[lit.[17] bp 109–111° (3 mm)]; ν_{max} 1682 cm^{-1}; nmr δ 0.6–2.0 (m, 9 H), 1.7 (d, J = 7.0 Hz, 3 H), 3.33 (m, 1 H), and 7.35 and 7.96 (m, 5 H each).

B. Phenyl 1-Phenyl-2-hexyl Ketone.—Treatment of the enolate **3** with benzyl chloride followed by work-up as described above produced phenyl 1-phenyl-2-hexyl ketone (for yields see Table I): bp 145° (0.55 mm); ν_{max} 1675 cm^{-1}; nmr δ 0.6–2.0 (m, 9 H), 2.91 (m, 2 H), 3.70 (m, 1 H), and 7.1–7.8 (m, 10 H). The product was identical in all respects with an authentic sample prepared by the benzylation of the enolate anion of caprophenone generated by treatment of caprophenone with sodium hydride in monoglyme.

Dialkylation of Diazocyclohexanone. Preparation of 2-Methyl-2-*n*-butylcyclohexanone.—To a solution of 1.82 g (14.7 mmol) of diazocyclohexanone[15] in 2 ml of tetrahydrofuran maintained under a nitrogen atmosphere was added 2.68 g (14.7 mmol) of tri-*n*-butylboron in 2 ml of tetrahydrofuran. The reaction mixture was stirred at room temperature for 2 hr. The reaction mixture was distilled under a nitrogen atmosphere giving 2.83 g (70%) of **4** as a pale yellow liquid: bp 97° (0.32 mm); ν_{max} 1687 cm^{-1} ($\nu_{C=C}$) with no absorption in the carbonyl region. The distillate was dissolved in 5 ml of tetrahydrofuran and the solution was cooled in an ice bath. A solution of *n*-butyllithium in hexane (20.8 mmol) was added dropwise and the resulting reaction mixture was allowed to stir at room temperature for 1 hr. Methyl iodide (2.9 g, 20.8 mmol) was then added and the reaction mixture was stirred for 30 min and was then worked up as described above. Analysis of the product by glpc indicated the presence of 2-methyl-2-*n*-butylcyclohexanone (61%) and 2-*n*-butylcyclohexanone[18] (6%). The 2-methyl-2-*n*-butylcyclohexanone was isolated by preparative glpc, ν_{max} 1705 cm^{-1}. The 2,4-dinitrophenylhydrazone had mp 140–141° (lit.[19] mp 139–140°).

Dialkylation of Methyl Vinyl Ketone. Preparation of 3-Methyl-2-octanone.—To a solution of 3.59 g (15.1 mmol) of **7** in 9 ml of tetrahydrofuran maintained at 0° was added dropwise 11.3 ml of 2.67 M (30.2 mmol) *n*-butyllithium in hexane. The reaction mixture was allowed to stir at room temperature for 1 hr. A solution of 4.29 g (30.2 mmol) of methyl iodide in 1 ml of tetrahydrofuran was added and the resulting mixture was stirred at room temperature for 30 min, whereupon the reaction mixture was worked up as described above. Analysis of the product mixture by glpc showed the presence of 3-methyl-2-octanone (59%), 3-nonanone (16%), 2-octanone (10%), and 3% of unidentified products. The 3-methyl-2-octanone was isolated by preparative glpc: ν_{max} 1710 cm^{-1}; nmr δ 0.7–1.8 (m, 14 H), 2.12 (s, 3 H), and 2.47 (m, 1 H); mass spectrum m/e 142, 127, 99, 72.

Registry No.—**1**, 29128-31-2; **4**, 29199-34-6; **7**, 29199-35-7; diazoacetophenone, 3282-32-4; tri-*n*-butylboron, 122-56-5; diazocyclohexanone, 3242-56-6; methyl vinyl ketone, 78-94-4.

