

*Rearrangement of 4-Allyl-2,6-di-*t*-butyl-4-methylcyclohexadien-1-one-3,5-*d*₂.* 4-Allyl-2,6-di-*t*-butyl-4-methylcyclohexadien-1-one-3,5-*d*₂ (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 usual¹ 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-methylphenol¹⁶ 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,¹ except for the absence of the peak at τ 3.1.

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(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 Rearrangements¹

Bernard Miller

*Contribution from the Chemical Research and Development Laboratories,
Agricultural Division, American Cyanamid Company, Princeton, New Jersey.
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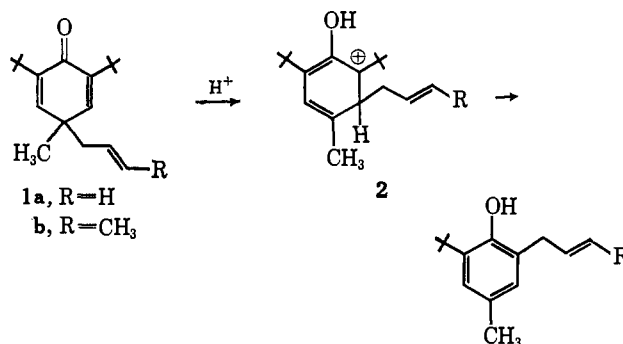
Formation of phenols by acid-catalyzed rearrangement of cyclohexa-2,4-dienones and cyclohexa-2,5-dienones results in both 1,2- and 1,3-migration of allyl and crotyl groups. While the 1,2-migrations proceed without allylic rearrangement of crotyl groups, 1,3-rearrangements result in complete allylic inversion 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."^{2,3} The migrating groups in reactions closely related to carbonium ion rear-

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

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 1a⁷ actually proceeds by a sequence of two 1,2-shifts.¹ 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.

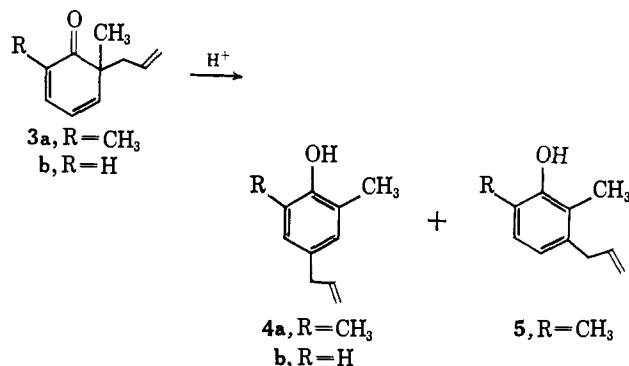
(5) (a) Y. Pocker in ref. 2, pp. 1-26; (b) J. A. Benson, ref. 2, pp. 111-232.

(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).

of the rearrangement of a *p*-cyclohexadienone in which a substituent migrates a second time even though the carbonium ion initially formed (2) could lose a proton to give an aromatic molecule.

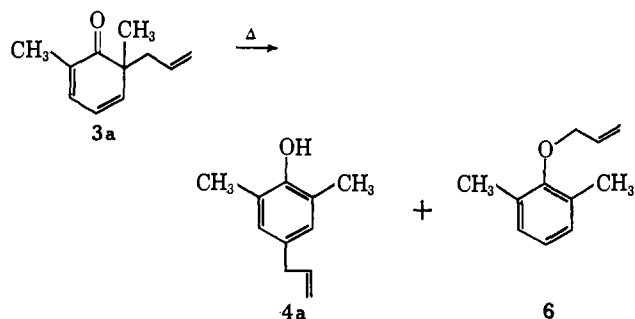
Fahrni, Habich, and Schmid, however, had previously reported that the *o*-cyclohexadienone **3a** gives a mixture of the 1,2-rearrangement product **5** and the



1,3-rearrangement product **4a** in acid,^{3a} while Leitch isolated only **4b** from the acid-catalyzed rearrangement of **3b**, although the presence of 1,2-rearrangement products was not excluded.⁸ Analogy with the rearrangements of **1** would suggest that formation of **4a** and **4b** results from two 1,2-shifts of the allyl group. It was previously suggested, however, that migration of the allyl group in carbonium ion **2**, in preference to loss of a proton, was due to the presence of the adjacent *t*-butyl group, which would inhibit formation of a planar system by loss of a proton.^{1,7} No such factor should favor 1,3-rearrangements in **3a** and **3b**. The migrations of allyl groups in some *o*- and *p*-cyclohexadienones lacking *t*-butyl groups were therefore examined, to determine the nature of the 1,3-migrations and the importance of *t*-butyl groups in determining the nature of the rearrangements of **1**.

