Since oxygen is more electronegative than sulfur,[28] it is not surprising to find that the C–H, Si–H, and Ge–H proton resonances in the ether derivatives are found at lower fields than they are for the corresponding thio derivatives.[29] The difference in chemical shifts between the oxygen and sulfur systems is greatest for the C–H protons followed by Ge–H protons and the least amount of change is observed for the Si–H protons. This trend is also observed in comparing electronegativity and proton nmr data for the halide derivatives of CH_4, SiH_4, and GeH_4.[30]

Ebsworth and Turner[31] have pointed out that for a series of SiH_3 compounds, there is a general decrease of τ_{SiH} as the electronegativity of the substituent increases. A similar relationship is found for CH_3 compounds.[32] However, plots of electronegativity *vs.* chemical shift values for the two series of compounds differ quite significantly.[31] One of the key differences in the two systems occurs with the sulfur derivatives. The chemical shift of $(CH_3)_2S$ is very close to that of CH_3I (sulfur and iodine have about the same electronegativity values, 2.5–2.6); however, the chemical shifts of $(SiH_3)_2S$ (τ 5.65) and SiH_3I (τ 6.56) are significantly different. In the present work, we wanted to ascertain the position of $(GeH_3)_2S$ with respect to GeH_3I. A plot of the proton chemical shifts of most of the known GeH_3 compounds *vs.* electronegativity of the substituents is given in Figure 2.[33] The pattern obtained is strikingly similar to that of the analogous plot for SiH_3 compounds.[31] Thus, we conclude that when considering electronegativity effects alone, the chemical shifts of SiH_3 and GeH_3 compounds follow similar trends, which are different in certain respects from trends of simple carbon compounds. We prefer to delay an explanation of the differences until the factors which determine the Si–H and Ge–H chemical shifts are better understood.

Acknowledgments.—The authors are grateful to Professor Sei Sujishi for communications on the unpublished work of his research group and to Mr. Sam Wrbican for obtaining the mass spectrum. J. T. Wang wishes to thank the Mobay Chemical Co. for a research fellowship.

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[28] H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).

[29] We are grateful to Dr. Stephen Cradock and Mr. Gerst Gibbon for providing us with their unpublished $(GeH_3)_2O$ (τ 4.72) nmr data.

[30] E. A. V. Ebsworth, S. G. Frankiss, and A. G. Robiette, *J. Mol. Spectry.*, **12**, 299 (1964).

[31] E. A. V. Ebsworth and J. J. Turner, *J. Phys. Chem.*, **67**, 805 (1963).

[32] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

[33] Chemical shifts used are those obtained for dilute (5–10% v/v) solutions of the compounds in cyclohexane.

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Nuclear Magnetic Resonance Chemical Shifts of the Acid Protons in Silyl-Substituted Benzoic Acids and Phenols and the Question of $(\pi \rightarrow d)-\pi$ Interaction in the Silicon–Phenyl Bond[1]

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The electrical effects of *para-* and *meta-*substituted trimethylsilylphenols and -benzoic acids have been investigated by nmr techniques designed to elucidate these effects in the ground-state, neutral molecules, and the data have been compared to those for phenol and benzoic acid themselves and for the *p-* and *m-t-*butyl derivatives. Results from measurement of the chemical shifts of the acidic protons of the substituted benzoic acids in an inert solvent (CCl_4) give the same order of hydrogen bonding as for the strong donor solvent pyridine: H > *m-* and *p-t-*butyl > *p-* and *m-*trimethylsilyl. For the analogous phenols the hydrogen-bonding strength in both types of solvents decreases, H > *p-*trimethylsilyl, but while *p-*trimethylsilylphenol is weaker than *p-t-*butylphenol in dilute solution in carbon tetrachloride, the reverse order is observed in dimethyl sulfoxide.

