

**Reaction of 2-Methylpropenyllithium with Methylene Chloride.**—2-Methylpropenyllithium (0.70 mole) was prepared from 1-bromo-2-methylpropene (135 g., 1.0 mole) and lithium (20 g., 2.9 g. atoms) in ether (1000 ml.).<sup>30</sup> The lithium compound precipitated partially as a slightly yellow powder. Most of the ether (800 ml.) was removed by distillation under reduced pressure (80 mm.). To the remaining lithium compound was added tetrahydrofuran (700 ml.) and the solution was cooled to  $-30^{\circ}$ . Methylene chloride (24 g., 0.28 mole) was slowly added under vigorous stirring keeping the solution between  $-35$  and  $-30^{\circ}$ . After the addition was complete the solution was kept an additional 10 minutes at this temperature. Then part of the solvent (600 ml.) was distilled into a trap cooled with liquid nitrogen under reduced pressure (1 mm.) thus removing most of the isobutene. During this distillation the reaction mixture was kept below  $-10^{\circ}$ . Heptane (100 ml.) was added to the residue followed by ice-water. The organic layer was separated and washed three times with ice-water (200 ml.) keeping the separatory funnel in an ice-bath. After drying over magnesium sulfate, the most volatile components were distilled from the heptane solution using a 3-ft. Helipack column kept in a room below  $15^{\circ}$ . The cooling water of the reflux cold finger had a temperature of  $3^{\circ}$ .

(30) E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 3324 (1955).

The gas outlet of the distillation head was connected with a trap cooled with Dry Ice and acetone. The fraction boiling at  $12-16^{\circ}$  was collected (3.8 g.). Comparison of the infrared and n.m.r. spectra of this material with those obtained from a pure sample of 3,3-dimethylcyclopropene (b.p.  $14.5^{\circ}$ )<sup>2</sup> obtained by the base-catalyzed decomposition of the tosylhydrazone of  $\beta$ -methylcrotonaldehyde showed the presence of about 60% 3,3-dimethylcyclopropene (12% yield). The main impurities were isobutene and ether. The final purification was achieved by v.p.c. using a 5-ft. column with silicon 710 on firebrick, at  $30^{\circ}$ . The sample was trapped in the conventional manner; n.m.r. spectrum: triplet, centered at  $9.07 \tau$  (0.7 c.p.s. separation) septuplet: centered at  $3.00 \tau$  (0.7 c.p.s. separation); infrared spectrum: C=C stretching,  $1632 \text{ cm}^{-1}$ .

**Hydrogenation of 3,3-Dimethylcyclopropene.**—3,3-Dimethylcyclopropene (0.478 g., 0.007 mole) was dissolved in ethanol (3 ml.) and hydrogenated over 5% palladium-on-charcoal (50 mg.) at  $0^{\circ}$ . Hydrogen uptake (0.0064 mole) was complete within 7 minutes; v.p.c. analysis showed the hydrogenation product to consist of 95% 1,1-dimethylcyclopropane with only one other component (unidentified). Isolation of the cyclopropane by v.p.c. was carried out on 12-ft. column using TCP on firebrick as substrate at  $22^{\circ}$ . The material was identified by comparison of its infrared and n.m.r. spectrum with an authentic sample of 1,1-dimethylcyclopropane.

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## Substituent Effects in the Solvolysis and Thiosulfate Reactions of 3-, 4- and 3,5-Substituted $\alpha$ -Chlorotoluenes

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The rates of reaction of a series of 3-, 4- and 3,5-substituted  $\alpha$ -chlorotoluenes with sodium thiosulfate in 60% acetone at  $30^{\circ}$ , and the rates of solvolysis in 50% ethanol at  $60^{\circ}$  have been measured. The present data together with previous work provide information on more than twenty compounds. The thiosulfate reaction rates may be represented by a series of U-shaped Hammett equation plots. 3-Substituents possess an intrinsic rate-depressing ability compared with 4-substituents of similar  $\sigma$ , and this effect is additive in the 3,5-disubstituted compounds. 4-Substituents capable of strong mesomeric electron release enhance rates compared with other substituents of similar  $\sigma$ . The solvolysis rates may be represented by a Hammett plot vs.  $\sigma^+$  as three lines, or, alternatively, as a single curved line. The mechanistic implications are discussed.

