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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Table I. Chlorine Isotope Ratios and KIE[a]

reaction	run	% reaction	I.R.	k^{35}/k^{37}
pyridine with CH_3Cl	1	9.18	0.318703	1.00352
	2	9.18	0.318707	1.00350
	3	9.18	0.318654	1.00368
	4	6.07	0.318696	1.00348
	5	6.07	0.318664	1.00358
2,6-lutidine with CH_3Cl	1	9.79	0.318583	1.00392
	2	9.79	0.318700	1.00354
	3	9.79	0.318688	1.00358
	4	6.02	0.318482	1.00417
	5	6.02	0.318614	1.00374
	6	6.02	0.318508	1.00409

[a] Natural abundance ratio is 0.319770.

(KIE)[6] in the closely analogous methylations of pyridine and 2,6-lutidine with methyl chloride. The large rate decreases which occur upon further increases in substitution in the 2,6 positions make it impossible to carry out the reaction with the other pyridines mentioned above under the same conditions of solvent and temperature. The reactions were carried out in bromobenzene solution[7] in sealed glass ampules at 100.0 ± 0.1 °C; they were allowed to proceed to about 6–10% of completion.[8] For analysis, the product ionic chloride was isolated, purified, and completely reconverted[9] into methyl chloride.

Experimental Section

Materials. Bromobenzene (Mallinkrodt) was fractionally distilled at atmospheric pressure. A middle fraction was thoroughly washed with concentrated sulfuric acid and concentrated ammonia (the latter by stirring overnight), dried, passed through a basic alumina column, and refractionated under nitrogen. Fractionation from CaH_2 followed by refractionation gave material of bp 156.0–156.5 °C (uncorr); GC indicated no detectable impurities. Methyl chloride was a Linde high-purity research grade. The gas was passed through a CaH_2/$CaSO_4$ drying tube before use; GC showed no detectable impurities. Reagent grade 2,6-lutidine was obtained from K & K; lutidine from other commercial sources contained an impurity which gave a violet color under the Menschutkin reaction conditions, and which could not be removed by distillation and chromatography. The K & K lutidine was fractionated, and the middle fraction was stirred overnight with CaH_2 and refractionated. A middle fraction was then filtered through activated basic alumina and refractionated under nitrogen: bp 144.0–144.1 °C (uncorr); GC showed no detectable impurities. Reagent grade pyridine was purified analogously to the lutidine: bp 115.0 °C; GC showed no detectable impurities. All other chemicals were reagent grade and used without further purification. Water was glass-distilled.

Kinetics. The kinetics were run under the same experimental conditions as the KIE experiments so that the fraction of reaction could be determined from the rate constant. A well-stirred oil bath was used at 100.0 ± 0.1 °C in all kinetic experiments. The reactions were run in sealed glass ampules of approximately 3-mL volume. Before use the ampules were thoroughly cleaned with detergent and dilute nitric acid, dried in an oven, and stored in a desiccator.

Samples were prepared as follows. Methyl chloride was passed through a long needle into a tared volumetric flask containing bromobenzene. Absorption of the gas was very rapid, and any bubbles formed did not reach the surface of the solution. The amount of CH_3Cl was determined by weight to give a concentration of approximately 1 M. The respective amines were added by volume as standard solutions in bromobenzene to give final solutions of approximately 0.2 M for pyridine and 0.5 M for lutidine. The volume was brought up to the mark by adding bromobenzene. Aliquots were then transferred to the sample ampules via a buret loaded by argon pressure and fitted with a long needle delivery tip. The samples were frozen in liquid nitrogen and sealed with a flame. The reactions are sufficiently slow at room temperature that insignificant reaction occurs during this procedure. The samples were then placed in the oil bath at 100 °C. The exact concentration of CH_3Cl was determined by adding a large excess of piperidine to extra duplicate samples, which were otherwise treated as above; the reaction with piperidine is rapid even at room temperature and thus gives the infinity titer for chloride. Product analysis was by the Volhard method (back titration of excess Ag^+ with SCN^-).

The reactions were cleanly second order. NMR analysis (D_2O solvent) of the solid product of the lutidine reaction showed no detectable impurities. Analysis of the rate data was by linear least squares. The rate constant for the pyridine reaction is $3.84 \pm 0.04 \times 10^{-5}$ M^{-1} s^{-1} with a correlation coefficient of 0.9998. The rate constant for the lutidine reaction is $2.1 \pm 0.1 \times 10^{-6}$ M^{-1} s^{-1} with a correlation coefficient of 0.997.

