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Rearrangements of Allyl-Substituted Naphthalenones with Oxygen at the Migration Origin[1]

Bernard Miller* and Whei-Oh Lin

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

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Replacement of alkyl substituents at quaternary carbons of β-naphthalenones by methoxy or acetoxy groups significantly changes the reactions of these molecules. Thermal migration of an allyl group proceeds by a 3,4 shift, rather than the expected 3,3 shift, when a methoxy group is at the migration origin. Acid-catalyzed migration of the allyl group proceeds by the expected 3,4 path, although at a rate which is accelerated by the presence of the methoxy substituent. Migration of a crotyl group in the methoxy-substituted naphthalenone also proceeds solely by 3,4 shifts in acetic acid or acetic anhydride, with no evidence for the 1,5 or 1,4 shifts observed in the absence of a methoxy substituent. The presence of an acetoxy substituent at C-1 invariably leads to reduction, rather than rearrangement of a β-naphthalenone. Rationales are offered to explain the effects of methoxy groups at C-1 on the reactions of β-naphthalenones.

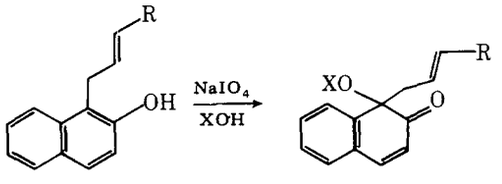
Miller and Saidi have shown that migrations of allyl groups in acid-catalyzed rearrangements of α- and β-naphthalenones can proceed by 1,2, 1,3, 1,4, 1,5, 3,3, or 3,4 shifts. The choice of routes in each reaction depends on the nature of the migrating group and of the solvent.[2,3]

Up to this time, there have been no investigations of the effects of substituents at the migration origins on the nature and rates of migrations of allyl groups in naphthalenones. Alkoxy and hydroxy groups, in particular, would be expected to have marked effects on the course of rearrangement since they can significantly stabilize the carbonium ions formed by allyl migration.

The syntheses of naphthalenones bearing allyl groups and oxygen atoms on the quaternary carbons have not been reported, and few examples are known of cyclohexadienones with this type of substitution.[4]

In this paper we report the syntheses and rearrangements of α- and β-naphthalenones bearing methoxy and allyl groups at the quaternary carbons.

Syntheses. Attempts to oxidize **1** and **2** to **3a** and **4a** were unsuccessful (see Experimental Section) as were attempts to hydrolyze the acetates, **3c** and **4c,** despite reported success in analogous cases.[5] However, sodium periodate oxidation of **1** and **2** in 1:1 water–methanol solutions gave **3b** and **4b** in 13 and 10% yields, respectively.

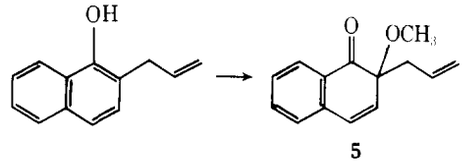


1, R = H
2, R = CH_3

3a, R = H; X = H
b, R = H; X = CH_3
c, R = H; X = C(=O)CH_3

4a, R = CH_3; X = H
b, R = CH_3; X = CH_3
c, R = CH_3; X = C(=O)CH_3

Oxidation of 2-allyl-1-naphthol gave naphthalenone **5** in



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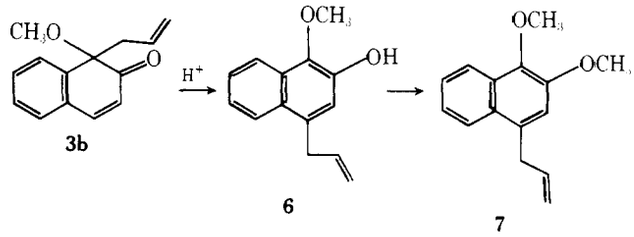
0.53% yield. The low yield is not surprising since a free para position in the naphthol is available for oxidation.

Rearrangements. Rearrangement of **3b** in a 1% solution of sulfuric acid in acetic acid at room temperature gave a single product, which was a phenol isomeric with **3b.** The same phenol was obtained by thermal rearrangement of **3b** in refluxing *N,N*-dimethylaniline for 24–48 h. The infrared and NMR spectra of the product were consistent with those expected of the formal 1,4 or 3,4 migration product **6.** The assignment of structure **6** to this phenol was confirmed by its



3b **6** **7**

methylation to **7,** which was identical with the diether formed by methylation of **7a,** obtained by thermal or acid-catalyzed

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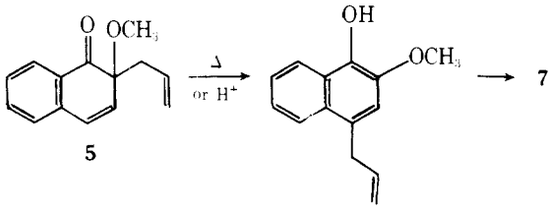
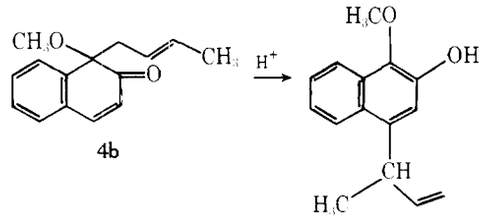
rearrangement of the naphthoquinol ether **5**. Formation of **7a** from **5** via a 3,3 shift, of course, has ample precedent.[2,6]



5 **7a**

Since formation of **6** from **3b** might have proceeded either by 3,4 or 1,4 shifts, the partially deuterated derivative **3b**-d_2 was synthesized as shown in Scheme I. Its NMR spectrum showed the presence of 0.70 ± 0.05 atom of residual hydrogen at the terminal vinyl positions. Acid-catalyzed rearrangement of **3b**-d_2 gave **6** with 0.62 ± 0.09 atom of hydrogen at the allylic methylene group. Similarly, the thermal rearrangement of **3b**-d_2 was shown to proceed with inversion of the allyl group. Within experimental error, therefore, the formation of **6** proceeded entirely by 3,4 migration with inversion of the allyl group.

