(41.5%) of hydrogen and the formation of a white precipitate which was soluble in excess acid solution. The clear colorless mixture was refluxed and yielded 2.84 g. (0.0167 mole, 53.7%) of C_3F_7H. The presence of a small amount of hydrogen sulfide was apparent. Distillation of the dried ether layer produced a fraction, b.p. 70–80°, $n^{20}D$ 1.3722, containing fluorine and iodine. Qualitative tests for fluoride ion on the aqueous layer were negative.

In an attempt to isolate and further characterize the complex $LiAl(C_3F_7)H_2I$, about half of the ether was removed by distillation at atmospheric pressure when a violent decomposition occurred. Addition of water to the remaining solid produced no evolution of gas. Aluminum powder, lithium iodide, hydrogen and probably C_3F_7H were formed. An alternate method of isolation was attempted by evaporating most of the solvent *in vacuo* to a slush, adding benzene and removing by filtration through a sintered glass funnel the remaining undissolved solid. The filtered white solid was lithium iodide only. The benzene filtrate on standing for 0.5 hour under nitrogen decomposed spontaneously. An aliquot previously taken produced C_3F_7H on the addition of water.

Reaction of Perfluoropropyl Iodide with Lithium Aluminum Hydride in a 3:1 Molar Ratio.—To 35 ml. (0.0392 mole) of lithium aluminum hydride solution at −78° was slowly added 34.72 g. (0.1170 mole) of perfluoropropyl iodide in 150 ml. of anhydrous ether with the evolution of 0.0378 mole (96.4%) of hydrogen. The reaction solution was allowed to remain at −80° to −20° for two hours and at 0° for one hour and then the solution gently refluxed for three hours and flushed intermittently with nitrogen. The original clear colorless solution became red, a crystalline substance was deposited and the sulfuric acid trap in the system also became markedly red. The colorless material collected in the trap was passed through distilled water, redried and condensed to yield 6.6 g. (0.0388 mole) of C_3F_7H, 99% of theory in accordance with equation 2. Several additional runs also produced stoichiometric amounts of C_3F_7H according to equation 2 before the addition of water. The distilled water above was acidic, liberated CO_2 from a bicarbonate solution and gave a strong silver iodide precipitate. This conforms with the fact that a product of equation 3 is hydrogen iodide.

The reaction solution was then cooled to −10° and a 1% sulfuric acid solution added slowly under nitrogen. Hydrogen gas was evolved in the small amount corresponding to the slight deficiency (<3:1) of iodide used. The mixture was then refluxed for two hours and an additional 3.3 g. (0.020 mole) of C_3F_7H was obtained. The aqueous acid layer contained no fluoride ion. The ether layer was dried over magnesium sulfate, decolorized with silver powder and distilled to yield 1 g. of a fraction, b.p. 70–80°, $n^{21}D$ 1.3714, and 4 g. of a product b.p. 50–51° (20 mm.), $n^{23}D$ 1.4970. Both fractions liberated iodine on standing.

In a reaction of 0.0476 mole of perfluoropropyl iodide with 0.0111 mole of lithium aluminum hydride, the C_3F_7H produced by equation 2 was collected after decomposition with water and amounted to 0.022 mole (66.7%). C_3F_7I in excess of the 3:1 ratio was recovered. The C_3F_7H obtained above represents 100% from equation 2 and therefore 50% from equation 3 after the addition of water.

Reaction of Trifluoromethyl Iodide with Lithium Aluminum Hydride.—To 50 ml. (0.0550 mole) of lithium aluminum hydride solution at −78° was added 8.4 g. (0.0429 mole) of trifluoromethyl iodide in a system similar to the above, with liquid nitrogen used as the refrigerant. The hydrogen collected was 0.0393 mole (91.5% of theory for equation 6). The reaction solution contained a white solid which dissolved when the temperature was raised to 0°. The reaction mixture was allowed to stand at 0° for two hours. A trace of material (CHF_3) was present in the liquid nitrogen-cooled trap.

The solution was then decomposed with 5% sulfuric acid and 0.0460 mole of hydrogen was evolved. A white precipitate formed which dissolved in the excess acid solution. Upon refluxing the mixture there was obtained methane, mol. wt. calcd. 16, found 16 (gas density balance), and CF_3H, mol. wt. calcd. 70, found 70 ± 1 (gas density balance); b.p. (lit.[9]) −84°, found *ca.* −80°. There were some losses in handling these low boiling gases. However, the methane and CF_3H were obtained in approximately equimolar quantities which amounted to about 50% of theory for equation 7. Qualitative tests for fluoride ion on the decomposed solution were positive.

