

Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. IX.¹ Aryl Derivatives of Metalloids

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Abstract: Integrated intensities for the ν_{16} mode of monosubstituted phenyl derivatives of metals and metalloids are tabulated together with derived σ_R° values. The variation of σ_R° with the position in the periodic table is discussed. *m*- and *p*-fluorophenyl derivatives are investigated for elements of group IVb, and σ_R° values derived from ir and nmr methods are compared and discussed.

We recently reported³ σ_R° values derived from the integrated infrared intensities of monosubstituted benzenes (using eq 1) for 110 substituents ring-linked by halogen, oxygen, sulfur, nitrogen, and carbon. We have now measured a range of phenyl derivatives of other elements, to clarify the nature of mesomeric ring-substituent interactions for substituents linked to the

$$A_{\text{mono}} = 17,600(\sigma_R^\circ)^2 + 100 \quad (1)$$

ring by a wide range of atoms. For the tetraphenyl derivatives of group IVb, the infrared intensities were too low to allow accurate σ_R° values to be deduced, and for these elements a series of *meta*- and *para*-substituted derivatives were also measured. Such studies also allow the determination of the sign of σ_R° , and a quantitative measure of substituent-substituent interactions.

Previous work⁴ on substituent interactions involving these elements has shown that the second and later row elements of the b subgroups display electron-acceptor properties into d orbitals. This evidence is reviewed below.

Results and Discussion

Spectral data for the compounds presently studied are collected in Tables I-III. No previous precise infrared intensity data of these compounds are available for comparison. The σ_R° values calculated for the compounds PhMPh_(x-1) are shown in Table IV which includes previously² determined values.

For the disubstituted benzenes, the data have been treated by eq 2⁵ and 3;⁶ eq 3 applies to *para*-disubsti-

$$A_{\text{meta}} = 19,000\{(\sigma_R^\circ 1)^2 + (\sigma_R^\circ 2)^2 + \sigma_R^\circ 1 \sigma_R^\circ 2\} + 340 \quad (2)$$

$$A_{\text{para-X/D}} = 11,800\{\sigma_R^\circ \text{D} - \sigma_R^\circ \text{X} + K_x \sigma_R^\circ \text{D}\}^2 + 170 \quad (3)$$

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(3) R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Am. Chem. Soc.*, **90**, 1757 (1968).

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(5) A. R. Katritzky, M. V. Sinnott, T. T. Tidwell, and R. D. Topsom, *J. Am. Chem. Soc.*, **91**, 628 (1969).

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tuted compounds where a donor substituent is paired with a d-orbital acceptor. Table V gives σ_R° values for groups calculated from the *meta*-substituted derivatives where no interaction between the substituents is expected. These disagree markedly with the values found by the ¹⁹F nmr method⁷ which utilized *para*-substituted fluorobenzenes. The same situation was found previously⁶ for the heavy halogens and for SMe. As argued before,⁶ direct resonance interaction between the substituents in the *p*-fluoro compound is given by the correction of $K_x \sigma_R^\circ \text{D}$ in eq 3: this extra resonance is the result of the fluorine acting as a stronger donor than in fluorobenzene with an effective σ_R° value of $\sigma_R^\circ \text{F} \cdot (1 + 0.5K_x)$ and the other substituent showing developed electron-acceptor properties with an effective σ_R° value of $(-\sigma_R^\circ \text{X} + 0.5K_x \sigma_R^\circ \text{F})$. Hence the difference between the ir-derived values of $\sigma_R^\circ \text{X}$ and the ¹⁹F-derived σ_R° values should be given by $0.5K_x \sigma_R^\circ \text{F}$; good agreement is usually found as shown by the last two columns in Table V.

Substituents Ring-Linked by Group VI and V Atoms.

