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.

Acknowledgment. I wish to thank the donors of the Petroleum Research Fund, Administered by the American Chemical Society, and the National Science Foundation for grants in support of this work.

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.

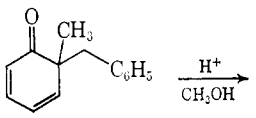
ticity of the benzene ring. Only [1,2] and [1,5] migrations should be feasible, and the effects of substitution on the dienone ring and of changes in reaction conditions upon these migrations should be readily determined.

We were further encouraged to examine the rearrangements of benzyl-substituted cyclohexadienones by the reports that benzyl groups actually migrate more slowly than methyl groups in the solvolysis of neopentyl tosylates[4] and in the reactions of diazomethane with ketones.[5] This contrasts with our observations[2,6] that allyl groups, which might, *a priori*, be expected to have migratory aptitudes similar to those of benzyl groups, are very effective migrating groups in the dienone–phenol rearrangement.

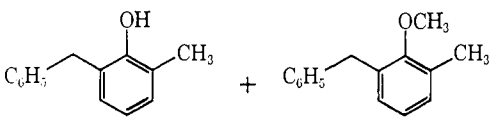
Results

Several linearly conjugated cyclohexadienones were prepared by Claisen alkylation of the corresponding phenols with benzyl bromide or benzyl chloride in benzene solution, or by silver ion catalyzed alkylation of the phenols.

Rearrangement of the simplest benzyl-substituted cyclohexadienone, 6-benzyl-6-methylcyclohexa-2,4-dien-1-one (**1**),[7] was carried out in methanolic HCl as was previously described[2] for the corresponding allyl derivatives. The completeness of the rearrangement was checked by ir analysis of the product before any further analyses were carried out. Vpc analysis of the crude reaction product showed the presence of four overlapping peaks at low retention times. These had retention times which corresponded to those for benzyl chloride, benzyl methyl ether, *o*-cresyl methyl ether, and *o*-cresol. No attempt was made to isolate these products, which amounted to about one-third (by vpc estimate) of the total reaction product. The two major products of the reaction had peaks at longer retention times, in the area ratio 1:1. These products were isolated by vpc. The component with the greater retention time was found to be 2-benzyl-6-methylphenol (**2**), which was identical with a sample prepared by Claisen alkylation of *o*-cresol with benzyl bromide.[7]



1

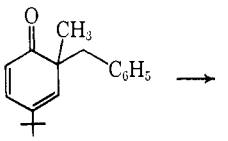


2

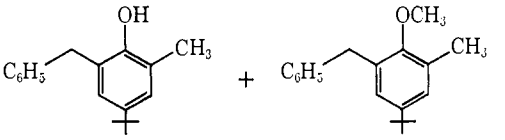
The component with the lower retention time lacked phenolic or carbonyl absorption in the ir, but showed the presence of a methoxy peak at τ 6.30 in its nmr spectrum. In view of the formation of **2** as the other major product from rearrangement of **1**, the methyl ether of **2** was prepared by alkylation of 2-benzyl-6-methylphenoxide ion with methyl iodide in DMSO solution. The product was identical with the ether obtained from the rearrangement of **1**.

The rearrangement of **1** was also carried out in acetic acid–sulfuric acid solution and in aqueous dioxane containing sulfuric acid. Both reactions gave rise to a single rearrangement product, which in each case was isolated and identified as **2**. We have found that **2** can also be obtained by thermal rearrangement of **1**. As with all rearrangements reported in this paper, however, ir analysis of the crude reaction product showed that all of the starting dienone had disappeared before vpc analysis was attempted, and **2** must therefore have been obtained entirely from the acid-catalyzed rearrangement.

Rearrangement of the 4-*t*-butyldienone **3** in 0.5 *N* methanolic HCl gave a mixture of six components, which were isolated by preparative vpc. The first four components were identified by comparison of their ir and nmr spectra and vpc retention times with those of authentic samples as benzyl methyl ether, benzyl chloride, 4-*t*-butyl-2-methylphenyl methyl ether, and 4-*t*-butyl-2-methylphenol, all resulting from fragmentation of **3**. The last two components, which were isolated in approximately equal amounts, were identified as 2-benzyl-4-*t*-butyl-6-methylphenol (**4**), identical with the principal product from Claisen alkylation of 4-*t*-butyl-2-methylphenol, and its methyl ether, **5**, identical



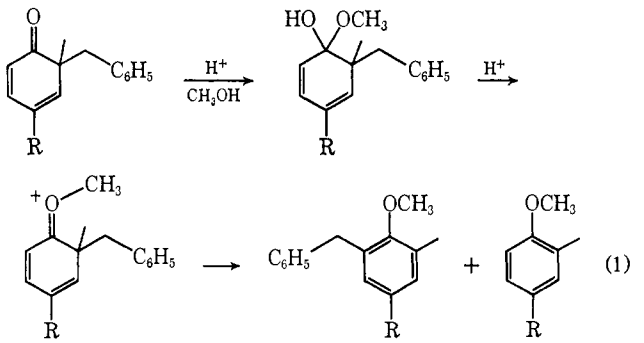
3



4 5

with the product obtained by reaction of the potassium salt of **4** with methyl iodide in DMSO solution. Approximately twice as much of the dienone reacted by rearrangement as by fragmentation processes.

As expected, it was found that neither phenol **2** nor **4** formed a methyl ether in methanolic HCl under the conditions used for the rearrangements of **1** and **3**. The methyl ethers obtained in these reactions must therefore have arisen from addition of methanol to the carbonyl group of the dienone, as is shown in reaction 1.



(1)

The absence of any products of [1,2] migration of a substituent to C-5 in the rearrangement of dienone **3**

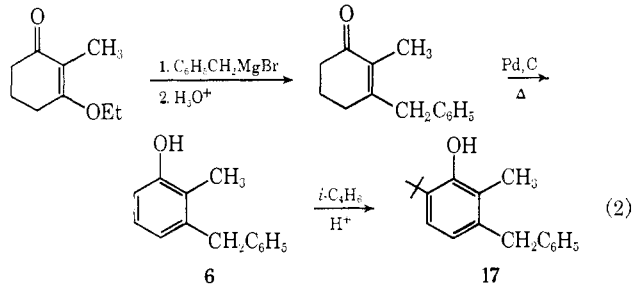
(4) (a) P. Warrick, Jr., and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **84**, 4095 (1962); (b) J. R. Owen and W. H. Saunders, Jr., *ibid.*, **88**, 5809 (1966).

