G. Reaction with Palladium on Carbon. Indoline (0.18 g, 1.5 mmol) was dissolved in 3 ml of water containing hydrochloric acid and the pH was adjusted to approximately 2. Palladium on carbon (0.3 g, 0.3 mg-atom) was added and the mixture was refluxed under nitrogen for 24 h. The mixture was then filtered, extracted with benzene, and treated with picric acid yielding indole picrate, 0.07 g (12% yield).

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Registry No.—Diethylamine, 109-89-7; triethylamine, 121-44-8; palladium dichloride, 7647-10-1; gold trichloride, 13453-07-1.

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London Force and Related Coulombic Interactions in the Displacement Reaction with Substituted Benzyl Chlorides

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The reaction rate constants for the displacement reactions with ortho- and para-substituted benzyl chlorides (CH_3, Cl, Br, and I) and the nucleophiles, MeO^-, PhS^-, and I^-, are presented. After accounting for the electrical effects of the substituents, all the trends in the values of the k_o:k_p rate ratios are best explained by considering two opposing factors operating in the transition state structure, steric effects, and London and related coulombic interactions between the nucleophiles and the ortho substituents.

London forces and related coulombic interactions have long been recognized as factors affecting equilibria and reaction rates.[1] Bunnett,[2] in a theoretical paper, suggested the operation of London forces in several bimolecular nucleophilic reaction series. He attributed the enhancement of reaction rate to London forces when the transition state structure is such as to bring highly polarizable groups close to one another. Bunnett and Reinheimer[3] estimated these forces in the reaction of the *o*-bromo- and *o*-methylbenzyl chlorides with the nucleophiles, MeO^-, PhS^-, and I^-. Sisti,[4] simultaneously with Reinheimer,[5] offered a new method of comparing the rates from that of Bunnett.[3] Reinheimer[5] examined the *o*-CH_3:*p*-CH_3 and *o*-Br:*p*-Br reaction rate ratios of benzyl chlorides with the same nucleophiles and obtained a better correlation of theory and experimental results than Bunnett.[3] He demonstrated that calculations of the magnitude of London forces operating in the transition state indicated that the differences in the rate ratios with MeO^-, PhS^-, and I^- for a given substituent may be assigned to these forces. However, it was pointed out by Sisti[4] that comparison of the *o*-CH_3:*p*-CH_3 and *o*-Br:*p*-Br rate ratios with any given nucleophile did not show the trends expected from London interactions alone, i.e., charged nucleophiles invariably gave higher ortho:para rate ratios with the less polarizable methyl group than with the more polarizable bromo group.

This paper reports the results of studies of the reaction of the nucleophiles MeO^-, PhS^-, and I^- with other ortho- and para-substituted benzyl chlorides. The purpose of the study was to determine if the trends still persist in the rate ratios and to discuss their possible origins.

Results

The reaction rate constants for the nucleophilic displacement of chloride from the ortho- and para-substituted benzyl chlorides are presented in Table I. Comparison of the results with the literature shows moderate to good agreement. Some comparisons are presented in Table I. We have confidence in our results since VPC analysis of the benzyl chlorides indicated that they were at least 99%pure. Also, the reaction rates of the nucleophiles with benzyl chloride were measured and only when found to be in acceptable agreement with the literature values were the analytical methods applied to the kinetic determinations for the substituted benzyl chlorides. The observed rate constants for the lithium methoxide runs are composites of the methoxide and solvolysis reactions. Thus, the rate constants presented in Table I are those which have been corrected for solvolysis by the method of Bunnett.[3]

Discussion

It will first be demonstrated that the trends in the k_o:k_p values (Table II) for a given ortho substituent with different nucleophiles and for any given nucleophile with different ortho substituents cannot be explained from consideration of the polar and steric effects of the substituents. A new consideration will be suggested which can, together with steric effects, satisfactorily explain the trends in the k_o:k_p values.

