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INTRAMOLECULAR BONDING IN β-SILYL KETONES?

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SUMMARY

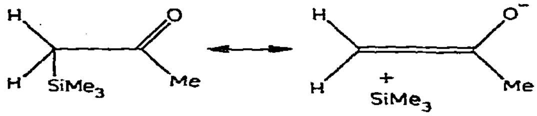
A comparison of the infrared carbonyl group absorption of 2-(triphenylsilyl)-cyclohexanone and of 2-(triphenylmethyl)cyclohexanone provided evidence of intramolecular interaction between the silicon atom and the carbonyl group. A similar interaction was found in the analogous 2-(triphenylsilyl)- and 2-(triphenylgermyl)-cyclohexanols.

In 1964 Brook and Pierce[1] reported a study of the position of the infrared carbonyl group absorption [ν(CO)] in ketones with the general formula $Ph_3Si(CH_2)_n$-COPh. They concluded that the shift in the position of the ν(CO) to lower frequency as n decreased from 2 to 0 was due to an increase in the inductive effect of the silicon on the carbonyl group.

In 1966 Musker and Larson[2] on the basis of the relationship proposed by Thompson and Jameson[3], $\nu(CO) = 1720 + 15\,\Sigma\sigma^*$, concluded that the inductive effect of silicon in (trimethylsilyl)acetone was of less importance than intramolecular interaction involving the nonbonding electrons of the carbonyl oxygen and the d-orbitals of silicon.

In a later paper Musker and Ashby[4] reported that the intensification of the $n \rightarrow \pi^*$ transition of the β-silyl ketones relative to that of their carbon analogs provided additional support for such intramolecular bonding.

More recently Taylor[5] has suggested that neither inductive effects nor intramolecular interaction of the type suggested by Musker and co-workers[2,4] are as important in determining the carbonyl stretching force constant in β-silyl ketones as are resonance contributors such as those shown below:



This problem seemed worthy of additional study for the following reasons: Musker and co-workers based their conclusions in part upon the relationship of Thompson and Jameson[3] which can only give an approximate value for the position of the ν(CO) since it was derived on the basis of the position of the ν(CO) of many compounds such as CCl_3COCl in which field and other effects may be more important than inductive effects. In addition a review of the literature in relationship to other β-substituted ketones in which exaltation of the $n \rightarrow \pi^*$ transition is observed indicates that the factors involved are complex[6] and can be unrelated to the factors causing shifts in the position of the ν(CO)[7]. If strong interactions of the types proposed by either Musker and co-workers[2,4] or by Taylor[5] are important in β-silyl ketones they may be of even greater importance in other compounds such as 2-silylcarboxylic acids. Since Taft[8] calculated the value for σ^* of $(CH_3)_3SiCH_2$– from the K_a of trimethylsilylacetic acid, such interactions would tend to lead to an incorrect value for σ^*.

Infrared spectral studies of the α-halocyclohexanones have been especially valuable in separating the inductive effect of the halogen from other factors effecting the carbonyl group[7]. By analogy it was hoped that a study of a 2-silylcyclohexanone might aid in assessing the interaction of the β-silicon atom with the carbonyl group. The triphenylsilyl ketone was chosen for this study since a reasonable synthetic pathway was available for its preparation and for the preparation of the carbon analog and because as can be seen in Table 1 the ν(CO) of silyl ketones is not greatly effected when a methyl on silicon is replaced by a phenyl.

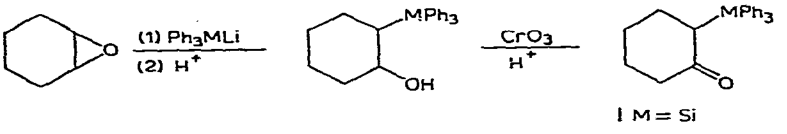
TABLE 1

ν(CO) OF SILYL KETONES

Compound	ν(CO) (cm^{-1})	Compound	ν(CO) (cm^{-1})
$Me_3SiCOMe$	1645	$Ph_3SiCOMe$	1645
$Me_3SiCOPh$	1618	$Ph_3SiCOPh$	1618
$Me_3SiCH_2COCH_3$	1694	$Ph_3SiCH_2COCH_3$	1695
Me_3SiCH_2COPh	1666	Ph_3SiCH_2COPh	1667

