hexane. On concentration and chilling 2.35 g. (94%) of white crystals was obtained. The infrared spectra of the deuterated and undeuterated sulfones were very similar except that the peak at 11.00 μ was more intense for the undeuterated sample and a new small peak appeared at 10.08 μ in the deuterated sample.

Deuterium Analysis. A. Cyclohexyl *p*-Tolyl Sulfone.—A 50.0-mg. portion of the sample was dissolved in 0.50 ml. of chloroform and the infrared spectrum determined between 10 and 11 μ using 0.1-cm. matched cells with the instrument which had been set at 100% transmittance with chloroform in both sample and the solvent cell. A calibration curve was constructed by determining the spectra of known mixtures of deuterated and undeuterated sulfone and plotting percentage transmittance at 10.62 μ against percentage of deuterated compound in the mixture. The limits were 52.5% transmittance for the most highly deuterated sample and 98% transmittance for the undeuterated sulfone. Since the various samples used varied widely in their deuterium content, the range for a kinetic run was not always this large.

B. Cyclopentyl *p*-Tolyl Sulfone.—A 70.0-mg. sample of the sulfone was dissolved in 0.50 ml. of chloroform and the spectrum between 10.4 and 11.2 μ run as before except that slow speed was used instead of normal speed. A calibration curve was obtained as before except that the peak at 11.00 μ was used. The range of percentage transmittance was from 48.5% for the undeuterated compound to 80% for the most highly deuterated compound.

Kinetic Procedure.—A solution about 0.05 *N* in sulfone and of known concentration (about 0.45 *N*) of potassium hydroxide in 50% by volume of dioxane–water was prepared. For runs at 40 and 50° this was placed in a glass-stoppered flask in a constant temperature bath and samples withdrawn at appropriate intervals and the sulfone isolated. For runs at higher temperatures samples were placed in Pyrex vials, frozen in a Dry Ice–acetone-bath, and sealed. The vials were placed in a constant temperature bath and at appropriate times withdrawn and placed in an ice-bath to stop the reaction. The sulfone was then isolated and analyzed.

The sulfone was isolated by making the solution acidic with hydrochloric acid, removing the solvents under reduced pressure and extracting the residue with hot hexane. The hexane was then filtered and evaporated to dryness. The sulfone then crystallized and was analyzed for deuterium content as described above. It was shown that deuterium exchange did not proceed during isolation.

Since the hydroxide ion is a catalyst, its concentration does not change during the course of the reaction, so the exchange followed first-order kinetics. The second-order rate constants were obtained by dividing the observed first-order rate constants by the hydroxide ion concentration.

PHILADELPHIA 1, PENNA.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Rates of Solvolysis of the *m*- and *p*-Phenyl-, *m*- and *p*-Methylthio-, and *m*- and *p*-Trimethylsilylphenyldimethylcarbinyl Chlorides. Steric Inhibition of Resonance as a Factor in Electrophilic Substituent Constants[1,2]

BY HERBERT C. BROWN, Y. OKAMOTO[3] AND T. INUKAI[4]

