Benzyl and Methoxy Migrations in Acid-Catalyzed Rearrangements of Naphthalenones[1]

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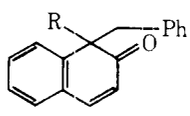
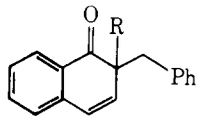
Miller and Saidi[2] have shown that rearrangements of naphthalenones **1a** and **2a** in acid give products resulting from 1,4 and 1,3 benzyl migrations, respectively. Rearrangement



1a, R = CH_3
b, R = OCH_3



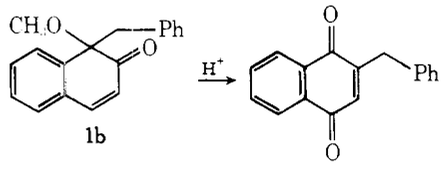
2a, R = CH_3
b, R = OCH_3

of **1a** gave, in addition, a phenol which was considered to be the product of 1,5 migration to C-3, but which was not unequivocally identified. In neither case were products of "normal" 1,2 benzyl shifts obtained.[2]

We recently reported that products of migration of allyl groups in acid-catalyzed and thermal rearrangements of naphthalenones were markedly changed by replacing methyl groups at the migration origins by methoxy groups.[3] In this paper, we report the products of acid-catalyzed migrations of benzyl groups in naphthalenones with methoxy groups at the migration origins.

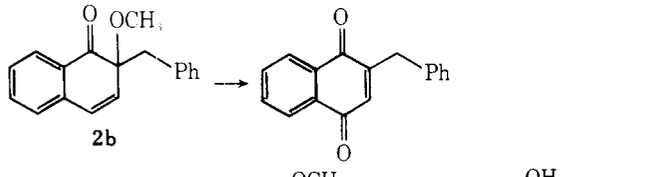
Naphthalenones **1b** and **2b** were prepared by sodium periodate oxidation of 1-benzyl-2-naphthol and 2-benzyl-1-naphthol, respectively, in aqueous methanol.[3] The structures of the products were clearly established by their spectra (see Experimental Section) which showed the presence of conjugated carbonyl groups, methoxy groups, and benzyl groups on quaternary carbons in each isomer. The NMR spectrum of **2b** showed the signal for the C-8 proton at an unusually far downfield position, due to the presence of the carbonyl at C-1. This feature was absent in the spectrum of **1b**.

Rearrangement of naphthalenone **1b** in a 3% solution of sulfuric acid in acetic acid gave 2-benzyl-1,4-naphthoquinone as the only detectable product. Rearrangement of 1-methoxy-1-methyl-2-naphthalenone in 10% sulfuric acid in acetic acid similarly gave 2-methyl-1,4-naphthoquinone.

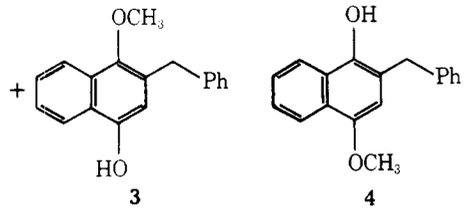


1b

Rearrangement of naphthalenone **2b** under the conditions employed for rearrangement of **1b** gave a 3:1 mixture of 2-benzyl-1-methoxy-4-naphthol (**3**) and 2-benzyl-1,4-naphthoquinone.



