in 0.1 *N* methanolic hydrochloric acid gave a quantitative yield of the cross-conjugated cyclohexadienone **4**. Rearrangement of **3** under the same conditions gave a 50% yield of **5**, accompanied by an equal amount of pentamethylphenol, resulting from loss of a butenyl group. The structures assigned to **4** and **5** are supported by their nmr spectra, which are listed in Table I.

Formation of dienone **5** can readily be rationalized as proceeding by a sequence of two Wagner–Meerwein shifts of the crotyl group, as in eq 1. Many apparent



5 (1)

[1,3] shifts in the rearrangements of cross-conjugated cyclohexadienones have been shown to proceed by similar sequences of [1,2] shifts.[7] It is not immediately evident, however, whether the allyl group in **2** migrates to C-4 by a single Cope rearrangement or by a sequence of Wagner–Meerwein shifts similar to that in eq 1. To get additional information about this point, dienone **6** was rearranged in 0.1 *N* HCl in methanol. Rather surprisingly, an almost quantitative yield of the cross-conjugated dienone **7** was obtained, accompanied by



6 **7** **8**

no more than 2–3% of the "normal" dienone–phenol rearrangement product, 3-allyl-2,4,6-trimethylphenol. After much longer reaction times, or in stronger acid, **7**, in turn, rearranges to 3-allyl-2,4,6-trimethylphenol.[2,3]

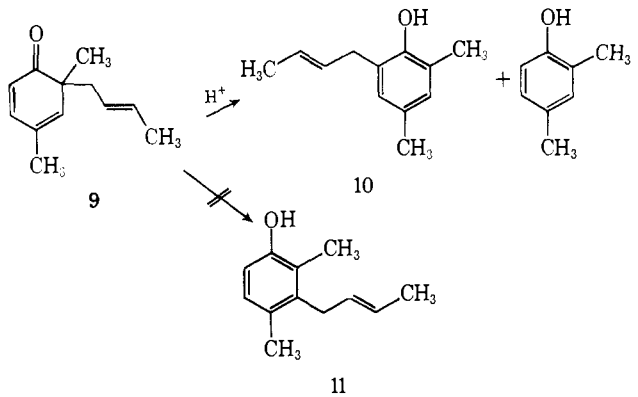
Formation of **7** from **6** almost certainly results from an acid-catalyzed Cope migration of the allyl group, rather than from two successive 1,2-shifts, since, in the absence of very exceptional steric effects,[8,9] migration of an allyl group in carbonium ions such as **8** cannot compete with loss of a proton to form an aromatic product. By analogy with the reaction of **6**, it appears likely that formation of **5** in the acid-catalyzed rearrangement of **3** also proceeds by a single Cope migration of the allyl group, rather than by a sequence of 1,2-shifts.

The formation of **5** as the exclusive rearrangement product from **3** suggests that crotyl groups, unlike allyl groups, will not undergo acid-catalyzed Cope migrations to C-4 when that position is already occupied by a methyl group. Failure to obtain the products of Cope rearrangement could readily be explained as due

(7) B. Miller in "Mechanisms of Molecular Migrations," Vol. I, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, pp 247–313.
(8) B. Miller and H. Margulies, *J. Amer. Chem. Soc.*, **87**, 5106 (1965).
(9) B. Miller, *ibid.*, **87**, 5111 (1965).

to steric repulsions between the methyl groups on the ring and on the migrating group. An alternative explanation, however, is that Cope migration of a crotyl group to C-4 does occur readily and reversibly even when C-4 is occupied by a methyl group, but that the equilibrium lies too far to the side of the *o*-dienone to allow observation of the rearrangement product.

To test this possibility, dienone **9** was prepared and rearranged in acid. Two products were obtained in the ratio 5:1. The minor product was identified as 2,4-dimethylphenol, resulting from fragmentation of the dienone. The nmr spectrum of the major product, a cryptophenol, showed the presence of two aromatic methyl groups, an unrearranged crotyl group, and two aromatic protons *meta* to each other. This suggested that the structure was 2-crotyl-4,6-dimethylphenol (**10**). The structural assignment was confirmed by preparation of **10** by reaction of a suspension of sodium 2,4-dimethylphenoxide with 1-bromo-2-butene, and comparison of its ir and nmr spectra and vpc retention times with those of the rearrangement product. No evidence could be found for formation of the "normal" product, **11**.