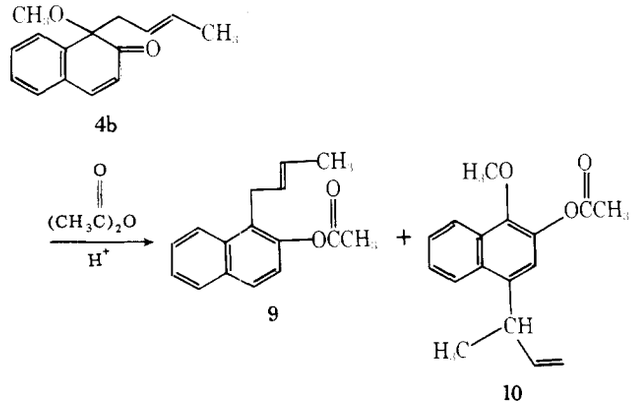
Rearrangement of naphthalenone **4b** in a solution of sulfuric



4b **8**

acid in acetic acid similarly proceeded with inversion of the crotyl group to give naphthol **8** as the only product. The structure of **8** was demonstrated by its NMR spectrum, which showed the presence of the 1-methylallyl group and had a one-proton singlet at δ 7.05 characteristic of a proton in a β position on the substituted ring.[2]

While rearrangement of 1-allyl-1-methyl-2-naphthalenone in acetic anhydride gave only the product of 1,4 crotyl migration,[2] rearrangement of **4b** in acetic anhydride catalyzed by sulfuric acid gave no evidence for 1,4 migration. Instead, two products were obtained in approximately a 1:1 molar ratio. The lower molecular weight component was the reduction product **9**, which was independently prepared by acetylation of naphthol **2**. It seems probable that the reducing agent in the formation of **9** was the enol of acetic anhydride. If that is so,

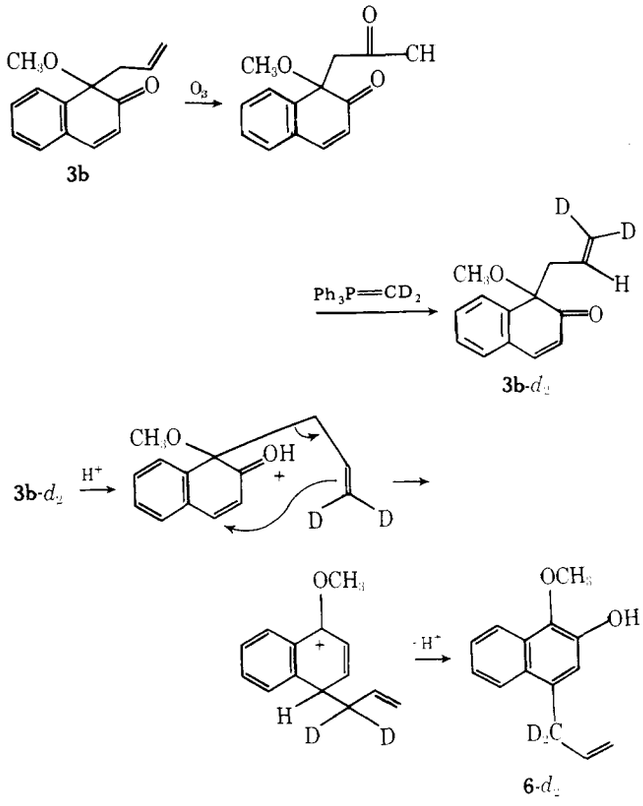


4b **9** **10**

the reduction of **4b** in the presence of acetic anhydride, but not of acetic acid, can be accounted for by the more ready enolization of the anhydride.

The second product from rearrangement of **4b** in acetic

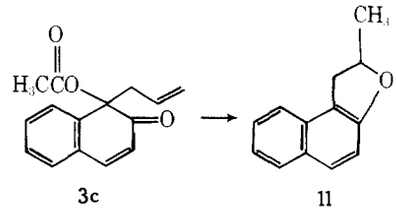
Scheme I



anhydride was the 3,4 rearrangement product **10**, which was identified by its spectrum and by independent synthesis by acetylation of **8**.

Attempted thermal rearrangement of **4b** in refluxing *N*,*N*-dimethylaniline also gave about 10% of the reduction product **2**, but the principal product was identified as 1-methoxy-2-naphthol, resulting from loss of a crotyl group from **4b**. To see whether loss of a crotyl group was catalyzed by *N*,*N*-dimethylaniline, **4b** was heated at 175 °C for 12 h in the absence of any solvent. 1-Methoxy-2-naphthol was the sole product isolated, but this reaction gave a good deal of tarry material which could not be identified.

Attempted rearrangement of the naphthoquinol acetate **3c** in 10% sulfuric acid in acetic acid at room temperature for 4 days, or in boron trifluoride etherate for 1 week, gave the cyclized reduction product, dihydronaphthofuran **11**,[8] as the only product. Similarly, attempted thermal rearrangement at 150 °C for 3 days in the absence of solvent gave **11** and recovered **3c**.