Synthesis of Cyclohexadienones. 6-Allylcyclohexa-2,4-dienones are readily prepared by alkylation of phenoxide anions in nonpolar solvents.⁹ At the time this work was started, however, no convenient synthesis of 4-allylcyclohexa-2,5-dienones was available.

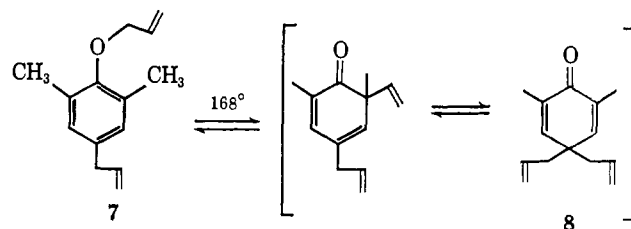
It seemed possible that the cross-conjugated cyclohexadienones might be prepared by careful thermal rearrangement of the linearly conjugated isomers. Curtin and Crawford had shown that dienone **3a** rearranges to a mixture of **4a** and **6** at temperatures much lower than those usually required for Cope rearrangements,⁹ while Schmid and his co-workers had



(8) J. Leitch, *Monatsh.*, **92**, 1167 (1961).

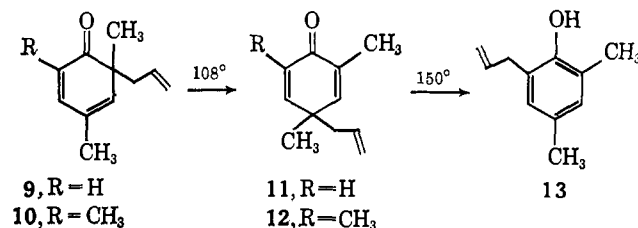
(9) D. Y. Curtin and R. J. Crawford, *J. Am. Chem. Soc.*, **79**, 3156 (1957).

demonstrated that, at the much higher temperatures of the Claisen rearrangement, the presence of a substituent in the *para* position of **7** did not prevent formation of



8 as a transient intermediate. If the *p*-cyclohexadienones are more stable than the *o*-cyclohexadienones¹⁰ conversion of an *o*-dienone such as **9** to the *p*-dienone **11** might occur more rapidly than further rearrangement of **11** to **13**.

In practice, dienones **9** and **10** were rearranged very smoothly by 2–3 hr. of heating at 100–110° to give

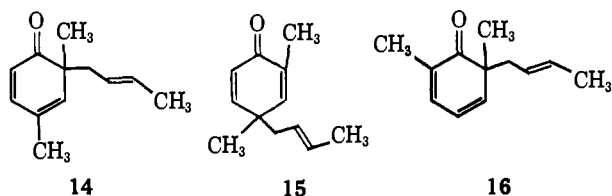


11 and **12**. The course of the reaction could conveniently be followed by observing the disappearance of the peaks at 310–320 $m\mu$ in the ultraviolet spectra of **9** and **10**. The cross-conjugated dienones **11** and **12** could be isolated in *ca.* 70% yields by chromatography on Florisil. Since our interest was centered on the synthesis of **11** and **12**, no attempt was made to determine the other products of the rearrangement. The work of Curtin and Crawford,⁹ however, leaves little doubt that rearrangement to ethers constitute the principal side reactions.

Since isolation of **9** and **10** was tedious and inefficient, it proved convenient for synthetic purposes to heat the crude mixtures from reaction of allyl bromide with salts of mesitol or 2,4-xylene⁹ until the peaks at 310 to 320 $m\mu$ had gone. Chromatography then gave **11** and **12** in yields of 50 and 20%, respectively, in essentially one step.