For several decades there has been available a considerable body of rate data pertaining to the reactions of nucleophiles with benzyl halides ( $\alpha$ -halotoluenes), and the effect of *m*- and *p*-substituents therein.<sup>2</sup> Attempted correlations with the Hammett equation have been unsuccessful in two ways: (1) plots of the reactivity of *p*-substituted benzyl halides with anions are U-shaped,<sup>2a,b,c,f,g,h</sup> with the unsubstituted compound at the rate minimum, and for the reactions with amines the plots may be still more complex,<sup>2d</sup> although tending to give negative values of  $\rho$ . (2) The rates of reaction of *m*-substituted benzyl halides<sup>2a-f</sup> are consistently lower than would be predicted on the basis of  $\sigma$ -values, and are in certain cases<sup>2b-e</sup> below that of the unsubstituted compound. There is also the possibility that the dissociation of salts in media of low ion-solvating ability, and, hence, the rate of nucleophilic attack by anions, may be affected by the polar nature of certain substituents.<sup>2f,h</sup> This possibility has been greatly reduced in the present study by the choice of 60% acetone-40% water as the solvent. The use of the powerful nucleophile thiosulfate has also precluded solvolysis as a successfully competing reaction in all cases excepting that of the *p*-methoxy compound.

(1) Based on the Ph.D. dissertation of D.M.C., The University of Texas, 1962.

(2) (a) H. Franzen, *J. prakt. Chem.*, [2] **97**, 82 (1918); H. Franzen and I. Rosenberg, *ibid.*, [2] **101**, 333 (1921); (b) W. T. Miller, Jr., and J. Bernstein, *J. Am. Chem. Soc.*, **70**, 3600 (1948); (c) S. C. J. Olivier and W. P. Weber, *Rec. trav. chim.*, **53**, 869 (1934); (d) J. W. Baker, *J. Chem. Soc.*, 2631 (1932); 1128 (1933); 1448 (1936); (e) C. G. Swain and W. P. Langsdorf, *J. Am. Chem. Soc.*, **73**, 2813 (1951); (f) G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1815 (1935); A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, **47**, 25 (1951); (g) R. Fuchs and A. Nisbet, *J. Am. Chem. Soc.*, **81**, 2371 (1959); (h) Other, less extensive series are cited in A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

The effect of substituents in the SN2 reactions of benzyl compounds has been considered by Swain<sup>3</sup> in terms of "loose" and "tight" transition states. Electron-releasing substituents are said to facilitate the former by stabilization of the fractional positive charge developed on the benzylic carbon atom in the transition state; electron-withdrawing substituents place a fractional positive charge on the benzylic carbon atom of the initial state, and stabilize the somewhat more negative charge in the "tight" transition state. The rate-enhancing effect of +R substituents has been attributed in part to neighboring orbital overlap<sup>2h</sup> when the entering and leaving groups are not first row elements; partial bonding of the nucleophile may occur at C-1 of the benzene ring of benzyl chlorides, with mesomeric delocalization of the fractional negative charge to a *p*-nitro group.

A recent publication<sup>4</sup> further indicates that  $\sigma$ -values do not serve as a satisfactory basis for prediction of the rates of reaction of several 4-substituted 3-nitrobenzyl chlorides with thiosulfate. The Hammett plot for this series (using experimentally determined  $\sigma$ -values for 3-nitro-4-substituents<sup>5</sup>) describes a separate U-shaped curve similar to that for the 4-substituted benzyl chlorides. It was concluded<sup>4</sup> that the 3-nitro group in each compound of the series exerts only a rather small effect on the absolute and relative rates of reaction.

Data on the rates of solvolysis of benzyl series are also available.<sup>2c,f,h,6</sup> The solvolysis of  $\alpha,\alpha$ -dimethyl-

(3) C. G. Swain and W. P. Langsdorf, Jr., *J. Am. Chem. Soc.*, **73**, 2813 (1951).

(4) R. Fuchs and D. M. Carlton, *J. Org. Chem.*, **27**, 1520 (1962).