RECEIVED FEBRUARY 28, 1958

Rates of solvolysis in 90% aqueous acetone have been determined for *m*- and *p*-phenyl-, *m*- and *p*-methylthio-, and *m*- and *p*-trimethylsilylphenyldimethylcarbinyl chlorides. At 25° the *m*-phenyl substituent decreases the solvolysis rate by a factor of 0.32. In the *para* position the phenyl group increases the rate by a factor of 6.5. The relatively small activating effect of *p*-phenyl is attributed to low resonance interactions arising from the non-coplanarity of the biphenyl system. In the *meta* position, the methylthio substituent decreases the solvolysis rate at 25° by a factor of 0.192, whereas in the *para* position the substituent increases the rate by a factor of 553. The ratio $k_{p-\mathrm{CH_3S}}/k_{m-\mathrm{CH_3S}}$ is very nearly equal to the ratio, $k_{p-\mathrm{CH_3O}}/k_{m-\mathrm{CH_3O}}$, in spite of the fact that resonance interactions of the oxygen atom with aromatic systems are presumably much larger than the corresponding interactions of the sulfur atom. The similarity in the *para/meta* rate ratios is attributed to decreased resonance in the *p*-methoxy derivative arising from the non-coplanarity of the *p*-methoxy group. Because of the larger size of the sulfur atom, such inhibition of resonance is far less important. Finally, in both the *meta* and *para* positions the trimethylsilyl substituent has very little effect on the rate ($k_{m-\mathrm{(CH_3)_3Si-}}/k_{\mathrm{H}} = 0.895$; $k_{p-\mathrm{(CH_3)_3Si-}}/k_{\mathrm{H}} = 0.806$). This observation is in accord with the negligible directive influence reported for the trimethylsilyl group in aromatic substitution. Electrophilic substituent constants for these groups are calculated.

Recently we suggested that the solvolysis of substituted *t*-cumyl chlorides[5] might provide a convenient route to electrophilic substituent constants.[6] The substituent constants previously evaluated [Me, Et, *i*-Pr, *t*-Bu, β-naphthyl, F, Cl, Br, I, CH_3O, NO_2] appeared highly promising in correlating the available data on electrophilic aromatic substitution[7a] and electrophilic side-chain reactions.[7b] We were thereby encouraged to evaluate additional electrophilic substituent constants to provide a more extensive test of their utility in these correlations.

Considerable scepticism has been expressed with respect to the possibility of developing such a set of electrophilic substituent constants. The prevailing view has been that resonance interactions by the substituent will vary widely from reaction to reaction, so that the electronic contribution of the substituent could not possibly be represented by a single constant.[8]

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(1) Directive Effects in Aromatic Substitution. XXVI.

(2) This research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

(3) Post-doctorate research assitant on a National Science Foundation Grant (G-2752), 1956–1957.

(4) Research assistant on a grant from the Petroleum Research Fund, 1956–1958.

(5) It is convenient to adopt the shorter term, *t*-cumyl-, to refer to the phenyldimethylcarbinyl [$C_6H_5C(CH_3)_2-$] moiety.

(6) (a) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, THIS JOURNAL, **79**, 1897 (1957); (b) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1903 (1957); (c) H. C. Brown, Y. Okamoto and G. Ham, *ibid.*, **79**, 1906 (1957); (d) Y. Okamoto and H. C. Brown, *ibid.*, **79**, 1909 (1957).

(7) (a) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957); (b) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

(8) P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954); J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953); N. C. Deno and A. Schriesheim, *ibid.*, **77**, 3051 (1955). More favorable views have been expressed by D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952); N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, , **60**, 164 (1956); N. C. Deno and W. L. Evans, THIS JOURNAL, **79**, 5804 (1957).

TABLE I

RATE CONSTANTS AND DERIVED DATA FOR THE SOLVOLYSIS OF *m*- AND *p*-PHENYL-, *m*- AND *p*-METHYLTHIO- AND *m*- AND *p*-TRIMETHYLSILYL-*t*-CUMYL CHLORIDES IN 90% AQUEOUS ACETONE

Substituent	Rate constant, k, sec.$^{-1}$ × 10^5 −45.5°	−31.8°	−18.4°	0.0°	25.0°	35.0°	40.0°	55.0°	Rate ratio at 25°	E_{act}	log A	$\Delta H \ddagger$	$\Delta S \ddagger$
Hydrogen[a]				0.600	12.4	36.1			1.00	19.5	10.4	18.8	−12.5
m-Phenyl					3.97		20.3	85.8	0.320	19.9	10.2	19.3	−13.9
p-Phenyl				4.56	80.8				6.52	18.6	10.6	18.0	−12.2
m-Methylthio				0.0990	2.38		12.4		0.192	20.5	10.4	20.0	−12.8
p-Methylthio	76.7	15.3	2.11		6860[b]				553	15.5	10.2	15.0	−13.3
m-Trimethylsilyl				0.533	11.1	31.9			0.895	19.4	10.2	18.8	−13.5
p-Trimethylsilyl				0.514	10.0	13.3			0.806	19.4	10.2	18.8	−13.7

[a] Data from ref. 6a. [b] Calculated from rate constants at lower temperatures.