On the evidence of diphenyl selenide, Se behaves very similarly to S. Although no results are available for the benzenedimethylsulfonium cation itself, values obtained for the *m*-fluoro derivative allow an estimation of the σ_R° value of the SMe₂⁺ substituent. It appears to be a weak resonance donor, a result rather analogous to that found for the NMe₃⁺ substituent previously reported.⁶ The intensity observed for the (*p*-fluorophenyl)dimethylsulfonium cation indicates that the SMe₂⁺ substituent accepts electrons when opposed by a strong donor, and a K_x value of 0.67 is obtained compared to the value of 0.44 obtained for the SMe substituent. This result can presumably only be explained in terms of acceptance of electrons into the d orbitals of the sulfur atom. A similar result is found with the triphenylphosphonium substituent although the analysis of these results is not quite so straightforward. The intensity values of the appropriate monosubstituted benzenes in Table I indicate an approximate σ_R° value of 0.075. Assuming that the contribution to the total intensity made by the three phenyl groups of the (*m*-fluorophenyl)triphenylphosphonium cation is similar to that observed in the tetraphenylphosphonium cation, a somewhat smaller resonance contribution for the PPh₃⁺ substituent in the *m*-fluoro-substituted ring is suggested.

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Table I. Spectral Data and Calculated σ_R° Values for Monosubstituted Benzenes

Compound	Solvent	$\pm\sigma_R^\circ$ calcd ^a	—1600 band—		—1585 band—		A^c	ϵ^d	—1500 band—		A^e
			ν	ϵ_A^b	ν	ϵ_A			ν	ϵ_A	
Ph ₂ Se	CHCl ₃	0.190	1577	60			737	713	1477	114	965
PhPCl ₂	CHCl ₃	0.059	1586	11.5			164		1480	11.5	
PhPMe ₂	C ₆ H ₁₂	0.076	1590	7	1580	5	169	210	1495	32	
Ph ₃ P	CCl ₄	0.063	1586	16	1572	2	175	146	1480	34	447
PhPMe ₃ +Cl ⁻	D ₂ O	0.080	1590	9			225		1494	9.3	
Ph ₄ P+Br ⁻	CHCl ₃	0.075	1588	24			199		1484	5	
PhP(O)OHSiMe ₃	CHCl ₃	0.092	1595	28			248	289			
PhPO(OH) ₂	D ₂ O	0.080	1597	19			183				
PhP(O)OHGeMe ₃	CHCl ₃	0.075	1592	25			201				
Ph ₃ P	CHCl ₃	0.031	1587	4	1575	4	127	6	1481	37	355
Ph ₄ As	CHCl ₃	0.070	1581	16			198	172	1483	59	368
Ph ₃ As	CHCl ₃	0.044	1580	12	1569	4	151	117	1482	25	355
Ph ₃ Sb	CHCl ₃	0.070	1578	22			191	151	1479	28	245
Ph ₃ Sb	CHCl ₃	0.063	1573	15			174	116	1479	44	311
Ph ₃ Bi	CHCl ₃	0.100	1572	44	1558	6	276	266	1475	30	296
PhSiMe ₃	CCl ₄	0.0 ^f	1592				95				
Ph ₄ Si	CHCl ₃	0.0 ^f	1589	4			59	64	1481	15	77
PhGeMe ₃	CCl ₄	0.096	1598				257				
Ph ₄ Ge	CHCl ₃	0.0 ^f	1584	3			39	13	1486	34	176
Ph ₄ Sn	CHCl ₃	0.0 ^f	1576	2			40	36	1481	36	162
Ph ₄ Pb	CHCl ₃	0.0 ^f	1572	10			78	83	1477	31	192
PhBCl ₂	CCl ₄	0.298	1597	157			1703		1491	8.9	
PhB(OH) ₂	DMSO	0.227	1602	58	1573	11	1030		1494		
Ph ₄ B ⁻ Na ⁺	DMSO	0.129	1581	24	1562	2	393		1480	31	
Ph ₃ B	Ether	0.221	1595	85	1574	7	965	912	1486		
Ph ₃ Al	Ether	0.109	1598	41	1582	12	315	369			
Ph ₂ Zn	Ether	0.109	1597	19	1568	4	321	429			
Ph ₂ Cd	Ether	0.104	1593	17	1570	3	307	424			
Ph ₂ Hg	CHCl ₃	0.031	1578	8	1569	2	121	56	1481	29	144
PhLi	Ether	0.144	1597	55	1569	11	480	767			

