Allyl and Benzyl Migrations in the Rearrangements of Naphthalenones[1]

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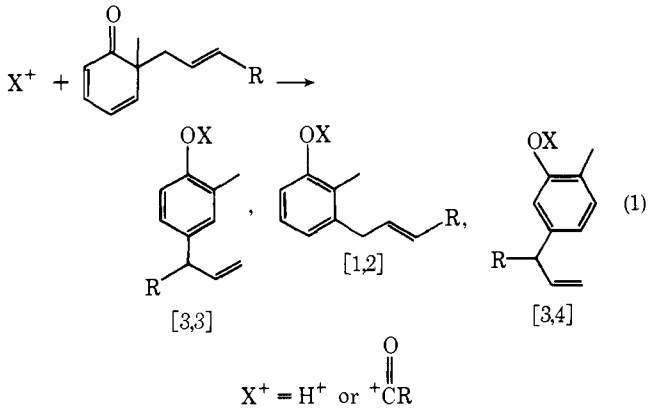
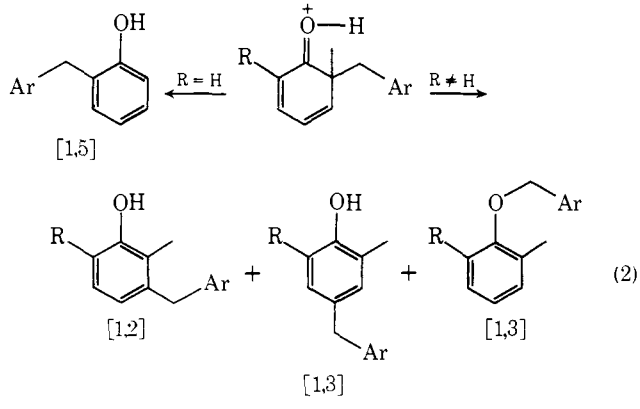
Abstract: The acid-catalyzed rearrangement of 1-allyl-1-methyl-2-naphthalenone in acetic acid, ether, or acetic anhydride solution gives 4-allyl-1-methyl-2-naphthol or its acetate as the only rearrangement product. Deuterium labeling experiments demonstrate that these reactions proceed by [3,4] migrations of the allyl group. Rearrangements of 1-(*trans*-2-butenyl)-1-methyl-2-naphthalenone in protic solvents give mixtures of the [3,4] migration product and of the [1,5] migration product, 3-(*trans*-2-butenyl)-1-methyl-2-naphthol, but rearrangement in acetic anhydride gives only the [1,4] migration product, 4-(*trans*-2-butenyl)-1-methyl-2-naphthol. Rearrangement of 1-benzyl-1-methyl-2-naphthalenone in acetic anhydride gives 2-acetoxy-4-benzyl-1-methylnaphthalene, while rearrangement of 2-benzyl-2-methyl-1-naphthalenone gives 1-acetoxy-4-benzyl-2-methylnaphthalene. It is suggested that formally forbidden [1,3] and [1,4] migrations are facilitated by the electron-withdrawing effect of acetylation of the carbonyl group and by the effects of electron-donating substituents on the migrating groups.

Allyl and benzyl groups undergo unusually rapid migrations in acid-catalyzed dienone–phenol rearrangements, giving products which differ markedly from those obtained from "normal" [1,2] shifts of alkyl groups.[2-4] When the rearrangements are carried out in protic solvents, allyl groups usually undergo [3,3] shifts. Occasionally, smaller amounts



(1)

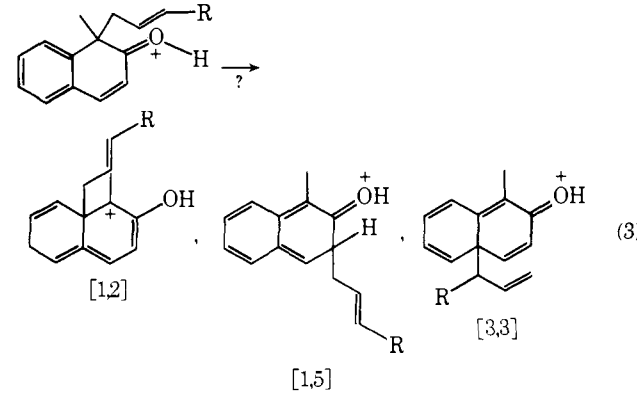
of products arising from [1,2] migrations are obtained.[2,5] When acid anhydrides are employed as the solvents, and acyl groups thus presumably react with the carbonyl oxygen, [1,2] and [3,4] migrations become more important, although [3,3] migrations still predominate[5,6] (eq 1). Benzyl groups in linearly conjugated cyclohexadienones normally undergo [1,5] migrations in acid.[3] If [1,5] migrations are precluded by the structure of the dienone (or are undetectable due to the symmetry of the molecule), [1,2] and [1,3] migrations (including migrations to oxygen) are observed (eq 2).[3,7]



(2)

It is still not clear why so many types of migrations occur, or what factors determine which types of migrations will be favored in a given reaction. It has been suggested[6,8] that "carbonium ion type" migrations[9] (i.e., [1,2] and [3,4] shifts) will be relatively favored by reaction conditions which place a large positive charge on the dienone ring, while "thermal type" migrations[9] ([3,3] or [1,5] shifts) are more likely to predominate when there is a smaller charge on the ring. However, there is little agreement as to why changes in the structure of the migrating groups affect the types of reactions observed.

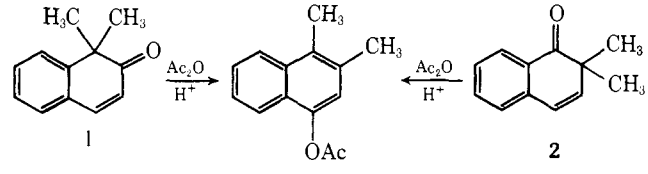
Rearrangements of naphthalenones should differ markedly from those of monocyclic dienones. In 2-naphthalenones, for instance, [1,5], [3,3], or "normal" [1,2] shifts to



(3)

the end of the dienone chain would all give intermediates in which the aromaticity of the benzene ring is destroyed (eq 3). [3,3] migrations in linearly conjugated 1-naphthalenones would be feasible, but [1,5] or "normal" [1,2] migrations would be inhibited.

Prior to our preliminary publication of part of this work,[10] the only study of the rearrangements of linearly conjugated naphthalenones had been that of Marvell and Stephenson, who showed that the very slow rearrangement of naphthalenone **1** in acetic anhydride results in migration of a methyl group to the carbonyl carbon, accompanied by migration of the oxygen function to C-4.[11] Rearrangement of naphthalenone **2** gives the same product.[12]

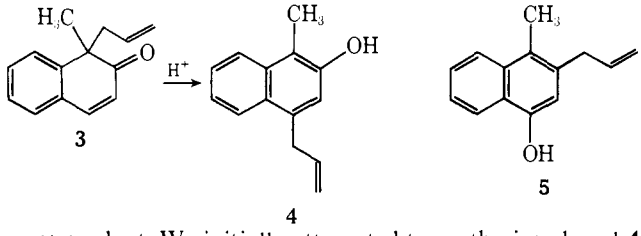


1 2

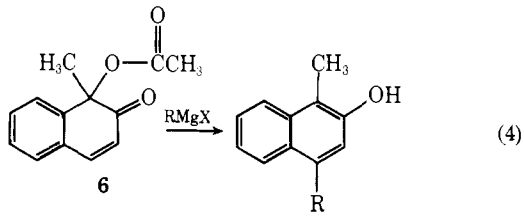
We have investigated the acid-catalyzed rearrangements of several naphthalenones in which allyl or benzyl groups might undergo migration. These studies have resulted in quite unexpected observations of the effects of structure and reaction conditions upon the nature of the resulting rearrangements.

Allyl Group Migrations in 2-Naphthalenones. Naphthalenone **3** was readily prepared by Claisen alkylation of the lithium salt of 1-methyl-2-naphthol. In contrast to its monocyclic analog, which rearranged rapidly in 0.01 M hydrochloric acid in methanol, **3** was stable in methanolic acid. However, it did rearrange with a half-life of ca. 6 h in a 1 M solution of sulfuric acid in acetic acid. After 24 h, two rearrangement products, a phenol and its acetate, were obtained. At shorter reaction times, the ratio of phenol to acetate increased, indicating that the acetate was obtained from the initially formed phenol.

The NMR spectrum of the phenol showed, in addition to signals for the methyl and allyl groups on an aromatic ring, a one-proton singlet at τ 3.17 far upfield from the multiplet for the other aromatic protons. The deshielded position of this signal suggested that it was both ortho to the hydroxyl group and in a β position on the naphthalene ring. Since it was assumed that the position of the methyl group had not changed during the rearrangement, two possible structures, **4** and **5**, were considered for the structure of the rearrangement product. We initially attempted to synthesize phenol **4** by reaction of allylmagnesium bromide with the quinol acetate **6**, according to the general procedure of Wessely and his coworkers,[13] but obtained an inseparable mixture of products together with recovered **6**. Problems with conjugate addition of allyl Grignard reagents to quinol acetates have been reported previously.[13b] The rearrangement product was therefore hydrogenated to form the propyl derivative. The two possible hydrogenation products, **7a** and **8**, were independently synthesized as shown in eq 4 and 5.



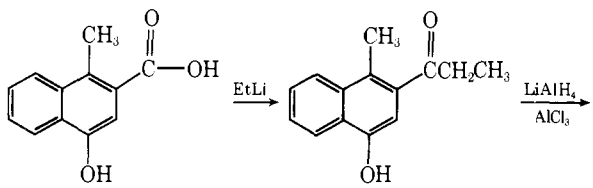
3 4 5

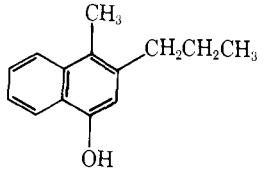


6

7a, R = *n*-Pr
b, R = *sec*-Bu

(4)





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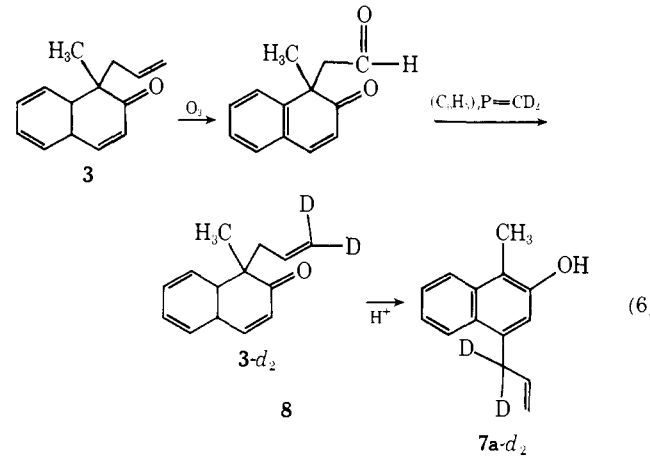
(5)

The NMR spectrum of phenol **7a** showed a triplet for the benzylic methylene group at τ 7.10, while the corresponding triplet in **8** was at τ 7.40. The lower field position for this signal in **7a** showed that the propyl group was in the α position, and in the β position in **8**.[14]

The phenol obtained by hydrogenation of the product of acid-catalyzed rearrangement of **3** was found to be identical with **7a**, and clearly different from **8**.

Rearrangement of **3** in the presence of boron trifluoride in ether similarly gave phenol **4** as the only rearrangement product. Rearrangement of **3** in 0.3 M sulfuric acid in acetic anhydride again gave a single product, which was found to be the acetate of **4**.