(5) H. O. House, E. J. Grubbs, and W. F. Gannon, *ibid.*, **82**, 4099 (1960).

(6) (a) B. Miller and H. Margulies, *ibid.*, **87**, 5106 (1965); (b) B. Miller, *ibid.*, **87**, 5115 (1965).

(7) D. Y. Curtin and M. Wilhelm, *J. Org. Chem.*, **23**, 9 (1958).

might reasonably be explained by steric interference with the *t*-butyl group at C-4. The apparent absence of any migration of a benzyl or methyl group to C-5 in the rearrangement of **1**, however, was unexpected. To determine whether any [1,2] migration product might be hidden under the vpc peak for **2**, 3-benzyl-2-methylphenol (**6**), which would arise from migration of a benzyl group to C-3, was synthesized as shown in sequence 2. (Since the evidence presented in this paper indicates that a benzyl group is a much better migrator in the dienone–phenol rearrangement than is a methyl group, it was not considered necessary to synthesize the alternate [1,2] migration product, 2-benzyl-3-methylphenol.) It was found that **6** has a significantly higher retention time on an SE 30 vpc

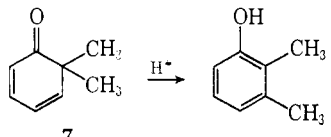


(2)

6 17

column than does **2**. Less than 1% phenol **6** could readily be detected in a synthetic mixture with **2**. Despite this, no detectable quantities of **6** could be found in the products from rearrangement of **1**.

This result was quite surprising, since the work of Marvell and Magoon[8] had previously indicated that rearrangement of dienone **7** gives the [1,2] methyl migration product, **8**. Since the reported yield[8] of



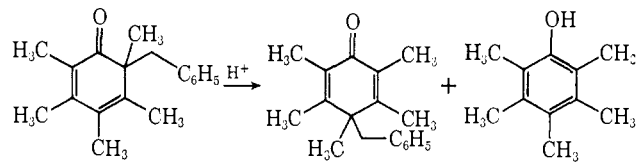
7 8

the phenylurethan of **8** was only 9%, however, it seemed possible that significant amounts of 2,6-dimethylphenol might actually have been produced during the rearrangement of **7**. Repetition of the rearrangement of **7** in acetic anhydride–sulfuric acid, according to the procedure of Marvell and Magoon,[8] or in acetic acid–sulfuric acid, under conditions similar to those used for the rearrangement of **1**, however, gave **8** as the only rearrangement product. Vpc analysis showed that less than 1% 2,6-dimethylphenol could have been produced.

Rearrangement of **1** to **2** might, in theory, have proceeded by migration of either a benzyl group or a methyl group to C-2. A decision between these two types of processes was made by consideration of the relative rates of rearrangement of dienones **1** and **7**. It was found that dienone **1** reacted in a clean first-order process with a half-life of 90 min in 0.5 *N* HCl in 80% aqueous methanol. Dienone **7**, on the other hand, did not significantly react in the same time period, but underwent a slow disappearance of its absorption maximum at 312 mμ on standing in aqueous methanol in the absence of added acid. The reaction was roughly first order, and had a half-life of *ca.* 175 hr. The reaction rate was not noticeably changed in 0.5 *N* HCl. It could be determined that any acid-catalyzed reaction was at least 10^3, and probably 10^4, times as slow as the rearrangement of **1**.

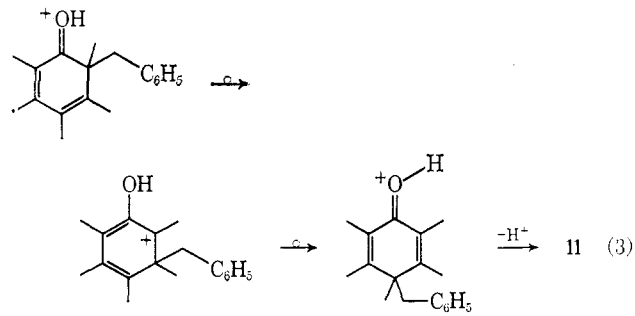
The only plausible explanation for the great difference in reaction rates of these two very similar compounds is that the benzyl group migrates in **1**, while a methyl group must move in **7**. Thus, rearrangement of **1** results exclusively in a [1,5] shift of the benzyl group, while rearrangement of **7** results exclusively in a [1,2] shift of the methyl group.

In order to determine whether migration of a benzyl group is faster than that of a methyl group if both undergo [1,2] migrations, the rearrangements of dienones **9** and **10** were studied. Rearrangement of



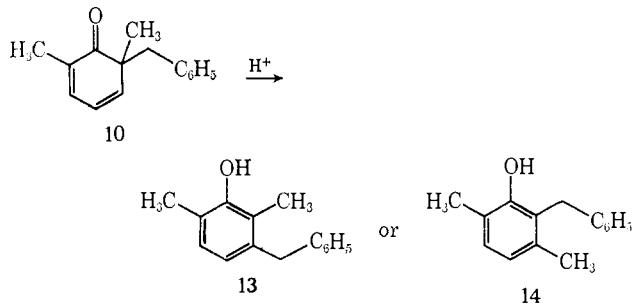
9 11 12

dienone **9** in methanolic HCl resulted in approximately equal percentages of cleavage to pentamethylphenol (**12**) and rearrangement to a new, cross-conjugated cyclohexadienone, **11**. The nmr spectrum of **11** clearly showed that the benzyl group was attached to the quaternary carbon at C-4, and thus that the reaction had proceeded exclusively *via* migration of the benzyl group. Although formation of **11** is formally the result of a [1,3] migration of the benzyl group, it seems almost certain that its formation, like those of the many similar [1,3] migrations in cross-conjugated cyclohexadienones,[9] proceeds by a sequence of two [1,2] shifts, as is shown in reaction 3.