^a Calculated using $\sigma_R^\circ = [(A - 100)/17,600]^{1/2}$. ^b Peak extinction coefficient; $\epsilon_A = a_{\max}/cl$ where a_{\max} is absorbance at peak maximum, c is concentration, and l is cell length. ^c ϵ , ϵ_A , and A values are divided by the number of benzene rings. ^d The integrated intensity of the 1600- and 1585-cm⁻¹ band; $A = \Sigma a_{\max}/cl$; for compounds with several equivalent rings, the A value quoted is that per ring. ^e ϵ is an estimate of the integrated intensity given by $\epsilon = \epsilon_A \Delta\nu^{1/2}$. ^f The integrated intensity of the 1500-cm⁻¹ band. ^g Larger uncertainty; see text and Table II.

Table II. Spectral Data for *para*-Disubstituted Benzenes

Substituents		Solvent	—1600 band—		A^b	—1500 band—	
			ν	ϵ_A^a		ν	ϵ_A
F	S ⁺ (Me) ₂ BF ₄ ⁻	CH ₃ CN	1590	237	2524	1500	357
F	P ⁺ (Ph) ₃ BF ₄ ⁻	CHCl ₃	1595	343 ^c	5130 ^c	1502	407 ^c
F	SiMe ₃	CCl ₄	1592	261	2697	1500	441
F	GeMe ₃	CCl ₄	1588	381	2522	1496	233
F	SnMe ₃	CCl ₄	1580	178	2722	1492	231
F	Sn(Me) ₂ (<i>p</i> -FC ₆ H ₄)	CCl ₄	1580	276	2687	1488	174
F	Sn(Me)(<i>p</i> -FC ₆ H ₄) ₂	CCl ₄	1583	278	2545	1494	270
F	SnEt ₃	CCl ₄	1582	374	2842	1488	175
F	Sn(Et) ₂ (<i>p</i> -FC ₆ H ₄)	CCl ₄	1582	325	2666	1490	226
F	Sn(Et)(<i>p</i> -FC ₆ H ₄) ₂	CCl ₄	1581	303	2721	1490	303
F	Sn(<i>p</i> -FC ₆ H ₄) ₃	CCl ₄	1583	290	3269	1492	345
Me	Sn(Et) ₂ (<i>p</i> -MeC ₆ H ₄)	CCl ₄	1585	27	256	1492	

^a ϵ_A is the peak extinction coefficient; $\epsilon_A = a_{\max}/cl$ where a_{\max} is the absorbance at peak maximum, c is the concentration, and l is the cell length. ^b A is the integrated intensity of the 1600- and 1585-cm⁻¹ band. ^c ϵ , ϵ_A , and A values are divided by the number of equivalent benzene rings. ^d These values have not been divided by the number of benzene rings as one ring is *para* substituted.

Table III. Spectral Data for *meta*-Disubstituted Benzenes

Substituents		Solvent	—1600 band—		A^b	—1500 band—	
			ν	ϵ_A^a		ν	ϵ_A
F	S ⁺ (Me) ₂ ClO ₄ ⁻	CH ₃ CN	1594	170	3240	1480	
F	P ⁺ (Ph) ₃ BF ₄ ⁻	CHCl ₃	1853	225 ^c	3186 ^c	1480	238 ^c
F	SiMe ₃	CCl ₄	1578	159	2858	1480	159
F	GeMe ₃	CCl ₄	1574	206	3147	1474	213
F	SnMe ₃	CCl ₄	1570	178	3370	1470	134
F	Sn(Me) ₂ (<i>m</i> -FC ₆ H ₄)	CCl ₄	1582	206	4527	1472	172
F	SnEt ₃	CCl ₄	1568	160	3745	1470	152
F	Sn(Et) ₂ (<i>m</i> -FC ₆ H ₄)	CCl ₄	1572	179	3325	1474	160
F	Sn(<i>m</i> -FC ₆ H ₄) ₃	CCl ₄	1572	167	3435	1474	177
Me	Sn(Et) ₂ (<i>m</i> -MeC ₆ H ₄)	CCl ₄	1586	39	763	1480	

^{a-c} Footnotes as in Table II.