To decide whether the rearrangements of **3** had proceeded with or without inversion of the allyl group, the deuterated dienone **3**-d_2 was prepared as shown in eq 6. Rearrangements of **3**-d_2 catalyzed by sulfuric acid in acetic acid or acetic anhydride, or by boron trifluoride in ether, each gave **7a**-d_2 with the deuterium located, within experimental error, on the benzylic methylene group. Thus each rearrangement had proceeded by an overall [3,4] shift of the allyl group. After publication of the preliminary report of our work, workers at the University of Zurich reported that rearrangement of **3** in chlorobenzene, catalyzed by boron trichloride, similarly proceeds with inversion of the allyl group to give **7a**.[5]



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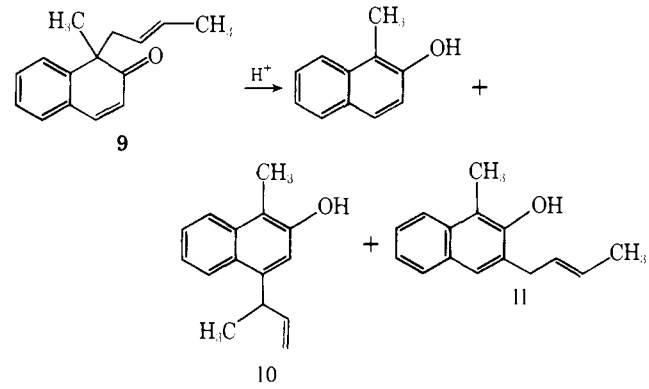
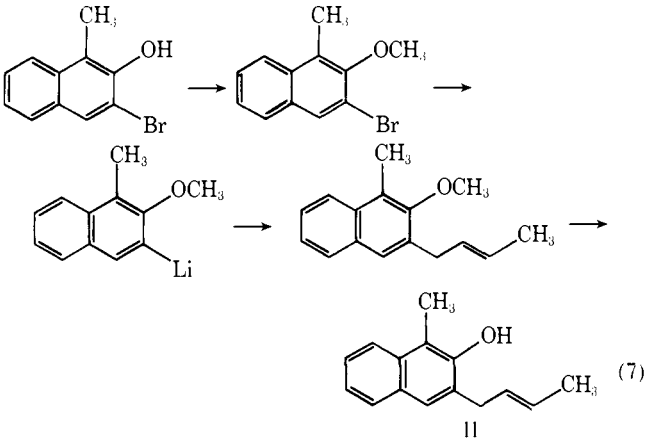
Rearrangement of naphthalenone **9** proceeded appreciably more rapidly than that of **3**. In either 0.1 M sulfuric acid in acetic acid, or 1.5 M sulfuric acid in aqueous ethanol, a mixture of three phenolic products was obtained.



These products were isolated by preparative GLC. The product with the lowest retention time was identified as the cleavage product, 1-methyl-2-naphthol. The NMR spectrum of the product with highest retention time, a phenol, showed the presence of a monosubstituted vinyl group and a three hydrogen doublet at τ 8.50, indicating that the crotyl

group had inverted during the rearrangement. In other respects, its spectrum resembled that of **7a.** This product thus seemed likely to be the [3,4] rearrangement product **10.** The correctness of this structural assignment was confirmed by hydrogenation of **10** to the *sec*-butyl derivative **7b,** which was independently synthesized by reaction of *sec*-butylmagnesium bromide with **6.**

The NMR spectrum of the rearrangement product with intermediate retention time showed the presence of an uninverted crotyl group. Its spectrum differed from that of **7a** and **10** in the absence of a high-field aromatic singlet for a proton ortho to the hydroxyl group. The most probable structure for this product appeared to be **11,** which would result from a [1,5] (or two [1,2]) migrations in **9.** Naphthol **11** was independently synthesized as shown in eq 7, and the

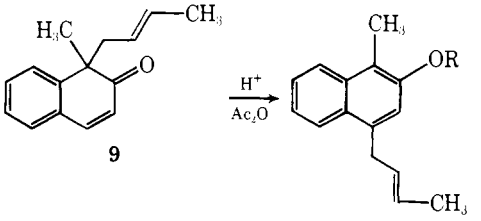


(7)

11

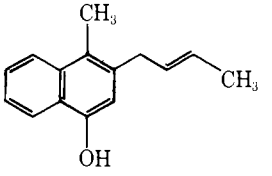
product was shown to be identical with the product obtained from the rearrangement of **9.**

While rearrangement of naphthalenone **3** gave similar results in acetic acid or acetic anhydride solutions, rearrangement of **9** in a 0.2 M solution of sulfuric acid in acetic anhydride gave, in addition to 1-methyl-2-naphthyl acetate, a single acetate **12b** as the only rearrangement product. On hydrolysis, **12b** gave a phenol which was different from ei-



9

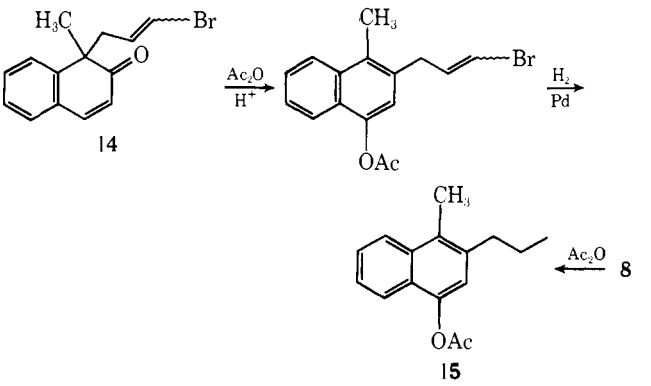
12a, R = H
b, R = $COCH_3$



13

ther naphthol obtained from rearrangement of **9** in acetic acid. Its NMR spectrum showed that the crotyl group had not inverted during the rearrangement, but, unlike the spectrum on **11,** showed a high-field aromatic singlet similar to those in the spectra of **7a** and **10.** Two possible structures for this phenol were **12a** and **13.** To distinguish between them, the double bond in the side chain of the rearranged phenol was hydrogenated, and the two possible butyl derivatives which might result were synthesized by methods similar to those shown in eq 4 and 5. The product obtained from the reaction of *n*-butylmagnesium bromide with **6** was found to be identical with that obtained from hydrogenation of the rearrangement product. Thus, although rearrangement of **3** in acetic anhydride had yielded only the [3,4] migration product, rearrangement of **9** gave only the [1,4] migration product.

To study the effect of an electron-withdrawing substituent on the migration of an allyl group, the 3-bromoallylnaphthalenone **14** was prepared by reaction of lithium 1-



14

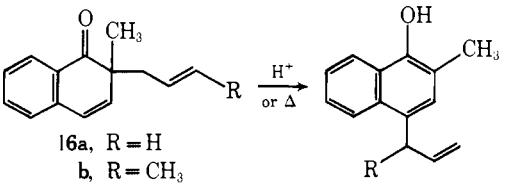
15

methyl-2-naphthoxide with 1,3-dibromopropene. Unfortunately, we were unable to effect any significant separation of the cis and trans isomers of the dibromopropene or of **14.** Rearrangement studies, therefore, were carried out on a mixture of the two isomers of **14.** Fortunately, the two isomers appeared to react in precisely the same manner (see below), so that the use of a mixture of stereoisomers presents no ambiguity in interpretation of the results.

Naphthalenone **14** did not rearrange in a 2 M solution of sulfuric acid in acetic acid even after several days at room temperature. However, it did rearrange slowly in 1.2 M sulfuric acid in acetic anhydride to give a mixture of rearrangement products, which were assumed to be cis-trans isomers from the similarity of their NMR spectra. Hydrogenation of the product mixture converted it to a single propyl derivative **15,** demonstrating that the products did indeed differ solely in the geometry around the double bond. The ratio of isomers in the product mixture (determined from the ratio of the signals for the methyl groups in the two isomers) was almost exactly the same as in naphthalenone **14.**

The structure of **15** was demonstrated by its independent synthesis by acetylation of 4-methyl-3-propyl-1-naphthol (**8**), whose synthesis is shown in eq 5. Thus, rearrangement of **14** proceeded by a [1,2] migration of the bromoallyl group to the carbonyl carbon, followed by migration of the oxygen function to C-4.

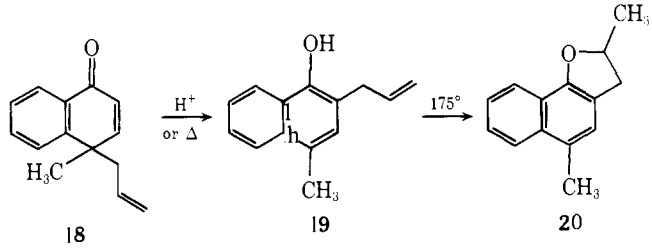
Allyl Migrations in 1-Naphthalenones. Rearrangement of naphthalenones **16a** and **16b** in acid gave products whose spectra corresponded to those expected of the [3,3] rearrangement products **17a** and **17b.** The structures of these products were confirmed by their formation by thermal Cope rearrangements of **16a** and **16b.**



16a, R = H
b, R = CH_3

17a, R = H
b, R = CH_3

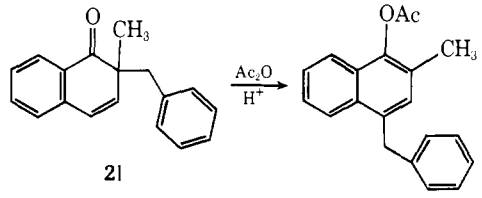
Rearrangement of the cross-conjugated naphthalenone **18** in a 0.3 M solution of sulfuric acid in acetic acid gave a product whose spectra corresponded to those expected of



18 19 20

the [3,3] rearrangement product **19.** An attempt to prepare **19** by thermal rearrangement of **18** at 175° gave only the dihydrobenzofuran **20.** Thermal rearrangement of **18** at 145°, however, gave a phenol whose spectra were identical with those of the product from acid-catalyzed rearrangement.

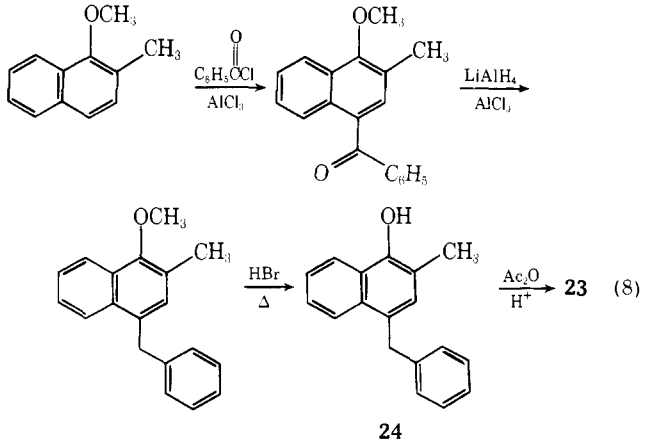
Migrations of Benzyl Groups. Rearrangements of the benzyl-substituted naphthalenones **21** and **22** proceeded



21 23

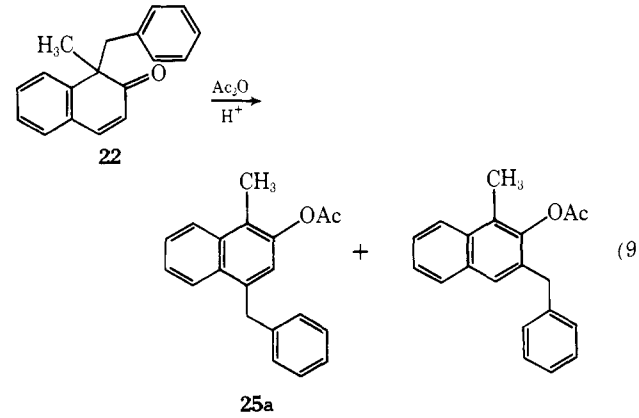
very slowly in 1 M sulfuric acid in acetic acid. In each case, unrecovered dienone (together with an inseparable mixture of reaction products) was obtained even after several days exposure to the acid solutions. Dienone **21** did rearrange slowly in a 1 M solution of sulfuric acid in acetic anhydride, giving, in addition to the cleavage product 1-acetoxy-2-methylnaphthalene, a mixture of two apparent rearrangement products in the ratio 5:1. The minor rearrangement product could not be isolated or identified. The major product was isolated by preparative GLC. Its NMR spectrum showed a singlet for the benzhydryl methylene group at τ 5.74, an unusually low-field position which suggested that the benzyl group was in the α position. The acetate **23** was therefore synthesized as shown in eq 8 and was found to be identical with the acetate obtained from rearrangement of **21.**

The boron trifluoride catalyzed rearrangement of **21** in ether similarly gave two apparent rearrangement products in the ratio ca. 7:1. The major product was isolated by GLC and identified as phenol **24.**



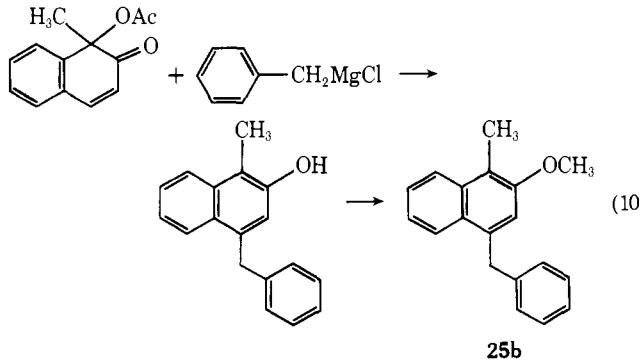
24 (8)