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[17] T. I. Temnikova, A. K. Petryaeva, and S. S. Skorokhodov, *Zh. Obshch. Khim.*, **25**, 1575 (1955).

[18] Identified by comparison with an authentic sample obtained by the hydrolysis of vinyloxyborane **4**.

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Enthalpies of Transfer of Transition States in the Menshutkin Reaction from a Polar Protic to a Dipolar Aprotic Solvent[1]

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The rates of the reaction of pyridine with six benzyl halides in methanol and dimethylformamide (DMF) were determined at 25.0 and 50.0°. The heats of solution of the reactants in these two solvents were determined at 25.0°. From these data the enthalpies of transfer of the transition states of these reactions from methanol to dimethylformamide were calculated. In all cases the lower activation enthalpy in the dipolar aprotic solvent was found to be caused *entirely* by greater solvation of the transition state in the dipolar aprotic solvent rather than by solvation effects on the reactants. Some effects upon this transition state of changes in the leaving group and in the substrate are discussed.

The Menshutkin reaction has long been regarded as one of the best examples of solvent effects upon reaction rate. Since ions are formed from neutral reactants in this reaction, large increases in rate have been observed with increases in the polarity of the solvent.[3] In addition to correlation of rates with dielectric constant,[4] Z values,[5] and polarizability,[6] it appears that there is an interesting effect on change from a polar protic to a dipolar aprotic solvent of similar dielectric constant.

The effect of this solvent change on the free energies of activation of S$_N$2 reactions has been the subject of thorough studies by Parker and coworkers,[7] and, in the case of the Menshutkin reaction, by Abraham.[3b] These authors discuss this solvent effect in terms of the free energy of transfer of the transition state in these reactions from a polar protic to a dipolar aprotic solvent. Another variable, namely the solvent effect on the volume of activation of the Menshutkin reaction, has been studied by Brower.[8]

Although the effect on rate of a change from a polar protic to a dipolar aprotic solvent is not great and both rate increases[9] and rate decreases[9,10] have been reported, there does seem to be a consistent decrease in the enthalpy of activation in the dipolar aprotic solvent.[9,10] This decrease in the $\Delta H^{\ddagger}$ can be attributed to two possible causes.

The first, and most common, explanation is that desolvation of the nucleophile or base in the aprotic solvent relative to the protic solvent raises the energy of the reactants, thus diminishing the energy gap between the reactants and the transition state. The second explanation is that the lowering of the activation energy

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[1] (a) A preliminary report of a part of this work appeared in *Chem. Commun.*, 194 (1968). (b) This work was supported in part by the National Science Foundation under its Undergraduate Science Education Program, 1963–1965.

[2] Taken in part from the M. A. thesis of A. Nudelman, Brooklyn College, Feb 1964.

[3] (a) N. Menschutkin, *Z. Phys. Chem.*, **5**, 589 (1890); (b) for a more recent discussion, see M. H. Abraham, *Chem. Commun.*, 1307 (1969).

[4] S. Eagle and J. Warner, *J. Amer. Chem. Soc.*, **61**, 488 (1939).

[5] E. M. Kosower, *ibid.*, **80**, 3267 (1958).

[6] J. D. Reinheimer, J. D. Harley, and W. W. Meyers, *J. Org. Chem.*, **28**, 1575 (1963).

[7] E. C. F. Ko and A. J. Parker, *J. Amer. Chem. Soc.*, **90**, 6447 (1968), and earlier papers.

[8] K. R. Brower, *ibid.*, **85**, 1401 (1963); see also H. Heydtman, *Z. Phys. Chem.*, **54**, 237 (1967).

[9] (a) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 519 (1935); (b) B. O. Coniglio, D. E. Giles, W. R. McDonald, and A. J. Parker, *J. Chem. Soc., B*, 152 (1966).