In order to determine whether any inversion of allyl groups occurs during dienone–phenol rearrangements, we attempted to prepare cross-conjugated cyclohexadienones with substituted allyl groups at C-4. Synthesis of cross-conjugated cyclohexadienones by rearrangement of linearly conjugated cyclohexadienones, however, appears to be limited to compounds in which the terminal position of the allyl group is unsubstituted. Heating a crude alkylation mixture containing dienone **14** until the 320- $m\mu$ peak was gone resulted in a product containing no carbonyl band in the infrared. Presumably rearrangement went either entirely to the ether, or, *via* the cross-conjugated dienone, to 2-(2-butenyl)-4,6-dimethylphenol. This point was not investigated. Fortunately, while this work was in progress Schmid and his co-workers reported the syn-

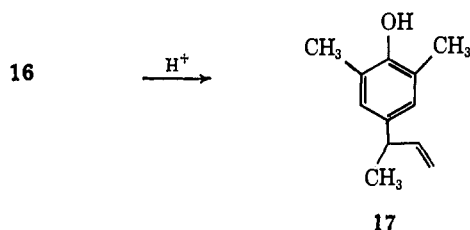
(10) 6-Bromocyclohexa-2,4-dienones rearrange completely to 4-bromocyclohexa-2,5-dienones on standing: L. Denivelle and R. Fort, *Compt. rend.*, **240**, 2423 (1955).



thesis of *p*-cyclohexadienones by direct alkylation of phenols.¹¹ Using a modification of their procedure, **15** was prepared in 1% yield by reaction of 2,4-dimethylphenol with crotyl bromide in the presence of silver carbonate.

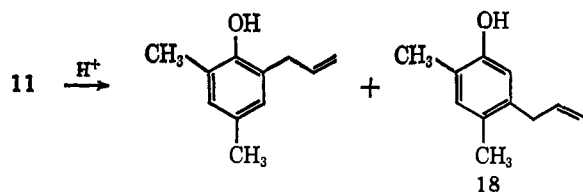
Rearrangements. Unlike 2,6-di-*t*-butylcyclohexadienones (**1**), which required several hours in a 10% solution of sulfuric acid in acetic acid to rearrange completely,⁷ dienones **11**, **15**, and **16** rearranged almost instantaneously in acetic acid containing 1% sulfuric acid. Ultraviolet spectra taken within 3 min. of addition of acid to the dienones showed the complete absence of the 320-m μ peak of **16**, and a marked decrease in the absorption at 242 m μ in the spectra of **11** and **15**. No further change in the spectra occurred after 0.5 hr. in acid at room temperature.

Rearrangement of **16** gave a single phenol in almost quantitative yield. The same phenol was obtained by thermal rearrangement of **16**, indicating that this product had structure **17**. The structure of **17** was



confirmed by its n.m.r. spectrum (in CDCl₃) which showed a single aromatic peak (2 H) at τ 3.20, a monosubstituted ethylene group, and a methyl group attached to a methylene carbon (doublet at τ 8.65, $J = 7$ c.p.s.).

Rearrangement of **11** in acetic acid containing 1% of sulfuric acid gave two phenols in the ratio 1.5:1.0. The major product was identified as 2-allyl-4,6-dimethylphenol, identical with the sole product of thermal

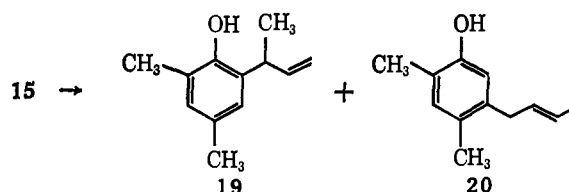


rearrangement of **11**. The n.m.r. spectrum of the minor product showed, in addition to the allyl and methyl groups, two very sharp singlets (1 H apiece) at τ 3.16 and 3.47, indicating the presence of hydrogens *ortho* and *meta* to the hydroxyl group. In view of the demonstrated efficacy of the allyl group as a migrating group, this phenol was assigned structure **18**, rather than a possible isomer in which the methyl group had

(11) R. Barner, A. Boller, J. Borgulya, E. G. Herzog, W. von Philipsborn, C. von Planta, A. Fürst, and H. Schmid, *Helv. Chim. Acta*, **48**, 94 (1965).

migrated. No evidence for the presence of an isomer with two adjacent hydrogens could be detected.