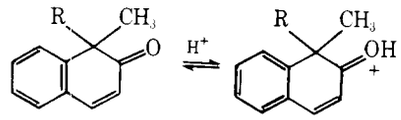
3c **11**

Effects of Methoxy Groups at C-1 on Rearrangement Rates of β-Naphthalenones. 3,4 Migrations of allyl groups in acid-catalyzed rearrangements of **3b** and **4b** must generate positive charges at C-1. These rearrangements would therefore be expected to proceed extremely rapidly compared to those of analogues lacking methoxy groups at C-1 since formation of β-alkoxy carbonium ions has been observed to proceed ca. 10^9–10^{14} times as rapidly as formation of analogous ions lacking stabilization by oxygen functions.[9] However, a kinetic study showed that rearrangement of **3b** in a 0.3 M solution of

sulfuric acid in acetic acid was only 2.8 times as fast as rearrangement of **12c** (Table I).

The apparently small effect of the methoxy group on the rate of rearrangement of **3b,** however, might be due to its efficacy in reducing the basicity of the carbonyl oxygen toward protonation prior to migration.[10] The actual effect of the methoxy group on the rate of the migration step could only be determined therefore if the relative basicities of **3b** and **12c** were known.

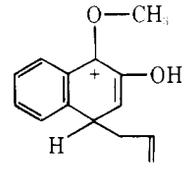
It proved impossible to measure those basicities since **12c** and **3b** rearrange rapidly even in acids too weak to allow detection of their protonated forms. Naphthalenones **12a** and



12a, R = CH_3
b, R = OCH_3
c, R = $CH_2CH{=}CH_2$

12b were therefore employed as models to determine the effects of methoxy substituents on the basicities of β-naphthalenones. The H_0 value for half protonation of **12a** was determined by the procedure of Vitullo and Logue[11] to be −5.56 and that of **12b** to be −7.23. Thus, substitution of a methoxy group for a methyl group at C-1 reduced the basicity of **12b** by a factor of 47 compared to **12a.** While the absolute basicities of **12c** and **3b** would be different from (and presumably slightly smaller than) those of **12a** and **12b,** it can safely be assumed that the ratio of their basicities would be very similar to the ratio of the basicities of these models. By combining the ratio of their basicities with the relative rates of rearrangement of **12c** and **3b,** it can be concluded that protonated **3b** rearranges approximately 10^2 times as rapidly as protonated **12c.**

Although formation of an α-methoxy carbonium ion by rearrangement of protonated **3b** is thus, as expected, faster than formation of the corresponding ion from protonated **12c,** the rate factor of 10^2 is not particularly impressive. In contrast, substitution of a methoxy group for an ethyl group on solvolysis of propyl chloride in ethanol increases its rate of solvolysis by a factor of ca. 10^{13}.[12] The relatively small effect of the methoxy group on the rate of rearrangement of protonated **3b** may be due, in part, to the leveling effects of the coplanar aromatic ring and double bond in carbonium ion **13,** which



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should reduce the "electron demand" on the methoxy group compared to solvolysis of a primary alkyl halide. The relatively small rate increase due to the methoxy group might also reflect some difficulty in achieving coplanarity between the methoxy group and the ring in formation of ion **13.** Unfortunately, it does not seem possible to decide whether these factors are entirely responsible for the small rate enhancement due to the methoxy group or whether this effect also indicates that a rather small charge resides on C-1 in the transition state leading to **13.**

Discussion

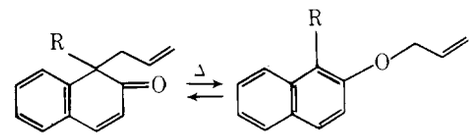
As expected, alkoxy and acetoxy groups on the quaternary carbons do indeed significantly affect the nature (as well as the rates) of the reactions of allyl-substituted naphthalenones. For instance, they afford reduction pathways which can compete with the thermal and acid-catalyzed rearrangement pathways available to other naphthalenones. This is particularly true of the naphthoquinol acetate **3c,** which is a better oxidizing agent than its methoxy-substituted analogues.

Table I. Rates of 3,4 Allyl Migrations of Naphthalenones in 0.3 M H_2SO_4 in HOAC[a]

naphthalenone	k, min^{-1}	$t_{1/2}$, min
3b	21.5 ± 0.35	322
12c	7.78 ± 0.02	891

[a] T = 29.6 ± 0.5 °C.

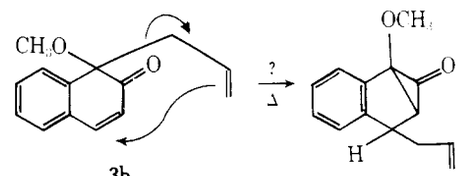
A more surprising change is the fact that **3b** undergoes a novel thermal 3,4 allyl shift to form **6.** In contrast, naphthalenone **12c,**[13a] as well as 1,1-diallyl-2-naphthalenone,[13b] simply equilibrates with the corresponding allyl



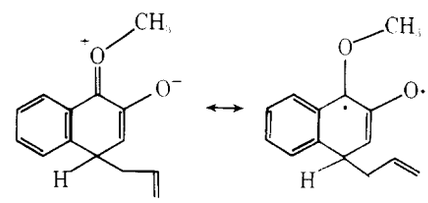
R = CH_3, $CH_2CH{=}CH_2$

naphthyl esters via reverse Claisen rearrangements on heating, with no evidence for any 3,4 shifts even after prolonged heating at 175 °C.