KIE Experiments. The KIE experiments were run under conditions closely analogous to the kinetic runs. Larger glass ampule and solution volumes were used with the smaller fractions of reaction so as to give approximately 1 mmol of chloride for all runs; the ampule volumes were approximately 5 and 7 mL. Concentrations of the amines were as in the kinetic runs. The gas volume above the solutions was 2–3% of the sealed ampules at 100 °C. The fraction of reaction f was determined from the rate constants k and elapsed time t, and the expression for chloride concentration was $[Cl^-] = ab(e^{kt(a-b)} - 1)/(ae^{kt(a-b)} - b)$, where a is the initial CH_3Cl concentration (determined from the infinity titer with piperidine) and b is the initial amine concentration. The reaction fractions and times (to the nearest 10 s) were as follows: pyridine, 6%, 9840 s; pyridine, 9%, 16 740 s; lutidine, 6%, 69 600 s; lutidine, 10%, 120 600 s.

The reactions were quenched by cooling at the above times, and the ampules were broken open. The mixture was washed with bromobenzene, benzene, and hexane. The chloride was precipitated at high ionic strength with Ag^+ according to the literature procedure.[10] The mixture was centrifuged, and the compact AgCl was washed and dried. The fractions of reaction were checked (with less precision) by gravimetric analysis of the AgCl.

The product chloride was converted to CH_3Cl by reaction with CH_3I according to the literature procedure,[10] which was not changed in any essential way; the technique is routine, and the conversion yields are claimed to be 99%. The converted CH_3Cl was collected at liquid nitrogen temperature and then purified by GC, which employed an Apiezon L stationary phase (itself chromatographed on alumina as an n-pentane solution to give a colorless grease) on silanized Chromosorb P (Johns-Manville) in a 10 mm × 250 cm glass column with helium carrier gas at room temperature. All of the chromatographed samples contained CH_3Br (M_r 94 and 96; cf. M_r 50 and 52 for CH_3Cl) as an impurity that was not removed due to the similar retention time to CH_3Cl. There was no obvious relationship between CH_3Br concentration and reaction time within a series; however, the lutidine series as a whole possibly contained more CH_3Br. [It should be pointed out that if CH_3Br^{2+} (m/e 48) fell in significant intensity on the detector plate, this could *lower* the observed isotope ratio.] The mass spectrum indicated that the total ion flux corresponding to the CH_3Br was at most 10% of that corresponding to CH_3Cl. A control experiment had previously been conducted in which the purified bromobenzene solvent was reacted under the KIE conditions with piperidine; no bromide product was detectable by the Volhard method.

Mass Spectrometry. Isotope ratios were determined with a Nuclide Model RMS-6-60 isotope ratio mass spectrometer, which has been described elsewhere.[10] This instrument has been used extensively before for chlorine KIE determinations. The instrument uses a dual channel inlet system, one for sample and one for reference standard, with electromagnetic switching between inlets. The dwell between automatic alternate switching between sample and standard was about 2 min, and at least five (generally six) switchings were made per run in Table I. Ions of m/e 48, 49, 50, and 51 fall on the detector plate when m/e 52 is centered in the Faraday cup; the ratio of the cup/plate ion current gives the observed mass ratio, which is then corrected. The instrument gives the first four digits of the isotope ratio directly in digital form; the last two digits in Table I were determined graphically from the instrument chart recorder trace used to establish the null condition between plate and cup.

Results and Discussion

The results are recorded in Table I.

The mean KIE's and standard deviations are 1.00355 ± 0.00008 and 1.00384 ± 0.00026 for the methylations of pyridine and 2,6-lutidine, respectively; the difference in means is significant at the 95% confidence limit (by the t test[11]). It is furthermore compatible with the trend in the activation volumes; if we accept Fry's proposition[12] that the chlorine KIE increases monotonically and essentially linearly from 1 to 1.020 as a function of C–X bond order, the change in KIE

observed here is quite comparable to that noted earlier in the activation volume. We therefore feel justified in concluding that the chlorine KIE supports the notion expressed earlier that the special effect of pressure on hindered Menschutkin reactions reflects the differences in position of the transition states along the reaction coordinate.