11 (3)

Some support for this mechanism is provided by the rearrangement of dienone **10**, which gives (in addition



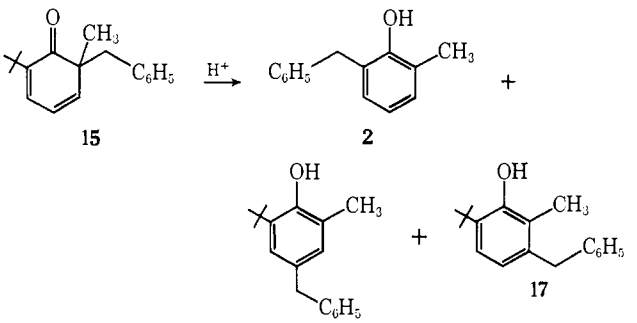
10 13 14

(8) E. N. Marvell and E. Magoon, *J. Amer. Chem. Soc.*, 77, 2542 (1955).

(9) B. Miller in "Mechanisms of Molecular Migrations," B. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, pp 275–285.

to fragmentation products) a single rearrangement product, whose nmr and ir spectra are consistent with either structure **13** or **14**. In view of the exclusive migration of the benzyl groups in dienone **9** and in dienone **15** (described below) it seems most probable that the rearrangement product is actually **13**. Definitive proof of this structural assignment has not been obtained, however.

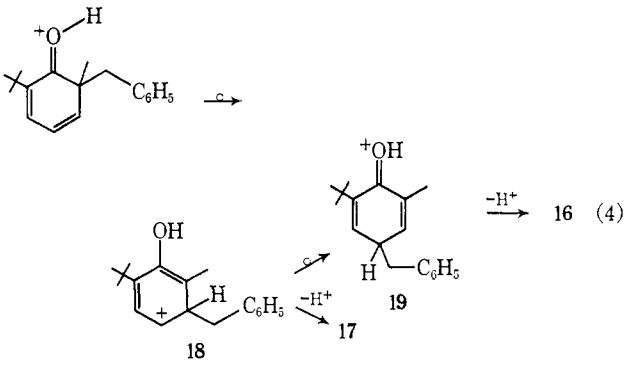
Finally, the rearrangement of dienone **15** in 2 *N* methanolic HCl was studied. This reaction gave not only the normal fragmentation products, benzyl chloride, benzyl methyl ether, and 2-*t*-butyl-6-methylphenol, but gave three products with higher vpc retention times in the mole ratio 5:2:7. These were isolated by vpc and their ir and nmr spectra examined. The product with the lowest retention time was identified as phenol **2**. Thus migration of a benzyl group to C-2 can be a major migration pathway even when C-2 is already occupied by a *t*-butyl group. The next component, which was obtained in the lowest yield, was also found to be a phenol. Its nmr spectrum showed the presence of *t*-butyl, methyl, and benzyl substituents on the phenolic ring, and also showed singlets (1 H) at τ 3.2 and 3.45, which were tentatively assigned to protons at the *meta* positions of the phenol ring. It was therefore considered that the product might have the benzyl group in the *para* position. 4-Benzyl-2-*t*-butyl-6-methylphenol (**16**) was readily synthesized by reaction of 4-benzyl-2-methylphenol with isobutylene in the presence of sulfuric acid. The product had identical nmr and ir spectra and vpc retention times with the minor product from rearrangement of **15**. The final (and major) product from the rearrangement of **15** was again a phenol with *t*-butyl, methyl, and benzyl substituents. Its nmr spectrum showed the presence of one-proton doublets (J = 8.0 cps) at τ 3.1 and 3.5. It seemed probable, therefore,



that the product was the expected 3-benzyl-6-*t*-butyl-2-methylphenol (**17**). Alkylation of 3-benzyl-2-methylphenol (**6**) with isobutylene in the presence of sulfuric acid gave **17**, identical with the product obtained by rearrangement of **15**.

Discussion

The work described above shows that acid-catalyzed rearrangements of linearly conjugated cyclohexadienones can result in overall [1,2], [1,3], and [1,5] migrations of benzyl groups. The apparent [1,3] migration to C-4 normally occurs when the presence of a substituent at C-5 prevents formation of the product of a [1,2] migration by loss of a proton from an intermediate carbonium ion. The only exception to this rule is the formation of phenol **16** as a minor product from the rearrangement of dienone **15**. In the absence of any other evidence that a direct [1,3] shift of a benzyl group can occur, it seems probable that formation of **16** proceeds by way of two successive [1,2] shifts, as in reaction 4. Apparently a second migration of the benzyl group in carbonium ion **18** to give **19** can compete with loss of a proton to give **17**. It is not clear



why loss of a proton from the intermediate carbonium ion should be slower (relative to migration of a benzyl group) when the carbonyl group is flanked by a *t*-butyl group than when the *t*-butyl group is replaced by a methyl group. It is possible that approach of solvent for removal of the proton is hindered by the presence of a *t*-butyl group on the other side of the ring. Alternatively, it is possible that steric interference between substituents on the ring are less pronounced in the nonplanar carbonium ion **18** than in phenol **17**. This might slow down loss of a proton from **18** sufficiently to enable some migration of the benzyl group to C-4 to occur.

In any case, it is clear from the absence of methyl migration in any of the rearrangements we have studied that migrations of benzyl groups in the acid-catalyzed rearrangements of cyclohexadienones are appreciably faster than migrations of methyl groups. This is in marked contrast to the more rapid migration of the methyl group in simpler Wagner–Meerwein migrations.[4,5] Saunders has suggested[4a] that the migrating group in the rearrangement of the neopentyl carbonium ion bears little positive charge. In contrast, it seems reasonable to picture the transition state for the dienone–phenol migration as involving a great deal of aromatic character in the six-membered ring, and a great deal of positive charge localized on the migrating group. It is therefore not surprising that a benzyl group should migrate appreciably more readily than a methyl group.[10]

The most interesting aspect of the migrations of benzyl groups in the rearrangements of cyclohexadienones is the occurrence of formal [1,5] sigmatropic shifts of the benzyl group to C-2, to the exclusion, whenever feasible, of the "normal" [1,2] migrations.

