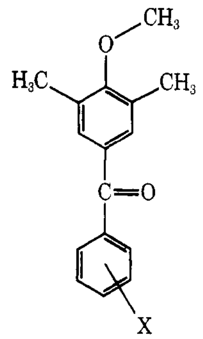
Table V. NMR Spectra of 4-Methoxybenzophenones[a]



Registry no.	X	ArCH$_3$ (s)	OCH$_3$	ArH	Mp, °C
14753-87-8	H	2.29	3.75	7.3–7.9 (m, 7 H)	
61259-83-4	p-CH$_3$	2.30 (6 H) 2.41 (3 H)	3.75	7.48 (s, 2 H) 7.30 (d, J = 8 Hz, 2 H) 7.70 (d, J = 8 Hz, 2 H)	75–77 (hexane)
61259-84-5	p-Cl	2.30	3.75	7.45 (s, 2 H) 7.46 (d, J = 9 Hz, 2 H) 7.68 (d, J = 9 Hz, 2 H)	93.5–94.5 (hexane)
61259-85-6	m-Cl	2.30	3.74	7.46 (s, H) 7.4–7.7 (m, 4 H)	
61259-86-7	m,p-di-Cl	2.30	3.76	7.45 (s, 2 H) 7.57 (d, J = 1 Hz, 2 H) 7.86 (d, J = 1 Hz, 1 H)	101.5–102.5 (hexane)

[a] Satisfactory C, H analyses were reported for all compounds.

was evaporated leaving 0.40 g of dark brown oil. GLC analysis on column A showed the presence of a single major component, which was isolated as a pale yellow oil by preparative GLC on column C. Its NMR spectrum showed peaks at δ 2.02 (s, 3 H), 2.18 (s, 3 H), 3.91 (s, 2 H), 4.4 (bs, 1 H) 6.58 (d, J = 8 Hz, 1 H), 6.81 (d, J = 8 Hz, 1 H), 7.01 (d, J = 8 Hz, 2 H), 7.11 (d, J = 8 Hz, 2 H). Small peaks at δ 2.16 and 3.78 showed the presence of some 4-(4-chlorobenzyl)-2,6-dimethylphenol.

3-(3-Chlorobenzyl)-2,6-dimethylphenol. Concentrated sulfuric acid (1 drop) was added to a solution of dienone **9d** (0.30 g) in 5 ml of glacial acetic acid. After 0.5 h, water was added and the mixture was extracted with methylene chloride. The organic layer was washed with sodium bicarbonate solution and dried over magnesium sulfate, and the solvent was evaporated to give 0.26 g of phenol **8d** as a dark brown oil. An analytical sample of the product was isolated as an oil by preparative GLC on column C. Its NMR spectrum showed peaks at δ 2.04 (s, 3 H), 2.19 (s, 3 H), 3.93 (s, 2 H), 4.54 (bs, 1 H), 6.59 (d, J = 8 Hz, 1 H), 6.81 (d, J = 8 Hz, 1 H), 7.1 (m, 4 H).

Acknowledgment. We thank the Research Corporation for a Cottrell Grant in partial support of this work.

Registry No.—**9c**, 61259-87-8; **9d**, 61259-88-9; 2,6-dimethylanisole, 1004-66-6; 4-methylbenzoyl chloride, 874-60-2; 2,6-dimethylcyclohex-2-en-1-one, 4079-59-5; 2,6-dimethyl-3-(4-methylbenzyl)cyclohexanone, 61259-89-0; 4-chlorobenzyl chloride, 104-83-6; 2,6-dimethylphenol, 576-26-1; 3-chlorobenzyl chloride, 620-20-2.

