

as zero in setting up the determinant. For purposes of evaluating the related exchange integrals, they were not taken as zero.

The resonance or exchange integrals, the non-diagonal elements, were taken as zero for all orthogonal adjacent p-orbitals and all nonadjacent orbitals, and were taken as 1.00 (in units of beta) between all adjacent p-orbitals in the same plane except for the adjacent orbitals 13-14, 14-15 and 15-16. Because in the latter cases the hybridizations and interatomic distances differ from the usually encountered sp^2 - sp^2 interaction, a correction was made. The method of Mulliken²⁷ was used to determine the overlap of the adjacent orbitals 13-14, 14-15 and 15-16 in I. The interatomic distance 13-14 = 15-16 was taken as 1.34 Å, while the 14-15 distance was taken as 1.20 Å. From the tables,²⁷ $S_{13-14} = S_{15-16} = 0.273$ and $S_{14-15} = 0.338$.

The exchange integrals used in the determinants were

(27) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

evaluated by making use of the equation $(H_{1l}/H_{kl}) = (S_{1l}/S_{kl})(1 + S_{kl})/(1 + S_{1l})$, relating exchange to overlap integrals.²⁸ In this case, k and l were taken to refer to a pair of adjacent benzene carbon atoms; thus $H_{kl} = \beta$ and $S_{kl} = 0.247$. The values (in units of beta) of the exchange integrals obtained were $H_{13-14} = H_{15-16} = 1.08\beta$ and $H_{14-15} = 1.27\beta$. The molecular orbitals available for delocalization in X and XI (in terms of beta) are indicated in Fig. 2.

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(28) M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, **76**, 18 (1954); F. Wilcox, Jr., S. Winstein and W. G. McMillan, *ibid.*, **82**, 5450 (1960).

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY, UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, N. C.]

ortho Effects in Reactions of Nucleophiles with Benzyl Chlorides¹

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Rates of reactions of LiOCH_3 , LiSC_6H_5 , KI and $(\text{CH}_3)_3\text{N}$ with benzyl chloride and its *o*-methyl and *o*-bromo derivatives have been measured; ΔH^\ddagger and ΔS^\ddagger values have been determined. The reagents of higher polarizability (I^- and $\text{C}_6\text{H}_5\text{S}^-$) are especially reactive, relative to CH_3O^- , with substrates carrying *ortho* substituents of higher polarizability. London interactions in the transition state are tentatively judged to be responsible. Experimental $\Delta\Delta\Delta F^\ddagger$ values agree rather well with $\Delta\Delta\Delta H^\ddagger$ values reckoned from London theory. In the case of trimethylamine reagent, steric interaction with *ortho* substituents obscures the effects of London forces.

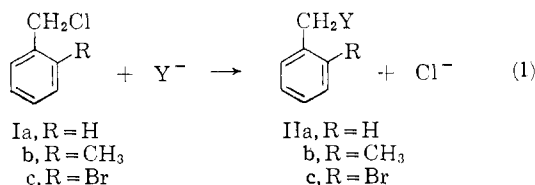
An earlier paper⁴ called attention to an interesting relationship: nucleophiles of high polarizability are, relative to those of low polarizability, especially reactive with substrates carrying high-polarizability substituents near the reaction site. This trend was discerned in the reactions of $\text{C}_6\text{H}_5\text{S}^-$ (*vs.* CH_3O^-) with 1-halo-2,4-dinitrobenzenes (1-substituent varied),⁵ of Br^- (*vs.* Cl^-) and I^- (*vs.* Br^-) with alkyl halides (displaced halogen varied), and in the reactions of $\text{C}_6\text{H}_5\text{S}^-$ or I^- (*vs.* CH_3O^-) with α -substituted methyl halides (α -substituent or displaced halogen varied).⁴ This regularity was then sought and found in the reactions of $\text{C}_6\text{H}_5\text{S}^-$ (*vs.* CH_3O^- or OH^-) with 2-substituted 1-fluoro-4-nitrobenzenes (2-substituent varied).⁶

This relationship is thought to represent reduction of transition state free energy by London forces acting between attacking nucleophile and nearby substrate substituents.^{4,6} On that view, the energetic advantage should be proportional to the polarizabilities of the reagent and the substituent and inversely proportional to the sixth power of their distance of separation.⁷ Accordingly, this factor should be negligible in the initial

state where the reagent and substrate are widely separated, and should benefit the transition state the more as the polarizabilities of reagent and substituent are greater.

