

t-Butyl chloride (kindly supplied by S. J. Tauber) was fractionally distilled from CaO, a center cut of b.p. 51.0° being taken, n_D^{20} 1.3854, lit.¹³ n_D^{20} 1.3855. The mixtures of aqueous methanol were made up in the same way as those used for the persulfonate runs.

(b) **Kinetic Procedure.**—The solvolysis was carried out in sealed tubes and followed by the appearance of HCl, using a titrimetric method of Fainberg and Winstein. In this method, the contents of the tube were washed into 25 ml. of acetone and titrated with methanolic NaOH to a brom phenol blue end-point (very sharp color change from yellow to green). The methanolic NaOH was standardized against standard HCl under the same conditions. The tubes held 5-ml. aliquots for the most part, 10-ml. aliquots being used at the beginning of the reaction when the acid concentration was still low. The solvent was kept in the constant temperature bath at least an hour before each run. Zero time was taken at the addition of *t*-butyl chloride to the solvent. Immediately after the *t*-butyl chloride was mixed with the solvent, the infinity point was taken by pipetting three or four 5-ml. aliquots into 35 ml. of water and letting the resulting solution stand for 4 to 5 hours. The acid content was determined by titration with methanolic NaOH to a phenolphthalein end-point, the base having been standardized against standard HCl under the same conditions. Fainberg and Winstein used brom thymol blue indicator, but

this proved unsatisfactory here since the color change was not in the least sharp. Of a series of other indicators tried, only phenolphthalein gave an acceptable precision of 0.1 ml. in 15 to 20 ml. of titrant used. The rate constants were evaluated graphically from a plot of $\log(A_\infty - A)$ versus time, where A_∞ is the "infinity" acid concentration and A the acid concentration at time t . Each plot had 8 to 10 points to determine the line.

Y-Values.—Because of the increasing reference value of the rate constants for solvolysis of *t*-butyl chloride, presented in Table I are the new values for the methanol-water system of mixed solvents, together with a comparison with the results for the less closely spaced solvent mixtures reported by Fainberg and Winstein¹³ and by Cropper, Spieth and Olson.²² The values calculated from the empirical equation of Fainberg and Winstein are also shown.

Acknowledgment.—This investigation was supported by a grant from the Higgins Fund of Harvard University, and by a Fellowship from the National Institutes of Health to the junior author.

(22) W. H. Cropper, F. Spieth and A. R. Olson, *THIS JOURNAL*, **76**, 6248 (1954).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

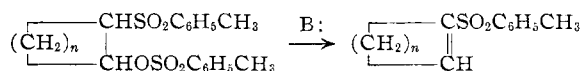
cis Elimination Mechanisms: The Base-catalyzed Deuterium Exchange of Cycloalkyl *p*-Tolyl Sulfones

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The rates of base-catalyzed exchange of deuterium for hydrogen alpha to the sulfone in cyclopentyl and cyclohexyl *p*-tolyl sulfone have been measured at several temperatures, and activation energies for the reaction obtained. Comparison of these rates with those of the base-catalyzed elimination reactions of the corresponding *trans*-sulfone tosylates which undergo *cis*-elimination shows that deuterium exchange is from 10^{-3} to 10^{-6} as rapid, and thus that carbanion formation cannot be the rate-determining step in the elimination reactions. It was found that for deuterium exchange the cyclopentyl system reacts about 1.5 times faster than the cyclohexyl system, while in the *cis* elimination reactions of *trans*-sulfone tosylates the ratio is about 60. This suggests that there is no relief of strain in the transition state in the cyclopentyl system when going to the anion, but that there is relief of strain in going to the transition state leading to olefin. Hence, there is partial double bond formation in the transition state leading to elimination and a free carbanion intermediate seems excluded.