Acknowledgment.—The financial support of the Office of Naval Research is gratefully acknowledged.

[9] O. Ruff, O. Bretschneider, W. Luchsinger and G. Miltshitzky, *Ber.*, **69**, 299 (1936).

Philadephia, Pennsylvania

[Contribution from the Chemical Laboratories of Purdue University]

Factors Influencing the Resonance Contribution of an Expanded Valence Shell. A Comparison of the Electrical Effects of the Triphenylsilyl and Triphenylgermanyl Groups on an Aromatic Ring

By Robert A. Benkeser, Charles E. DeBoer, Robert E. Robinson and Dale M. Sauve

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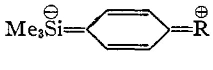
Hammett sigma values for the *meta* and *para* triphenylsilyl and triphenylgermanyl groups have been determined from a series of reaction rates. These values indicate that both groups function principally through a −I effect, and when conjugated to a strong electron supplying group *both* central atoms are capable of valence shell expansion to ten electrons. The contribution of this expanded valence structure is approximately the same in both the aforementioned groups, indicating that the atomic radius of the central element does not influence such structures appreciably. It is demonstrated further that the expanded valence structure is affected little by the nature of the R group attached to the central element, but that these substituents do play a role in determining the over-all electrical effect of the R_3M– group.

The electrical effects of the trimethylsilyl group on an aromatic nucleus and side chains attached to it have been reported.[1] These studies indicated that this group exerts its influence mainly as an electron-supplying group (+I effect). When it is substituted *para* to strongly electron-releasing groups such as hydroxyl, amino and dimethylamino, however, the trimethylsilyl group functions as an electron-withdrawing group. This latter effect has been interpreted as involving a resonance interaction between the electron-releasing group and the trimethylsilyl group in which the silicon atom has expanded its valence shell to accommodate ten electrons.


I

The above results prompted a study of the electrical effects of the triphenylsilyl group. The purpose of the study was threefold: (1) to determine

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[1] R. A. Benkeser and H. R. Krysiak, This Journal, **75**, 2421 (1951), and references reported therein.

what effect substitution of phenyl for methyl groups has on the inherent electron-releasing properties of the silicon atom; (2) to determine whether the triphenylsilyl group, like the trimethylsilyl is capable of resonance interaction when substituted *para* to electron-releasing groups; and (3) to determine in what way this resonance effect, if present, is affected by substitution of phenyl for methyl groups. Thus, in regard to the latter point, one might be led to predict that the inherent electron attracting ability of the phenyl groups would tend to favor a ten-electron silicon structure with a formal negative charge residing on the silicon atom I.

The effects of the triphenylgermanyl group on side chains attached to an aromatic nucleus were also studied. This was done for several reasons. First, since the electronegativities of Si (1.8) and Ge (1.7) are nearly identical,[2] it was of interest to determine how the inductive effects of these two groups would compare. Second, it was also of interest to determine whether the germanium atom is capable of expanding its valence shell to ten electrons and to what extent, if any, the increase in atom size in going from silicon to germanium would affect this ability for valence shell expansion.

Probably the most convenient method of studying the electrical effect of various substituents on an aromatic nucleus and a side chain attached to it is through the use of the Hammett equation[3,4] in which the effect of the group under study is expressed in terms of the Hammett sigma constant. A positive value of the sigma constant for a particular substituent indicates that group to be electron-withdrawing while a negative value indicates an electron-supplying group.

Evidence of resonance interaction between the substituent and electron-releasing groups is obtained in reactions of phenols and anilines if a substituent constant, $\sigma_p{}^*$, is observed which is different from the value of σ_p observed in substituted benzoic acid derivatives.[5,6]

In order to determine such sigma values the rates of the following reactions were studied