Table IV. σ_R° Values for Substituents $\cdot\text{MPh}_{(x-1)}$ Calculated from Infrared Intensities of Compounds MPh_x

MPh	MPh ₂	MPh ₃	MPh ₄	MPh ₅	MPh ₆	MPh
Li +0.144	Be ...	B +0.221	C -0.130 ^a	N -0.438 ^a	O -0.364 ^a	F -0.341 ^a
	Mg ...	Al +0.109	Si <i>ca.</i> 0.0	P -0.063 ^b (+0.031) ^{b,c}	S -0.189 ^a	Cl -0.217 ^a
	Zn +0.109	...	Ge <i>ca.</i> 0.0	As -0.070 (+0.044) ^c	Se -0.190	Br -0.231 ^a
	Cd +0.104	...	Sn <i>ca.</i> 0.0	Sb -0.080 (+0.063) ^c	Te ...	I -0.221 ^a
	Hg <i>ca.</i> 0.0	...	Pb <i>ca.</i> 0.0	Bi -0.100

^a Values from ref 3 calculated using equation $(\sigma_R^\circ)^2 = (A - 100)/17,600$ (A values are divided by the number of benzene rings). ^b Signs for the group V substituents are tentative. ^c These refer to measurements on compound MPh_5 .

Table V. Interactions in *meta*- and *para*-Disubstituted Benzenes $\text{XC}_6\text{H}_4\text{Y}$

Substituents Y X		Infrared method (<i>meta</i> compounds)		¹⁹ F nmr method ^a			Infrared method (<i>para</i> compounds)			
		\bar{R}_m^b	$\sigma_R^\circ\text{X calcd}$	$\delta^{19}\text{F para}$	$\delta^{19}\text{F meta}$	$\sigma_R^\circ\text{X}^c$	\bar{R}_p^d	K_X^e	$0.5K_X\sigma_R^\circ\text{Y}$	Δ^f
F	SiMe ₃	0.13	-0.04	-0.51	+0.83	+0.04	0.21	0.48	0.08	0.08
F	GeMe ₃	0.15	-0.08	+0.56	+0.75	+0.01	0.20	0.56	0.10	0.09
F	SnMe ₃	0.16	-0.10	+0.15	+0.55	+0.01	0.22	0.65	0.11	0.11
F	SnEt ₃	0.18	-0.13	+0.23	+0.51	+0.01	0.23	0.79	0.13	0.14
F	Sn(Et) ₂ C ₆ H ₄ F	0.16	-0.09	-0.76	-0.32	+0.01	0.21	0.81	0.14	0.10
F	Sn(Me) ₂ C ₆ H ₄ F	0.22	-0.19	-0.83	-0.22	+0.02	0.21	0.92	0.16	0.21
F	S(Me ₂) ⁺ Z ⁻	0.15 ^g	-0.09	-5.46 ^h	-0.57 ^h	+0.16 ^h	0.20 ⁱ	0.67	0.11	0.25
F	P(Ph ₃) ⁺ Z ⁻	0.12 ^k	0.00	-7.61 ^j	0.00 ^j	+0.26 ^j	0.61 ^k	0.79	0.14	0.26

^a δ values in parts per million (ppm), data taken from ref 27. ^b $\bar{R}_m = [(A - 340)/19,000]^{1/2}$ (A values are divided by the number of equivalent benzene rings). ^c Calculated as in ref 7; $\delta_{Fm} - \delta_{Fp} = +29.5\sigma_R^\circ$. ^d $\bar{R}_p = [(A - 170)/11,800]^{1/2}$ (A values are divided by the number of equivalent benzene rings). ^e For definitions see eq 3; Y is a strong donor. ^f $\Delta = |\sigma_R^\circ\text{X(nmr)} - \sigma_R^\circ\text{X(ir)}|$. ^g Z = ClO₄. ^h Z = BF₄. ⁱ Z = ClO₄ (in CH₃CN), result communicated by R. W. Taft and J. Rakshys. ^j Z = BF₄ (in CH₂Cl₂), result communicated by R. W. Taft and J. Rakshys. ^k Z = BF₄; this result was calculated assuming that the three monosubstituted rings in this compound each contribute 199 units to the intensity (cf. Table I).