Rearrangement of naphthalenone **22** in 1 M sulfuric acid in acetic anhydride gave a mixture of two rearrangement products (in addition to the cleavage product 1-methyl-2-naphthyl acetate) in the ratio 4:1. The two acetates could not be separated, nor could the phenols obtained from them by hydrolysis. However, the methyl ethers obtained from



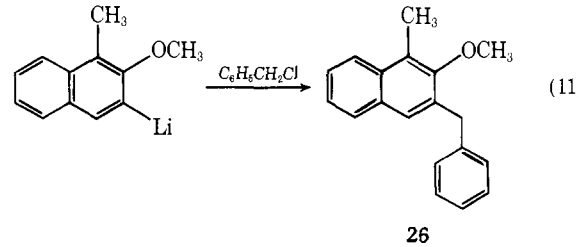
22 25a (9)

the phenols could be partially separated by preparative GLC. The major (lower retention time) isomer was obtained essentially pure. Its NMR product was characterized by the presence of a high-field aromatic singlet at τ 3.03, assigned to a proton in the β position and ortho to the acetoxy group, and by a benzhydryl methylene signal in a low-field position at τ 5.74. This spectrum suggested the possible structure **25b,** which was confirmed by synthesis as shown in eq 10. The second isomeric ether could not be ob-



25b (10)

tained pure, but was obtained as the major component in a mixture containing ca. 35% of **25b.** The spectrum of the mixture was characterized by the absence of a high-field aromatic singlet (except for that ascribed to ether **25b**) and the presence of a benzhydryl methylene singlet at τ 5.92, suggesting that the benzyl substituent was in the β position. Ether **26** was therefore synthesized as shown in eq 11. Its



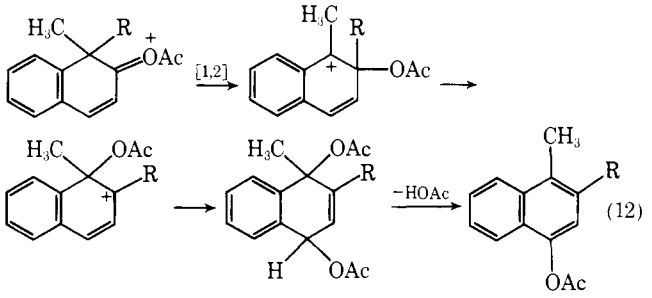
26 (11)

retention times on several GLC columns were found to be identical with those of the ether obtained from the minor rearrangement product, and the NMR spectrum of a mixture of **25b** and **26** was identical with the spectrum of the mixture of ethers obtained from the products of rearrangement of **22.** However, the ir spectrum of the mixture of ethers obtained from the rearrangement products showed two small peaks which were not present in the mixture of **25b** and **26.** It seems probable that the minor rearrangement product is indeed that resulting from a [1,5] migration of the benzyl group, but a definitive structural assignment cannot now be made.

Discussion

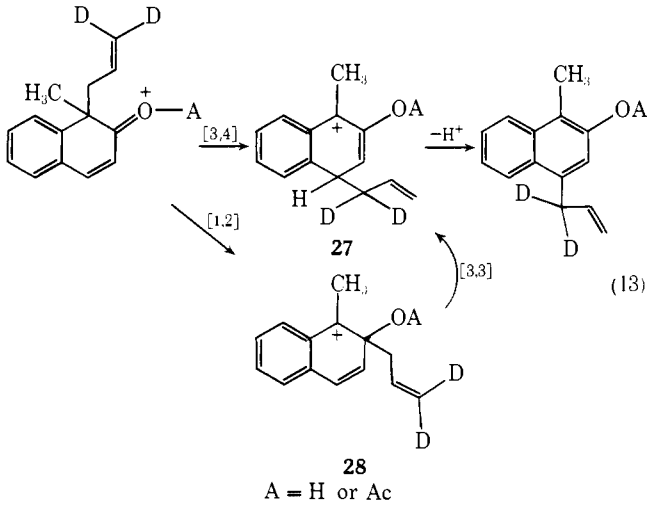
Allyl and benzyl groups thus undergo a variety of types of migrations in acid-catalyzed rearrangements of naphthalenones. The actual rearrangement observed in any instance is determined by the catalyst and solvent employed in the reaction and by the nature of substituents on the allyl group, when the migrating groups are allylic. Reasonable mechanisms can be written for most of these reactions. We can only begin to explain, however, why apparently minor changes in the structures of the migrating groups or in the reaction conditions can produce such dramatic changes in the types of rearrangements which take place.

Individually, most of these reactions are readily understood. Migration of a bromopropenyl group in **14,** for instance, directly parallels the migration of a methyl group in the rearrangement of naphthalenone **1**. In each case, rearrangement in acetic anhydride results in a [1,2] shift of the migrating group to the carbonyl carbon, followed by a migration of the oxygen function, which ultimately winds up at C-4. The mechanism proposed by Marvell and Stephenson[11] (eq 12) accounts adequately for these reactions, with



the minor cavil that the acetate migration to C-4 may be intramolecular rather than intermolecular.

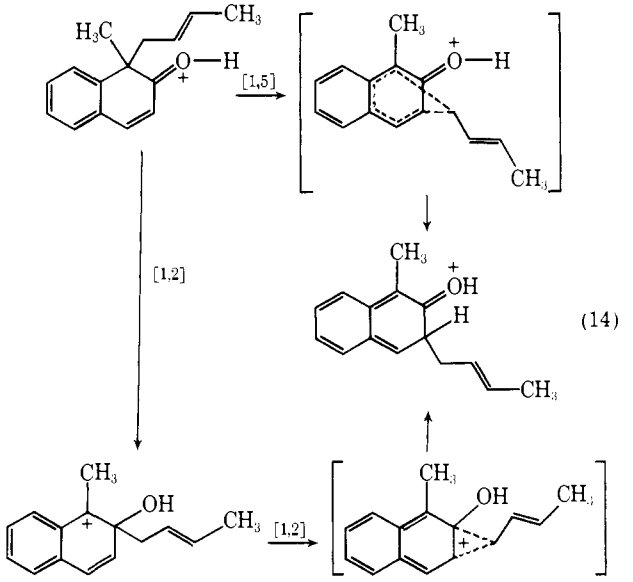
In contrast to the exclusive migration of a 1-bromopropenyl group to C-2, an allyl group migrates exclusively to C-4 with inversion of the allyl structure. This reaction can be accounted for either by a direct [3,4] migration or by a [1,2] migration to the carbonyl carbon, followed by a [3,3] shift in the resulting carbonium ion (eq 13).



Allyl groups have been shown to undergo [3,4] migrations almost as rapidly as [1,2] migrations in cyclohexadienyl carbonium ions[15] and in rearrangements of *o*-cyclohexadienones in trifluoroacetic anhydride.[6] A direct [3,4] migration would appear to be particularly favorable in the rearrangement of **3**, since carbonium ion **27,** which would be formed from a [3,4] shift, should be more stable than **28,** which would result from a [1,2] shift. It seems likely, therefore, that at least a major portion of the migration of an allyl group in **3** proceeds by a direct [3,4] shift.

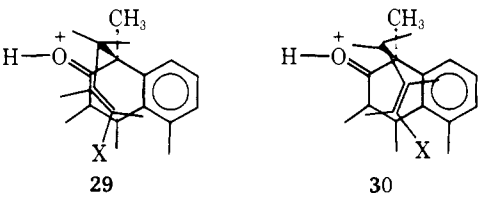
[3,4] migration of a 1-bromopropenyl group may be inhibited by steric repulsions between the bromine atom and the C-H bond at C-5 in **14,** particularly for the *Z* isomer. Alternatively, substitution of a bromine atom on the double bond may favor the mode of migration which maintains the more substituted double bond (although the energy difference between a bromine on a double bond or an sp^3 carbon appears to be quite small[16]).

Two possible mechanisms may be proposed for formation of naphthol **11** from naphthalenone **9**: a direct [1,5] migration of the crotyl group from C-1 to C-3, or a sequence of two [1,2] shifts (eq 14). Since the transition states for both

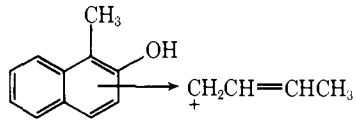


reactions resemble quinonoid, rather than aromatic, structures, both processes should require relatively high activation energies.

It is difficult to rationalize formation of **11** from rearrangement of naphthalenone **9**, but not of the corresponding product from rearrangement of **3**, on the basis of the sequential [1,2] shift mechanism. In rearrangements of cyclohexadienones in trifluoroacetic anhydride,[5] crotyl groups give approximately the same ratios of [1,2] to [3,4] migrations as allyl groups. In these reactions, therefore, neither the stabilizing effect of the methyl group on the double bond nor its steric effect significantly hinders inversion of a crotyl group. There seem to be no special steric effects attributable to the fused benzene rings in **3** and **9**, since inspection of molecular models indicates little repulsion between the methyl group (X) and the aromatic ring in transition state **29.** (The alternative transition state **30** seems likely to be less favorable than **29,** even for migration of an allyl group, due to the greater interaction between the migrating group and the aromatic ring.)



It might be suggested that transition state **31** resembles structure **31a,** in which stabilization of the transition state by the methyl on the side chain would be significant. However, similar "nonbonded" structures can be written for the transition state for [3,4] migration, or for [3,3] migration



31a

after an initial [1,2] migration. As was mentioned above, in rearrangements of cyclohexadienones crotyl groups do not give higher ratios of [3,4] to [1,2] migrations than do allyl groups.[5] Crotyl groups actually give higher ratios of [3,3] to [1,2] migrations than do allyl groups.[2] Thus, the suggestion that **11** is formed from **9** via a series of [1,2] shifts does not seem to account for the failure of **3** to rearrange to products similar to **11.**

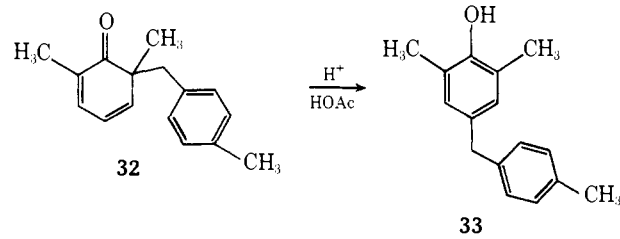
On the basis of the n vs. π protonation hypothesis, one of us has suggested that good migrating groups in acid-catalyzed rearrangements of linearly conjugated cyclohexadienones should undergo "thermal type" [1,5] migrations, while poor migrating groups should be more likely to undergo "carbonium ion type" [1,2] or [3,4] migrations.[3,8] The formation of a [1,5] migration product from rearrangement of **9** but not of **3** is at least consistent with this hypothesis.

Formation of the 4-crotylnaphthol **12b** from rearrangement of **9** in acetic anhydride offers problems of its own. Whether **12b** is formed by a direct [1,4] shift or by a [1,2] followed by a [1,3] migration, either a formally forbidden suprafacial migration or an unusual low-temperature antarafacial migration must take place. A satisfactory explanation for this reaction should account both for the different products obtained from reaction of **9** in acetic acid and in acetic anhydride, and for the difference between the reactions of **3** and **9** in acetic anhydride.

We suggest that the effects of the medium and the migrating group can both be understood if the migrations are presumed to proceed by suprafacial paths. Recent theoretical arguments indicate that formally forbidden rearrangements can proceed with relatively low activation energies if the highest occupied orbital of one fragment of the rearranging molecule (conceptually split at the migrating bond) and the lowest unoccupied orbital of the other fragment are similar in energy.[16,17] When a carbon-carbon bond is migrating, such a correspondence of energies of occupied and unoccupied orbitals can be achieved by having strongly electron-donating groups on one fragment of the molecule, and strongly electron-accepting groups on the other. Since an acetyl group is more electron withdrawing than a proton, the acylated ketone which would result from reaction of **9** with acetic anhydride should have a lower lying LUMO than the protonated ketone. Rearrangement of **9** in acetic anhydride thus appropriately gives more **12b** than does its rearrangement in protic solutions. Comparison of the results of rearrangement of **9** with that of rearrangement of **3** indicates that a more electron-donating substituent (which would raise the energy of the HOMO) on the other molecular fragment similarly favors the formally forbidden [1,4] or [1,3] shift.

While the effects of changes in the reaction conditions and migrating group are in the direction predicted by theory, we must admit that the magnitude of the effects is a surprise.