Spinner⁸ has also discussed London forces as a factor affecting nucleophilic displacement rates.

This paper describes the search for, and discovery of, this regularity in some $\text{S}_\text{N}2$ displacements in *o*-substituted benzyl chlorides (eq. 1). The nucleophiles concerned are the methoxide, thio-



phenoxide and iodide ions and the trimethylamine molecule. The *o*-substituents are hydrogen, methyl and bromine. We confess that, before experimental work was commenced, data already in the literature⁹ were extrapolated to a promise of success in this search.

Experimental

Benzyl chloride was a commercial product re-distilled through a good column; b.p. 61.9° (12 mm.).

o-Xylyl chloride was prepared by sulfuryl chloride chlorination of *o*-xylene.¹⁰ The *o*-xylene was purified by sulfonation, recrystallization of the sodium salt of the sulfonic acid, and

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(2) Brown University, Providence, R. I.

(3) On Research Leave from the College of Wooster, 1957-1958.

(4) J. F. Bunnett, *J. Am. Chem. Soc.*, **79**, 5969 (1957).

(5) J. F. Bunnett and W. D. Merritt, Jr., *ibid.*, **79**, 5967 (1957).

(6) J. D. Reinheimer and J. F. Bunnett, *ibid.*, **81**, 315 (1959).

(7) (a) K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953, pp. 198-201; (b) K. S. Pitzer, in "Advances in Chemical Physics," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1959, pp. 59ff.

(8) E. Spinner, *Austral. J. Chem.*, **13**, 218 (1960).

(9) Reference 4, Table IV.

(10) M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2142 (1939).

then desulfonation.¹¹ It had b.p. 67.7–68.0° (8–9 mm.), lit.¹³ b.p. 84° (14 mm.).

***o*-Bromobenzyl Chloride.**—*o*-Bromotoluene was brominated by the procedure of Goerner and Nametz.¹³ The reaction mixture was poured into water and heated three days at reflux. On cooling, *o*-bromobenzyl alcohol crystallized. It was thrice recrystallized from petroleum ether (90–100°); yield 58%, m.p. 79.5–81.5°. Treatment of this alcohol with thionyl chloride by Newman's procedure¹² furnished *o*-bromobenzyl chloride, b.p. 65.8–66.2° (4–5 mm.), in 60% yield; lit.¹⁴ b.p. 105–106° (12 mm.).

The benzyl chlorides were stored in a desiccator over calcium chloride and sodium hydroxide.

Trimethylamine, a commercial product, was purified by the method of Brown, *et al.*¹⁵ Trimethylamine hydrochloride: the Eastman Kodak white label product was recrystallized from chloroform and dried at 110° for 0.5 hour. **Acetone**: commercial analytical grade was dried over Drierite. **Potassium Iodide**: commercial analytical grade was dried at 110° for 3 hours. **Methanol**: Commercial analytical grade was dried over Drierite for at least 1 day, and then distilled from Drierite. **Lithium methoxide** solutions were prepared by dissolving clean lithium metal in purified methanol, and standardizing against potassium hydrogen phthalate; they were protected from the atmosphere by soda-lime drying tubes during storage.

Kinetic Measurements.—Reaction solutions were carefully prepared (at thermostat temperature) by standard procedures.

In lithium methoxide runs, initial concentrations of Ia, b or c and of LiOCH₃ were 0.0542 *M* except in two Ib runs where they were 0.0692 *M*. Aliquots (5 cc.) were withdrawn at recorded times and quenched in chilled beakers containing 20 cc. of 0.1 *M* nitric acid and 30 cc. of (chloride-free) U.S.P. ethyl ether. The chloride content of the aqueous layer was determined by potentiometric titration with silver nitrate. Rates of solvolysis in methanol were determined for Ib and Ic with use of virtually the same analytical procedure.