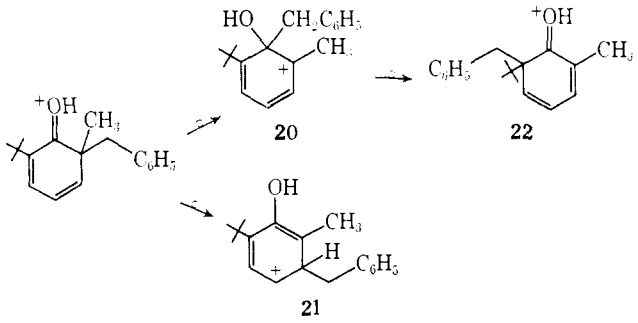
As was pointed out in the preceding paper,[2] a formal [1,5] migration might, in theory, proceed by either a single step process or by initial migration to the carbonyl

(10) In contrast to its migration to carbon, migration of a benzyl group to positive oxygen in the Baeyer–Villager rearrangement is faster than that of a methyl group.[11] In view of the high electronegativity of oxygen (and the high bond strength of the carbonyl π bond) it seems reasonable that the transition state for migration to oxygen should also involve appreciable double bonding between the oxygen and carbon atoms, and appreciable positive charge on the migrating group.

(11) M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *J. Amer. Chem. Soc.*, **89**, 6393 (1958).

carbon, followed by a second migration to C-2. Such processes are quite difficult to distinguish, since at some point in the single step process the benzyl group must pass close to the carbonyl carbon, in a structure which closely resembles the intermediate in the two-step process. We feel, however, that the formation of phenol **2** from dienone **15** offers significant evidence against the possibility that the benzyl group migrates first to the carbonyl carbon and then to C-2.

Comparison of the intermediate carbonium ions **20** and **21** (resulting from migration of the benzyl group to the carbonyl carbon and to C-5, respectively) shows no obvious reason to expect migration to the carbonyl carbon to be preferred over migration to C-5. Indeed,



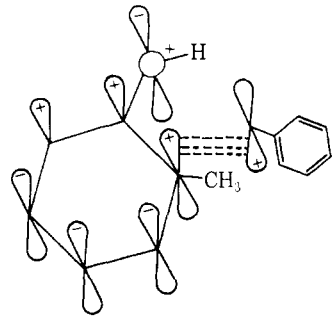
carbonium ion **21** seems to be somewhat superior to carbonium ion **20**, since **21** has enolic resonance possibilities absent in **20**. The principal factor distinguishing these two carbonium ions, however, is the very strong steric repulsion between the *t*-butyl group and the groups on the adjacent carbon atom in **20**. Other work in the dienone–phenol rearrangement has shown that steric interference between a migrating group and a methyl[12,6b] group or bromine atom[13] on a carbon adjacent to the migration terminus plays an important role in determining the direction in which a migrating group will move. Repulsion between a *t*-butyl group and a migrating benzyl group should be much larger than the repulsions in the reactions previously studied[6b,12,13] and one would expect a benzyl group to migrate to a position adjacent to a *t*-butyl group only when there is no reasonable alternative. Since migration of the benzyl group in **15** to C-5 is a very viable alternative, no significant amount of migration to the carbonyl carbon should take place.

In contrast to the double Wagner–Meerwein migration path, the direct [1,5] migration of the benzyl group to C-2 yields the protonated dienone **22** rather than a carbonium ion. While this process is also subject to appreciable steric interference by the *t*-butyl group, as is demonstrated by the occurrence of [1,2] migration to C-5 as the principal process, the advantage in energy in being able to proceed directly to **22** is so great that appreciable formation of **2** by this route is not unreasonable. This argument therefore strongly supports the assumption that **2** is formed by a direct [1,5] sigmatropic shift of the benzyl group to form **22**.

This conclusion brings us to the basic question raised by this work. Why does the benzyl group normally undergo only [1,5] migration, while the methyl group undergoes only [1,2] migration?

(12) P. J. Kropp, *Tetrahedron Lett.*, *No.* **25**, 1671 (1963).
(13) F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **29**, 509 (1964).

The Woodward–Hoffmann rules for conservation of orbital symmetry during sigmatropic shifts[14] offer an explanation for the specific [1,5] migrations of benzyl groups. If the highest occupied molecular orbital of the protonated cyclohexadienone is assumed to have orbital symmetries identical with those of the unprotonated dienone (A),[2] [1,5] migration to C-2 would be allowed while [1,3] migration to C-4 or to the oxygen



A

atom would not. This qualitative orbital symmetry argument, however, does not account for the striking difference between the migrations of methyl and benzyl groups, and suggests that [1,2] migration to C-5 should be forbidden to any migrating group.

In the preceeding paper we suggested that migrations of substituents in acid-catalyzed rearrangements of cyclohexadienones can proceed by initial protonation of the carbonyl group either on the nonbonded electrons or on the electrons of the π bond, and that these two types of protonation can result in different types of rearrangements.[2] This concept offers an explanation for the observed preference of benzyl groups in cyclohexadienones for [1,5] migration and of methyl groups for [1,2] migration.

The rapid migrations of benzyl groups, according to this concept, would take place in the "normal"[15] n-protonated ketone, and would thus result exclusively in [1,5] migration. (The slower rearrangement of **15**, in which the [1,5] migration is hindered by the *t*-butyl group at C-2, would proceed from both n- and π-protonated dienones.) Protonation of the nonbonded electrons, however, would result in only a relatively minor change in the electron distribution in the dienone, and would not activate the molecule sufficiently to result in migration of a methyl group. Instead, the methyl-substituted dienone would await the occasional protonation of the π bond of the carbonyl, which results in effective removal of the orbital on oxygen from the conjugated system. π Protonation therefore converts the dienone ring to a cyclohexadienyl carbonium ion, in which [1,2] migration but not [1,5] migration can occur.[16]

It seems difficult to conceive of another reasonable explanation for the exclusive [1,2] migration of methyl groups and exclusive [1,5] migration of benzyl groups in the acid-catalyzed rearrangements of cyclohexadienones. On the other hand, the theory presented above

(14) R. B. Woodward and R. Hoffmann, *Accounts Chem. Res.*, **1**, 17 (1968).
(15) G. A. Olah, D. H. O'Brien, and M. Calin, *J. Amer. Chem. Soc.*, **89**, 3582 (1967); G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, **89**, 3586 (1967).
(16) H.-J. Hansen, B. Sutter, and H. Schmid, *Helv. Chim. Acta*, **51**, 828 (1968).

appears to be completely consistent with all the evidence now available.

We are presently attempting to test other predictions derived from the hypothesis that cyclohexadienone rearrangements can proceed through both n- and π-protonated carbonyls.