The polar effect for a substituent will be identical from the para and ortho positions and will cancel in the ratio, k_o:k_p, if the susceptibility constants, ρ and ρ^*, are identical. The equivalence of ρ and ρ^* has been observed to be generally true.[6] Also, the equivalence of σ_p and σ^*, a property confirmed

Table I. Rate Constants for Reactions of Substituted Benzyl Chlorides at 20 °C ($k_2 \times 10^5$ l./mol s)

Nucleophile/solvent		Substituents CH$_3$	Cl	Br	I
LiOMe/MeOH	*p*-	2.70[a]	1.74	1.66[b]	1.60
	o-	3.58[c]	1.41[d]	1.37[c]	1.35[d]
LiSPh/MeOH	*p*-	2930[e]	3300	3500[f]	3460
	o-	7120[c]	3960[d]	3860[c]	4650[d]
NaI/Me$_2$CO[g]	*p*-	40.2[h]	78.0[i]	85.7[j]	81.7[k]
	o-	321[c]	146[d,l]	156[c,l]	153[d,l]
MeOH[m]	*p*-	6.53[n]	1.85	2.88[o]	3.01
	o-	15.6[p]	1.17	1.21[q]	1.36

[a] Average of two runs; extrapolated value from data in ref 5, 2.63×10^{-5}. [b] Extrapolated value from data in ref 5, 1.54×10^{-5}. [c] Value obtained by extrapolation from data in ref 3. [d] Value obtained by extrapolation to 20 °C from unpublished results of J. F. Bunnett, W. Greizerstein, D. J. McLennan, and A. A. Shiragian. [e] Average of two values; extrapolated value of 2770×10^{-5} from data in ref 5. [f] Average of two runs; extrapolated value of 3390×10^{-5} from data in ref 5. [g] For the reactions with NaI the rate constants were also (see Experimental Section) obtained from the slopes of the plots of $1/[I^-]$ vs. time. Linear plots to about 40% reaction were obtained. Beyond approximately 40% reaction the observed rates generally decreased until equilibrium was attained. All rate constants with iodide, therefore, were determined from the data obtained between 5 and 40% reaction. The concentrations of NaI employed were between 0.03 and 0.05 M.[3,5,20,d] [h] Average of two runs; extrapolated value of 38.4×10^{-5} with NaI in acetone from data in ref 5. [i] A value of 77.7×10^{-5} with KI in acetone at 20 °C from ref 20. [j] A value of 86.6×10^{-5} with KI in acetone at 20 °C from reference in *i*. [k] A value of 82.8×10^{-5} with KI in acetone at 20 °C obtained from reference in *i*. [l] Value was in good agreement with the one obtained in KI in acetone at 20 °C by reference in *i*. [m] k, in $s^{-1} \times 10^8$. [n] A value of 6.54×10^{-8} obtained by extrapolation of data in ref 5. [o] An extrapolated value of 2.94×10^{-8} from ref 5. [p] An extrapolated value of 15.9×10^{-8} from ref 3. [q] An extrapolated value of 1.23×10^{-8} from ref 3.

Table II. Reaction Rate Ratios for Substituted Benzyl Chlorides at 20 °C

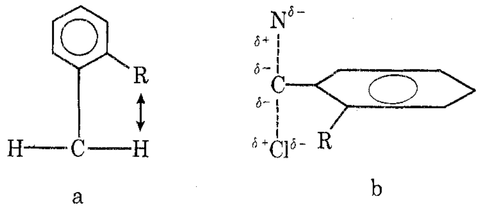
Nucleophile (N)	Solvent	k_o:k_p CH$_3$	Cl	Br	I
MeO$^-$	MeOH	1.33[a]	0.81	0.83[b]	0.84
PhS$^-$	MeOH	2.43[c]	1.20	1.10[d]	1.35
I$^-$	Me$_2$CO	8.00[e]	1.87[f]	1.82[f]	1.87[f]

[a] A value of 1.43 obtained by ref 5. [b] A value of 0.84 obtained by ref 5. [c] A value of 2.61 obtained by ref 5. [d] A value of 1.18 obtained by ref 5. [e] A value of 8.16 obtained by ref 5. [f] Values for the k_o:k_p rate ratios for the substituents Cl, Br, and I with KI in acetone at 20 °C obtained from data in ref 20 were 1.88, 1.69, and 1.85, respectively.

by Taft,[6] offers further support that the k_o:k_p rate ratio should cancel the total polar effect. Table II, composed from the kinetic data in Table I, presents the k_o:k_p ratios for the substituents with each of the nucleophiles employed.