An equivalent analysis for the intensity value observed for the (*p*-fluorophenyl)triphenylphosphonium cation indicates additional electron movement into the charged substituent.

Although the quantitative agreement between $0.5K_X \cdot \sigma_R^\circ\text{F}$ and the determined Δ values (Table V) is less satisfactory for the substituents SMe_2^+ and PPh_3^+ , the qualitative agreement that these quantities are all positive supports the treatment.

The σ_R° values of the substituents MPh_2 , where M is an element of group V, are all small, but increase in magnitude gradually from M = P to M = Bi; all these substituents are probably weak resonance donors, although polysubstituted compounds are not presently available to check this. The contrast with the strong donor properties of the group NPh_2 is very marked; we believe that this is a result of d-orbital acceptor properties being superimposed on the lone-pair donor character of the heavier elements. The value obtained for the σ_R° value of the PPh_2 substituent is in accord with the small ¹⁹F shift observed⁸ in (*p*-fluorophenyl)diphenylphosphine compared to fluorobenzene. Schindlbauer⁹ assigned a σ_p value of +0.31 to this substituent from the observed shift using the formula⁹

$$\sigma_p = -0.560\delta_p + 0.271$$

This formula, however, only gives approximate results¹⁰

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and the small shift in the *para* compound taken together with the report that the *m*-fluoro derivative shows an almost identical change¹¹ suggests a very low σ_R° value and in fact that the σ_I value is also close to zero. Later work¹² on ¹⁹F nmr indicates a low σ_R° , but σ_I *ca.* +0.17. Low σ° and σ_p values (+0.03 and -0.01) were reported recently¹³ and are in poor agreement with the previous values of σ_p of +0.68¹⁴ and +0.21.¹⁵ In the three available pentavalent derivatives MPh_5 , the σ_R° values for the groups MPh_4 are *smaller still* than the corresponding trivalent derivatives, and show a similar small increase in magnitude for M = P to M = Sb. These groups are probably weak electron acceptors.

We have also examined a few other phosphorus substituents. Signs cannot be rigorously assigned in the absence of measurements on disubstituted derivatives, but we believe that PMe_2 (-0.076) and PCl_2 (-0.059) are resonance donors, whereas PMe_3^+ (+0.080), PPh_3^+ (+0.075), and $\text{PO}(\text{OH})_2$ (+0.080) are resonance acceptors.

There is previous evidence of the participation of the phosphorus d orbitals in conjugation involving electron acceptance. Thus the decreased uv intensity of *p*-

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 (14) H. L. Retcofsky and C. E. Griffin, *Tetrahedron Letters*, 1975 (1966).
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methoxyphenylphosphine¹⁶ and the bathochromic shift found for tris- α -furylphosphine oxide and related compounds¹⁷ as well as the proton nmr chemical shifts of the acetylenic hydrogen of HC \equiv CP derivatives¹⁸ and ¹⁹F shifts and coupling constants for C₆F₅P derivatives¹⁹ all indicate electron withdrawal. However, the conclusions from work involving a strong resonance donor group such as F¹⁹ ($\sigma_R^\circ = -0.34$) or OMe¹⁶ ($\sigma_R^\circ = -0.43$) *para* to the phosphorus substituent indicated that the latter is a stronger acceptor than in fact it is, for the reasons mentioned above; this is demonstrated later in this paper for compounds involving Si, Ge, and Sn atoms. In fact, uv spectra of unsubstituted phenylphosphorus compounds give little evidence of interaction.²⁰ The rule proposed¹⁹ for distinguishing between a π -electron donor and a π -electron acceptor does *not* generally allow conclusions to be made regarding unperturbed substituents in aromatic rings. Evidence for electron withdrawal by substituents containing phosphorus and other second and third row elements is available from electrophilic substitution reactions: protodesilylation²¹ and nitration.²²