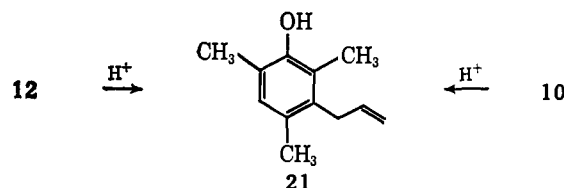
Rearrangement of **15** again gave two isomeric phenols, in the ratio 2.0:1.0. The principal product was the



same as the product of thermal rearrangement of **15**, and its n.m.r. spectrum (2 H singlet at τ 3.20, 3 H doublet at τ 8.65, $J = 7$ c.p.s.) agreed with that expected of structure **19**. The second isomer showed sharp 1 H singlets at τ 3.13 and 3.44, an allylic methylene as a doublet at 6.83 ($J = 5$ c.p.s.), and an allylic methyl group as a doublet at 8.31 ($J = 5$ c.p.s.). It was therefore assigned structure **20**. Again, no evidence for migration of the allylic group into the position between the two methyl groups was observed.

The rearrangement rates of **11** and **15** were too fast to be measured in acetic acid-sulfuric acid. However, the rates of disappearance of the 242-m μ peaks in the ultraviolet spectra of **11** and **15** were easily measured in methanolic hydrochloric acid. The half-life of **11** in 1 *N* acid at room temperature was *ca.* 2 hr. The disappearance of **15** in 1 *N* acid at room temperature was inconveniently fast, but in 0.01 *N* acid it had a half-life of *ca.* 3 hr. The very fast migration of the crotyl group, compared to the allyl group, agreed with that observed in the rearrangement of dienone **1**.⁷

Rearrangement of dienone **12** gave **21**^{3a} in quantita-

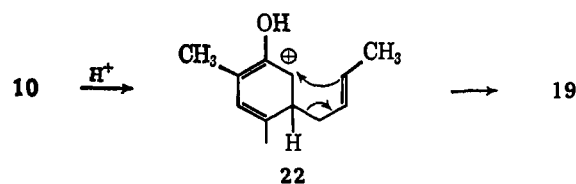


tive yield. Rearrangement of **10** in acid gave the same product. Rearrangement of **12** was appreciably slower than that of **11**, since appreciable amounts of **12** were recovered unchanged from 1% H₂SO₄ in acetic acid after 15 min. Complete conversion to **21**, however, was observed after 1 hr.

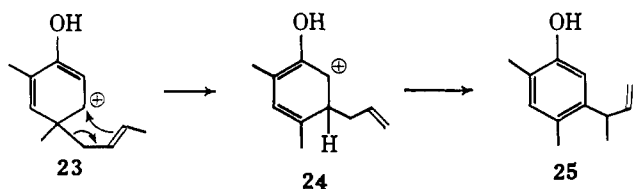
Discussion

The 1,3-migrations of crotyl groups in the rearrangements of **11** and **15** clearly differ from ordinary carbonium ion rearrangements, since they involve complete inversion of the migrating butenyl groups. Two possible modes of migration can be considered for the 1,3-shifts: they can proceed in a single step, or by two successive 1,2-migrations.

If the 1,3-migrations do occur by two 1,2-migrations, just one of the two steps must involve inversion of the



allylic system. Such a rearrangement of, for instance, the carbonium ion (**22**) formed by a 1,2-shift of the crotyl group of **15**, seems more probable than a similar process in the rearrangements of **1**,⁷ in that no appreciable steric interference should inhibit it. However, the question must be raised as to why a similar cyclic rearrangement should not occur initially to give carbonium ion **24**, and, finally, phenol **25**. It is true that **22** is a more reactive carbonium ion than **23**, and might



therefore follow reaction paths which do not occur in **23**. It seems quite improbable, however, that rearrangement of **22** should proceed entirely by inversion of the allylic group, while the allylic group of **23** migrates entirely by a normal shift, without any of the alternative process occurring in either case.

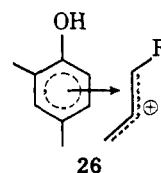
If, on the other hand, it is assumed that the initial migration does take place both with allylic rearrangement, to give **24**, and without rearrangement, to give **22**, it must then be assumed that the methylallyl group in **24** migrates infinitely fast, compared to loss of a proton, and migrates entirely without allylic rearrangement, while the crotyl group of **22** either does not migrate at all or migrates entirely with allylic rearrangement. These conditions seem far too stringent to be at all probable.

It is much simpler to assume that the 1,3-shifts of the crotyl groups of **15** and **16** (and presumably, the allyl group of **11**) occur in single-step processes competing with the normal 1,2-migrations.