References and Notes

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Solvent Effects in the Benzylation of Aniline

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Second-order rate constants for the reaction of benzyl chloride with aniline were measured in various solvents: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2,2-methylpropanol, benzyl alcohol, ethylene glycol, water, N-methylformamide, dimethyl sulfoxide, and some mixtures of alcohols with acetonitrile. The kinetic results depend on the dielectric constant and on the electrophilic parameter E_T of the reaction medium. The protic solvent acts also a reaction catalyst, by favoring the displacement of the chloride ion by hydrogen bonding. The reaction is third order overall depending on the concentrations of the substrate, of the nucleophile, and of the protic solvent (electrophile), in agreement with the "push–pull" termolecular mechanism.

Solvent effects on the rate of a bimolecular nucleophilic substitution cannot easily be predicted on the basis of the electrostatic properties of the solvent, considered as a continuum dielectric. The solvent, in fact, can exert many kinds of specific interactions on the reagent and on the transition state.[1] However, if these effects are well understood, the study of the solvent effects is a useful diagnostic tool to elucidate the reaction mechanism.

Table I. Rate Constants and Activation Parameters for the Reactions of Benzyl Chloride with Aniline in Various Solvents

Registry no.	Solvent	ϵ^a	n^a	$E_T{}^a$	$10^5 k_2$, L mol^{-1} s^{-1} 30 °C	40 °C	50 °C	60 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}
67-56-1	1 Methanol	32.6	1.329	55.5	5.15	11.4	23.9		14.3	−31.2
64-17-5	2 Ethanol^b	24.3	1.361	51.9		6.55	14.2	26.7	14.0	−33.0
71-23-8	3 1-Propanol	20.1	1.385	50.7			13.4			
67-63-0	4 2-Propanol	18.3	1.377	48.6		6.36	10.8	19.3	11.2	−42.2
71-36-3	5 1-Butanol	17.1	1.399	50.2			13.0			
75-65-0	6 2-Methyl-2-propanol	12.2	1.384	43.9			6.07			
100-51-6	7 Benzyl alcohol	13.1	1.540	50.8			16.4			
107-21-1	8 Ethylene glycol	37.7	1.432	56.3			141			
7732-18-5	9 Water	78.5	1.333	63.1			870			
123-39-7	10 *N*-Methylformamide	182.4	1.431	54.1			130			
67-68-5	11 Dimethyl sulfoxide	48.9	1.478	45.0			17.8			
75-05-8	12 Acetonitrile^c	37.5	1.344	46.0	1.37	2.72	4.04	5.59	8.7	−52.0

[a] References 9, 10. [b] Reference 5b. [c] Reference 5a.

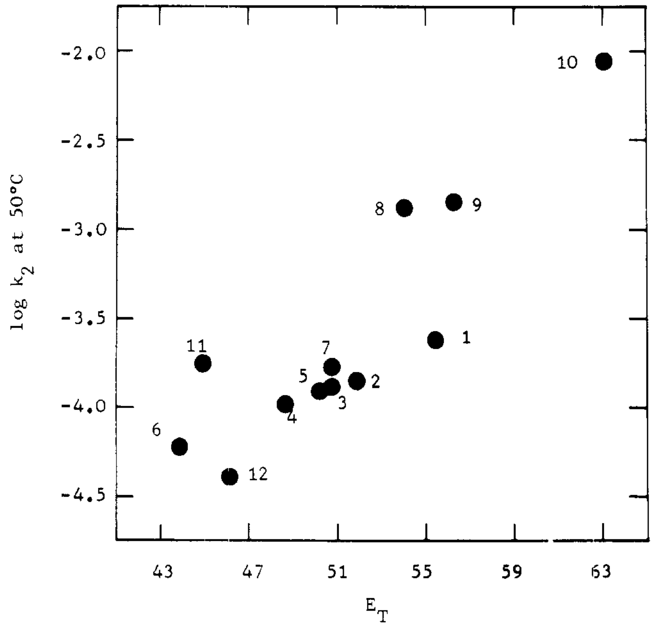


Figure 1. Correlation between log k_2 and Dimroth–Reichardt parameter, E_T, for the reaction of benzyl chloride with aniline at 50 °C in the solvents 1–12, as in Table I.