In lithium thiophenoxide runs, initial concentrations of Ia, b or c and of LiSC₆H₅ were 0.0585 *M*, and there was free thiophenol in excess. Samples (4.90 cc.) were taken by means of a fast-delivery pipet and quenched in chilled glass-stoppered erlenmeyer flasks which contained 20 cc. of 0.1 *M* nitric acid and 10 cc. of carbon tetrachloride. After shaking, the aqueous layer was separated and extracted with 30 cc. of ethyl ether; the ether layer was rinsed with water, and the rinse water was combined with the aqueous layer. Four or five drops of concentrated nitric acid and again of 30% hydrogen peroxide were added, and the next day the chloride content was determined by potentiometric titration.

In trimethylamine runs, initial concentrations of Ia, b or c and of trimethylamine were 0.0590 *M* and trimethylamine hydrochloride (0.00373 *M*) was also always present. Aliquots (5 cc.) were discharged into beakers containing 20 cc. of 0.1 *M* nitric acid and ca. 30 cc. of ether. The ether layer was washed twice with water, and the combined water layers titrated potentiometrically for chloride ion. Chloride ion released by the reaction was reckoned by subtracting the titer of a zero-time sample.

In potassium iodide runs, acetone was the solvent; the initial concentration of KI was 0.0271 and of the substrate 0.06–0.07 *M*. Aliquots (10 cc.) were pipetted into a quenching mixture of 20 cc. of water and 10 cc. of carbon tetrachloride. The aqueous layer was extracted thrice more with carbon tetrachloride, and the iodide ion content was determined by potentiometric titration. For one aliquot from each substrate, representing about 50% reaction, the titration was continued through the chloride ion end-point. The amount of chloride ion liberated checked excellently with the amount of iodide consumed.

All thermostat thermometers were calibrated *versus* one certified by the National Bureau of Standards.

Reaction Products. **Benzyl Chloride and Lithium Methoxide.**—Lithium metal (1.5 g.) was dissolved in 90 cc. of

methanol, 10 cc. of benzyl chloride was added, and the mixture was kept a week at 46°. The product was isolated by standard procedures. It had b.p. 168–169° (757 mm.), *d*₂₀²⁵ 0.960; the literature values¹⁶ for benzyl methyl ether are b.p. 170.5°, *d*₂₀²⁵ 0.9643.

Benzyl Chloride and Lithium Thiophenoxide.—The unused remains of several kinetic reaction solutions were poured into glacial acetic acid to which some 30% hydrogen peroxide was then added. The mixture was heated on the steam-bath for 1 hour. Benzyl phenyl sulfone, m.p. 145–147° (lit.¹⁷ 148°), was isolated by standard procedures.

***o*-Bromobenzyl Chloride and Lithium Thiophenoxide.**—Similarly, phenyl *o*-bromobenzyl sulfone, m.p. 94.5–96.0° (from dilute ethanol), was obtained.

Anal. Calcd. for C₁₃H₁₁BrO₂S: C, 50.17; H, 3.56. Found¹⁸: C, 50.09; H, 3.56.

Reaction of *o*-Chlorobenzyl Chloride in Methanol-*O*-D Solution.¹⁹—Methanol-*O*-D was prepared by combining 34.6 g. (0.33 g.) of methyl borate, 23 g. (1.15 moles) of deuterium oxide and 10.6 g. (0.1 mole) of anhydrous sodium carbonate, allowing the mixture to stand overnight at room temperature, heating it at reflux for 4 hours, and finally distilling the CH₃OD away from the residue.²⁰ The CH₃OD was dried by the magnesium method.²¹ *o*-Chlorobenzyl chloride (1.151 g., 0.00715 mole) and 5 cc. of a 1.55 *M* solution of sodium methoxide in CH₃OD were combined in a 10-cc. volumetric flask which was then filled to the mark with CH₃OD. After the reaction had been allowed to proceed at 50° for 2 hours, the solution was poured into 20 cc. of 0.16 *M* nitric acid and 20 cc. of benzene. The benzene layer was thrice washed with water. The solvent was evaporated and the residue distilled; b.p. 93.5–94° (17 mm.). The infrared spectrum, determined on a middle fraction, was identical with that of a normal sample of methyl *o*-chlorobenzyl ether; there was no indication of C–D bonds.