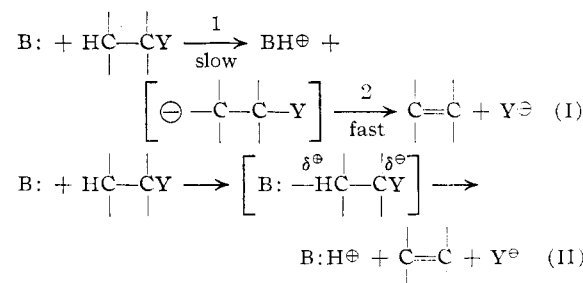
In a study of the base-catalyzed elimination reactions of *cis*- and *trans*-2-(*p*-tolylsulfonyl)-cycloalkyl *p*-toluenesulfonates² (I) we have found that although the *trans* elimination using hydroxide ion as the base goes 400 times faster than *cis* elimination in the cyclohexyl system, and 20 times faster in the cyclopentyl system, both *cis* and *trans* eliminations are subject to general base catalysis. This indicated that no carbanion which existed long enough to revert to sulfone tosylate was present as



Ia, *trans*-cyclohexyl
Ib, *trans*-cyclopentyl
Ic, *cis*-cyclohexyl
Id, *trans*-cyclopentyl

an intermediate, and that removal of a proton was involved in the rate-determining step. However, this work did not show whether a short lived carbanion was involved as an intermediate (mechanism

I) or if the reaction was concerted in the sense that the removal of the proton was made more facile by the simultaneous departure of the leaving group (mechanism II).



Other workers in this field³⁻⁵ have suggested that the results previously obtained would be consistent with mechanism I^{3,4} or mechanism II in which the C-Y bond has barely begun to break. The present work was undertaken as part of an effort to obtain evidence concerning the extent of concertedness, if any, of the elimination reactions

(3) H. L. Goering, D. I. Relyea and K. L. Howe, *ibid.*, **79**, 2502 (1957).

(4) S. J. Cristol and E. F. Hoegger, *ibid.*, **79**, 3438 (1957).

(5) W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957).

(1) Research and Development Division, Smith, Kline and French Laboratories, Philadelphia 1, Pa. This paper was presented at the Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, Pa., February 5, 1958.

(2) J. Weinstock, R. G. Pearson and F. G. Bordwell, *THIS JOURNAL*, **78**, 3468, 3473 (1956).

previously studied. We have tried to estimate the rate of step 1 of mechanism I by means of a deuterium exchange study.

In order to study the rate of base-catalyzed ionization of the cycloalkyl *p*-tolyl sulfones, the deuterated sulfones were prepared and their rate of exchange to the protium compound in 50% water-dioxane studied. The usual assumption is made that the rate of exchange is equal to the rate of ionization. Cyclohexyl-1-*d*₁ *p*-tolyl sulfone was prepared by obtaining the magnesium iodide salt of cyclohexyl *p*-tolyl sulfone by reaction with a Grignard reagent and treating it with 99.5% deuterium oxide. The abstraction of the hydrogen in the 1-position is expected by analogy with earlier work of Field.⁶ If isopropyl *p*-tolyl sulfone is treated with ethylmagnesium bromide a salt is obtained which gives 1-substituted products on treatment with carbonyl compounds or with a halide. The amount of deuteration was often low by this procedure, so base-catalyzed exchange of the sulfone with 99.5% deuterium oxide also was used by us. This gave the same deuterated product as before, but with a higher recovery of material and usually with a greater amount of deuterium exchange. Cyclopentyl-1-*d*₁ *p*-tolyl sulfone was prepared by the second method.

The assignment of the position of the deuterium also was supported by the differences in the infrared spectrum of the deuterated and undeuterated compounds. Bellamy⁷ states that the —C—H bending results in a weak band close to 1340 cm.^{-1} . The spectrum of cyclohexyl *p*-tolyl sulfone has a weak band at 1340 cm.^{-1} which is much less intense (reverts to a shoulder) in cyclohexyl-1-*d*₁ *p*-tolyl sulfone. The spectrum of cyclopentyl *p*-tolyl sulfone has a shoulder at 1337 cm.^{-1} which becomes less intense in the spectrum of the deuterated sulfone. Bellamy⁷ states that the C—CH_3 group has a symmetrical deformation mode of the hydrogen which gives rise to a band at $1370\text{--}1385\text{ cm.}^{-1}$ in the cyclopentyl and the cyclohexyl compounds the spectrum of both the deuterated and the undeuterated samples have a peak at about 1387 cm.^{-1} of about equal intensity. This indicates that no deuteration has occurred on the methyl group on the benzene ring.