(5) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(6) (a) S. C. J. Olivier, *Rec. trav. chim.*, **41**, 301, 646 (1921); **42**, 516

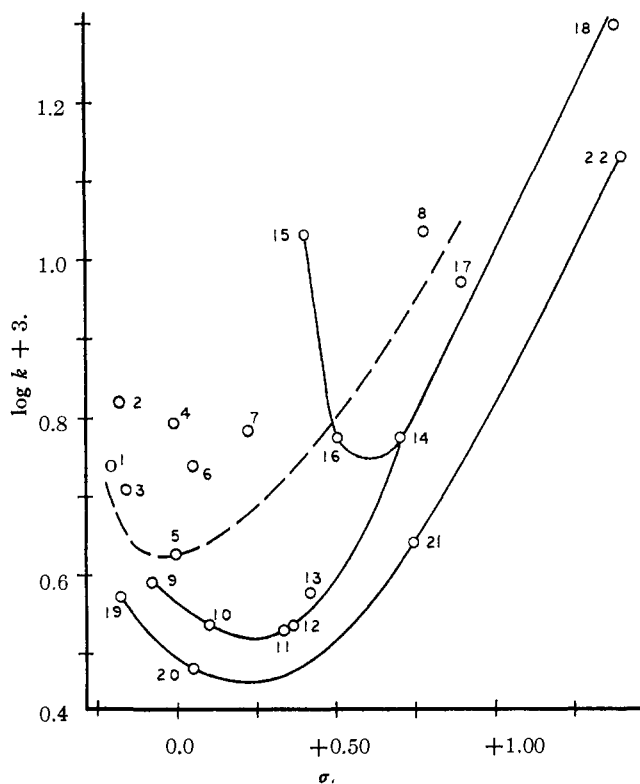


Fig. 1.—Rates of reaction of benzyl chlorides with thiosulfate in 60% acetone at 30°. Numbers refer to compounds in Table I.

benzyl chlorides in 90% aqueous acetone<sup>6b</sup> has been used as the basis of  $\sigma^+$ -constants which are applicable to a number of electrophilic aromatic substitution reactions and electrophilic reactivities at benzylic carbon atoms. A problem of mechanistic interpretation arises in the solvolyses of benzyl chlorides<sup>4,6a</sup> and tosylates,<sup>6c</sup> wherein no simple correlation with  $\sigma^+$ -exists. Plots of  $\log k$  vs.  $\sigma^+$  for these series result in a line with definite curvature,<sup>6c</sup> which has been attributed<sup>7</sup> to two different mechanisms of solvolysis. The data have also been represented<sup>6c</sup> as two "straight" lines vs.  $\sigma^+$ , with the line of greater slope ( $\rho$ ) falling at negative and slightly positive values of  $\sigma^+$ , or as a straight line vs.  $\sigma^+$  ( $\sigma^+ < 0.2$ ) and a curved line vs.  $\sigma^+$ .

Stereochemical studies with benzyl- $\alpha$ -*d* tosylate<sup>8</sup> indicate that the reaction with ethoxide ion and the solvolyses in 80% and 100% ethanol proceed with essentially complete inversion. While it has frequently been suggested that the inversion results from direct displacement by solvent molecules<sup>9</sup> and that cases of partial inversion result from the simultaneous operation of carbonium ion and direct displacement mechanisms, a more recent postulate<sup>10</sup> involves a solvated (ion-pair) intermediate which, depending on the energetics, may react with the solvent with inversion, may become solvent-separated with formation of a symmetrically solvated carbonium ion leading to racemization, or both. Hammond<sup>6c</sup> feels that the

(1923); 49, 697 (1930); (b) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958), and earlier papers; (c) G. S. Hammond, C. E. Reeder, F. T. Fang and J. K. Kochi, *ibid.*, **80**, 568 (1958), and previous papers cited therein; (d) G. S. Hammond, J. Peloquin, F. T. Fang and J. K. Kochi, *ibid.*, **82**, 443 (1960).

(7) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

(8) A. Streitwieser, Jr., and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **81**, 4912 (1959).

(9) See, for example I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 173 (1946). Evidence for the simultaneous operation of first- and second-order processes in diphenylmethyl bromide reactions has been published by Y. Pocker, *ibid.*, 3939 (1959).

(10) W. E. Doering and H. H. Zeiss, *J. Am. Chem. Soc.*, **75**, 4733 (1953).

