the estimation of the $\Delta H_f°(Co(CO)_8)$ might be a source of considerable error. Bidinosti and McIntyre have reported[29] that the Co–Co bond energy (76 kcal/mol) cited by Winters and Kiser[27] for $Co_2(CO)_8$ is too large. These authors[29] find the Co–Co dissociation energy to be 11.5 kcal/mol. Thus, the reaction

$$Co_2(CO)_8 \longrightarrow 2Co(CO)_4$$

has a heat of reaction of 14 kcal/mol. If this heat of reaction is used together with Winters and Kiser's estimate of $\Delta H_f°(Co_2(CO)_8)$, a value of −163 kcal/mol is found for $\Delta H_f°(Co(CO)_4)$. At present, it is impossible to decide which of the values for $\Delta H_f°(Co(CO)_4)$ is correct; therefore, two values for the dissociation energies of several silylcobalt tetracarbonyls are shown in Table V. As can be seen, the dissociation energies are large for both values of $\Delta H_f°(Co(CO)_4)$; however, the energies based on the $\Delta H_f°(Co(CO)_4) = -164$ kcal/mol appear to be more reasonable. It should be noted that while the absolute values of the DE are questionable owing to the large errors, the differences between the DE's reported are thought significant to ±15 kcal/mol.

In conclusion, the mass spectral results reported here and previously[13–15] are not inconsistent with the postulation that partial $(d \rightarrow d)\pi$ double-bond character exists in the R–Co linkage. Furthermore, they are consistent with an intramolecular interaction that exists between the R substituent and the equatorial groups. It should be stressed than an experimental determination of $\Delta H_f°(Co_2(CO)_8)$ is needed before any confidence can be given to the absolute values of DE reported here.

Acknowledgment. The authors thank Dr. John M. Ruth of the Pesticide Chemical Research Branch, U. S. Department of Agriculture for the high-resolution mass measurements. We also wish to acknowledge the help of Alan D. Berry and James F. Bald, Jr., of the Department of Chemistry, University of Pennsylvania, for supplying the compounds reported here.

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Electron Spin Resonance Studies of Substituent Effects.[1] III. Electron Withdrawal by Group IV and Group VI Elements

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Contribution from the Mobil Research and Development Corporation, Field Research Laboratory, Dallas, Texas 75221. Received October 31, 1969

Abstract: Electron withdrawal by group IV and group VI elements was studied by incorporating the elements in substituents and determining the effect of these substituents on methyl hyperfine splitting in 1-phenyl-1,2-propanesemidiones. The following order of electron withdrawal is found: p-OCH_3 < m,p-di-OCH_3 < p-OPh < p-$C(CH_3)_3$ < p-H < p-SCH_3 ≈ p-$SeCH_3$ ≈ m-OCH_3 < p-$Ge(CH_3)_3$ < p-$Si(CH_3)_3$ < p-SPh ≈ p-SePh < p-$SOCH_3$. It is argued that splitting constants in all aromatic radical systems will follow an additivity relationship on substitution, similar to that found in nmr, and the splittings in the m-OCH_3 derivative are partially assigned by this procedure. Contrary to the predictions of σ constants, the p-$Si(CH_3)_3$ and p-$Ge(CH_3)_3$ substituents are moderately good electron-withdrawing groups. The p-$Si(CH_3)_3$ substituent in this system withdraws spin about as well as p-Cl. The p-OCH_3 group is a better electron donor than the p-OPh group in these radicals, reversing the order predicted by σ constants. There is little esr evidence for $d\pi$–$p\pi$ bonding within the p-$SOCH_3$, p-SCH_3, and p-$SeCH_3$ substituents. The p-SPh and p-SePh groups, however, are powerful electron withdrawers, better than the *meta* halogens. The σ^- constants derived from esr data are 0.40 ± 0.03 and 0.42 ± 0.02, respectively, as compared to the 0.29 value for p-SPh obtained from phenol ionization. This result is best explained by invoking $d\pi$–$p\pi$ bonding within the p-SPh and p-SePh substituents. The rehybridization at the divalent atom apparently is a consequence of the conjugative effect of the phenyl group. Molecular orbital calculations were performed on the derivatives which gave results consistent with the above conclusions.

The question of participation of 3d orbitals in bonding involving elements in the third row of the periodic table is of continuing interest. In recent years attempts have been made to attack this problem by electron spin resonance (esr) spectroscopy.[3] There is strong esr evidence that the d orbitals of silicon can contribute to free-radical stabilization. Compared to analogous carbon radicals, silicon appears more capable of delocalizing spin.[4–6] More recent work has shown the remarkable fact that decamethylcyclopentasilane forms a stable anion radical.[7] Studies of 1,4-disilacyclohexadiene anion radical[8] and other silyl-substituted

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(1) (a) Part II: E. T. Strom, A. L. Bluhm, and J. Weinstein, *J. Org. Chem.*, 32, 3853 (1967); (b) presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(2) Author to whom inquiries should be addressed.

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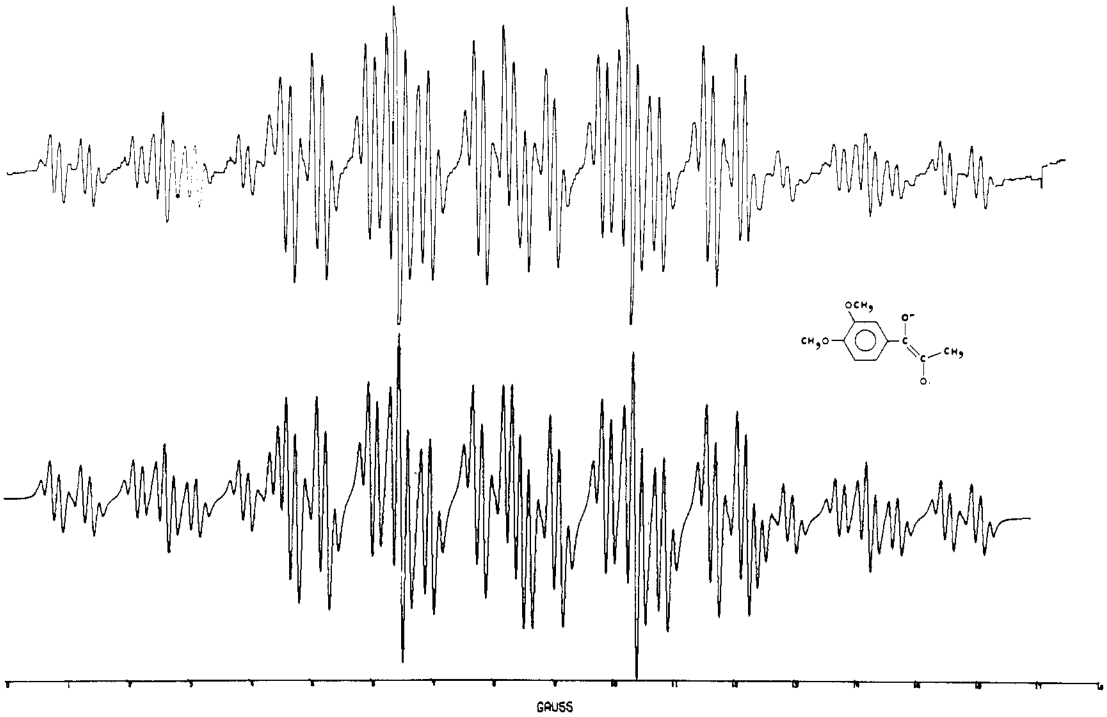
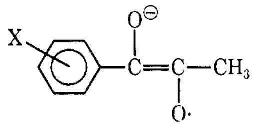


Figure 1. Experimental (top) and simulated (bottom) spectra for the radical formed by the oxidation of *m,p*-dimethoxypropiophenone.

anion radicals[9–12] reinforce the conclusion that the d orbitals of silicon are quite active in delocalizing spin.