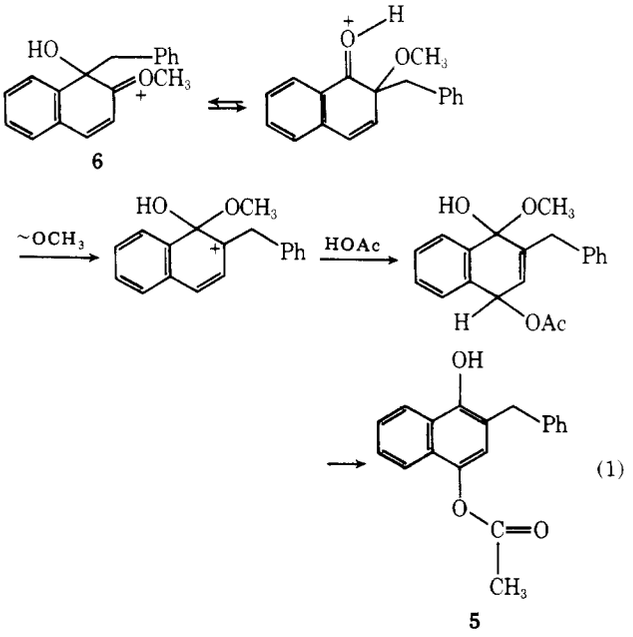
2b



3 **4**

The structure of **3**, except for the relative positions of the methoxy and hydroxy groups, was confirmed by its methylation to form 2-benzyl-1,4-dimethoxynaphthalene, which was independently prepared by reduction and methylation of 2-benzyl-1,4-naphthoquinone. To determine the location of the methoxy group, the two possible monomethyl ethers **3** and **4** were independently synthesized as described in the experimental section, and the structure of the rearrangement product was established as **3**.

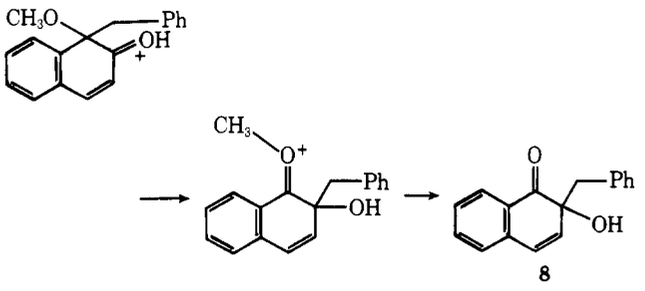
The mechanism in eq 1 appears to offer the simplest path for formation of a derivative of 4-methoxy-3-benzyl-1-naphthol by acid-catalyzed rearrangement of **2b**. The 1,2 migration of a methoxy group required by the mechanism is not unprecedented.[4] However, the correctness of this mechanism



6 **5** (1)

seemed questionable, since it should give rise to the monoacetate **5**, rather than naphthol **3**. When a sample of **5** was stirred at room temperature in a 3% solution of sulfuric acid in acetic acid, however, it was found to be quantitatively converted to **3**. Since the acetate group in **5** is thus unusually easily cleaved, the mechanism of eq 1 appears to be a satisfactory explanation for formation of **3** during rearrangement of **2b**. Since a methoxy group has previously been found to migrate less rapidly than a *methyl* group in the acid-catalyzed rearrangement of 4-methoxy-4-methylcyclohexadien-1-one,[5] we suggest that the benzyl group migrates rapidly but reversibly between C-1 and C-2 in **2b**, while the product of the slower migration of the methoxy group reacts more rapidly with solvent to yield a stable, aromatic product.

In view of the ready conversion of acetate **5** to **3**, it seemed possible that 1,4-diacetoxy-2-benzylnaphthalene (**7**) might be an intermediate in formation of 2-benzyl-1,4-naphthoquinone from **1b**. However, it was found that **7** was cleaved to 4-acetoxy-3-benzyl-1-naphthol under the conditions of the rearrangement, with 2-benzyl-1,4-naphthoquinone a minor product of the reaction. It also seems unlikely that carbonium



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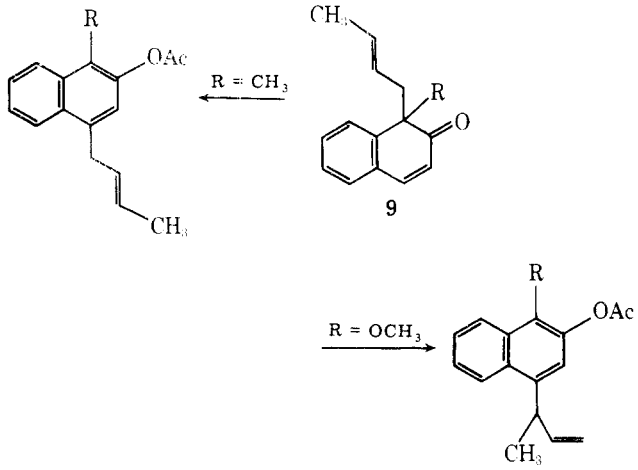
ion **6** is an intermediate in rearrangement of **1b**, since **6** is presumably a precursor of **3** in rearrangement of **2b**. The most probable mechanism for formation of 2-benzyl-1,4-naphthoquinone from **1b** appears to be loss of a methyl group to give ketol **8**, which then undergoes allylic rearrangement of the hydroxy group and oxidation by sulfuric acid.