RESULTS AND DISCUSSION

2-(Triphenylsilyl)cyclohexanone, I, and its carbon analog, 2-(triphenylmethyl)cyclohexanone, (II), were prepared by the reaction sequence outlined below:



I M = Si
II M = C

The IR spectra of I and of II were determined in nujol mulls and in carbon tetrachloride solution. In the mull the ν(CO) of the carbon ketone was a singlet at 1709 cm^{-1} while that of the silicon ketone was at 1678 cm^{-1}. In carbon tetrachloride solution the ν(CO) of the carbon ketone was a singlet at 1720 cm^{-1} while that of the silicon ketone was a broad absorption from 1682 to 1692 cm^{-1}. The solution spectrum of the silicon compound was run under a variety of conditions including very slow scanning and scale expansion on a Perkin–Elmer 421 Spectrometer adjusted for maximum resolution and in each case results similar to those shown in Fig. 1. were obtained.

The ν(CO) of the silicon ketone was relatively concentration independent over a range of concentrations of from 0.2–10% indicating that the broadening was not due to intermolecular interaction. Another possible source of doublets in systems such as this is Fermi resonance[9]. While this possibility cannot be completely discounted it seems unlikely since the ν(CO) of the mull was not a doublet.

If the observed results are due to conformer equilibration it would be expected that the relative intensities of the two peaks should be temperature dependent. As can be seen in Fig. 1 the predicted change was observed. At 0° the two peaks are of equal intensity and as the temperature is raised to 50° the intensity of the peak at 1682 cm^{-1} decreases relative to that at 1692 cm^{-1}. The temperature dependence of the ν(CO) was determined at several concentrations and in each case analogous results were obtained.

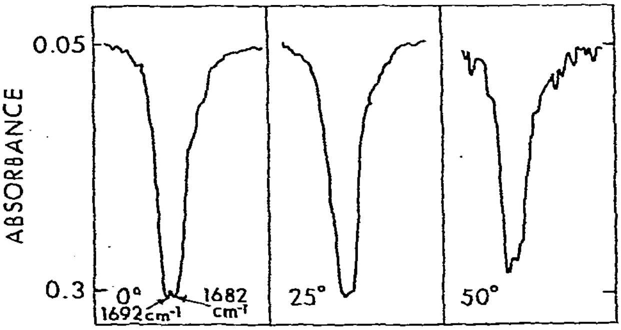


Fig. 1. ν(CO) of 2-(triphenylsilyl)cyclohexanone in CCl_4.

The inductive effect of the silicon will be virtually independent of the conformation of the cyclohexanone ring. However, only in conformations in which the silicon is equatorial* would interaction of the type proposed by Musker[2,4] be possible and only when the silicon is axial* would resonance contributors of the type proposed by Taylor[5] be important.

Therefore the observed results can be rationalized on the basis of a large inductive effect of the silicon causing a shift of 28 cm^{-1} for the ν(CO) of the silicon ketone relative to that of the carbon ketone plus a weaker effect of either the type proposed by Musker[2,4] or by Taylor[5] causing an additional shift of 10 cm^{-1} in the position of the ν(CO) for one of the conformers of the silicon ketone. A second explanation would be that both the interaction proposed by Musker[2,4] and that proposed by Taylor[5] are possible. The shift of 28 cm^{-1} in the relative position of the ν(CO) of the carbon and silicon ketones would then arise from one type of interaction while the shift of 38 cm^{-1} would arise from the other type of interaction.

In effort to obtain evidence for some interaction in a related system the ν(OH) of 2-(triphenylmethyl), of 2-(triphenylsilyl), and of 2-(triphenylgermyl)cyclohexanol were determined in the absence and in the presence of weak bases. The results are given in Table 2.

West, Baney and Powell[10] and Matwiyoff and Drago[11] have previously used

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* It is possible that boat or skew boat conformations could be involved in which case the substituents would be pseudo axial or pseudo equatorial.

