were effectively infinitely dilute for this solute; in each case the two solutions were compared by placing them in the two compartments of a Wilmad coaxial sample cell, spinning in the magnetic field.

If an internal reference is used, the operational definition of the reference-independent solvent shift (for which we suggest the notation $\bar{\Delta}_y^x$) is

$$\bar{\Delta}_y^x = \Delta_y^x + \sigma_{loc}(\text{ref, y}) - \sigma_{loc}(\text{ref, x}) \qquad (9)$$

The tabulated values of σ_{loc} differences for TMS (Table II) can be used in eq 9 to convert internally referenced solvent shifts Δ_y^x to reference-independent shifts $\bar{\Delta}_y^x$ (*e.g.*, see last column of Table I).

Where the solvent shift is measured by an external referencing procedure, one can use an alternative definition of $\bar{\Delta}_y^x$ as that shift obtained by subtracting the bulk susceptibility contribution for the appropriate solvent pair from the total observed shift.

By reporting $\bar{\Delta}_y^x$ rather than other more arbitrary forms of the solvent shift, comparison between results obtained with different referencing procedures is facilitated.

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Received September 9, 1969

Acid-Catalyzed Rearrangements of Cyclohexa-2,4-dien-1-ones. Competitive [1,2] and [1,5] Migrations[1]

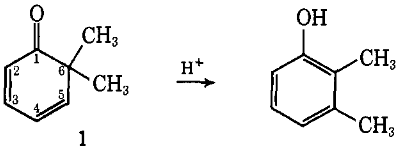
Sir:

The acid-catalyzed rearrangements of cross-conjugated cyclohexadienones have been extensively investigated.[2] In contrast, the rearrangements of linearly conjugated cyclohexadienones have not received much attention, except for the special, and very complicated, cases in which allyl groups migrate.[1,3] In the few reactions studied involving other migrating groups, the products of [1,2] shifts of the migrating group to C-5 have been obtained.[4]

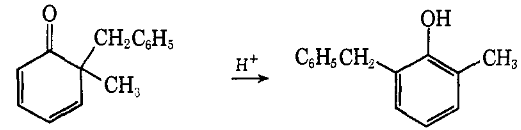
I now wish to report that acid-catalyzed rearrangements of linearly substituted cyclohexadienones can result in either [1,2] or [1,5] shifts of the migrating group.[5] The type of rearrangement occurring is remarkably dependent on the nature of the migrating group.

Marvell and Magoon found that rearrangement of dienone **1** in acetic anhydride–sulfuric acid gave (after hydrolysis) a low yield of 2,3-dimethylphenol.[4a] Repetition of this reaction, both under the literature conditions and in acetic acid–sulfuric acid, showed that 2,3-dimethylphenol is indeed the only product detectable by vpc analysis.

In contrast, rearrangement of dienone **2** at 25° in acetic acid containing 1% sulfuric acid (reaction time = 20 min), or in aqueous dioxane catalyzed by HCl, gives 2-benzyl-6-methylphenol[7] as the only detectable rearrangement product.[8] Vpc analysis showed that no more than 0.5% of 3-benzyl-2-methylphenol[9] could have been produced during the reaction. Similarly, rearrangement of 6-benzyl-4-*t*-butyl-6-methylcyclohexa-2,4-dien-1-one (**3**) in 0.5 *N* methanolic HCl gives 2-benzyl-4-*t*-butyl-6-methylphenol[9] and its methyl ether[9] as the only rearrangement products.



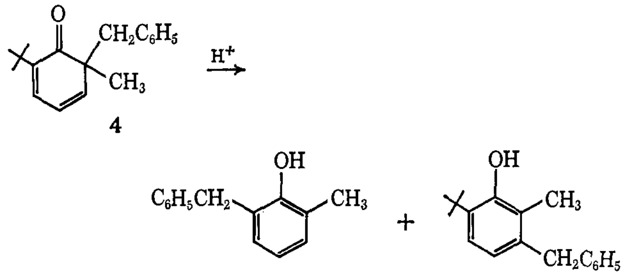
1



2

The rearrangements of **2** and **3** could proceed by migration of either the benzyl or methyl groups. However, rearrangement of **2** in 0.5 *N* HCl in 80% aqueous methanol has been found to be at least 10^3 times as rapid as that of **1**. This rate difference can only be explained if the benzyl group migrates during the rearrangement of **2**.