The rate of exchange of the deuterium for hydrogen catalyzed by hydroxide ion was measured in a 50% by volume mixture of dioxane and water. Since hydroxide ion is not used up by the exchange, the reaction follows pseudo first-order kinetics. Consequently it was not necessary to know the isotopic purity of the starting sulfone. It is only necessary to be able to determine the relative rate of disappearance of deuterio sulfone in terms of its initial concentration. The exchange was followed by isolating samples of sulfone after appropriate time intervals and determining the intensity of an appropriate peak in its infrared spectrum. A calibration curve was constructed using known mixtures

and the relative deuterium content could be determined from this. Considering the method of analysis, it is estimated that the rates are accurate to at least 10%. The results and the mean deviations are shown in Table I. The energies of activation, the entropies of activation and the calculated rates at 25° also are given.

TABLE I
RATES, ACTIVATION ENERGIES AND ACTIVATION ENTROPIES
FOR DEUTERIUM EXCHANGE OF SULFONES

| <i>p</i> -Tolyl sulfone | <i>T</i> , °C. | Initial % D ^a | $k \times 10^3$, l. mole ⁻¹ sec. ⁻¹ | $E_{\text{act.}}$, kcal./mole | ΔS^\ddagger , e.u. |
|--------------------------------------|-------------------|-----------------------------|---|-----------------------------------|-------------------------------|
| Cyclohexyl-1- <i>d</i> ₁ | 40 | 32 | 0.218 ± 0.003 | 25.2 | -5.3 |
| | 50 | 100 | $1.11 \pm .04$ | | |
| | 70 | 42 | $8.43 \pm .72$ | | |
| | 79.2 | 38 | 22.5 ± 2.2 | | |
| | 25 ^b | | 0.0412 | | |
| Cyclopentyl-1- <i>d</i> ₁ | 50 | 80.5 | 1.67 ± 0.08 | 25.1 | -4.9 |
| | 59.9 | 81 | $5.25 \pm .22$ | | |
| | 70.8 | 100 | $16.7 \pm .68$ | | |
| | 25 ^b | | 0.0620 | | |

^a In terms of the most completely deuterated sample obtained. ^b Calculated using the rate at 50° and the activation energy.

In order to compare the exchange data with the elimination data it is first necessary to estimate the isotope effect in order to be able to estimate the rate of exchange of the protium sulfones. It is also necessary to estimate the acid-strengthening effect of the tosylate group due to its inductive effect since this would increase the rate of hydrogen abstraction.

In a number of cases of base-catalyzed ionization, it has been found that $k_{\text{H}}/k_{\text{D}}$ has values ranging from 1.5 to about 7.⁸ Since we are interested comparing orders of magnitude, the larger value will be taken as a limiting case. There seems to be no direct estimate of the inductive effect of the tosylate group available. However, it must be less acid strengthening than chloride as judged from the fact that the rate of elimination of 2-chloro-cycloalkyl sulfones is about the same as for the corresponding sulfone tosylate.³ Since in pure displacement reactions tosylates are much more reactive than chlorides, the conclusion that the inductive effect is less must be drawn to explain the elimination data. It also has been shown⁹ that in the phenethyl series tosylates eliminate much more slowly than bromides or iodides.

An estimate of the possible rate-enhancing effect of the chloro group due to its inductive effect can be obtained from data on the rate of ionization of pseudo acids collected by Pearson and Dillon.¹⁰ The ratio of the rate of ionization in water of chloroacetone to that of acetone is 118. The same ratio for nitroethane and chloronitroethane is 15.5. Again taking the higher figure and correcting for the fall-off of the inductive effect in moving the activating group from an α -carbon to a β -carbon,

(6) L. Field and J. W. McFarland, *THIS JOURNAL*, **75**, 5582 (1953); L. Field, *ibid.*, **78**, 92 (1956).

(7) L. J. Bellamy, "The Infrared-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 20.

(8) (a) W. D. Emmons and M. F. Hawthorne, *THIS JOURNAL*, **78**, 5593 (1956); (b) J. Hine and N. W. Burske, *ibid.*, **78**, 3337 (1956); J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, **79**, 1406 (1957).

(9) C. H. De Puy and D. R. Froemsdorf, *ibid.*, **79**, 3710 (1957).