Treatment of Data.—The reactions of Ia, b and c with methanolic lithium methoxide are slow enough so that solvolysis is an appreciable side reaction. However, good linear plots of 1/(*a* – *x*) vs. *t* were obtained. Correction for solvolysis was made by a simple method derived as shown

$$dx/dt = k_1(a - x) + k_2(a - x)^2$$

$$\frac{dx}{(a - x)^2} = \left(\frac{k_1}{a - x} + k_2 \right) dt$$

As *x* → 0

$$\frac{dx}{(a - x)^2} = \left(\frac{k_1}{a} + k_2 \right) dt$$

It follows that *k*_{app} (the slope of the plot of 1/(*a* – *x*) vs. *t*) is, when the reaction has not progressed very far, approximately equal to *k*₂ (the true bimolecular rate coefficient) plus *k*₁/*a*; *k*₁ is the solvolysis rate coefficient. The *k*₂ values reported are *k*_{app} less *k*₁/*a*. Since *k*_{app} were based on 40–60% of reaction, the corrections are somewhat approximate. On the other hand, the corrections were at highest about 7% of *k*_{app}; thus uncertainty due to the approximation is at most but slightly greater than experimental error.

For solvolysis of Ia, solvolysis values computed from those in the literature²² were used. For Ib and Ic, *k*₁ values were determined experimentally.

Reactions of lithium thiophenoxide and of trimethylamine with Ia, b and c were so fast that the methanolysis correction would have been within experimental error. It was therefore neglected. Since initial concentrations of substrate and reagent were equal, second-order rate coefficients were taken from the slopes of plots of 1/(*a* – *x*) against time. Data for reactions of Ia, b and c with potassium iodide in acetone were treated by means of a standard expression.

(16) W. H. Perkin, *J. Chem. Soc.*, **69**, 1190 (1896).

(17) E. Knoevenagel, *Ber.*, **21**, 1344 (1888).

(18) Analysis by Micro-Tech Laboratories, Skokie, Ill.

(19) This experiment was performed at Brown University by Dr. Walter Greizerstein, to whom we express our gratitude.

(20) Cf. J. F. Bunnett, M. M. Rauhut, D. Knutson and G. E. Bussell, *J. Am. Chem. Soc.*, **76**, 5755 (1954).

(21) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

(22) At 25.0°, S. Altscher, R. Baltzly and S. W. Blackman, *J. Am. Chem. Soc.*, **74**, 3649 (1952); see also R. A. Clement, J. N. Naghizadeh and M. R. Rice, *ibid.*, **82**, 2449 (1960); at 50.0°, S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(11) J. A. Riddick, E. E. Toops, Jr., A. Weissberger and E. S. Proskauer, "Organic Solvents," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1955, p. 321.

(12) M. S. Newman, *J. Am. Chem. Soc.*, **62**, 2295 (1940).

(13) G. L. Goerner and R. C. Nametz, *ibid.*, **73**, 2940 (1951).

(14) G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1815 (1935).

(15) H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *J. Am. Chem. Soc.*, **66**, 435 (1944).

Results and Discussion

Our data concerning reactions of Ia, Ib and Ic with four nucleophiles are displayed in Tables I and II. Rates for each reaction were determined at two temperatures. The derived enthalpies and entropies of activation are set forth in Table IV.

TABLE I
REACTIONS OF *o*-SUBSTITUTED BENZYL CHLORIDES WITH LITHIUM METHOXIDE IN METHANOL

<i>o</i> -Subst.	Temp., °C.	$10^6 k_{app},^a$ 1. mole ⁻¹ sec. ⁻¹	$10^7 k_1,^b$ sec. ⁻¹	$10^6 k_2,^c$ 1. mole ⁻¹ sec. ⁻¹
H	24.60	2.46, 2.41	0.62	2.33 ± 0.03
	46.25	30.0, 29.1	7.7	$28.2 \pm .5$
CH ₃	24.60	7.21, 7.08	2.85	$6.62 \pm .07$
	46.25	82.0, ^d 80.0, ^d 82.0	35	$75.8 \pm .8$
Br	24.60	2.54, 2.44	0.22 ^e	$2.45 \pm .05$
	46.25	30.3, 30.6	2.7	$30.0 \pm .2$

^a k_{app} is the slope in a plot of $1/(a-x)$ vs. t . ^b Solvolysis rate coefficient. ^c Corrected second-order rate coefficient. ^d In these two runs, $[Ib]_0 = [LiOCH_3]_0 = 0.0692 M$. ^e Extrapolated from 46.25° with assumption of the same activation energy as for Ia and Ib solvolysis.