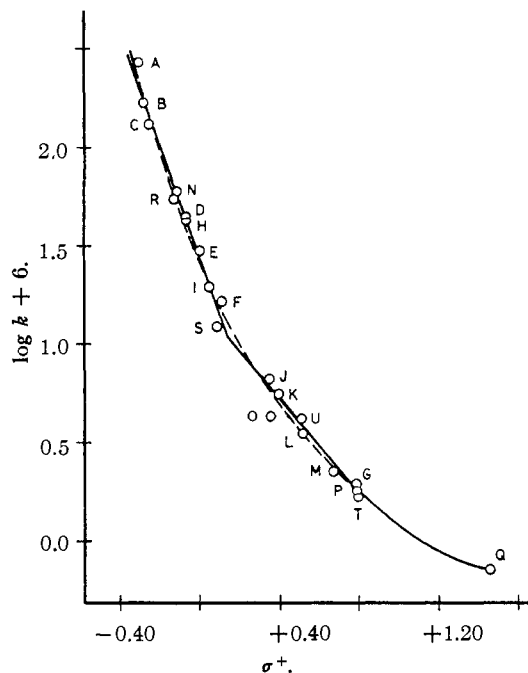


Fig. 2.—Rates of solvolysis of benzyl chlorides in 50% ethanol at 60°; letters refer to compounds in Table II.

solvolysis of benzyl tosylates may well represent gradations in the ion-pair mechanism (rather than two distinct mechanisms) consistent with a curved plot against  $\sigma^+$ . There appears to be agreement that the hydrolysis of benzyl chloride is not limiting, but some question exists as to the identity of the preferred alternative. Based on deviations from the Winstein-Grunwald relationship, Fierens<sup>11</sup> has found in this reaction "nucleophilic action," which is the rate enhancement due to the incursion of an SN2 process over that rate which would be anticipated from an SN1 process. From measurements of thermodynamic quantities of activation and the relative reactivities of benzyl and allyl halides, Robertson<sup>12</sup> concluded that the hydrolysis of benzyl chloride is not SN1 limiting, but takes place by a bimolecular displacement involving a highly polar transition state.

## Results

In the present study the rates of reaction with sodium thiosulfate in 60% acetone at 30° (Table I, Fig. 1), and the rates of solvolysis in 50% ethanol at 60° (Table II, Fig. 2) have been measured for a series of 3-, 4- and 3,5-substituted benzyl chlorides. Together with previous rate data for other 4-substituted and 4-substituted-3-nitrobenzyl chlorides,<sup>4</sup> the present data constitute a larger and more varied series than any previously examined. The *p*-methoxy compound, which solvolyzed too rapidly to measure in 50% ethanol, and hydrolyzed considerably in the presence of thiosulfate, is omitted from the tables. The range of  $\sigma$ -values has been considerably extended at the positive end by the inclusion of the dinitrobenzyl chlorides.

## Discussion

**The Thiosulfate Reaction.**—The data of Table I are plotted in Fig. 1, using ordinary  $\sigma$ -values. The  $\sigma$ -values representing disubstituted benzyl chlorides are those reported by Jaffé,<sup>5</sup> which have been experimentally determined. These values are no more than 0.04 sigma unit less positive than the algebraic sum of the two individual sigma constants, except in the case of

(11) L. Wilputte-Steinert and P. J. C. Fierens, *Bull. soc. chim. Belg.*, **65**, 719 (1956).

(12) R. E. Robertson and J. M. W. Scott, *J. Chem. Soc.*, 1596 (1961).