If our suggestion that a benzyl group rapidly shifts between C-2 and C-1 in **2b** is correct, benzyl groups in both **1b** and **2b** undergo only 1,2 migrations, while benzyl groups in **1a** and **2a** undergo formally forbidden 1,3 and 1,4 migrations. This result is reminiscent of our observations that rearrangement of naphthalenone **9** in acetic anhydride proceeds by a forbidden 1,4 shift when R = CH_3, but by an allowed 3,4 shift when R = OCH_3.[2,3] We suggest that the electron-donating methoxy group exerts its effect in both benzyl and allyl migrations by decreasing the difference in polarity between the "acceptor" cyclohexadienone ring and the "donor" migrating group in the transition state for rearrangement, thereby increasing the "forbiddenness" of the 1,4 or 1,3 migrations.[6]



Experimental Section

IR spectra were taken on a Beckman IR 10 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. × ¼ 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) several times, dry over anhydrous magnesium sulfate, filter, and remove the solvent under vacuum.

1-Benzyl-1-methoxy-2-naphthalenone (1b). A solution of sodium periodate (6.68 g, 0.0312 mol) in 100 mL of water was added drop by drop to a solution of 2-benzyl-1-naphthol[7] in 270 mL of methanol. A white precipitate formed immediately. The mixture was stirred at room temperature for 5 days, filtered, and extracted with three 40-mL portions of methylene chloride. The organic layer was worked up to give 4.84 g of brown oil, which was chromatographed on 80 g of neutral alumina, eluting with a 20% methylene chloride–80% petroleum ether mixture. Naphthalenone **1b** (0.58 g, 16%) was obtained as a light yellow powder, mp 94.5–96 °C. Its IR spectrum showed a carbonyl peak at 1670 cm^{-1} and a conjugated double bond peak at 1620 cm^{-1}. Its NMR spectrum showed multiplets between δ 6.96 and 7.34 (8 H) and 6.50 and 6.65 (2 H), a doublet at 5.88 (1 H, J = 9 Hz), and singlets at 2.97 (3 H) and 3.0 (2 H). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 82.09; H, 6.42.

Rearrangement of 1b in Acid. A solution of naphthalenone **1b** (0.24 g., 0.91 mmole) in 10 mL of a 3% solution of sulfuric acid in acetic acid was stirred at room temperature for 2 days. Methylene chloride was added and the mixture worked up to give 0.198 g of a brown oil, which was shown by VPC analysis (200 °C, 67 mL/min) to consist of two components, retention times 234 and 444 s, in the area ratio 1:22. The components were isolated by preparative VPC and found to be recovered **1b** and 2-benzyl-1,4-naphthoquinone, identified by comparison with a sample synthesized by the procedure of Jacobsen and Torsell,[8a] mp 81–82 °C (lit.[8b] mp 82 °C).

2-Benzyl-2-methoxy-1-naphthalenone (2b). A solution of sodium periodate (17.2 g, 0.080 mol) in 200 mL of water was added dropwise to a solution of a mixture of 2-benzyl-1-naphthol (80%) and 4-benzyl-1-naphthol[7] (18.0 g, 0.077 mol) in 200 mL of methanol. The solution was stirred at room temperature for 3 days and worked up to give 19 g of brown oil, which was chromatographed on 360 g of neutral alumina (activity III), eluting with petroleum ether. Naphthalenone **2b** (0.12 g, 0.454 mmol, 0.57%) was obtained as a light brown powder, mp 93–94 °C. Its IR spectrum showed a carbonyl peak at 1660 cm^{-1} and a conjugated vinyl peak at 1600 cm^{-1}. Its NMR spectrum showed multiplets between δ 7.92 and 8.07 (1 H) and 7.00 and 7.65 (9 H), a doublet at 6.35 (1 H, J = 9 Hz), and singlets at 3.00 (3 H) and 3.10 (2 H). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.19. Found: C, 81.69; H, 5.97.

Rearrangement of 2b in Acid. Naphthalenone **2b** (0.175 g) was dissolved in 10 mL of a 3% solution of sulfuric acid in acetic acid. The solution was stirred at room temperature for 48 h, water was added, and the mixture was extracted with two 10-mL portions of methylene chloride. The organic solutions were worked up to give 0.15 g of brown oil. The oil was dissolved in methylene chloride and extracted with potassium hydroxide solution. The neutral layer was worked up to give 0.03 g (17%) of 2-benzyl-1,4-naphthoquinone. The basic layer was acidified and extracted with methylene chloride. The methylene chloride solution was worked up to give **3-benzyl-4-methoxyl-1-naphthol (3)** (0.113 g, 64%) as a brown oil. Its IR and NMR spectra were identical with those of a synthetic sample.