The rearrangements of **21** to **23** and of **22** to **25a** probably proceed by similar [1,3] and [1,4] shifts. No other mechanism seems reasonable for the formation of **25a,** since mechanisms involving initial dissociation of **23** (to yield either radicals or a benzyl carbonium ion) would not be expected to yield the products of recombination at C-4, meta to the acetoxy group. The possibility of a dissociative mechanism for the rearrangement of **21** has not been eliminated. However, it was recently shown that the acid-catalyzed rearrangement of **32** to give **33** proceeds by a concerted [1,3] shift.[18] The analogous reaction of **21** therefore seems most likely to proceed by a similar mechanism.



32 33

Experimental Section

General. NMR spectra were taken on Varian A-60 or Perkin-Elmer R12A spectrometers in carbon tetrachloride solution (unless otherwise indicated) using TMS as an internal standard. Ir spectra were taken on Beckman IR-10 or Perkin-Elmer 273B spectrometers. Mass spectra were taken on a Hitachi Perkin-Elmer RMU-6L instrument.

Elemental analyses were carried out by the University of Massachusetts Microanalytical Laboratory, Amherst, Mass.

GLC analyses and separations were carried out on a Varian Aerograph Model 202c instrument using one of the following columns: column A, 6 ft × ¼ in., 5% SE-30 on Chromosorb W; column B, 5 ft × ⅜ in., 5% SE-30 on Chromosorb W; column C, 6 ft × ¼ in., 5% diethylene glycol glutarate (DEGG) on Chromosorb W; column D, 6 ft × ⅜ in., 5% SE-52 on Chromosorb W. Column temperature and carrier gas flow rates are described in parentheses for each separation.

Melting points were taken on a Mel-Temp apparatus and are uncorrected.

For syntheses of naphthalenones, the phrase "worked up as usual" means that water was added to the reaction mixture and the organic layer was washed with 10% sodium hydroxide and then with water. The solution was then dried over anhydrous magnesium sulfate and the solvent evaporated.

For acid-catalyzed rearrangements of naphthalenones, the phrase "worked up as usual" means that water was added to the reaction mixture, which was then extracted with methylene chloride. The organic layer was washed with aqueous sodium bicarbonate solution, then with water, and dried over anhydrous magnesium sulfate, and the solvent was evaporated.

Preparation of 2-Naphthalenones. 1-Methyl-2-naphthol was most conveniently prepared by dissolving 2-naphthol (7.2 g, 0.050 mol) in 200 ml of dry benzene under a nitrogen atmosphere and adding a hexane solution of *n*-butyllithium (0.050 mol). After the mixture had been stirred at room temperature for 10 min, dimethyl sulfate (6.3 g, 0.050 mol) was added and the reaction mixture was refluxed for 4 h. Water was cautiously added to the cooled mixture and the organic layer extracted with 3 N sodium hydroxide solution. The basic extract was acidified and extracted with methylene chloride, and the organic solution was dried over magnesium sulfate and evaporated to give 2.1 g of crude product. GLC on column A showed the product to consist of 2-naphthol and 1-methyl-2-naphthol in a molar ratio of 1:3. The product was dissolved in methylene chloride and extracted with 3 N sodium hydroxide solution containing 0.0034 mol of base (equal to the number of moles of 2-naphthol in the product). The methylene chloride layer was washed with water, dried over magnesium sulfate, and evaporated to give 1.55 g (0.0098 mol, 20%) of essentially pure 1-methyl-2-naphthol, mp 108–109° (lit.[19] mp 111 °C).

1-Allyl-1-methyl-2-naphthalenone (3). *n*-Butyllithium (10 ml of a 2.1 M solution in hexane) was added to a solution of 1-methyl-2-naphthol (3.2 g, 0.02 mol) in 100 ml of dry benzene, and the mixture stirred under nitrogen for 10 min. Allyl bromide (3.0 g, 0.025 mol) was added and the mixture was stirred at room temperature for 16 h and worked up as usual. The crude product (3.7 g) was chromatographed on 100 g of Florisil, eluting with pentane containing 5% by volume of methylene chloride. The first fraction obtained (0.3 g) consisted of a mixture of allyl 1-methyl-2-naphthyl ether and **3**. Continued elution gave pure **3** (2.7 g, 0.0137 mol, 69%) as a pale yellow oil. Its ir spectrum had a carbonyl peak at 1650 cm^{-1}. Its NMR spectrum had signals at τ 2.68–2.90, 4.02 (d,

J = 8 Hz, 1 H), 3.6–4.6 (m, 1 H), 4.82–5.47 (m, 2 H), 7.06–7.77 (m, 2 H), and 8.60 (s, 3 H).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.56; H, 7.33.

1-(*trans*-2-Butenyl)-1-methyl-2-naphthalenone (9) was prepared in 55% yield by a similar procedure. Its ir spectrum had a carbonyl peak at 1650 cm^{-1}. Its NMR spectrum ($CDCl_3$) had signals at τ 2.52–2.75 (m, 5 H), 3.86 (d, J = 8.5 Hz, 1 H), 4.35–5.15 (m, 2 H), 7.05–7.54 (m, 2 H), 8.53 (d, J = 4 Hz, 3 H), and 8.56 (s, 3 H).

Anal. Calcd for $C_{15}H_{16}O$: C, 84.90; H, 7.58. Found: C, 84.71; H, 7.80.

1,3-Dibromopropene. Attempts to prepare 1,3-dibromopropene by dehydration of 1,3-dibromo-2-propanol[20] gave only tarry products. Instead, a mixture of 1-bromo-1-propene (60 g, 0.5 mol), *N*-bromosuccinimide (80 g, 0.45 mol), and benzoyl peroxide (0.2 g) in 250 ml of carbon tetrachloride was stirred under reflux while being irradiated by a 250-W incandescent lamp. After 5 h the mixture was washed with water and dried over magnesium sulfate; the solvent was evaporated to give 87 g (87%) of dark yellow fluid. GLC on column A (60°, 50 ml/min) showed two peaks with retention times of 2.4 and 2.9 min, in the area ratio 3:2. The components could not be separated by fractional distillation. Preparative GLC on column B (60°, 55 ml/min) gave pure samples of both products. The product with the lower retention time had NMR signals at τ 6.18–6.50 (m, 2 H) and 3.9–4.1 (m, 2 H). The compound with the higher retention time had NMR signals at τ 6.31–6.49 (m, 2 H) and 3.8–3.94 (m, 2 H). These spectra correspond to those expected for 1,3-dibromopropene, but stereochemical assignments for the two isomers could not be made.

1-(3-Bromoallyl)-1-methyl-2-naphthalenone (14) was prepared in 59% yield as a mixture of cis and trans isomers, using the mixture of stereoisomeric 1,3-dibromopropenes prepared above as the alkylating agent, in a procedure otherwise identical with that used for the preparation of **3**. The product had an ir peak at 1655 cm^{-1}. Its NMR spectrum had signals at τ 2.54–2.82 (m, 5 H), 3.92 (d, J = 10 Hz), 4.18–4.62 (m, 2 H), 7.02–7.56 (m, 2 H), and 8.55 and 8.60 (two singlets, together 3 H). Its mass spectrum had peaks at m/e 280 (M^+).

1-Benzyl-1-methyl-2-naphthalenone (22). The reaction of lithium 1-methyl-2-naphthoxide and benzyl bromide was carried out on a 0.06 molar scale using the procedure described above for the preparation of **3**. Chromatography of the product on 200 g of activity III neutral alumina, eluting with a 95:5 (by volume) mixture of 30–60° petroleum ether and methylene chloride gave 7.4 g (0.03 mol, 53%) of naphthalenone **22** as a white solid, mp 62–64 °C (from petroleum ether). Its ir spectrum had a carbonyl peak at 1660 cm^{-1}. Its NMR spectrum had signals at τ 2.68–3.70 (m, 10 H), 4.29 (d, J = 9.0 Hz, 1 H), 6.67 and 7.11 (each a doublet, J = 10.0 Hz), and 8.51 (s, 3 H).

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.97; H, 6.25.

1-Methyl-1-(2-oxoethyl)-2-naphthalenone (34). A solution of naphthalenone **3** (10.0 g, 0.05 mol) in 500 ml of methylene chloride was kept in a dry ice–acetone bath and stirred for 2 h while ozone was passed through it at a rate of 0.4 l./min. The solution was then warmed to room temperature and a 10% solution of sodium sulfite in water (200 ml) was added. The mixture was stirred for 1 h and the organic layer was then washed with water and dried and the solvent evaporated to give 10.1 g of a yellow oil. The crude product was chromatographed on Florisil (110 g), eluting with a 90:10 (by volume) mixture of 30–60° petroleum ether and methylene chloride. After a mixture of naphthalenones **3** and **34** (3.9 g) was collected, further elution gave essentially pure **34** (6.0 g, 0.03 mol, 60%) as a pale yellow oil. Its ir spectrum showed carbonyl peaks at 1720 and 1650 cm^{-1}. Its NMR spectrum had signals at τ 0.65 (broad s, 1 H), 2.55 (d, J = 8.5 Hz), 2.75 (s, 4 H), 3.80 (d, J = 8.5 Hz), 6.62 (d, J = 18.1 Hz, 1 H), 6.79 (d of d, J = 18.1 and 1.3 Hz), and 8.65 (s, 3 H).

1-(3,3-Dideuterioallyl)-1-methyl-2-naphthalenone (3-d_2). A solution of 2.1 M *n*-butyllithium in hexane (14 ml, 0.028 mol) was added to a solution of trideuteriomethyltriphenylphosphonium bromide (9.5 g, 0.027 mol) in 150 ml of anhydrous ether. The mixture was kept under nitrogen and stirred for 5 h, after which a solution of aldehyde **34** (4.5 g, 0.023 mol) in 100 ml of ether was added. The reaction mixture was stirred under nitrogen for 3 days. Water was added and the ether layer was again washed with water, dried over anhydrous magnesium sulfate, and evaporated to give 3.9 g of yellow oil. Chromatography on 80 g of activity III neutral alumina gave 2.8 g (0.014 mol, 62%) of naphthalenone **3**-d_2. Its NMR spectrum was identical with that of **3**, except for the decreased area of the peaks for the terminal vinyl protons around τ 5. The number of residual hydrogens at the terminal vinyl position was calculated to be 0.79 ± 0.12, based on internal comparison of the area of the signals for the terminal vinyl protons with the area of the signals for the vinyl proton at C-3, and 0.73 ± 0.11 residual hydrogen atoms based on comparison with the signals for the secondary vinyl proton in the allyl group.

Rearrangement of 2-Naphthalenones. Rearrangement of 1-Allyl-1-methyl-2-naphthalenone. (A) In Acetic Acid. Naphthalenone **3** was dissolved in 6 ml of 1 M sulfuric acid in acetic acid. The resulting mixture was allowed to stand at room temperature for 24 h and worked up as usual to give 0.4 g of a brown oil. VPC on column A (170°, 60 ml/min) showed the presence of peaks with retention times of 2.6, 9.9, and 11 min. The area ratios were 7:31:10. The products were isolated on column B (200°, 65 ml/min). The first component was the starting ketone **3**. The second compound (t_R 9.9 min.) (naphthol **4**) crystallized on standing and was recrystallized from petroleum ether, mp 102–103 °C. Its ir spectrum showed a hydroxy peak at 3330 cm^{-1}. Its NMR spectrum (in $CDCl_3$) had signals at τ 2.1–2.22 (m, 2 H), 2.56–2.79 (m, 3 H), 3.17 (s, 1 H at C-3), 3.78–4.29 (m, 1 H), 4.70–5.17 (m, 2 H), 6.31 (d, τJ = 5.5 Hz, 2 H), and 7.54 (s, 3 H).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.54; H, 6.95.

The third component (t_r 11 min.) was identified as 2-acetoxy-4-allyl-1-methylnaphthalene by comparison with a sample prepared as described below.

(B) Catalyzed by BF_3. Naphthalenone **3** (0.50 g) was dissolved in 10 ml of a 3 M solution of boron trifluoride in ether. The mixture was stirred at room temperature for 2.5 h and worked up as usual to give 0.5 g of 4-allyl-1-methyl-2-naphthol.

(C) In Acetic Anhydride. Naphthalenone **3** (0.50 g) was dissolved in 10 ml of a 0.3 M solution of sulfuric acid in acetic anhydride. The resulting mixture was stirred at room temperature for 2 h and was then poured into cold water and worked up as usual to give 0.6 g of 2-acetoxy-4-allyl-1-methylnaphthalene, identified by comparison with the sample prepared as described below.