Experimental Section

All vpc analyses and separations were carried out on a Varian Aerograph Model 202c chromatograph, using one of two columns: column A, a 6 ft × 1/4 in., 3% SE30 column at a flow rate of 45 cc/min, and column B, a 5 ft × 3/8 in. 20% SE30 column at a flow rate of 200 cc/min. Either temperature programmed or isothermal modes were employed, as described below. The relative areas of peaks from the vpc are given below in parentheses, following the retention times. Nmr spectra were taken on a Varian A60 instrument, in CCl_4 solution unless otherwise noted. Ultraviolet spectra were taken on a Cary Model 14 spectrophotometer using methanol as the solvent, and ir spectra were taken on a Perkin-Elmer Model 137 spectrophotometer. Analyses were done by Charles Meade at the University of Massachusetts Microanalysis Laboratory, or by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Melting points and boiling points are corrected.

Preparation of 6-Benzyl-4-*t*-butyl-6-methylcyclohexa-2,4-dien-1-one (3) and 2-Benzyl-4-*t*-butyl-6-methylphenol (4). Benzyl bromide (17.1 g, 0.10 mol) and 4-*t*-butyl-2-methylphenol (16.4 g, 0.10 mol) were suspended in 250 ml of water and the mixture stirred rapidly. A solution of silver nitrate (20.0 g, 0.118 mol) in 30 ml of water was added, resulting in immediate precipitation of a small amount of silver chloride. The amount of precipitate increased very rapidly. The mixture was stirred for 5 hr. Ammonium chloride solution was then added, and the silver chloride filtered off and washed with petroleum ether. The aqueous layer was extracted with petroleum ether, and the combined organic layers were extracted with Claisen alkali solution, washed with water, dried over magnesium sulfate, filtered, and evaporated to give 10.4 g of yellow oil. The product was chromatographed on Florisil. Elution with petroleum ether and then with a mixture of petroleum ether and methylene chloride gave an impure product whose nmr spectrum suggested that it might contain 2,6-dibenzyl-4-*t*-butyl-6-methylcyclohexa-2,4-dien-1-one. Further elution with methylene chloride gave 1.1 g (4.3×10^{-3} mol, 4.0%) of **3** as a pale yellow oil, λ_{max} 314 mμ (log ϵ = 3.62). *Anal.* Calcd for $C_{18}H_{22}O$: C, 85.0; H, 8.72. Found: C, 85.0; H, 8.91. The Claisen alkali extracts were diluted with water, acidified with dilute hydrochloric acid, and extracted with methylene chloride. The methylene chloride layer was washed with water, dried over magnesium sulfate, and evaporated to give 4.7 g of yellow oil. This was chromatographed on Florisil. The column was eluted with petroleum ether, and the eluents were discarded. Further elution with 25% methylene chloride–petroleum ether gave 2.6 (0.01 mol, 10%) of **4** as a yellow oil, as well as an additional 0.5 g which contained some 4-*t*-butyl-2-methylphenol. The nmr spectrum showed singlets at τ 8.87 (9 H, *t*-Bu), 8.02 (3 H, CH_3), 6.25 (2 H, $ArCH_2Ar$), 5.80 (1 H, OH), 3.16 (2 H, *meta* protons on phenol ring), and 2.99 (5 H, phenyl group). *Anal.* Calcd for $C_{18}H_{22}O$: C, 85.0; H, 8.72. Found: C, 84.9; H, 8.66.

Preparation of 6-Benzyl-1,2,3,4,5,6-pentamethylcyclohexa-2,4-dien-1-one (9). Sodium methoxide (9.9 g, 0.184 mol) was added to a solution of pentamethylphenol (30.0 g, 0.183 mol) in 700 ml of benzene. The mixture was stirred while benzene was distilled out until the distillate was completely clear. The reaction mixture was then cooled to 40°, and benzyl chloride (23.4 g, 0.185 mol) was added. The mixture was stirred for 14 hr at room temperature, and then refluxed for 24 hr. It was cooled in ice and washed with water. The solvent was removed in a rotary evaporator under vacuum, and the residue dissolved in petroleum ether (bp 30–60°) and extracted with Claisen alkali. Acidification of the alkaline solution gave 3.8 g of recovered pentamethylphenol. The organic layer was washed with water, dried over magnesium sulfate, and the solvent evaporated to give 44.0 g of a brown liquid. Part of this liquid (22.0 g) was chromatographed on Florisil. Elution with petroleum ether gave 3.9 g (0.0154 mol, 20% based on recovered phenol) of benzyl pentamethylphenyl ether, mp 73–74° (from hexane). The nmr spectrum had peaks at τ 8.92 (broad singlet, 15 H), 5.45 (s, 2 H) and 2.6–2.9 (m, 5 H). *Anal.* Calcd for $C_{18}H_{22}O$: C, 85.0; H, 8.72. Found: C, 84.7; H, 8.44.

Further elution with methylene chloride, and then with chloroform, gave 11.7 g (0.046 mol, 56%) of **9**, λ_{max} 335 mμ (log ϵ = 3.61). *Anal.* Calcd for $C_{18}H_{22}O$: C, 85.0; H, 8.72. Found; C, 84.8; H, 8.80.

Preparation of 6-Benzyl-2,6-dimethylcyclohexa-2,4-dien-1-one (10). The procedure of Curtin, *et al.*,[17] was followed on a 0.25-mol scale, except that benzyl chloride was substituted for benzyl bromide. Chromatography on Florisil gave a 3.9-g yield of **2** (λ_{max} 312 mμ, log ϵ = 3.52). Our product crystallized to yellow needles, mp 70–71° (from methanol). The crystalline product was stable for 1 week at room temperature, and for several months in an ice chest, but condensed in the solid phase on prolonged standing at room temperature to give the dimer, mp 172°, reported previously.[17]

Preparation of 6-Benzyl-2-*t*-butyl-6-methylcyclohexa-2,4-dien-1-one (15). Dienone **15** was prepared on a 0.2-mol scale as described above for the preparation of **9**. The crude product was chromatographed on neutral alumina. Elution with petroleum ether gave carbonyl-free material which was discarded. Elution with methylene chloride gave 3.9 g of **15** as a yellow oil, λ_{max} 314 mμ (log ϵ = 3.61). *Anal.* Calcd for $C_{18}H_{22}O$: C, 85.0; H, 8.72. Found: C, 85.0; H, 8.78. An additional 0.8 g of slightly less pure product was obtained from earlier and later fractions.

