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PMR studies of silylcarbinols and related compounds

Since the report by Chapman and King[1] on the use of dimethyl sulfoxide as a solvent for identifying alcohols numerous papers have appeared[2-5], including a recent one on the classification of organosilanols[3]. In this connection it seems appropriate to report some correlations we have observed involving α-silylcarbinols, compounds synthesized in connection with our investigations of the acid[6]- and base[7]-catalyzed rearrangements of these compounds, and also some carbinols and organosilanols.

The shift of the hydroxyl resonance of an alcohol to low field in dimethyl sulfoxide has been attributed to strong hydrogen bonding which also results in a decrease in the OH proton exchange rate, thereby enabling first order splitting to be observed. The frequency of the OH resonance appears to be related to the intrinsic acidity of the alcohol, although steric factors which may affect the ability of the solvent to hydrogen-bond undoubtedly also affect the resonance frequency[2,5]. Numerous other effects due to the neighbouring substituents, including electronegativity, magnetic anisotropy, and the number of α-carbon–carbon bonds, may also play important roles in determining the magnetic shielding of protons. Thus the resonance frequency of thiophenols[8] have been related to σ, of aliphatic thiols[8] to σ^* and n, the number of α-carbon–carbon bonds, where the first effect dominated, and of silanes[9] to σ^* and n, where the effect of n predominated. Substituted methyl- and ethyl-silanes and -germanes have also been correlated[10] with $\Sigma\sigma^*$.

TABLE 1

HYDROXYL RESONANCE FREQUENCIES OF *p*-SUBSTITUTED PHENYL SILYLCARBINOLS[a]

Series A[b]		*Series B*[b]	
$Ph_3SiC(OH)Me(C_6H_4$–OMe)	310	$Ph_3SiC(OH)Ph(C_6H_4$–OMe)	363
$Ph_3SiC(OH)Me(C_6H_4$–$CMe_3)$	313.5	$Ph_3SiC(OH)Ph(C_6H_4$–$CMe_3)$	366
$Ph_3SiC(OH)Me(C_6H_4$–H)	318.5	$Ph_3SiC(OH)Ph(C_6H_4$–H)	372
$Ph_3SiC(OH)Me(C_6H_4$–F)	324.5	$Ph_3SiC(OH)Ph(C_6H_4$–F)	375
$Ph_3SiC(OH)Me(C_6H_4$–Cl)	328	$Ph_3SiC(OH)Ph(C_6H_4$–Cl)	379
Series C[c]		*Series D*[b]	
$Ph_3SiCH(OH)(C_6H_4$–OMe)	332.5	$Ph_3SiC(OH)(CH_2Ph)(C_6H_4$–OMe)	250
$Ph_3SiCH(OH)(C_6H_4$–$CMe_3)$	333	$Ph_3SiC(OH)(CH_2Ph)(C_6H_4$–$CMe_3)$	252
$Ph_3SiCH(OH)(C_6H_4$–H)	339.5	$Ph_3SiC(OH)(CH_2Ph)(C_6H_4$–H)	261
$Ph_3SiCH(OH)(C_6H_4$–F)	344	$Ph_3SiC(OH)(CH_2Ph)(C_6H_4$–F)	272
$Ph_3SiCH(OH)(C_6H_4$–Cl)	346.5	$Ph_3SiC(OH)(CH_2Ph)(C_6H_4$–Cl)	273
Series E[b]		*Series F*[b]	
$Ph_3SiC(OH)Ph(CH_2C_6H_4$–OMe)	252	$Ph_3SiC(OH)(C_6H_4$–OMe)$(CH_2C_6H_4$–OMe)	244
$Ph_3SiC(OH)Ph(CH_2C_6H_4$–$CMe_3)$	260.5	$Ph_3SiC(OH)(C_6H_4$–$CMe_3)(CH_2C_6H_4$–$CMe_3)$	253
$Ph_3SiC(OH)Ph(CH_2C_6H_4$–H)	261	$Ph_3SiC(OH)(C_6H_4$–H)$(CH_2C_6H_4$–H)	261
$Ph_3SiC(OH)Ph(CH_2C_6H_4$–F)	270	$Ph_3SiC(OH)(C_6H_4$–F)$(CH_2C_6H_4$–F)	275
$Ph_3SiC(OH)Ph(CH_2C_6H_4$–Cl)	273	$Ph_3SiC(OH)(C_6H_4$–Cl)$(CH_2C_6H_4$–Cl)	283

[a] Positions are in cps below TMS. All substituents are in the *para* position. [b] All OH signals in this series were singlets. [c] All OH signals in this series were doublets, $J = 4.5$ cps.