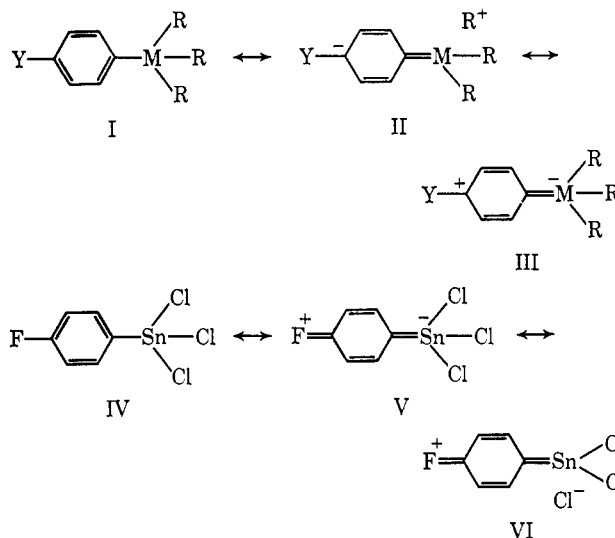
Relatively few σ values for P-containing groups have been reported (and still less for As, etc.); for a summary of early work see ref 23. More recently Schiemenz has derived σ values from the $\nu(\text{Ar-O})$ of *p*-methoxyphenyl derivatives,²⁴ from various properties of *p*-dimethylamino derivatives,²⁵ and from other infrared band frequency shifts.²⁶ Magnetic resonance ¹³C determinations have also yielded¹⁴ σ_p values. The values of σ^+ for trivalent phosphorus substituents vary considerably between *p*-methoxyphenyl and *p*-dimethylaminophenyl derivatives, being considerably smaller in the former case.

Substituents Linked by Group IV Atoms. The substituents MPh₃ (M = Si, Ge, Sn, Pb) have σ_R° values too small to be deduced from the infrared intensities of monosubstituted phenyl compounds (Table I). The σ_R° values for the corresponding groups MMe₃ are also small and are best obtained from the *meta*-substituted derivatives which show clearly that the groups are all net resonance donors (Table V). From available ¹⁹F results,²⁷ it was possible to calculate nmr-derived σ_R° values for the groups MMe₃. Although these indicate the groups to be weak electron acceptors this arises from the presence of substituent-substituent interaction in the *p*-fluorophenyl compounds. The situation is comparable to that found earlier for the heavier halogens.⁵

Good previous evidence for d-orbital participation in aryl-silicon compounds and other group IV element derivatives is available for compounds in which direct con-

jugation can occur with a powerful donor group. The uv intensity criterion has been applied to *p*-methoxyphenylsilane²⁸ and to a series of *p*-methoxyphenyltrimethyl derivatives of Si, Ge, and Sn.²⁹ Other evidence is available from uv frequency shifts,³⁰ reduction potentials for substituted quinones,³¹ esr spectra,^{32,33} and acidity measurements.³⁴ However, doubts have been raised as to the reality of π -d delocalization at least in Si-N bonds, even quite recently.³⁵ The earlier, less conclusive, evidence is surveyed in ref 28 and 33 and a review³⁶ is available on the applicability of σ constants to silicon derivatives.

We can conclude from our own and the literature evidence that whereas in unsubstituted phenyl derivatives resonance interactions of type II outweigh those of III, for compounds in which Y is a strong donor we have III > II. The figures in Table II suggest that this electron acceptance, when *para* to a strong donor, is greater for the trimethylsilyl substituent than for the trimethylstannyl one in accordance with dipole moment evidence.³⁷ It was previously shown³⁸ by nmr that in the case of *p*-fluorophenylchlorostannanes, (FC₆H₄)_n-SnCl_{4-n}, where the fluorine atom behaves as a strong resonance donor, structures such as V and VI are favored.



Substituents Linked by Group I, II, and III Atoms. The group substituents, MPh₂ (M = B and Al) and MPh (M = Zn, Cd, Hg, and Li), all show rather small σ_R° values which decrease with increasing atomic weight of the metal atom. They are presumably all resonance

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electron acceptors as suggested by the downfield chemical shifts³⁹ of the *p*-hydrogens in phenyllithium and diphenylzinc. However, the ¹⁹F shifts of the *m*- and *p*-fluoro-substituted diphenylmercury indicated⁴⁰ a very slight electron donation by the HgC₆H₄F substituent. For boron, confirmation of this acceptance is available from other substituents; thus the group B(OH)₂ ($\sigma_R^\circ = +0.227$) is almost the same as BPh₂ ($+0.221$), whereas BCl₂ ($+0.298$) is a stronger acceptor. The BPh₃⁻ group is probably a resonance donor ($\sigma_R^\circ = -0.129$): it would be expected to be similar to CPh₃ (-0.130).