Rearrangement of Dienone 1. Dienone **1** (0.40 g) was dissolved in 5 ml of 0.5 *N* hydrochloric acid in methanol. The solution was allowed to stand overnight at room temperature, and then diluted with water and extracted with methylene chloride. The methylene chloride layer was washed with water, dried over magnesium sulfate, and evaporated to give 0.40 g of yellow oil, which showed the presence of peaks with vpc retention times of 3.0, 3.1, 3.7, 4.1 (combined area 232), 14.0 (90), and 16.0 (98) min on column A (starting at 90° with the temperature rising 8°/min). The first four peaks (in order of increasing retention times) had retention times corresponding to those of benzyl methyl ether, benzyl chloride, *o*-cresyl methyl ether, and *o*-cresol. The last two components were isolated by preparative vpc on column B at 225°. They were identified as phenol **2**[7] and 2-benzyl-6-methylphenyl methyl ether by comparison of their ir and nmr spectra and vpc retention times with those of authentic samples.

The rearrangements were similarly carried out in 80% aqueous dioxane and in acetic acid, catalyzed in each case by 1 drop of sulfuric acid. (In the last case, the reaction time was 5 min.) They were worked up as described above, and the high retention time peak (**2** in both reactions) was isolated by vpc.

Preparation of 2-Benzyl-6-methylphenyl Methyl Ether. Potassium *t*-butoxide (0.57 g, 5.08 mmol) was added to a solution of phenol **2** (1.0 g, 5.05 mmol) in 10 ml of dimethyl sulfoxide. The mixture was shaken until a clear solution was obtained, and 3 ml of methyl iodide was added. After 5 min the solution was poured into water and the aqueous mixture extracted with methylene chloride. The methylene chloride layer was washed three times with water, dried, and evaporated to give 1.0 g (0.47 mmol, 93%) of almost pure ether. An analytical sample was obtained by preparative vpc on column B at 225°. Its nmr spectrum had peaks at τ 7.94 (s, 3 H), 6.65 (s, 3 H), 6.22 (s, 2 H) 3.15–3.42 (m, 3 H), 3.03 (broad singlet, 5 H). *Anal.* Calcd for $C_{15}H_{16}O$: C, 84.9; H, 7.60. Found: C, 84.8; H, 7.65.

Rearrangement of Dienone 3. Dienone **3** (0.7 g) was dissolved in 10 ml of methanol and 0.5 ml of *ca.* 12 *N* aqueous hydrochloric acid was added. The mixture was allowed to stand overnight, poured into water, and extracted with methylene chloride. The methylene chloride solution was washed with sodium bicarbonate solution and with water, dried over magnesium sulfate, and evaporated to give 0.65 g of yellow oil, which showed no carbonyl band in the ir. Vpc analysis on column A, temperature programmed at 6°/min (starting temperature 120°) showed the presence of six components. Their retention times in minutes were: (A) 5.0 (21), (B) 5.5 (7.2), (C) 12.5 (48), (D) 13.2 (15), (E) 29 (40), (F) 31.7 (40). The products were isolated by preparative vpc on column B, starting at 150° with the temperature programmed to rise at 4°/min. All the products were identified by comparison of their nmr and ir spectra and vpc retention times with those of authentic samples, with the exception of product B, which was identified by its ir spectra and vpc retention times only. The products were (A) benzyl methyl ether, (B) benzyl chloride, (C) 4-*t*-butyl-2-methylphenyl methyl ether, (D) 4-*t*-butyl-2-methylphenol, (E) 2-benzyl-4-*t*-butyl-6-methylphenol (**4**), and (F) 2-benzyl-4-*t*-butyl-6-methylphenyl methyl ether (**5**).

Preparation of 2-Benzyl-4-*t*-butyl-6-methylphenyl Methyl Ether. 2-Benzyl-4-*t*-butyl-6-methylphenol (**4**) (0.50 g, 1.97 mmol) was dis-

(17) D. Y. Curtin, R. J. Crawford, and M. Wilhelm, *J. Amer. Chem. Soc.*, 80, 1391 (1958).

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

Compd	Substituents at[c] C_2	C_3	C_4	C_5	CH_3-C<	$-CH_2OC_6H_5$
1	Hm, 4.1	Hm, 3.45	Hm, 4.1	Hm, 4.1	s, 8.97	d, 7.01 (J = 13.0) d, 7.49
3	Hd, 4.31 (J = 10.0)	Hdd, 3.27 (J = 10.0, 2.8)	Bs, 9.06	Hd, 4.14 (J = 2.8)	s, 8.93	d, 7.00 (J = 13.0) d, 7.49
9	Ms, *ca.* 8.3[a]	Ms, 8.10	Ms, *ca.* 8.3[a]	Ms, *ca.* 8.3[a]	s, 8.78	d, 6.94 (J = 13.3) d, 7.30
10	Md, 8.30 (J < 1.0)	Hm, 3.63	Hm, 4.1	Hm, 4.1	s, 8.83	d, 6.95 (J = 12.5) d, 7.40
11	Ms, 8.35	Ms, 8.06	*b*	Same as C-3	s, 8.75	s, 7.12
13	Bs, 8.97	Hdd, 3.54 (J = 2.5, 5.5)	Hm, 4.1	Hm, 4.1	s, 8.97	d, 6.96 (J = 13.0) d, 7.50

[a] Apparently three overlapping singlets. [b] Quaternary methyl + methylene substituents. [c] Substituents: B = *t*-butyl, H = hydrogen, M = methyl; splitting: d = doublet, m = multiplet centered at given value, s = singlet.

solved in 10 ml of dimethyl sulfoxide. Potassium *t*-butoxide (0.22 g, 2.0 mmol) was added, and the mixture shaken for 2 min. Methyl iodide (2.5 g, 17.5 mmol) was added, and the mixture shaken for 10 min. It was then poured into water, extracted with methylene chloride, and the methylene chloride solution washed with water, dried over magnesium sulfate, and evaporated to give 0.50 g (1.87 mmol, 95%) of **5** as a nearly colorless oil, shown to be almost pure by vpc. For analysis, the product was chromatographed through a 1-in. column of alumina to give a colorless oil, identical with the crude product in its nmr and ir spectra. *Anal.* Calcd for $C_{19}H_{24}O$: C, 85.0; H, 9.01. Found: C, 84.9; H, 8.90. The nmr spectrum had peaks at τ 8.88 (s, 9 H), 7.95 (s, 3 H), 6.63 (s, 3 H), 6.19 (s, 2 H), 3.13 (broad singlet, 1 H), and 3.00 (broad singlet, 1 H).