A classic example of solvent effect is the reaction of alkyl halides with tertiary amines (Menschutkin reaction),[2] where the importance of electrostatic and nonelectrostatic (polarizability, hydrogen bonding, etc.) effects on the reagents and the transition state solvation has been recently pointed out.[3]

The reaction of alkyl halides with primary and secondary amines has been extensively studied kinetically,[4,5] while the available data on the solvent effect, for the reaction of aliphatic amines with alkyl iodides,[6] cannot be generalized.

The difference between the reactions with primary or secondary amines and that of tertiary amines, apart from the nucleophiles' intrinsic reactivity, might seem negligible as both reactions go from neutral reagents to a transition state of similar structure:

$$\mathrm{RCH_2X + R_3'N \rightarrow RCH_2N^+R_3'\,X^-} \quad (1)$$

$$\mathrm{RCH_2X + R'NH_2 \rightarrow RCH_2N^+H_2R'\,X^- \rightarrow RCH_2NHR' + HX} \quad (2)$$

However, differences between these reactions were observed in the solvent effects and in the reaction mechanism.

In reaction 1, in fact, the rate in dipolar aprotic solvents is higher than in the protic ones,[3] while the opposite trend is observed for reaction 2.[4,5]

Moreover, the reaction of benzyl chloride with aniline in aprotic solvents (acetonitrile and benzene) follows third-order kinetics, first order with respect to the substrate and second order with respect to the nucleophile.[5a,7] In protic solvents, instead, the reaction is second order, first order with respect to each reactant.[4,5b] Then, the reaction seems to proceed through a different mechanism, depending on the protic or the aprotic solvent.

We are interested in the study of the solvent effects on the rate of nucleophilic reactions, by the empirical multiple correlations approach;[8] we now report kinetic data on the reaction of benzyl chloride with aniline in various solvents and solvent mixtures, to determine the empirical solvent parameters responsible for the observed reactivity and to obtain information on the reaction mechanism.

Results and Discussion

The reaction of benzyl chloride with aniline in seven aliphatic alcohols, water, ethylene glycol, *N*-methylformamide, and dimethyl sulfoxide yields *N*-benzylaniline quantitatively. The solvolysis reactions are always negligible with respect to the nucleophilic substitution. The rate was followed by titration of anilinium chloride formed in the reaction.

The reactions, carried out in a large excess of aniline, follow a pseudo-first-order kinetics to at least 65% completion. k_{obsd} values are linearly correlated with the aniline concentration, indicating that the reaction is second order overall, first order with respect to each reagent, according to the simple rate law

$$k_{\mathrm{obsd}} = k_2[\mathrm{C_6H_5NH_2}] \quad (3)$$

Second-order rate constants were calculated from the slope of the plot of k_{obsd} vs. aniline concentration, obtained from four to six kinetic runs. Table I reports k_2 values in various solvents, together with the corresponding polarity parameters (ϵ, n, E_T).

Dielectric constants, refraction indexes, and some of their functions do not correlate log k_2 values in the solvents 1–11. A poor correlation is found with E_T parameters (Figure 1).

The best statistical two parameters correlation is given by eq 4:

$$\log k_2 = 0.0865E_T + 10.87\frac{\epsilon - 1}{2\epsilon + 1} - 13.125 \quad (4)$$

The observed reactivity depends both on $\epsilon - 1/2\epsilon + 1$

Table II. Second-Order Rate Constants ($10^4 k_2$, L mol^{-1} s^{-1}) at 50 °C for the Reaction of Benzyl Chloride with Aniline in Some ROH–CH_3CN Mixtures