at or near the reaction site.^{4,6} For example, the rate ratios k_{PhS^-}/k_{MeO^-} have been considered. The idea behind the taking of such rate ratios is that polar effects of the substituents in question on reaction rates would thereby be cancelled. We have previously shown⁶ this procedure to be legitimate if the reaction series involving the various nucleophiles all have the same Hammett ρ (or Taft ρ^*) value.²⁶

Although Hammett correlations of rates of SN2 reactions of *m*- and *p*-substituted benzyl chlorides with σ -values are not altogether tidy, it is clear from numerous studies²⁷ that substituent effects are generally small ($|\rho| < 0.8$). The requirement that the several reaction series should have the same ρ -value thus is met, at least approximately.

Table IV presents rate ratios k_Y/k_{MeO^-} at 24.6°. Methoxide ion has been selected as the comparison nucleophile of low polarizability. Table IV also presents adjusted rate ratios

$$(k_Y/k_{MeO^-})_R / (k_Y/k_{MeO^-})_H$$

TABLE II
REACTIONS OF *o*-SUBSTITUTED BENZYL CHLORIDES WITH LITHIUM THIOPHENOXIDE, TRIMETHYLAMINE AND POTASSIUM IODIDE

Reagent and solvent	<i>o</i> -Substit.	Rate coefficient, 1. mole ⁻¹ sec. ⁻¹ × 10 ²		
		0.0°	24.60°	46.25°
LiSC ₆ H ₅ in CH ₃ OH	H		22.0 ± 0.05	152 ± 3
	CH ₃	9.25 ± 0.13	115 ± 5	
	Br	4.83 ± 0.04	62.7 ± 1.3	
(CH ₃) ₃ N in CH ₃ OH	H		0.711 ± 0.019	4.04 ± 0.12
	CH ₃		$1.13 \pm .01$	$6.61 \pm .03$
	Br		$0.399 \pm .011$	$2.54 \pm .02$
KI in acetone	H		$0.560 \pm .004^a$	
	CH ₃	0.418 ± 0.004^b	$5.22 \pm .12$	
	Br		$2.54 \pm .2^c$	

^a Ref. 23 gives 0.521×10^{-3} at 25.1°, and 0.595×10^{-3} at 24.6° is extrapolated from data in ref. 24. ^b Ref. 25 gives $0.386 \pm 0.014 \times 10^{-3}$ for reaction with NaI at 0°. ^c 2.35×10^{-3} at 24.6° is extrapolated from data in ref. 24.

TABLE III
ACTIVATION PARAMETERS FOR REACTIONS OF *o*-SUBSTITUTED BENZYL CHLORIDES WITH VARIOUS REAGENTS (AT 24.60°)

Reagent and solvent	<i>o</i> -Subst.	ΔH^\ddagger , kcal.	ΔS^\ddagger , cal./deg.
LiOCH ₃ in CH ₃ OH	H	21.2	- 8.7
	CH ₃	20.7	- 8.2
	Br	21.3	- 8.2
LiSC ₆ H ₅ in CH ₃ OH	H	16.3	-11.5
	CH ₃	16.0	- 9.3
	Br	16.2	- 9.5
(CH ₃) ₃ N in CH ₃ OH	H	14.6	-24.0
	CH ₃	14.8	-22.2
	Br	15.6	-21.8
KI in acetone	H	17.7 ^a	-14.0
	CH ₃	16.0	-15.2
	Br	17.2 ^b	-12.7

^a Datum from ref. 24, confirmed by ref. 23. ^b Datum from ref. 24.

The relationship with which this paper is concerned has been recognized by considering the relative reactivity of a nucleophile of high polarizability with respect to one of low polarizability, as a function of the polarizabilities of substituents

(23) P. J. C. Fierens, H. Hannaert, J. Van Rysselberge and R. H. Martin, *Helv. Chim. Acta*, **38**, 2009 (1955).

(24) G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1914 (1935).

(25) J. C. Charlton and E. D. Hughes, *ibid.*, 855 (1956).