4-*t*-Butyl-2-methylphenyl methyl ether was prepared by alkylation of 4-*t*-butyl-2-methylphenol in dimethyl sulfoxide solution, as described for the preparation of **5**, in 87% yield. It had bp 84–86° (3 mm); n^{25}D 1.5079 (lit.[18] bp 82° (2.5 mm), n^{20}D 1.5098).

Rearrangement of Dienone 7. The sulfuric acid catalyzed rearrangement of **7** was carried out in acetic anhydride, according to the published procedure, and in acetic acid, using a procedure similar to that described for the rearrangement of **1**. Vpc analysis of the crude, crystalline, product from each reaction showed it to be essentially pure 2,3-dimethylphenol.[19]

Rearrangement of Dienone 9. Preparation of 4-Benzyl-2,3,4,5,6-pentamethylcyclohexa-2,5-dien-1-one (11). Dienone **9** (5.0 g, 0.020 mol) was dissolved in 50 ml of methanol, and 5 ml of 12 *N* aqueous hydrochloric acid was added. The mixture was allowed to stand at room temperature for 24 hr, and then poured into water and the aqueous layer extracted with petroleum ether. The organic layer was extracted with Claisen alkali. The alkaline solution was diluted with water, acidified with hydrochloric acid, and extracted with methylene chloride. Evaporation of the methylene chloride left 1.4 g (8.4 mmol, 42%) of pentamethylphenol.

The petroleum ether layer was washed with water, dried, and evaporated to give 3.7 g of yellow oil, which was chromatographed on neutral alumina. Elution with petroleum ether gave 0.9 g of colorless oil, which was shown by vpc and ir analysis to be largely benzyl methyl ether. Elution with methylene chloride gave 2.3 g (9.1 mmol, 46%) of 4-benzyl-2,3,4,5,6-pentamethylcyclohexa-2,5-dien-1-one (**11**) as white crystals, mp 83.5–84.5° (from hexane). *Anal.* Calcd for $C_{18}H_{22}O$: C, 85.0; H, 8.72. Found: C, 84.7; H, 8.84.

Rearrangement of Dienone 15. Dienone **15** was dissolved in 10 ml of methanol, and 1 ml of concentrated HCl was added. The solution was allowed to stand at room temperature for 8 days, and then worked up as described for the rearrangement of dienone **3** to give 0.3 g of oil, which showed no carbonyl band in its ir spectrum. Vpc analysis showed the presence of six components, which were isolated by preparative vpc on column B. The first three components were obtained at 175°, and the column temperature was then raised to 230° to isolate the remaining products. The products (in order of elution from the column) were identified by comparison of their ir and nmr spectra and vpc retention times with those of authentic samples as benzyl methyl ether, benzyl chloride, 2-*t*-butyl-6-methylphenol, 2-benzyl-6-methylphenol (**2**), 4-benzyl-2-*t*-butyl-6-methylphenol (**16**), and 3-benzyl-2-*t*-butyl-6-methylphenol (**17**). Comparison with synthetic mixtures showed that the molar ratios of the last four components (by vpc) were 9:5:2:7.

Preparation of 4-Benzyl-2-*t*-butyl-6-methylphenol (16). A mixture of 4-benzyl-2-methylphenol[20] (3.2 g, 0.016 mol) and concentrated sulfuric acid (0.3 g) was stirred at 50° while isobutylene was bubbled slowly into the reaction mixture. The reaction was followed by vpc and introduction of isobutylene stopped after 1 hr, when the reaction was almost complete. The reaction mixture was dissolved in methylene chloride, washed with water, dried over magnesium chloride, and the solvent evaporated to give 3.7 g of a yellow oil, which was almost pure by vpc analysis. A pure sample was isolated by preparative vpc on column B at 225°, R_t = 17 min. *Anal.* Calcd for $C_{18}H_{22}O$: C, 85.0; H, 8.72. Found: C, 85.1; H, 8.81. The nmr spectrum had peaks at τ 8.70 (s, 9 H), 7.97 (s, 3 H), 6.30 (s, 2 H), 5.70 (s, 1 H), 3.43 (d, J = 2 cps), 3.20 (d, J = 2 cps), and 2.95 (broad singlet, 5 H).

Preparation of 3-Benzyl-2-methylphenol (6). A solution of 10.0 g (0.065 mol) of 3-ethoxy-2-methylcyclohexenone[21] in 25 ml of ethyl ether was added to a stirred, ice-cooled solution of benzyl magnesium chloride (0.065 mol) in ether. The mixture was allowed to stand at room temperature overnight. It was then cooled in ice and a solution of dilute hydrochloric acid added. The two layers were separated and the ether layer was washed with water, dried over magnesium sulfate, and the solvent evaporated to give 7.5 g of yellow liquid with a strong ir peak at 5.92 μ. It contained only one component on vpc analysis. The product was dissolved in 20 ml of mesitylene, and 2.0 g of 10% palladium on charcoal was added. The mixture was refluxed until vpc analysis showed dehydrogenation to be essentially complete (8 hr). The mixture was cooled, filtered, and extracted with 3 *N* sodium hydroxide solution. The alkaline solution was acidified with dilute hydrochloric acid and extracted with methylene chloride. The methylene chloride solution was washed with water, dried over magnesium sulfate, and the solvent evaporated to give 3.5 g of brown oil. This was distilled to give 1.4 g of **6** (7.06 mmol, 11%) as a yellow oil, bp 153–156° (1.5 mm). Its ir spectrum was almost identical with that of the undistilled product. *Anal.* Calcd for $C_{14}H_{14}O$: C, 84.8; H, 7.12. Found: C, 84.9; H, 7.22. The nmr spectrum had peaks at τ 8.05 (s, 3 H), 6.23 (s, 2 H), 4.05 (broad absorption, 1 H), 3.15–3.75 (m, *ca.* 3 H), and 3.03 (broad singlet, 5 H).