ROH,	CH_3OH					C_2H_5OH					2-C_3H_7OH				
vol %	X^a	Mol L^{-1}	$E_T{}^b$	k_2	$\Delta \log k_2$	X^a	Mol L^{-1}	$E_T{}^b$	k_2	$\Delta \log k_2$	X^a	Mol L^{-1}	$E_T{}^b$	k_2	$\Delta \log k_2$
100	1.0	24.7	55.5	2.39	0.00	1.0	17.2	51.9	1.42	−0.05	1.0	13.1	48.6	1.08	0.00
90	0.92	22.2	54.7	1.96	−0.05	0.89	15.5	51.3	1.19	−0.09	0.86	11.8	48.2	0.894	−0.06
80	0.84	19.8	54.0	1.54	−0.12	0.78	13.8	50.6	0.950	−0.15	0.73	10.4	47.9	0.803	−0.09
70	0.75	17.3	53.1	1.15	−0.20	0.68	12.0	50.0	0.729	−0.24	0.62	9.1	47.6	0.678	−0.15

[a] Molar fraction of ROH in the ROH–CH_3CN mixture. [b] The E_T values for the solvent mixtures were calculated by the equation. $E_{T(\mathrm{mixt})} = E_{T(S_1)}X_{(S_1)} + E_{T(S_2)}X_{(S_2)}$; where $E_{T(S_1)}$ and $E_{T(S_2)}$ are the E_T values for the pure solvents (S_1 and S_2) and $X_{(S_1)}$ and $X_{(S_2)}$ are the respective molar fractions in the mixture.

(Kirkwood's function) and E_T (Dimroth–Reichardt parameter); in fact the higher rates were measured in water, ethylene glycol, and N-methylformamide, solvents which exhibit high ϵ and E_T values; in dimethyl sulfoxide the balance between the high ϵ and the low E_T gives a rate constant similar to that of 1-butanol (low ϵ, high E_T).

For the reactions in aliphatic alcohols (solvents 1–7) a satisfactory correlation with E_T is found (eq 5), the effect of the dielectric constant being negligible:

$$\log k_2 = 0.0512E_T - 6.458 \qquad (5)$$

E_T measures the ability of the solvent to solvate specifically negative charges;[9,10] the positive coefficient indicates an electrophilic stabilization of the transition state with respect to the initial state, where no negative charge is present. The protic solvent, then, favors the chloride ion displacement probably through a determining solvation via hydrogen bonding.

The reactivity sequence in the various solvents (protic > dipolar aprotic) is opposite with respect to that observed for the Menschuntkin reaction with tertiary amines.[3] In the latter case, owing to the formation of a stable addition product (eq 1), the solvation of the reagents should be important. In the reaction with primary amines, where the addition step is followed by elimination of the chloride ion (eq 2), hydrogen bonding between the protic solvent and the leaving group (Cl^-) probably overcomes the reagents solvation.

The reaction in dimethyl sulfoxide is not third order as in the other aprotic solvents.[5a,7] To interpret this behavior a general consideration can be given. The catalytic activity of dimethyl sulfoxide in nucleophilic substitutions, owing to the polarity and to direct chemical effects, is in fact well known;[11] moreover, being a base of medium strength[12] and an hydrogen bonding acceptor,[13] it can well solvate structures with extended charges as the transition states.[14,15]

In order to verify if the solvent acts only as a solvation medium or also as a catalyst, kinetics in alcohol mixtures with acetonitrile were carried out. The results are reported in Table II.

If the hypothesis is correct, changes in k_2 at various solvent compositions should depend not only on the medium polarity, but also on the alcohol concentration.

k_2 values can be "cleaned" for the medium effect, by subtracting log k_2 values calculated by eq 5 from the observed k_2. The differences, Δ log k_2 (Table II), are linearly correlated with log [ROH] (Figure 2). The slope is very close to 1, indicating a first-order dependence on the alcohol concentration. The rate law is then

$$k_{\mathrm{obsd}} = k_3[C_6H_5NH_2][ROH] \qquad (6)$$

These results indicate that the protic solvent favors the stabilization of the transition state through the same catalytic effect which in aprotic solvents was exerted by the second aniline molecule.[5a]