Unlike reverse Claisen rearrangements of 1-allyl-2-naphthalenones, which can lead directly to stable products, thermal 3,4 shifts in these molecules must proceed by means of at least one high energy intermediate. This intermediate might conceivably be a cyclopropane (**14a**) or its "open" form, which can be written as a dipolar ion (**14b**) or a singlet dirad-



3b **14a**

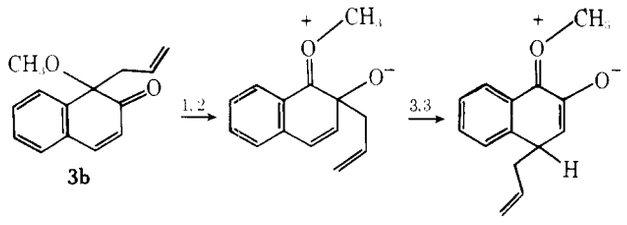


14b **14c**

ical (**14c**). A dipolar ion would clearly be significantly stabilized by the presence of a methoxy group at C-1. A diradical would also be stabilized by the methoxy group, although stabilization would presumably be smaller than for a dipolar structure since a hydroxy group stabilizes a primary radical by ca. 6 kcal/mol and a secondary radical by ca. 4 kcal/mol compared to an alkyl group.[4] It is easy to see why no 3,4 allyl shifts to form **14b** or **14c** would occur in the absence of stabilization by a methoxy group. In contrast, it is difficult to see why formation of a cyclopropanone should be significantly favored by the presence of a methoxy group rather than a methyl group at C-1 of the naphthalenone.

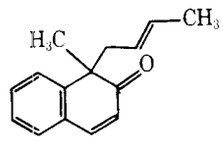
We therefore suggest that the intermediate in the thermal rearrangement of **3b** is an open form (presumably best formulated as **14b** rather than **14c**) and that the transition state leading to this intermediate is markedly stabilized by the presence of the methoxy group at C-1.

Formation of **14b** could proceed by consecutive 1,2 and 3,3 shifts of the allyl group in **3b** (eq 1). We see no way to distinguish between this path and a single step migration.



3b **14b** (1)

The acid-catalyzed rearrangements of **4b** are also affected by the presence of the methoxy group at C-1. Whereas **15** gives



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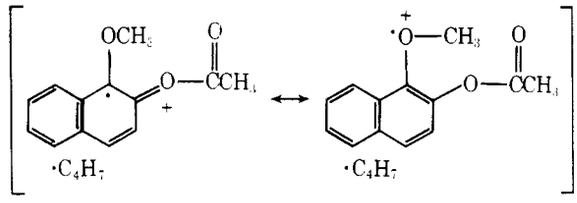
a mixture of 3,4 and 1,5 rearrangement products,[2] **4b** not unexpectedly gives solely a 3,4 migration product on rearrangement in acetic acid. Rearrangement of **4b** in acetic anhydride solution proceeds solely by a 3,4 shift of the crotyl group, while under the same conditions naphthalenone **15**, lacking a methoxy group at C-1, gives exclusively the product of a 1,4 crotyl shift. Miller and Saidi[2] have suggested that the occurrence of the "forbidden" 1,4 crotyl migration in rearrangement of **15** may be accounted for by the large difference in polarity between the acylated cyclohexadienone ring and the migrating crotyl group. Apparently minor changes, such as replacement of the acyl group on oxygen by a proton or a crotyl group by an allyl, were sufficient to eliminate rearrangement by the forbidden path, presumably by reducing the polarity differences between the migration framework and the migrating group. We can explain the effect of a methoxy group at C-1 in preventing a 3,4 shift by a similar argument. If, following Epiotis' reasoning,[15] we consider the transition state (**16**) for the 1,4 shift to be formed by combination of a



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crotyl radical and an acylated naphthalenone radical, the electron-donating effect of the methoxy group should reduce the electron affinity of the "acceptor" radical. By thus reducing the difference in polarity between the two segments of the transition state (and increasing the difference in energy between the acceptor LUMO and the donor HOMO), the methoxy group apparently increases the "forbiddeness" of the 1,4 shift and only the allowed 3,4 migration is observed.

Experimental Section

IR spectra were taken on a Beckman IR10 spectrometer or on a Perkin-Elmer Model 727 infrared spectrometer. NMR spectra were recorded on a Varian Associates A60 spectrometer or on a Perkin-Elmer Model R12-A spectrometer, employing tetramethylsilane (Me_4Si) as an internal standard in carbon tetrachloride solution unless otherwise noted. VPC analyses were carried out on a Varian Aerograph Model 202C chromatograph using a 6 ft × 0.25 in. 5% SE-30 column. Column temperature and carrier gas flow rate are described in parentheses. Melting points were recorded on a Mel-temp laboratory device without correction. Analyses were carried out by the Microanalytical Laboratory, University of Massachusetts, Amherst, Mass.

The general workup procedure was to wash organic solutions with water (and with sodium bicarbonate solution if the solution was acidic) and then dry over anhydrous magnesium sulfate, filter, and remove the solvent under vacuum.

Synthesis of 1-Allyl-1-methoxy-2-naphthalenone (3b). 1-Allyl-2-naphthol (4.5 g, 0.0244 mol) was dissolved in 50 mL of methanol, and a solution of sodium periodate (10.5 g, 0.0488 mol) in 50 mL of water was added drop by drop. The mixture was stirred at room temperature for 3 days. Some white precipitate formed during the stirring. At the end of the reaction, ethylene glycol (8 mL) was added to destroy the excess sodium periodate, 100 mL of water was added, and the mixture was stirred for 30 min more and then extracted with methylene chloride. The organic solution was worked up to give 4.2 g of crude product which was chromatographed on 60 g of Florisil, eluting with a 10% methylene chloride–90% petroleum ether mixture. **1-Allyl-1-methoxy-2-naphthalenone** (0.70 g, 3.3 mmol, 14%) was obtained as a yellow oil. Its IR spectrum showed a carbonyl peak at 1670 cm^{-1}. Its NMR spectrum showed two multiplets between δ 7.24–7.61 (5 H) and 4.63–5.30 (3 H), doublets at δ 6.13 (1 H, J = 10 Hz) and 2.56 (2 H, J = 7 Hz), and a sharp singlet at δ 3.03 (3 H). Anal. ($C_{14}H_{14}O_2$) C,H.

