

## INTRAMOLECULAR INTERACTION INVOLVING GROUP IV ELEMENTS. SPECTRAL PROPERTIES OF 1-(TRIMETHYLSILYL)-2-PROPANONE

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### INTRODUCTION

The recent report by Krüger and Rochow<sup>1</sup> on the synthesis and spectral properties of the O-silyl-substituted enol form of acetone, 2-trimethylsilyloxypropene, prompted us to report the infrared and NMR spectra of the isomeric C-substituted compound, 1-(trimethylsilyl)-2-propanone. In contrast to these authors, we have had little difficulty in preparing this ketone by the method of Hauser and Hance<sup>2</sup>. However, the compound reacted rapidly with water, alcohol and HCl in non-polar solvents at room temperature and has decomposed on distillation at atmospheric pressure.

In a recent ultraviolet study it was suggested<sup>3</sup> that the intensification of the  $n \rightarrow \pi^*$  transition in  $\beta$ -silyl ketones [ $\lambda(\text{C}_6\text{H}_{12}) = 283$ ,  $\epsilon = 81$ ] relative to simple ketones [ $\lambda(\text{C}_6\text{H}_{12}) \sim 280$ ,  $\epsilon = 20$  to  $30$ ]<sup>4</sup> could be interpreted as an indication of an interaction between the  $d$ -orbitals of silicon and the non-bonding electrons of the carbonyl oxygen (see ref. 5 for additional references to orbital interaction in  $\beta$ -substituted ketones).

It is suggested that the position of the carbonyl band in the infrared spectrum of this ketone not only reflects the low electronegativity of the trimethylsilyl group but is additional evidence for intramolecular interaction.

### EXPERIMENTAL

#### *Chemicals*

The 1-(trimethylsilyl)-2-propanone was synthesized by the method of Hauser and Hance<sup>2</sup>, 4-(trimethylsilyl)-2-butanone by the method of Sommer and Marans<sup>5</sup>, and 4,4-dimethyl-2-pentanone was purchased from K and K Laboratories, New York, N.Y. All compounds were purified by preparative gas chromatography using an Aerograph Model A-90-P3 chromatograph with a silicone column (20% SF-96 on 60/80 Firebrick).

#### *Infrared spectra*

The high-resolution infrared spectra were obtained with a Beckman IR-12 Infrared Spectrophotometer calibrated with a polystyrene film. The gas samples were observed in a 10 cm gas cell with sodium chloride windows which was initially evacuated and then filled from a high-vacuum line. The carbonyl region was scanned slowly (1.6  $\text{cm}^{-1}/\text{min}$ ) and the error in the absorption maximum is estimated to be

$\approx 1 \text{ cm}^{-1}$ . Dilute solutions of the ketones (1 to 2% by volume) were observed in a 0.062 cm cell.

The spectrum of 1-(trimethylsilyl)-2-propanone (liquid film, Fig. 1) was obtained with a Perkin-Elmer 237-B Infrared Spectrophotometer.

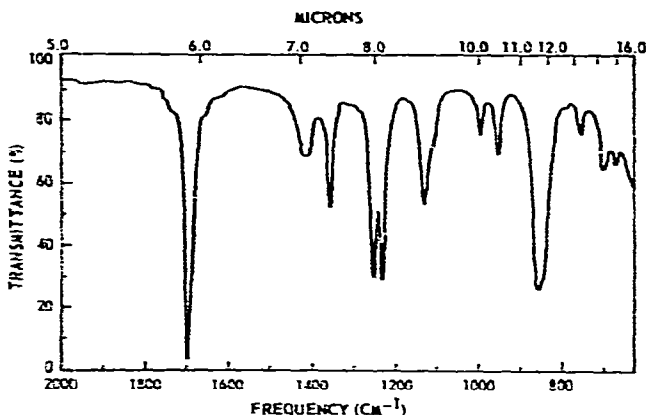


Fig. 1. Infrared spectrum ( $2000\text{--}650 \text{ cm}^{-1}$ ) of 1-(trimethylsilyl)-2-propanone (liquid-film).