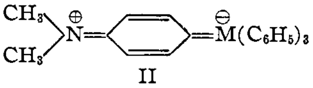
$$R\text{—}C_6H_4N(CH_3)_2 + CH_3I \xrightarrow[35°]{\text{Acetone}} R\text{—}C_6H_4N(CH_3)_3{}^+I^- \quad (1)$$

$$R\text{—}C_6H_4ONa + C_2H_5I \xrightarrow[35°]{\text{Ethanol}} R\text{—}C_6H_4OC_2H_5 + NaI \quad (2)$$

$$R\text{—}C_6H_4CO_2H + (C_6H_5)_2CN_2 \xrightarrow[30°]{\text{Ethanol}} R\text{—}C_6H_4CO_2CH(C_6H_5)_2 + N_2 \quad (3)$$

$$R\text{—}C_6H_4COCl + 2C_6H_5NH_2 \xrightarrow[25°]{\text{Benzene}} R\text{—}C_6H_4CONHC_6H_5 + C_6H_5NH_3{}^+Cl^- \quad (4)$$

In reactions 1 and 2, if the substituents "R" are electron-releasing the rates would be expected to be faster than for dimethylaniline or sodium phenoxide and would result in a negative σ-value; however, if the substituents are electron-withdrawing, the rates would be expected to be slower than for the unsubstituted compounds and would be reflected in a positive σ-value. Furthermore, if any resonance interaction is involved between the electron-releasing dimethylamino and oxide groups and the triphenylsilyl and triphenylgermanyl groups, the rates of the *meta* substituted compounds should be faster than the *para* and this would result in a larger value ($\sigma_p{}^*$) for the *para* than the *meta* substituent. In reactions 3 and 4, where the inductive effect is of primary importance and resonance may be considered negligible, an electron-releasing group will hinder the reaction while an electron-withdrawing group will facilitate the reaction. From this series the "normal" σ_p and the σ_m may be obtained. The difference between $\sigma_p{}^*$ and σ_p should then be a measure of the ability of the triphenylsilyl and triphenylgermanyl groups to conjugate with electron-releasing substituents on an aromatic nucleus. This may be interpreted as involving resonance structures such as II and III where the silicon and germanium atoms have expanded their valency shells to accommodate ten electrons.



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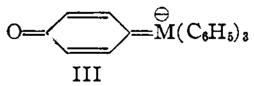

III

Experimental

Preparation of Compounds.—All compounds used for the kinetic studies except those containing silicon or germanium were prepared or treated as follows. The dimethylanilines were obtained by purification of commercial products or prepared by treatment of the free amines with methyl iodide followed by decomposition of the resulting methiodides. In each case, the tertiary amine was treated with acetic anhydride and carefully fractionated under reduced pressure. The phenols and benzoic acids were obtained commercially and further rectified or recrystallized. The benzoyl chlorides were prepared from the acids using thionyl chloride and were fractionated under reduced pressure.

***m*-Dimethylaminophenyltriphenylsilane.**—This material was prepared by the method of Gilman and co-workers[7]; yield 40%, m.p. 97–98°.

***p*-Dimethylaminophenyltriphenylsilane.**—This was prepared by the procedure utilized in the synthesis of the *meta* isomer. After recrystallization from methanol, the amine melted 148–149° and gave a large melting point depression with triphenylsilanol; yield 53%.

Anal. Calcd. for $C_{26}H_{25}NSi$: Si, 7.39. Found: Si, 7.39.

***p*-Dimethylaminophenyltriphenylgermane.**—Under a nitrogen atmosphere a solution of *p*-dimethylaminophenyllithium was prepared in 100 ml. of anhydrous ether from 15 g. (0.075 mole) of *p*-bromodimethylaniline and 1.4 g. (0.2 g. atom) of lithium. The solution was refluxed for one-half hour after all the bromo compound had been added. To the ethereal solution of the lithium compound was added 24.2 g. (0.063 mole) of triphenylbromogermane dissolved in benzene. The solution was refluxed for two hours, after which the ether was removed and replaced by benzene. The solution was refluxed overnight and then carefully decomposed by the addition of water. The organic layer was separated and concentrated to yield crystals of *p*-dimethylaminophenyltriphenylgermane. The product was crystallized from petroleum ether (b.p. 90–100°)-benzene to yield 20.9 g. (79%), m.p. 140–141°; literature[8] 140–141°.

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[2] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, pp. 58.

[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 184.

[4] For an excellent review of the Hammett Equation see H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

[5] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 250.

[6] F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952).

[7] S. V. Sunthankar and H. Gilman, *J. Org. Chem.*, **15**, 1200 (1950).

[8] W. K. Orndorff, D. L. Tabern and L. M. Dennis, THIS JOURNAL, **49**, 2512 (1927).