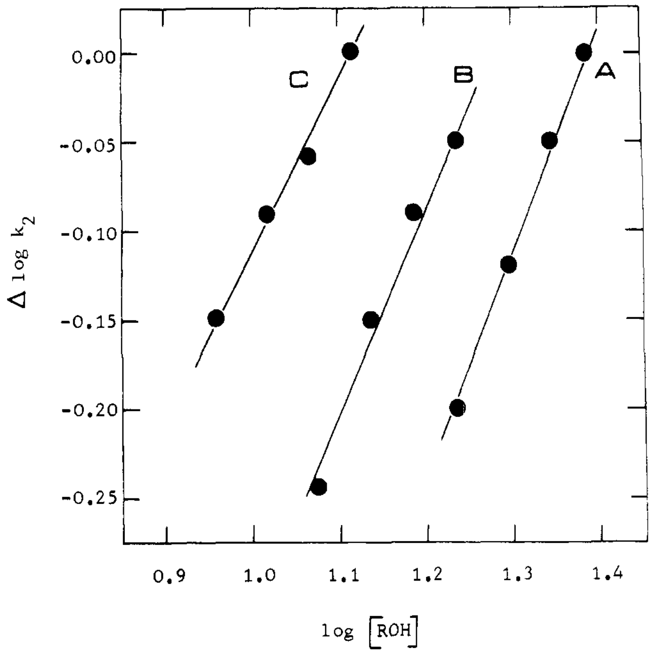
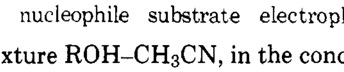


Figure 2. Reaction orders with respect to ROH for the reactions of benzyl chloride with aniline in (A) CH_3OH–CH_3CN; (B) C_2H_5OH–CH_3CN; (C) 2-C_3H_7OH–CH_3CN.

The data are in agreement with the termolecular "push-pull" mechanism proposed by Swain for nucleophilic substitutions[16] and provide a unitary explanation for the reaction mechanism in protic and aprotic solvents, notwithstanding the apparent difference in the reaction order (eq 7).



$$\underset{\text{nucleophile}}{C_6H_5NH_2}\cdots\underset{\substack{|\\ C_6H_5 \\ \text{substrate}}}{CH_2}\cdots Cl\cdots\underset{\text{electrophile}}{HOR} \qquad (7)$$

nucleophile substrate electrophile

In the mixture ROH–CH_3CN, in the concentration range 100–70% ROH, used to calculate the order with respect to ROH, the reaction order with respect to aniline is 1. The order with respect to aniline was measured in the concentration range 0–100% CH_3OH–CH_3CN. Table III lists the order with respect to aniline, the rate constants, and the activation parameters. This order, calculated by the initial rates method,[17] is 1 up to 40% CH_3OH; on increasing the CH_3CN percentage, the apparent order increases, and is 2 in 100% CH_3CN. The catalysis of nucleophile (in the concentration range 0.25–1.0 mol L^{-1}) becomes effective below 5 mol L^{-1} of methanol.

This trend is represented in eq 8, where methanol- and aniline-catalyzed reactions are shown:

Table III. Orders with Respect to Aniline (*n*), Rate Constants at 30 °C, and Activation Parameters for the Reactions of Benzyl Chloride with Aniline[a] in CH_3OH–CH_3CN Mixtures

CH_3OH Vol %	CH_3OH Mol L^{-1}	*n*	$10^5 k_2$, L mol^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}
100	24.7	1.0	5.15	14.3	−31.2
90	22.2	1.0	4.68	13.4	−34.4
80	19.8	1.0	4.25	12.0	−39.2
70	17.3	1.0	3.73	10.4	−44.7
60	14.8	1.0	2.93		
40	9.89	1.0	1.86		
20	4.94	1.2			
10	2.47	1.4			
5	1.24	1.6			
0	0.00	2.0	1.37[b]	8.7	−52.0