#### Nuclear magnetic resonance spectra

The  $^1\text{H}$  NMR spectra of 15% solutions in carbon tetrachloride were obtained using a Varian A-60A spectrometer. The  $^{13}\text{C}$  NMR data was obtained using a Varian HR-60 spectrometer at a fixed frequency of 15.085 Mc/sec by measuring the natural abundance  $^{13}\text{C}$  resonance of the carbonyl carbon atom of the ketones as the neat liquid<sup>7</sup>.

## RESULTS AND DISCUSSION

#### Infrared spectra

The infrared spectrum of the silyl propanone showed that the carbonyl absorption band is significantly lowered in energy from its position in acetone, 4,4-dimethyl-2-pentanone, 4-(trimethylsilyl)-2-butanone and other simple acetone derivatives<sup>4</sup> in both the vapor phase and in non-polar solvents (see Table I), and is similar to the absorption maximum observed for mesityl oxide<sup>8</sup>, a conjugated ketone.

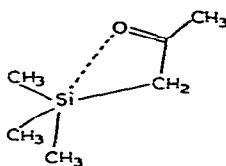
TABLE I

THE POSITION OF THE CARBONYL ABSORPTION FREQUENCY OF METHYL KETONES<sup>a</sup>

Solvent	Acetone <sup>b</sup>	4,4-Dimethyl-2-pentanone	4-(Trimethylsilyl)-2-butanone	1-(Trimethylsilyl)-2-propanone	Mesityl oxide
Vapor	1738	1736	1736	1715	1715 <sup>c</sup>
Liquid	1715	1710	1728	1699	1687
Cyclohexane	1724	1723	1727	1698	
Carbon tetrachloride	1719	1719	1723	1698	1697 <sup>c</sup>
Acetonitrile	1715	1712-1702	1713-1705	1684	

<sup>a</sup> All  $\nu$  are expressed in  $\text{cm}^{-1}$ . <sup>b</sup> Compiled by Bellamy and Williams<sup>9</sup>. <sup>c</sup> Ref. 8.

A lowering of the carbonyl frequency in 1-(trimethylsilyl)-2-propanone might be attributed entirely to an inductive effect<sup>10,11</sup> resulting from the low electronegativity of the trimethylsilyl group. In order to approximate the position of the carbonyl stretching frequency in 1-(trimethylsilyl)-2-propanone due to the inductive effect, we attempted to equate the position of the carbonyl stretching frequency in carbon tetrachloride solvent to Taft's  $\sigma^*$  constant as proposed by Thompson and Jameson<sup>12</sup>. Using Thompson's equation [ $\nu(\text{CO}) = 1720 + 15 \Sigma\sigma^*$ ], the position of the maximum in carbon tetrachloride would be expected ( $\sigma^* = -0.26$ )<sup>13</sup> to be near  $1716 \text{ cm}^{-1}$  [obs.  $\nu(\text{CO}) = 1698 \text{ cm}^{-1}$ ]. Although numerous compounds have carbonyl stretching frequencies which deviate from the value predicted by this equation, it was hoped that in the absence of intermolecular interactions and solvent effects, a lowering of the frequency due only to the inductive effect could be estimated. Since the position of absorption in 4,4-dimethyl-2-pentanone, the carbon analog, is not shifted significantly\*, steric effects seem unimportant. Thus, the large deviation from the calculated value in the silyl ketone may result from a significant interaction between the carbonyl oxygen and the silicon atom which would also contribute to the lowering of the force constant and, consequently, to an additional lowering of the carbonyl stretching frequency.



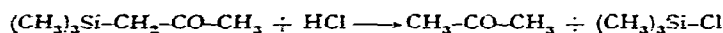
In order to insure that solvent effects and intermolecular interactions were not entirely responsible for the observed lowering of the carbonyl stretching frequency, the spectrum of 1-(trimethylsilyl)-2-propanone was determined in the vapor phase and compared with other ketones (Table I). Acetone, 4,4-dimethyl-2-pentanone, and 4-(trimethylsilyl)-2-butanone all exhibit their carbonyl stretching frequency near  $1738 \text{ cm}^{-1}$  and compounds having strongly electronegative groups attached to the  $\alpha$ -carbon of acetone exhibit their carbonyl stretching frequency\*\* only slightly higher than acetone, e.g. chloroacetone ( $1743 \text{ cm}^{-1}$ )<sup>14</sup>, (trifluoromethyl)acetone ( $1748 \text{ cm}^{-1}$ )<sup>15</sup> and 1,3-dichloroacetone ( $1746 \text{ cm}^{-1}$ )<sup>16</sup>. Since in 1-(trimethylsilyl)-2-propanone the carbonyl stretching frequency in the gas phase is lowered  $23 \text{ cm}^{-1}$  from its position in acetone, factors other than the inductive effect of the trimethylsilyl group seem to be operating here. These observations suggest that coordination between silicon and carbonyl group is important even in the gas phase.