It must also be shown that the trends in the k_o:k_p rate ratios cannot be explained by the steric consideration between the ortho substituent and the nearest benzyl hydrogen (Chart I).

Chart I



R = CH$_3$, Cl, Br, and I; N = MeO$^-$, PhS$^-$, and I$^-$

Examination of the k_o:k_p rate ratios for different substituents with any given nucleophile reveals that the steric effect cannot be solely responsible for their trends. It is observed (Table II) that with any given nucleophile the k_o:k_p values for the methyl group are higher than the values for the bromo group of equal size[3] and higher than the values for the smaller chloro group. The trends in the k_o:k_p values for the Cl, Br, and I groups with any given nucleophile are not to be expected from consideration of their steric effects alone. Also note that most k_o:k_p rate ratios are >1 and increase from MeO$^-$ to I$^-$ for a given ortho substituent. These values and trends are also not to be expected from the steric consideration alone.[5] Solvent effects would obviously cancel in the k_o:k_p ratios for a given substituent with different nucleophiles if all the data were available in the same solvent. Since this is not the case, one must consider what changes would occur in the value of the ratio $(k_o:k_p)_{I^-}$ with a change in solvent (acetone to methanol). The changes in reaction rate which accompany a change in the dielectric constant of the solvent would be incorporated in the numerator and denominator of the preceding ratio and thus its value should remain essentially unchanged.[7]

A suggested explanation for the trends in the k_o:k_p rate ratios for a given ortho substituent with different nucleophiles and for different ortho substituents with a given nucleophile is that favorable London and related coulombic interactions between the nucleophile and the ortho substituent (and between ortho substituent and leaving chloride) are offsetting the steric effect in varying amounts.[8]

The polarizabilities of the nucleophiles (α_N) are suggested by the values for the ions, H-O$^-$ 1.89, H-S$^-$ 5.28, and I$^-$ 7.10 (all units cm$^3 \times 10^{-24}$); the polarizabilities of the ortho substituents ($\alpha_{o\text{-sub}}$) are CH$_3$ 2.19, Cl 2.28, Br 3.34, O-R 0.64, and I 5.11.[9] The model for the transition state structure is one in which the entering and departing groups are on a line perpendicular to the plane of the benzene ring (Chart I). Pearson's[10] discussion of polarizability leads to a reasonable inference that a dipole should exist between N and C and Cl and C in the transition state structure (Chart Ib). The essence of the discussion[10] was that a nucleophile of high polarizability can more effectively polarize its bonding electrons in the direction from N → C, thereby permitting better electrostatic interaction with a minimum of electrostatic repulsion between the remaining electrons on N and the covalent electrons on C. Thus, the more polarizable nucleophile, N, will have the larger dipole moment, μ ($\mu = qr$, q is the charge and r the distance between the charges) in the transition state structure since r will be larger (Chart Ib).

When considering the trends in the k_o:k_p rate ratios for a given ortho substituent the steric effect between the given ortho substituent and the benzyl hydrogen (Chart I) should be the same for each of the nucleophiles. Three coulombic forces operating in the transition state can account for the trends in the k_o:k_p values increasing toward the more polarizable nucleophile with a given ortho substituent (Table II).