[10] H. Essex and O. Gelomini, *J. Amer. Chem. Soc.*, **48**, 883 (1926).

is caused by increased solvation of the transition state in the dipolar aprotic solvent. A combination of both effects is also conceivable. A direct means of distinguishing between these possibilities, as demonstrated in the work of Arnett,[11] is to determine the difference in the enthalpies of activation of a reaction in a pair of solvents, $\delta\Delta H^{\ddagger}$, and to compare them to the enthalpies of transfer of the reactants from one solvent to the other, $\delta\Delta H_s$.

The decrease in the $\Delta H^{\ddagger}$ for the Menshutkin reaction on going from a polar protic to a dipolar aprotic solvent is quite large and is of the same order of magnitude as that observed for SN2 reactions having a negatively charged nucleophile and a neutral electrophile.[9,12] Recently we were able to show[13] that for some SN2 reactions of this second type the decrease in $\Delta H^{\ddagger}$, which accompanies the very large rate enhancement of these reactions in dipolar aprotic solvents, was caused principally by increased solvation of the transition state rather than by decreased solvation of the nucleophile in the dipolar aprotic solvent. This was particularly true when the nucleophile was a *weak* base.

The purpose of the present work was to measure the dipolar aprotic solvent effect for the Menshutkin reaction as a function of leaving group and substrate variation and to determine to what degree the effect upon the $\Delta H^{\ddagger}$ in each particular case was caused by an effect on the enthalpies of solvation of the reactants and of the transition state. For this purpose we chose methanol and dimethylformamide (DMF), two solvents having very similar dielectric constants, in order to focus, as much as possible, solely upon the differences between a protic and a dipolar aprotic solvent.

Results and Discussion

The solvent effect upon the rates of reaction of six benzyl halides with pyridine can be seen in Table I. There is a substantial rate enhancement by the dipolar aprotic solvent on the rates of the bromides but none on the rates of the chlorides. The rate-enhancing effect is increased by an electron-withdrawing group and diminished by an electron-donating group. The thermodynamic activation parameters are listed in Table II. A plot of $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ for the chlorides in each solvent and for the bromides in each solvent yielded four parallel lines with an isokinetic temperature of 355°K. The rate increases are reflected in a substantial lowering of the $\Delta H^{\ddagger}$ in DMF; however, this effect is even more pronounced for the chlorides than for the bromides. Again the effect is increased by an electron-withdrawing group and diminished by an electron-donating group.

To determine whether the effect is caused by a lowered enthalpy of the transition state in DMF or by a lower enthalpy of the reactants in methanol, we determined the enthalpy of transfer of the reactants from methanol to DMF. Table III contains the heats of solution, ΔH_s, of the reactants in the two solvents measured at the concentration at which the kinetic measurements were made and the enthalpy of transfer, $\delta\Delta H_s$, of the reactants from methanol to DMF. As can be seen, the endothermic $\delta\Delta H_s$ of pyridine from methanol to DMF (attributable to H bonding by methanol to the nucleophile) is cancelled by approximately equal exothermic $\delta\Delta H_s$ values for the benzyl halides (except for the nitro compounds where this effect is about twice as large). Thus the total $\delta\Delta H_s$ of the reactants from the one solvent to the other is nearly zero (except for the nitro compounds where the reactants actually have a slightly higher enthalpy in methanol than in DMF). The enthalpy of transfer of a transition state from one solvent to another, δH^t, is obtained from the relation $\delta H^t = \delta\Delta H_s + \delta\Delta H^{\ddagger}$, where $\delta\Delta H_s$ is the enthalpy of transfer of the reactants from one solvent to the other and $\delta\Delta H^{\ddagger}$ is the difference in the activation enthalpies

TABLE I

RATE CONSTANTS FOR THE REACTION OF PYRIDINE WITH VARIOUS BENZYL HALIDES IN METHANOL AND DIMETHYLFORMAMIDE AT 25.0 AND 50.0°