_m_-Dimethylaminophenyltriphenylgermane.—Following the procedure described above for the *para* isomer, *m*-dimethylaminophenyltriphenylgermane was prepared in 71% yield from *m*-dimethylaminophenyllithium and triphenylbromogermane, m.p. 92–93°.

Anal. Calcd. for $C_{26}H_{25}NGe$: Ge, 17.1. Found: Ge, 17.3.

_p_-Hydroxyphenyltriphenylsilane.—This compound was prepared following the directions of Gilman and Melvin.[9] A solution of *p*-hydroxyphenyllithium in 300 ml. of ether was prepared from 0.436 mole of *n*-butyllithium and 37.65 g. (0.218 mole) of *p*-bromophenol.[10] The mixture was refluxed for 1.5 hours at which time 24.35 g. (0.0825 mole) of triphenylchlorosilane in 200 ml. of benzene was added. The mixture was refluxed with stirring for 24 hours and hydrolyzed with 250 ml. of 1:3 hydrochloric acid. The organic layer was separated and extracted with 10% sodium hydroxide, then dried and concentrated. Addition of petroleum ether precipitated the sodium salt which was dissolved in ethanol and neutralized with hydrochloric acid. The phenol was filtered and recrystallized from 400 ml. of ethanol yielding 15 g. (52%) melting at 229–230°. A benzoyl derivative melted 174.5–175.5°.

Anal. Calcd. for $C_{31}H_{24}O_2Si$: Si, 6.15. Found: Si, 6.02.

_m_-Hydroxyphenyltriphenylsilane.—This was prepared by a procedure similar to that described for the *para* isomer. This yielded 30% of the desired compound melting at 225–226°.

Anal. Calcd. for $C_{24}H_{20}OSi$: Si, 7.96. Found: Si, 7.70.

_p_-Ethoxyphenyltriphenylsilane.—This was isolated by distillation of the ethanol and excess ethyl iodide from the solution used to determine the rate constant for the reaction of sodium *p*-triphenylsilyl phenoxide with ethyl iodide. After recrystallization from ethanol it melted 146–147°.

Anal. Calcd. for $C_{26}H_{24}OSi$: Si, 7.38. Found: Si, 7.37.

_m_-Ethoxyphenyltriphenylsilane.—This was isolated from the solution used for the kinetic study by the method described for the *para* isomer. It melted 122–123°.

Anal. Calcd. for $C_{26}H_{24}OSi$: Si, 7.38. Found: Si, 7.45.

_p_-Tolyltriphenylsilane.—A solution of *p*-tolyllithium in ether was prepared from 86 g. (0.5 mole) of *p*-bromotoluene and 8.0 g. (1.1 g. atoms) of lithium. To this was added a solution of 100 g. (0.35 mole) of triphenylchlorosilane in benzene. The resulting mixture was heated under reflux for two hours. After hydrolysis with dilute hydrochloric acid, the organic material was recovered, the solvent distilled and the residual solid recrystallized from petroleum ether (b.p. 90–100°) to yield 81 g. (67%) of *p*-tolyltriphenylsilane, m.p. 139–140°.

_p_-Triphenylsilylbenzoic Acid.—A suspension of 24.6 g. (0.07 mole) of *p*-tolyltriphenylsilane in 230 ml. of a 50-50 mixture of acetic anhydride and acetic acid was cooled to −5° in an ice-salt-bath. To the stirred mixture was added cautiously 17 ml. of concentrated sulfuric acid, at a rate slow enough to maintain the temperature below 5°. When the temperature had again fallen to −5°, 20 g. (0.2 mole) of chromium trioxide was added, and the resulting mixture was stirred one hour at −5°, one hour at 12° and one hour at 20°. The solution was poured onto crushed ice. The resulting precipitate was recrystallized once from glacial acetic acid and several times from petroleum ether (b.p. 90–100°). The yield of pure acid, m.p. 211–212°, was 3.3 g. (12%).

Anal. Calcd. for $C_{25}H_{20}O_2Si$: Si, 7.38. Found: Si, 7.32.

_p_-Triphenylsilylbenzoyl Chloride.—A solution of 3.0 g. of *p*-triphenylsilylbenzoic acid in 30 ml. of thionyl chloride was refluxed for 45 minutes. The thionyl chloride was distilled, the last traces being removed with an aspirator. The residue was recrystallized from petroleum ether (b.p. 90–100°) to yield 1.8 g. (57%) of the acid chloride melting 149–150°.