The coulombic interaction, dipole$_N$–induced dipole$_{o\text{-sub}}$ ($F \propto \mu_N{}^2\alpha_{o\text{-sub}}/r^7$), between the nucleophile and ortho substituent should be favorable and become larger as the α_N increases since the more polarizable nucleophile should have the larger μ (see above and Chart Ib). The London interaction, induced dipole$_{o\text{-sub}}$–induced dipole$_N$ ($F \propto \alpha_N\alpha_{o\text{-sub}}/r^7$), between the nucleophile and ortho substituent should be favorable and increase as the α_N becomes larger. Lastly, the ion$_N$–induced dipole$_{o\text{-sub}}$ ($F \propto q_N\alpha_{o\text{-sub}}/r^5$) should be favorable but it is assumed that this force is the same for each of the nucleophiles.[11,12]

The trends in the k_o:k_p values (Table II) for a given nucleophile with the different halo substituents can be explained by considering two opposing factors present in the transition state, namely, the steric effect (*o*-halo group and benzyl hydrogen), and the London and related coulombic forces. Specifically, the increase in the steric interactions (Cl to I) is compensated for, in varying amounts, by an increase in the coulombic forces (London, dipole$_N$–induced dipole$_{o\text{-sub}}$, and ion$_N$–induced dipole$_{o\text{-sub}}$) caused by the increase in the $\alpha_{o\text{-halo group}}$ from Cl to I.[13]

Further examination of the k_o:k_p rate ratios for any given nucleophile with different ortho substituents shows that the values for the less polarizable methyl group are invariably higher relative to the more polarizable halogens. Contrary trends would have been expected from consideration of coulombic interactions together with the varying steric effect of the methyl and halo groups since the methyl group is less polarizable and larger than the chloro group and is less polarizable and equal in size to the bromo group.[3] Indeed, one would have expected the k_o:k_p values to be higher for the halogens relative to the methyl group[14] (with the possible exception of the larger and more polarizable iodo group). Three additional coulombic forces are deemed responsible for the higher values for the methyl group because of the favorable dispositions of the *o*-methyl group dipole ($\leftarrow\!\!\!+$ CH$_3$) with the dipole and with the charge of the nucleophile. These favorable dispositions do not occur with the dipole of the *o*-halo group ($+\!\!\!\rightarrow$ X) (Chart Ib). The specific forces involved are believed to be dipole$_N$–dipole$_{\leftarrow\!\!+\, o\text{-CH}_3}$ ($F \propto \mu^2{}_N\mu^2{}_{\leftarrow\!\!+\, o\text{-CH}_3}/r^7$) which should also increase from MeO$^-$ to I$^-$ since μ_N should become larger with an increase in α_N; dipole$_{\leftarrow\!\!+\, o\text{-CH}_3}$–induced dipole$_N$ ($F \propto \mu^2{}_{\leftarrow\!\!+\, o\text{-CH}_3}\ \alpha_N/r^7$) which should also increase as the α_N increase from MeO$^-$ to I$^-$; and the important intermediate range force, ion$_N$–dipole$_{\leftarrow\!\!+\, o\text{-CH}_3}$ ($F \propto q_N\mu^2{}_{\leftarrow\!\!+\, o\text{-CH}_3}/r^5$), which is presumed to be the same for each nucleophile.[12,15,16]

In summary, all the trends in the k_o:k_p rate ratios seem best explained by invoking the steric consideration together with offsetting London and related coulombic interactions between the nucleophile and the ortho substituent. These coulombic interactions vary in magnitude with α_N and $\alpha_{o\text{-sub}}$. Three additional forces are involved when the dispositions of the dipole$_{o\text{-sub}}$ with the dipole and with the charge of the nucleophile[16] are favorable. Specifically, the London, dipole$_N$–induced dipole$_{o\text{-sub}}$, and ion$_N$–induced dipole$_{o\text{-sub}}$[12] coulombic interactions increase with a given ortho substituent as the α_N increases, and they also increase with any given nucleophile as the $\alpha_{o\text{-sub}}$ increases. Three additional interactions, dipole$_N$–dipole$_{o\text{-CH}_3}$, dipole$_{o\text{-CH}_3}$–induced dipole$_N$, and ion$_N$–dipole$_{o\text{-CH}_3}$ favoring the methyl group, are deemed responsible for the higher k_o:k_p values for the less polarizable methyl group relative to the more polarizable halogens.[17] All of the coulombic forces discussed can be visualized from the model of the transition state structure (Chart Ib) which assumes the presence of a dipole between N and C and C and Cl.