Benzyl halide	Solvent	Temp, °C	$k_2^a \times 10^5$ l. mol^{-1} sec^{-1}
p-Nitrobenzyl chloride	Methanol	25.0	0.122
		50.0	3.10
	DMF	25.0	0.251
		50.0	2.64
Benzyl chloride	Methanol	25.0	0.346
		50.0	4.39
	DMF	25.0	0.374
		50.0	2.37
p-Methylbenzyl chloride	Methanol	25.0	0.820
		50.0	7.95
	DMF	25.0	0.950
		50.0	5.62
p-Nitrobenzyl bromide	Methanol	25.0	4.91
		50.0	44.7
	DMF	25.0	58.4
		50.0	348
Benzyl bromide	Methanol	25.0	9.64
		50.0	55.5
	DMF	25.0	84.6
		50.0	394
p-Methylbenzyl bromide	Methanol	25.0	27.8
		50.0	151
	DMF	25.0	128
		50.0	569

[a] Standard deviations were generally within ±4%.

TABLE II

ACTIVATION PARAMETERS[a] FOR THE REACTION OF BENZYL HALIDES WITH PYRIDINE IN METHANOL AND DIMETHYLFORMAMIDE

Benzyl halide	Solvent	$\Delta H^{\ddagger}$,[b] kcal mol^{-1}	$\Delta S^{\ddagger}$,[b] mol^{-1} deg^{-1}	$\delta\Delta H^{\ddagger}$,[c] kcal mol^{-1}
p-Nitrobenzyl chloride	Methanol	24.1	−4.45	
	DMF	17.3	−25.6	−6.8
Benzyl chloride	Methanol	18.8	−20.1	
	DMF	13.5	−37.7	−5.3
p-Methylbenzyl chloride	Methanol	16.7	−25.3	
	DMF	13.0	−37.7	−3.7
p-Nitrobenzyl bromide	Methanol	16.2	−23.4	
	DMF	13.0	−29.3	−3.2
Benzyl bromide	Methanol	12.8	−33.8	
	DMF	11.1	−34.8	−1.7
p-Methylbenzyl bromide	Methanol	12.3	−34.6	
	DMF	10.9	−34.8	−1.4

[a] At 25.0°. [b] $\Delta H^{\ddagger}$, ±0.6 kcal mol^{-1}; $\Delta S^{\ddagger}$, ±1.5 cal mol^{-1} deg^{-1} or better. [c] $\delta\Delta H^{\ddagger} = \Delta H^{\ddagger}$ in DMF − $\Delta H^{\ddagger}$ in methanol.

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[11] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Amer. Chem. Soc.*, **87**, 1541 (1965).

[12] N. Tokura and Y. Kondo, *Bull. Chem. Soc. Jap.*, **37**, 133 (1964).

[13] P. Haberfield, L. Clayman, and J. Cooper, *J. Amer. Chem. Soc.*, **91**, 787 (1969).

TABLE III
HEATS OF SOLUTION OF BENZYL HALIDES AND PYRIDINE IN METHANOL AND DIMETHYLFORMAMIDE AT 25°

Reagent	ΔH_s (CH_3OH), kcal/mol	ΔH_s (DMF), kcal/mol	$\delta\Delta H_s$,[a] kcal/mol
p-Nitrobenzyl chloride	5.97	4.16	−1.81
Benzyl chloride	0.44	−0.39	−0.83
p-Methylbenzyl chloride	0.60	−0.26	−0.86
p-Nitrobenzyl bromide	7.03	4.72	−2.31
Benzyl bromide	0.76	−0.44	−1.20
p-Methylbenzyl bromide	5.12	4.17	−0.95
Pyridine	−0.95	−0.09	0.86

[a] The enthalpy of transfer from methanol to DMF, $\delta\Delta H_s = \Delta H_s$ (DMF) − ΔH_s (CH_3OH); standard deviations were generally within 0.05 kcal/mol.

of the reaction in the two solvents. Table IV lists these quantities for the six Menshutkin reactions which we have examined.