The situation is ambiguous as regards group VI. In compounds of bivalent group VI elements, the presence of lone-pair electrons in orbitals capable of overlapping with π systems could obscure any interaction of the d orbitals. Strom and Russell[13] found that d-orbital and p-orbital models for sulfur gave analogous results in an HMO treatment of the anion radical of 2,1,3-benzothiadiazole. More sophisticated calculations on this system did not demonstrate a need to invoke d orbitals in explaining the experimental results.[14–16] Furthermore, Gerdil and Lucken[17] found that the Longuet-Higgins d-orbital model[18] for sulfur gave an incorrect prediction of the spin distribution in dibenzothiophene anion radical.

We felt that a fruitful approach to the question of d-orbital participation in π bonding might lie in an esr study of substituent effects on hyperfine splitting constants (hfsc's) in which the substituents contained group IV and group VI elements. It is known that the methyl hfsc's in substituted 1-phenyl-1,2-propanesemidiones (I) give an excellent correlation with σ constants.[19]



I

Therefore, we studied the phenyl and methyl *para*-substituted group VI derivatives and the trimethyl *para*-substituted group IV derivatives, forming the radicals by base-catalyzed oxidation of the corresponding propiophenones.

Results

Oxidation of *p-t*-Butylpropiophenone. The potassium *t*-butoxide catalyzed oxidation of this ketone, and all the ketones below, in 80% dimethyl sulfoxide–20% *t*-butyl alcohol resulted in the following color changes: on initial contact with the base, the ketone solution became yellow. The yellow deepened to a golden color, quickly becoming deep brown. Occasionally, the deep brown color would change to reddish brown. An esr spectrum was observed with 30 peaks. The spectrum could be analyzed as arising from the methyl group on the semidione side chain and the four ring protons. The splitting constants were as follows: $a^{H}{}_{CH_3} = 3.65 \pm 0.02$, $a^{H}(2H) = 1.53 \pm 0.02$, and $a^{H}(2H) = 0.53 \pm 0.01$ G. The line width of nonoverlapped lines was about 200 mG. The corresponding widths in the unsubstituted radical were 80–100 mG. The extra breadth in the *t*-butyl derivative can be reasonably attributed to an unresolved hyperfine splitting from the *t*-butyl protons. Any elementary consideration of resonance delocalization of the spin or any simple molecular orbital calculation predicts that the larger of the

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Table I. Splitting Constants for Radical Anions

Substituent	$a^H_{CH_3}$	$a^H_{o\text{-}H}$	$a^H_{m\text{-}H}$	$a^H_{p\text{-}H}$	a_{sub}	σ^a
p-C(CH$_3$)$_3$	3.65 ± 0.02	1.53 ± 0.02	0.53 ± 0.01	. . .	. . .	−0.197 ± 0.02
p-Si(CH$_3$)$_3$	3.25 ± 0.02	1.59 ± 0.02	0.50 ± 0.02	. . .	. . .	−0.07 ± 0.1
p-Ge(CH$_3$)$_3$	3.36 ± 0.02	1.59 ± 0.01	0.51 ± 0.01	. . .	. . .	0.0 ± 0.1
p-OCH$_3$	3.88 ± 0.02	1.54 ± 0.02	0.51 ± 0.01	. . .	0.15 ± 0.01	−0.268 ± 0.02
m-OCH$_3$	3.39 ± 0.02	1.43 ± 0.03, 1.75 ± 0.03[b]	0.51 ± 0.01	1.60 ± 0.03[b]	. . .	0.115 ± 0.02
m,p-DiOCH$_3$	3.84 ± 0.02	1.35 ± 0.02, 1.72 ± 0.02[b]	0.50 ± 0.01	. . .	0.145 ± 0.01	. . .
p-SCH$_3$	3.40 ± 0.02	1.65 ± 0.02	0.58 ± 0.02	. . .	0.15 ± 0.01	0.00 ± 0.1
p-SeCH$_3$	3.39 ± 0.02	1.65 ± 0.02	0.58 ± 0.02	. . .	. . .	0.0 ± 0.1
p-SOCH$_3$	2.81 ± 0.02	1.76 ± 0.02	0.54 ± 0.02	. . .	0.17 ± 0.01	0.49 ± 0.1
p-OPh	3.73 ± 0.04	1.67 ± 0.03	0.54 ± 0.02	. . .	. . .	−0.320 ± 0.02
p-SPh	3.01 ± 0.03	1.75 ± 0.04	0.56 ± 0.02	. . .	. . .	0.075 ± 0.02[c]
p-SePh	2.98 ± 0.02	1.67 ± 0.02	0.54 ± 0.01	. . .	. . .	. . .
p-H[d]	3.43 ± 0.02	1.59 ± 0.02	0.54 ± 0.01	1.84 ± 0.02	. . .	. . .

[a] Taken from ref 30. [b] See text for assignment. [c] Taken from ref 39. [d] Taken from ref 20.

two splittings arising from two hydrogens should be assigned to the *ortho* position. This is proven by the disappearance of one small splitting on *meta* substitution (*vide infra*). We shall therefore assign the larger of the two proton splittings to the *ortho* positions for all the *para*-substituted radicals.

Oxidation of *p*-Trimethylsilylpropiophenone. This ketone gave on oxidation an unstable radical with a 27-peak spectrum. The analysis was the following: $a^H_{CH_3}$ = 3.25 ± 0.02, $a^H_{o\text{-}H}$ = 1.59 ± 0.02, $a^H_{m\text{-}H}$ = 0.50 ± 0.02 G. The nonoverlapped lines were ~240 mG in width, which is consistent with an unresolved splitting from the trimethylsilyl protons. The radical decayed rapidly.

Oxidation of *p*-Trimethylgermylpropiophenone. This derivative gave a relatively stable radical. All of the expected 36 lines were resolved. The hyperfine splittings were: $a^H_{CH_3}$ = 3.36 ± 0.02, $a^H_{o\text{-}H}$ = 1.59 ± 0.01, $a^H_{m\text{-}H}$ = 0.51 ± 0.01 G. The width of the lines was ~100 mG, indicating no unresolved splitting from the trimethylgermyl protons.

Oxidation of *p*-Methoxypropiophenone. This compound on oxidation gave a spectrum in which 96 of the possible 144 lines were observed. The spectrum was readily analyzed and interpreted on the basis of a 3.88 ± 0.02 G splitting from the methyl protons, a 1.54 ± 0.02 G splitting from the *ortho* protons, a 0.51 ± 0.01 G coupling from the *meta* protons, and a 0.15 ± 0.01 G splitting from the methoxy protons. Since the methoxy splitting is *ca.* one-third of the *meta* splitting, 48 of the expected lines disappeared by overlap. The observed splitting were identical with those in the literature.[20]

Oxidation of *m*-Methoxypropiophenone. In the absence of resolvable methoxy splittings, 64 lines would be expected from the radical formed by oxidation of this compound. A spectrum was recorded in which 44 of the 64 lines were observed. The spectrum was analyzed as follows: $a^H_{CH_3}$ = 3.39 ± 0.02, $a^H_{ring\text{-}H}$ = 0.51 ± 0.01, 1.43 ± 0.03, 1.60 ± 0.03, and 1.75 ± 0.03 G.

Oxidation of *m,p*-Dimethoxypropiophenone. The experimental spectrum recorded when this compound is oxidized is shown in Figure 1 together with a theoretical spectrum, calculated with $a^H_{CH_3}$ = 3.84 ± 0.02, $a^H_{p\text{-}OCH_3}$ = 0.145 ± 0.01, and $a^H_{ring\text{-}H}$ = 1.72 ± 0.02, 1.35 ± 0.02, and 0.50 ± 0.01 G. The theoretical spectrum was generated with the computer program of Stone[21] using a line width of 80 mG, as measured from the wing peaks. Correspondence of the experimental spectrum with the theoretical spectrum is excellent at almost every point. The main incongruities are that the 21st, 22nd, and 23rd lines from the ends of the theoretical spectrum coalesce to the 21st and 22nd lines from the ends of the experimental spectrum, and the quartet at the center of the theoretical spectrum coalesces to a triplet in the experimental spectrum. These discrepancies stem from the assumption of constant line width. The line width of components with relative intensity three is 130 mG rather than 80 mG.