Several arguments suggest that the 1,3-migrations are intramolecular, rather than processes involving cleavage of the dienones to allyl or crotyl carbonium ions and phenols, followed by realkylation of the phenols by the carbonium ions. It has previously been shown that rearrangement of **1a** is completely intramolecular, even though the reaction takes place in much more concentrated acid than those reported in this paper, and requires much longer reaction times.⁷ If cleavage of an allyl group from a dienone were a facile process, some evidence for it might have been expected during rearrangement of **1a**. Furthermore, the work of Schmid and his co-workers strongly suggests that alkylation of phenols by crotyl carbonium ions should give the crotylphenol, rather than the 1-methylallyl derivative.¹¹ Finally, rearrangement of **15** in the presence of 6 equiv. of thiophenol resulted in no change in the reaction. The highly nucleophilic sulfur atom would have been expected to trap any carbonium ions, if any were present.

We are left, therefore, with a direct, 1,3-migration which, in the geometry of its transition state at least, must resemble the Cope rearrangement. Unlike the typical thermal "no mechanism" rearrangement,² however the migrating allyl group in these acid-catalyzed Cope rearrangements must bear an appreciable positive charge. It has been previously shown that rearrangement of a crotyl carbonium ion in **1** is more than 100 times as fast as that of an allyl carbonium

ion.^{1,7} If it is assumed that the rearrangements of **11** and **15** are first order in both dienone and acid, their half-lives show the rate constant for rearrangement of **15** in methanolic HCl to be *ca.* 70 times that of that of **11**. Such relationships would be expected of the 1,2-migrations, since the migrating groups bear appreciable carbonium ion character.⁵ The somewhat higher percentage of 1,3-migration observed in the rearrangement of **15** compared to **11**, and the absence of any 1,2-migration in **16**, while **3a** undergoes appreciable 1,2-migration, suggests that the migrating groups in the 1,3-migrations bear even more positive charge than in the 1,2-shifts. To accommodate these observations, the transition state for 1,3-migrations must resemble a π -complex of an allylic carbonium ion with a phenolic ring (**26**).

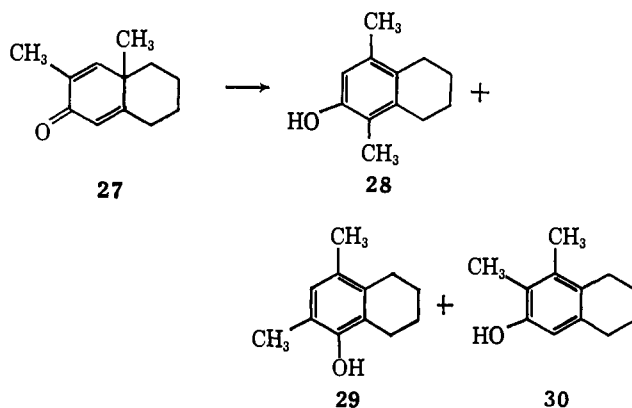


We have previously suggested a similar transition state for the rearrangements of another group of cyclohexadienones, the *p*-quinamines.¹² In the quinamine rearrangement, however, it appears probable that a π -complex is an intermediate in the reaction. There is no evidence as yet to indicate whether the acid catalyzed Cope rearrangement proceeds through any intermediates.

As was stated in the previous paper,⁷ the absence of any 1,3-migration of the unrearranged crotyl group in **15** demonstrates that the *t*-butyl groups of **1** are essential to a second shift of the migrating group from the *meta* to the *ortho* position. Clearly, in the absence of a large steric effect inhibiting formation of a planar system, migration of even such a stable carbonium ion as the crotyl group cannot compete with loss of a proton from **22**.

The observation that 1,2-migration of allyl and crotyl groups occurs exclusively toward C-5 of dienones **11** and **15** and away from the methyl group at C-1 is rather surprising. While some interference by the methyl group might have been anticipated, such complete control is unusual.