TABLE IV
ENTHALPIES OF TRANSFER (δH^t) OF THE TRANSITION STATES IN THE MENSHUTKIN REACTION FROM METHANOL TO DIMETHYLFORMAMIDE

Reaction	$\delta\Delta H_s$, kcal/mol	$\delta\Delta H^{\ddagger}$, kcal/mol	δH^t, kcal/mol
Pyridine + *p*-nitrobenzyl chloride	−0.95	−6.8	−7.8
Pyridine + benzyl chloride	0.03	−5.3	−5.3
Pyridine + *p*-methylbenzyl chloride	−0.00	−3.7	−3.7
Pyridine + *p*-nitrobenzyl bromide	−1.45	−3.2	−4.7
Pyridine + benzyl bromide	−0.34	−1.7	−2.0
Pyridine + *p*-methylbenzyl bromide	−0.09	−1.4	−1.5

The most important conclusion to be drawn from these data is that the very substantial decreases in the enthalpy of activation for the Menshutkin reaction on going from a polar protic to a dipolar aprotic solvent are caused *entirely* by enhanced solvation of the transition state in the dipolar aprotic solvent and not by desolvation of the reactants. Several other observations can be made.

(1) It is interesting that the dipolar aprotic rate enhancement effect is greater for bromides than for chlorides, whereas the dipolar aprotic $\Delta H^{\ddagger}$ lowering is greater for chlorides than for bromides. The lack of rate enhancement for the chlorides appears to be caused by a very high negative entropy of activation for the reaction in DMF relative to that in methanol (Table II). This may be caused by a more tight transition state in DMF, a medium providing no H-bonding stabilization to the leaving group. This lack of stabilization for the leaving group would be more important for Cl^- than for Br^-.

Another,[9b] more obvious, explanation for the rate effect, namely that the transition state is well solvated by hydrogen-bonding interactions with methanol and that these interactions would be stronger for Cl than for Br, is inconsistent with the $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$ values. These clearly indicate that there is a decrease in the $\Delta H^{\ddagger}$ in DMF for both halides which is, however, vitiated by an unfavorable change in the $\Delta S^{\ddagger}$ values on going to DMF in the case of the chlorides. Abraham[3b] has shown that in the reaction of trimethylamine with *p*-nitrobenzyl chloride the rate enhancement in a dipolar aprotic solvent was caused by transition state stabilization in the dipolar aprotic solvent, *i.e.*, that $\delta\Delta G^{\ddagger} = \delta G^t$. Since we have shown that for our reactions $\delta\Delta H^{\ddagger} = \delta H^t$ this suggests that $\delta\Delta S^{\ddagger} = \delta S^t$. The lack of rate enhancement of benzyl chlorides in DMF is then clearly a consequence of an unfavorable entropy of transfer of the transition state from methanol to DMF rather than greater stabilization of the transition state in methanol than in DMF.

The rule of Swain and Thornton,[14] applied to our reactions, predicts the tightest transition state for *p*-nitrobenzyl chloride. This is the reaction for which we find our most negative $\delta\Delta S^{\ddagger}$ value. This suggests that the compound which is predicted to have the least bond breaking in the SN2 transition state is most sensitive to a solvent effect which tightens that transition state.

(2) Electron withdrawal at the central carbon increases the rate enhancement as well as the $\Delta H^{\ddagger}$ lowering by the dipolar aprotic solvent. We believe that this is caused by a shift toward products in the transition state structure.[15] In the Menshutkin reaction this would mean a more dipolar transition state and hence one having the greatest degree of solvation by a dipolar aprotic solvent.