Migration of a benzyl group to C-2 can proceed even when C-2 is occupied by a *t*-butyl group. Rearrangement of dienone **4** in 2 *N* HCl in 80% aqueous methanol results in partial elimination of a *t*-butyl group to give 2-benzyl-6-methylphenol and 5-benzyl-2-*t*-butyl-6-methylphenol[9] in the ratio 5:7.[10]



4

Migration of the benzyl groups in **2** and **4** to C-2 might, in principle, proceed by either direct [1,5] acid-catalyzed sigmatropic shifts (path a) or by a sequence of two Wagner–Meerwein shifts of the benzyl group—

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[1] Reactions of Cyclohexadienones. XXIII. Part XXII: *J. Amer. Chem. Soc.*, **91**, 2170 (1969).

[2] (a) B. Miller in "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Interscience Publishers, New York, N. Y., 1968, pp 275–310; (b) A. J. Waring, *Advan. Alicyclic Chem.*, **1**, 207–215 (1966).

[3] (a) J. Leitich, *Monatsh. Chem.*, **92**, 1167 (1960); (b) P. Fahrni, A. Habich, and H. Schmid, *Helv. Chim. Acta*, **43**, 448 (1960); (c) B. Miller, *J. Amer. Chem. Soc.*, **87**, 5115 (1965); (d) B. Miller, *Chem. Commun.*, 1435 (1968).

[4] (a) E. N. Marvell and E. Magoon, *J. Amer. Chem. Soc.*, **77**, 2542 (1955); (b) E. Schinzel and F. Wessely, *Monatsh. Chem.*, **86**, 912 (1955).

[5] Occurrence of [1,5] shifts have been previously reported[1,6] but only in dienones in which the "normal" [1,2] shifts are difficult or impossible.

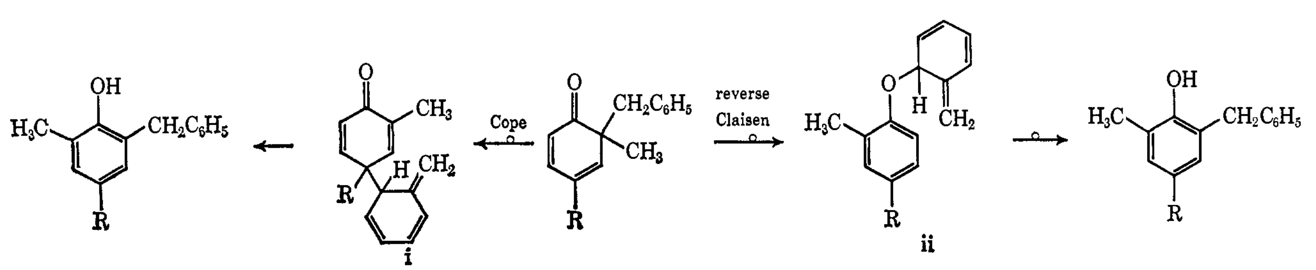
[6] T. Suehiro, *Chem. Ber.*, **100**, 915 (1967).

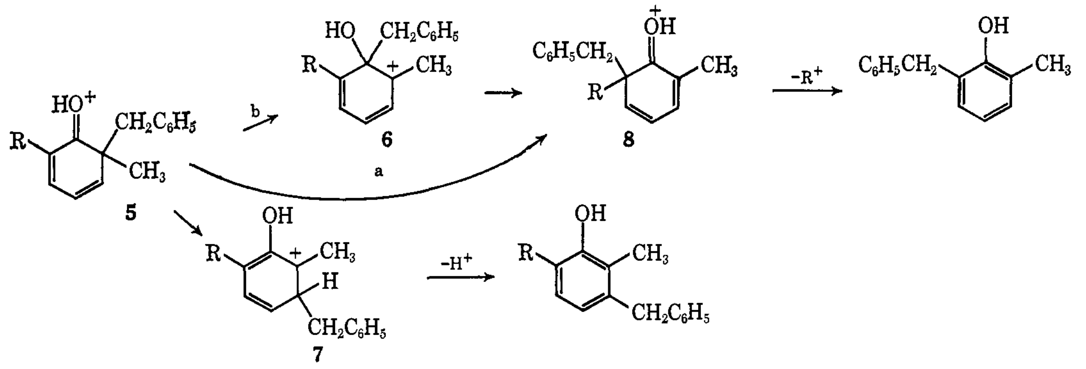
[7] T. Schorigin, *ibid.*, **58**, 2028 (1925).

