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NOTE

INTRAMOLECULAR INTERACTION IN GROUP IV ALCOHOLS

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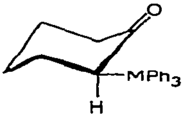
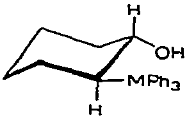
INTRODUCTION

During a recent study of 2-substituted cyclohexanones (I) and cyclohexanols (II), M=C, Si, Ge we found spectroscopic evidence that, when M=Si or Ge, interaction occurred between M and the vicinal oxygen[1]. In an effort to learn more about the extent of this interaction in conformationally more mobile systems we have extended our studies to include the homologous series of alcohols $Ph_3M(CH_2)_nOH$, M=C, Si, Ge; n=0, 1, 2.



(I)



(II)

As with the cyclohexanols[1], (II), the shift in frequency of the IR hydroxyl group absorption [$\Delta\nu$(OH)] upon the addition of a weak base was assumed to be proportional to the relative acidities of the alcohol. The basis for this correlation has been discussed by previous workers in their studies of the relative acidities of Ph_3MOH[2,3] and Ph_3MSH[4].

The shift of the hydroxyl resonance to low field in the PMR spectra of a dilute solution of an alcohol in DMSO has been attributed to strong hydrogen bonding between the alcohol and the DMSO[5]. Brook and Pannell related the magnitude of the shift relative to TMS to the acidity of the alcohol[6]. They realized that many factors such as magnetic anisotropy may also play an important role in the magnetic shielding of the hydroxyl proton and they were able to rationalize their results only in the case of structurally similar secondary and tertiary carbinols. We decided to determine if the validity of this correlation could be extended to other systems by comparing the hydroxyl resonance frequency of the alcohol in DMSO to that at infinite dilution in carbon tetrachloride. It was hoped that this would minimize anisotropy and other extraneous effects and maximize the differences directly attributable to the formation of the OH–DMSO hydrogen bond.

INFRARED RESULTS

The shift in the position of the IR hydroxyl group absorption of the alcohols upon hydrogen bonding to THF and DMSO are shown in Table 1.

TABLE 1

HYDROGEN BONDING IN GROUP IV ALCOHOLS

Compound[a]	ν(OH)[b]	$\Delta\nu$(DMSO)[c]	$\Delta\nu$(THF)[d]
Ph_3COH	3609		208[e]
Ph_3SiOH	3677		338[e]
Ph_3GeOH	3651		211[e]
Ph_3CCH_2OH	3590	190	140
Ph_3SiCH_2OH	3615	205	160
Ph_3GeCH_2OH	3605	230	170
$Ph_3CCH_2CH_2OH$	3630	220	165
$Ph_3SiCH_2CH_2OH$	3630	220	155
$Ph_3GeCH_2CH_2OH$	3625	220	160
2-$Ph_3CC_6H_{10}OH$	3590	190	140
2-$Ph_3SiC_6H_{10}OH$	3610	235	170
2-$Ph_3GeC_6H_{10}OH$	3610	240	180

[a] Solutions at 0.03 *M* in the alcohol and 0.25 *M* in DMSO or THF. [b] Frequency of the free OH in cm^{-1}. [c] Frequency shift upon hydrogen bonding to DMSO, cm^{-1}. [d] Frequency shift upon hydrogen bonding to THF, cm^{-1}. [e] From ref. 2.

For the three homologous carbon alcohols the magnitude of the $\Delta\nu$(OH) increases $Ph_3CCH_2OH < Ph_3CCH_2CH_2OH < Ph_3COH$. The order of acidity expected as a result of the inductive withdrawal of electrons by the phenyl groups[7] is $Ph_3CCH_2CH_2OH < Ph_3CCH_2OH < Ph_3COH$. Steric hindrance of solvation should be least in the case of $Ph_3CCH_2CH_2OH$. The observed order can obviously be rationalized in terms of a compromise between inductive and steric factors.