(3) Although the enthalpies of transfer of the transition states from methanol to DMF (δH^t's) are all exothermic, there is a very considerable variation in the values (from −1.5 to −7.8 kcal/mol). We see this mainly as a consequence of a continuous shift toward products in transition state structure with increasing exothermicity of the δH^t values. The transition states which are furthest along the reaction coordinate have the greatest degree of dipolar character and are therefore best solvated by a dipolar aprotic solvent.[16]

(4) SN2 transition states having a net zero charge (Menshutkin reaction) and those having a net negative charge[13] both appear to have large exothermic δH^t values from methanol to DMF, but only the second type show large rate enhancements in the dipolar aprotic solvent. This seems to be the consequence of a much more negative δS^t (from methanol to DMF) for the neutral transition states than for the negatively charged ones.

Experimental Section

Materials.—Dimethylformamide was dried over anhydrous P_2O_5, decanted, and distilled using a 90-cm, glass helix packed column at 12-mm pressure. Methanol was distilled from magnesium. Pyridine (Baker) was dried over KOH and distilled, $n^{20}D$ 1.5092. Benzyl chloride (Baker) was decanted from anhydrous $NaHCO_3$ and distilled at reduced pressure, $n^{15}D$ 1.5416. Benzyl bromide (Eastman) was decanted from anhydrous Na_2CO_3 and fractionated at reduced pressure, $n^{20}D$ 1.5757. *p*-Methylbenzyl chloride was decanted from anhydrous Na_2CO_3 and fractionated, $n^{20}D$ 1.5323. *p*-Methylbenzyl bromide was sublimed at reduced pressure, mp 38.0–38.7°. *p*-Nitrobenzyl chloride was recrystallized from benzene, mp 73.0–73.5°. *p*-

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[14] C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, **84**, 217 (1962).

[15] Such a substituent effect on the transition state structure is predicted by the rules suggested by J. C. Harris and J. L. Kurz, *ibid.*, **92**, 349 (1970). These authors predict that an electron-withdrawing substituent will have a bond-strengthening effect on the nucleophile and a bond-weakening effect on the leaving group, whereas the Swain–Thornton rule predicts a bond-strengthening effect on both the entering and the leaving groups.

[16] In the case of the nitro compounds, it is useful to consider a contribution to the δH^t value by the NO_2 group itself, aside from its influence on the transition state of complex. This way of looking at it can be justified by the large exothermic enthalpies of transfer of the reactants, *p*-nitrobenzyl chloride and *p*-nitrobenzyl bromide. Another example of the affinity of a dipolar aprotic solvent for molecules having nitro groups is the $\delta\Delta H_s$ (methanol to DMF) of 2,4-dinitrochlorobenzene which is −3.45 kcal/mol.[13]

Nitrobenzyl bromide was recrystallized from benzene, mp 98.0–98.7°.

Rates.—The concentrations of reactants ranged from 0.02 to 0.50 *M*. The concentration of the benzyl halide was equal to that of pyridine in each run. Rates were determined by following the disappearance of base or the appearance of halide ion. In some instances both methods were employed for the same reaction to provide an added check. The base concentration was determined by titration with perchloric acid in glacial acetic acid solvent. To determine the halide concentration, an aliquot of the reaction mixture was added to a mixture of ice water and ligroin in a separatory funnel. After two countercurrent washings, the aqueous phases were titrated for halide using the Volhard method. The second-order rate constants obtained in the usual manner invariably showed an upward drift. We attributed this to concurrent solvolysis in most cases and therefore treated our data by the method reported by Young and Andrews.[17] The yields and melting points of the products were determined for most runs at 25.0° and are listed in Table V.

Heats of Solution.—The calorimeter vessel was a 250-ml dewar flask, 11 cm deep and 6-cm i.d., equipped with a rubber stopper and placed within a styrofoam box for added insulation. The stopper had five holes drilled into it to accommodate the following items: a 24.0–26.0°, 30-cm-long thermometer (Brooklyn Thermometer Co.); a stirrer passing through a bushing made of a ball and socket joint, made from a 3-mm glass rod shaped into a 3-cm propeller pitched to drive liquid downward and attached to a stirring motor; two pieces of 16-gauge copper wire joined at the bottom by a 3-cm length of 38-gauge Nichrome-V wire; an 8-cm-o.d. length of glass tubing ending in a fragile glass bulb, containing the solute and a glass breaker rod passing through a rubber septum at the top.