Consequently, it appeared that groups capable of strong resonance interactions would provide the most rigorous test of the utility of these constants. Accordingly, it was decided to examine the behavior of the *m*- and *p*-phenyl[9,10] and the *m*- and *p*-methylthio[11] substituents. The trimethylsilyl substituent exhibits quite unusual electrical characteristics.[12] This group also was included in the present study.

Results

The *t*-cumyl chlorides desired were synthesized by treating the substituted phenyldimethylcarbinol or the corresponding olefin with hydrogen chloride at 0°. Since the tertiary chlorides are unstable and difficult to purify, we were content to prepare pure samples of the tertiary alcohols or olefin, and to utilize the crude tertiary chlorides directly, without further treatment. It had been demonstrated previously that this procedure has no observable effect on the measured rate of solvolysis.[6a]

3-Isopropenylbiphenyl was obtained from the reaction of acetone with 3-bromomagnesium biphenyl. 4-Acetobiphenyl, from the acetylation of biphenyl, was treated with methylmagnesium iodide, to form the carbinol. The synthesis of the *m*- and *p*-methylthio derivatives proceeded through the corresponding benzoic acids, transformation into the methyl esters, followed by treatment with the methyl Grignard reagent. Finally, *m*- and *p*-bromophenyltrimethylsilanes were prepared from the reaction of the *m*- and *p*-halophenylmagnesium halides with trimethylchlorosilane. The two halides were transformed into the corresponding Grignard reagents and treated with acetone to form the *m*- and *p*-trimethylsilylphenyldimethylcarbinols.

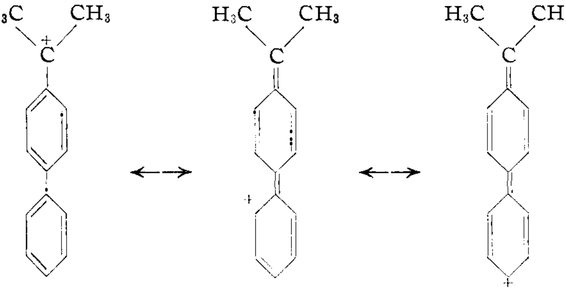
In the case of the latter compounds we were concerned over the possibility that the trimethylsilyl groups might be lost in the process of converting the tertiary carbinol into the chloride. However, the crude chloride from *p*-trimethylsilylphenylcarbinol analyzed for 95% tertiary chloride. After solvolysis, the pure trimethylsilylphenyldimethylcarbinol, m.p. 61–63°, could be isolated from the solution. As a result, it was concluded that protonolysis of the trimethylsilyl group does not occur under the mild conditions used for the preparation of the chloride.

The tertiary chlorides prepared from these derivatives were dissolved in 90% aqueous acetone and the rates of hydrolysis determined, usually at three temperatures. Because of the very fast rate exhibited by the *p*-methylthio- derivative, it was necessary to measure its rate at low temperatures (−45.5°, −31.8° and −18.4°) and to extrapolate the observed rate constants to 25°. The rate constants, relative rates at 25° and the derived data are summarized in Table I.

Discussion

In the *meta* position, the phenyl group reduces the rate of hydrolysis at 25° by a factor of 0.32, as compared to the parent compound. This is in accord with the recognized electron-withdrawing inductive effect of the phenyl group.[13]

In the *para* position, instead of a rate decrease, there is observed an increase in rate, with the *p*-phenyl-*t*-cumyl chloride undergoing solvolysis at a rate some 6.5 times greater than that of the parent compound. This increase in rate is reasonably attributed to stabilization of the carbonium ion by diffusion of the charge into the phenyl substituent (I).