Synthesis of 1-Allyl-1-acetoxy-2-naphthalenone (3c). 1-Allyl-2-naphthol (4.5 g, 0.0244 mol) was dissolved in 60 mL of glacial acetic acid and the solution heated in an oil bath at 74 °C. Lead tetroxide (Pb_3O_4; 18.4 g, 0.0269 mol) was added, and the mixture was stirred at 74 °C for 30 minutes to give a brown solution which was cooled and neutralized with dilute sodium hydroxide solution. Some white precipitate formed during neutralization and was filtered out. The solution was extracted with three 30-mL portions of ether. The organic extracts were combined and worked up to give 5.5 g of dark oil which was chromatographed on 50 g of neutral alumina, eluting with petroleum ether. **1-Allyl-1-acetoxy-2-naphthalenone** (4.40 g, 18.2 mmol, 75%) was obtained as a yellowish liquid. Its IR spectrum showed carbonyl peaks at 1740 and 1670 cm^{-1}. Its NMR spectrum showed multiplets between δ 7.13—7.50 (5 H) and 4.88–5.30 (3 H), doublets at δ 6.16 (1 H, J = 10 Hz) and 2.68 (2 H, J = 6.8 Hz), and a singlet at δ 2.09 (3 H). Anal. ($C_{15}H_{14}O_3$) C,H.

Synthesis of 1-(3,3-Dideuterioallyl)-1-methoxy-2-naphthalenone 3b-d_2. Naphthalenone **3b** (5.61 g, 0.026 mol) was dissolved in 200 mL of methylene chloride, and the solution was cooled in a dry ice–acetone bath. Ozone was generated and passed into the solution for 1 h at the rate of 0.4 L/min. The solution was warmed to room temperature, 50 mL of 10% aqueous sodium sulfite solution was added, and the mixture was stirred for 1 h. The organic portion was separated and worked up to give 5.21 g of yellowish product. This product was not further purified. Its IR spectrum showed the presence of two carbonyl absorptions at 1720 and 1670 cm^{-1}. Its NMR spectrum showed the absence of vinyl protons and the presence of an aldehyde proton at δ 9.7.

n-Butyllithium (18 mL, 2.15 M in hexane) was added to a solution of trideuteriomethyltriphenylphosphonium bromide (9.05 g, 0.024 mol) in 220 mL of anhydrous ether. The mixture was stirred at room temperature under nitrogen for 5 h, and a solution of the crude product (5.21 g) from ozonization of **3b** in 50 mL of anhydrous tetrahydrofuran was added. The resulting mixture was stirred at room temperature under a nitrogen atmosphere for 91 h. Water (15 mL) was added, and the organic portion was separated and worked up to give 2.66 g of crude product. It was purified by column chromatography on activity III neutral alumina, eluting with petroleum ether. The deuterated naphthalenone **3b-d_2** (0.17 g, 0.787 mmol, 3.4%) was obtained as a pale yellow oil. Its NMR spectrum showed the presence of 0.70 ± 0.05 residual hydrogen atom at the terminal methylene group, based on the ratio of terminal vinyl protons to protons in the methoxy group.

In a second run, following the same procedure, a 10% yield of **3b-d_2** containing 0.49 ± 0.03 atom of residual hydrogen in the terminal methylene group was obtained.

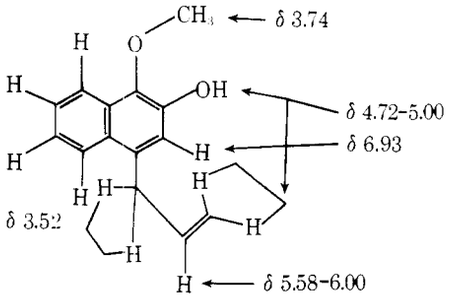
Synthesis of 1-(*trans*-2-Butenyl)-2-naphthol. 2-Naphthol (12.80 g, 0.096 mol) was dissolved in a solution of sodium hydroxide (3.86 g, 0.096 mol) in 100 mL of water. *trans*-1-Bromo-2-butene (12.96 g, 0.096 mol) was added drop by drop. A precipitate formed immediately. This mixture was stirred overnight. It was then filtered, and the filtrate was extracted with two 50-mL portions of methylene chloride. The organic solution was extracted with Claisen alkali, and the basic solution was neutralized and extracted with methylene chloride. The organic solution was worked up to give 9.00 g of crude product which was chromatographed on 200 g of silica gel, eluting with methylene chloride–petroleum ether. **1-(*trans*-2-Butenyl)-2-naphthol** (3.5

g, 0.0177 mol, 18%) was obtained, mp 72–74 °C (from petroleum ether). Its NMR spectrum showed multiplets between δ 7.10–7.80 (6 H) and 5.40–5.57 (2 H), a broad signal at δ 3.60 (2 H), a doublet at δ 1.55 (3 H, J = 5.0 Hz), and a singlet at δ 5.10 (1 H).