After 200 ml of solvent was placed into the dewar flask, the apparatus was assembled and temperature readings were taken at 30-sec intervals until a steady base line was established. The glass breaker rod was now pushed through the fragile glass bulb containing the solute, the ensuing rise or fall of temperature times the heat capacity being the heat of solution. The heat capacity of the calorimeter was now determined by passing current through the heater for 15 or 30 sec, using two cells of a lead storage battery as the current source. The voltage drop across the heater was measured during the heating period and the resistance of the heater was determined before and after a run. The amount of electrical energy supplied divided by the temperature rise was the heat capacity of the system. When the calorimeter was tested by measuring the heat of solution of KCl in water, the literature value was duplicated with an average deviation of 30 cal/mol. The concentration of solute employed ranged from 0.01 to 0.1 *M*.

TABLE V

YIELDS AND MELTING POINTS OF PRODUCTS FOR RATES AT 25.0°

Product	Solvent	Yield, %	Mp, °C[a]
p-Nitrobenzylpyridinium chloride	Methanol	>96	211–213[b]
	DMF	>96	
Benzylpyridinium chloride	Methanol	98	127–129
	DMF	96	
p-Methylbenzylpyridinium chloride	Methanol	94	
	DMF		
p-Nitrobenzylpyridinium bromide	Methanol	>98	226–228[c]
	DMF	>98	
Benzylpyridinium bromide	Methanol	97	110–111[d]
	DMF	93	
p-Methylbenzylpyridinium bromide	Methanol	96	123–124
	DMF		

[a] All melting points are uncorrected and are for recrystallized samples. [b] Lit. mp 207° [C. G. Raison, *J. Chem. Soc.*, 2070 (1949)]. [c] Lit. mp 218–219° [F. Kröhnke and K. Ellegant, *Chem. Ber.*, **86**, 1556 (1953)]. [d] Lit. mp 110–111° [J. A. Berson, E. M. Evleth, Jr., and Z. Hamlet, *J. Amer. Chem. Soc.*, **87**, 2887 (1965)].

Registry No.—Pyridine, 110-86-1; *p*-nitrobenzyl chloride, 100-14-1; benzyl chloride, 100-44-7; *p*-methylbenzyl chloride, 104-82-5; *p*-nitrobenzyl bromide, 100-11-8; benzyl bromide, 100-39-0; *p*-methylbenzyl bromide, 104-81-4; benzylpyridinium chloride, 2876-13-3; *p*-methylbenzylpyridinium bromide, 29182-75-0.

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(17) (a) W. G. Young and L. J. Andrews, *J. Amer. Chem. Soc.*, **66**, 421 (1944); (b) N. K. Vorobev and G. F. Titova [*Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.*, **9** (2), 218 (1966); *Chem. Abstr.*, **65**, 12074*g* (1966)] also report an upward drift in the second-order rate constant for the reaction of benzyl bromide with pyridine in methanol and report a rate constant at 25° of $k_2 = 20.5 \times 10^{-5}$ l. mol^{-1} sec^{-1}. This compares with a value of $k_2 = 17.7 \times 10^{-5}$ l. mol^{-1} sec^{-1} which we obtain by extrapolating our apparent second-order rate constant to zero time but, of course, does not agree with the k_2 calculated by the method of Young and Andrews. It is gratifying to note that the same reaction in DMF, where solvolysis should be less important, gives similar values for both methods of calculation, namely 84.6×10^{-5} l. mol^{-1} sec^{-1} (our data, method of calculation of Young and Andrews), 73.9×10^{-5} l. mol^{-1} sec^{-1} (our data, extrapolation of apparent k_2 to zero time), and 79.2×10^{-5} l. mol^{-1} sec^{-1} (Vorobev and Titova).