TABLE I  
RATES OF REACTION OF SUBSTITUTED  $\alpha$ -CHLOROTOLUENES WITH  
THIOSULFATE IN 60% ACETONE AT 30°

Substituent	No.	$k^a$	$\sigma^b$
4- <i>t</i> -C <sub>4</sub> H <sub>9</sub>	1	5.52	-0.20
4-CH <sub>3</sub>	2	6.68 <sup>c</sup>	- .17
4- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	3	5.16 <sup>c</sup>	- .15
4-C <sub>6</sub> H <sub>5</sub>	4	6.28	- .01
Unsubstd.	5	4.27 <sup>c</sup>	.00
4-F	6	5.52	+ .06
4-Cl	7	6.10 <sup>c</sup>	.23
4-NO <sub>2</sub>	8	10.9	.78
3-CH <sub>3</sub>	9	3.93	- .07
3-OCH <sub>3</sub>	10	3.47	+ .11
3-F	11	3.42	.34
3-Cl	12	3.46	.37
3-CF <sub>3</sub>	13	3.82	.42
3-NO	14	5.98 <sup>c</sup>	.71
3-NO <sub>2</sub> -4-OCH <sub>3</sub>	15	10.8 <sup>c</sup>	.41
3-NO <sub>2</sub> -4-CH <sub>3</sub>	16	6.00 <sup>c</sup>	.51
3-NO <sub>2</sub> -4-Cl	17	9.45 <sup>c</sup>	.90
3,4-(NO <sub>2</sub> ) <sub>2</sub>	18	20.0 <sup>c</sup>	1.38
3,5-(CH <sub>3</sub> ) <sub>2</sub>	19	3.77	-0.17
3,5-(OCH <sub>3</sub> ) <sub>2</sub>	20	3.05	+ .05
3,5-Cl <sub>2</sub>	21	4.42	.75
3,5-(NO <sub>2</sub> ) <sub>2</sub>	22	13.6	1.40

<sup>a</sup> Second-order rate constants (l. mole<sup>-1</sup> sec.<sup>-1</sup>)  $\times 10^3$ . All values are averages of two or more determinations. At time of mixing (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) = 0.04 M, (RCl) = 0.025 M; stated temperature regulated to  $\pm 0.02^\circ$ . Solvent is 40% water + sufficient acetone to make up total volume. <sup>b</sup> Sigma values for 3- and 4-substituents are those of H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958); values for 3,4- and 3,5-disubstituents are experimentally determined combined values of Jaffé (ref. 5). <sup>c</sup> Ref. 4.

3,5-dimethoxyl substitution, which does not appreciably affect the shape of the 3,5-disubstituted curve, and the case of 3,4-dinitro substitution, in which the measured value is 0.11 less positive, presumably due to an appreciable steric inhibition of the +R effect of the 4-nitro group. It is probably true that no usual set of  $\sigma$ -values is completely appropriate for 4-substituents. The rate order 4-CH<sub>3</sub> > 4-*t*-C<sub>4</sub>H<sub>9</sub> > 4-*i*-C<sub>3</sub>H<sub>7</sub> suggests that -R effects play a somewhat more important role than is reflected in ordinary  $\sigma$ -values, but not to the extent that  $\sigma^+$  is appropriate. The successful application of the latter is generally considered to require that the magnitude of the positive charge on or adjacent to the benzene ring be constant throughout the series, a situation which is unlikely in the present system.<sup>3</sup> The appropriate value of  $\sigma_{p\text{-NO}_2}$  is also uncertain; to the extent that neighboring orbital overlap occurs, an exalted value greater than  $\sigma$ , but probably less than  $\sigma^-$ , would be anticipated.

It has been pointed out previously<sup>4</sup> that points on the Hammett equation plot representing the *p*-substituted *m*-nitrobenzyl chlorides describe a U-shaped line; the rates are, in general, quite different from those of *p*-substituted benzyl chlorides of similar  $\sigma$ -value. The *m*-substituted benzyl chlorides fall on a U-shaped plot below the "line" for the *p*-substituted compounds. With the exception of the *m*-nitro compound all *m*-substituted benzyl chlorides react with thiosulfate at a slower rate than does the unsubstituted compound. This holds true for five compounds ( $\sigma$ -values -0.07 to +0.42) in the present study. The rate minimum in the *meta* series, shown (Fig. 1) at  $\sigma = 0.2$ , is not well defined, since the rates for the *m*-methoxy, *m*-fluoro and *m*-chloro compounds are not significantly different. The 3,5-disubstituted benzyl chlorides describe a line below that for the *meta* compounds. Thus, the 3-substituents appear to have an intrinsic ability to decrease the rate of the thiosulfate reaction, and this