Anal. Calcd. for $C_{25}H_{19}ClOSi$: Si, 7.03. Found: Si, 7.04.

The amide melted at 174–174.5°.

Anal. Calcd. for $C_{25}H_{21}ONSi$: N, 3.69. Found: N, 3.58.

_m_-Tolyltriphenylsilane.—This was prepared from *m*-tolyllithium and triphenylchlorosilane by the procedure described for the *para* isomer. After recrystallization from methanol–benzene there was obtained 69% of the desired compound melting 148–149°.

Anal. Calcd. for $C_{25}H_{22}Si$: Si, 8.01. Found: Si, 8.03.

_m_-Triphenylsilylbenzoic Acid.—This material was prepared by the procedure described for the *para* isomer, the same amounts of starting materials being used. After repeated recrystallizations from petroleum ether, the acid melted at 178–179° and weighed 3.9 g. (14%).

Anal. Calcd. for $C_{25}H_{20}O_2Si$: Si, 7.38. Found: Si, 7.28.

_m_-Triphenylsilylbenzoyl Chloride.—This substance was prepared by the procedure described for the *para* isomer, the same amounts of starting materials being used. The acid chloride after crystallization from pentane at 0°, weighed 2.1 g. (67%) and melted 84–85°.

Anal. Calcd. for $C_{25}H_{19}ClOSi$: Si, 7.03. Found: Si, 7.14.

The amide melted at 161–162° and the anilide at 184–185°.

Anal. Calcd. for $C_{25}H_{21}ONSi$: Si, 7.39; N, 3.69. Found: Si, 7.37; N, 3.78.

Anal. Calcd. for $C_{31}H_{25}SiON$: Si, 6.15; N, 3.08. Found: Si, 6.24; N, 3.26.

_p_-Bromophenyltriphenylgermane.—To a solution of 17.9 g. (0.076 mole) of *p*-dibromobenzene in ether in a flask immersed in a Dry Ice slurry maintained at −30° to −35° was added 0.07 mole of *n*-butyllithium at a rate of 5 ml. per minute. The solution was allowed to stir for one-half hour after the addition and then 25.7 g. (0.056 mole) of triphenylbromogermane in ether was added. After the addition the bath was removed and the mixture was stirred for 3.5 hours before refluxing overnight. The mixture was hydrolyzed with dilute hydrochloric acid. The solid obtained by concentration of the ether layer was crystallized three times from petroleum ether (b.p. 90–100°) to yield 14.2 g. (55%) of *p*-bromophenyltriphenylgermane, m.p. 159–160°.

Anal. Calcd. for $C_{24}H_{19}BrGe$: Ge, 15.8. Found: Ge, 15.5.

_p_-Triphenylgermanylbenzoic Acid (I).—To a solution of 9.2 g. (0.02 mole) of *p*-bromophenyltriphenylgermane in 120 cc. of ether and 25 cc. of benzene was added 0.56 g. (0.08 g. atom) of lithium. After 9.5 hours of refluxing with stirring, the mixture was poured into a slurry of crushed Dry Ice in anhydrous ether. When the ether solution had warmed to room temperature, it was acidified with dilute hydrochloric acid and the ether layer separated. Evaporation of the ether left a brown solid which was recrystallized from benzene–petroleum ether (b.p. 90–100°) and decolorized with charcoal. This yielded 1.25 g. of *p*-triphenylgermanylbenzoic acid, m.p. 201–202°.

Anal. Calcd. for $C_{25}H_{20}O_2Ge$: Ge, 17.1. Found: Ge, 16.7.

The acid chloride melted 143–145°. The amide melted 171–172°.

Anal. Calcd. for $C_{25}H_{21}ONGe$: N, 3.31. Found: N, 3.50, 3.52.

_p_-Hydroxymethylphenyltriphenylgermane.—The general procedure described by Gilman and Melstrom[11] for the preparation of the corresponding lead compound was followed. From 15.9 g. (0.085 mole) of *p*-bromobenzyl alcohol 0.17 mole of *n*-butyllithium and 27.8 g. (0.072 mole) of triphenylbromogermane, there was isolated 11.5 g. (39%) of *p*-hydroxymethylphenyltriphenylgermane, m.p. 108.5–110°.