Oxidation of *p*-Methylthiopropiophenone. The oxidation of this compound gave a radical with ~100 of the 144 possible lines resolved. The coupling with the thiomethoxy protons was 0.15 ± 0.01 G. The other splittings were $a^H_{CH_3}$ = 3.40 ± 0.02, $a^H_{o\text{-}H}$ = 1.65 ± 0.02, and $a^H_{m\text{-}H}$ = 0.58 ± 0.02 G.

Oxidation of *p*-Methylselenopropiophenone. This ketone gave a 27-peak esr spectrum on oxidation. The measured splittings were $a^H_{CH_3}$ = 3.39 ± 0.02, $a^H_{o\text{-}H}$ = 1.65 ± 0.02, and $a^H_{m\text{-}H}$ = 0.58 ± 0.02 G.

Oxidation of *p*-Methylsulfinylpropiophenone. This radical gave a well-resolved spectrum with observable splitting from the methylsulfinyl protons. The amount of this splitting was 0.17 ± 0.01 G. The other coupling constants were $a^H_{CH_3}$ = 2.81 ± 0.02, $a^H_{o\text{-}H}$ = 1.76 ± 0.02, and $a^H_{m\text{-}H}$ = 0.54 ± 0.02 G.

Oxidation of *p*-Phenoxypropiophenone. The spectrum obtained from this compound consisted of all 36 expected lines. The analysis was as follows: $a^H_{CH_3}$ = 3.73 ± 0.04, $a^H_{o\text{-}H}$ = 1.67 ± 0.03, $a^H_{m\text{-}H}$ = 0.54 ± 0.02 G.

Oxidation of *p*-Phenylthiopropiophenone. A moderately resolved spectrum was obtained in which some 28 lines were observed. The analysis was $a^H_{CH_3}$ = 3.01 ± 0.03, $a^H_{o\text{-}H}$ = 1.74 ± 0.04, $a^H_{m\text{-}H}$ = 0.56 ± 0.02 G. The line widths of the nonoverlapped lines were 100–130 mG.

Oxidation of *p*-Phenylselenopropiophenone. A well-resolved spectrum was obtained in which all 36 lines were observable. The methyl splitting was 2.98 ± 0.02 G. The *ortho* and *meta* splittings were 1.67 ± 0.02 and 0.54 ± 0.01 G, respectively. The data for all the radicals, together with the pertinent σ constants, are given in Table I. The data for the unsubstituted parent radical are also given for comparison.

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Assignment of Splitting Constants in *meta*-Substituted Radicals. Conclusive assignment of the splitting constants in the *meta*-substituted radicals can only be obtained by specific deuteration, but strongly suggestive support for certain assignments can be acquired by other means. Venkataraman, *et al.*, were able to arrive at a consistent assignment for various methyl- and chloro-substituted *p*-benzosemiquinones by assuming that the effect of the methyl or chloro substituent on various ring splitting constants was additive.[22] Barton and Fraenkel assigned splitting constants for methyl-substituted dihydropyrazine cation radicals by this same procedure.[23] We believe that these are specialized cases of a general phenomenon. We suggest that ring splitting constants will follow an additive relationship in all substituted aromatic radical systems. There are precedents for this hypothesis in the additivity relationships found for the chemical shifts of ring protons in substituted benzenes.[24,25] An important factor determining the proton chemical shifts in these benzenoid derivatives is the π electron density at various ring positions. If changes in π electron density are additive, it is reasonable that changes in unpaired π electron density will also be additive, and it is mainly the unpaired π electron density which determines the splitting constant.

There are two obvious situations where an additivity relationship will break down. When two large substituents are located *ortho* to each other, steric effects will distort any additivity relationship. Also, a substituent which can attract spin better than the parent substituent will not merely perturb spin density; it will drastically rearrange it.

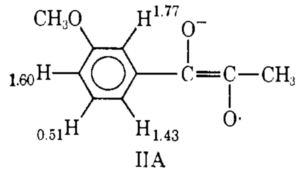
The procedure of Venkataraman, *et al.*, entailed assigning a characteristic, additive change (compared to the unsubstituted radical) to a ring position on substitution. The data from multiply substituted radicals allowed the determination of a unique set of parameters. The phenylsemidione system differs from the semiquinone and dihydropyrazine cation radical systems in that incremental changes will be different for *para* and *meta* substitution. The changes introduced by substitution of a *p*-methoxy group, as referenced to the unsubstituted derivative, are as follows: $\delta^{\alpha}{}_{p\text{-OCH}_3} = -0.03$, $\delta^{\beta}{}_{p\text{-OCH}_3} = -0.05$ G. For the *m*-methoxy derivative $\delta^{\beta}{}_{m\text{-OCH}_3} = -0.03$ G, but there are six possible ways of assigning $\delta^{\alpha}{}_{m\text{-OCH}_3}$, $\delta^{\alpha'}{}_{m\text{-OCH}_3}$, and $\delta^{\gamma}{}_{m\text{-OCH}_3}$. Elimination of certain of these combinations is accomplished by assuming additivity of splitting constants and calculating the ring splitting constants for the *m,p*-dimethoxy derivative from eq 1 and 2. Normally, one

$$a^{\mathrm{H}}{}_{o}\text{ (next to methoxy)} = 1.59 + \delta^{\alpha}{}_{m\text{-OCH}_3} + \delta^{\beta}{}_{p\text{-OCH}_3} \quad (1)$$

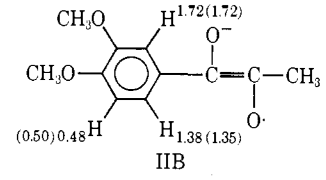
$$a^{\mathrm{H}}{}_{o}\text{ (other)} = 1.59 + \delta^{\gamma}{}_{m\text{-OCH}_3} + \delta^{\beta}{}_{p\text{-OCH}_3} \quad (2)$$

might fear deviations from additivity in the case of *ortho* disubstitution, but the methoxy methyls can orient themselves so as to minimize steric repulsions. Lending credence to this view is the result that the increase in the side-chain methyl splitting in the *meta,para* derivative, when compared to the unsubstituted compound, 0.41 ± 0.04 G, is equal to the algebraic sum of the corresponding changes for the *meta* and *para* derivatives, *i.e.*, 0.45 − 0.04 = 0.41 ± 0.04 G.

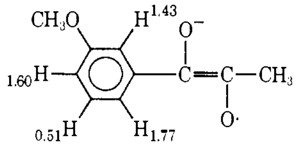
Only two splitting assignments for the *meta* derivative are found to give reasonable splitting constants for the disubstituted derivative. The assignments and resultant predicted splitting constants are shown below with the experimental values in parentheses. This is as far as the assumption of additivity of substituent effects will take us. Data for the di-*m*-methoxy derivative will not allow a choice between these two assignments, while substitution of a methoxy group at an *ortho* position completely distorts the spin distribution because of steric effects.[26] We favor assignments IIIA and IIIB.



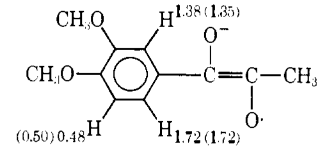
IIA



IIB



IIIA



IIIB

The increments used in IIIA are $\delta^{\alpha}{}_{m\text{-OCH}_3}$ (*ortho* to the semidione) = −0.16, $\delta^{\alpha'}{}_{m\text{-OCH}_3}$ (*para* to the semidione) = 0.24, $\delta^{\beta}{}_{m\text{-OCH}_3} = -0.03$, and $\delta^{\gamma}{}_{m\text{-OCH}_3} = +0.18$ G. The *m*-methoxy substituent has decreased spin density at the α and β positions and increased spin density at the position γ to it. The other assignment (II) would indicate that the methoxy group has increased spin density at one α position and *decreased* it at the other. We feel this is highly improbable, but molecular orbital calculations (*vide infra*) do support assignment II. The problem will have to be resolved by deuterium substitution.