2-Benzyl-1,4-Naphthalenediol. A solution of 2-benzyl-1,4-naphthoquinone (11.0 g, 0.443 mol) in 100 mL of water was heated on a water bath at 70–80 °C. Sodium hydrosulfite (25 g) in 150 mL of water was added in small portions. The solution was cooled, water was added, and the solution was extracted with methylene chloride. The organic solution was extracted with 10% aqueous sodium hydroxide solution, the alkaline solution acidified and extracted with methylene chloride, and the methylene chloride solution worked up to give **2-benzyl-1,4-naphthalenediol** (7.71 g, 0.031 mol, 70%), mp 157–159 °C (from methanol). Its NMR spectrum showed multiplets at δ 8.05–8.22 (2 H) and 7.07–7.37 (7 H), a singlet at 6.47 (1 H), and a singlet at 4.1 superimposed on a broad peak at 4.4 (4 H). Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.58; H, 6.04.

2-Benzyl-1,4-dimethoxynaphthalene. Potassium *tert*-butoxide (1.68 g, 15 mmol) was added to a solution of 2-benzyl-1,4-naphthalenediol (1.5 g, 6.0 mmol) in 25 mL of dimethyl sulfoxide. The mixture was stirred at room temperature for two hours, methyl iodide (2.2 g, 15 mmol) was added, and stirring was continued for 2 h. Water was added and the mixture was extracted with methylene chloride and worked up to give 1.95 g of crude **2-benzyl-1,4-dimethoxynaphthalene.** An analytical sample was isolated by preparative VPC. Its NMR spectrum showed multiplets at δ 8.28–7.97 (2 H) and 7.58–7.00 (7 H) and singlets at 6.48 (1 H), 4.13 (2 H), and 3.76 (6 H). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.73; H, 6.93.

2-Benzoyl-1-methoxynaphthalene. 2-Benzoyl-1-naphthol (4.0 g, 0.016 mol) was converted to its methyl ether using 2.75 g of potassium *tert*-butoxide and 4.0 g of methyl iodide in 30 mL of dimethyl sulfoxide by the procedure used for methylation of 1,4-naphthalenediol. **2-Benzoyl-1-methoxynaphthalene** (4.21 g, 0.016 mol, 100%) was obtained as a yellow liquid. Its IR spectrum showed a carbonyl peak at 1650 cm^{-1}. Its NMR spectrum showed multiplets at δ 8.32–8.17 (1 H), 7.96–7.77 (3 H), and 7.70–7.30 (7 H) and a singlet at 3.83 (3 H). Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 6.38. Found: C, 82.22; H, 5.59.

2-Benzyl-1-methoxynaphthalene. 2-Benzoyl-1-methoxynaphthalene (4.15 g, 16.0 mmol) in 35 mL of dry ether was added drop by drop over a 15-min period to a suspension of lithium aluminum hydride (0.677 g, 17.8 mol) in 40 mL of anhydrous ether. The mixture was stirred at room temperature for 40 min. Aluminum chloride (2.5 g, 17.8 mmol) was added in small portions. After addition was complete, the mixture was stirred at room temperature for 30 min. Water (10 mL) and then 3 M sulfuric acid solution (10 mL) were added slowly. The layers were separated, the aqueous layer extracted with ether, and the ether fractions combined and worked up to give 4.15 g of yellow oil, which was dissolved in 35 mL of benzene. Thionyl chloride (4.0 g, 33.9 mmol) was added and the solution was stirred at room temperature overnight and then heated on a steam bath for 5

min. Water (60 mL) was added and the mixture stirred for 15 min. The layers were separated and the organic layer worked up to give 3.97 g of oil, whose IR spectrum showed no hydroxy or carbonyl peaks. The oil was dissolved in 50 mL of anhydrous ether and added drop by drop to a suspension of lithium aluminum hydride (0.834 g, 21.9 mol) in 50 mL of anhydrous ether, at a rate sufficient to maintain gentle refluxing. After completion of the addition, the mixture was stirred for 1 h and worked up as before to give 2.63 g of yellow oil, which was chromatographed on 50 g of neutral alumina, eluting with petroleum ether. **2-Benzyl-1-methoxynaphthalene** (1.63 g, 6.57 mmol, 41%) was obtained as pale yellow crystals, mp 50–52 °C (from methanol). Its NMR spectrum showed multiplets at δ 8.10–8.25 (1 H) and 7.17–7.92 (10 H) and singlets at 4.22 (2 H) and 3.87 (3 H).