I


A methyl group in the *para* position increases the rate of solvolysis of *t*-cumyl chloride by a factor of 26.[5] It is quite surprising that a methyl group in this system appears to be a considerably better source of electrons to stabilize the carbonium ion than is the electron-rich phenyl substituent.

In the α-phenylethyl chlorides, $C_6H_5CR_1R_2Cl$, both methyl and phenyl groups (R_1, R_2) markedly increase the rate of hydrolysis. However, in this system, phenyl substituents are far more effective than methyl substituents. This conclusion is sub-

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(9) P. B. D. de la Mare and M. Hassan, *J. Chem. Soc.*, 3004 (1957).

(10) M. T. S. Dewar, T. Mole and E. W. T. Warford, *ibid.*, 3572 (1956).

(11) F. G. Bordwell and P. J. Boutan, THIS JOURNAL, **78**, 854 (1956).

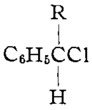
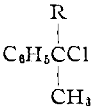
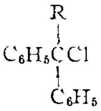
(12) C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 939 (1954); L. H. Sommer, J. R. Gold, G. M. Goldberg and N. S. Marans, THIS JOURNAL, **71**, 1509 (1949); H. Soffer and T. DeVries, *ibid.*, **73**, 5817 (1951).

(13) N. N. Lichtin and H. P. Leftin, *ibid.*, **74**, 4207 (1952).

stantiated by the results summarized in Table II.[14]

TABLE II

RELATIVE RATES OF SOLVOLYSIS OF PHENYL AND METHYL SUBSTITUTED α-PHENYLETHYL CHLORIDES

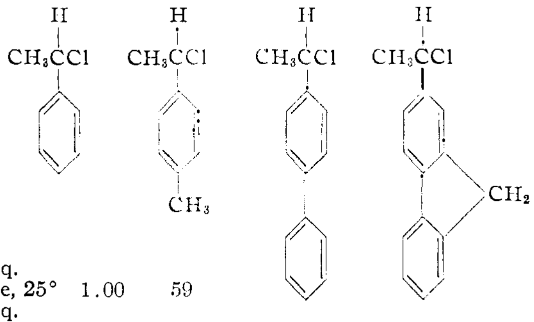
Structure	Relative rate[a] $k_1^{\mathrm{Ph}}/k_1^{\mathrm{Me}}$
 $\mathrm{C_6H_5\overset{R}{\underset{H}{C}}Cl}$	390[b]
 $\mathrm{C_6H_5\overset{R}{\underset{CH_3}{C}}Cl}$	56[c]
 $\mathrm{C_6H_5\overset{R}{\underset{C_6H_5}{C}}Cl}$	39[d]

[a] The rates are compared for R = Ph with R = Me. [b] In 90% aqueous acetone (wt. %) at 25°. [c] In 90% aqueous acetone (wt. %) at 0°. [d] In 97% aqueous acetone (wt. %) at 0°.

A similar inversion in the relative activating effects of *p*-Me and *p*-Ph has been observed in aromatic substitution by de la Mare and Hassan.[9] These authors have suggested that the lower activating effect of the *p*-Ph substituent may arise from the conflicting inductive and resonance effects of this substituent, whereas in the case of *p*-Me these two effects reinforce each other. Unfortunately, the much larger activating effect of α-phenyl substituents in the α-arylethyl chloride system does not appear to be consistent with this otherwise plausible interpretation.