TABLE II  
RATES OF SOLVOLYSIS OF SUBSTITUTED  $\alpha$ -CHLOROTOLUENES IN  
50% ETHANOL AT 60°

Substituent	No.	$k^a$	$\sigma^{+b}$
4-CH <sub>3</sub>	A	27.3 <sup>c</sup>	-0.31
4- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	B	17.2 <sup>c</sup>	- .28
4- <i>t</i> -C <sub>4</sub> H <sub>9</sub>	C	13.4	- .26
4-F	D	4.48	- .07
Unsubstd.	E	3.02 <sup>c</sup>	.00
4-Cl	F	1.69 <sup>c</sup>	+ .11
4-NO <sub>2</sub>	G	0.198 <sup>c</sup>	.79
3-CH <sub>3</sub>	H	4.38	- .07
3-OCH <sub>3</sub>	I	1.98	+ .05
3-F	J	0.678	.35
3-Cl	K	.570	.40
3-CF <sub>3</sub>	L	.362	.52
3-NO <sub>2</sub>	M	.231 <sup>c</sup>	.67
3-NO <sub>2</sub> -4-OCH <sub>3</sub>	N	6.05 <sup>c</sup>	- .11
3-NO <sub>2</sub> -4-CH <sub>3</sub>	O	0.437 <sup>c</sup>	+ .36
3-NO <sub>2</sub> -4-Cl	P	.183 <sup>c</sup>	.79
3,4-(NO <sub>2</sub> ) <sub>2</sub>	Q	.0726 <sup>c</sup>	1.46
3,5-(CH <sub>3</sub> ) <sub>2</sub>	R	5.58	-0.13
3,5-(OCH <sub>3</sub> ) <sub>2</sub>	S	1.25	+ .09
3,5-Cl <sub>2</sub>	T	0.172	.80
3,4-Cl <sub>2</sub>	U	0.427	.51

<sup>a</sup> First-order rate constants (sec.<sup>-1</sup>)  $\times 10^3$ . All values are averages of two or more determinations. At time of mixing (RCl) = 0.005 M; stated temperatures regulated to  $\pm 0.02^\circ$ . Solvent is 50% commercial absolute alcohol-50% water by volume. <sup>b</sup>  $\sigma^+$ -Values of H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958). Values given for 3,4- and 3,5-substitution are sums of the individual values, and are not experimentally determined. <sup>c</sup> Ref. 4.

property is approximately additive in the 3,5-disubstituted benzyl chlorides, which, as a series have the lowest order of reactivity. We can offer nothing approaching a complete explanation of this behavior. It is possible to discount a steric factor of *m*-substituents, whether in terms of hindrance to transition state solvation or to approach of the nucleophile, by the observation that substituents of various sizes (F, Cl, CF<sub>3</sub>) affect reactivity only slightly differently, and in a manner related to  $\sigma$ . Within the framework of *m*-substituent rate inhibition it is observed that, as in all series, pronounced electron release or electron withdrawal by the substituent enhances the rate of the thiosulfate reaction above the rate minimum for the series. Thus, *m*-methyl and *m*-nitro groups in the *m*-substituted benzyl chloride series enhance reactivity compared with the *m*-methoxy or *m*-halogen substituents, but not to the extent that any compound of the series is as reactive as a *p*-substituted benzyl chloride having a substituent of similar  $\sigma$ .

The reactivity of *p*-substituted benzyl chlorides tends to increase with electron-releasing and electron-withdrawing power. However, a smooth curve cannot be drawn through the points. We have drawn (Fig. 1) a broken line representing a hypothetical "*para* line," which is roughly an indication of the reactivity which might be anticipated in the absence of mesomeric effects due to the *p*-substituent. Real substituents enhance rates to a greater extent, and that extent is approximately proportional to  $-\Delta\sigma$ , where  $\Delta\sigma = \sigma_p^+ - \sigma_p$ . The rate enhancement amounts to about 0.10 unit in log  $k$  for each 0.10 unit in  $\Delta\sigma$ . The relationship holds reasonably well for six -R substituents; the situation is ambiguous for the +R *p*-nitro group, if as mentioned above, the appropriate  $\sigma$ -value is open to question. From this point of view the Hammett equation cannot be relied upon to provide useful interpolative data in this particular series. The reactivity of each *p*-substituted *m*-nitrobenzyl chloride

is reasonably consistent with a combination of mesomeric rate enhancement (proportional to  $-\Delta\sigma$ ) and inhibition due to the *m*-nitro substituent, acting on the hypothetical reactivity of a compound with the same  $\sigma$ -value of substituents, but having neither *m*-substituents nor  $-R$  *p*-substituents.