Anal. Calcd. for $C_{25}H_{22}OGe$: Ge, 17.7. Found: Ge, 17.5.

_p_-Triphenylgermanylbenzoic Acid (II).—The procedure of Gilman and Melstrom[11] for the preparation of *p*-triphenylplumbylbenzoic acid was followed. From 9.55 g. (0.0233 mole) of *p*-hydroxymethylphenyltriphenylgermane and 5.42 g. (0.0343 mole) of potassium permanganate, 5.14 g. (52%) of *p*-triphenylgermanylbenzoic acid was obtained.

_m_-Tolyltriphenylgermane.—This was prepared by the procedure described for the silicon analog. From 15.4 g. (0.09 mole) of *m*-bromotoluene, 1.6 g. (0.23 g. atom) of lithium and 28.5 g. (0.074 mole) of triphenylbromogermane

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(9) H. Gilman and H. W. Melvin, private communication.

(10) H. Gilman and C. E. Arntzen, This Journal, **69**, 1537 (1947).

(11) H. Gilman and D. S. Melstrom, *ibid.*, **72**, 2953 (1950).

was obtained 26.0 g. (89%) of the desired compound, m.p. 136–138°, reported m.p. 136–138°.[12]

***m*-Triphenylgermanylbenzoic Acid.**—To a mixture of 200 ml. of glacial acetic acid and 200 ml. of acetic anhydride was added 18 ml. of concentrated sulfuric acid. The solution was cooled to 5° and 27 g. (0.068 mole) of *m*-tolyltriphenylgermane was added. Over a three-hour period, 19.6 g. (0.196 mole) of chromium trioxide was added while keeping the temperature between 35 and 40°. After all the chromium trioxide had been added, the solution was stirred for an additional 45 minutes and poured onto a large volume of cracked ice. After standing overnight the yellow solid was filtered, dried and dissolved in benzene. The benzene solution was treated with an aqueous solution of potassium hydroxide. The solid product which resulted was filtered and dried. This material did not melt and proved to be the potassium salt of the acid. The salt was dissolved in 95% ethanol, the solution decolorized with activated charcoal and filtered. The filtrate was carefully acidified with dilute hydrochloric acid and the solution was concentrated. Water was added slowly to the warm solution to give a milky suspension from which a white crystalline product was obtained on cooling. This material was crystallized from ethanol–petroleum ether (b.p. 35–37°) and then from cyclohexane–ethanol to yield 2.8 g. (10%) of *m*-triphenylgermanylbenzoic acid, m.p. 168–169°.

Anal. Calcd. for $C_{25}H_{20}O_2Ge$: C, 70.59; H, 4.71. Found: C, 70.50; H, 4.79.

The amide melted at 162–163°.

Anal. Calcd. for $C_{25}H_{21}ONGe$: C, 70.75; H, 4.93; N, 3.31. Found: C, 70.40; H, 5.18; N, 3.44.

Diphenyldiazomethane.—This compound was prepared from benzophenone hydrazone and mercuric oxide.[13]

Determination of Rate Constants in Reactions of the Dimethylanilines with Methyl Iodide.—The experimental procedure of Davies and Lewis[14] was used, with the following modifications: (1) the solvent was pure acetone rather than 90% aqueous acetone; (2) the aliquot portions withdrawn were analyzed for iodide by the Volhard, rather than the Mohr, method; and (3) the temperature was maintained at 35 ± 0.05°. The calculated values of the second-order rate constants are listed in Table I.

TABLE I

RATE CONSTANTS FOR REACTION OF DIMETHYLANILINES WITH METHYL IODIDE IN ACETONE AT 35°

Substituent	100 k_2 (l./mole min.)	Substituent	100 k_2 (l./mole min.)
p-CH_3O	9.0	*p*-Cl	0.39
p-CH_3	3.4	*p*-Br	.37
m-CH_3	1.85	*p*-$(C_6H_5)_3Ge$	.36
H	1.17	*p*-$(C_6H_5)_3Si$	.29
m-CH_3O	1.03	*m*-Cl	.16
m-$(C_6H_5)_3Si$	0.71	*m*-Br	.14
m-$(C_6H_5)_3Ge$	.60		