Synthesis of 1-Methyl-4-propyl-2-naphthol (7a). A solution of 1-acetoxy-1-methyl-2-naphthalenone[21] (1.50 g, 7.0 mmol) in 50 ml of dry ether was added slowly to a stirred solution of propylmagnesium bromide (0.05 mol) and cuprous chloride (80 mg) in 50 ml of dry ether under a nitrogen atmosphere. After all the naphthalenone had been added (ca. 15 min), the mixture was refluxed for 2 h and then poured into ammonium chloride solution. The organic layer was washed with dilute hydrochloric acid, then with water, and dried over magnesium sulfate. GLC of the product on column A (175°, 55 ml/min) showed two major peaks with retention times of 2.53 (1-methyl-2-naphthol) and 6.69 min, in the area ratio 3:2. These products were isolated by preparative GLC on column B (200°, 60 ml/min). The component with higher retention time (1-methyl-4-propyl-2-naphthol) solidified on standing, mp 107–108 °C. Its ir spectrum showed a hydroxy peak at 3370 cm^{-1}. Its NMR spectrum had signals at τ 2.06–2.31 (m, 2 H), 2.51–2.90 (m, 3 H), 3.22 (s, 1 H), 7.10 (t, J = 5 Hz, 2 H), 7.51 (s, 3 H), 8.11 (m, 2 H), 8.97 (t, J = 5 Hz, 3 H).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.60; H, 8.39.

2-Acetoxy-4-allyl-1-methylnaphthalene. 4-Allyl-1-methyl-2-naphthol (28 mg) was dissolved in 3 ml of acetic anhydride containing 25 mg of sodium acetate. After 18 h, 25 ml of water was added; the mixture was stirred at room temperature for 2 h and then extracted with methylene chloride. The organic layer was washed with water, then with sodium bicarbonate, and again with water and dried over magnesium sulfate; the solvent was evaporated to give 33 mg (93%) of pale yellow oil. GLC on column A (170°, 58 ml/min) showed the presence of a single component with a retention time of 11.4 min. Its ir spectrum showed a carbonyl peak at 1765 cm^{-1}. Its NMR spectrum had signals at τ 2.02–2.20 (m, 2 H), 2.57–2.79 (m, 2 H), 3.13 (s, 1 H), 3.74–4.43 (m, 1 H), 4.80–5.15 (m, 2 H), 6.28 (d, J = 5.0 Hz, 2 H), 7.58 (s, 3 H), and 7.71 (s, 3 H).

Rearrangement of 1-(3,3-Dideuterioallyl)-1-methyl-2-naphthalenone (3-d_2). (A) In Acetic Acid. Naphthalenone 3-d_2 (0.4 g) was dissolved in 6 ml of 0.5 M sulfuric acid in acetic acid. The solution was allowed to stand at room temperature for 3 days, and was then worked up as usual to give 0.35 g of a brown oil. GLC analysis showed the presence of 3-d_2, 4-d_2, and the acetate of 4-d_2 in the ratio 11:82:7. The major component was isolated by GLC on column B (200°, 65 ml/min). Its NMR spectrum was identical with that of 4-allyl-1-methyl-2-naphthol, except for the decreased intensity of the allylic methylene doublet at τ 6.31. The hydrogen content at this position was found to be 0.74 ± 0.15 atom by comparison of the area of these signals with that of the methyl group.

(B) Catalyzed by BF_3. Naphthalenone 3-d_2 (0.2 g) was dissolved in 10 ml of a 20% solution of boron trifluoride in ether. The mixture was stirred at room temperature for 2.5 h and worked up as usual to give 0.2 g of crystalline 4-allyl-1-methyl-2-naphthol. The hydrogen content of the allylic methylene group was found to be 0.81 ± 0.16 atom.

(C) In Acetic Anhydride. Naphthalenone 3-d_2 (0.2 g) was dissolved in 10 ml of acetic anhydride containing 3% (by weight) of sulfuric acid. The solution was stirred at room temperature for 2 h and worked up as usual to give 0.25 g of 4-allyl-1-methyl-2-naphthyl acetate. The hydrogen content of the allylic methylene group was found to be 0.71 ± 0.15% atom.

Rearrangement of 1-(*trans*-2-Butenyl)-1-methyl-2-naphthalenone (9). (A) In Acetic Acid. Naphthalenone **9** (0.50 g, 2.4 mmol) was dissolved in 10 ml of 0.1 M sulfuric acid in acetic acid. After standing at room temperature for 24 h, the deep orange-red solution was worked up as usual to give 0.50 g of yellow oil. GLC analysis on column C (185°, 55 ml/min) showed three peaks with retention times of 8.1, 11.8, and 21.5 min, in the ratio 1:0.35:0.48, respectively. These compounds were isolated by preparative chromatography on column C. The component with lowest retention time was found to be 1-methyl-2-naphthol. The second (intermediate retention time) component was identified as 3-(*trans*-2-butenyl)-1-methyl-2-naphthol (**11**) by comparison of its GLC retention times and ir and NMR spectra with those of a sample prepared as described below.

The third component, 4-(1-methylallyl)-1-methyl-2-naphthol (**10**), was obtained as a yellow oil. Its ir spectrum had an OH peak at 3400 cm^{-1}. Its NMR spectrum had signals at τ 1.9–2.18 (m, 2 H), 2.54–2.83 (m, 2 H), 3.12 (s, 1 H), 3.60–5.10 (m, 4 H), 5.5–5.9 (m, 1 H), 7.51 (s, 3 H), and 8.50 (d, J = 7 Hz, 3 H).

(B) In Aqueous Ethanol. A solution of naphthalenone **9** (0.50 g) in 2 ml of ethanol was slowly dropped into 10 ml of 1 M sulfuric acid in water. The solution was stirred for 24 h and then worked up as usual to give 0.40 g of a pale yellow oil. GLC on column C showed four peaks in relative areas 10:2.0:2.1:1.2. These products were isolated by preparative VPC and identified as naphthalenone **9**, 1-methyl-2-naphthol, **11**, and **10**.

(C) In Acetic Anhydride. Naphthalenone **9** (1.8 g, 0.084 mol) was dissolved in 10 ml of 2% sulfuric acid in acetic anhydride; the solution was stirred at room temperature for 2 h and then worked up as usual to give 1.8 g of dark brown oil. This was dissolved in 30 ml of a 10% solution of potassium hydroxide in 1:1 ethanol–water and refluxed for 1 h. After acidification 1.7 g of brown oil was obtained. Extraction of the crude material with 1% sodium hydroxide and acidification of the basic extract gave 0.5 g (0.032 mol, 38%) of 1-methyl-2-naphthol. The residual material (1.1 g) showed GLC peaks at 2.9 and 8.7 min, in the area ratio 1:15. The major component was isolated as a colorless oil by preparative GLC on column C, (200°, 60 ml/min). Its ir spectrum had an OH peak at 3400 cm^{-1}. Its NMR spectrum ($CDCl_3$) had peaks at τ 1.9–2.85 (m, 4 H), 3.10 (s, 1 H), 3.6–4.05 (m, 2 H), 4.77 (s, 1 H), 6.24–6.62 (m, 2 H), 7.50 (s, 3 H), and 8.23–8.44 (m, 3 H). Its mass spectrum had a peak at m/e 212 (M^+). This compound was identified as 4-(*trans*-2-butenyl)-1-methyl-2-naphthol (**12a**) as described below.

Proof of Structures of Products of Rearrangement of 9. Hydrogenation of 1-Methyl-4-(1-methylallyl)-2-naphthol (10). A solution of **10** (31 mg) in 10 ml of benzene containing 20 mg of 5% palladium on charcoal was stirred at room temperature under an atmosphere of hydrogen until hydrogen uptake was complete (ca. 25 min). The mixture was filtered and the solvent evaporated to give 30 mg of yellow oil. GLC on column A showed a single peak. The ir and NMR spectra of the product were identical with those of 4-*sec*-butyl-1-methyl-2-naphthol.

4-*sec*-Butyl-1-methyl-2-naphthol. A solution of 1-acetoxy-1-methyl-2-naphthalenone[21] (1.0 g, 4.5 mmol) in ether was added slowly to a solution of 14.5 mmol of *sec*-butylmagnesium bromide in 100 ml of ether. After stirring for 1 h, the reaction mixture was poured onto a mixture of ice and hydrochloric acid. The ethereal layer was washed with water and dried and the solvent evaporated to give 0.75 g of brown oil. Its ir spectrum showed no carbonyl peaks. GLC on column A (205°, 55 ml/min) showed three peaks in the area ratios 1:0.9:2.6. These products were isolated by preparative VPC on column B (205°). The first component was found to be 1-methyl-2-naphthol and the second to be *sec*-butyl-1-methyl-2-naphthyl ether. The component with the highest retention time, a yellow oil, was assigned the structure 4-*sec*-butyl-1-methyl-2-naphthol. Its NMR spectrum had signals at τ 1.85–2.20 (m, 2 H), 2.45–2.90 (m, 2 H), 3.08 (s, 1 H), 4.90 (s, 1 H), 6.35–6.85 (m, 1 H), 8.1–ca. 8.8 (m, ca. 2 H), 8.65 (d, J = 7 Hz, 3 H), and 9.11 (t, J = 7 Hz, 3 H).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.46. Found: C, 83.77; H, 8.50.

3-Bromo-1-methyl-2-naphthyl Methyl Ether. Potassium *tert*-butoxide (5.0 g, 0.045 mol) was added to a solution of 3-bromo-1-methyl-2-naphthol[22] (10.0 g, 0.045 mol) in 80 ml of dimethyl sulfoxide. The mixture was stirred at room temperature for 15 min and methyl iodide (2.7 ml, 0.045 mol) was added. After 1 h the mixture was poured into water and extracted with methylene chloride; the organic layer was washed with water and dried and the solvent evaporated, leaving 11.0 g of yellow fluid. Chromatography on Florisil (110 g) eluting with 30–60° petroleum ether, gave 6.3 g (0.025 mol, 55%) of 3-bromo-1-methyl-2-naphthyl methyl ether as a colorless fluid. Its ir spectrum showed no carbonyl or hydroxy peaks.

3-(*trans*-2-Butenyl)-1-methyl-2-naphthyl Methyl Ether. A 2.1 N solution of *n*-butyllithium in hexane (3 ml, 6.3 mmol) was added to a solution of 3-bromo-1-methyl-2-naphthyl methyl ether (1.0 g, 3.98 mmol) in 20 ml of ether. The solution was stirred at room temperature under nitrogen for 2 h, and then cooled in ice. A solution of *trans*-1-bromo-2-butene (0.92 g, 6.8 mmol) in 10 ml of ether was added and the mixture stirred at room temperature for 2 h. Water was added, the organic layer was dried over magnesium sulfate, and the solvent was evaporated to give 0.83 g of brown oil. GLC analysis on column A (200°, 55 ml/min) showed two peaks which were isolated by preparative GLC and identified as methyl 1-methyl-2-naphthyl ether and 3-(*trans*-2-butenyl-1-methyl-2-naphthyl methyl ether, respectively. The latter compound had NMR peaks at τ 2.0–2.9 (m, 5 H), 4.2–4.45 (m, 2 H), 6.22 (s, 3 H), 6.4–6.6 (m, 2 H), 7.39 (s, 3 H), and 8.30 (broad doublet, J = 4 Hz).

3-(*trans*-2-Butenyl)-1-methyl-2-naphthol. The crude mixture of naphthyl methyl ethers prepared in the above procedure (0.69 g) was dissolved in 10 ml of *N,N*-dimethylformamide (DMF) and added to a solution of potassium *tert*-butoxide (1.1 g, 9.9 mmol) and thiophenol (1.1 g, 10 mmol) in 15 ml of DMF. The mixture was refluxed for 1 h under an atmosphere of nitrogen, cooled to room temperature, and poured into a dilute hydrochloric acid solution. Methylene chloride was added and the organic layer was extracted with Claisen alkali. The alkaline layer was acidified and extracted with methylene chloride, the organic layer washed with water and dried over magnesium sulfate, and the solvent evaporated to give 0.43 g of brown oil. GLC analysis showed the presence of two compounds in the area ratio 1.5:1.0. These were separated by preparative GLC on column C. The product with the lower retention time was found to be 1-methyl-2-naphthol, and that with the higher retention time was assigned the structure 3-(*trans*-2-butenyl)-1-methyl-2-naphthol. Its ir spectrum had an OH peak at 3450 cm^{-1}. Its NMR spectrum had peaks at τ 2.05–3.07 (m, 5 H), 3.65–4.86 (m, 3 H), 6.38 (m, 2 H), 7.52 (s, 3 H), and 8.34 (m, 3 H).

Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.59. Found: C, 85.11; H, 7.80.