Table 1 reports the OH resonance frequency in cycles per second below tetramethylsilane for six different series of triphenylsilyl-*p*-substituted phenylcarbinols in dimethyl sulfoxide. In all cases, the *para*-substituents clearly influence the hydroxyl resonance in a manner related to their electron-withdrawing or -releasing character and, as shown in Fig. 1, excellent linear correlations exist between the position of the hydroxyl resonance and the Hammett σ_p substituent constant[11], correlation coefficients of 0.98, 0.99, 0.97 and 0.99 being obtained for series *A*, *B*, *C* and *D*, respectively. Since within a given series, no significant differences at the hydroxyl group appear to be involved except those due to the electronic effects of the *para*-substituents, it appears reasonable to relate the hydroxyl resonance positions to relative acidities. In series *E* and *F*, where *p*-substituted benzyl groups are involved, rather more scatter of the points is observed about the best straight lines (correlation coefficients, 0.92, 0.96, respectively), possibly due to conformational effects, but the same general relationship that electron-withdrawing substituents cause a shift of the OH resonance to lower field, is observed.

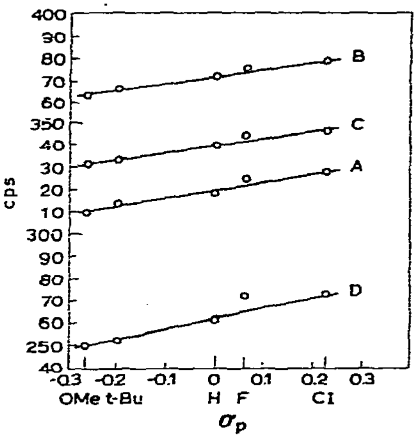

Fig. 1. OH-proton resonance frequencies (cps below TMS) *vs.* Hammett σ_p substituents for α-silylcarbinols series in DMSO. A, $Ph_3SiC(OH)MeC_6H_4X$-*p*; B, $Ph_3SiC(OH)PhC_6H_4X$-*p*; C, $Ph_3SiCH(OH)C_6H_4X$-*p*; D, $Ph_3SiC(OH)(CH_2Ph)C_6H_4X$-*p*.

The nature of the groups attached to the silicon atom of α-silylcarbinols also affects the frequency of the hydroxyl resonance in a predictable way. Thus, when phenyl groups on silicon are successively replaced by methyl groups, the hydroxyl resonance signal moves regularly toward higher field, as shown in Table 2 for a series of silyldiphenylcarbinols. This will be referred to again later.

TABLE 2

HYDROXYL RESONANCE FREQUENCIES OF VARIOUS METHYLPHENYLSILYLDIPHENYLCARBINOLS

Ph_3SiCPh_2OH	372 cps	$PhMe_2SiCPh_2OH$	336 cps
$Ph_2MeSiCPh_2OH$	353 cps	Me_3SiCPh_2OH	323 cps

Similarly, substituents on phenyl groups attached to silicon effect small changes in the resonance frequency. Thus, as shown in Table 3, *p*-chlorophenyl groups attached to the silicon atom of silylcarbinols shift the resonance to lower field relative to the phenyl compounds, whereas *p*-tolyl groups result in a shift to higher field, as expected if electronic effects were the dominating effect present.

TABLE 3

HYDROXYL RESONANCE FREQUENCIES OF (*p*-SUBSTITUTED PHENYL)$_3$SILYLCARBINOLS

$Ph_3SiCHPhOH$	339.5[a] cps	$Ph_3SiCMePhOH$	318[b]
$(p\text{-}Cl\text{-}C_6H_4)_3SiCHPhOH$	343[a]	$(p\text{-}Cl\text{-}C_6H_4)_3SiCMePhOH$	330[b]
$Ph_3SiCHMeOH$	282[a]		
$(p\text{-}CH_3\text{-}C_6H_4)_3SiCHMeOH$	276.5[a]		

[a] Doublet, *J* 4.5 cps. [b] Singlet.

Changing the nature of the groups directly attached to the carbinol-carbon profoundly affects the hydroxyl resonance frequency of the carbinols as shown by the series of triphenylsilylcarbinols given in Table 4. Our studies have been restricted to the three groups, phenyl, hydrogen and methyl, but for this limited series of compounds a linear correlation exists, as shown in Fig. 2, between the OH resonance frequency and the sum of the appropriate Taft polar substituent constants σ^{*}[12,13] for the varying groups* which are attached to the carbinol carbon in each case**.