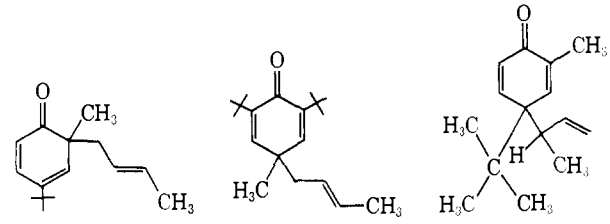


9 **10** **11**

Several possible mechanisms could be considered for the rearrangement of **9** to **10**. The possibility that **10** was formed by dissociation of **9** into 2,4-dimethylphenol and a crotyl carbonium ion seemed unlikely, since reaction of the carbonium ion with the solvent should be very rapid. A more plausible possibility was that the protonated dienone **9** itself might have acted as an alkylating agent toward 2,4-dimethylphenol, while carrying on a chain reaction by formation of another molecule of 2,4-dimethylphenol in the same step. Both types of intermolecular mechanisms were dismissed, however, when it was found that rearrangement of **9** in the presence of 10 molar excesses of phenol or of *p*-cresol did not reduce the yield of **10**. Any intermolecular mechanism should result in preferential alkylation of phenol or *p*-cresol rather than alkylation of the comparatively small amounts of 2,4-dimethylphenol formed in the reaction.

Two possible intramolecular mechanisms could account for formation of **10** from **9**. Phenol **10** might be formed by a direct *ortho–ortho'* migration of the crotyl group, or by a sequence of two acid-catalyzed Cope migrations of the crotyl group, first to C-4 and then to C-2.

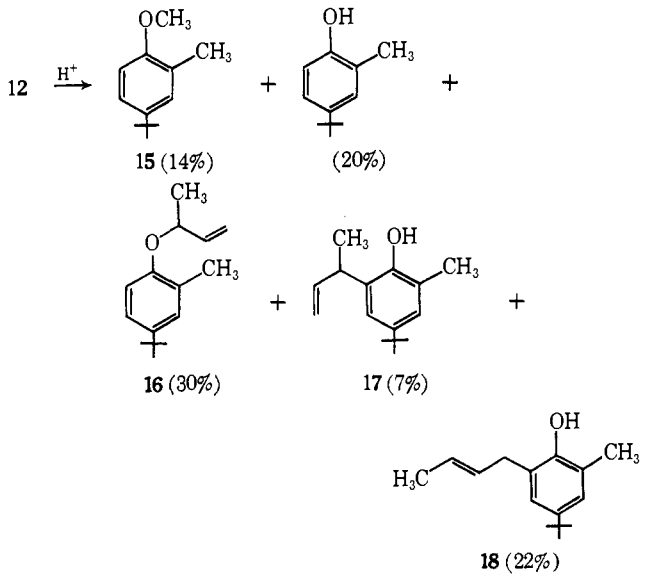
In order to distinguish between these possibilities, it was decided to carry out the rearrangement with dienone **12**, in which C-4 is substituted with a *t*-butyl group. We have previously shown that the presence of *t*-butyl groups at C-2 and C-6 in the cross-conjugated cyclohexadienone **13** completely prevents any acid-



12 **13** **14**

catalyzed Cope migration of a crotyl group to that position.[8] We therefore expected the strong steric repulsions between the migrating 1-methylallyl group and the *t*-butyl group to prevent similarly any Cope migration to form the intermediate dienone **14** from **12**.

Rearrangement of **12** under the usual conditions in 0.1 *N* HCl in methanol occurred readily to give a mixture containing six components, which were isolated by vpc. The nmr spectrum of the first compound evolved (14% yield) showed, in addition to three aromatic protons, a nine proton singlet for the *t*-butyl group, and a three proton singlet at τ 7.93 for a methyl group on an aromatic ring, a three proton singlet at τ 6.38. Its ir spectrum showed no carbonyl or hydroxyl absorptions. These spectra suggested that the compound was 4-*t*-butyl-2-methylphenyl methyl ether (**15**) and this assignment was confirmed by synthesis of **15** by methylation of 4-*t*-butyl-2-methylphenol and comparison of its spectra and vpc retention times with that of the product from rearrangement of **12**. The second product was found to be 4-*t*-butyl-2-methylphenol (20%). The third product in order of evolution was the major component (30% yield). Its nmr spectrum again showed three aromatic hydrogens, an aromatic methyl group, and a *t*-butyl group. In addition, it had three to four protons in the region τ 4.5–5.8, and a three proton doublet (J = 6.5) at τ 8.85. It showed no hydroxyl peak in the ir. This information strongly suggested that its structure was **16**, and this was confirmed by the independent preparation of **16** by the thermal rearrangement of **12** at 120°. The fourth product (7%) was a phenol whose spectrum showed, in addition to aromatic methyl, hydroxyl, and *t*-butyl peaks, a two proton aromatic peak at τ 3.22, two to three vinyl protons at τ 4.5–5.5, a one proton multiplet around τ 6.4, and a three proton doublet at τ 8.77. This spectrum agreed with that expected for structure **17**, and this assignment was confirmed by synthesis of **17** by Claisen rearrangement of *trans*-2-butenyl 4-*t*-butyl-2-methylphenyl ether at 200° in dimethylaniline. The fifth product was the second largest fraction (22%). Its nmr spectrum, which showed the presence of an unrearranged crotyl group and two aromatic protons *meta* to each other, as well as *t*-butyl, hydroxyl, and aromatic methyl peaks, suggested that it had structure **18**, and this was confirmed by comparison of its spectra and vpc retention times with that of **18** prepared by Claisen alkylation of 4-*t*-butyl-2-methylphenol. The final product was obtained in low yield (4%), and could not be sufficiently separated from **18** to be identified. Its nmr spectrum appeared, in general, to be similar to that of **18**.