We have been led to take an agnostic view toward supposed large $(p \rightarrow d)-\pi$ contributions to the bonds silicon forms with nitrogen on the basis of experiments involving nuclear magnetic resonance techniques.[3] Apart from the silicon–nitrogen bond, convincing evidence for large π interactions in fourth-group bonds comes from studies of silicon–phenyl systems. Here the argument involves the electrical effect of silicon as a substituent. Current electronegativity tables agree that the silicon atom should donate electrons to the phenyl group. Should there be large $(\pi \rightarrow d)-\pi$ interactions in the silicon–phenyl bond, however, then this inductive electron release would be offset by the drift of π-electron density from the phenyl ring, and the result might be a net reversal of the expected electrical effect of the silicon atom.

In their classic paper Chatt and Williams reported the results of a careful study of the strengths of the acids

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[1] A preliminary report of this work was presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

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[3] E. W. Randall, J. J. Ellner, and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 622 (1966); E. W. Randall and J. J. Zuckerman, *Chem. Commun.*, 732 (1966); C. H. Yoder and J. J. Zuckerman, *Inorg. Chem.*, **6**, 103 (1967); E. W. Randall and J. J. Zuckerman, *J. Am. Chem. Soc.*, **90**, 3167 (1968).

p-$R_3MC_6H_4COOH$ [M = C, Si, Ge, or Sn, and R = CH_3 or C_2H_5]. They found the acids containing Si, Ge, and Sn to be stronger than p-$R_3CC_6H_4COOH$, and they concluded that the M–phenyl bond must involve a $(\pi \rightarrow d)-\pi$ contribution and that this contribution is large enough to overcome the positive inductive effect due to the greater electropositive character of silicon relative to carbon. The data were the thermodynamic dissociation constants of the acids in 60.1% by weight aqueous ethanol.[4]

The dissociation of acids in aqueous media is complex. The data of Chatt and Williams differ from those obtained by Benkeser, *et al.*, and by Roberts, *et al.*, for p-trimethylsilyl as against benzoic acid itself. Roberts found p-$(CH_3)_3SiC_6H_4COOH$ to be of about the same strength acid as benzoic ($pK_a = 5.85$ and 5.75, respectively) in 50% aqueous ethanol[5] (values were later corrected to 5.80 for both).[6] Benkeser, *et al.*, found the silicon-containing acid to be weaker than benzoic ($pK_a = 4.27$ and 4.20, respectively) in 10^{-5} *M* aqueous solution,[7] whereas Chatt and Williams found pK_a's of 5.955 and 5.979, respectively. We agree with Chatt and Williams that solvent effects play a role.[4]

We present in this paper the results of experiments designed to test the hypothesis of large $(\pi \rightarrow d)-\pi$ interactions in the silicon–phenyl bond. Nuclear magnetic resonance spectroscopy offers an improved method for determining the polar effects of substituent groups in ground-state, neutral molecules. Such spectroscopic measurements are relatively free from the complications inherent in the use of chemical reactions as a test of substituent effects, although results from nmr studies do parallel those from chemical studies on similar systems. Thus the chemical shifts of the hydroxyl protons of 29 substituted phenols dissolved in dimethyl sulfoxide were shown to correlate extremely well with values of the Hammett σ constant established by other methods, and this technique offers a method of determining new σ constants with unusual ease.[8] Likewise the chemical shifts of the acidic protons of a large number of substituted benzoic acids dissolved in pyridine have been shown to correlate extremely well with established Hammett σ values.[9]

We have attempted two different types of experiments. The first involves measuring the chemical shifts of the acid protons on variously substituted benzoic acids and phenols in an inert solvent (carbon tetrachloride). In the second type of experiment we measure the chemical shifts of the acidic protons as they are undergoing a hydrogen-bonding interaction with a Lewis base (dimethyl sulfoxide or pyridine). While in the first type of experiment we hoped to study a parameter characteristic of the dissolved molecules themselves—an intrinsic parameter—in the second type of experiment our measured values arise from the interaction of our acids with a Lewis base. The interaction parameter is a differential quantity referred to the free acid or phenol and the free Lewis base. In this view the sequences of intrinsic acidities would resemble the realized sequences of acidity only if the interaction energies also follow the intrinsic parameter.[10]