Synthesis of 1-(*trans*-2-Butenyl)-1-methoxy-2-naphthalenone (4b). 1-(*trans*-2-Butenyl)-2-naphthol (8.70 g, 0.044 mol) was dissolved in 200 mL of methanol, and a solution of sodium periodate in 100 mL of water was added drop by drop. The mixture was stirred at room temperature for 48 h. It was worked up as usual to give 9.00 g of crude product which was chromatographed on 180 g of silica gel, eluting with 10% methylene chloride–petroleum ether solution. Naphthalenone **4b** (0.98 g, 4.3 mmol, 10%) was obtained as a yellowish oil. Its IR spectrum showed a carbonyl peak at 1670 cm^{-1}. Its NMR spectrum showed multiplets between δ 7.44–7.75 (5 H) and 5.21–5.37 (2 H), three doublets at δ 6.23 (1 H, J = 11 Hz), 2.48 (2 H, J = 3.5 Hz), and 1.55 (3 H, J = 4 Hz), and a sharp singlet at δ 3.08 (3 H). Anal. ($C_{15}H_{16}O_2$) C,H.

Synthesis of 2-Allyl-2-methoxy-1-naphthalenone (5). A solution of sodium periodate (32.1 g, 0.15 mol) in 200 mL of water was added drop by drop to an ice-cooled solution of 2-allyl-1-naphthol (27.86 g, 0.15 mol) in 500 mL of methanol. The solution was stirred for 3 days at room temperature, filtered, extracted with methylene chloride, and worked up to give 30.0 g of dark oil, which was chromatographed on 600 g of neutral alumina (activity III). The column was eluted with 10% methylene chloride in petroleum ether to yield 0.146 g (0.68 mmol, 0.50%) of **5** as a brownish oil. Its IR spectrum showed a carbonyl peak at 1660 cm^{-1}. Its NMR spectrum showed multiplets between δ 8.00–8.12 (1 H), 7.71–7.18 (3 H), and 4.88–5.98 (3 H), three doublets at δ 6.8 (1 H, J = 8.3 Hz), 6.15 (1 H, J = 8.3 Hz), and 2.52 (2 H, J = 6.15 Hz), and a sharp singlet at δ 3.19 (3 H). Anal. ($C_{14}H_{14}O_2$) C,H.

Acid-Catalyzed Rearrangement of 3b. A solution of naphthalenone **3b** (0.40 g) in 10 mL of a 1% solution of sulfuric acid in acetic acid was stirred at room temperature for 3 days. Methylene chloride was added, and the solution was worked up to yield 0.218 g of brown oil. VPC analysis (170 °C, 67 mL/min) showed two peaks with retention times of 175 and 345 s in an area ratio of 1:5.7. The two components were isolated by preparative VPC. The component with the lower retention time was identified as **3b.** The compound with the higher retention time was assigned the structure **4-allyl-1-methoxy-2-naphthol (6).** Its IR spectrum showed strong peaks at 3400, 1620, 1540, 1610, 1370, 1220, and 750 cm^{-1}. Its NMR spectrum showed multiplets between δ 7.36–7.87 (2 H), 7.08–7.28 (2 H), 5.58–6.00 (1 H), and 4.72–5.00 (3 H), a doublet at δ 3.52 (2 H, J = 5 Hz), and singlets at δ 3.74 (3 H) and 6.93 (1 H). Anal. ($C_{14}H_{14}O_2$) C,H.



Acid-Catalyzed Rearrangement of 3b-d_2. Acid-catalyzed rearrangement of **3b**-d_2 was carried out as described for the rearrangement of **3b,** employing 0.15 g of the naphthalenone and 10 mL of 1% sulfuric acid–acetic acid solution. The NMR spectrum of the product was the same as that of the undeuterated rearrangement product except for the decreased intensity of the doublet at δ 3.52 (which contained 0.62 ± 0.09 proton). Its IR spectrum showed strong peaks at 3530, 3400, 2950, 1620, 1600, 1460, 1370, 1340, 1220, 1175, 1100, 910, and 860 cm^{-1}.

Thermal Rearrangement of 3b. Napthalenone **3b** (0.20 g) was dissolved in 10 mL of N,N-dimethylaniline and the solution refluxed for 2 days. Methylene chloride was added, and the mixture was washed several times with 5% hydrochloric acid solution. (Compound **3b** was shown to be stable in this acid solution for at least 6 h.) A trace of solid material was filtered out, and the organic solution was worked up to give 0.20 g of brown oil. VPC analysis (180 °C, 67 mL/min) showed a single component, which was isolated by preparative VPC and identified by its IR and NMR spectra and VPC retention time as naphthol **6.**

Thermal Rearrangement of 3b-d_2. Naphthalenone **3b**-d_2 (0.14 g), containing 0.49 ± 0.03 atom of residual hydrogen at the terminal methylene position, was refluxed in 10 mL of N,N-demethylaniline for 30 h. It was worked up as described above to give 0.13 g of **6.** NMR analysis showed it to contain 0.51 ± 0.06 atom of hydrogen at the benzylic methylene position.

Acid-Catalyzed Reactions of 1-Acetoxy-1-allyl-2-naphthalenone (3c). (a) In 3% Sulfuric Acid–Acetic Acid Solution. Compound **3c** (1.0 g) was dissolved in 15 mL of a 3% solution of sulfuric acid in acetic acid, and the solution was stirred at room temperature for 2 days. It was worked up to give 0.9 g of product, whose VPC analysis and IR and NMR spectra showed that only unchanged **3c** was present.