Determination of the Rate Constants in Reactions of Sodium Phenoxides with Ethyl Iodide.—A solution 0.1 *N* in the sodium phenoxide was prepared by adding 5 ml. of a 1 *N* solution of sodium ethoxide in absolute ethanol to 0.005 mole of the phenol in a 50-ml. volumetric flask. The solution was brought to volume at 35° by the addition of absolute ethanol and transferred to the reaction vessel. This was the same bulb previously used for the reaction of the dimethylanilines with methyl iodide. Then 50 ml. of freshly distilled ethyl iodide was added; the mixture was shaken, and the time of half addition of the ethyl iodide recorded. At various time intervals aliquots were withdrawn into 50 ml. of benzene. The benzene solutions were extracted twice with water, acidified with nitric acid and analyzed for iodide ion by the Volhard method. The calculated values of the pseudo first-order rate constants obtained are listed in Table II.

TABLE II

RATE CONSTANTS FOR REACTION OF SODIUM PHENOXIDES WITH ETHYL IODIDE IN ETHANOL AT 35°

Substituent	10^3k_1 (min.$^{-1}$)	Substituent	10^3k_1 (min.$^{-1}$)
p-CH_3O	10.4	*p*-Br	3.56
p-CH_3	8.48	*p*-$(C_6H_5)_3Si$	3.16
m-CH_3	7.53	*m*-Cl	2.79
H	5.71	*p*-NO_2	0.427
m-$(C_6H_5)_3Si$	5.06		

Determination of Rate Constants for Reaction of Substituted Benzoic Acids with Diphenyldiazomethane.—The rates were followed spectrophotometrically by the method previously described by Roberts, McElhill and Armstrong.[15] The solutions used were all 0.00179 *N* in diphenyldiazomethane while the concentrations of acids ranged from 0.0161 to 0.0221 *N*. The pseudo-unimolecular rate constants were obtained from the slope of the best straight line from a plot of logarithm optical density *versus* time. The final second-order rate constants listed in Table III were obtained by dividing the pseudo-unimolecular constants by the corresponding acid concentrations.

TABLE III

RATE CONSTANTS FOR REACTION OF BENZOIC ACIDS WITH DIPHENYLDIAZOMETHANE IN ETHANOL AT 30°

Substituent	k_2 (l./mole min.)	Substituent	k_2 (l./mole min.)
m-CH_3	0.96	*p*-$(C_6H_5)_3Si$	1.34
m-$(C_6H_5)_3Si$	1.01	*p*-Cl	1.67
H	1.07	*p*-Br	1.99
m-$(C_6H_5)_3Ge$	1.21	*m*-Br	2.60
p-$(C_6H_5)_3Ge$	1.24	*m*-NO_2	5.21
m-CH_3O	1.29	*p*-NO_2	5.32

Determination of Rate Constants for Reaction of Substituted Benzoyl Chlorides with Aniline.—The procedure followed was a modification of that described by Williams and Hinshelwood.[16] Into each of several 60-ml. glass-stoppered bottles was introduced by means of volumetric pipets 20 ml. each of 0.0100 *N* aniline and 0.00500 *N* acid chloride in benzene. The bottles were immediately stoppered, shaken and suspended in a bath at 25 ± 0.05°. At regular intervals, bottles were withdrawn, wiped dry and their contents extracted with 20–30 ml. of water. The water extracts were then analyzed for chloride ion by the Volhard method. The calculated values of the second-order rate constants are listed in Table IV.

TABLE IV

RATE CONSTANTS FOR REACTION OF BENZOYL CHLORIDES WITH ANILINE IN BENZENE AT 25°

Substituent	100 k_2 (l./mole sec.)	Substituent	100 k_2 (l./mole sec.)
p-CH_3O	1.49	*p*-$(C_6H_5)_3Si$	6.6
p-CH_3	3.1	*p*-Cl	9.3
m-$(C_6H_5)_3Si$	4.4	*p*-Br	10.1
m-CH_3	4.6	*m*-I	15.4
H	6.2	*m*-Br	16.5

Determination of the Substituent Constants.—The values of ρ and log k_0 for the four reactions were determined in the usual way[3,4] using the method of least squares. Using these and the rate constants obtained for the triphenylsilyl and triphenylgermanyl substituted compounds, the values of the sigma constants for these groups were calculated. The results are listed in Table V.