Experimental Section[18]

Preparation and Purification of Materials. The *p*-chloro-, *p*-bromo-, and *p*-methylbenzyl chlorides were commercially available and were purified by fractionation[18] or by repeated recrystallizations: *p*-chlorobenzyl chloride, bp 59 °C (0.6 mm) (lit.[19] bp 222 °C), mp 28.5–29 °C (lit.[20] mp 29 °C); *p*-bromobenzyl chloride was recrystallized from petroleum ether, mp 38 °C (lit.[5] mp 38–39 °C); *p*-methylbenzyl chloride, bp 42 °C (0.5 mm) [lit.[5] bp 68.5–69 °C (6 mm)].

p-Iodobenzyl chloride was prepared as follows: *p*-iodotoluene was brominated according to the procedure of Goerner and Nanetz.[21] The crude benzyl bromide was then hydrolyzed with 50% aqueous acetone by refluxing for 60 h. The *p*-iodobenzyl alcohol obtained upon cooling was recrystallized (three times) from petroleum ether, mp 72 °C (lit.[20] mp 71–72 °C). The alcohol was then converted to the *p*-iodobenzyl chloride according to the procedure of Newman.[22] The chloride was recrystallized (two times) from petroleum ether, mp 53 °C (lit.[20] mp 53 °C).

Acetone, reagent grade, was treated with potassium permanganate under reflux (3 h), filtered, and distilled from anhydrous calcium oxide. Methanol, reagent grade, was distilled from sodium methoxide. The sodium iodide, reagent grade, was dried at 110 °C for 1 h prior to use. Lithium methoxide solutions were prepared by dissolving clean lithium metal in purified methanol and they were standardized against potassium hydrogen phthalate to a phenolphthalein end point. Lithium thiophenoxide solutions were prepared by dissolving thiophenol [reagent grade, bp 168–169 °C (lit.[23] bp 169 °C)] in standard solutions of lithium methoxide. In all the thiophenoxide runs a slight excess (10%) of free thiophenol was maintained. The silver nitrate and mercuric nitrate solutions were standardized against weighed amounts of sodium chloride. The bromophenol blue–diphenylcarbazone indicator was prepared by the method of Swain and Langsdorf.[24]

Evaluation of Rate Constants. With Lithium Methoxide. Runs at 20 °C were carried out in a glass-stoppered volumetric flask in a water bath regulated to ±0.05 °C. Initial concentrations of methoxide and substrate in methanol were equal in all cases at 0.050 M. The benzyl chloride was weighed into a 25-ml volumetric flask and dissolved in methanol up to the mark. The lithium methoxide solution was prepared and standardized as already mentioned. The concentrations of the nucleophile and substrate solutions were such that when 10 ml of organic chloride (1.00 M) and 50 ml of methoxide ion (0.200 M) solutions were pipetted into a 250-ml volumetric flask containing 140 ml of methanol it gave an overall concentration of 0.050 M in nucleophile and substrate. Ten-milliliter aliquots were taken (at different time intervals) and released into a 250-ml separatory funnel containing 80 ml of water, 5 ml of 0.2 N nitric acid, and 100 ml of ether. The aqueous layer was separated and titrated for chloride ion content using mercuric nitrate and 5 drops of bromophenol blue–diphenylcarbazone indicator as described by Swain.[24]

Individual apparent second-order rate constants (k_{app}) were calculated by substitution of the data obtained at each time interval into the second-order rate equation. The average k_{app} was obtained from a minimum of 12 individual k_{app} values calculated for each substrate, with no one k_{app} value deviating from another by more than 2%. All reactions were followed to 60–80% of the half-lives. The solvolytic rate constants (k_1) were determined at 20 °C by the same procedure described above. The solvolytic reactions were followed to 35–50% of the half-lives.