TABLE IV
REACTIONS OF *o*-SUBSTITUTED BENZYL CHLORIDES WITH VARIOUS REAGENTS RATE RATIOS AND ADJUSTED RATE RATIOS AT 24.6°

Reagent and solvent	k_Y/k_{MeO^-}			$(k_Y/k_{MeO^-})_R / (k_Y/k_{MeO^-})_H$		
	H	CH ₃	Br	H	CH ₃	Br
LiSC ₆ H ₅ in CH ₃ OH	944	1740	2560	1.00	1.84	2.71
(CH ₃) ₃ N in CH ₃ OH	30.5	17.1	16.3	1.00	0.56	0.53
KI in acetone	24.0	78.9	103.7	1.00	3.28	4.32

in which inherent differences in nucleophilicity among the nucleophiles are cancelled out, leaving only differences stemming from local interactions (London, steric or whatever else may be significant) between nucleophile and *o*-substituent.

The trimethylamine entries in Table IV indicate that this reagent is relatively less reactive with *o*-methyl- and *o*-bromobenzyl chlorides than with the parent molecule. Presumably adverse steric interactions are responsible. The steric effect

(26) J. F. Bunnett, in S. L. Friess, E. S. Lewis and A. Weissberger, "Investigation of Rates and Mechanisms of Reactions," 2nd ed., Part I, Interscience Publishers, Inc., New York, N. Y., 1961, pp. 210 ff.

(27) Summaries have been given by H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953); C. G. Swain and W. P. Langsdorf, *J. Am. Chem. Soc.*, **73**, 2813 (1951); R. Fuchs, *ibid.*, **79**, 6531 (1957).

may be offset to some extent by London attraction. The fact that the rate ratios for *o*-CH₃ and *o*-Br are nearly the same does not necessarily mean that the steric and London effects of the two groups are equal.²⁸ It may be that the opposing effects are rather different in the two cases, but combine so as to give nearly the same sum.

The thiophenoxide and iodide entries in Table IV display the trends expected from London interactions. The polarizabilities of the three nucleophiles are suggested by those of three ions: OH⁻, 1.89; SH⁻, 5.28; I⁻, 7.10 (all in cm.³ × 10⁻²⁴).³¹ The polarizabilities of the three *o*-substituents are: H, 0.42; CH₃, 2.19; Br, 3.34 (same units).³⁰ The rate ratios and adjusted rate ratios in Table V show that the nucleophiles of higher polarizability are relatively more reactive with the benzyl chlorides bearing *o*-substituents of higher polarizability.

The Possibility of Competing α -Elimination.—It was conceivable that some of the reactions proceeded *via* carbene intermediates to an appreciable extent.^{32,33} With an eye to the mechanism of formation of carbenes from trihalomethanes in alcoholic media,³⁴ we should expect carbene formation to be most serious when the strongest base (in the thermodynamic sense) and the most strongly electron-attracting substituent were involved, that is, in the reaction of *o*-bromobenzyl chloride with lithium methoxide. This possibility was checked by examining for deuterium content the methyl *o*-chlorobenzyl ether formed by reaction of *o*-chlorobenzyl chloride with sodium methoxide in methanol-*O*-D. To the extent that the reaction proceeded *via* a carbene intermediate, the product would contain deuterium on benzylic carbon. The infrared spectrum of the product obtained showed it to be deuterium-free. α -Elimination is therefore at most an insignificant complication.

Reactivity of Methylated Benzyl Chlorides with Potassium Iodide.—Charlton and Hughes,²⁵ who studied rates of reaction of several mono-, di- and trimethylbenzyl chlorides with potassium iodide in acetone, found that those bearing *o*-methyl groups were unusually reactive. For example, 2,6-dimethylbenzyl chloride was four times as reactive as its 2,4-isomer. They commented: "...we assume the presence of some kind of direct polar effect of *o*-methyl groups, plausibly one deriving from an electrostatic attraction between methyl hydrogen and the semi-ionic halogen atoms in the transition state." We suggest that their "direct

polar effect" is the same factor that concerns us, presumably London interactions.