The procedure used above should apply to other substituents and other aromatic radical systems. We hope to test it.

Discussion

How will the interaction of the d orbitals of sulfur and its isologs or the d orbitals of the group IV elements with the π-electron system of I reflect itself in the esr spectrum? Whether the interaction is that of "vacant" d orbitals with the π systems or that of rehybridized dp orbitals, each containing one electron as in the Longuet-Higgins treatment,[18] we would expect withdrawal of spin density by resonance. In Hammett treatments of systems where direct resonance is possible between a substituent and the functional group, electron withdrawal by resonance results in a correlation with σ^- rather than σ. Clearly I is a system in which direct resonance interactions are possible, *e.g.*, see IV.

In the earlier study[19] on substituted anion radicals of structure I, it was found that 16 substituents gave an excellent correlation with σ. For the substituents *m*-CN, *m*-CF$_3$, *m*-Br, *m*-Cl, *m*-F, *p*-Br, *p*-Cl, *m*-OCH$_3$,

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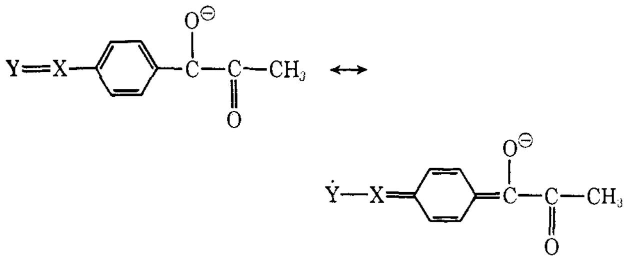
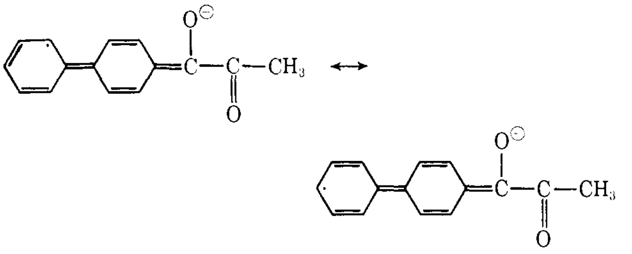


IV

p-H, m-CH_3, m-NH_2, p-CH_3, p-$C(CH_3)_3$, p-OMe, p-NH_2, and m-O^-, the correlation coefficient of σ with the methyl hfsc was 0.995. The p-CN, p-CF_3, p-Ph, p-F, and p-NMe_2 substituents deviated markedly. The "well-behaved" substituents all have one property in common. They do not strongly withdraw electron density by resonance. It might be expected that the deviation of the "ill-behaved" substituents stems from resonance interactions not accounted for by σ constants.

This expectation proves very reasonable for four of the five deviating substituents.[27] It is well known that the p-CN group withdraws electron density by resonance. Recent evidence also indicates that the p-CF_3 substituent is capable of resonance electron withdrawal *via* p-π conjugation.[28] Although σ values would indicate that p-Ph can weakly donate electrons, one can obviously draw many structures in which a p-Ph substituent could delocalize spin, as shown below (V). Finally, even though the p-F substituent has a small positive σ constant, it is known that this group can donate electrons by resonance.[29]



V

In Figure 2 we show the least-squares line for the 16 "well-behaved" substituents. The equation of this line is $a^H_{CH_3} = -1.178\sigma + 3.477$. The data for the p-CN, p-CF_3, p-Ph, and p-F substituents were also plotted. Points for these substituents were obtained using both σ and σ^- constants. The σ^- constants were derived both from ionization of phenols and anilinium ions. It can be seen that the σ^--type points were brought much closer to the correlation line. The deviation of the p-CN, p-CF_3, and p-Ph substituents can be attributed to strong electron withdrawal by resonance. The deviation of p-F stems from electron donation by resonance. With these data we can develop the following criterion. If a substituent of I gives an $a^H_{CH_3}$ value appreciably *less* than that predicted by the σ constant and the correlation equation, then that substituent withdraws electron density by resonance. If a σ^- constant is available, we would expect it to decrease the deviation. We will use this reasoning in attempting to detect spin delocalization *via* d orbitals.

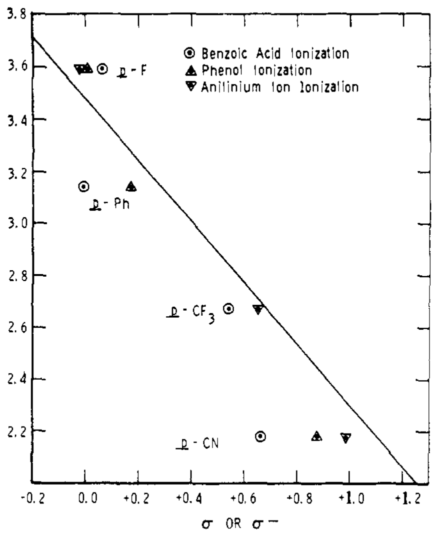


Figure 2. Plot of σ and σ^- *vs.* methyl hfsc for "ill-behaved" points together with the least-squares line for "well-behaved" points. The σ values are from ref 30. The σ^- point for p-CF_3 is from W. A. Sheppard, *J. Amer. Chem. Soc.*, **85**, 1314 (1963). The σ^- point for p-Ph is calculated from data in "Dissociation Constants of Organic Acids in Aqueous Solution," G. Kortum, W. Vogel, and K. Andrussow, Ed., Butterworth & Co., Ltd., London, 1961. All other σ^- points are from A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).

Using the data in Table I and the correlation equation, one can calculate σ values of +0.19 and +0.10, respectively, for the p-$Si(CH_3)_3$ and p-$Ge(CH_3)_3$ substituents. The corresponding literature values are −0.07 and 0.0.[30] The discrepancy for the p-$Si(CH_3)_3$ substituent is less, however, if one compares the esr values with σ^- constants. The σ^- constants derived from phenol and anilinium ion ionization are in the +0.07 to +0.11 range.[31] (We are not aware that any σ^- constants have been measured for the p-$Ge(CH_3)_3$ substituent.) Values of +0.17[32] and +0.19[33] have been derived from other reactions. Since these two substituents have proven to be electron withdrawing in system I, while the p-$Si(CH_3)_3$ substituent is predicted to be electron supplying on the basis of its σ constant with the p-$Ge(CH_3)_3$ substituent predicted to be neutral, the electron withdrawal can only be rationalized on the basis of overlap by vacant d orbitals of Si and Ge with the π system. The d-orbital overlap is greater for Si than Ge. This conclusion is consistent with that reached by Bedford, *et al.*,[5a] in their classical study of group IV substituted benzene anion radicals. Certain data on nucleophilic displacement reactions can also be rationalized on this basis.[34]

Data for the series p-OCH_3, m-OCH_3, p-SCH_3, and p-$SeCH_3$ agree quite well with the predictions of σ constants. The p-OCH_3 group is a strong electron donor, while the m-OCH_3 group is a weak electron withdrawer.

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(27) We feel that deviation of the p-NMe_2 substituent is quite possibly steric in origin, involving steric inhibition of lone-pair electron donation; therefore, this substituent will not be further treated in this paper. The methyl hfsc's in I for the series p-NH_2, p-NMe_2, and p-morpholinyl are 4.30, 4.12, and 3.94 G, respectively.

(28) W. A. Sheppard, *J. Amer. Chem. Soc.*, **87**, 2410 (1965).

(29) See, for example, C. M. Sharts, *J. Chem. Educ.*, **45**, 185 (1968); A. Ault, *ibid.*, **43**, 329 (1966).

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

(31) R. A. Benkeser and H. R. Krysiak, *J. Amer. Chem. Soc.*, **75**, 2421 (1953).

(32) F. Mares and A. Streitwieser, Jr., *ibid.*, **89**, 3770 (1967).

(33) C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 126 (1955).

(34) J. R. Chipperfield and R. H. Prince, *ibid.*, 3567 (1963).