Rate constants observed (k_{app}) for the lithium methoxide runs are composites of the methoxide and solvolysis reactions. To correct the observed rate constants (k_{app}) for solvolysis the quantity $k_1/[\mathrm{RCl}]_0$ is substracted from each according to Bunnett.[3] The k_2 values so obtained are given in Table I.

With Lithium Thiophenoxide. Initial concentrations of all benzyl chlorides and of lithium thiophenoxide were 0.050 M, and there was free thiophenol in excess (10%) (under N$_2$). Ten-milliliter samples were taken out by means of a fast delivery syringe and quenched by discharging into a 250-ml separatory funnel containing 20 ml of 0.1 N nitric acid, 80 ml of water, and 100 ml of ether. The ether layer was rinsed with water and the rinse water was combined with the aqueous layer. Five drops of concentrated nitric acid was then added, followed by the addition of 5 ml of 30% hydrogen peroxide. The next day the chloride ion content was determined potentiometrically.

Individual second-order rate constants, k_2, were calculated as described above. The average k_2 was obtained from a minimum of eight individual k_2 values for each substrate with no one k_2 value deviating from another by more than 4%. The reactions were followed to 55–65% of the half-lives. The values so obtained (at 20°) are given in Table I.

With Sodium Iodide. Initial concentrations of iodide ion and substrate in acetone were equal in all cases (0.050 M). Ten milliliters each of iodide and of substrate solutions were pipetted into 180 ml of acetone at 20 °C to yield an overall concentration of 0.050 M in each reactant. The reaction was quenched by discharging 10 ml of the reaction mixture into a 250-ml separatory funnel containing 80 ml of water and 100 ml of ether. The ether layer was extracted twice with water and the water extracts were combined. The aqueous layer was then titrated potentiometrically for iodide ion content. Occasionally the iodide ion was checked with the chloride ion liberated, and excellent agreement was obtained.

Individual second-order rate constants, k_2, were calculated as described above. The average k_2 was obtained from a minimum of nine individual k_2 values for each substrate with no one k_2 value deviating from another by more than 3%. The reactions were followed to 55–65% of the half-lives. The values so obtained are presented in Table I.

Reaction Products. Adequate representative product studies were done by Bunnett[3] and by Reinheimer[5] with various ortho- and para-substituted benzyl chlorides and each of the nucleophiles employed.

Registry No.—LiOMe, 865-34-9; LiSPh, 2973-86-6; NaI, 7681-82-5; MeOH, 67-56-1; *p*-methylbenzyl chloride, 26519-66-4; *p*-chlorobenzyl chloride, 104-82-5; *p*-bromobenzyl chloride, 589-17-3; *p*-iodobenzyl chloride, 54589-53-6; *o*-methylbenzyl chloride, 552-45-4; *o*-chlorobenzyl chloride, 611-19-8; *o*-bromobenzyl chloride, 578-51-8; *o*-iodobenzyl chloride, 59473-45-9.

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(7) One may argue that the k_o:k_p rate ratios for I^- may be altered due to the solvent change indicated and thus the trends in the values of the k_o:k_p rate ratios for a given substituent with different nucleophiles may be altered so that no need arises for the consideration of any new factor(s). However, the trends in the k_o:k_p values with different substituents for a given nucleophile (examine the table horizontally) in a given solvent cannot be explained because of a solvent change or steric and electrical considerations (see also ref 8).