4′-Methoxy-1′-methyl-2′-butyronaphthone (34a). A solution of *n*-propyllithium (0.2 mol) in 80 ml of ether was slowly added to a solution of 4-methoxy-1-methyl-2-naphthoic acid[23] (10.8 g, 0.05 mol) in 300 ml of dry benzene. The mixture was refluxed under a nitrogen atmosphere for 2 h, and then carefully poured onto a mixture of 200 g of ice and 30 ml of concentrated hydrochloric acid.

The organic layer was washed several times with water and aqueous sodium bicarbonate solution and dried over magnesium sulfate; the solvent was evaporated to give 9.8 g of black oil. GLC on column A (210°, 55 ml/min) showed the product to have a single main component which was isolated by preparative GLC on column B (220°, 65 ml/min). Its ir spectrum had a carbonyl peak at 1680 cm^{-1}. Its NMR spectrum had peaks at τ 1.65–2.05 (m, 2 H), 2.4–2.61 (m, 2 H), 3.03 (s, 1 H), 5.99 (s, 3 H), 7.18 (t, J = 6.6 Hz, 2 H), 7.4 (s, 3 H), 7.5–8.40 (m, 4 H), 8.97 (t, J = 6.6 Hz, 3 H).

2-*n*-Butyl-1-methyl-4-methoxynaphthalene (35). Lithium aluminum hydride (1.0 g, 0.025 mol) was suspended in 50 ml of anhydrous ether, and anhydrous aluminum chloride (3.3 g, 0.025 mol) in 20 ml of dry ether was added. The mixture was stirred under an atmosphere of nitrogen for 5 min, and a solution of crude **34a** (6.1 g, 0.025 mol) in 50 ml of ether was added. The mixture was refluxed for 4 h. Water was added cautiously to the cooled mixture, and then 10 ml of 3 M sulfuric acid solution was added. The layers were separated, the organic fraction was washed with water and dried, and the solvent was evaporated to give 5.9 g of dark brown oil. GLC on column A (200°, 55 ml/min) showed three peaks with retention times of 4.2, 5.9, and 8.1 min, with areas in the ratio 30:48:22, respectively. An attempt to separate these products by chromatography on Florisil was unsuccessful. Samples of the three components were isolated by preparative GLC on column B (220°, 65 ml/min). The components with the highest and lowest retention times showed strong hydroxyl peaks at 3430 cm^{-1}, respectively, in their ir spectra, and were not further investigated. The NMR spectrum of the component with a retention time of 5.9 min had peaks at τ 1.75–2.20 (m, 2 H), 2.41–2.73 (m, 2 H), 3.49 (s, 1 H), 6.05 (s, 3 H), 7.25 (t, J = 6.6 Hz, 2 H), 7.51 (s, 3 H), 8.1–8.81 (m, 4 H) and 9.02 (t, J = 5 Hz, 3 H). Its mass spectrum had a peak at m/e 228 (M^+). It was assigned the structure 2-butyl-1-methyl-4-methoxynaphthalene.

4-Butyl-1-methyl-2-naphthol. 1-Acetoxy-1-methyl-2-naphthalenone[21] (2.2 g, 0.010 mol) in 50 ml of ether was added to a solution of butylmagnesium bromide (0.015 mol) in 30 ml of ether. After completion of the addition (5 min) the mixture was refluxed for 2 h and worked up as described for the preparation of 1-methyl-4-propyl-2-naphthol. The crude product was extracted with 1% sodium hydroxide solution to remove 1-methyl-2-naphthol. The ether solution was dried and the solvent evaporated to give 1.3 g (6.1 mmol, 61%) of crude 4-butyl-1-methyl-2-naphthol. An analytical sample was isolated as a pale yellow oil by preparative GLC on column B (220°, 65 ml/min). Its ir spectrum had an OH peak at 3300 cm^{-1}. Its NMR spectrum ($CDCl_3$) had peaks at τ 1.90–2.12 (m, 2 H), 2.41–2.76 (m, 2 H), 3.05 (s, 1 H), 5.14 (broad s, 1 H), 7.01 (t, J = 6.6 Hz, 2 H), 7.50 (s, 3 H), 8.17–8.81 (m, 4 H), and 9.04 (t, J = 5.5 Hz, 3 H).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.06; H, 8.46. Found: C, 84.44; H, 8.48.

4-Butyl-2-methoxy-1-methylnaphthalene (36). Potassium *tert*-butoxide (1.0 g, 8.9 mmol) was added to a solution of crude 4-butyl-1-methyl-2-naphthol (1.2 g, 5.5 mmol) in 50 ml of dimethyl sulfoxide. When the alkoxide had completely dissolved, methyl iodide (5 ml) was added and the mixture was stirred at room temperature for 2 h. Water was added and the mixture was extracted with methylene chloride. The organic layer was washed with water, dried, and evaporated to give 1.3 g of brown oil. GLC on column A (200°, 55 ml/min) showed the presence of a single major peak. A sample of the product (4-butyl-2-methoxy-1-methylnaphthalene) was isolated by preparative GLC on column B (220°, 65 ml/min). Its ir spectrum showed no carbonyl or hydroxy peaks. Its NMR spectrum had signals at τ 2.01–2.17 (m, 2 H), 2.47–2.79 (m, 2 H), 2.98 (s, 1 H), 6.10 (s, 3 H), 6.97 (t, J = 6.5 Hz, 2 H), 7.53 (s, 3 H), 8.14–8.82 (m, 4 H), and 9.02 (t, J = 6 Hz, 3 H).

Methylation and Hydrogenation of 4-(*trans*-2-Butenyl)-1-methyl-2-naphthol (12a). Potassium *tert*-butoxide (1.0 g, 89 mmol) was added to a solution of naphthol **12a** (1.1 g, 5.0 mmol) in 30 ml of dimethyl sulfoxide. After the mixture had been stirred at room temperature for 10 min, methyl iodide (7 ml) was added, and stirring was continued for another 2 h. The reaction was worked up as in the preparation of **36** to give 1.2 g of brown oil. The oil was dissolved in 50 ml of benzene and a small amount of 5% palladium on charcoal was added. The mixture was stirred under an atmosphere of hydrogen until uptake of hydrogen had ceased and was then filtered; the solvent was evaporated, leaving 1.2 g of deep yellow oil. A sample of the single major component of this material was isolated by GLC on column B and identified as 4-butyl-2-methoxy-1-methylnaphthalene by comparison of its GLC retention time and ir and NMR spectra with those of the compound prepared as described above.

Rearrangement of 1-(3-Bromoallyl)-1-methyl-2-naphthalenone (14). Naphthalenone **14** (1.0 g) was dissolved in 12 ml of acetic anhydride containing 12% (by weight) of sulfuric acid. The reaction mixture was stirred at room temperature for 3 days and then worked up as usual to give 1.0 g of brown oil. GLC analysis on column A (200°, 55 ml/min) showed two peaks in the area ratio 11:89. The products were isolated by glc on column B (220°, 60 ml/min). The minor component was identified by its ir and NMR spectra as 2-acetoxy-1-methylnaphthalene. The major component had a carbonyl peak in its ir spectrum at 1665 cm^{-1}. Its NMR spectrum ($CDCl_3$) had peaks at τ 1.94–2.3 (m, 2 H), 2.43–2.73 (m, 2 H), 2.95 and 3.01 (two singlets, together 1 H), 3.55–4.20 (m, 2 H), 6.30–6.60 (m, 2 H), 7.46 and 7.51 (two singlets, together 3 H), and 7.66 (s, 3 H).

Hydrogenation of the Product of Acid-Catalyzed Rearrangement of Naphthalenone 14. The crude product obtained from acid-catalyzed rearrangement of naphthalenone **14** was hydrogenated and worked up as described for hydrogenation of the rearrangement product from **3**. The major product of the hydrogenation was isolated by GLC on column B (200°, 60 ml/min) and identified as 4-acetoxy-1-methyl-2-propylnaphthalene by comparison of its GLC retention times and ir and NMR spectra with those of the sample whose preparation is described below.

4′-Hydroxy-1′-methyl-2′-propionaphthone. A 1.2 M solution of ethyllithium in benzene (125 ml, 0.15 mol) was added slowly to a solution of 4-hydroxy-1-methyl-2-naphthoic acid[24] (6.1 g, 0.03 mol) in 250 ml of benzene. The reaction mixture was refluxed under nitrogen for 1 h and then poured onto a mixture of 200 g of ice and 30 ml of concentrated hydrochloric acid. After all the ice had melted, the organic layer was washed with water and aqueous sodium bicarbonate solution and then extracted with 15% potassium hydroxide solution. The basic extracts were acidified with hydrochloric acid to give a crystalline product, which was washed several times with methylene chloride and recrystallized from 50:50 benzene–methylene chloride to give 0.8 g (3.4 mmol, 11%) of 4′-hydroxy-1′-methyl-2′-propionaphthone, mp 170–172 °C. Its ir spectrum (Nujol) had peaks at 3350 and 1660 cm^{-1}. Its NMR spectrum (acetone-d_6) had peaks at 1.57–1.99 (m, 2 H), 2.35–2.54 (m, 2 H), 3.03 (s, 1 H), 7.13 (q, J = 6.6 Hz, 2 H), 7.45 (s, 3 H), and 8.85 (t, J = 6 Hz, 3 H).

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.47; H, 6.58. Found: C, 78.24; H, 6.42.

1-Methyl-2-propyl-4-naphthol (8). A solution of 4′-hydroxy-1′-methyl-2′-propionaphthone (0.65 g, 3.0 mmol) in 20 ml of ether was added to a mixture of anhydrous aluminum chloride (0.80 g, 6 mmol) and lithium aluminum hydride (0.25 g, 6 mmol) in 30 ml of anhydrous ether. The mixture was refluxed for 4 h and worked up as described for the preparation of **35** to give 0.60 g of yellow oil. GLC on column A (200°, 55 ml/min) showed two peaks with retention times of 2.8 and 4.0 min, in the area ratio 33:17. These products were isolated by GLC on column B. The minor component, which appeared to be an alcohol, was not further investigated. The major component had a peak in its ir spectrum at 3380 cm^{-1}. Its NMR spectrum had peaks at 1.95–2.36 (m, 2 H), 2.53–2.72 (m, 2 H), 3.41 (s, 1 H), 7.23 (t, J = 6 Hz, 2 H), 7.49 (s, 3 H), 8.14–8.54 (m, 2 H), and 8.98 (t, J = 6 Hz, 3 H).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.59; H, 8.38.

4-Acetoxy-1-methyl-2-propylnaphthalene (15). A solution of 1-methyl-2-propyl-4-naphthol (0.10 g), acetic anhydride (20 ml), and concentrated sulfuric acid (0.20 g) was stirred at room temperature for 4 h, then poured into water and extracted with methylene chloride. The organic layer was washed with water and with sodium bicarbonate solution and dried and the solvent evaporated to give 0.11 g of brown oil, which showed a single peak by GLC. An analytical sample was obtained by preparative GLC on column B (200°, 60 ml/min). Its ir spectrum had a carbonyl peak at 1665 cm^{-1}. Its NMR spectrum had peaks at τ 2.02–2.32 (m, 2 H), 2.53–2.77 (m, 2 H), 3.00 (s, 1 H), 7.31 (t, J = 6.6 Hz, 2 H), 7.53 (s, 3 H), 7.70 (s, 3 H), 8.20–8.75 (m, 2 H), 9.04 (t, J = 6.5 Hz, 3 H). Its mass spectrum had a peak at m/e 242 (M^+).

2-Acetoxy-1-methyl-4-propylnaphthalene. A solution of 1-methyl-4-propyl-2-naphthol (0.50 g) in 50 ml of acetic anhydride containing 1 ml of concentrated sulfuric acid was stirred at room temperature for 18 h. The reaction was worked up as described for the preparation of **15** to give essentially pure 2-acetoxy-1-methyl-4-propylnaphthalene (0.60 g) as a brown oil. Its is spectrum had a carbonyl peak at 1750 cm^{-1}. Its NMR spectrum had peaks at τ 1.84–2.16 (m, 2 H), 2.45–2.23 (m, 2 H), 3.07 (s, 1 H), 7.02 (t, J = 8 Hz, 2 H), 7.60 (s, 3 H), 7.74 (s, 3 H), 8.01–8.60 (m, 2 H) and 8.98 (t, J = 6.5 Hz, 3 H).