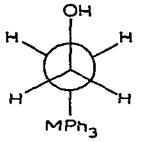
The order observed for the homologous silicon containing alcohols is $Ph_3SiCH_2OH < Ph_3SiCH_2CH_2OH \ll Ph_3SiOH$. Since silicon is more electropositive than carbon[8] the order of acidity predicted as a result of the inductive release of electrons will be $Ph_3SiOH < Ph_3SiCH_2OH < Ph_3SiCH_2CH_2OH$. In addition the steric hindrance of solvation should also be least in $Ph_3SiCH_2CH_2OH$. The enhanced acidity of triphenylsilanol in this series is additional evidence to support the suggestion of d_π–p_π bonding in triphenylsilanol[2,3].

For the homologous germanium alcohols the magnitude of $\Delta\nu$(OH) decreases $Ph_3GeCH_2CH_2OH < Ph_3GeCH_2OH < Ph_3GeOH$ which is the reverse of the order predicted as a result of the inductive release of electrons by germanium[8] and the steric hindrance of solvation. The enhanced acidity of triphenylgermanol again suggests a contribution from d_π–p_π bonding[2,3]. The enhanced acidity of Ph_3GeCH_2OH may indicate some interaction between the vacant *d*-orbitals of the germanium and the non-bonding electrons of the oxygen. A similar interaction has been proposed to account for the low Lewis basicity of $H_3GeCH_2\ddot{O}CH_3$ relative to the carbon analog[9].

The importance of d_π–p_π bonding in determining the observed order of acidity $Ph_3COH < Ph_3GeOH \ll Ph_3SiOH$ has been discussed by previous workers[2,3].

For the analogs of 2,2,2-triphenylethanol the observed order of acidity decreases $Ph_3GeCH_2OH > Ph_3SiCH_2OH > Ph_3CCH_2OH$. Because of the inductive release of electrons by the electropositive germanium and silicon[8] it would be predicted that Ph_3CCH_2OH would be most acidic. Since the difference in steric effect between the silicon and germanium alcohols will be relatively small, the enhanced acidity of Ph_3GeCH_2OH again supports the earlier suggestion[9] of direct interaction between the germanium and oxygen. The enhanced acidity of the silicon alcohol may be partially the result of a similar interaction[9], however, steric factors may also be a major consideration.

The acidity of all the analogs of 3,3,3-triphenylpropanol were effectively the same. Variation in inductive effects through two methylene groups should be small and the influence of differences in steric effects negligible. In the absence of an intramolecular interaction stabilizing a skew or eclipsed conformation the trans conformation (III) would be expected to be energetically most stable. In the 2-substituted cyclohexanols, (II), where in the preferred conformation the silicon and the germanium must be skew to the hydroxyl group the IR results indicate an increase in acidity[1]. Since no similar increase in acidity is observed in the cases of $Ph_3GeCH_2CH_2OH$ and $Ph_3SiCH_2CH_2OH$ it seems reasonable to conclude that such an interaction is not sufficiently strong to stabilize a skew conformation for these alcohols.



(III)

The IR results therefore indicate the presence of significant back donation of electron density from oxygen to the metalloid atom in Ph_3SiOH with much weaker back donation for Ph_3GeOH and Ph_3GeCH_2OH and for those Ph_3Ge–C–C–OH and Ph_3SiC–C–OH systems where gauche or eclipsed conformations are preferred.

PMR RESULTS

The hydroxyl resonance frequencies of the various alcohols were determined on a Varian Associates HA-100 spectrometer at 40°. At the concentration used the resonance positions were not shifted more than a few Hz by small variations in concentration indicating that the relative population of the ROH–DMSO species does not change[10]. The positions of the hydroxyl resonance frequencies of the various alcohols in carbon tetrachloride were plotted against concentration. A typical plot is shown in Fig. 1. With the exception of triphenylsilanol all the plots were essentially linear over the range of concentrations studied. Previous workers[11], have demonstrated that the extrapolation of such plots to infinite dilution gives a reasonable value for the resonance frequency of the unassociated alcohol.