The ratio of products obtained from rearrangement of **18** is not appreciably affected by the presence of a 20-fold excess of phenol in the reaction mixture, again suggesting that the rearrangements are intramolecular in character.

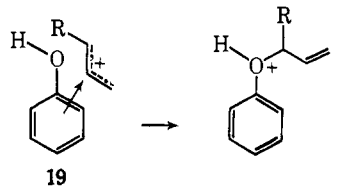
Isolation of **18** therefore provides strong evidence that a direct migration of a crotyl group across the "top" of a cyclohexadienone ring from C-6 to C-2 is possible. At present, however, it cannot be decided whether **10** is formed from **9** by a direct migration of the crotyl group or by a twofold Cope migration.

Discussion

The results of this study show that the acid-catalyzed migrations of allyl groups in linearly conjugated cyclohexadienones can give rise to a wide variety of rearrangements, in addition to fragmentation processes. Two types of migration—a Wagner–Meerwein shift to C-5 and a Cope migration to C-4, have been previously observed, while acid-catalyzed reverse-Claisen migrations and migration of the allyl group across the "top" of the ring to C-2 have been observed for the first time in this work.

It is clear that formation of ether **16** and phenols **17** and **18** from dienone **12** does not fit into a "normal" pattern for acid-catalyzed rearrangements, since there is no reasonable manner in which C-2 or the oxygen atom can be pictured as electron-deficient sites. (Since several of these products can also arise by thermal rearrangement of **12**, it is perhaps again worth stressing that no rearrangement will occur at room temperature in the absence of acid. Ir analysis shows clearly that all **12** is consumed before vpc analysis of the product, and the product composition is independent of the reaction time once **12** has disappeared. Finally, the products from rearrangement of **12** do not interconvert during vpc analysis.)

Formation of ether **16** from **12** presumably proceeds *via* a single [3,3] sigmatropic shift whose transition state (**19**), like those for the Cope migration to C-4,[2] may be regarded as a complex of a phenol ring and an allyl carbonium ion. (The exact charge distribution in the transition state, however, will not affect the symmetry arguments which follow.)



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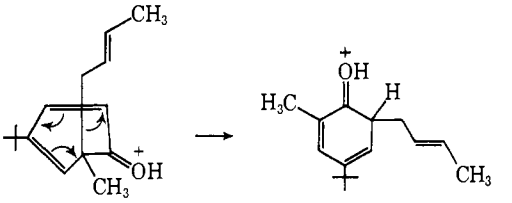
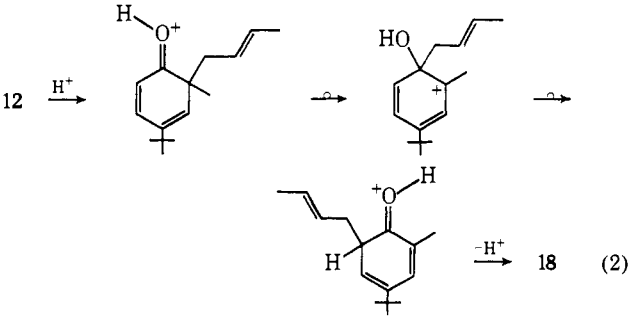
Formation of phenol **18** might also proceed in a single step *via* a [1,5] sigmatropic shift, as in transition state **20**. It is not yet certain, however, that formation



20

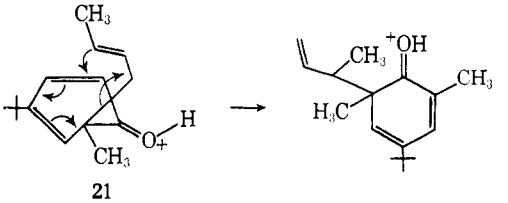
of **18** does proceed in a single step. The evidence detailed above suggests that **18** is not formed by a sequence of two Cope migrations, but is instead obtained by migration of the crotyl ring from C-6 to C-2 without any inversions. This is strongly supported by the observation of similar migrations of benzyl groups,[10] which cannot undergo Cope rearrangements. The possibility remains, however, that **18** is formed by a sequence of two Wagner–Meerwein shifts proceeding through the carbonyl group, as in eq 2. Migration of substituents from a quaternary carbon atom



(2)

to the carbonyl carbon has been previously observed in the rearrangements of naphthalenones,[7] since other migrations would be precluded by loss of aromaticity in the benzene ring. There is no direct evidence at present which would enable us to distinguish between the direct [1,5] shift and the double Wagner–Meerwein migration. In the following paper, however, we will offer evidence which suggests that benzyl groups can migrate *via* direct [1,5] shifts, and we therefore favor this mechanism for formation of **18**.