Rearrangement of 1-Benzyl-1-methyl-2-naphthalenone (22). (A) In Acetic Acid. 1-Benzyl-1-methyl-2-naphthalenone (0.90 g) was dissolved in 15 ml of 1 M sulfuric acid in acetic acid. The solution was allowed to stand at room temperature for 7 days and was then worked up as usual to give 1.0 g of brown oil. This was dissolved in methylene chloride and washed with 1% potassium hydroxide solution to extract 1-methyl-2-naphthol. The organic layer was washed with water and dried, and the solvent was evaporated to give 0.4 g of brown oil. GLC on column A (200°, 60 ml/min) showed peaks at 2.4, 3.9, 4.7, 6.5, 7.7, 9.8, and 11.8 min. These products could not be isolated or identified.

(B) Catalyzed by Boron Trifluoride. A solution of naphthalenone **22** (0.50 g) was dissolved in 10 ml of 20% boron trifluoride in ether, and allowed to stand at room temperature for 16 h. The mixture was worked up as usual to give 0.45 g of brown fluid. GLC on column A showed peaks at 1.7, 4.6, 6.1, and 11.6 min. These products could not be isolated or identified.

(C) In Acetic Anhydride. Naphthalenone **22** (2.5 g) was dissolved in 25 ml of 1 M sulfuric acid in acetic anhydride. The reaction mixture was stirred at room temperature for 4 days and was then worked up as usual to give 2.8 g of dark brown oil. GLC on column A (225°, 60 ml/min) showed peaks at 1.0 min (isolated and identified as 2-acetoxy-1-methylnaphthalene), 11.6, and 12.1 min. The two peaks at high retention times could not be separated by preparative GLC or column chromatography.

The reaction product was dissolved in 100 ml of a 5% solution of potassium hydroxide in 50% aqueous ethanol, and the solution refluxed for 1 h. It was acidified with hydrochloric acid and extracted with methylene chloride, and the solvent was evaporated to give 2.0 g of brown oil. GLC on column A showed peaks with retention times of 1.2 (1-methyl-2-naphthol), 14.1, and 14.9 min, in the area ratio of 3:5:1.3. The two high retention time components again could not be separated. The products were washed with 1% sodium hydroxide solution to extract 1-methyl-2-naphthol, and the insoluble portion (1.5 g) was dissolved in 50 ml of dimethyl sulfoxide. Potassium *tert*-butoxide (1.5 g) was added, the solution was stirred at room temperature for 10 min, and methyl iodide (7 ml) was added. After the mixture was stirred at room temperature for 2 h, water was added and the product extracted with methylene chloride. The organic fraction was washed with water and dried and the solvent evaporated to give 1.6 g of yellow oil. GLC on column A (210°, 55 ml/min) showed peaks with retention times of 8.8 and 10.1 min. Chromatography on Florisil (20 g) resulted in no separation of the two components. The lower retention time component was isolated by GLC on column B and identified as 4-benzyl-2-methoxy-1-methylnaphthalene by comparison of its spectra and retention time with those of the compound synthesized below. The second component could not be isolated in a pure form. The ir spectrum and VPC retention times of a 2:1 mixture of the components with higher and lower retention times were very similar to those of an appropriate mixture of 4-benzyl-2-methoxy-1-methylnaphthalene (**25b**) and 3-benzyl-2-methoxy-1-methylnaphthalene (**26**).

4-Benzyl-1-methyl-2-naphthol. 1-Acetoxy-1-methyl-2-naphthalenone[23] (1.5 g, 7.0 mmol) in 30 ml of ether was added to a solution of 0.02 mol of benzylmagnesium bromide in 30 ml of ether. The mixture was refluxed for 2 h and then poured into ammonium chloride solution. The organic layer was washed with dilute hydrochloric acid, water, and 1% sodium hydroxide solution. The neutral fraction was then extracted with Claisen alkali. The alkaline solution was acidified with 10% hydrochloric acid and extracted with methylene chloride. The organic layer was washed with water and dried and the solvent evaporated to give 0.60 g (2.4 mmol, 35%) of 4-benzyl-1-methyl-2-naphthol, mp 112–114 °C (from petroleum ether). Its ir spectrum had a hydroxy peak at 3400 cm^{-1}. Its NMR spectrum had peaks at τ 1.96–2.24 (m, 2 H), 2.45–2.85 (m, 7 H), 3.2 (s, 1 H), 5.65 (s, 2 H), and 7.51 (s, 3 H).

4-Benzyl-2-methoxy-1-methylnaphthalene (25b). 4-Benzyl-1-methyl-2-naphthol (0.60 g, 2.4 mmol) was dissolved in 20 ml of dimethyl sulfoxide, and potassium *tert*-butoxide (0.50 g, 4.5 mmol) was added. After the mixture was stirred at room temperature for 10 min, methyl iodide (5 ml) was added and stirring was continued for 2 h. The reaction was worked up as described for preparation of **36** to give 0.65 g of yellow fluid. GLC on column A (220°, 55 ml/min) showed one peak with a retention time of 11.8 min. An analytical sample was prepared by GLC on column B. The ir spectrum showed no OH or CO peaks. Its NMR spectrum had peaks at τ 2.03–2.25 (m, 2 H), 2.55–2.94 (m, 7 H), 3.06 (s, 1 H), 5.74 (s, 2 H), 6.35 (s, 3 H), and 7.55 (s, 3 H). Its mass spectrum had a peak at *m/e* 262 (M^+).

3-Benzyl-2-methoxy-1-methylnaphthalene (26). A solution of 2.2 N butyllithium in hexane (27 ml, 0.06 mol) was added to a solution of 3-bromo-2-methoxy-1-methylnaphthalene (5.1 g, 0.02 mol) in 100 ml of ether. The mixture was stirred under nitrogen for 2 h, then cooled, and benzyl bromide (10.3 g, 0.06 mol) in 20 ml of dry ether was added. After the mixture had stirred at room temperature for 15 h, the reaction was quenched with water, the organic fraction was dried, and the solvent was evaporated to give 4.6 g of yellow oil. GLC on column A (225°, 55 ml/min) showed peaks with retention times of 1.4 min (1-methyl-2-methoxynaphthalene) and 8.6 min. The peak with higher retention time was isolated by GLC on column D (230°, 65 ml/min). Its ir spectrum had no OH or CO peaks. Its NMR spectrum had peaks at τ 2.1–2.88 (m, 10 H), 5.92 (s, 2 H), 6.42 (s, 3 H), and 7.48 (s, 3 H). Its mass spectrum had a peak at *m/e* 262 (M^+).

Synthesis of 1-Naphthalenones. 1-Allyl-2-methyl-1-naphthalenone (16a). Sodium methoxide (1.4 g, 0.026 mol) was added to a solution of 2-methyl-1-naphthol (4.1 g, 0.026 mol) in 50 ml of dry benzene. The mixture was stirred for 15 minutes under an atmosphere of nitrogen, and allyl bromide (10 ml, 0.050 mol) was added. The mixture was stirred at room temperature for 24 h and then worked up as usual to give 3.1 g of brown oil. This was chromatographed on 60 g of activity III neutral alumina, eluting with petroleum ether. After initial elution of a mixture of **16a** and allyl 2-methyl-1-naphthyl ether, continued elution with a 95:5 mixture of petroleum ether–methylene chloride gave 1.4 g of 2-allyl-2-methyl-1-naphthalenone (0.007 mol, 27%) as a pale yellow oil. Its ir spectrum had carbonyl peaks at 1680 and 1650 cm^{-1}. Its NMR spectrum had peaks at τ 1.91–2.08 (m, 1 H), 2.50–2.94 (m, 3 H), 3.50 (d, J = 10 Hz, 1 H at C-4), 3.95 (d, J = 10 Hz, 1 H at C-3), 4.32–5.24 (m, 3 H), 7.20–8.01 (m, 2 H), and 8.8 (s, 3 H).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81, H, 7.12. Found: C, 84.92; H, 7.15.

2-(*trans*-2-Butenyl)-2-methyl-1-naphthalenone (16b) was prepared in 30% yield via a similar procedure. Its ir spectrum had a carbonyl peak at 1665 cm^{-1}. Its NMR spectrum had signals at τ 1.87–2.07 (m, 1 H), 2.50–2.94 (m, 3 H), 3.48 (d, J = 11 Hz, 1 H), 3.94 (d, J = 11 Hz, 1 H), 4.24–4.80 (m, 2 H), 7.29–8.0 (m, 2 H), 8.51 (d, J = 6 Hz, 3 H), and 8.81 (s, 3 H).

2-Benzyl-2-methyl-1-naphthalenone (21) was prepared as a yellow oil in 54% yield following a procedure similar to those used for the preparation of **16a** and **16b**. Its ir spectrum had a carbonyl peak at 1660 cm^{-1}. Its NMR spectrum had peaks at τ 1.95–2.13 (m, 1 H), 2.60–3.10 (m, 9 H), a pair of doublets at 3.56 and 3.98 (J = 10 Hz, 2 H), a pair of doublets at 6.86 and 7.28 (J = 12 Hz, 2 H), and 8.74 (s, 3 H).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.94. Found: C, 87.04; H, 6.49.

Rearrangements of 1-Naphthalenones. Rearrangement of 2-Allyl-2-methyl-1-naphthalenone. (A) In Acid. A solution of 2-allyl-2-methyl-1-naphthalenone (0.40 g) in 6 ml of 3 M sulfuric acid in acetic acid was kept at room temperature for 45 h, and then worked up as usual to give 0.35 g of brown oil. GLC on column A (175°, 55 ml/min) showed two peaks with retention times of 8.6 and 6.4 min, in the area ratio 77:14. The major component was isolated by GLC on column B (175°, 60 ml/min) and identified as 4-allyl-2-methyl-1-naphthol (**17a**). Its ir spectrum had a strong OH peak at 3400 cm^{-1}. Its NMR spectrum had signals at τ 1.83–1.99 (m, 1 H), 2.10–2.30 (m, 1 H), 2.58–2.80 (m, 2 H), 3.08 (m, 1 H), 3.62–5.20 (m, 4 H), 6.39 (d, J = 6 Hz, 2 H), and 7.78 (s, 3 H). The spectra of the crude rearrangement product were essentially identical with those of pure **17a**. When a sample of pure **17a** (iso-

lated by GLC) was reinjected onto column A (through an injector port at 225°) it again showed two peaks at 8.6 and 6.4 min, in an area ratio identical with that of the crude product. The component with retention time of 6.4 min was therefore considered to result from reaction of **17a** in the chromatograph, and its structure was not further investigated.

(B) Thermal Rearrangement. A solution of 2-allyl-2-methyl-1-naphthalenone (0.20 g) in 0.5 ml of *N,N*-dimethylaniline was heated at 150° in a sealed tube for 24 h. The cooled solution was poured into 50 ml of 10% hydrochloric acid solution and the mixture extracted with methylene chloride. The organic layer was dried over magnesium sulfate and the solvent evaporated to give 0.20 g of brown oil. GLC on column A (175°, 55 ml/min) showed a single peak with a retention time of 8.5 min and a minor peak with a retention time of 6.4 min. The major component was isolated by GLC. Its ir and NMR spectra were identical with those of 4-allyl-2-methyl-1-naphthol.

Rearrangement of 2-(*trans*-2-Butenyl)-2-methyl-1-naphthalenone (16b). (A) In Acid. A solution of naphthalenone **16b** (0.30 g) in 6 ml of 0.1 M sulfuric acid in acetic acid was kept at room temperature for 5 h. It was then worked up as usual to give 0.25 g of brown oil. GLC on column A (175°, 55 ml/min) showed peaks with retention times of 1.0 (2-methyl-1-naphthol), 3.4, and 4.0 min, in the area ratios 6:3:64. The component with the highest retention time was isolated by GLC on column B (180°, 60 ml/min) and identified as 4-(1-methylallyl)-2-methyl-1-naphthol (**17b**). Its ir spectrum had a strong hydroxy peak at 3400 cm^{-1}. Its NMR spectrum had peaks at τ 1.74–2.20 (m, 2 H), 2.54–2.81 (m, 2 H), 2.96 (s, 1 H), 3.58–5.17 (m, 4 H), 5.75–6.05 (m, 1 H), 7.66 (s, 3 H), and 8.56 (d, J = 8 Hz, 3 H). Its mass spectrum had a peak at *m/e* 212 (M^+).

When the rearrangement was carried out for longer periods, the yield of 2-methyl-1-naphthol increased, indicating that **17b** cleaves on prolonged contact with acid.

(B) Thermal Rearrangement. A solution of naphthalenone **16b** (0.2 g) in 0.5 ml of *N,N*-dimethylaniline was heated in a sealed tube for 2 h at 190°. It was worked up as described for the rearrangement of **16a** to give a brown fluid. GLC on column A (175°, 55 ml/min) showed three peaks with retention times of 1.2 (2-methyl-1-naphthol), 3.1, and 4.2 min, in the area ratios 38:12:50. The spectra of the major component were identical with those of naphthol **17b**.