An alternative explanation for the unexpectedly low resonance stabilization of the *p*-Ph substituent is suggested by the non-coplanarity of the biphenyl system. Thus, biphenyl has been reported to exist in the gas phase in a non-planar configuration with an angle of approximately 45° between the planes of the two aromatic rings.[15] This configuration presumably arises in order to minimize steric interactions of the four *ortho* hydrogen atoms. Such a non-coplanar system should greatly reduce the resonance contributions of the *p*-Ph substituent.[16]

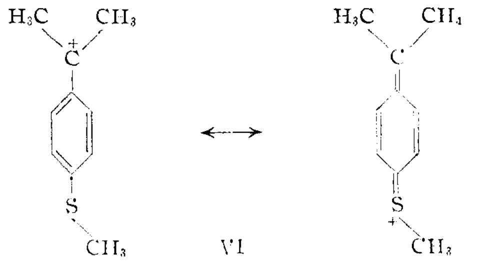
Strong evidence in support of this interpretation is provided by recent results of Berliner and Shieh.[17] Whereas a *m*-Me substituent increases the rate of solvolysis (in 70% aqueous acetone at 25°) of α-phenylethyl chloride (II) by a factor of 1.9, and a *p*-Me substituent (III) by a factor of 59,[14] a *p*-Ph substituent (IV) increases the rate (in 80% aqueous acetone at 25°) by a factor of only 11.[17] On the other hand, in the corresponding 2-fluorenyl derivative V, where the two aromatic rings of the biphenyl system are constrained to be coplanar by the methylene bridge, the rate of solvolysis is some 700-fold greater than that of the parent compound, α-phenylethyl chloride.



	II	III	IV	V
70% aq. acetone, 25°	1.00	59		
80% aq. acetone, 25°	1.00		11	700

In the *meta* position the methylthio substituent decreases the rate of hydrolysis by a factor of 0.192. Consequently, the *m*-methylthio group has a relatively powerful electron-withdrawing effect, significantly greater than that of the methoxy group. This is also indicated by the Hammett σ-constants for these groups.[11] In the *para* position the methylthio group has a marked activating effect—the solvolysis of the *p*-methylthio-*t*-cumyl chloride proceeds at a rate some 550 times greater than the parent compound.

Presumably this greatly enhanced rate of solvolysis of the *p*- as compared to the *m*-methylthio derivative is the result of resonance stabilization of the carbonium ion VI.



VI

However, the high rate of solvolysis observed was unexpected. It is generally considered that first row elements, such as fluorine and oxygen, are far more able to engage in resonance interactions with aromatic rings than are second row elements, such as chlorine and sulfur.[18] If we take 2.303 RT log $(k_{\mathrm{p}}/k_{\mathrm{m}})$ as a measure of the resonance stabilization provided by the respective *para* substituents, we see that *p*-fluoro is indeed considerably more effective than *p*-chloro (Table III). On the other hand, there is a much smaller difference between *p*-methoxy and *p*-methylthio (Table III).

TABLE III

RESONANCE CONTRIBUTIONS OF *m*- AND *p*-SUBSTITUENTS

Substituent	$k_{\mathrm{p}}/k_{\mathrm{m}}$ (25°)	2.303 RT log $(k_{\mathrm{p}}/k_{\mathrm{m}})$
Fluoro	85.2	2.6
Chloro	19.5	1.8
Methoxy	5500	5.1
Methylthio	2800	4.7

It has been suggested that the resonance contri-

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[14] Y. Okamoto, Ph.D. Thesis, Purdue University, 1957.

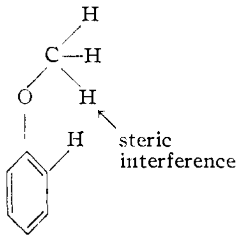
[15] O. Bastiansen, *Acta. Chem. Scand.*, **3**, 408 (1949); **4**, 926 (1950).

[16] See G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 157 ff., for a detailed discussion of steric inhibition of resonance with pertinent literature references.

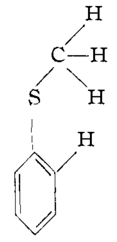
[17] E. Berliner and N. Shieh, THIS JOURNAL, **79**, 3849 (1957).