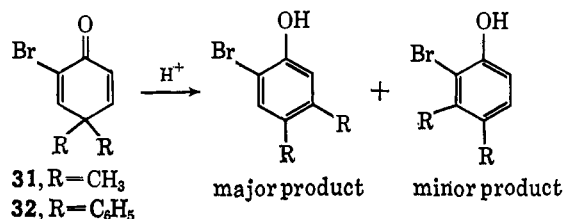
Kropp has reported that the presence of a methyl group in the *ortho* position of dienone **27** can partially



(12) B. Miller, *J. Am. Chem. Soc.*, **86**, 1127 (1964).

force the angular methyl group to migrate to the other angular position, and ultimately to form the unusual product **28** as well as the expected **29** and **30**.¹³

Bordwell and Wellman have reported that rearrangement of dienones **31** and **32** give predominantly phenols resulting from migration of substituents to the less substituted double bond.¹⁴ They believed the influence of the bromine atom to be largely due to polar



effects. Since both methyl groups and bromine atoms tend to repel migrating groups, however, the effect must be principally steric in origin.¹⁵

The repelling effects of substituents at C-1 suggest that these substituents will tend to slow down the absolute rearrangement rates of dienones. The rearrangement rate of **1** is indeed very much slower than those of dienones lacking the *t*-butyl groups. While it is tempting to ascribe this to repulsion of migrating groups by the *t*-butyl groups, however, the presence of the *t*-butyl groups will presumably also inhibit rearrangement by decreasing the basicity of the dienones. Dienone **12**, however, would not be expected to be appreciably less basic than **11**. The much slower rearrangement rate of **12** supports the view that substituents at C-1 materially retard migration of substituents from C-4 to C-3.

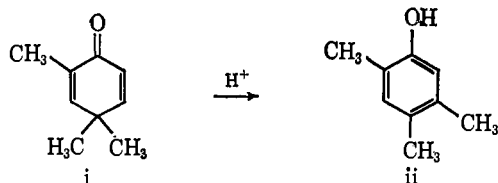
Experimental Section^{16,17}

Synthesis of Cyclohexadienones. *6-Allyl-2,4,6-trimethylcyclohexa-2,4-dienone (10)*. To a solution of 2,4,6-trimethylphenol (30.0 g., 0.221 mole) in 600 ml. of benzene was added 12.0 g. of sodium methoxide (0.222 mole). The mixture was stirred and distilled until 200 ml. of solvent was collected. It was then stirred in an ice bath while allyl bromide (50.0 g.) was added slowly, and then stirred for 26 hr. at room temperature. The mixture was then neutral to indicator paper. It was washed with water, extracted twice with Claisen alkali, and dried over magnesium sulfate. Evaporation of the solvent left 36.2 g. of yellow fluid, of which 12.0 g. was chromatographed on Florisil to give 7.0

(13) P. J. Kropp, *Tetrahedron Letters*, No. 25, 1671 (1963).

(14) F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **29**, 509 (1964).

(15) M. Yanagita and S. Inayama, *ibid.*, **19**, 1724 (1954), found that only ii could be isolated from rearrangement of i. The very low yield (23% of crude product) however makes it difficult to draw conclusions from this report.



(16) All melting points are corrected. Boiling points are uncorrected. Microanalyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Ultraviolet spectra were taken in methanol solution unless otherwise indicated.

(17) The author wishes to thank Mr. Richard Wayne for his assistance in interpretation of n.m.r. spectra.

g. of **10** (0.0397 mole, 54% based on the amount chromatographed) as a yellow oil, λ_{max} 319 m μ (ϵ 4830), b.p. 60–63° (0.15 mm.).

Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}$: C, 81.8; H, 9.08. Found: C, 80.9; H, 9.41.

The reaction between allyl bromide and 2,4-dimethylphenol was carried out in a similar manner to give a 7% yield of *6-allyl-4,6-dimethylcyclohexa-2,4-dienone (9)*, λ_{max} 318 m μ (ϵ 4620), b.p. 57° (0.1 mm.).

Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}$: C, 81.5; H, 8.64. Found: C, 81.8; H, 8.81.

The alkylation of 2,6-dimethylphenol with 1-bromo-2-butene was carried out as described for the preparation of **10**, except that the product was purified by two distillations through a three-plate Snyder column followed by chromatography on basic alumina (activity III). *6-(trans-2-Butenyl)-2,6-dimethylcyclohexa-2,4-dienone (16)*, λ_{max} 309 m μ (ϵ 4170), b.p. 72–73° (0.2 mm.), n_{D}^{25} 1.5071, was obtained in 10% yield.

Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}$: C, 81.8; H, 9.09. Found: C, 81.7; H, 8.95.