Reactions of γ -Substituted Allyl Chlorides with Sodium Ethoxide and Potassium Iodide.—Hatch and co-workers³⁵ have prepared and characterized the *cis* and *trans* isomers of a number of γ -substituted allyl chlorides, and determined their reactivities with sodium ethoxide in ethanol and with potassium iodide in acetone. They have noted that *cis* and *trans* isomers react at similar rates with sodium ethoxide, but that the *cis* isomers (III) are



appreciably more reactive than the *trans* (IV) with potassium iodide. This is true for both alkyl and halogen γ -substituents. For example, with γ -bromine the *cis* isomer reacts twice as fast with NaOC₂H₅ but 17.1 times as fast with KI. With γ -methyl, the corresponding figures are 1.16 (NaOC₂H₅) and 5.36 (KI).

These observations are remarkable because steric hindrance should, if anything, make the *cis* isomers *less* reactive than the *trans*. Hatch and Noyes³⁶ noted the resemblance of their observations to those of Charlton and Hughes (*vide supra*). Like the British authors, they felt that "some kind of direct polar effect" was responsible. We should like to point out that the kinetic effects of Hatch, *et al.*, approximate the expectations from London theory.³⁷

Quantitative Comparison of Kinetic Effects with the London Theory.—The adjusted rate ratios in Table IV can alternatively be expressed as $\Delta\Delta\Delta F^\ddagger$ values. These may be compared with $\Delta\Delta\Delta H^\ddagger$ values calculated, on assumption of reasonable transition state structures, from the formula⁷

$$-W_{\text{YR}} = 2.1 \frac{3\alpha_Y\alpha_R}{2r^6} \left(\frac{I_Y I_R}{I_Y + I_R} \right) \quad (2)$$

$-W_{\text{YR}}$ is the energy of attraction between atoms Y and R, α_Y and α_R their polarizabilities, r their distance of separation, and I_Y and I_R their ionization potentials. Equation 2 differs from the expression usually given by the factor 2.1. Pitzer⁷ has reported that whereas the usual expression (without the 2.1 factor) gives a good account of the viscosities of hydrogen and helium, eq. 2 gives better agreement for gases containing atoms of greater atomic weight. Since the usual expression is but an approximation, the introduction of the empirical factor 2.1, which makes it give better answers, is welcomed.

For the calculation, the following transition state characteristics were assumed: (a) the Y^δ---C---Cl^δ bonds linear and perpendicular to a plane in which the ring carbons and the methylene hy-

(35) L. F. Hatch, H. D. Weiss and T. P. Li, *J. Org. Chem.*, **26**, 61 (1961), and earlier papers.

(36) L. F. Hatch and P. R. Noyes, *J. Am. Chem. Soc.*, **79**, 345 (1957).

(37) We are grateful to Mr. Anthony J. Sisti for calling our attention to γ -substituted allyl chloride reactions.

(28) The methyl and bromo groups are similar in size. Racemization rates of optically active biphenyls²⁹ suggest bromine to be somewhat larger than methyl, while van der Waals radii (Br, 1.95 Å.; CH₃, 2.0 Å.)³⁰ indicate the opposite.

(29) R. L. Shriner, R. Adams and C. S. Marvel, in H. Gilman, "Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., Vol. 1, p. 362.

(30) J. A. A. Ketelaar, "Chemical Constitution," 2nd ed., Elsevier Publishing Co., New York, N. Y., 1958, pp. 91 and 201.

(31) Values taken from Landolt-Börnstein.

(32) S. A. Hanna, Y. Iskander and Y. Riad, *J. Chem. Soc.*, 217 (1961).

(33) C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83**, 4033 (1961).

(34) J. Hine and F. P. Prosser, *ibid.*, **80**, 4282 (1958), and preceding papers.

drogens lie²⁵; (b) the C---Y^{δ-} distance 1.15 times the normal covalent C-Y distance³⁸; (c) the polarizability and ionization potential of Y^{δ-} in the transition state halfway between values for the Y⁻ ion and the -Y atom. Polarizability and ionization potential values from Landolt-Börnstein were used, supplemented where necessary by values from Ketelaar³⁰ or Ingold.³⁹ However, for I_R (*o*-substituent) a constant value of 225 kcal. per mole was used throughout. Except for bonds undergoing formation or breaking, bond lengths were considered to be normal, and were taken from those tabulated for suitable analogs.⁴⁰

The London attraction between Y and R in each transition state was reckoned. This may be considered as a ΔH^\ddagger value: the amount by which the transition state enthalpy is lowered by the London interaction in question. With R held constant, ΔH_{MeO^\ddagger} was then subtracted from ΔH_{Y^\ddagger} , giving a pair of $\Delta\Delta H^\ddagger$ values for each substrate. Finally $\Delta\Delta H^\ddagger$ values for Ia were subtracted from those for the other two substrates, giving (in all) four $\Delta\Delta\Delta H^\ddagger$ values.