2-Benzyl-1-methoxy-4-nitronaphthalene. A solution of nitric acid (0.4 mL) in 1 mL of acetic acid was added drop by drop to a solution of 2-benzyl-1-methoxynaphthalene (0.63 g, 25 mmol) in 5 mL of acetic acid. The solution was stirred overnight at room temperature. Water (20 mL) was added and the mixture was extracted with methylene chloride and worked up to give **2-benzyl-1-methoxy-4-nitronaphthalene** (0.63 g, 2.15 mmol, 86%) as a yellow oil. Its NMR spectrum showed multiplets at δ 8.52–8.68 (1 H), 7.53–7.70 (2 H), and 8.13–8.29 (1 H) and singlets at 8.13 (1 H), 7.22 (5 H), 4.20 (2 H), and 3.90 (3 H).

3-Benzyl-4-methoxy-1-naphthol. Hydrochloric acid (12 M, 10 mL) was added to a solution of 2-benzyl-1-methoxy-4-nitronaphthalene (12.6 g, 43 mmol) in 10 mL of ethanol. The mixture was heated to 70–80 °C and zinc dust (32 g) was added in small portions. When addition was complete, the mixture was stirred at 70–80 °C for 30 min, filtered, and neutralized (pH 7). The mixture was extracted with methylene chloride and worked up to give 7.9 g of crude **4-amino-2-benzyl-1-methoxynaphthalene** as a brown oil. Its NMR spectrum showed multiplets at δ 8.03–8.18 (1 H) and 7.15–7.82 (8 H) and singlets at 6.45 (1 H), 4.12 (2 H), and 3.82 (3 H). This product was immediately diazotized by the procedure below.

A solution of crude 4-amino-2-benzyl-1-methoxynaphthalene (6.0 g, 22 mmol) in 50 mL of 3 M sulfuric acid was cooled at 0 °C. Ice (20 g) was added, and a solution of sodium nitrite (1.4 g, 20 mmol) in 20 mL of water (previously cooled to 0 °C) was added drop by drop. The mixture was shaken vigorously in an ice bath for 5 min and then added drop by drop to 60 mL of boiling 1% aqueous sulfuric acid solution. The solution was boiled for 5 min after completion of the addition, cooled, and extracted with ether. The ether solution was extracted with two 10-mL portions of Claisen alkali. The basic extract was acidified with 3 M hydrochloric acid and extracted with methylene chloride and the methylene chloride layer was worked up to give 0.15 g (0.57 mmol, 26%) of **3-benzyl-4-methoxy-1-naphthol** as a brown oil. An analytical sample was isolated by preparative VPC. Its IR spectrum showed a hydroxy peak at 3520 cm^{-1}. Its NMR spectrum showed multiplets at δ 8.10–8.25 (2 H) and 7.58–7.42 (2 H) and singlets at 7.25 (5 H), 6.54 (1 H), 4.15 (2 H), and 3.85 (3 H). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.56; H, 6.19.

2-Benzyl-4-methoxy-1-naphthol (4). 4-Methoxy-1-naphthol (10.0 g, 57.4 mmol) was dissolved in 100 mL of benzene and a 2.0 M solution of *n*-butyllithium in hexane (50 mL, 0.10 mol) was added. The reaction was stirred under an atmosphere of nitrogen for 20 min and benzyl chloride (7.84 g, 62.2 mmol) was added. The mixture was refluxed for 48 h, cooled, neutralized, washed with water, and extracted with Claisen alkali. The basic layer was neutralized, extracted with methylene chloride, and worked up to give 2.7 g (10.7 mmol, 19%) of **2-benzyl-4-methoxy-1-naphthol** as a brown oil. A pure sample was prepared by preparative VPC. Its NMR spectrum showed multiplets at δ 8.28–7.97 (2 H) and 7.53–7.36 (2 H) and singlets at 7.22 (6 H), 6.58 (1 H), 4.12 (2 H), and 3.89 (3 H).