(8) Recently, M. Charton [*J. Am. Chem. Soc.*, **91**, 6649 (1969)] has offered evidence that the electrical effect of a substituent from the ortho and para positions is not the same and, therefore, it may be reasonably argued that the increasing trends in the k_o:k_p rate ratios ($MeO^- \rightarrow I^-$) for a given substituent can be attributed to the different responses of each nucleophile to this electrical difference, the latter, instead of coulombic interactions between the nucleophile and the ortho substituent, being the factor offsetting the steric effect. However, two arguments can demonstrate that all the observed trends in the k_o:k_p rate ratios cannot be explained because of this electrical difference. First, since it is known that PhS^- and I^- respond more[5,20] favorably to the electron-withdrawing para halogens (relative to hydrogen) than to the electron-donating *p*-methyl group (relative to hydrogen), the k_o:k_p rate ratios for the chloro and bromo groups should be larger than for the methyl group as a result of steric considerations and any electrical difference from the two positions (the substituent's electrical effect is assumed greater at the ortho position). The latter conclusion is contrary to the experimental results. Second, since any electrical difference between *o*-Cl and *p*-Cl, *o*-Br and *p*-Br, and *o*-I and *p*-I groups should be essentially the same, $(\sigma_p - \sigma^*_o)_X \simeq$ constant (ref 6, p 591), the response of a given nucleophile to the same electrical difference should be identical and is, therefore, incorporated in each of the k_o:k_p values to the same extent. The effect then of any electrical difference from the two positions on the k_o:k_p values for the different halo groups with a given nucleophile (examine Table II horizontally) has been cancelled or accounted for.

(9) Values taken from Landolt-Bronstein and J. A. A. Ketelaar, "Chemical Constitution", 2d ed, American Elsevier, New York, N.Y., 1958, pp 91 and 201.

(10) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

(11) These interactions should also occur between the leaving group and a given ortho substituent. Since these forces should occur in the ground state and the transition state, their effect on the k_o:k_p rate ratio will be determined by whether the difference favors the transition state or the ground state. The difference should favor the transition state because both μ_{C-Cl} and α_{Cl} should be larger in the transition state. However, whatever the increment in the k_o:k_p rate ratio as a result of these interactions, it should be the same for each nucleophile with a given ortho substituent.

(12) It is difficult to qualitatively determine the relative centers of negative charge, q_N, in the transition state involving nucleophiles of different polarizabilities and different $N \cdots C$ bond lengths and, therefore, difficult to assess the relative distances, *r*, between q_N and the ortho substituent. This force is thus assumed to be essentially the same for each nucleophile with a given ortho substituent (*r* is essentially the same for each nucleophile).

(13) As mentioned in ref 11, these interactions also obtain between the leaving group and *o*-halo substituents and should occur in the ground state as well as the transition state. However, with different $\alpha_{o\text{-sub}}$ the magnitude of the difference favoring the transition state (see ref 11) will not be the same for any given nucleophile. The difference favoring the transition state should become larger as the $\alpha_{o\text{-sub}}$ increases and will also offset the increasing steric effect (Cl to I).

(14) Similarly, the same conclusion would result from consideration of the varying steric effect of the methyl and halo groups together with the coulombic interactions (thus far discussed) between the leaving group and *o*-halo and *o*-methyl groups. The difference between the leaving group–ortho-substituent interactions in the ground state and transition state favors the latter and should become larger as the $\alpha_{o\text{-sub}}$ increases (see ref 11 and 13).

(15) These additional interactions should also occur between the leaving group and the *o*-methyl group. Since these additional forces should occur in the ground state and the transition state, their effect on the k_o:k_p rate ratio will be determined by whether the difference favors the transition state or the ground state. The difference should favor the transition state because both μ_{C-Cl} and α_{Cl} should be larger in the transition state. However, whatever the increment in the k_o:k_p rate ratio as a result of these interactions, it should be the same for each nucleophile.