The esr evidence would indicate that the p-SCH$_3$ and p-SeCH$_3$ substituents may withdraw unpaired electron density better than p-H, but considering the error limits of the esr data and the σ constants, the effect cannot be large and may not be real. The thiomethyl proton splitting in the p-thio derivative is equal to the methoxy splitting in the p-methoxy derivative. One might expect a larger splitting from the thiomethyl protons if dπ–pπ bonding delocalized spin on sulfur. There seems to be *no* evidence for unexpected electron withdrawal by the p-SCH$_3$ group.

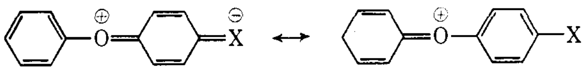
The same considerations apply to the p-SOCH$_3$ group. The σ constant calculated from the correlation equation is 0.57 ± 0.02 while the literature value[30] is 0.49 ± 0.1. When one considers the error limits in the splitting constant and the σ constant, there is no strong evidence for an unusual electron-withdrawing effect. The splitting from the sulfinylmethyl protons is quite small, close to the values of thiomethyl and methoxy splitting. This is inconsistent with the presence of large amounts of spin density within the sulfinyl group. We conclude that there is no compelling esr evidence for dπ–pπ bonding within the sulfinyl group.

This conclusion is consistent with certain other evidence. For the methylsulfinyl group, $\sigma_m > \sigma_p$.[30] This is expected when inductive effects predominate over resonance effects. The separation of field and resonance effects performed by Swain and Lupton[35] indicates that the substituent effect of methylsulfinyl is almost exclusively inductive in nature.

The evidence from phenol ionization, however, indicates that the methylsulfinyl group can exert an electron-withdrawing resonance effect from the *para* position. The σ^- constants for methylsulfinyl derived from the ionizations of phenols in H$_2$O at 25° are σ^-_p = 0.73 and σ_m = 0.53.[36] The σ^- constants for thiomethyl, measured in an identical fashion, are $\sigma^-_p = \sigma_m$ = 0.16.[37] These results are particularly disturbing since we showed that σ constants derived from phenol ionization correlated well with methyl hfsc's for substituents exerting a strong resonance effect. Values of σ^-_p for -SCH$_3$ and -SOCH$_3$ can be calculated from the chemical shift of the phenolic protons in DMSO, using the experimental data and σ^-_p correlation equation of Tribble and Traynham.[38] The calculated values are 0.52 for -SOCH$_3$ and 0.06 for -SCH$_3$, rather close to the esr results. We cannot explain the discrepancy with the ionization constant data at this time.

While *all* of the methyl-substituted group VI substituents gave esr results consistent with σ constant predictions, *none* of the phenyl-substituted group VI substituents did. In system I the p-phenoxy group is not as good an electron donor as the p-methoxy group. This is contrary to σ constant predictions. One can calculate from the correlation equation σ constants of 0.40 ± 0.03 and 0.42 ± 0.02 for the p-PhS and p-PhSe substituents. We are not aware of a σ constant for the p-PhSe substituent derived from the ionization of benzoic acids. However, a value of 0.075 ± 0.02 has been obtained from benzoic acid ionizations for the p-PhS substituent.[39] The σ^- value measured from phenol ionization is 0.29.[40]

The result that p-OCH$_3$ is a better electron donor in the phenylmethylsemidione system than p-OPh, while reversing the order of the σ constants, is in accord with chemical intuition. The strong electron-donating properties of ethereal oxygen in the *para* position stems from resonance involving the lone-pair electrons. With a p-PhO group, however, such electron donation to a functional group should be diminished by similar resonance involving the other benzene ring, as in VI. The discrepancy may involve the main weakness of the σ treatment. The σ constant is composed of a substituent effect on electron density in a benzoic acid *and* a substituent effect on electron density in a benzoate anion. The esr data, by contrast, are concerned with a substituent effect on a single physical property of a *single* species. The above complication of the σ treatment cannot be a serious limitation because the σ treatment is valid in so many systems and reaction series. Nevertheless, it may account for the failure of the σ methodology for isolated substituents.



VI

Charton has suggested that the correct σ constant for p-OPh is −0.14.[41] The σ constants calculated for p-OCH$_3$ and p-OPh from the esr data and the correlation equation are, respectively, −0.342 and −0.215. The deviation for p-OCH$_3$ is the greatest for all the 16 "well-behaved" substituents. The difference between the two constants, 0.127, however, is essentially identical with the difference between the McDaniel and Brown[30] value for $\sigma_{p\text{-OCH}_3}$ and Charton's value for $\sigma_{p\text{-OPh}}$, $-0.269 - (-0.14) = 0.129$. We interpret the esr result as additional support for Charton's suggested value for $\sigma_{p\text{-OPh}}$.

The electron-withdrawing effect of the p-PhS substituent is far greater than would be predicted even by σ^- constants. The most reasonable explanation is that for this group the d orbitals do participate in π bonding. This explanation was also advanced by Meyers to account for the acidities of the substituted phenols.[40] Theoretical calculations[42,43] suggest that the 3d orbitals of atomic sulfur are too diffuse for good overlap with π systems. This result need not necessarily hold for sulfur in a molecule, however. Other calculations predict that substitution of sulfur with highly electronegative atoms can contract the d orbitals so that they can participate in molecular bonding.[44–46] This same conclusion was drawn by Beishline,[47] who also felt that the substitution of sulfur with conjugative groups would enhance dπ–pπ bonding. Beishline concluded that dπ–pπ bonding was important for the p-SCN and p-SCOCH$_3$ substituents. Our results signify that the

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(35) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

(36) F. G. Bordwell and P. J. Boutan, *ibid.*, **79**, 717 (1957).

(37) F. G. Bordwell and G. D. Cooper, *ibid.*, **74**, 1058 (1952).

(38) M. T. Tribble and J. G. Traynham, *ibid.*, **91**, 379 (1969).

(39) H. H. Szmant and G. Suld, *J. Amer. Chem. Soc.*, **78**, 3400 (1956).

(40) C. Y. Meyers, *Gazz. Chim. Ital.*, **93**, 1206 (1963).

(41) M. Charton, *J. Chem. Soc.*, 5884 (1964).

(42) D. W. J. Cruickshank, B. C. Webster, and D. F. Mayers, *J. Chem. Phys.*, **40**, 3773 (1964).

(43) For discussions of this topic see C. A. Coulson, *Nature*, **221**, 1106 (1969); K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).

(44) D. P. Craig and C. Zauli, *J. Chem. Phys.*, **37**, 601, 609 (1962).

(45) D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, 4895 (1965).

(46) K. A. R. Mitchell, *ibid.*, *A*, 2676 (1968).

(47) R. R. Beishline, *J. Org. Chem.*, **26**, 2533 (1961).

phenyl group can also contract the d orbitals of sulfur. Analogous conclusions must hold for the PhSe group. The inductive effect of phenyl is not large enough, however, that one would care to attribute enhanced electron withdrawal by phenyl-substituted sulfur and selenium solely to the electronegativity of the phenyl group. Clearly the conjugative effect of phenyl is crucial. The increase in π-electron delocalization available when two phenyl groups are linked by a transmitting moiety apparently favors rehybridization of bivalent sulfur from sp^3 to a hybrid containing some d character. A special transmission effect for sulfur has recently been noted in the nmr of substituted diphenyl sulfides.[48]

The conclusions we have drawn concerning the electronic effect of the phenylthio group are in marked contrast to those drawn by Lucken.[49] Lucken measured the esr spectra of various aryl- and benzylthio-1,4-benzosemiquinones and concluded that the phenylthio group was electron releasing. Since the arylthio group in the semiquinone system is of necessity *ortho* to a carbonyl group, Lucken's conclusions may lack generality because of steric effects. We should note that *our* conclusions may be only valid for properties affected mainly by the lowest antibonding molecular orbital. These d-orbital effects may not be apparent in the properties that are solely a function of the filled bonding molecular orbitals.