**The Solvolysis Reaction.**—The rates of solvolysis of the four series of benzyl chlorides in 50% ethanol at 60° (Table II, Fig. 2) can be satisfactorily treated in either of two ways. Since each Hammett equation correlation has a different mechanistic implication, the data do not definitively elucidate the mechanistic pathway. A satisfactory plot represents the data as: (1) a straight line *vs.*  $\sigma^+$  ( $\rho = -3.0$ ) at values of  $\sigma^+$  less than 0.12, (2) a second straight line ( $\rho = -1.25$ ) *vs.*  $\sigma^+$  in the range 0.12 to 0.8, and (3) a curved line at greater values of the substituent constant. Only one point (3,4-dinitro) falls on the latter portion of the plot, and it is not possible to say whether  $\sigma$  or  $\sigma^+$  is appropriate in this range. It should be noted that complete inhibition of the  $+R$  effect of the 4-nitro group would not place the 3,4-dinitro point on the extension of line 2. The over-all average deviation in  $\sigma^+$  is about  $\pm 0.02$ . These lines could be taken as consistent with three mechanisms of solvolysis, possibly involving benzyl cations, a less limiting reaction of ion-pairs, and nucleophilic attack by solvent, respectively. Alternatively, the data can be about equally precisely represented as a single curve (of somewhat variable radius), as has been done for the solvolysis of benzyl tosylates,<sup>6c</sup> with the implication of gradations in the ion-pair mechanism. In view of the rather extensive evidence that Hammond has presented<sup>6c,d</sup> against a direct displacement solvolysis of the tosylates, it appears more probable that a similar situation also holds true for the benzyl chloride solvolysis. We wish to point out at this time only that the rate data herein presented is not mechanistically definitive.

A recent study of chlorine isotope effects in the reactions of benzyl chlorides<sup>13</sup> has demonstrated that a somewhat larger isotope effect ( $Cl^{35}/Cl^{37}$ ) occurs with first-order reactions (about 1.0078) than with second-order reactions (1.0058). Isotope effects of about 1.0078 for *p*-methoxy-, *p*-methyl-, unsubstituted, *p*-chloro- and *p*-nitrobenzyl chlorides suggest that all hydrolyze in 80% aqueous dioxane by first-order reactions which occur by a mechanism which is very close to ideal  $SN_1$ . Stereochemical evidence indirectly opposes the three-mechanism hypothesis. As in the present work if the solvolysis of benzyl tosylates<sup>6c</sup> is represented by straight lines *vs.*  $\sigma^+$ , the intersection occurs at a  $\sigma^+$ -value of about 0.1, regardless of the nature of the solvent mixture. Streitwieser<sup>8</sup> has found essentially complete inversion in the solvolysis of benzyl- $\alpha$ -*d* tosylate in 80% ethanol. Since the unsubstituted benzyl compound falls on the line of largest slope, the adoption of a three-mechanism hypothesis requires the inconsistency of a more-or-less limiting solvolysis *via* the carbonium ion which proceeds with complete inversion! We do not see an obvious alternative choice of three mechanisms which would obviate this difficulty.

(13) J. W. Hill and A. Fry, *J. Am. Chem. Soc.*, **84**, 2763 (1962).

## Experimental

The kinetic measurements in the thiosulfate reactions<sup>2a</sup> and in the solvolyses<sup>4</sup> have been previously described, as has the purification of several of the benzyl chlorides.<sup>2a</sup> The following commercial compounds were distilled before use:  $\alpha$ -chloro-3-fluorotoluene (b.p. 70° at 36 mm.),  $\alpha$ ,3,4-trichlorotoluene (b.p. 71° at 1 mm.) and  $\alpha$ -chloro-4-fluorotoluene (b.p. 73° at 18 mm.).

**$\alpha$ ,3-Dichlorotoluene.**—3-Chlorobenzaldehyde was reduced with sodium borohydride in aqueous 1,2-dimethoxyethane solution in 80% yield to 3-chlorobenzyl alcohol, b.p. 77° at 26 mm. The alcohol was converted by a 25% excess of thionyl chloride in refluxing carbon tetrachloride (hereafter referred to as procedure A) to the chloride, b.p. 44° at 0.3 mm.,<sup>14</sup> in 77% yield.

**$\alpha$ -Chloro-*m*-xylene.**—*m*-Toluic acid was reduced with lithium aluminum hydride in ether solution (hereafter referred to as procedure B) in 69% yield to 3-methylbenzyl alcohol, b.p. 122° at 43 mm. The alcohol was converted by procedure A to the chloride, b.p. 96° at 23 mm.,<sup>15</sup> yield 56%.