(b) In 10% Sulfuric Acid–Acetic Acid Solution. Compound **3c** (0.40 g) was dissolved in 10 mL of a 10% sulfuric acid in acetic acid solution, and the mixture was stirred at room temperature for 48 h. The solution was worked up as described in method a to give 0.31 g of brown oil. VPC analysis (180 °C, 67 mL/min) showed two peaks with retention times of 170 and 247 s in an area ratio of 1:2.77. The components were separated by preparative gas chromatography and identified as **11**[10] and **3c.**

(c) In Boron Trifluoride Etherate. Naphthalenone **3c** (0.50 g) was dissolved in 10 mL of boron trifluoride etherate, and the solution was stirred at room temperature for 1 week. It was worked up to give 0.341 g (76%) of **11.**

Thermal Reactions of 3c. Naphthalenone **3c** was sealed in a glass tube and heated in an oil bath at 150 °C for 72 h. The product was dissolved in 10 mL of methylene chloride and filtered. VPC analysis (180 °C, 67 mL/min) showed three peaks with retention times of 165, 222, and 274 s in an area ratio of 2.60:1.12:0.07. The two major components were isolated by preparative VPC and identified as **11** and recovered **3c.**

Acid-Catalyzed Rearrangements of 4b. (a) In Acetic Acid Solution. Naphthalenone **4b** (0.53 g, 0.023 mol) was dissolved in 20 mL of a 1% solution of sulfuric acid in acetic acid, and the solution was allowed to stand at room temperature for 48 h. It was worked up as described for the rearrangement of **3b** to give 0.52 g of dark liquid. VPC analysis (175 °C, 67 mL/min) showed a single component with a retention time of 534 s. A pure sample was isolated by preparative VPC. The product was assigned the structure **4-(1-methyl-2-propenyl)-1-methoxy-2-naphthol (8).** Its NMR spectrum showed multiplets at δ 8.11–8.30 (2 H), 7.36–7.67 (2 H), 6.02–6.58 (2 H), 5.04–5.38 (2 H), and 4.16–4.42 (1 H), singlets at δ 7.05 (1 H) and 3.98 (3 H), and a doublet at δ 1.50 (3 H, J = 2 Hz). Anal. ($C_{15}H_{16}O_2$).

(b) In Acetic Anhydride Solution. A 1% solution of sulfuric acid (10 mL) in acetic anhydride was added to a solution of naphthalenone **4b** (0.62 g, 0.0027 mol) in 10 mL of acetic anhydride. The solution was stirred at room temperature for 1.5 h and then poured into 200 mL of water. The mixture was stirred for 20 min and then worked up to give 0.60 g of dark oil. VPC analysis (195 °C, 75 mL/min) showed two peaks with retention times of 120 and 330 s in an area ratio of 1:0.93. These components were isolated by preparative VPC. The component with the lower retention time was assigned the structure **9.** Its IR spectrum showed a strong carbonyl peak at 1775 cm^{-1}. Its NMR spectrum showed a multiplet at δ 7.35–8.30, a doublet at δ 7.20 (2 H, J = 8 Hz), and singlets at δ 4.0 (3 H) and 2.40 (3 H).

The component with the higher retention time was assigned the structure **4-(1-methyl-2-propenyl)-1-methoxy-2-naphthyl acetate (10).** Its IR spectrum showed a carbonyl peak at 1755 cm^{-1}. Its NMR spectrum showed multiplets between δ 7.00 and 8.50 (5 H), 4.9–6.5 (3 H), and 4.1–4.4 (ca. 1 H), singlets at δ 3.97 (3 H) and 2.38 (3 H), and a doublet at δ 1.45 (3 H, J = 6.5 Hz). Anal. ($C_{17}H_{18}O_3$).

Synthesis of 9. 2[7] (0.16 g, 0.92 mmol) was dissolved in 5 mL of acetic anhydride. Sulfuric acid (1 drop) was added, and the solution was kept overnight at room temperature. It was then poured into 100 mL of acetic anhydride, and the mixture was stirred for 1 h. It was worked up to give 0.17 g (0.79 mol, 86%) of **9,** whose IR and NMR spectra and retention time were identical with those of **9** obtained from rearrangement of **4b** in acetic anhydride.

Synthesis of 4-(1-Methyl-2-propenyl)-1-methoxy-2-naphthyl Acetate (10). Naphthol **8** (0.090 g, 0.394 mmol) was dissolved in 5 mL of acetic anhydride. A solution of 1 drop of sulfuric acid in 1 mL of acetic anhydride was added, and the mixture was stirred overnight at room temperature. It was poured into 100 mL of acetic anhydride and stirred at room temperature for 2 h. It was worked up to give 0.102 g (0.389 mol, 99%) of **10,** whose IR and NMR spectra and VPC retention time were identical with those of **10** obtained from rearrangement of **4b** in acetic anhydride.

Thermal Rearrangements of 4b. (a) Without Solvent. Naphthalenone **4b** (0.0875 g, 0.384 mmol) in a sealed test tube was heated in an oil bath at 175 °C for 12 h. VPC analysis (175 °C, 67 mL/min) showed two peaks with retention times of 130 and 315 s in an area ratio of 2.7:10. These components were isolated by preparative VPC. The component with the longer retention time was identified

as recovered **4b**. The component with the shorter retention time was identified from its IR and NMR spectra as **1-methoxy-2-naphthol.**[7] Its NMR spectrum showed a multiplet at δ 7.20–7.96 and sharp singlets at δ 5.90 (1 H) and 3.84 (3 H).

(b) In *N,N*-Dimethylaniline. A solution of **4b** (0.20 g, 0.878 mmol) in 10 mL of *N,N*-dimethylaniline was refluxed for 22 h. Methylene chloride was added, and the solution was extracted with 6 M hydrochloric acid solution and worked up to give 0.16 g of brown liquid. VPC analysis (205 °C, 48 mL/min) showed two peaks with retention times of 65 and 190 s in an area ratio of 7.0:3.8. The components were isolated and identified as **1-methoxy-2-naphthol** and **1-(*trans*-2-butenyl)-2-naphthol.**

Acid-Catalyzed Rearrangement of 5. Naphthalenone **5** (0.116 g, 0.54 mmol) was dissolved in 10 mL of a 1% solution of sulfuric acid in acetic acid and stirred overnight at room temperature. The solution was worked up to give 0.101 g of a brown oil. VPC analysis showed a single peak. The product was isolated by preparative VPC and assigned the structure **4-allyl-2-methoxy-1-naphthol.** Its NMR spectrum showed four multiplets between δ 5.76–6.30, 4.86–5.14 (4 H), 7.80–8.28 (2 H), and 7.30–7.60 (2 H), two sharp singlets at δ 7.06 (1 H) and 3.86 (3 H), and a doublet at δ 3.71 (2 H, J = 5.0 Hz). Anal. ($C_{14}H_{14}O_2$) C,H.