[18] A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 103.

butions of *p*-methoxy are lower than they should be because of steric interactions between the methyl group and the *ortho* hydrogen atoms which force the methoxy group out of the plane of the aromatic ring (VII).[19] On this basis, the larger covalent radius of sulfur should decrease this steric interference and permit a closer approach to the coplanar configuration most favorable for resonance stabilization of the carbonium ion.



VII



VIII

The strengths of *m*- and *p*-trimethylsilylbenzoic acid are reported to be slightly lower than that of benzoic acid in 50 (vol.)% aqueous ethanol.[20,21] On the other hand, Chatt and Williams found the strength of *p*-trimethylsilylbenzoic acid in 60.1 (wt.)% aqueous ethanol to be slightly stronger than that of benzoic acid.[22]

In spite of these minor differences there is general agreement that the electrical effects of the trimethylsilyl group are small and the Hammett σ-constants are close to zero.

Even in the case of aromatic substitution the available evidence is that the trimethylsilyl group has no significant directive effect. For example, Benkeser and Brumfield observed that the nitration of phenyltrimethylsilane with copper nitrate yielded 30% *o*-, 40% *m*- and 30% *p*-nitrophenyltrimethylsilane.[23] Similarly, Speier noted that fuming nitric acid in formic acid at −10° yielded a phenyltrimethylsilane–benzene reactivity ratio of 1.64 with 20% *o*-, 30% *m*- and 50% *p*-orientation.[24]

In the solvolysis study, the introduction of the *m*- and *p*-trimethylsilyl substituents results in small decreases in rate, by factors of 0.9 and 0.8, respectively. These small effects of the trimethylsilyl substituent are qualitatively in agreement with the negligible directive effect observed in aromatic substitution. Unfortunately, data are not available which would permit a quantitative examination of the correlation.

Taking ρ for the solvolysis of the substituted *t*-cumyl chlorides in 90% acetone as −4.54[25] and the relative rates listed in Table I, values of the electrophilic substituent constants have been calculated with the aid of the expression

$$\sigma^+ = \frac{1}{\rho} \log (k/k_H)$$

The resulting constants are listed in Table IV, along with the related Hammett substituent constants.[26]

TABLE IV

SUBSTITUENT CONSTANTS FOR THE *m*- AND *p*-PHENYL, *m*- AND *p*-METHYLTHIO AND *m*- AND *p*-TRIMETHYLSILYL GROUPS

Substituent	σ_m	σ_m^+	σ_p	σ_p^+
Phenyl	0.06	0.109	−0.01	−0.179
Methylthio	.15	.158	.00	− .604
Trimethylsilyl	− .04	.011	− .07	.021

The utility of these electrophilic substituent constants in correlating the available data on electrophilic aromatic substitution and electrophilic side chain reactions is explored in the final paper of this group.

Experimental Part

3-Isopropenylbiphenyl.—*m*-Bromoaniline was converted into 3-bromobiphenyl, b.p. 155–158° at 11 mm., n^{20}_D 1.6412, by adapting the procedure used for the synthesis of 3-nitrobiphenyl.[27] The product from the reaction of acetone with 3-bromomagnesium biphenyl lost water upon distillation. Consequently, the mixture of olefin and carbinol was refluxed with acetic anhydride to complete the dehydration. In this way, 3-isopropenylbiphenyl, b.p. 160.5–161.5 at 11.5 mm., n^{20}_D 1.6136, was obtained in 51% yield.[28]

4-Diphenylyldimethylcarbinol.—4-Acetobiphenyl, m.p. 121–122°, from the Friedel–Crafts acylation of biphenyl,[29] was converted by methyl magnesium iodide into the carbinol, m.p. 91.5–92.5° (lit.[28] 92–93°) in 62% yield.