Rearrangement of 1-Methoxy-1-methyl-2-naphthalenone. A solution of 1-methoxy-1-methyl-2-naphthalenone[3] (0.391 g) in 15 mL of 10% sulfuric acid in acetic acid was stirred at room temperature for 72 h. Methylene chloride was added and the reaction worked up to give 0.20 g of brown oil. VPC analysis (180 °C, 67 mL/min) showed the presence of two components in the area ratio 2:1, with retention times of 113 and 130 s. These components were isolated by preparative VPC. The component with the longer retention time was identified as unreacted 1-methoxy-1-methyl-2-naphthalenone. The major component was identified as **2-methyl-1,4-naphthoquinone** by comparison with a sample obtained from the Aldrich Chemical Co.

2-Benzyl-1,4-diacetoxynaphthalene (7). A solution of 2-benzylnaphthalene-1,4-diol (0.20 g, 0.80 mmol) and sodium acetate (0.516 g) in 10 mL of acetic anhydride was stirred under nitrogen at room temperature for 2 days. Water (20 mL) was added, the mixture was stirred for 20 min and then extracted with ether, and the ether layer was worked up to give **2-benzyl-1,4-diacetoxynaphthalene** (0.21 g, 6.3 mmol, 79%) as white crystals, mp 108–109.5 °C (from methanol). Its IR spectrum showed a carbonyl peak at 1740 cm^{-1}. Its NMR spectrum showed multiplets at δ 7.90–7.67 (2 H) and 7.50–7.35 (2 H) and singlets at 7.20 (5 H), 7.05 (1 H), 4.0 (2 H), 2.30 (3 H), and 2.26 (3 H). Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43. Found: C, 75.49; H, 5.66.

4-Acetoxy-2-benzyl-1-methoxynaphthalene. A solution of sodium acetate (0.10 g) and 3-benzyl-4-methoxy-1-naphthol (0.09 g) in 10 mL of acetic anhydride was stirred at room temperature for 48 h. Water was added and the mixture was extracted with methylene chloride and worked up to give 0.07 g of a brown oil. Its IR spectrum showed no hydroxy peak, but did show a carbonyl peak at 1760 cm^{-1}. Its NMR spectrum showed multiplets at δ 8.10–8.27 (2 H) and 7.35–7.61 (3 H) and singlets at 4.20 (2 H), 3.87 (3 H), and 2.20 (3 H), in addition to a multiplet for the aryl hydrogens. The product was therefore assigned the structure **4-acetoxy-2-benzyl-1-methoxynaphthalene.** Attempts to purify this compound resulted in its hydrolysis to 3-benzyl-4-methoxy-1-naphthol.

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Registry No.—**1b,** 68707-60-8; **2b,** 68707-61-9; **3,** 68707-62-0; **4,** 68707-63-1; **5,** 68707-64-2; **7,** 33440-69-6; 2-benzyl-1-napthol, 36441-32-4; 2-benzyl-1,4-naphthoquinone, 33440-68-5; 2-benzyl-1,4-naphthalenediol, 35100-89-1; 2-benzyl-1,4-dimethoxynaphthalene, 68707-65-3; 2-benzoyl-1-methoxynaphthalene, 43073-56-9; 2-benzoyl-1-naphthol, 21009-99-4; 2-benzyl-1-methoxynaphthalene, 68707-66-4; 2-benzyl-1-methoxy-4-nitronapthalene, 68707-67-5; 3-benzyl-4-methoxy-1-naphthol, 68707-62-0; 4-amino-2-benzyl-1-methoxynaphthalene, 68707-68-6; 4-methoxy-1-naphthol, 84-85-5; 1-methoxy-1-methyl-2-naphthalenone, 67464-79-3; 2-methyl-1,4-naphthoquinone, 58-27-5.

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Chlorine Kinetic Isotope Effects in the Methylation of Pyridine and 2,6-Lutidine[1]

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When the rates of methylation of 2,6-dialkylpyridine with methyl iodide are measured under pressure, a remarkable descendence in activation volume is observed in the series R = H, Me, Et, *i*-Pr, and *t*-Bu, the extremes being −22 and −50 cm^3/mol, respectively.[3] A subsequent study[4] revealed no anomalies in the partial volumes of either the reactants or the products. The overall reaction volumes are in all instances approximately −50 cm^3/mol, and it was therefore proposed that the increase in $\Delta V^{\ddagger}$ in the series is a manifestation of the phenomenon described by the Hammond postulate,[5] the most hindered and slowest reaction possessing the "latest" (most product-like) transition state.

In order to further test this conclusion, it seemed desirable to gather independent information regarding the location of the transition state along the reaction coordinate, and accordingly we have measured the chlorine kinetic isotope effect

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