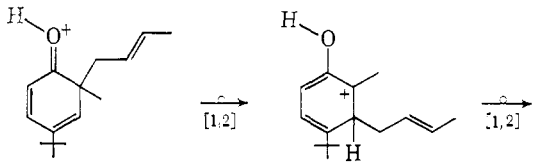
The formation of phenol **17** from **12** can proceed by a direct [3,5] sigmatropic shift, as in transition state **21** or by the complex mechanism shown in eq 3, in which



21

(10) B. Miller, *J. Amer. Chem. Soc.*, **92**, 6252 (1970).

the crotyl group first undergoes two successive Wagner–Meerwein shifts to C-4, and then a Cope migration to C-2. The twofold Wagner–Meerwein migration of the



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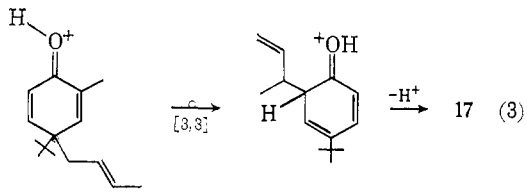


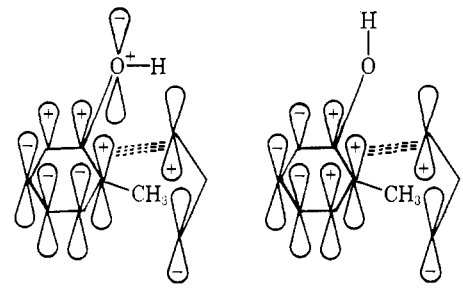
crotyl group to C-4 closely resembles the migration of a crotyl group to C-2 in the acid-catalyzed rearrangement of dienone **13**.[8] As in the rearrangement of **13**, failure of the carbonium ion **22** to lose a proton to give a phenol could be attributed to the difficulty of forcing a *t*-butyl group into the same plane as the adjacent crotyl group. Instead, the crotyl group should undergo a second migration to C-4. The final Cope migration to C-2 has ample precedent.[2]

We cannot, at present, distinguish between these two possible mechanisms for the formation of **17** in the acid-catalyzed rearrangement of **12**.

It is noteworthy that all of the rearrangements of cyclohexadienones, with the exception of the migrations to C-2, proceed with complete selectivity in regard to inversion of retention of the migrating allyl group. Migration to C-5 occurs solely with retention, while migration to C-4 or to oxygen occurs solely with inversion. The last two observations are particularly striking since migration to C-2 occurs principally with retention.

It is of interest to attempt to correlate the occurrence or nonoccurrence of inversion with predictions from molecular orbital symmetry considerations.[5] One possible way to arrive at an orbital symmetry picture of the protonated dienone is to consider protonation to take place on the nonbonded (n) electrons of the oxygen atom. This should, in fact, be the normal mode of protonation of the carbonyl group, as is indicated by the detection of *cis* and *trans* forms of protonated carbonyl compounds by Olah and his coworkers.[11,12] Although the effective electronegativity of the oxygen atom will be increased, it seems likely that the orbital symmetries will not be appreciably changed, in this model, from those of the unprotonated dienone. The orbital symmetry pattern for the frontier orbital, consisting of ψ_4 for a phenoxyl radical and ψ_2 for the allyl radical,[5] is shown in structure A.[13,14]

According to this model, therefore, [3,3] migrations to C-4 and to oxygen and [1,5] migrations to C-2 would be allowed in the acid-catalyzed as well as the thermal rearrangements. If we assume that formation of **17** occurs *via* the mechanism shown in eq 3, these predictions are thus far in agreement with our observations. However, the [1,2] migration to C-5 would not be allowed.[15]



A B

An alternative possibility is that protonation of the ketone takes place on the carbonyl π bond, rather than on a pair of nonbonded electrons.[16] This would incorporate one exocyclic π orbital in a σ bond, and effectively remove the orbital on oxygen from the π-orbital system. To a first approximation, the π-protonated cyclohexadienone can be considered to react as a simple cyclohexadienyl carbonium ion, of the type whose rearrangements have recently been elegantly explored by Schmid and his coworkers.[17] The molecular orbital symmetries of the frontier orbital,[17] consisting of ψ_3 for the ring and ψ_2 for the allyl radical, are shown in diagram B. It will be seen that migration of the crotyl group to C-5 without inversion, and to C-4 and C-2 with inversion, are allowed. In fact, Schmid's work[17] shows that both of these types of migrations do occur in simpler systems. Migration to C-2 without inversion of the crotyl group might also occur by the double Wagner–Meerwein shift through the carbonyl group. Since the orbital on the oxygen atom has been removed from the system, however, there is no way to account for reverse-Claisen migration.