Experimental Section

Nmr data were obtained using a Varian A-60 spectrometer with the chemical shifts measured relative to an internal TMS standard. The purity of commercially available reagent grade benzoic acids and phenols was determined by the melting point method, and recrystallization was repeated to constant melting point. Fresh solutions, prepared and manipulated under an atmosphere of dry nitrogen, were used throughout. Pyridine was distilled from potassium hydroxide pellets and stored over Linde 4A Molecular Sieves. Dimethyl sulfoxide and carbon tetrachloride were distilled from magnesium sulfate and similarly stored.

p-Trimethylsilylbenzoic acid (mp 116–118°) was prepared from p-trimethylsilylbromobenzene[11] by the Grignard method of Roberts, *et al.*[5] This acid was also prepared from the silyl-substituted bromobenzene using a lithium reagent: n-butyllithium (13 ml of a 16% solution in hexane) was slowly added to the bromobenzene (4.84 g, 0.021 mol) in dry ether (50 ml) under nitrogen and stirred at −20° for 2 hr. The reaction mixture was poured onto crushed Dry Ice and the excess CO_2 was evaporated. The residue was acidified with dilute sulfuric acid and extracted with ether. The ether was evaporated and the residue was treated with sodium bicarbonate solution; the solution was filtered and acidified, and the resulting solid was filtered. p-Trimethylsilylbenzoic acid (2.5 g, 60.8% yield) was recrystallized successively from ether–ligroin and petroleum ether (bp 60–70°) as white needles.

m-Trimethylsilylbenzoic Acid.[5]—n-Butyllithium (52 ml of a 16% solution in hexane) was added to 1,3-dibromobenzene (21.4 g, 0.091 mol) in dry ether at −78° in a nitrogen atmosphere. Trimethylchlorosilane (10 g, 0.092 mol) in ether was added over 10 min, and the reaction mixture was stirred at room temperature overnight. The mixture was hydrolyzed with distilled water and dried over magnesium sulfate; the ether was evaporated and the remaining solution was distilled at 94–96° (5 mm) to yield m-trimethylsilylbromobenzene (12.2 g, 57.1% yield). The lithium derivative was then prepared from the silyl-substituted bromobenzene (4.84 g) by a method analogous to that used above for p-trimethylsilylbenzoic acid and carbonated to give m-trimethylsilylbenzoic acid (2.1 g, 51.3% yield).

p-Trimethylsilylphenol (mp 75–76°) was prepared by the method of Neville[12] and was sublimed *in vacuo* to yield a pure, dry sample.

m-Trimethylsilylphenol.[5]—A mixture of 3-bromophenol (21.6 g, 0.125 mol), anhydrous benzene (22.5 ml), and pyridine (9.9 g, 0.125 mol) was cooled in an ice bath to 0–5°, and a solution of trimethylchlorosilane (13.6 g, 0.125 mol) in benzene (12.5 ml) was added dropwise, care being taken to keep the temperature in the range 0–20°. After stirring the mixture for 3 hr and allowing it to stand overnight, the precipitate of pyridinium chloride was filtered and the benzene solvent was stripped. The remaining liquid was distilled *in vacuo* to yield m-trimethylsiloxybromobenzene, bp 112–114° (15 mm) (18.6 g, 35.4% yield).

Magnesium turnings (1.85 g, 0.08 g-atom), sodium-dried tetrahydrofuran (5 ml), and methyl iodide (0.4 ml) were warmed until the Grignard reaction began and then a further 10 ml of

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(4) J. Chatt and A. A. Williams, *J. Chem. Soc.*, 4403 (1954).

(5) J. D. Roberts, E. A. McElhill, and R. Armstrong, *J. Am. Chem. Soc.*, **71**, 2923 (1949).

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

(7) R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 2421 (1953).

(8) J. G. Traynham and G. A. Knesal, *J. Org. Chem.*, **31**, 3350 (1966).

(9) Y. Kondo, K. Kondo, T. Takemoto, and T. Ikenoue, *Chem. Pharm. Bull.* (Tokyo), **12**, 514 (1964); **14**, 1332 (1966).

(10) We have already employed this approach with regard to the Lewis base strengths of fourth-group organometallic amines: E. W. Randall, C. H. Yoder, and J. J. Zuckerman, *Inorg. Chem.*, **6**, 744 (1967).

(11) C. A. Burkhard, *J. Am. Chem. Soc.*, **68**, 2103 (1946).