Table 2 contains the results obtained. The purpose of this study was to determine if the correlation suggested by Brook and Pannell[6] between the acidity of the

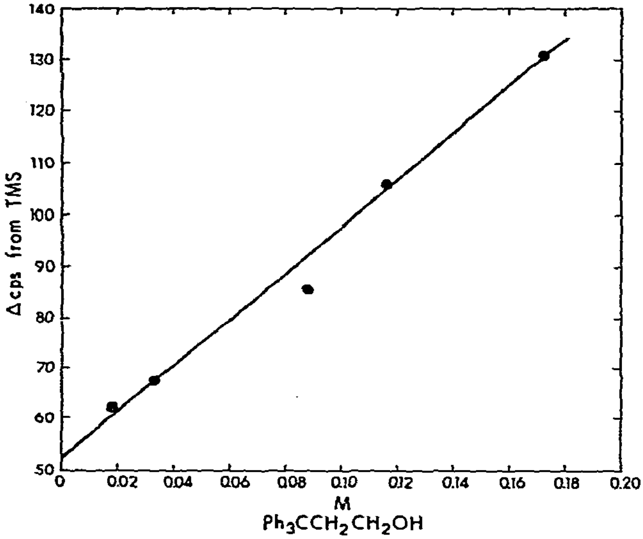


Fig. 1. Dilution curve for O–H shift of 3,3,3-triphenylpropanol in carbon tetrachloride.

TABLE 2

HYDROXYL RESONANCE FREQUENCIES OF $Ph_3M(CH_2)_nOH$

Compound	δ(DMSO)	$\delta(CCl_4)$	δ(DMSO)-$\delta(CCl_4)$
Ph_3COH	6.45	2.40	4.05
Ph_3SiOH	7.15	2.15	5.00
Ph_3GeOH	5.00	1.00	4.00
Ph_3CCH_2OH	5.00	1.20	3.80
Ph_3SiCH_2OH	4.65	0.80	3.85
Ph_3GeCH_2OH	4.25	0.80	3.45
$Ph_3CCH_2CH_2OH$	4.55	0.55	4.00
$Ph_3SiCH_2CH_2OH$	4.60	0.75	3.85
$Ph_3GeCH_2CH_2OH$	4.30	0.85	3.45

alcohol and δ(DMSO) could be made more general by using δ(DMSO)–$\delta(CCl_4)$. This would make the approach analogous to the method used in the IR studies where it is the difference between the free and the hydrogen bonded hydroxyl resonance which is significant rather than the relative positions of the hydrogen bonded absorption. Brook and Pannell's results[6] would be comparable only in those cases where the values of $\delta(CCl_4)$ for the alcohols studied were fortuitously the same. In general they were able to rationalize their results for closely related secondary and tertiary alcohols, but not for primary alcohols. A notable exception was the Ph_3MOH series of tertiary alcohols where, as can be seen in Table 2, the value of δ(DMSO) for Ph_3GeOH appears to be very low in comparison with the infrared data. The values of δ(DMSO)–$\delta(CCl_4)$ for Ph_3MOH are in agreement with the relative acidities suggested by the IR results. However this agreement may be fortuitous rather than significant.

In a recent study of alcohol–bromide ion complex formation[11], $ROH-Br^-$, it was shown that a reasonable correlation was possible between the association constant and the inductive effect of the substituents. The values of the limiting chemical shift on complex formation by comparison showed no consistent correlation with substituent effects and orders were reversed in different systems *e.g.*, $CH_3CH_2OH < (CH_3)_2CHOH < (CH_3)_3COH < Ph(CH_3)_2COH < Ph(CH_3)CHOH < PhCH_2OH$.

In addition they observed[11] that "the limiting shifts of the OH complexes are remarkably independent of the structure of the alcohol". A similar conclusion can be drawn from Table 2 where with the exception of Ph_3SiOH, Ph_3GeCH_2OH, and $Ph_3GeCH_2CH_2OH$ all of the values observed for $\delta(DMSO)-\delta(CCl_4)$ are well within the experimental uncertainty.