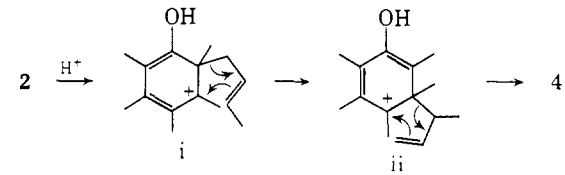
(11) G. A. Olah, D. H. O'Brien, and M. Calin, *J. Amer. Chem. Soc.*, **89**, 3582 (1967).

(12) G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, **89**, 3586 (1967).

(13) M. R. Sandner, E. Hedaya, and D. J. Trecker, *ibid.*, **90**, 7249 (1968).

(14) H.-J. Hansen and H. Schmid., *Chem. Brit.*, **5**, 111 (1969).

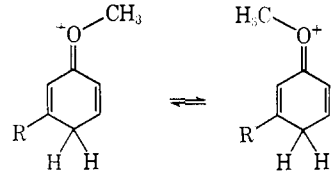
(15) A referee has suggested that formation of dienone **4**, which we have proposed proceeds by a sequence of [1,2] shifts, might proceed by a series of [2,3] shifts (**2** → i → ii). This ingenious proposal does not, however, account for the occurrence of [1,2] shifts in linearly conjugated



i ii

cyclohexadienones when allylic migrations to C-5 are not possible (*cf.* ref 10).

(16) The rotations of methoxy groups in C-protonated anisoles



iii iv

(*e.g.*, iii → iv) presumably proceed through π-methylated cyclohexadienones, which can serve as models for our proposed π-protonated forms. Since the π-methylated dienones should be minima in the energy path for rotations, measurements of the activation energies for these rotations would provide maximum values for the differences in energies of n- and π-methylated cyclohexadienones. The very rapid rotation of the methoxy group in iii (D. M. Brouwer, E. L. Mackor, and C. MacLean, *Recl. Trav. Chim. Pays-Bas.*, 85, 114 (1966)) indicates that the difference in energies is small. This, in turn, suggests that π-protonation of a cyclohexadienone is an energetically feasible process.

(17) H.-J. Hansen, B. Sutter, and H. Schmid., *Helv. Chim. Acta*, **51**, 828 (1968).

This analysis therefore suggests that no one protonated cyclohexadienone structure can give rise to all the products of acid-catalyzed allyl group migrations in 2,4-cyclohexadienones. All the observed rearrangements can be explained, however, if it is assumed that rearrangements proceed from both n-protonated and π-protonated dienones. This hypothesis can also account for the observation that [3,3] migrations are more likely to occur when the migrating group is a crotyl group than when it is an allyl group.[2] Since protonation of a nonbonded electron pair on a carbonyl group will be the predominant pattern, good migrating groups would be expected to migrate largely from that structure. Poorer migrating groups, however, might have to await (at least in part) formation of the more reactive π-protonated dienone. Since [1,2] migrations would occur only from the π-protonated dienone, poorer migrating groups would undergo higher percentages of [1,2] migration.

The evidence obtained thus far is therefore consistant with the hypothesis that rearrangements of allyl groups in cyclohexadienones can proceed from both n- and π-protonated carbonyls, but obviously does not compel its acceptance. Our belief that this hypothesis is, in fact, the explanation for the observed phenomena is supported by its success in accounting for the unexpected observations on the migrations of benzyl groups in cyclohexadienones, which are reported in the following paper.

Experimental Section

Unless otherwise noted, all uv spectra were recorded in methanol solution and nmr spectra in CCl_4. Melting points are corrected and boiling points uncorrected. Microanalyses were performed by Charles Meade, University of Massachusetts, Microanalytical Laboratory, Amherst, Mass., and by Galbraith Laboratories, Knoxville, Tenn.

Preparation of Cyclohexa-2,4-dien-1-ones. 6-Allyl-2,3,4,5,6-pentamethylcyclohexa-2,4-dien-1-one (2). Pentamethylphenol (30.0 g, 0.183 mol) was dissolved in 1000 ml of benzene. Sodium methoxide (9.9 g, 0.183 mol) was added. The mixture was distilled while being stirred until *ca.* 300 ml of distillate was collected. The residue was then cooled in ice and allyl bromide (25.0 g, 0.206 mol) was added. The mixture was stirred at room temperature for 70 hr and then washed with water, dried over magnesium sulfate, and the benzene evaporated. The residual oil (39.2 g) was dissolved in petroleum ether (bp 30–60°) and extracted with Claisen alkali. Acidification of the alkaline solution gave 4.2 g of recovered pentamethylphenol. The alkali insoluble layer was washed with water, dried, and the solvent evaporated to give 34.9 g of yellow oil, which was chromatographed on Florisil. Elution with petroleum ether (30–60°) gave 18.1 g (0.0888 mol, 56% based on recovered phenol) of the desired dienone as a yellow oil, λ_{max} 333 mμ (log ε = 3.63). *Anal.* Calcd for $C_{14}H_{20}O$: C, 82.4; H, 9.80. Found: C, 82.5; H, 9.83.