***m*- and *p*-Methylthiophenyldimethylcarbinols.**—Diazotized *p*-aminobenzoic acid was treated with sodium disulfide to form the bis-*p*-carboxyphenyl disulfide, which was reduced with zinc powder and glacial acetic acid to *p*-mercaptobenzoic acid.[30] The product was converted to the methylthio derivative with dimethyl sulfate[31] and esterified with methanol, m.p. 81–82° (lit.[32] 82°). The ester was treated with methylmagnesium iodide to form *p*-methylthiophenyldimethylcarbinol in 93% yield, m.p. 62.9–63.4°.

Anal. Calcd. for $C_{10}H_{14}OS$: C, 65.89; H, 7.74. Found: C, 65.88; H, 7.83.

Diazotized *m*-aminobenzoic acid was treated with potassium methyl xanthate. The crude *m*-methylthiobenzoic acid, m.p. 120–125° (lit.[33] m.p. 126°) was converted into the methyl ester,[31] b.p. 125° at 4 mm., n^{20}_D 1.5774 (lit.[31] b.p. 132° at 4 mm.). The ester was recrystallized from pentane at low temperatures and redistilled. No change in the physical constants was observed. The ester was treated with methylmagnesium iodide and *m*-methylthiophenyldimethylcarbinol, b.p. 114° at 1 mm., n^{20}_D 1.5762, was obtained in 90% yield.

Anal. Calcd. for $C_{10}H_{14}OS$: C, 65.89; H, 7.74. Found C, 66.32; H, 7.74.

***m*- and *p*-Trimethylsilylphenyldimethylcarbinols.**—*p*-Dibromobenzene and *m*-bromoiodobenzene were transformed into the monoGrignard reagents and treated with trimethyl-

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[19] G. Baddeley, N. H. P. Smith and M. A. Vickars, *J. Chem. Soc.*, 2455 (1956).

[20] R. A. Benkeser and H. R. Krysiak, THIS JOURNAL, **75**, 2421 (1953).

[21] J. D. Roberts and C. M. Regan, *ibid.*, **75**, 4102 (1953).

[22] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 4402 (1954).

[23] R. A. Benkeser and P. E. Brumfield, THIS JOURNAL, **73**, 4770 (1951).

[24] J. L. Speier, *ibid.*, **75**, 2930 (1953).

[25] This value differs slightly from the value used previously, $\rho = -4.62$ (ref. 5). The reason for the selection of the new value is presented in the final paper of this group, H. C. Brown and Y. Okamoto, THIS JOURNAL, **80**, 4979 (1958).

[26] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

[27] W. E. Bachmann and R. A. Hoffman, Chapt. 6, Vol. 2, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., p. 249.

[28] D. T. Mowry, J. Dazzi, M. Renoll and R. W. Shortridge, THIS JOURNAL, **70**, 1916 (1948), report b.p. 160–161° at 12 mm., n^{20}_D 1.6128.

[29] C. V. Ferris and E. E. Turner, *J. Chem. Soc.*, 1147 (1920).

[30] The procedure was identical to that described for thiosalicylic acid: C. F. H. Allen and D. D. MacKay, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 580.

[31] The procedure for the related *meta* derivative was followed: K. Brand, W. Gabel and E. Rosenkranz, *Ber.*, **70**, 305 (1937).

[32] K. Brand and O. Stallmann, *J. prakt. Chem.*, [2] **107**, 378 (1924).

[33] V. Baliah, S. Shanmuganathan and R. Varadachin, *J. Phys. Chem.*, **61**, 1013 (1957).

chlorosilane to form *m*- (b.p. 72–75° at 2.2 mm., n^{20}_D 1.5458) and *p*-bromophenyltrimethylsilanes (b.p. 75–77° at 4 mm., n^{20}_D 1.5303).[34]

p-Bromophenyltrimethylsilane was converted into the Grignard reagent and treated with acetone. *p*-Trimethylsilylphenyldimethylcarbinol was obtained in a yield of 42%. After recrystallized from hexane, the product exhibited m.p. 52–52.5°.