Preparation of 5-Benzyl-2-*t*-butyl-6-methylphenol (17). A mixture of **6** (1.0 g, 5.1 mmol) and 2 drops of concentrated sulfuric

(18) M. S. Carpenter, W. M. Easter, and T. F. Wood, *J. Org. Chem.*, 16, 586 (1951).

(19) Obtained for comparison from the Aldrich Chemical Co., Milwaukee, Wis.

(20) H. Meyer and K. Bernhauer, *Monatsh. Chem.*, 53, 735 (1922).

(21) E. G. Meek, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 811 (1953).

acid was heated to 70°, and isobutylene was bubbled through the mixture until vpc analysis showed almost all **6** to have reacted (*ca.* 20 min). The product was washed with water and then with 3 *N* sodium hydroxide solution. It was dried and evaporated to give 1.2 g (4.7 g, 92%) of **17** as a yellow viscous oil, which showed only one significant peak in the vpc. An analytical sample was obtained by vpc on column B (220°, R_t 21 min). Its ir and nmr spectra were identical with those of the crude product. *Anal.* Calcd for $C_{18}H_{22}O$: C, 85.0; H, 8.72. Found: C, 85.0; H, 8.62. The nmr spectrum had peaks at 8.70 (s, 9 H), 8.15 (s, 3 H), 6.23 (s, 2 H), 3.50 (d, J = 9.0 cps, 1 H), 3.13 (d, partially hidden), 3.00 (broad singlet, 5 H).

Rearrangement of Dienone 10. A solution of dienone **10** (0.30 g) in 10 ml of 1.0 *N* HCl in methanol was allowed to stand at room temperature for 24 hr. The uv spectrum of the solution then showed the absence of any unreacted **10**. The reaction was worked up as usual to give 0.3 g of yellow oil. Vpc analysis of the product on column A, starting at 120° with the temperature rising at 4°/min, showed the presence of four peaks with retention times of 1.8 (2.7), 2.0 (1.5), 3.4 (6.4), and 20.6 (5.1) min. The four components were isolated by preparative vpc on column B at 225°, and identified as benzyl methyl ether, benzyl chloride, 2,6-dimethylphenol, and an unidentified phenol, presumably either **13** or **14**. The phenol had nmr peaks at τ 7.92 and 7.97 (s, totaling 6 H), 6.33 (s, 2 H), 6.21 (s, 1 H), 3.2–3.5 (m, *ca.* 2 H), and 3.02 (broad absorption, 5 H). *Anal.* Calcd for $C_{15}H_{16}O$; C, 84.9; H, 7.60. Found: C, 84.7; H, 7.51.

Kinetics. Samples of dienones **1** and **7** were dissolved in 0.50 *N* HCl in 80% aqueous methanol, using concentrations such that the uv spectrum of the solutions could be measured directly, without further dilution. The solutions were kept in a constant-temperature bath at 25.8 ± 0.1°, and samples pipeted out at intervals for uv analysis. The disappearance of the absorption maxima at 308 mμ was followed. The reaction rates of **1** and **7** in the absence of acid were also followed. **1** was found to be unchanged after 14 hr in the absence of acid, while **7** disappeared at the same rate in neutral and in acid solution.

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Unsymmetrical Substitution and the Direction of the Di-π-methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry. LVI[1]

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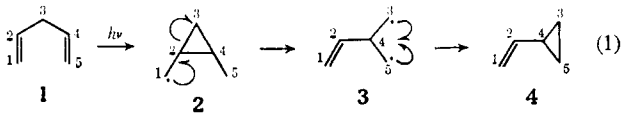
Abstract: 1,1-Diphenyl-3,3,5-trimethyl-1,4-hexadiene (**5**) was synthesized in order to study the effect of substitution on the direction of the di-π-methane rearrangement. Direct irradiation of diene **5** gave 1,1-dimethyl-2,2-diphenyl-3-(2-methylpropenyl)cyclopropane (**6**), whose structure was established by its spectral properties and by degradation. No 1,1,2,2-tetramethyl-3-(2,2-diphenylvinyl)cyclopropane (**7**) was formed (<3%). The absence of vinylcyclopropane **7** was not due to its destruction, either in a process leading to the observed product vinylcyclopropane (**6**) or in reactions giving further products. This was established by the near perfect mass balance for the direct photolysis and by the photochemical behavior of independently synthesized vinylcyclopropane **7**. It was found that the singlet excited state of diene **5** undergoes the di-π-methane rearrangement smoothly and cleanly with a quantum efficiency of 0.097 while T_1 rearranges only with difficulty (ϕ = 0.008). The photochemistry of the vinylcyclopropanes **6** and **7** was explored. The photochemistry of **6** involved two types of carbene fission. In contrast the irradiation of vinylcyclopropane **7** led to a unique rearrangement involving three-ring fission and methyl migration to give 1,1-diphenyl-4,5,5-trimethyl-1,3-hexadiene (**13**) as the major product.

Previously we have described a number of examples of the di-π-methane rearrangement[2–6] and have noted that the rearrangement is general, occurring whenever two π moieties are bonded to one sp^3 hybridized carbon atom. Thus far we have advanced tentative correlations between molecular structure and the multiplicity of the reacting excited state. Also, in the case of bicyclic systems, we have described initial efforts toward determining which two π moieties bridge preferentially when more than two bridging processes are *a priori* possible.[3,5]



(1)

In the present investigation we have turned our attention to another facet of the problem, namely the direction of rearrangement in an unsymmetrically substituted divinylmethane. Thus, for example, if carbon atoms 1 and 5 of the system in eq 1 were differently substituted, after bridging to give species **2** there would exist not only the possibility of bond 2–3 fission as shown but also bond 3–4 cleavage. Different vinylcyclopropanes would then be potential products. We felt it of practical interest and also of importance in understanding the electronic details of the mechanism

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(2) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969).

(3) H. E. Zimmerman and C. O. Bender, *ibid.*, **91**, 7516 (1969).

(4) (a) H. E. Zimmerman and G. E. Samuelson, *ibid.*, **91**, 5307 (1969); (b) H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schröder, *ibid.*, **89**, 5973 (1967).

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(6) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).