Rearrangement of 2-Benzyl-2-methyl-1-naphthalenone (21). (A) In Acetic Anhydride. A solution of naphthalenone **21** (0.50 g) in 10 ml of 1 M sulfuric acid in acetic anhydride was stirred at room temperature for 22 h. It was then worked up as usual to give 0.6 g of brown oil. GLC on column A (210°, 55 ml/min) showed peaks with retention times of 1.3, 6.8, 8.7, and 9.2 min, in the area ratios 7:4:72:14. The products were isolated by GLC on column B (240°, 65 ml/min) and identified as (in order of increasing retention time) 1-acetoxy-2-methylnaphthalene, naphthalenone **21**, 1-acetoxy-4-benzyl-2-methylnaphthalene, and a product of undetermined structure.

(B) Catalyzed by Boron Trifluoride. Naphthalenone **21** (0.50 g) was dissolved in 10 ml of a solution of boron trifluoride in ether. The mixture was kept at room temperature for 18 h and worked up as usual to give 0.5 g of brown oil. GLC on column A (210°, 60 ml/min) showed peaks at 1.0 (2-methyl-1-naphthol), 8.6, and 9.0 min, in the area ratios 4:82:14. The major component was isolated by GLC on column B (230°, 65 ml/min) and identified as 4-benzyl-2-methyl-1-naphthol by comparison of its ir and NMR spectra and GLPC retention times with those of the sample prepared as described below.

4-Benzoyl-1-methoxy-2-methylnaphthalene. Aluminum chloride (4.6 g, 0.035 mol) was added in small portions to a solution of benzoyl chloride (4.8 g, 0.035 mol) and 1-methoxy-2-methylnaphthalene[25] (5.1 g, 0.03 mol) in 40 ml of nitrobenzene. After the aluminum chloride was added, the mixture was warmed to room temperature and stirred overnight. Water was added, and the organic layer was dried over magnesium sulfate. The nitrobenzene was distilled off under vacuum to give 7.6 g of dark brown fluid which was chromatographed on 100 g of Florisil to give 6.8 g of 4-benzoyl-1-methoxy-2-methylnaphthalene (0.024 mol, 80%) as a yellow oil. Its ir spectrum had a carbonyl peak at 1650 cm^{-1}. Its NMR spectrum had peaks at τ 1.76–1.96 (m, 2 H), 2.07–2.24 (m, 2 H), 2.50–2.56 (m, 5 H), 2.61 (s, 1 H), 6.07 (s, 3 H), and 7.57 (s, 3 H).

4-Benzyl-1-methoxy-2-methylnaphthalene. Anhydrous aluminum chloride (1.4 g, 0.10 mol) in 10 ml of ether was added to a suspension of lithium aluminum hydride (0.40 g, 0.105 mol) in 20 ml of ether. The mixture was stirred under nitrogen at room temperature for 5 min and a solution of 4-benzoyl-1-methoxy-2-methylnaphthalene (2.8 g, 0.01 mol) in ether was added. The mixture was refluxed overnight and cooled to room temperature; water was added. Dilute sulfuric acid was then added, the layers were separated, and the organic layer was washed with water and dried and the solvent evaporated to give 2.2 g of brown oil. The product was chromatographed on 40 g of Florisil. Elution with petroleum ether gave 0.50 g of 4-benzyl-1-methoxy-2-methylnaphthalene (0.007 mol, 21%) as a pale yellow oil. Its is spectrum had no carbonyl or hydroxy peaks. Its NMR spectrum ($CDCl_3$) had peaks at τ 1.65–2.25 (m, 2 H), 2.6–2.84 (m, 2 H), 2.94 (s, 5 H), 3.0 (s, 1 H), 5.78 (s, 2 H), 6.26 (s, 3 H), and 7.74 (s, 3 H).

4-Benzyl-2-methyl-1-naphthol (24). A solution of 4-benzyl-1-methoxy-2-methylnaphthalene (0.26 g, 1.0 mmol) and 7 ml of 40% aqueous hydrobromic acid in 50 ml of acetic acid was refluxed for 16 h. It was cooled, water was added, and the mixture was extracted with methylene chloride. The organic layer was washed with water and sodium bicarbonate solution and dried, and the solvent was evaporated to give 0.2 g of brown oil. The product was dissolved in methylene chloride and the solution extracted with Claisen alkali. The alkaline layer was acidified and extracted with methylene chloride, the organic layer was washed with water and dried, and the solvent was evaporated to give 0.15 g of 4-benzyl-2-methyl-1-naphthol (0.64 mmol, 64%) as a brown oil. Its ir spectrum had a hydroxy peak at 3450 cm^{-1}. Its NMR spectrum ($CDCl_3$) had peaks at τ 1.71–2.30 (m, 2 H), 2.4–2.9 (m, 7 H), 2.98 (s, 1 H), 4.2 (broad s, 1 H), 5.68 (s, 2 H), and 7.7 (s, 3 H).

1-Acetoxy-4-benzyl-2-methylnaphthalene (23). A solution of naphthol **24** (0.10 g, 0.41 mmol) in 10 ml of acetic anhydride containing 5 drops of concentrated sulfuric acid was stirred at room temperature for 4 h and worked up as described for the preparation of **15** to give 0.10 g of 1-acetoxy-4-benzyl-2-methylnaphthalene as a brown oil. An analytical sample was collected by GLC on column B (240°, 65 ml/min). Its ir spectrum had a carbonyl peak at 1760 cm^{-1}. Its NMR spectrum had peaks at τ 2.05–2.22 (m, 2 H), 2.41–2.92 (m, 8 H), 5.71 (s, 2 H), 7.59 (s, 3 H), and 7.71 (s, 3 H). Its mass spectrum had a peak at *m/e* 290 (M^+).

4-Allyl-4-methyl-1-naphthalenone (18). Following the general procedure of Hansen et al.,[15] a suspension of 4-methyl-1-naphthol[26] (4.0 g, 0.025 mol) and potassium hydroxide (1.45 g, 0.025 mol) in 25 ml of water and 10 g of glycerol was stirred very rapidly for 10 min until a clear solution was obtained. Allyl bromide (3.1 g, 0.025 mol) was added and the mixture was stirred rapidly at room temperature for 4 h. The mixture was extracted with methylene chloride. The organic layer was washed with Claisen alkali and then with water and dried; the solvent was evaporated to give 1.9 g of brown fluid. The product was chromatographed on 50 g of activity III neutral alumina. Elution with a 90:10 mixture of petroleum ether–methylene chloride gave 1.4 g of 4-allyl-4-methyl-1-naphthalenone (7.0 mmol, 28%) as a colorless oil. Its ir spectrum had a carbonyl peak at 1665 cm^{-1}. Its NMR spectrum had signals at τ 1.72–1.92 (m, 1 H), 2.45–2.78 (m, 3 H), 3.20 (d, J = 8.5 Hz, 1 H), 3.60 (d, J = 8.5 Hz, 1 H), 4.27–5.37 (m, 3 H), 7.18–7.77 (m, 2 H), and 8.58 (s, 3 H).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.56; H, 7.33.

Rearrangement of 4-Allyl-4-methyl-1-naphthalenone. (A) In Acid. A solution of naphthalenone **18** (0.40 g) in 6 ml of 0.3 M sulfuric acid in acetic acid was allowed to stand at room temperature for 10 h and then worked up as usual to give 0.26 g of brown oil, whose ir and NMR spectra were identical with those of 4-allyl-4-methyl-1-naphthol prepared from the thermal rearrangement of **18**.

(B) Thermal Rearrangement at 175°. A solution of naphthalenone **18** (0.20 g) in 0.5 ml of *N,N*-dimethylaniline was heated at 175° in a sealed tube for 7 h and then worked up as described for the thermal rearrangement of **16a**. GLC on column A (175°, 55 ml/min) showed a single peak with a retention time of 4.1 min. An analytical sample was isolated by GLC on column B (200°, 65 ml/min). Its ir spectrum had no carbonyl or hydroxy peaks. Its NMR spectrum had peaks at τ 2.0–2.26 (m, 2 H), 2.52–2.70 (m, 2 H), 2.99 (s, 1 H), 4.90–5.20 (m, 1 H), 6.58–7.22 (m, 2 H), 7.51 (s, 3 H), 8.53 (d, J = 5 Hz, 3 H). Its mass spectrum had a peak at

m/e 198 (M^+). It was assigned the structure 2,5-dimethylnaphthol[1,2-*b*]2,3-dihydrofuran.

(C) Thermal Rearrangement at 145°. A solution of naphthalenone **18** (0.20 g) in 5 ml of *N,N*-dimethylaniline was heated at 145° in a sealed tube for 2 h and worked up as usual to give 0.15 g of 2-allyl-4-methyl-1-naphthol as a brown oil. Its ir spectrum had a hydroxy peak at 3550 cm^{-1}. Its NMR spectrum had peaks at τ 1.78–2.00 (m, 1 H), 2.12–2.38 (m, 1 H), 2.55–2.82 (m, 2 H), 3.13 (s, 1 H), 3.67–5.25 (m, 4 H), 6.60 (d, J = 6 Hz, 2 H), and 7.52 (s, 3 H).

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Vinylic Cations from Solvolysis. XXIII.[1] Degenerate β-Anisyl Rearrangement during the Solvolysis of 2-Anisyl-1,2-diphenylvinyl Bromides. Free Ions as Intermediates

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Abstract: The solvolysis of *trans*-2-anisyl-2-pentadeuteriophenyl-1-phenylvinyl bromide (**6***-Br) in 60% EtOH, 80% EtOH, and TFE buffered by 2,6-lutidine and in AcOH–AgOAc is accompanied by an extensive (>85%) degenerate β-anisyl rearrangement. A 7:3 mixture of the cis and trans isomers and pure **6***-Br give the same extent of rearrangement in 60% EtOH, suggesting that the rearrangement proceeds via the free vinyl cation **13***. The migratory aptitudes of anisyl and phenyl groups in the vinylic system are normal, and rearrangement ratios $k_{r(An)}/k_{r(Ph)}$ of 76–120 were obtained from the internal competition in the ion **13*** or by comparison with the migration in the triphenylvinyl cation. The migration origin, the migration terminus, and the bridged transition state for the migration are stabilized better by anisyl than by phenyl group. The degenerate migration is not an important contributor to the selectivity of the ion **13***. The use of mass spectral and NMR analyses for determining the extent of the degenerate rearrangement is discussed.

Several processes which accompany the heterolytic ionization of triarylvinyl halides were recently studied. These include external ion return and ion pair return with isomerization to the geometrical isomer,[2] capture of the ion by the solvent or by other nucleophiles,[2,3] and β-aryl rearrangement across the double bond of the intermediate cation to form a more stable triarylvinyl cation.[4] When we began our work we were interested as to whether degenerate rearrangements also occur in these systems. Meanwhile, degenerate β-anisyl and β-phenyl rearrangement in triarylvinyl cations were observed.[5,6]

Eight β-aryl rearrangements are possible in the ion **1**, when Ar^1, Ar^2, and Ar^3 are all possible combinations of phenyl and anisyl groups (eq 1). Two of these, phenyl rearrangement when Ar^1 = An, Ar^2 = Ar^3 = Ph and the anisyl rearrangement when Ar^1 = Ar^2 = An, Ar^3 = Ph, were not

$$Ar^3Ar^2C{=}\overset{+}{C}{-}Ar^1 \longrightarrow \underset{1}{} \quad Ar^2{-}\overset{+}{C}{=}CAr^3Ar^1 \text{ or } Ar^3{-}\overset{+}{C}{=}CAr^2Ar^1 \qquad (1)$$

observed since they lead to a less stable α-arylvinyl cation than the precursor ion. Two rearrangements which lead from an α-phenyl to an α-anisylvinyl cation were observed. In the solvolysis of the bromide **2** via ion **3**, both the product ion **4** and the transition state for the rearrangement are stabilized by anisyl groups and only rearranged products were formed[4] (eq 2). β-Phenyl rearrangement during the solvolysis of *cis*- and *trans*-2-anisyl-1,2-diphenylvinyl bromides

$$\underset{2}{An_2C{=}C(Br)Ph} \longrightarrow \underset{3}{An_2C{=}\overset{+}{C}{-}Ph} \longrightarrow \underset{4}{An{-}\overset{+}{C}{=}C(Ph)An} \qquad (2)$$