Ebsworth[8] has recently discussed some of the problems associated with attempting to correlate NMR chemical shifts in organometallic systems with factors such as $d_\pi-p_\pi$ bonding and electronegativity of substituents and concludes that because of uncertainty as to the origin and magnitude of the factors involved that such correlations "must be regarded with suspicion". We can but concur.

EXPERIMENTAL

The IR spectra were run on a Perkin Elmer 421 grating spectrophotometer in matched solution cells with sodium chloride windows.

The PMR spectra were determined on a Varian Associates HA100 spectrometer using TMS as an internal reference. The variable temperature probe was maintained at 40°. Resonance positions were determined using an electronic counter in conjunction with a variable oscillator. The DMSO-d_6 used was supplied by Merck, Sharp and Dohme of Canada Ltd.

The triphenylmethanol used was obtained from Aldrich Chemical Company Ltd.

The triphenylsilanol[12] and triphenylgermanol[13] were prepared by hydrolysis of the corresponding halides.

The 2,2,2-triphenylethanol[14], (triphenylsilyl)methanol[15], and (triphenylgermyl)methanol[16] were prepared by the addition of the corresponding organolithium reagent to formaldehyde.

The 3,3,3-triphenylpropanol[17], 2-(triphenylsilyl)ethanol[18], and 2-(triphenylgermyl)ethanol, m.p. 83–85°, (Found: C, 68.6; H, 5.90. $C_{20}H_{20}GeO$ calcd.: C, 68.8; H, 5.78%.) were prepared by the addition of the organolithium reagents to ethylene oxide.

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REFERENCES

1 G. J. D. Peddle, *J. Organometal. Chem.*, 14 (1968) 115.
2 R. West, R. H. Baney and D. L. Powell, *J. Amer. Chem. Soc.*, 82 (1960) 6269.
3 N. A. Matwiyoff and R. S. Drago, *J. Organometal. Chem.*, 3 (1965) 393.

4 R. M. SALINGER AND R. WEST, *J. Organometal. Chem.*, 11 (1968) 631.
5 O. L. CHAPMAN AND R. W. KING, *J. Amer. Chem. Soc.*, 86 (1964) 1256.
6 A. G. BROOK AND K. H. PANNELL, *J. Organometal. Chem.*, 8 (1967) 179.
7 R. W. TAFT, JR., in M. S. NEWMAN (Ed.), *Steric Effects in Organic Chemistry*, Wiley, New York, 1956, pp. 556–659.
8 E. A. V. EBSWORTH, in A. G. MACDIARMID (Ed.), *Organometallic Compounds of the Group IV Elements*, Vol. 1, Dekker, New York, 1968, pp. 1–89.
9 G. A. GIBBON, J. T. WANG AND C. H. VAN DYKE, *Inorg. Chem.*, 6 (1967) 1989; J. T. WANG AND C. H. VAN DYKE, *Inorg. Chem.*, 6 (1967) 1741.
10 C. P. RADER, *J. Amer. Chem. Soc.*, 88 (1966) 1713.
11 R. D. GREEN, J. S. MARTIN, W. G. MCCASSIE AND J. B. HYNE, *Can. J. Chem.*, in press.
12 H. GILMAN AND R. M. CLARK, *J. Amer. Chem. Soc.*, 68 (1946) 1675.
13 A. G. BROOK AND H. GILMAN, *J. Amer. Chem. Soc.*, 76 (1954) 77.
14 S. WINSTEIN, B. K. MORSE, E. GRUNWALD, K. C. SCHREIBER AND J. CORSE, *J. Amer. Chem. Soc.*, 74 (1952) 1113.
15 A. G. BROOK AND B. IACHIA, *J. Amer. Chem. Soc.*, 83 (1961) 827.
16 H. GILMAN AND C. W. GEROW, *J. Amer. Chem. Soc.*, 77 (1955) 5740.
17 W. D. MCPHEE AND E. G. LINDSTROM, *J. Amer. Chem. Soc.*, 65 (1943) 2177.
18 H. GILMAN, D. AOKI AND D. WITTENBERG, *J. Amer. Chem. Soc.*, 81 (1959) 1107.