[a] Reagent concentrations: benzyl chloride, 0.02 mol L^{-1}; aniline, 0.25–1.0 mol L^{-1}. [b] k_3 value in acetonitrile (L^2 mol^{-2} s^{-1}): ref 5a.

$$C_6H_5CH_2Cl + C_6H_5NH_2 \xrightarrow[k'_3[C_6H_5NH_2]]{k_3[CH_3OH]} \text{products} \qquad (8)$$

Experimental support for the proposed catalytic mechanism is provided by the kinetic experiments in pure acetonitrile for the reaction of benzyl chloride with *o*-phenylendiamine (OPDA). In this nucleophile, in fact, both amino groups can react with the substrate exerting an intramolecular catalysis, and the predicted reaction order with respect to the nucleophile is 1. The geometry of the transition state (Figure 3) does not exclude this internal catalysis.

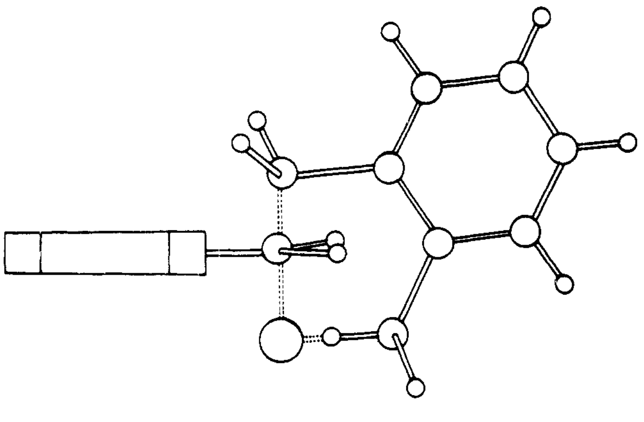


Figure 3. Geometry of the transition state for the reaction of benzyl chloride with *o*-phenylenediamine.

Experimental results confirmed the above hypothesis: the order with respect to OPDA, calculated by the initial rates method, is very close to 1.[18]

Experimental Section

Starting Materials. Benzyl chloride and aniline, commercially available samples, were distilled before use. The solvents (Carlo Erba RP) were used without further purification.

Kinetic Procedure. Rate measurements were done conductometrically by continuous titration of the acid produced with 0.1 M sodium hydroxide, following the procedure already described.[19] The reagent concentrations were 0.002 mol L^{-1} for the benzyl chloride and 0.1–1.0 mol L^{-1} for the aniline. Pseudo-first-order rate constants (k_{obsd}, s^{-1}) were obtained from the slope of conventional plots of log $(a - x)$ vs. time, calculated by the least squares method. The estimated precisions were ±5% for k_{obsd}, ±0.5 kcal mol^{-1} for $\Delta H^{\ddagger}$, and ±3 cal mol^{-1} K^{-1} for $\Delta S^{\ddagger}$ values.

Reaction Product. Benzyl chloride (0.05 mol) and aniline (0.11 mol) in the same solvents used for the kinetic runs were allowed to react at 50 °C for 2–4 h, depending on the reaction rate. Solvent was evaporated, and then the residue treated with anhydrous ether; the solution was separated from the anilinium chloride, insoluble in ether, and evaporated. The residue was crystallised from light petroleum–*N*-benzylaniline, yield ca. 90%, mp 36–37 °C.[5,20]

Registry No.—Benzyl chloride, 100-44-7; aniline, 62-53-3.

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(18) Calculated on keeping constant the benzyl chloride concentration (0.02 mol L^{-1}) and varying the OPDA one (0.2–1.0 mol L^{-1}) [log V_0, log [OPDA]: −6.54, −0.644; −6.20, −0.312; −5.87, −0.099; −5.76, 0.00]. The slope of the linear plot is 1.2 ($r = 0.996$; $s = 0.08$).
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