Thermal Rearrangement of 5. Naphthalenone **5** (0.10 g) in a glass tube was kept in an oil bath overnight at 150 °C. It was cooled and 5 mL of methylene chloride was added to dissolve the crude product. The solution was filtered, and the solvent was removed to give 0.7 g of brown liquid. VPC on column A (175 °C, 67 mL/min) showed only one peak with a retention time of 350 s. This compound was isolated and identified as naphthol **8.**

Synthesis of 1,2-Dimethoxy-4-allylnaphthalene (7). The crude product obtained from acid-catalyzed rearrangement of **3b** (0.438 g) was dissolved in 15 mL of dimethyl sulfoxide, and potassium *tert*-butoxide (0.003 mol, 0.337 g) was added. The solution was stirred at room temperature for 2 h. Methyl iodide (0.003 mol, 4.2 g) was added drop by drop. The solution was stirred overnight and worked up to give 0.41 g of product. VPC on column A (170 °C, 67 mL/min) showed a peak with a retention time of 318 s, which was isolated by preparative gas chromatography and identified as **7.** Its NMR spectrum showed four multiplets between δ 7.80–8.37 (2 H), 7.58–7.30 (2 H), 5.79–6.33 (1 H), and 4.92–5.22 (2 H), two sharp singlets at δ 7.15 (1 H) and 3.95 (6 H), and a doublet at δ 3.72 (2 H, J = 5 Hz). Anal. ($C_{15}H_{16}O_2$) C,H.

Methylation of naphthol 8 was carried out in the same manner to give **7.**

Synthesis of 1-Methyl-1-methoxy-2-naphthalenone (12b). A solution of 42.7 g (0.20 mol) of sodium periodate in 300 mL of water was added drop by drop to a solution of 1-methyl-2-naphthol (15.8 g, 0.10 mol) in 300 mL of methanol. The solution was stirred at room temperature for 3 days. Methylene chloride was added and the reaction worked up to give 10.5 g of yellow oil. Addition of 20 mL of ethyl ether to the crude product resulted in precipitation of 3.68 g of yellowish crystals, which consisted principally of 1-methyl-2-naphthol. The mother liquor was chromatographed on neutral alumina to give 2.00 g (0.0106 mol, 10.6%) of **12b** as a yellow oil. Its IR spectrum showed a carbonyl peak at 1670 cm^{-1}. Its NMR spectrum showed a multiplet at δ 7.16–7.50 (5 H), a doublet at δ 5.93 (1 H, J = 8 Hz), and singlets at δ 2.84 (3 H) and 1.32 (3 H). Anal. ($C_{12}H_{12}O_2$) C,H.

Basicity Studies. Studies of the basicities of naphthalenones **12a** and **12b** were carried out in 72.00, 74.50, 77.40, and 79.48% aqueous sulfuric acid solutions at room temperature, following the procedure of Vitullo and Logue.[11] Acidity functions were taken from the literature.[17] Concentrations of the protonated naphthalenones were determined from their UV absorbances at 380 mμ. The changes in absorbances were measured as functions of time and extrapolated to t = 0 to give absorbances at 0 time for each point. The H_0 value for half protonation of **12a** was determined to be −5.56 and for half protonation of **12b** to be −7.23.

Kinetic Studies of Acid-Catalyzed Rearrangements of Naphthalenones. Weighed amounts of naphthalenones **12c** or **3b** were dissolved in 40 mL of glacial acetic acid in 50-mL volumetric flasks. The solutions were kept in a water bath at 29.6 ± 0.5 °C overnight. A 5-mL aliquot of 3 M sulfuric acid in acetic acid solution was added to each flask, and the solutions were then diluted to the 50-mL marks with glacial acetic acid to give 0.3 M sulfuric acid solutions. The flasks were shaken vigorously, and the first points were taken when they were well mixed. At intervals, aliquots were removed by a pipet and quenched with sodium acetate in acetic acid–water (2:1) solution. The UV spectra were taken on a Cary 14 spectrometer. The rates of the reaction were followed by the disappearance of the maxima at 308–320 mμ. The rates were found to be first order and were calculated from eq 2.

$$\log \frac{A - A_\infty}{A_0 - A_\infty} = \frac{-kt}{2.30} + \text{constant} \qquad (2)$$

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Registry No.—**1,** 3697-96-9; **2,** 67464-72-6; **3b,** 67274-84-4; **3b-d_2,** 67247-85-5; **3c,** 67464-73-7; **4b,** 67464-74-8; **5,** 67274-88-8; **6,** 67274-87-7; **6-d_2,** 67464-75-9; **7,** 67274-89-9; **7a,** 67377-24-6; **8,** 67464-76-0; **9,** 67464-77-1; **10,** 67464-78-2; **11,** 67464-80-6; **12a,** 23230-52-6; **12b,** 67464-79-3; **12c,** 39094-46-7; 2-naphthol, 135-19-3; *trans*-1-bromo-2-butene, 29576-14-5; 2-allyl-1-naphthol, 28164-58-1; 1-methyl-2-naphthol, 1076-26-2.

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