(10) R. G. Pearson and R. L. Dillon, *ibid.*, **75**, 2440 (1953).

one can estimate that β -chloroethyl ketones might ionize as much as 15 times more rapidly than the corresponding ethyl ketones, and that this figure would be a high estimate for the inductive influence of the tosylate radical on the rate of ionization of I. Combining this figure with 7 for the isotope effect, it is calculated that the cycloalkyl-1- d_1 *p*-tolyl sulfones should ionize no more than 1/100 as fast as I would in the absence of a concerted elimination reaction. In Table II the rates of *cis* elimination of Ia and Ib and the rates of ionization are compared. The rates of elimination are at least 10^3 to 10^6 times faster than the calculated rates of ionization of Ia and Ib, and this excess rate must be ascribed to occurrence of carbon-oxygen bond breaking in the transition state for elimination.

TABLE II

| | Rate of deuterium exchange, 25° | Estd. max. rate of proton abstraction of I | Rate of <i>cis</i> elimination of I |
|-------------|---------------------------------|--|-------------------------------------|
| Cyclopentyl | 6.20×10^{-7} | 6×10^{-6} | 2.17 ^a |
| Cyclohexyl | 4.12×10^{-7} | 4×10^{-6} | 3.48×10^{-20} |

^a Data from reference 2.

The same conclusion is reached by considering the activation energies for deuterium exchange shown in Table I with the activation energies for *cis* elimination in a series of substituted benzene-sulfonates of 2-cyclohexyl *p*-tolyl sulfone in 50% dioxane-water.¹² These values are between 15.7 and 17.5 kcal. which are 5–7 kcal. smaller than for the ionization step after allowance is made for the deuterium and inductive effects.

The data in Table II may be looked at in another way. The rates of deuterium exchange are nearly the same for the cyclohexyl and cyclopentyl sulfones. This contrasts markedly with rates of ionization of the cycloalkyl ketones,⁸ keto esters and diketones,¹⁰ and nitro compounds,¹¹ in which the five-membered ring is always considerably more reactive than the six. These greater rates have been explained^{12,13} on the basis of relief of strain due to opposed hydrogens when unsaturation is introduced either *endo* or *exo* to a five-membered ring. It then follows that in the ionization of the sulfones there is no unsaturation due to π -bonding of the kind produced in the ionization of ketones and nitro compounds. Either the sulfone group does not π -bond or else the π -bonding involves *d*-orbitals with quite different geometrical requirements than *p*-orbitals.¹⁴ Table II shows that *cis* elimination is 63 times faster in the cyclopentyl case than in the cyclohexyl case. The logical explanation for this is that unsaturation is being produced in the transition states for elimination and that this results from the partial release of the tosylate group.

If unsaturation is already partly present in the transition state, then it must surely become com-

plete as the proton is completely removed; thus the formation of a carbanion intermediate which must rearrange in some manner before losing the tosylate group is very unlikely. The E1cB mechanism does not seem to operate even in this rather favorable case.

Experimental¹⁵

Cyclopentyl *p*-Tolyl Sulfide.—To a solution of 46.8 g. (0.377 mole) of *p*-thiocresol and 56.5 g. (0.377 mole) of cyclopentyl bromide in 150 ml. of alcohol was added a solution of 15 g. (0.377 mole) of sodium hydroxide in 65 ml. of water. The solution became hot and an oil came out of solution. About 5 ml. extra of bromide was added, the mixture shaken and allowed to stand at room temperature for 24 hours. The mixture was then concentrated, diluted with water, and extracted with ether. The ether solution was dried over magnesium sulfate and distilled. This gave 58.6 g. (82%) of an oil, b.p. 155–156° at 16 mm., n_D^{20} 1.5628.

Anal. Calcd. for $C_{12}H_{18}S$: C, 74.94; H, 8.38. Found: C, 75.25; H, 8.42.

Cyclopentyl *p*-Tolyl Sulfone.—A hot solution containing 58.6 g. (0.32 mole) of cyclopentyl *p*-tolyl sulfide dissolved in a mixture of 150 ml. of glacial acetic acid and 150 ml. of acetic anhydride was treated with 100 ml. of 30% hydrogen peroxide (0.96 mole) at such a rate as to maintain reflux. After the addition was complete the solution was refluxed for 1.5 hours, cooled, and poured into cold water. The crystals which formed were recrystallized from a methanol-water mixture to give 59.4 g. (87%) of white crystals, m.p. 52–55°. Recrystallization from hexane gave a 92% recovery of crystals of the same melting point.