[8] All rearrangements of benzylated dienones give products of cleavage to the parent phenol as well as rearrangement products.

[9] These compounds have been independently synthesized by unequivocal methods.

[10] A small amount of 4-benzyl-2-*t*-butyl-6-methylphenol is also produced in this reaction, presumably by a twofold migration of the benzyl group to C-4.





first to the carbonyl carbon and then to C-2 (path b). While these alternatives are quite difficult to distinguish, I believe that the migration of a benzyl group to C-2 in dienone **4** offers significant evidence that a direct [1,5] shift occurs. It has previously been shown that Wagner–Meerwein shifts in the dienone–phenol rearrangement are subject to strong steric inhibition by groups on carbons adjacent to the migration terminus.[1,3c,11] There is no obvious advantage to be gained by migration of a benzyl group to the carbonyl carbon of **4** (rather than to C-5) which would offset the strong steric repulsion by the *t*-butyl group adjacent to the carbonyl. Indeed, even in the absence of any steric considerations, the intermediate carbonium ion **6** should be somewhat less stable than the alternative ion **7** which would result from a shift of the benzyl group to C-5, since **6** lacks the enolic resonance of **7**. A direct [1,5]-sigmatropic shift of the benzyl group, however, would simply convert the protonated ketone **5** to the isomeric protonated ketone **8**. The much greater bond energy of **8**, compared with **7**, should more than compensate for steric compressions in the formation of **8**.

It remains to be explained why the benzyl group in **2** should undergo exclusive [1,5] migration to C-2, while the methyl group in the very similar dienone **1** undergoes exclusive [1,2] migration to C-5. A possible answer lies in the suggestion previously offered to account for the surprising variety and specificity of acid-catalyzed sigmatropic shifts of allyl groups in cyclohexadienones.[1] It was proposed that protonation of the carbonyl group of a cyclohexadienone can take place either on the unbonded (n) electrons or on the π electrons of the carbonyl oxygen. *The nature of the allowed migrations would then be determined by conservation of orbital symmetries*[12] *in these two types of protonated dienones.* According to this concept, the normal[13] n protonation would result in only a slight perturbation of the molecular orbital symmetry pattern of the dienone, and the allowed acid-catalyzed migrations would resemble the allowed thermal migrations in the dienone.[12,14] Since the benzyl group is a good migrator in these reactions, n protonation would be sufficient to cause rearrangement to occur, and thus a thermally allowed [1,5] migration would take place. Poorer migrating groups, such as methyl, would not rearrange in the n-protonated dienone, but would await protonation of the π bond. This would result in conversion of the dienone to a cyclohexadienyl carbonium ion, in which suprafacial [1,2] migrations are allowed, but [1,5] migrations are not.[14–16]

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

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(11) P. J. Kropp, *Tetrahedron Lett.*, 1671 (1963).

(12) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(13) 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).

(14) H.-J. Hansen and H. Schmid, *Chem. Brit.*, **5**, 111 (1968).

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

(16) A referee has suggested that the apparent [1,5] migrations may proceed by successive Cope migrations of the benzyl groups to C-4 (forming i) and then to C-2, or by a reverse Claisen rearrangement to oxygen (forming ii) followed by a Cope migration to C-2. The rapid [1,5] migration observed in dienone **3** (R = *t*-Bu), however, clearly does not proceed *via* a Cope migration to C-4. Intermediates such as ii should rearrange rapidly in acid to diphenyl ethers. No such ethers are observed, even when C-2 is blocked by a methyl group. In that case, only [1,2] migration is observed. Finally, it may be noted that [1,5] migrations of benzyl groups are approximately as fast as migrations of allyl groups.[1] Since the reverse Claisen migrations of allyl groups should be some 18 kcal more exothermic than those of benzyl groups, migrations of allyl and benzyl groups by this mechanism should have vastly different rates.

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Received August 27, 1969

The Preparation of Alkylmagnesium Fluorides

Sir:

All attempts in the past to prepare and isolate fluoro Grignard compounds have failed.[1] A recent report[2]

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(1) (a) H. Gilman, J. Peterson, and F. Schulze, *Rec. Trav. Chim.*, **47**, 19 (1928); (b) G. Schiemann and R. Pillarsky, *Chem. Ber.*, **64**, 134