Typical Calculation.—Reaction of I⁻ with Ic: I₁^{δ-} was taken as 156 kcal./mole, the average of 72 kcal. (for I⁻ ion) and 241 kcal. (for I atom); $\alpha_{I_1}^\delta$ was taken as 6.10×10^{-24} cc., the average of 7.10 (for I⁻ ion) and 5.11 (for I atom); α_{Br} was taken as 3.34×10^{-24} cc. The C...I^{δ-} length was taken as 2.47 Å. (1.15 times the normal C-I bond length of 2.15 Å.). The Br to I^{δ-} distance was reckoned as 3.97 Å. By eq. 2, the energy of London attraction was then computed as -1462 cal./mole.

Similarly, the London attraction energy in the CH₃O⁻ + Ic transition state was reckoned as -830 cal./mole. The difference in favor of the I⁻ + Ic transition state is 632 cal./mole. The London attraction energies in the transition states for I⁻ and CH₃O⁻ with Ia were reckoned as -288 and -187 cal./mole, respectively, an advantage of 101 cal./mole for the I⁻ + Ia reaction. The $\Delta\Delta\Delta H^\ddagger$ factor corresponding to the $(k_{I^-}/k_{MeO^\ddagger})_{Br}/(k_{I^-}/k_{MeO^\ddagger})_H$ ratio of rate ratios is then $632-101 = 531$, rounded off to 530 cal./mole.

(38) P. B. D. de la Mare, L. Fowden, E. D. Hughes, C. K. Ingold and J. D. H. Mackie, *J. Chem. Soc.*, 3200 (1955).

(39) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 119 ff.

(40) "Interatomic Distances," Special Publication No. 11, The Chemical Society (London), 1958.

If changes in the entropy of activation are negligible or have a negligible effect on adjusted rate ratios, these $\Delta\Delta\Delta H^\ddagger$ values should match the $\Delta\Delta\Delta F^\ddagger$ from experiment. The comparison is made in Table V.

TABLE V
LONDON INTERACTIONS IN TRANSITION STATES.
COMPARISON OF EXPERIMENT WITH THEORY

<i>o</i> -Substituent	—C ₆ H ₅ S ⁻ reaction—		—I ⁻ reaction—	
	$\Delta\Delta\Delta F^\ddagger$, cal. Found	$\Delta\Delta\Delta H^\ddagger$, cal. Calcd.	$\Delta\Delta\Delta F^\ddagger$, cal. Found	$\Delta\Delta\Delta H^\ddagger$, cal. Calcd.
CH ₃	-360	-340	-700	-350
Br	-610	-500	-870	-530

Although the calculated values do not agree precisely with those from experiment, they do concord as to order of magnitude and in the ranking of *o*-Br *vs.* *o*-CH₃. In view of the approximate character of eq. 2, and of the many assumptions involved in its application to transition states, the agreement is regarded as quite good.

Conclusions.—The concordance of experiment with predictions from London theory, as shown in Table V, indicates that London interactions can reasonably account for the kinetic effects observed. It does not, however, prove that London forces are principally responsible. For example, if Pitzer's factor of 2.1 is not legitimately employed in the present instance, or if the transition state C---Y bond length is appreciably longer than 1.15 times the normal C-Y length, London forces would fall considerably short of accounting for the experimental values. Therefore identification of the observed kinetic trends with London forces, though plausible, remains tentative.

NOTE ADDED IN PROOF.—Recent data of G. Klopman and R. F. Hudson, *Helv. Chim. Acta*, 44, 1914 (1961), show that for reactions with *para*-substituted benzyl bromides $(k_{PhS^-}/k_{MeO^\ddagger})_R/(k_{PhS^-}/k_{MeO^\ddagger})_H$ is 1.1 for *p*-CH₃ and 1.6 for *p*-Br. This makes it appear that a part, but only a part, of the effect observed with *o*-Br is of polar origin, while polar influences do not affect the adjusted rate ratios for *o*-CH₃. The principal conclusions of the present paper retain their validity.