**3-Chloromethylanisole.**—3-Methoxybenzyl alcohol was converted in 60% yield by procedure A to the chloride, b.p. 55° at 0.3 mm.<sup>16</sup>

**$\alpha$ -Chloro- $\alpha'$ , $\alpha'$ , $\alpha'$ -trifluoro-*m*-xylene.**—The Grignard reagent of *m*-bromo- $\alpha$ , $\alpha$ , $\alpha$ -trifluorotoluene was carbonated to give 3-trifluoromethyl-benzoic acid,<sup>17</sup> which was converted in 69% yield by procedure B to *m*-trifluoromethylbenzyl alcohol, b.p. 53° at 0.1 mm. The alcohol was converted by procedure A to the chloride, b.p. 87° at 28 mm., in 55% yield.

*Anal.* Calcd. for  $C_8H_8ClF_3$ : C, 49.4; H, 3.09. Found: C, 49.2; H, 3.21.

**$\alpha$ -Chloromesitylene.**—3,5-Dimethylbenzoic acid was converted in 73% yield by procedure B to 3,5-dimethylbenzyl alcohol, b.p. 71° at 0.6 mm. Procedure A was used to convert the alcohol to the corresponding chloride, b.p. 57° at 0.8 mm.<sup>18</sup> The yield was 50%.

**$\alpha$ ,3,5-Trichlorotoluene.**—3,5-Dichlorobenzoic acid was converted in 70% yield by procedure B to 3,5-dichlorobenzyl alcohol, which after recrystallization from ethanol-water melted at 78–79°. The alcohol was treated with a large excess of thionyl chloride without added solvent (hereafter called procedure C) to give a 30% yield of the chloride, b.p. 60° at 0.35 mm., m.p. 36.2–37.0°.<sup>19</sup>

**3,5-Dimethoxybenzyl Chloride.**—3,5-Dimethoxybenzoic acid was reduced in 47% yield by procedure B to 3,5-dimethoxybenzyl alcohol, b.p. 106° at 0.03 mm. The alcohol was treated by procedure A, except that the reaction mixture was cooled during the 3-hr. reaction time to give a 60% yield of the chloride, m.p. 48.2–48.7°.<sup>20</sup>

**$\alpha$ -Chloro-3,5-dinitrotoluene.**—3,5-Dinitrobenzoyl chloride was reduced with sodium borohydride in slightly aqueous dioxane solution to give very low yields<sup>21</sup> of 3,5-dinitrobenzyl alcohol, m.p. 91–92°. The alcohol was converted by procedure C to the chloride, m.p. 79.0–79.5°.<sup>22</sup>

**$\alpha$ -Chloro-4-*tert*-butyltoluene.**—Using procedures B and A *p*-*tert*-butylbenzoic acid was converted through the alcohol to the chloride, b.p. 69.5° at 0.7 mm.<sup>23</sup>

**4-Chloromethylbiphenyl.**—Using procedures B and A 4-biphenylcarboxylic acid was reduced to the alcohol and converted to the chloride, m.p. 68.4–68.8°.<sup>24</sup>

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(14) Reported 215–216° at 753 mm.; S. C. J. Olivier, *Rec. trav. chim.*, **41**, 309 (1924).

(15) Reported 85–87° at 16 mm.; T. Posner and Schreiber, *Ber.*, **57**, 1137 (1924).

(16) Reported 124° at 13 mm.; R. Pschorr, *Ann.*, **391**, 44 (1912).

(17) T. Swarts, *Rec. trav. chim.*, **24**, 423 (1906).

(18) Reported b.p. 215–220°; G. Robinet, *Compt. rend.*, **96**, 500 (1883).

(19) F. Assinger and G. Lock, *Monatsh.*, **62**, 344 (1933), reported m.p. 36°. Melting points in the present work are uncorrected.

(20) Reported m.p. 46°; R. Adams, U. S. Patent 2,509,387 (May 30, 1950).

(21) No product was obtained in dry dioxane or 1,2-dimethoxyethane.

(22) Reported m.p. 79.2–79.7°.

(23) Reported b.p. 115° at 16 mm.; G. Darzens and A. Levy, *Compt. rend.*, **199**, 1426 (1934).

(24) J. von Braun and H. Engel, *Ann.*, **436**, 299 (1924), reported m.p. 68°.