Anal. Calcd. for $C_{12}H_{16}SO_2$: C, 64.25; H, 7.19. Found: C, 64.61; H, 7.47.

Cyclohexyl *p*-Tolyl Sulfone.—Cyclohexyl *p*-tolyl sulfide (b.p. 170–172° at 17 mm.) was prepared from thiocresol, cyclohexyl bromide, and potassium hydroxide in 40% yield by the method used for the cyclopentyl analog. On oxidation a 90% yield of sulfone, m.p. 84–86°, after recrystallization from hexane, was obtained which had the same infrared spectrum as material previously prepared by another method.

Cyclohexyl-1- d_1 *p*-Tolyl Sulfone. Method A.—A solution of methylmagnesium iodide was prepared using 0.85 g. (0.07 mole) of magnesium, 5.5 g. (0.021 mole) of methyl iodide and 40 ml. of ether. A solution of 5.0 g. (0.021 mole) of cyclohexyl *p*-tolyl sulfone in 60 ml. of ether was added and the mixture refluxed for about 1 hour. Then 1.50 g. (0.075 mole) of 99.5% deuterium oxide was added, and after about 5 minutes the reaction poured into a saturated solution of ammonium chloride. The organic layer was washed with water and the solvent removed under reduced pressure. The residue was recrystallized from hexane to give 1.3 g. of sulfone, m.p. 84–86°, undepressed by admixture with starting sulfone. The infrared spectra of the deuterated and undeuterated sulfone differed in the region 9–12 μ , but no obvious difference was found in the region 3.8–5 μ .

Method B.—A mixture of 5.0 g. (0.021 mole) of cyclohexyl *p*-tolyl sulfone, 3.0 g. (0.15 mole) of deuterium oxide in which 150 mg. (0.006 mole) of sodium had been dissolved and 20 ml. of dioxane was sealed in a glass vial and placed in a steam-bath for 48 to 95 hours. The sulfone was recovered in about 70% yield by adding the mixture to concentrated hydrochloric acid, evaporating to dryness, and taking up the product in hot hexane. The infrared spectrum of the product deuterated in this way showed the same changes from the spectrum of the undeuterated sulfone as in the above method, but of course the degree of deuteration (and so the amount of change in the spectrum) differed from run to run.

Cyclopentyl-1- d_1 *p*-Tolyl Sulfone.—A solution of sodium deuterioxide was prepared by dissolving 60 mg. (0.0025 mole) of sodium in 2.60 g. (0.13 mole) of 99.5% deuterium oxide. To this was added a solution of 2.5 g. (0.013 mole) of cyclopentyl *p*-tolyl sulfone in 8 ml. of dioxane and the solution sealed in a glass vial and kept in a steam-bath for 24 hours. The solution was then added to excess 12 *N* hydrochloric acid, evaporated to dryness and the residue taken up in hot

(11) H. Stone, P. Flanagan, J. Traynham and H. Schechter, Abstracts of 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956, p. 82-O.

(12) T. F. Sullivan, private communication.

(13) H. C. Brown, J. H. Brewster and H. Schechter, *THIS JOURNAL*, **76**, 467 (1954).

(14) This conclusion is supported by other kinds of evidence: W. Doering and L. Levy, *ibid.*, **77**, 509 (1955); H. Zimmerman, T. Nevins and B. Thyagarajan, Abstracts of 132nd Meeting of the American Chemical Society, New York, N. Y., September, 1957, p. 39-P.

(15) Analyses by Miss Hilda Beck.

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 $11.00\ \mu$ was more intense for the undeuterated sample and a new small peak appeared at $10.08\ \mu$ 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 $11\ \mu$ 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 $10.62\ \mu$ 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 $11.2\ \mu$ 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 $11.00\ \mu$ 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.

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[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}

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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 $k_{p-\text{CH}_3\text{S}}/k_{m-\text{CH}_3\text{S}}$ is very nearly equal to the ratio, $k_{p-\text{CH}_3\text{O}}/k_{m-\text{CH}_3\text{O}}$, 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 ($k_{m-(\text{CH}_3)_3\text{Si-}}/k_{\text{H}} = 0.895$; $k_{p-(\text{CH}_3)_3\text{Si-}}/k_{\text{H}} = 0.806$). 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 chlorides⁵ 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, CH₃O, NO₂] 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

(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).

(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 assistant 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 [$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2$] 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).