(16) Unpublished results with neutral nucleophiles of low polarizabilities (pyridine and diethyl sulfide) lend support to the operation of these additional forces involving the *o*-methyl dipole and the dipole and charge of the nucleophile. The neutral nucleophiles gave values for the k_o:k_p rate ratios which were completely opposite to those herein, i.e., the values were higher for all the halo groups relative to the methyl group. The force deemed responsible is the intermediate range, $\text{ion}_N\text{–dipole}_{o\text{-halo group}}$, which in this case favors the halogens because of the favorable disposition of its dipole (+→ X) to the positive charge generated in the transition state with neutral nucleophiles. With nucleophiles of low polarizability the $\text{dipole}_N\text{–dipole}_{o\text{-}CH_3}$ and $\text{dipole}_{o\text{-}CH_3}\text{–induced dipole}_N$ interactions will be small (μ_N and α_N small) compared to the $\text{ion}_N\text{–dipole}_{o\text{-halo group}}$.

(17) The model for the transition state structure used for all the substituents throughout the discussion may be considered inadequate since no consideration was given to loose and tight transition state structures [A. J. Parker, *Chem. Rev.*, **69**, 1 (1969)]. Including consideration of variations in looseness and tightness of the transition state structures, the favorable coulombic interactions discussed together with the steric effect (benzyl hydrogen and ortho substituent, Chart Ia) can still explain all the trends in the k_o:k_p rate ratios. Whether the electrical effect of the substituent promotes a loose (methyl group) or tight (halo groups) transition state structure its effects will cancel in the k_o:k_p rate ratio for a given substituent with a given nucleophile. However, the looseness or tightness of the transition state structures should vary with the nucleophile used for a given substituent. This change in looseness or tightness with the nucleophile employed will only affect the size of the coulombic interactions between the different nucleophiles and a given ortho substituent (compared to the model used, Chart I) and not the trends expected from these interactions with the different nucleophiles and a given ortho substituent (no matter how the transition states differ in looseness or tightness for the three nucleophiles, the order of α and μ is I > PhS > MeO).[12] The coulombic forces between a given ortho substituent and the leaving group will not be the same for each of the nucleophiles[11] but will increase (compared to the model used, Chart I) as the looseness (methyl group) increases and as the tightness (halo groups) decreases in the transition state structure for the three nucleophiles since α_{Cl}, μ_{Cl}, and q_{Cl} would become accordingly larger. Since it is not obvious how the three nucleophiles vary in looseness or tightness for a given ortho substituent the trend for the latter increasing coulombic interactions with the nucleophiles cannot be indicated. The effect of the looseness or tightness of the transition state structure on the coulombic interactions between a given nucleophile with different ortho substituents must also be considered when comparing the k_o:k_p rate ratios for the methyl group (loose transition state structure) with those for the halo groups (tight transition state structures). The loose transition state structure would favor all the coulombic interactions between the *o*-methyl group with both a given nucleophile and leaving chloride even more than in the model employed (Chart I) because in the loose transition state structure the *q*, α, and μ for any given nucleophile and for the leaving chloride would be larger than either in the model used or in the tight transition state structure. In the k_o:k_p rate ratios for the halogen compounds with a given nucleophile the tightness of the transition state structures will result in a decrease in q_N, α_N, and μ_N (compared to the model employed). The latter will cause a lessening in the size of the increasing coulombic forces[13] ascribed to offsetting the increasing steric effect (Cl to I).

As assumed steric interaction between the nucleophile and ortho substituent should make the transition state structure looser for the *o*-methyl compound compared to the transition state structure for the *p*-methyl compound and the transition state structures for the *o*-halo compounds not as tight compared to the transition state structures for the *p*-halo compounds (reference above). Arguments can be presented to show that if the difference in looseness (methyl group) and the difference in tightness between the transition state structures for the ortho compound and para compound is assumed the favorable factor offsetting the steric effect, it cannot account for all the trends in the k_o:k_p rate ratios.

(18) All melting points and boiling points are uncorrected. All liquid benzyl chlorides were distilled using a 60 cm helix column. All organic compounds were used within 24 h after purification. Each of the benzyl chlorides was tested for purity by VPC and were thereby shown to be at least 99% pure.

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