The reaction between pentamethylphenol and *trans*-1-bromo-2-butene was carried out in a similar manner to give a 40% yield of **6-*trans*-2-butenyl-2,3,4,5,6-pentamethylcyclohexa-2,4-dien-1-one (3),** λ_{max} 331 mμ (log ε = 3.59). *Anal.* Calcd for $C_{15}H_{22}O$: C, 82.5; H, 10.2. Found: C, 82.4; H, 10.5.

The reaction between 2,4-dimethylphenol and 1-bromo-2-butene was carried out in the manner described for the preparation of **2** on a 0.5-mol scale. After evaporation of the benzene, the residual oil was dissolved in petroleum ether, washed with dilute sodium hydroxide solution, and extracted with Claisen alkali. Repeated chromatography of the alkali-insoluble product gave 3.11 g (0.018 mol, 4%) of **6-*trans*-2-butenyl-4,6-dimethylcyclohexa-2,4-dien-1-one (9)** as a pale yellow fluid, λ_{max} 325 mμ (log ε = 3.57). *Anal.* Calcd for $C_{12}H_{16}O$: C, 81.8; H, 9.10: Found: C, 81.8; H, 9.29.

The Claisen alkali extract was acidified with dilute hydrochloric acid and extracted with methylene chloride. The organic layer was washed with water, dried over magnesium sulfate, and the solvent evaporated to give 17 g of yellow oil, which was distilled at 5 mm to give 11.1 g (0.063 mol, 13%) of **2-(*trans*-2-butenyl)-4,6-dimethylphenol (10),** bp 136–139°. Its nmr spectrum showed three-proton singlets at τ 7.87 and 7.95, a three-proton multiplet at τ 8.34, a broad, two-proton peak at τ 6.83, a one-proton singlet at τ 5.3, a two-proton multiplet around τ 4.5, and two one-proton peaks at τ 7.37 and 7.46. *Anal.* Calcd for $C_{12}H_{16}O$; C, 81.8; H, 9.10. Found: C, 81.6; H, 9.25.

Alkylation of 4-*t*-butyl-2-methylphenol with 1-bromo-2-butene was carried out on a 0.2-mol scale in the usual manner. After evaporation of the benzene, the residual oil was dissolved in petroleum ether and washed with 2 *N* sodium hydroxide solution, and then extracted twice with Claisen alkali. The organic layer was washed with water, dried, and the solvent evaporated to give 29 g of yellow oil, which was chromatographed on Florisil. Eluting with petroleum ether gave 16.4 g of carbonyl-free product, which was discarded. Elution with 2:1 petroleum ether–methylene chloride then gave 2.1 g (9.0 mmol, 5%) of **6-(*trans*-2-butenyl)-4-*t*-butyl-6-methylcyclohexa-2,4-dien-1-one (12)** λ_{max} 323 mμ (log ε = 3.59). *Anal.* Calcd for $C_{15}H_{22}O$: C, 82.5; H, 10.2. Found: C, 82.3; H, 10.1.

The Claisen alkali layer was diluted with water, acidified with dilute hydrochloric acid, and extracted with methylene chloride. The organic layer was dried over magnesium sulfate and the solvent evaporated to give 9.2 g of yellow oil, which was distilled at 0.1 mm, to give 4.9 g (0.0228 mol, 11%) of **2-(*trans*-2-butenyl)-4-*t*-butyl-6-methylphenol (18),** bp 147–155°. *Anal.* Calcd for $C_{15}H_{22}O$: C, 82.5; H, 10.2. Found: C, 82.7; H, 10.0.

Preparation of 4-Allyl-2,3,4,5,6-pentamethylcyclohexa-2,5-dien-1-one (4). Dienone **2** (5.0 g, 0.025 mol) was dissolved in 150 ml of 0.1 *N* methanolic hydrogen chloride. After 6 hr, the absorption peak at 333 mμ had largely disappeared. The solution was diluted with water and extracted with methylene chloride. The methylene chloride layer was washed with sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to give 4.9 g of residue, which was chromatographed on neutral alumina. Elution with petroleum ether gave 0.5 g of a mixture of equal amounts of **4** and allyl pentamethylphenyl ether. Further elution with 1:1 petroleum ether (bp 30–60°)–methylene chloride gave 4.2 g (0.0206 mol, 83%) of pure **4**, as a colorless liquid, λ_{max} 247 mμ (log ε = 4.17). *Anal.* Calcd for $C_{14}H_{20}O$: C, 82.4; H, 9.80. Found: C, 82.7; H, 9.77.