TABLE 2

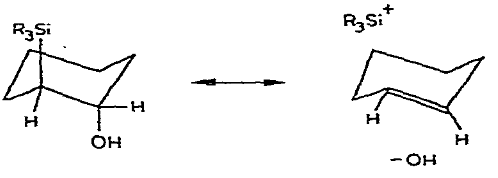
HYDROGEN BONDING PROPERTIES OF 2-SUBSTITUTED CYCLOHEXANOLS

Compound[a]	ν(OH)[b]	$\Delta\nu$(DMSO)[c]	$\Delta\nu$(THF)[d]
2-H-$C_6H_{10}OH$	3632	213	149
2-$Ph_3CC_6H_{10}OH$	3592	191	138
2-$Ph_3SiC_6H_{10}OH$	3612	235	170
2-$Ph_3GeC_6H_{10}OH$	3612	239	180

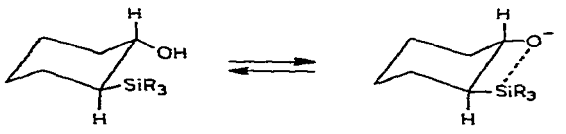
[a] Solutions are 0.03 *M* in the alcohol and 0.25 *M* in DMSO or THF. *b* Frequency of the free O–H in cm^{-1}. [c] Frequency shift upon hydrogen bonding to DMSO, cm^{-1}. [d] Frequency shift upon hydrogen bonding to THF, cm^{-1}.

a similar technique in which it is assumed that the magnitude of the frequency shift, $\Delta\nu$(OH), is related to the acidity of the alcohol, to obtain the relative acidity of Group IV alcohols. From the results shown in Table 2 it is apparent that the silyl and germyl alcohols are more acidic than the carbon analog. This cannot be a result of steric factors since the silyl and germyl alcohols are also more acidic than cyclohexanol. The inductive effect of the substituent would be expected to be relatively small since the metal atom is separated by two carbons from the hydroxyl group. However, any inductive release of electrons by the electropositive silicon or germanium atoms would be expected to be acid weakening. Since the silicon and germanium alcohols are stronger acids than the carbon analog it must be concluded that some intramolecular interaction is occurring.

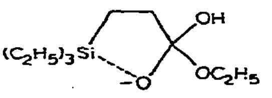
This interaction cannot be of the type proposed by Taylor[5] since such an interaction would be acid weakening.



Interaction of the type proposed by Musker[2,4] would stabilize the anion relative to the alcohol and be acid strengthening as observed.



Rijkens and co-workers[12] have proposed a similar weak intramolecular interaction to explain the facile hydrolysis of ethyl 3-(triethylsilyl)propanoate.



The interpretation of these results is complicated by the variety of different factors involved. Thus in addition to inductive effects[1], intramolecular bonding[2,4] and resonance contributors[5] other factors such as field effects need to be considered. Since Eaborn[13] has noted that a carbon–silicon bond is twice as polar as a carbon–chlorine bond it would be reasonable to expect a large shift in the ν(CO) of I simply on the basis of a field effect such as has been proposed by a number of groups of workers[14] for α-halo ketones.

The above results do demonstrate that the silicon in these compounds is capable of some intramolecular interaction in addition to its inductive effect. Studies to clarify the nature and magnitude of such interactions in related systems are at present underway.

EXPERIMENTAL

General

All reactions were carried out under an atmosphere of prepurified nitrogen. Melting points are uncorrected. Elemental analysis were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee or by Mrs. D. Mahlow and Mrs. A. Dunn, Department of Chemistry, University of Alberta. IR, UV and mass spectra were determined on Perkin–Elmer 421, Perkin–Elmer 202 and Metropolitan–Vickers MS-9 spectrometers, respectively.

Under the conditions which the IR spectra were run the Perkin–Elmer 421 grating spectrophotometer is capable of resolution of better than 2 cm^{-1}. Spectra were run in matched cells with sodium chloride windows, and cell thickness and concentration were varied so that ν(CO) absorbance varied from approximately 0.05 to 1.5 in various runs. In each case similar results were obtained. The temperature studies were carried out in a Barnes Engineering Company, Variable Temperature Chamber 104–0013.