TABLE 4

HYDROXYL RESONANCE FREQUENCIES OF TRIPHENYLSILYLCARBINOLS

Ph_3SiCPh_2OH	372[a] cps	Ph_3SiCH_2OH	278[c]
$Ph_3SiCHPhOH$	339.5[b]	$Ph_3SiCHMeOH$	282[b]
$Ph_3SiCMePhOH$	318[a]	Ph_3SiCMe_2OH	262[a]

[a] Singlet. [b] Doublet, *J* 4.5 cps. [c] Triplet, *J* 3.5 cps.

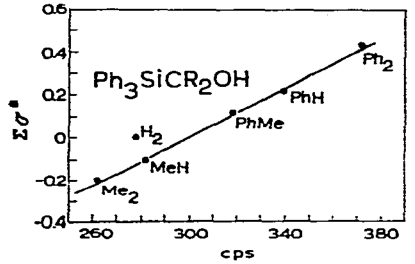

Fig. 2. $\Sigma\sigma^{*}$, sum of Taft polar substituent constants (excluding triphenylsilyl) *vs.* hydroxyl proton resonance frequency in cps below TMS for α-silylcarbinols in DMSO.

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* A value of σ^{*} for the triphenylsilylmethylene group, present in all members of this series, has not been reported to the best of our knowledge.

** The values of σ^{*} employed here are those for $Z\text{-}CH_2$ rather than Z itself, since we are concerned with the effects of substituents on the grouping C–O–H present in all compounds. It has been shown that σ^{*} values are additive (see Table XXI of ref. 14), and that for example, the value of σ^{*} for α-phenylethyl $(Ph\text{-}CH\text{-}CH_3) = Ph + H + CH_3$ attached to C, (0.105), is reasonably precisely derived as the sum of σ^{*} (benzyl $[=\underline{Ph}\text{-}CH_2$, (0.215)$]$ $+\sigma^{*}$ (methyl) $[=\underline{H}\text{-}CH_2\text{-}$, (0.00)$]$ $+\sigma^{*}$ (ethyl) $[=\underline{CH_3}\text{-}CH_2$, $(-0.100)] = 0.115$.

The observed order of proton resonance frequencies is qualitatively in accord with what would be expected as the order of relative acidities for the compounds where the substituents are exhibiting normal polar effects, uncomplicated by resonance interactions.

Similar linear correlations of σ^* with the hydroxyl proton resonance frequency (with correlation coefficients >0.99) are observed for simple methyl and phenyl secondary and tertiary carbinols and also for the related silanols (Table 5, Fig. 3),

TABLE 5

HYDROXYL PROTON RESONANCES OF SILANOLS AND CARBINOLS

Compound	*PMR resonance position (cps below TMS)*	*Infrared frequency shift ($\Delta\nu$ cm^{-1})*
PhOH	555^a	280^b
Ph_3SiOH	$429^{c,d}$	316^e, 311^b, 317^g
Ph_2SiHOH	412^d	322^b
$Ph_2MeSiOH$	389^d	
Ph_3COH	388^c	$174^{b,e}$, 176^g
Ph_2CHOH	$351^{c,f}$	177^b
$PhMe_2SiOH$	346^d	
Ph_2MeCOH	342.5^c	
Me_2HSiOH	332^a	
Me_3SiOH	312^d	238^b
$PhCH_2OH$	$310^{a,c}$	
PhMeCHOH	$309^{c,f}$	
Ph_3GeOH	298^c	198^e, 196^g
$PhMe_2COH$	297^c	
Me_2CHOH	261^a	
Me_2CHCH_2OH	261^c	
Me_3COH	$249^{a,c}$	122^b

[a] Ref. 1. [b] Ref. 16. [c] This work. [d] Ref. 3. [e] Ref. 17. [f] Doublet, J 4 cps. [g] Ref. 18.