(12) R. G. Neville, *J. Org. Chem.*, **25**, 1063 (1960).

THF was added prior to refluxing. The siloxybromobenzene (18.6 g, 0.75 mol) in THF (30 ml) was added over 1 hr, and the mixture was refluxed 1 hr. The mixture was cooled to 10° and trimethylchlorosilane (8.1 g, 0.75 mol) was added with stirring. The mixture was refluxed for 1 hr and cooled overnight. The precipitated magnesium salts were dissolved in water, the THF layer was separated and dried over magnesium sulfate, and *m*-trimethylsiloxytrimethylsilylbenzene was distilled at 60–62° (2 mm) (12.6 g, 69.4%). *m*-Trimethylsiloxytrimethylsilylbenzene was converted to *m*-trimethylsilylphenol by the method of Benkeser, *et al.*,[7] bp 69–71° (1 mm).

m- and *p*-diphenylphosphinobenzoic acids were kindly supplied by Dr. R. A. Baldwin. Melting points were checked against literature values.[13]

Results

The relative position of the acid proton resonance indicates a greater or lesser amount of hydrogen bonding, high field indicating less hydrogen bonding.

Table I lists, in decreasing order, the chemical shifts in ppm for the –OH protons of several substituted phenols in dimethyl sulfoxide solution together with the shift difference from phenol itself and the Hammett σ constants of the substituent group taken from the compilation of Jaffé.[14]

TABLE I

CHEMICAL SHIFT DATA FOR –OH SIGNALS FROM DMSO SOLUTIONS OF PHENOLS (1.0 *M*)

Substituted	Chemical shift, ppm	$\Delta\delta$, ppm	σ[a]
p-NO$_2$[b]	10.97	1.64	0.778
p-Cl[b]	9.60	0.27	0.227
p-H[b]	9.33	0.00	0.00
p-(CH$_3$)$_3$Si	9.25	−0.08	−0.072
m-(CH$_3$)$_3$Si	9.07	−0.26	−0.120
p-CH$_3$[b]	9.04	−0.29	−0.170
m-(CH$_3$)$_3$C	9.03	−0.30	−0.121
p-(CH$_3$)$_3$C	8.95	−0.38	−0.197
p-OCH$_3$	8.75	−0.58	−0.268

[a] From the compilation of H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953). [b] Thermodynamic data are now available for these acids: J. M. Wilson, N. E. Gore, J. E. Sawbridge, and F. Cardenas-Cruz, *J. Chem. Soc.*, *B*, 852 (1967).

Table II lists the chemical shifts, in decreasing order, of the acid protons of several *para*- and *meta*-substituted benzoic acids in pyridine solution at three different concentrations.[14a]

TABLE II

CHEMICAL SHIFTS OF BENZOIC ACIDS IN PYRIDINE SOLUTIONS(IN PPM)

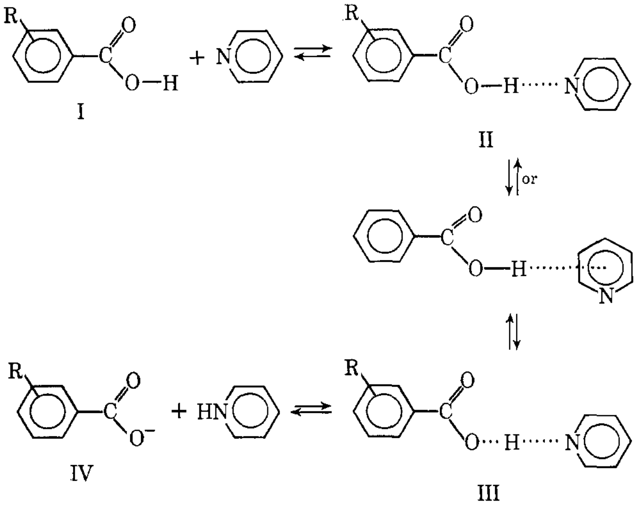
Substituent	2 *M*	1 *M*	0.5 *M*
p-Br[a]	15.23	. . .	. . .
H[a]	15.07	14.96	14.37
p-CH$_3$[a]	14.71	14.57	. . .
m-(CH$_3$)$_3$C	14.66	. . .	. . .
p-(CH$_3$)$_3$C	14.65	14.51	. . .
p-(CH$_3$)$_3$Si	14.44	14.33	13.90
p-OCH$_3$	14.43	. . .	. . .
m-(C$_6$H$_5$)$_2$P	14.40	14.13	. . .
m-(CH$_3$)$_3$Si	14.33	. . .	. . .
p-(C$_6$H$_5$)$_2$P	14.05	13.76	12.56

[a] See footnote *b* of Table I.