Discussion

The rate constants in Tables I and II indicate that the triphenylsilyl and triphenylgermanyl

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TABLE V

CONSTANTS FOR THE TRIPHENYLSILYL AND TRIPHENYLGERMANYL GROUPS

Reaction	ρ	log k_0[a]	r[b]	$(C_6H_6)_3Si$		$(C_6H_5)_3Ge$	
				σ_m	σ_p	σ_m	σ_p
1. Dimethylanilines with methyl iodide	−2.56	−3.615	0.057	0.12	0.27	0.15	0.24
2. Sodium phenoxides with ethyl iodide	−0.906	−4.000	.016	.08	.31		
3. Benzoic acids with diphenyldiazomethane	0.929	−1.745	.035	− .03	.10	.05	.08
4. Benzoyl chlorides with aniline	1.42	−1.311	.055	− .03	.09		

[a] The unit of time for all of the rate constants is seconds. [b] Median deviation of the sigma value.

groups are electron-attracting when substituted in either the *meta* or *para* positions of an aromatic nucleus. The relatively small σ_m values listed in Table V for reactions 1 and 2 show that the inductive effects of the triphenylsilyl and triphenylgermanyl groups are weakly electron-attracting. Since the trimethylsilyl group was found to exert an electron-supplying inductive effect,[1] the **electrical effect of a silicon atom attached to an aromatic nucleus appears to be determined by the nature of the groups attached to it.**

The more pronounced electron-withdrawing effect of the triphenylsilyl and triphenylgermanyl groups when substituted *para* to a dimethylamino group or oxide ion indicates resonance interaction of the type shown in II and III in addition to the inductive effect. The values of $\sigma_p - \sigma_m$ for the triphenylsilyl group in these reactions of $+0.15$ and $+0.23$ are similar to the value of $+0.16$ obtained for the trimethylsilyl group,[1] **indicating that the nature of the groups attached to the silicon atom has little influence on its ability to enter into resonance with an aromatic nucleus.** Thus it would appear that the inherent electron attracting power of the phenyl rings does not contribute appreciably to the expanded valence structure. Further evidence bearing on this point would be highly desirable and such investigations are presently underway.

The values of σ_p in Table V for the triphenylsilyl and triphenylgermanyl groups determined in reactions 3 and 4 are similar to the values of σ_m and considerably smaller than the values of σ_p determined in reactions 1 and 2. Since there can be no resonance interaction between these groups and the carboxy or carbonyl chloride groups, the observed electron-attraction must be due to an inductive effect. The values of $\sigma_p^* - \sigma_p$ for the triphenylsilyl group of $+0.2$ is nearly the same as the value of $+0.14$ found for the trimethylsilyl group again indicating that there is little difference in the effect of methyl and phenyl groups on the ability of silicon to enter into resonance.

The values of σ_m determined in reactions 3 and 4 seem to be inconsistent with the other values in Table V. The negative values for the *m*-triphenylsilyl group indicate an electron-supplying inductive effect whereas an electron-withdrawing inductive effect was observed in the σ_m values for reactions 1 and 2 and the σ_p values for reactions 3 and 4. The value of σ_m for the triphenylgermanyl group in reaction 3 is also smaller than the value of σ_p in the same reaction and considerably smaller than the value of σ_m determined in reaction 1, a fact inconsistent with an inductive effect.

A similar deactivating effect has been observed in studies of the influence of other bulky groups on the reactivity of aromatic acids and their derivatives and has been attributed to an effect which is steric rather than electronic in nature[17] ("bulk effect"). If this is indeed the case in these reactions, it is difficult to see why this effect was not observed in reactions 1 and 2. However, this possibility is being studied in this Laboratory by a determination of the effect of a triphenylmethyl group in these reactions. If this deactivation is due to a steric effect it should be observed for the triphenylmethyl group. If no such deactivation is observed, the effect must be electrical and of a nature which cannot be explained at the moment.

The data presented here indicate that the triphenylsilyl and triphenylgermanyl groups exert an electron-withdrawing inductive effect of about the same magnitude, a result which might have been predicted on the basis of the similar electronegativities of silicon and germanium. The $\sigma_p^* - \sigma_p$ values of $+0.2$ for the triphenylsilyl group and $+0.16$ for the triphenylgermanyl group **indicate that the amount of conjugation or resonance interaction and hence the double-bond character of the carbon–silicon and carbon–germanium bonds is essentially identical.** These results are in accord with recent theoretical predictions[18] and experimental evidence[19] that this type of bonding is independent of the relative sizes of the bonded orbitals.

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