Theoretical Calculations

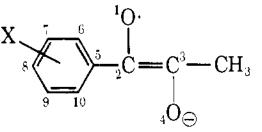
Molecular orbital theory has proven very useful in interpreting the esr spectra of free radicals. Spin densities at sp^2-hybridized carbon atoms substituted by a hydrogen atom or a methyl group can be estimated by either the McConnell[50] (eq 3) or McLachlan[51] (eq 4) equations. For radicals in which negative spin densities are

$$\rho_C = a^H{}_{C-H}/Q^H{}_{CH} \tag{3}$$

$$\rho_C = a^H{}_{C-CH_3}/Q^H{}_{C-CH_3} \tag{4}$$

present, McLachlan's modification of simple Hückel molecular orbital theory has given good results.[52] It was of interest to see if the spin densities within I could be reproduced by calculations of this type. Spin densities were evaluated using a $Q^H{}_{CH}$ of 22.5 G[53] and a $Q^H{}_{C-CH_3}$ of 20.0 G.[23,54] Larger values for both Q parameters[55,56] may be chosen, but, as we will evaluate spin densities in the same manner for all substituents, the exact choice is not that crucial. Our goal is to seek general trends in spin distribution rather than to force exact correspondence of theoretical spin densities with experimental spin densities. The numbering system is shown in VII. Note that of the ten atoms in the π system, we have spin density estimates for only five.

The parameters chosen for the semidione system were those found by Dehl and Fraenkel[57] to give good results for benzil anion radical. Those parameters were as follows: $\alpha_O = \alpha_C + 1.5\beta_{CC}$, $\beta_{C=O} = 1.6\beta_{CC}$, $\beta_{C-C^*} = \beta_{2-5} = 0.7\beta_{CC}$. The effect of the side-chain methyl is most easily taken into account with an inductive model for the methyl group. Streitwieser's suggested value of $h_{C-CH_3} = -0.5$ was used;[58] therefore, $\alpha_{C-CH_3} = \alpha_3 = \alpha_C - 0.5\beta_{CC}$. The parameter λ was taken as 1.2. When these parameters are used to calculate McLachlin spin densities in the unsubstituted radical, the following theoretical spin densities are computed: $\rho_3 = 0.173$, $\rho_6 = \rho_{10} = 0.065$, $\rho_7 = \rho_9 = -0.024$, $\rho_8 = 0.081$. The experimentally derived spin densities are: $\rho_3 = 0.172$, $\rho_6 = \rho_{10} = 0.070$, $\rho_7 = \rho_9 = -0.024$, $\rho_8 = 0.082$. This set of parameters does a reasonable job of reproducing the experimental spin density, but in treating substituted radicals we should accept *ortho* spin densities 0.05 less than the experimental value. These parameters were kept constant for the calculations described below.



VII

A series of generalized calculations was first undertaken to see the effect of attaching an atom X at position 8 and varying the parameters h_X and k_{CX}.[59] The extra molecular orbital resulting from atom X was at approximately a nonbonding level for $h_X = 0$, switching position from bonding to antibonding as h_X and k_{CX} were varied. Depending on the values of the parameters chosen, the new molecular orbital might be either higher or lower in energy than the orbital which *was* the lowest antibonding molecular orbital in the unsubstituted radical. Since the spin distribution in the new molecular orbital did not correspond to the experimental distributions, sharp limits were set on acceptable parameters. For a d-orbital model, negative values of h_X coupled with sizable values of k_{CX} gave unreasonable results while these same values were acceptable for a p-orbital model.

The first pair of substituents to be treated were the trimethylsilyl and trimethylgermyl groups. Parameters for these atoms for use with McLachlan theory have been derived by Curtis and Allred.[60] The silicon and germanium atoms are treated by a d-orbital model (atom X donates an atomic orbital but no electrons) with parameters $h_{Si} = -1.2$, $k_{C-Si} = 0.45$, $h_{Ge} = -1.05$, and $k_{C-Ge} = 0.3$. The attached carbon atom (atom 8) was assigned a Coulomb integral of $\alpha_C - 0.12\beta_{CC}$ for Si or $\alpha_C - 0.1\beta_{CC}$ for Ge. The calculated and experimental spin densities are given in Table II. The agreement is surprisingly good considering that Curtis and Allred derived their parameters from an entirely different radical system. The largest deviation is for the *ortho* position, but this position also gives the poorest agreement for the parent radical.

An effort was made to find a single set of parameters to treat the p-OCH$_3$, p-OPh, and m-OCH$_3$ derivatives using a p-orbital model for the oxygen atom. Preliminary results indicated that if k_{CO} was set $\leqq 1.0$ any

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(48) J. B. Hyne and J. W. Greidanus, *Can. J. Chem.*, 47, 803 (1969).

(49) E. A. C. Lucken, *J. Chem. Soc.*, 4240 (1964).

(50) H. M. McConnell, *J. Chem. Phys.*, 24, 632 (1956).

(51) A. D. McLachlan, *Mol. Phys.*, 1, 233 (1958).

(52) A. D. McLachlan, *ibid.*, 3, 233 (1960).

(53) T. R. Tuttle and S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 5342 (1958).

(54) E. T. Strom, G. A. Russell, and R. Konaka, *J. Chem. Phys.*, 42, 2033 (1965).

(55) M. R. Das and G. K. Fraenkel, *ibid.*, 42, 1350 (1965).

(56) R. W. Fessenden and R. Schuler, *ibid.*, 39, 2147 (1963).

(57) R. Dehl and G. K. Fraenkel, *ibid.*, 39, 1793 (1963).

(58) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 5.

(59) Defined in the usual way: $\alpha_X = \alpha_C + h_X\beta_{CC}$, $\beta_{CX} = k_{CX}\beta_{CC}$.

(60) M. D. Curtis and A. L. Allred, *J. Amer. Chem. Soc.*, **87**, 2554 (1965).

Table II. Calculated and Experimental Spin Densities for *para*-Trimethylsilyl- (and -germyl-) 1-phenyl-1,2-propanesemidiones

	ρ_3	ρ_6	ρ_7
p-Trimethylsilyl, exptl	0.162	0.070	−0.022
p-Trimethylsilyl, calcd	0.162	0.063	−0.020
p-Trimethylgermyl, exptl	0.168	0.070	−0.023
p-Trimethylgermyl, calcd	0.168	0.064	−0.023

reasonable value of h_O predicted, for the *m*-OCH_3 derivative, that the *ortho* position farthest from the -OCH_3 group had the lowest spin density of the three ring positions bearing sizable amounts of positive spin. The parameters $h_O = 0.8$ and $k_{CO} = 0.8$ gave a reasonable representation of the actual spin distribution in the three radicals. Parameters were also derived by another procedure. A computer program was used which sought parameters in an iterative fashion to minimize the differences between theoretical and experimental spin densities at the 3 and 6 positions of the *p*-OCH_3 radical. The derived parameters, $h_O = 1.43$, $k_{CO} = 1.15$, were then used in calculations on the *p*-OPh and *m*-OCH_3 radicals. Finally, calculations were performed using Streitwieser's recommended parameters for ethereal oxygen, $h_O = 2.0$, $k_{CO} = 0.8$.[58] With these latter parameters, an auxiliary inductive parameter of $\alpha_C + 0.2\beta_{CC}$ was assigned to the attached carbon. The results of these calculations are shown in Tables III and IV.

Table III. Calculated and Experimental Spin Densities for the *p*-Methoxy and *p*-Phenoxy Derivatives

	ρ_3	ρ_6	ρ_7
p-OCH_3, exptl	0.194	0.068	−0.023
p-OCH_3, calcd A[a]	0.193	0.062	−0.029
p-OCH_3, calcd B[b]	0.196	0.063	−0.029
p-OCH_3, calcd C[c]	0.175	0.064	−0.024
p-OPh, exptl	0.186	0.074	−0.024
p-OPh, calcd A	0.190	0.063	−0.029
p-OPh, calcd B	0.193	0.062	−0.029
p-OPh, calcd C	0.173	0.064	−0.024

[a] $h_O = 0.8$, $k_{CO} = 0.8$. [b] $h_O = 1.43$, $k_{CO} = 1.15$. [c] $h_O = 2.0$, $k_{CO} = 0.8$.