Similar chemical shift data for several variously substituted phenols and benzoic acids in carbon tetrachloride solutions at varying concentrations were measured and are discussed below.

Discussion

In pyridine solution the acidic proton of a benzoic acid may find itself in a number of different magnetic environments, as shown



and the measured chemical shift will be the weighted average of the resonance frequency in each situation except IV. Further, the magnetic anisotropy of the pyridine ring will affect the acidic proton chemical shift in a way which will not vanish with rotational averaging, and the quadrupolar N^{14} nucleus in the donor will broaden the acidic proton resonance.[15] Since all of our measurements are for benzoic acids with reference to the same Lewis base and are compared for equal concentrations, the assumption that the above-mentioned effects are constant is probably justified.

The sequence found, H > *m*- and *p*-*t*-butyl > *p*- and *m*-trimethylsilyl, would indicate a negative Hammett σ value for the trimethylsilyl group just as predicted on simple electronegativity grounds.

In the trimethylsilyl-substituted benzoic acids moving the substituent group from the *meta* to the *para* position diminishes the acid-weakening effect of the group. With *t*-butyl as the substituent group and no interaction other than the inductive possible, moving the substituent from the *meta* to the *para* position increases the acid-weaking effect. This reversal may indicate enough π-electron withdrawal in the silyl case to reverse the expected *meta* and *para* positions, but not enough to make the silylbenzoic acids stronger than their *t*-butyl analogs.

For the phenols we find a hydrogen-bonding order in dimethyl sulfoxide of: H > *p*- and *m*-trimethylsilyl > *m*- and *p*-*t*-butyl. Thus a negative value for the Ham-

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(13) R. A. Baldwin, M. T. Cheng, and G. D. Homer, *J. Org. Chem.*, **32**, 2176 (1967).

(14) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(14a) NOTE ADDED IN PROOF.—We learned after this report had been accepted for publication that independent work of a similar nature to our own with silyl-substituted benzoic acids in pyridine solution had been carried out simultaneously at Harvard University. We thank Drs. J. Schraml and E. G. Rochow for sharing their results with us.

(15) B. B. Howard, C. F. Jumper, and M. T. Emerson, *J. Mol. Spectry.*, **10**, 117 (1963).

mett σ constant is again indicated. However, the trimethylsilyl phenols appear to be stronger hydrogen-bonding agents than the *t*-butylphenols. In addition, moving the trimethylsilyl group from the *meta* to the *para* position diminishes the acid-weakening effect, just as with the benzoic acids.

These results may be rationalized by invoking a $(\pi \rightarrow d)-\pi$ contribution to the silicon–phenyl bond sufficiently large to reverse the sequence in dimethyl sulfoxide solution with respect to the *t*-butylphenol, but too small to have the silylphenol become stronger than phenol itself, *i.e.*, not large enough to overcome completely the silyl group inductive effect. In considering this view, it should be noted that: (a) The phenol OH group in dimethyl sulfoxide solution may bear a closer resemblance to its situation in the transition state for dissociation than to the ground-state, neutral molecule. (b) The more negative charge placed at the OH site of the phenol by the interaction with the Lewis base, the stronger the $(\pi \rightarrow d)-\pi$ interaction at the *para* position of the ring will likely be. This is to say that the bonding situation in the silicon–phenyl bond is solvent dependent. The *meta* positions should not be so affected, and the chemical shifts of the *m-t*-butyl and *m*-trimethylsilyl phenols do not differ greatly from one another. (c) Compared with the benzoic acids, in phenol the acid proton is closer to the substituent by one chemical bond.