4-Allyl-2,4,6-trimethylcyclohexa-2,5-dienone (12). **10** (4.0 g., 0.0227 mole) was heated at 108° until the extinction at 319 m μ had fallen below 500 (2.5 hr.). Chromatography on Florisil gave 2.85 g. of **12** (0.0162 mole, 71%), λ_{max} 244 m μ (ϵ 14,000), b.p. 40–42° (0.2 mm.).

Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}$: C, 81.8; H, 9.08. Found: C, 81.3; H, 9.31.

4-Allyl-2,4-dimethylcyclohexa-2,5-dienone (11) was similarly prepared in 68% yield by heating **9** at 105° for 2 hr. The product had λ_{max} 242 m μ (ϵ 13,850), b.p. 38–39° (0.15 mm.).

Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}$: C, 81.5; H, 8.64. Found: C, 80.9; H, 8.60.

4-(trans-2-Butenyl)-2,4-dimethylcyclohexadien-1-one (15). Silver nitrate (113.0 g., 0.667 mole) was dissolved in 1 l. of water in a three-necked flask covered with aluminum foil. Potassium carbonate (46.7 g., 0.334 mole) was added, and the mixture was stirred for 15 min. A solution of 2,4-dimethylphenol (100 g., 0.819 mole) in 300 ml. of ethanol was added. The reaction mixture was cooled in ice and stirred for 15 min. 1-Bromo-2-butene (50.0 g., 0.369 mole) was added drop by drop over a 15-min. period to the stirred solution. Stirring was continued for 1.5 hr. at room temperature. The mixture was then filtered, and the filtrates were extracted with methylene chloride. The methylene chloride layer was washed with 15% potassium hydroxide solution, dried, and evaporated. The residual liquid was chromatographed on Florisil. Elution with petroleum ether (b.p. 39–56°) and methylene chloride gave mainly ethers, which were discarded. Elution with chloroform gave 3.6 g. of ketone, which was distilled to give 1.0 g. (0.0057 mole, 0.7%) of **15**, b.p. 61–63° (0.2 mm.), n_{D}^{25} 1.5060, λ_{max} 242 m μ (ϵ 14,600).

Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}$: C, 81.8; H, 9.09. Found: C, 81.8; H, 9.33.

Rearrangements of Cyclohexadienones. *Reaction of 6-(trans-2-Butenyl)-2,6-dimethylcyclohexa-1,4-dienone (16) with Acid.* **16** (3.0 g., 0.0170 mole) was dissolved in 20 ml. of glacial acetic acid containing 1% (by volume) concentrated sulfuric acid. The ultraviolet spectrum of the solution 3 min. after mixing

showed no peak at 309 $m\mu$, but showed a strong band at *ca.* 270 $m\mu$. The solution was dissolved in water and extracted with methylene chloride. The methylene chloride layer was washed with sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to give 3.0 g. of yellow fluid. Distillation gave 2.5 g. (0.0142 mole, 83%) of 2,6-dimethyl-4-(1-methyl)allylphenol (**17**), b.p. 84–86° (0.35 mm.), n^{25}_D 1.5265.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.09. Found: C, 81.5; H, 9.17.

B. **16** (1.0 g., 0.0569 mole) was shaken in 10 ml. of 6 *M* sulfuric acid for 15 min. The mixture was extracted with methylene chloride and the methylene chloride layer was washed with sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to give 0.60 g. of **17**, identical in infrared and n.m.r. spectra and v.p.c. retention time (11.6 min. on a 6-ft., 10% diethylene glycol succinate on Gas Chrom Z column at 220°) with the product of procedure A.

Thermal Rearrangement of 16. **16** (3.0 g., 0.0170 mole) was heated to 105°, and maintained at that temperature for 1 hr. Distillation of the product gave 2.5 g. (0.0142 mole, 83%) of **17**, b.p. 82–88° (0.4 mm.), n^{25}_D 1.5261, identical with the product of the acid-catalyzed rearrangements.