2-(*Triphenylsilyl*)*cyclohexanone*

To a rapidly stirring solution of 2.3 g (0.0065 mole) of 2-(triphenylsilyl)cyclohexanol[15] in 100 ml of acetone 3.9 ml (0.0065 mole) of a 1.7 *M* solution of chromium trioxide in 2.6 *M* sulfuric acid was added*. A green colour developed immediately and a precipitate formed. The mixture was stirred for 5 min and then added to ether and a dilute solution of ammonium chloride. The ether layer was washed with water, dried with sodium sulfate and concentrated under reduced pressure. The resultant waxy solid was recrystallized from ethanol to obtain 0.33 g (15%) of 2-(triphenylsilyl)-cyclohexanone, I, m.p. 118–121°. (Found: C, 80.8; H, 7.00; mol. wt. mass spectrum, 356.1598. $C_{24}H_{24}OSi$ calcd.: C, 80.8; H, 6.79; mol. wt., 356.1596.)

The UV spectra (heptane) of I was a series of shoulders at 288 mμ (ε 115), 298 mμ (ε 97), 308 mμ (ε 69) and 318 mμ (ε 34).

2-(*Triphenylmethyl*)*cyclohexanol*

Addition of 5 ml (0.05 mole) of 1,2-epoxycyclohexane to 50 ml (0.02 mole) of a 0.4 *M* solution of triphenylmethyllithium in ethyl ether discharged the red color. Work-up as above followed by recrystallization from ethanol gave 3.8 g (56 %) of 2-(tri-

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* Excess chromic acid was used since it proved impossible to separate the product from unreacted starting material.

phenylmethyl)cyclohexanol, m.p. 168–170°. (Found: C, 87.7; H, 7.40. $C_{25}H_{26}O$ calcd.: C, 87.7; H, 7.65%.)

2-(*Triphenylmethyl*)*cyclohexanone*

Treatment of 1 g (0.003 mole) of 2-(triphenylmethyl)cyclohexanol in 50 ml of acetone with 1.8 ml (0.003 mole) of chromic acid solution followed by work-up as above gave 0.62 g (62%) of 2-(triphenylmethyl)cyclohexanone, II, m.p. 154–157°. (Found: C, 88.2; H, 7.19. $C_{25}H_{24}O$ calcd.: C, 88.2; H, 7.11%.) The UV spectrum (heptane) of II showed a shoulder at 292 mμ (ε 22).

2-(*Triphenylgermyl*)*cyclohexanol*

Addition of 10 ml (0.1 mole) of 1,2-epoxycyclohexane to the triphenylgermyllithium prepared from 7.7 g (0.02 mole) of triphenylbromogermane and 0.8 g (0.11 g-atom) of lithium in 50 ml of THF followed by work-up as above and recrystallization from methanol gave 4.6 g (57%) of 2-(triphenylgermyl)cyclohexanol m.p. 137–140°. (Found: C, 71.6; H, 6.54. $C_{24}H_{26}GeO$ calcd.: C, 71.5; H, 6.50%.)

Oxidation of 2-(*triphenylgermyl*)*cyclohexanol*

A. Treatment of 1.2 g (0.003 mole) of 2-(triphenylgermyl)cyclohexanol in 50 ml of acetone with 1.8 ml (0.003 mole) of chromic acid solution followed by acid workup gave 0.81 g (87%) of hexaphenyldigermoxane, m.p. 179–182°.

B. A mixture of 0.4 g (0.001 mole) of 2-(triphenylgermyl)cyclohexanol, 3 ml of DMSO, 0.824 g (0.004 mole) of *N*,*N*-dicyclohexylcarbodiimide, and 0.096 g (0.0005 mole) of pyridinium trifluoroacetate was stirred for 3 h, filtered and then the filtrate worked up as above. The resultant oil was chromatographed on silica gel eluted with heptane. A solid was obtained, m.p. 118–125°, which was free from *N*,*N*-dicyclohexylcarbodiimide. The IR spectrum showed absorption at 1720 cm^{-1} with a broad shoulder from 1700–1680 cm^{-1}. (Found: C, 70.6; H, 6.03. $C_{24}H_{24}GeO$ calcd.: C, 71.9; H, 6.03%.) Upon standing samples of the solid slowly lost their carbonyl group absorption.

ACKNOWLEDGEMENT

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