In dilute solution in carbon tetrachloride both the phenols and the acids are expected to be predominantly monomeric. However, dimerization or polymerization through hydrogen bonding may occur to a serious extent even at relatively low concentrations. The benzoic acid dimer may include cyclic and/or acyclic species with the open, acyclic dimer containing one free and one hydrogen-bonded proton. Thus the proton may find itself in one of several different magnetic environments, and the proton resonance will in both cases be the time averaged signal of a fast exchange between these states. As the concentration decreases, the observed frequency will approach that of the monomer.

Detailed agreement as to the order of hydrogen-bonding strength of the substituted phenols in carbon tetrachloride was lacking in the studies made. Using solutions 0.5, 0.25, and 0.10 *M*, the relative order of the *p-t*-butyl- and *p*-chlorophenols with respect to phenol crosses on dilution with the anticipated order found at the limiting dilution. At this limiting dilution the *p*-trimethylsilylphenol is the weakest hydrogen-bonding agent in the sequence: *p*-Cl > H > *p-t*-butyl > *p*-trimethylsilyl.

Infrared studies suggest that the benzoic acids may be present as the monomers in very dilute solutions (0.02 *M* or lower).[16] Unfortunately the concentration range of our nmr data is limited by the solubility of the acids in carbon tetrachloride and the signal-to-noise ratio of the spectrometer. The only measurements on the benzoic acid–carbon tetrachloride system using concentrations like ours did not give unambiguous results for the position of the monomer–dimer equilibrium.[17]

The chemical shifts of the acidic protons of the substituted benzoic acids in carbon tetrachloride at the concentrations 0.50, 0.25, and 0.10 *M* are consistent and lie in the same order as those measured in the strong-donor solvent pyridine: H > *p-t*-butyl > *p*-trimethylsilyl > *m*-trimethylsilyl.

The diphenylphosphine-substituted acids appear to be weaker than both benzoic acid itself and the *t*-butyl derivatives in both solvent systems. That this arises from π-electron release utilizing the lone-pair electrons of the phosphorus atom is supported by the observed enhancement of the acid-weakening effect on moving the group from the *meta* to the *para* position. This effect is opposite in sense to that postulated for the silyl group. Thus the change from inert to donor solvent should tend to suppress π interaction in the phosphorus–phenyl bond and enhance it in the silicon–phenyl bond. The net effect is to change the sequence from H > *p-t*-butyl > *p*-diphenylphosphine > *p*-trimethylsilyl at the limiting dilution in carbon tetrachloride to H > *p-t*-butyl > *p*-trimethylsilyl > *p*-diphenylphosphine in pyridine. The chemical shift values of the *m*-phosphine and -silyl isomers are closer and in the order *m*-diphenylphosphine > *m*-trimethylsilyl in pyridine. These comparisons are not exact, however, since they are drawn between methyl- and phenyl-substituted groups.

Conclusions

Based upon the customary benzoic acid standard, the value of the Hammett σ constant for the trimethylsilyl group should be negative in sign and greater in magnitude than that for the *t*-butyl group.

The contribution of the $(\pi \rightarrow d)-\pi$ interaction in the silicon–phenyl bond of *p*- and *m*-trimethylsilylbenzoic acids and -phenols does not predominate over the inductive effect.

While this view is corroborated for the phenol derivatives with respect to phenol itself, the silyl-substituted phenols appear to be stronger than their *t*-butyl analogs in dimethyl sulfoxide solution, and this can be interpreted as arising from a larger contribution from the $(\pi \rightarrow d)-\pi$ interaction in this case.

The $(p \rightarrow \pi)-\pi$ interaction of the phosphorus lone pair with the phenyl ring controls the acidity of the diphenylphosphine-substituted benzoic acids.

Acknowledgment.—This investigation was supported by National Science Foundation Grant GP-5025. Diphenylphosphine-substituted benzoic acids were kindly donated by Dr. R. A. Baldwin of the American Potash and Chemical Corp.

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[16] A. E. Martin, *Nature*, **166**, 474 (1950).

[17] J. C. Davis, Jr., and K. S. Pitzer, *J. Phys. Chem.*, **64**, 886 (1960).