Anal. Calcd. for $C_{12}SiH_{20}O$: C, 69.28; H, 9.65. Found: C, 69.38; H, 9.77.

m-Trimethylsilylphenyldimethylcarbinol was obtained through an identical procedure. After two recrystallizations from hexane, the product, m.p. 62–63°, was obtained in 41% yield.

Anal. Calcd. for $C_{12}SiH_{20}O$: C, 69.28; H, 9.65. Found: C, 69.01; H, 9.65.

Preparation of Tertiary Chlorides.—The olefin and carbinols were transformed into the tertiary chlorides by treatment with hydrogen chloride in methylene chloride solution, following the procedure previously described.[6c] All of the chlorides were liquids, except for *p*-phenyl-*t*-cumyl chloride, m.p. 64–65°. The chlorides were used directly for the rate measurement without further treatment.

Since the trimethylsilyl group is subject to protonolysis,[35] we examined the possibility that cleavage of this group might occur in the course of preparation of the tertiary chloride. *m*-Trimethylsilylphenyldimethylcarbinol, 4.0 g., was dissolved in 40 ml. of methylene chloride and treated with dry hydrogen chloride at 0° for 30 min. The aqueous phase was separated and the solvent phase dried over calcium chloride. The solvent was removed under reduced pressure. Two samples of the product, 0.3775 g. and 0.7227 g., were solvolyzed in 30 ml. of 60% aqueous acetone. The acid produced in the solvolysis required 14.60 and 27.85 ml. of 0.1087 *N* sodium hydroxide, corresponding to 95.3 and 95.0% of the amount calculated for $C_{12}H_{19}SiCl$. The solutions were combined and extracted with ethyl ether. Removal of the ether yielded yellowish crystals. After recrystallization from pentane, *m*-trimethylsilylphenyldimethylcarbinol, m.p. 61–63°, was obtained, and no melting point depression with the original carbinol, m.p. 62–63°, was observed.

Kinetic Measurements.—The procedures were similar to those previously described. The aqueous content of the 90% acetone was adjusted so as to yield a rate of solvolysis identical (±3%) with that observed in the earlier studies.[6a] Rate constants observed for the solvolysis of *t*-cumyl chloride were 0.435, 0.440, 0.437 and 0.434 hr.$^{-1}$ Typical kinetic data are presented in Table V.

TABLE V

RATE DATA FOR THE SOLVOLYSIS OF SUBSTITUTED *t*-CUMYL CHLORIDES IN 90% AQUEOUS ACETONE

Time, hr.	*x*, ml.	*a* − *x*, ml.	k_1, hr.$^{-1}$
A. *m*-Phenyl-*t*-cumyl chloride at 55.0°			
0	0.390	3.850	
0.133	1.630	2.610	2.92
.200	2.150	2.090	3.05
.267	2.550	1.690	3.08
.350	2.940	1.300	3.10
.417	3.190	1.050	3.12
.533	3.540	0.700	3.20
.633	3.710	0.530	3.12
∞	4.240		∞
		Average	3.09 ± 0.059
B. *p*-Methylthio-*t*-cumyl chloride at −45.5°			
0	0.865	7.375	
0.125	0.938	7.302	7.96 × 10^{-2}
.350	1.062	7.178	7.74
.683	1.228	7.012	7.39
1.083	1.440	6.800	7.49
1.417	1.596	6.644	7.37
∞	8.240		∞
		Average	7.59 ± 0.21
C. *p*-Trimethylsilyl-*t*-cumyl chloride at 35°			
0	0.180	4.970	
0.133	0.838	4.312	1.07
.250	1.360	3.790	1.08
.383	1.860	3.290	1.08
.500	2.280	2.870	1.10
.733	2.928	2.220	1.10
.900	3.310	1.840	1.10
1.050	3.590	1.560	1.10
∞	5.150		∞
		Average	1.09 ± 0.01

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