Table IV. Calculated and Experimental Spin Densities for the *m*-Methoxy Derivative

	ρ_3	ρ_6	ρ_8	ρ_9	ρ_{10}
Exptl	0.170	0.064 or 0.078	0.071	−0.023	0.078 or 0.064
Calcd A[a]	0.175	0.078	0.070	−0.023	0.054
Calcd B[b]	0.175	0.081	0.067	−0.021	0.050
Calcd C[c]	0.173	0.067	0.080	−0.023	0.064

[a] $h_O = 0.8$, $k_{CO} = 0.8$. [b] $h_O = 1.43$, $k_{CO} = 1.15$. [c] $h_O = 2.0$, $k_{CO} = 0.8$.

The parameters given by Streitwieser, being recommended for more general usage, do not give too good a representation of the actual spin density. The other parameters reproduce the spin-supplying effect of *para*-substituted ethereal oxygen, predict that *p*-OCH_3 is more spin-supplying than *p*-OPh, and, for the *m*-OCH_3 radical, reflect the fact that the *para* splitting is intermediate in value between the two *ortho* splittings. The parameters do not reproduce the weak spin-withdrawing effect of *m*-OCH_3, do not reflect the increased spin density at the *ortho* position in the *p*-OPh radical when compared to the *p*-OCH_3 radical, and do not give a good ratio of ρ_6 to ρ_7. Nevertheless, the fact remains that a p-orbital model for oxygen when applied to three different radicals gives a picture of spin distribution that is not grossly in error.

In treating the thiomethyl group, a d-orbital model for sulfur as well as a p-orbital model has to be considered. A d-orbital model like that used for Si and Ge was not even contemplated, as it is unrealistic to completely ignore the sulfur lone pairs. The easiest method of allowing for d–p hybridization is to use the Longuet-Higgins model for sulfur.[18] This latter model has to be modified to account for the fact that the sulfur is bonded to carbons of different hybridization. This can be done in a simple-minded but consistent fashion by treating the methyl inductively, as was done for the semidione side chain. The corresponding parameters are $\alpha_S = \alpha_C$, $\alpha_{S'} = \alpha_C - 0.5\beta_{CC}$, $\beta_{C-S} = 0.8\beta_{CC}$, and $\beta_{SS'} = \beta_{CC}$.[61] With a p-orbital model the parameters $h_X = 0.6$, $k_{CS} = 0.2$ gave the best fit. The results are shown in Table V. The d-orbital model gives slightly better results, but clearly there is not much to choose between the two models.

Table V. Calculated and Experimental Spin Densities for the *p*-Thiomethyl Derivative

	ρ_3	ρ_6	ρ_7
Exptl	0.170	0.073	−0.026
p-Orbital model	0.174	0.065	−0.024
d-Orbital model	0.169	0.063	−0.025

Finally, efforts were made to reproduce the 0.150 spin density at the β-carbonyl carbon in the *p*-SPh radical by treating sulfur with a p-orbital model. Plots of the spin density at the β-carbonyl carbon and the *ortho* position *vs.* various heteroatom parameters for a p-orbital model are shown in Figures 3 and 4. These plots indicate that *no* parameters will give a suitable spin density using a p-orbital model for sulfur. When a negative value of h_S gives a reasonable spin density at atom 3, the corresponding *ortho* spin density is wildly incorrect. Calculations using the Longuet-Higgins model for sulfur, however, do predict spin withdrawal by the *p*-SPh group. The amount of spin withdrawal is overestimated, with a calculated value of 0.124 for ρ_3. Calculations for the d-orbital model and for a p-orbital model, using the parameters which gave the best fit for *p*-SCH_3, are given in Table VI.

Table VI. Calculated and Experimental Spin Densities for the *p*-Thiophenyl Derivative

	ρ_3	ρ_6	ρ_7
Exptl	0.150	0.078	−0.025
p-Orbital model[a]	0.174	0.065	−0.024
d-Orbital model[b]	0.124	0.051	−0.007

[a] $h_S = 0.6$, $k_{C-S} = 0.2$. [b] $h_S = h_{S'} = 0$, $k_{C-S} = k_{C-S'} = 0.8$, $k_{S-S'} = 1.0$.

Presumably, an improvement in the d-orbital model calculations could be achieved by decreasing the param-

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[61] Alternatively, one could assign $\alpha_S = \alpha_{S'} = \alpha_C - 0.25\beta_{CC}$.

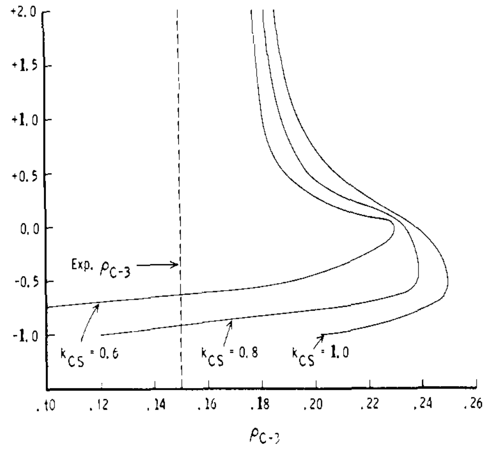

Figure 3. Plot of ρ_{C-3} in the *p*-thiophenyl derivative *vs.* h_S for several values of k_{C-S}.

eter k_{C-S}. This would not be an unreasonable procedure since the attached carbon p orbitals should be at a greater angle in this molecule than in the molecule for which the parameters were originally derived, thiophene.[18] Nevertheless, the salient point is not that a d-orbital model predicted an electron-withdrawing effect for the *p*-thiophenyl group. The inclusion of an extra atomic orbital was bound to have that effect. The important result is that *no* parameters in the p-orbital model gave a proper spin distribution in the *p*-SPh derivative.

The parameters which were used for the thiomethyl group would also be suitable for the selenomethyl group. The deficiencies in calculations on the thiophenyl derivatives would also be present in calculations on the selenophenyl derivative.

To summarize, the calculations on the silicon and germanium substituents give results consistent with the presence of d–π bonding in these radicals. The ethereal substituents can be treated adequately by a p-orbital model. The thiomethyl derivative can be treated reasonably well by either a p-orbital or d-orbital model, but *no* p-orbital model is satisfactory for the *p*-SPh substituent, if a reasonable range of parameters is used.

Experimental Section

A. Materials. **p-t-Butylpropiophenone.** The derivative was formed from *t*-butylbenzene and propionyl chloride by the procedure given for the synthesis of aceto-*p*-cymene,[62] n^{25}D 1.5140, lit.[63] 1.5138.

p-Trimethylsilylpropiophenone. This ketone was made by the procedure used for the synthesis of the corresponding acetophenone.[64] This entailed synthesis of the ethylene ketal of *p*-bromopropiophenone, formation of the Grignard reagent, and reaction of the Grignard reagent with trimethylsilyl chloride. The ketal was then hydrolyzed and the desired product purified by distillation. A liquid with a faint yellow color was obtained: n^{25}D 1.5122, lit.[65] 1.5120. The nuclear magnetic resonance (nmr) frequencies of the protons in this compound (and all compounds mentioned below) were obtained referenced to 3% TMS in CCl_4. The aromatic protons gave an A_2B_2 multiplet splitting with peaks at 7.86, 7.78, 7.54, and 7.46 ppm. A 1:3:3:1 quartet was found centered at 2.92 ppm, a 1:2:1 triplet was centered at 1.22 ppm, and a singlet corresponding to nine protons was observed at 0.34 ppm.