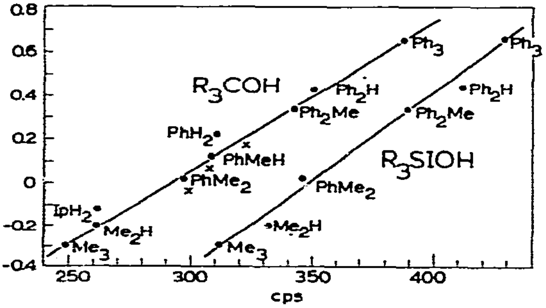

Fig. 3. $\Sigma\sigma^*$, sum of Taft polar substituent constants *vs.* hydroxyl proton resonance frequency in cps below TMS for carbinols and silanols in DMSO (Ip = isopropyl).

but here, as with the triphenylsilylcarbinol series, primary alcohols do not fit the correlation well. The fact that the slopes of the lines for the silanols and carbinols are approximately the same indicates that a change of substituent has approximately the same effect on the magnetic shielding of the hydroxyl protons in the two series of compounds regardless of whether silicon or carbon is the central atom. Furthermore, the good correlations with σ^* imply that neither steric nor anisotropic effects vary significantly from compound to compound within each series*.

The horizontal displacement of the points for similarly substituted carbinols and silanols (Fig. 3) is a reflection of the different properties (electronegativity, polarizability, ability to undergo d_π–p_π bonding, magnetic anisotropy of the bonds) associated with the atoms to which the substituents are attached. Because the empty and energetically accessible *d*-orbitals of silicon are capable of d_π–p_π bonding with unshared electrons on the oxygen of the hydroxyl group, thereby removing electron density, silanols are stronger acids than the corresponding carbinols as has been noted before[16,17] from infrared work.

Earlier work[2] indicated a fair correlation of chemical shifts of the OH resonances with the relative electron-attracting power of the substituent in an alcohol, except for compounds differing significantly in structure and geometry, or having highly polar substituents where anisotropic effects may be important.

While it is tempting to relate the OH resonance frequency of all compounds containing this group to the relative acidities of the various compounds, this is probably unwarranted because of other effects which may influence the magnetic shielding of the hydroxyl protons. Thus Table 5, which lists in decreasing order the PMR resonance frequencies of the compounds used in Fig. 3, shows some inconsistencies with the available infrared data[16–18] used as a measure of relating acidities. For example, the OH resonance frequency of the germanol in the series Ph_3MOH appears to be very low in comparison with the infrared data. Such a low frequency might reflect a lack of d_π–p_π bonding between germanium and the lone pair of electrons on oxygen so that inductive electron release is a major effect acting to make the germanol an even weaker acid than the infrared data infers. On the other hand, the changes in magnetic anisotropy involved in going from C → Si → Ge could well be primarily responsible for the differences in resonance frequency of the various Ph_3MOH compounds. However, within a given series, it does seem reasonable to relate relative OH resonance positions to relative acidities. We therefore suggest that the frequencies of the hydroxyl resonance of secondary or tertiary hydroxyl compounds in DMSO may, with judicious choice of reference compounds for comparison, be used as a method for establishing the relative acidities of these compounds.

All spectra were taken on a Varian Associates A-60 spectrometer using concentrations well below 20 mole % of the hydroxyl compounds in purified dimethyl

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* The only reported value of σ^* for a silylmethylene group is that for Me_3SiCH_2–, −0.26 (see ref. 12, p. 619; this value appears to have been derived from the work of Sommer *et al.*[15]). Using this value for computing $\Sigma\sigma^*$ for the compounds Me_3SiCPh_2OH, resonance frequency 324 cps, and, $Me_3SiCHPhOH$, resonance frequency 302 cps, it is found that these compounds fit the carbinol plot, Fig. 3, reasonably well. If the data from Table 2 are plotted on the carbinol graph, Fig. 3, values of σ^* for the various silylmethylene groups may be obtained:

Ph_3SiCH_2–	+0.09
$Ph_2MeSiCH_2$–	−0.06
$PhMe_2SiCH_2$–	−0.17
Me_3SiCH_2–	−0.26

Utilizing the results of Table 4 in the same manner, the σ^* value of +0.09 for Ph_3SiCH_2– places the various triphenylsilylcarbinols reasonably well on the carbinol line of Fig. 3. Thus it appears that this treatment of the data may provide a useful alternative method of establishing the value of σ^* for various groups.

sulfoxide. Small variations in concentration were demonstrated not to change the resonance frequency by more than a cycle or two. The temperature of the probe was 28°, and it was noted that as the temperature was raised to 80°, the hydroxyl resonance signals moved a few cycles upfield and became less sharp. The silylcarbinols employed were prepared by conventional procedures as described previously[7,19] and will be reported in a forthcoming publication.

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