Reaction of 4-trans-2-Butenyl-2,4-dimethylcyclohexadien-1-one (15) with Acid. **A.** **15** (0.30 g., 0.0017 mole) was dissolved in a solution of 20 ml. of glacial acetic acid and 0.2 ml. of concentrated sulfuric acid. After standing for 30 min., the mixture was worked up as described for **16**, to give 0.3 g. of colorless liquid. The infrared spectrum showed no carbonyl peak. V.p.c. analysis (6-ft., 2% SE30 silicone gum column at 150°) showed the presence of two peaks, retention times 6.0 and 11.9 min., in the area ratio of 2.0:1.0. The components were isolated by v.p.c. The major

component was shown by its n.m.r. and infrared spectra and v.p.c. retention times to be 2-(1-methylallyl)-4,6-dimethylphenol.¹⁸ The minor product crystallized in waxy, white needles, m.p. 57–59°. Its n.m.r. spectrum indicated it to be 3-(*trans*-2-butenyl)-4,6-dimethylphenol (**18**).

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.09. Found: C, 81.5; H, 9.17.

B. A mixture of 0.1 g. of **15** and 0.5 g. of thiophenol was reacted with acid and worked up as described in procedure A. V.p.c. analysis of the product showed the ratio of the two phenols to be 2.0:1.0. No 2-butenyl phenyl thioether could be detected.

Reaction of 4-Allyl-2,4-dimethylcyclohexa-2,5-dienone (11) with Acid. To an ice-cooled solution of 0.2 ml. of concentrated sulfuric acid in 20 ml. of glacial acetic acid was added 3.0 g. of **11** (0.0185 mole). After standing in ice for 15 min., the mixture was worked up as usual to give 3.0 g. of yellow fluid. V.p.c. analysis on a 6-ft., 20% diethylene glycol column at 225° showed the presence of two components in the ratio of 1.5:1.0. Chromatography on Florisil gave, on elution with methylene chloride, 1.4 g. (0.00865 mole, 47%) of the major component, which was found to have infrared and n.m.r. spectra identical with those of 2-allyl-4,6-dimethylphenol.¹⁹ Elution with chloroform gave 1.0 g. of a mixture containing approximately equal amounts of the two products. The minor product was isolated by v.p.c. as a colorless oil, n^{25}_D 1.5315. Its n.m.r. spectrum indicated that it was 3-allyl-4,6-dimethylphenol.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.5; H, 8.64. Found: C, 81.4; H, 9.03.

(18) Q. R. Bartz, R. F. Miller, and R. Adams, *J. Am. Chem. Soc.*, **57**, 371 (1935).

(19) L. Claisen and E. Tietze, *Ann.*, **449**, 81 (1926).

Carbonium Ions. XX. Acid-Catalyzed Cleavage Reactions

N. C. Deno and Edward Sacher

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The xanthylium cation, but not the less stable triphenylmethyl cation, is ejected from protonated primary, secondary, and tertiary alcohols and protonated ketones in 10–50% H_2SO_4 at 25°. This effect of the xanthylium cation, formally insulated from the functional group by a saturated carbon, shows that in the transition state the positive charge is delocalized throughout the xanthylium system, the forming olefin, and the leaving H_2O .

Introduction

The acid-catalyzed polymerization of olefins is one of the classic reactions of synthetic organic chemistry. Although the reaction is well known to be reversible,¹ examples where the products of reversal are dominant

(1) For a study demonstrating this reversibility, see J. E. Hofmann and A. Schriesheim, *J. Am. Chem. Soc.*, **84**, 953, 957 (1962).

are relatively rare. The most complete study of this latter type is that of Whitmore and Stahly,² who studied the fragmentation of alcohols and 1,3-diols. The successful examples were confined to tertiary alcohols, even for the 1,3-diols,^{2,3} which left the impression that fragmentation was possible only *via* relatively stable carbonium ions, specifically *t*-alkyl cations in the cases cited (of course, the reactant must be constituted so that it can eject a stable carbonium ion, the *t*-butyl in the cases cited, but this aspect of the reaction is not under discussion). A single example of cleavage of a ketone, the formation of 3-methyl-2-butanone from

(2) F. C. Whitmore and E. E. Stahly, *ibid.*, **55**, 4153 (1933); **67**, 2158 (1945); F. C. Whitmore, *Chem. Eng. News*, **26**, 668 (1948).

(3) A. N. Slovjanzov, *J. Russ. Phys. Chem. Soc.*, **39**, 140 (1907); *Chem. Abstr.*, **1**, 2077 (1907); A. Kalishev, *J. Russ. Phys. Chem. Soc.*, **46**, 428 (1914); *Chem. Abstr.*, **8**, 3186 (1914); L. S. Schmerling, B. S. Friedman, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **62**, 2446 (1940).