Our result is in agreement with that of Berg,[13] who deduced a similar variation in the transition state location in the methylation of 2-substituted pyridines on the basis of a selectivity relationship, and with that of Swain,[14] who found that amines and enolates have an earlier transition state than iodide as nucleophiles in their reactions with methyl chloride, but in contrast with another result by Swain:[15] the KIE in the reaction of methyl chloride with triethylamine is smaller than in the faster reaction with quinuclidine. The special explanation for this observation does evidently not apply in the reactions compared here.

Finally, it may be noted that our result is near the low end of the range of chlorine isotope effects reported so far (1.001–1.010).[16] The implication is that Menschutkin reactions have early transition states; this inference is supported by several other literature reports concerning this reaction.[17]

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Note Added in Proof: Further support for transition state progression along the reaction coordinate in a Menschutkin reaction as a function of substituents has recently been claimed on the basis of ^{14}C isotope effects. [H. Yamataka and T. Ando, *J. Am. Chem. Soc.*, **101**, 266 (1979)].

Registry No.—Pyridine, 110-86-1; CH_3Cl, 108-48-5; 2,6-lutidine, 74-87-3.

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Triple Bond Participation in the Solvolysis of Soluble Sulfonates in Water and Water–Sulfuric Acid

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The solvolysis of a sulfonate of 6-octyn-2-ol (**1**, X = (CH_3)) with triple bond participation to give **4** and **5** (Scheme I) was reported in our laboratories in 1966,[1] following our preliminary report of triple bond participation in the solvolysis of 6-heptyn-2-yl tosylate.[2] Other types of triple bond participation were reported at approximately the same time.[3]

The reaction of **1** to give the five-membered ring ketone **5** may be considered to be the model reaction for the formation of ring D in Johnsons' spectacular steroid syntheses involving olefinic and acetylenic cyclization.[4] The triple bond "terminator" has, in fact, been a key element in several studies from the Johnson group, since other likely terminators gave complex rearrangements, presumably involving 1,2 shifts.[5]

We have now studied the reaction of Scheme I in water (containing 2% acetone) and water–sulfuric acid, using the water-soluble *p*-(trimethylammonio)benzenesulfonate **1a** (amsylate) or the *p*-(dimethylamino)benzenesulfonate **1b** (damsylate?). The use of the quaternary sulfonates has recently been introduced by Sukenik and Bergman.[6] The relative amounts of products, **4** and **5**, from triple bond participation and that, **6**, from solvent displacement are given in Table I. The results of Table I correspond to 52% cyclization in water. Increasing cyclization occurs as increasing amounts of H_2SO_4 in water are used. In 67% H_2SO_4, quantitative cyclization (>99%) is the result. The uncyclized alcohol (**6**, OR=OH) is stable under the reaction conditions.

Since previous cyclizations were conducted in relatively nonnucleophilic solvents (CH_3CO_2H, HCO_2H, and particularly CF_3CO_2H), the substantial amount of cyclization in water may appear to be surprising. However, recent advances in the understanding of solvolysis reactions[7,8] allow us to replace intuition with quantitiative estimates of the relative amounts of participation and normal solvolysis (k_Δ/k_s, Scheme I). The k_Δ and k_s processes of Scheme I may be assumed to follow eq 1 and 2, respectively.

$$\log (k_\Delta^A/k_\Delta^B) = 0.86 Y_A^B \quad (1)$$

$$\log (k_s^A/k_s^B) = 0.3 N_A^B + 0.77 Y_A^B \quad (2)$$

Here N_A^B and Y_A^B are the respective changes in nucleophilicity and ionizing power upon changing from solvent A to solvent B. Numerical values for the sensitivities to nucleo-

Table I. Ratio of Cyclization to Substitution in the Solvolysis of 6-Octyn-2-yl Sulfonates in H_2O and H_2O–H_2SO_4

amsylate[a]		damsylate[b]	
% H_2SO_4 (w/w)	product ratio (cyclic/acyclic)	% of H_2SO_4 (w/w)	product ratio (cyclic/acyclic)
0.0	1.08	14.0	0.81
0.72	1.07	31.0	1.98
18.3	1.62	43.0	4.10
45.1	5.54	50.0	8.28
55.8	13.10	56.0	13.4
		59.0	16.5
		62.0	24.1
		65.0	57.5
		67.0	115

[a] *p*-(Trimethylammonio)benzenesulfonate (trifluoromethanesulfonate salt). [b] *p*-(Dimethylamino)benzenesulfonate.

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