We are presently studying further organometallic derivatives, particularly benzyl compounds, to determine the significance of metal hyperconjugation.

Experimental Section

Compounds were obtained commercially or prepared by known methods. Purities were checked by gas chromatography or melting point. Tetraphenylphosphonium bromide was prepared from triphenylphosphine and bromobenzene.⁴¹ Tetraphenylstannane, tetra-

phenylgermane, and tetraphenylsilane were kindly supplied by Professor J. C. Maire, Département de chimie organique, Marseille, France (for other compounds of Si, Ge, Sn see ref 28 and 42). Pentaphenylphosphorus, -arsenic, and -antimony were kindly supplied by Dr. D. Hellwinkel and Professor G. Wittig of the Institute für organische chemie der Universität, Heidelberg, Germany. The compounds of type C₆H₅PHO(OMR₃) where M = Si or Ge were kindly donated by Dr. J. F. Brazier, 11 Nouvelle Faculté des Sciences, Toulouse, France.

Spectra were obtained on a Perkin-Elmer 125 spectrophotometer under conditions similar to those previously specified and solvents were purified as before.⁴³ Intensity area *A* values quoted are the average of four readings, usually in two separate solutions; reproducibility of *A*^{1/2} was ± 1 unit. For compounds having more than one benzene ring, the *A*, ϵ_A , and ϵ values have been divided by the number of benzene rings. We have shown that for mono-³ and meta-disubstituted compounds⁵ the variation of the *A* values with solvent are generally small, although this does not hold for certain para-disubstituted derivatives.⁶ The accuracy of σ_R° values measured by the ir method has been discussed previously and attention drawn to the uncertainties with values <0.1 unit.

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Nuclear Magnetic Resonance Spectroscopy. ¹³C Spectra of Aliphatic Carboxylic Acids and Carboxylate Anions¹

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Abstract: The ¹³C chemical shifts of each of the carbons of the simple aliphatic carboxylic acids and their corresponding anions from formic to valeric acid have been measured in aqueous solution. Perhaps surprisingly, ionization of an aliphatic acid results in a downfield shift of its carbon resonances. The results have been correlated with other substituent effects, with ¹³C and H resonances in corresponding hydrocarbons, and with the distance between the carboxylic(ate) group and the carbons undergoing resonance absorption.

Despite the low sensitivity of the ¹³C nucleus for nmr detection,² ¹³C chemical shifts can be determined quite readily using ¹³C of natural abundance with the aid of proton decoupling in the digital-frequency-sweep spectrometer previously described,³ even in fairly dilute (0.5 *M*) solutions. The purpose of the present work was to determine if the electrostatic perturbation produced by carboxylate groups could be clearly distinguished on ¹³C chemical shifts. If this were possible, it might have important applications for determining sites of protonation of amine groups or deprotonation of carboxyl groups in peptide chains made up of basic or acidic amino acids.⁴ To this end, the ¹³C chemical

shifts of some continuous-chain carboxylic acids and the corresponding tetramethylammonium carboxylate salts have been determined in aqueous solution and are summarized in Table I.

The chemical shifts shown in Table I were measured against the ¹³C resonance of tetramethylammonium ion as internal standard at about 30–35° with a precision judged to be ± 0.1 ppm. These were converted to the carbon disulfide scale by adding 137.0 ppm. Positive chemical shifts represent upfield resonances from the carbon disulfide standard. All of the shifts were measured at three concentrations, 0.5, 1.0, and 2.0 *M*, but only the shifts of the carboxyl carbon were more sensitive than ± 0.1 ppm to concentration and for this reason the small upfield effects of concentration changes are only shown for the carboxyl carbons.

The differences in chemical shifts between corresponding carbons in the carboxylic acids studied in this

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