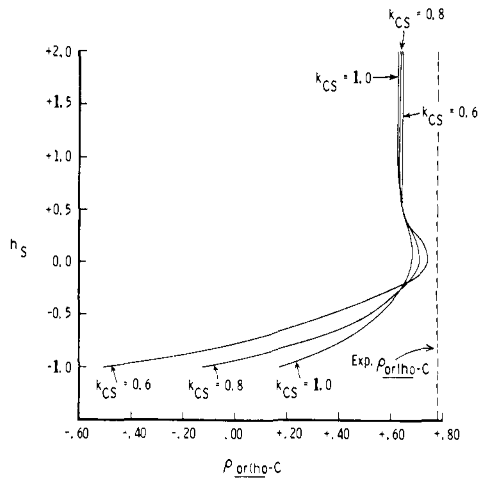

Figure 4. Plot of ρ_{o-C} in the *p*-thiophenyl derivative *vs.* h_S for several values of k_{C-S}.

p-Trimethylgermylpropiophenone. This isolog was synthesized in the same manner as the above silicon derivative. Distillation of the product gave a clear liquid, n^{25}D 1.5297. The nmr spectrum showed the A_2B_2 aromatic multiplet with peaks at 7.88, 7.80, 7.53, and 7.45 ppm. The quartet from the methylene protons was centered at 2.92 ppm, and the triplet from the methyl protons was centered at 1.23 ppm. The trimethylgermyl protons absorbed at 0.46 ppm.

p-Methoxypropiophenone. This chemical was obtained from Aldrich Chemical Co. and used without further purification.

m-Methoxypropiophenone. This compound was synthesized from *m*-hydroxypropiophenone by the procedure of Johnson, *et al.*,[66] $n^{23.5}$D 1.5300, lit. n^{25}D 1.5325.

m,p-Dimethoxypropiophenone. This derivative was made by the Freidel-Crafts reaction of veratrole and propionyl chloride in CS_2, mp 59–61°, lit.[67] 57.5°.

p-Methylthiopropiophenone. This material was formed from the Freidel-Crafts reaction of thioanisole and propionyl chloride using the procedure of Cagniant,[68] mp 57.5–58.0°; lit.[69] 59–60°.

p-Methylselenopropiophenone. Methyl phenyl selenide was synthesized using the procedures of Supniewski, *et al.*,[70] except that powdered commercial selenium was used in place of the recommended amorphous selenium. The methyl phenyl selenide obtained after distillation was a very faint yellow. The nmr spectrum showed a complex region at about 7.1–7.4 ppm corresponding to five protons and a singlet at 2.286 from three protons. The latter resonance was flanked by two satellites 4–5% the height of the central peak. These we attribute to splitting by the natural abundance of ^{77}Se. The value of $J_{^{77}Se-H'}$ was 11.3 cps. The measured value of $J_{^{77}Se-H'}$ in dimethyl selenide is +10.5 cps.[71] The desired ketone was synthesized by a Friedel-Crafts reaction with $AlCl_3$–propionyl chloride under the conditions used by Supniewski, *et al.*,[70] for the synthesis of the corresponding acetophenone. The compound was recrystallized from ethanol giving white crystals, mp 52.5–53.0°. The nmr spectrum consisted of an A_2B_2 type spectrum in the aromatic region with four prominent peaks at 7.82, 7.74, 7.41, and 7.33 ppm, a singlet at 2.36 ppm from the methyl on selenium, a 1:3:3:1 quartet centered about 2.88 ppm from the methylene protons, and a 1:2:1 triplet from the side chain methyl at 1.22 ppm. The selenomethyl peak was flanked by two satellites with $J_{^{77}Se-H'}$ = 11.4 cps.

p-Methylsulfinylpropiophenone. This compound was synthesized from the thiomethyl derivative by oxidation with iodosobenzene diacetate. The derivative was formed by the procedure used for the synthesis of thiaxanthone sulfoxide from thiaxanthone,[72] mp 95.5–96.5°, lit.[73] 96°.

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***p*-Phenoxypropiophenone.** This ketone was made by the procedure of Bun-Hoi, *et al.*,[74] mp (CH_3OH) 35.5–36.0°, lit. 36°.

***p*-Phenylthiopropiophenone.** This compound was synthesized by the Friedel–Crafts reaction of diphenyl sulfide and propionyl chloride using $AlCl_3$ as catalyst. The crude product contained some disubstituted material. The desired compound was separated by fractional crystallization and consisted of white crystals, mp 59–61°. The nmr spectrum showed an A_2B_2-type multiplet splitting from the disubstituted benzene ring with peaks at 7.81, 7.74, 7.21, and 7.13 ppm, a broad resonance from the monosubstituted benzene ring at 7.37 ppm, a 1:3:3:1 quartet from the methylene protons centered at 2.86 ppm, and 1:2:1 triplet at 1.20 ppm.

***p*-Phenylselenopropiophenone.** This compound was synthesized in the same manner as the corresponding sulfur derivative. Faint yellow crystals were obtained, mp 71–73°. The methylene and methyl resonances were centered at 2.850 and 1.17 ppm, respectively. The B-type lines of the A_2B_2 multiplet were obscured by the resonance from the monosubstituted benzene ring.

B. Procedures. Oxidations were carried out in the apparatus described earlier.[75] The concentrations of base and ketone were 0.1 and 0.05 *M*, respectively. Esr spectra were obtained with a Varian V-4500-10 esr spectrometer equipped with a 12-in. magnet and 100-kc/sec field modulation. Sweep rates were calibrated from the spectrum of *p*-benzosemiquinone in 1-butanol.[76]

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A Paramagnetic Monomeric Molybdenum(V)–Cysteine Complex as a Model for Molybdenum–Enzyme Interaction

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Abstract: A paramagnetic Mo(V)–cysteine complex has been studied anaerobically in 0.2 *M* phosphate buffer over a pH range from 6 to 10. Mo(V) and cysteine form a diamagnetic dimer at low pH which then dissociates slowly into a paramagnetic monomer on addition of base. Epr measurements of the isotopically enriched ^{95}Mo(V)–cysteine complex give the following parameters: $g = 1.975$, $g_{zz} = 2.029$, $g_{yy} = 1.972$, $g_{xx} = 1.931$; and $a = 0.0032$ (35 G), $A_{zz} = 0.0051$ (54 G), $A_{yy} = 0.0022$ (24 G), $A_{xx} = 0.0031\ \mathrm{cm}^{-1}$ (34 G). The g and a values, calculated on the basis of $g = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz})$ and $a = \frac{1}{3}(A_{xx} + A_{yy} + A_{zz})$, are in good agreement with those corresponding values measured at room temperature, suggesting that the paramagnetic complex possesses the same structure in both frozen and liquid solutions. A six-line hyperfine splitting follows the monomeric pattern. A line broadening which depends on the nuclear spin orientation was observed in solution at room temperature. The temperature dependence of the epr signals suggests that an equilibrium between the dimer and the monomer exists in solution. Results show the dioxo bridge of the dimer can be broken either by the attack of OH^- in solution or by heat in solid state. A broad weak band, tentatively assigned as a d–d transition, centered at 580 nm was observed for the paramagnetic monomer in solution. A possible structure for the paramagnetic monomer and the biological implications for molybdenum–enzyme interaction, especially in xanthine oxidase, are discussed.

An electron paramagnetic resonance (epr) signal, attributed to the d^1 system of monomeric molybdenum(V), has been found in a number of sulfhydryl enzymes such as xanthine oxidase,[1] aldehyde oxidase,[2] nitrate reductase,[3] and nitrogenase.[4] Molybdenum–sulfur binding at the active site due to the cysteine residue has been proposed.[1,2] This fact led us to study the paramagnetic monomeric Mo(V)–cysteine complex as a possible model for molybdenum–enzyme interaction. Although a few papers dealing with the Mo(V)–cysteine complex have recently appeared in the literature,[5–8] no stable epr signal which includes measurement of anisotropic parameters has been reported in this system. The study of molybdenum thiol complexes by Meriwether, *et al.*,[9] revealed that neither cysteine nor glutathione produces an epr signal in solution with Mo(V). Following the earlier work of Spence and Chang,[5] Kay and Mitchell[6] and Melby[8] independently isolated a diamagnetic Mo(V)–cysteine complex which contains the dimeric grouping $Mo_2O_4^{2+}$, with ligands coordinated to each Mo atom. The structure of this compound was determined by Knox and Prout,[7] and X-ray data suggest that the diamagnetism is due to the formation of a direct Mo–Mo bond. Recently, Mar-

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