Preparation of 4-(*trans*-2-Butenyl)-2,3,4,5,6-pentamethylcyclohexa-2,5-dien-1-one (5). a. Acid-Catalyzed Rearrangement of 3. Dienone **3** (3.1 g, 0.0143 mol) was dissolved in 100 ml of 0.1 *N* methanolic HCl. After 4 hr the solution was poured into water, and extracted with methylene chloride. The methylene chloride layer was washed with sodium bicarbonate solution, dried, and evaporated. The residue was dissolved in petroleum ether and extracted with Claisen alkali. Acidification of the alkaline solution gave an oil which crystallized on seeding with pentamethylphenol. Recrystallization from methanol gave 1.0 g (0.0061 mol, 43%) of pure pentamethylphenol. The alkaline insoluble layer was washed with water, dried, and evaporated to give 1.7 g of yellow oil, which crystallized on prolonged scratching. Recrystallization from pentane gave 1.4 g (0.0064 mol, 45%) of **5** as white needles, mp 85–87°.

b. Silver-Catalyzed Alkylation of Pentamethylphenol. Pentamethylphenol (50.0 g, 0.31 mol) was suspended in 700 ml of water. Silver nitrate (53.5 g, 0.31 mol) and potassium carbonate (22.0 g, 0.16 mol) were added. The reaction flask was covered with aluminum foil and the mixture stirred rapidly for 10 min. 1-Bromo-2-butene (40.5 g, 0.30 mol) was added over a 0.5-hr period. The mixture was stirred for 1 additional hr, sodium chloride was added, and the precipitated silver salts filtered off and washed with methylene chloride. The organic layer was extracted twice with Claisen alkali, washed with water, dried, and evaporated to give 41.0 g of yellow fluid. Chromatography on neutral alumina (eluting with petroleum ether) gave a yellow oil, which crystallized after standing to give a waxy solid. Recrystallization from *n*-hexane gave 3.1 g (0.0143 mol, 4.6%) of yellow needles, mp 84–87°.

Anal. Calcd for $C_{15}H_{22}O$: C, 82.5; H, 10.2. Found: C, 82.3; H, 10.2.

Acid-Catalyzed Rearrangement of 6-Allyl-2,4,6-trimethylcyclohexa-2,4-dien-1-one (6). Dienone **6** (2.10 g, 0.012 mol) was dissolved in 100 ml of 0.1 *N* methanolic HCl. After standing for 7 hr at room temperature, the solution was poured into water and extracted with methylene chloride. The organic layer was washed several times with water, dried over magnesium sulfate, and the solvent evaporated to give 2.10 g of yellow oil. Its ir and nmr spectra were essentially identical with those of 4-allyl-2,4,6-

trimethylcyclohexa-2,5-dien 1-one (7).[2] Chromatography on Florisil gave 1.92 g (0.011 mol, 92%) of pure 7.

Acid-Catalyzed Rearrangement of Dienone 9. A solution of **9** (1.0 g, 57 mmol) in 20 ml of 0.1 *N* methanolic HCl was allowed to stand at room temperature for 8 hr. The solution was then poured into water and extracted with methylene chloride. The methylene chloride layer was washed with water, dried over magnesium sulfate, and the solvent evaporated to give 0.90 g of yellow oil. Vpc analysis on a 5-ft, 3% SE 30 column at 150° showed the presence of two peaks at retention times of 2.6 and 7 min, in the ratio 1:5. The products were isolated by vpc on the same column and identified by their ir and nmr spectra and vpc retention times as 2,4-dimethylphenol and phenol **10**, respectively.

Acid-Catalyzed Rearrangement of Dienone 12. A solution of dienone **12** (0.90 g, 4.1 mmol) in 20 ml of 0.1 *N* methanolic HCl was allowed to stand at room temperature for 6 hr. The solution was worked up as usual to give 0.89 g of yellow oil. Vpc analysis on a 5-ft, 20% DC-550 column, at 185°, showed the presence of six peaks at retention times of 6.2, 7.7, 14.2, 18.3, 22.7, and 23.9 min. The first five components were isolated from the same column, with the first two components collected at 150°, and the temperature then raised to 185° for isolation of the succeeding components. The areas of the peaks on the chromatogram were then calibrated for per cent yield by the preparation of mixtures of the products. The five products (in the order in which they were obtained from the column) were identified as **15** (14% yield), 4-*t*-butyl-2-methylphenol (20%), **16** (30%), **17** (7%), and **18** (22%), by comparison of their spectra and vpc retention times with those of authentic samples. The sixth component was approximately 4% of the total.

Preparation of 4-*t*-Butyl-2-methylphenyl Methyl Ether (15). Potassium *t*-butoxide (1.4 g, 12.4 mmol) was added to a solution of 4-*t*-butyl-2-methylphenol (2.0 g, 12.2 mmol) in 15 ml of dimethyl sulfoxide. The mixture was shaken until all the base was dissolved. Methyl iodide (1.75 g, 12.3 mmol) was then added and the mixture was shaken for an additional 5 min. The mixture was poured into ice water, and extracted with methylene chloride. The organic layer was washed several times with water, dried over magnesium sulfate, filtered, and the solvent evaporated to give 2.1 g of yellow oil, which was distilled at 5 mm to give 1.3 g (7.3 mmol, 60%) of **15** as a colorless liquid, bp 124–127°. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.8; H.10.2. Found: C, 80.4; H, 9.85.

Preparation of 4-*t*-Butyl-2-methylphenyl 1-Methylallyl Ether (16). Dienone **12** (0.35 g) was heated at 150° for 0.5 hr. Vpc analysis showed the presence of only one compound, which was shown to be **16** by its ir and nmr spectra. For analysis, a sample was isolated from vpc on a 5-ft 20% DC 550 column at 185°. *Anal.* Calcd for $C_{15}H_{22}O$; C, 82.5; H, 10.2. Found: C, 82.8; H, 10.4.

Preparation of 4-*t*-Butyl-2-methyl-6-(1-methylallyl)phenol (17). To a solution of 4-*t*-butyl-2-methylphenol (1.45 g, 8.76 mmol) in 12 ml of dimethyl sulfoxide was added potassium *t*-butoxide (1.00 g, 8.80 mmol), and the mixture shaken until all the base had dissolved. 1-Bromo-2-butene (1.20 g, 8.80 mmol) was added, and the mixture shaken for 2 min and then worked up as described for the preparation of **15**, to give 1.75 g of yellow oil. Without further purification, this was dissolved in 5 ml of dimethylaniline and heated at 200° for 4 hr. The product was then dissolved in methylene chloride, and the solution washed with dilute hydrochloric acid and with water and dried over magnesium sulfate. The solvent was evaporated to give 1.70 g of yellow oil, which was shown by vpc to consist of two components in the ratio 3:1 (in addition to a small amount of 4-*t*-butyl-2-methylphenol). The major product was isolated by vpc on a 5-ft, 20% DC-550 column at 170°, and identified as **17** by its nmr and ir spectra. *Anal.* Calcd for $C_{15}H_{22}O$; C, 82.5; H, 10.2. Found: 82.6; H, 10.3.

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Acid-Catalyzed [1,2] and [1,5] Migrations in Linearly Conjugated Cyclohexadienones. Further Evidence for Differing Types of Migration from n- and π-Protonated Cyclohexadienones[1]

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Abstract: Acid-catalyzed rearrangement of dienone **7** results solely in [1,2] migration of a methyl group to C-5. In contrast, rearrangement of dienone **1** or its 4-*t*-butyl analog in acid gives [1,5] migration of the benzyl group to C-2 as the only rearrangement process. Even in dienone **15**, [1,5] migration of the benzyl group to C-2, displacing the *t*-butyl group, occurs to a significant extent, although in this case [1,2] migration is the major process. The benzyl group is a much better migrator than the methyl group in both [1,2] and [1,5] rearrangement processes. The occurrence of [1,5] migration in dienone **15** is considered evidence that migration of benzyl groups to C-2 occurs by a single step [1,5] migration, rather than by initial [1,2] migration to the carbonyl carbon and subsequent migration to C-2. The pronounced preference of the benzyl group for [1,5] migration and of the methyl group for [1,2] migration is explained by the hypothesis that the facile migration of the benzyl group proceeds from the n-protonated cyclohexadienone, while the much slower methyl migration requires protonation of the π bond of the carbonyl.

In the preceding paper it was reported that allyl groups can apparently undergo at least five different types of migrations in acid-catalyzed rearrangements of linearly conjugated cyclohexadienones.[2] These include the "normal" [1,2] shifts, Cope migrations to C-4, reverse Claisen migrations, and [1,5] and [3,5] sigmatropic shifts to C-2. In view of the complexity of this situation, we decided to examine the acid-catalyzed rearrangements of linearly conjugated cyclohexadienones bearing benzyl substituents in place of allyl groups. The benzyl group closely resembles the allyl group in its electronic structure and its reactivity in solvolysis reactions,[3] but the possibility of rearrangements involving allylic inversion should be greatly reduced, since such reactions would disrupt the aroma-

(1) Reactions of Cyclohexadienones. XXV. For Part XXIV, see ref 2.

(2) B. Miller, *J. Amer. Chem. Soc.*, **92**, 6246 (1970).

(3) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 74–81.