The remainder of the infrared spectrum is consistent with the keto form of the silyl propanone. No maxima are observed between  $1650$  and  $1425 \text{ cm}^{-1}$  indicating the absence of olefinic absorption<sup>1</sup> and none appears at  $1040 \text{ cm}^{-1}$  clearly demonstrating the absence of an Si-O-C grouping. The absorption near  $760$ ,  $840$  and  $1250 \text{ cm}^{-1}$  is assigned to the typical absorptions of the trimethylsilyl group<sup>17</sup>.

\* The calculated value for the carbonyl absorption in this compound is  $1717 \text{ cm}^{-1}$  using  $\sigma^* = -0.165$  for the neopentyl group (obs.  $\nu(\text{CO}) = 1723 \text{ cm}^{-1}$ ).

\*\* For  $\alpha$ -haloketones, only one peak is observed in the vapor phase rather than the doublet observed in both the liquid phase and upon solution in non-polar solvents. This doublet, which has been attributed to rotational isomers of the halo ketones<sup>15,16</sup>, is not observed in the silyl propanone, either in the vapor phase or in non-polar solvents.

The facile decomposition of 1-(trimethylsilyl)-2-propanone was noted throughout the infrared analysis. When ethyl alcohol was used as a solvent, two peaks were immediately observed in the carbonyl region; however, on standing in the infrared beam, the low energy peak disappeared and the high energy peak increased in intensity. The high energy peak has been assigned to acetone, the product resulting from cleavage of the silicon-carbon bond by solvent. This reaction was reported earlier by Hauser<sup>2</sup> using refluxing alcohol. In an attempt to determine the change in the fundamental stretching frequency of HCl on coordination, we found that, when either a carbon tetrachloride or methylene chloride solution of the silyl ketone was gassed with hydrogen chloride, the peak at 1698 cm<sup>-1</sup> disappeared and a peak at 1719 cm<sup>-1</sup> developed. Gas chromatographic analysis of the resulting solution has indicated that the primary products resulting from this treatment were acetone and trimethylchlorosilane.



#### Nuclear magnetic resonance spectra

The <sup>1</sup>H nuclear magnetic resonance spectra of 1-(trimethylsilyl)-2-propanone and related compounds were examined to prove the identity of this compound and to determine the position of the methylene protons. A comparison of the data for substituted acetones is given in Table 2. It appears to be impossible to detect any intramolecular interaction from the position of the methylene protons in 1-(trimethylsilyl)-2-propanone.

TABLE 2

<sup>1</sup>H AND <sup>13</sup>C NUCLEAR MAGNETIC RESONANCE SPECTRA OF SUBSTITUTED ACETONE

R of R-CO-CH <sub>3</sub>	<sup>1</sup> H (δ in ppm wrt TMS)	<sup>13</sup> C of CO (in ppm wrt <sup>12</sup> C <sub>6</sub> H <sub>6</sub> )
CH <sub>3</sub> -	a 2.09 <sup>b</sup>	-77.2 <sup>d</sup>
CH <sub>2</sub> CH <sub>2</sub> -		-78.4 <sup>d</sup>
(CH <sub>3</sub> ) <sub>3</sub> Si-CH <sub>2</sub> - <sup>a</sup>	a 1.92, b 2.08, c 0.05	-77.1
(CH <sub>3</sub> ) <sub>3</sub> C-CH <sub>2</sub> - <sup>a</sup>	a 1.92, b 2.20, c 0.89	-79.9
ClCH <sub>2</sub> -		-71.9 <sup>d</sup>
CH <sub>3</sub> -S-CH <sub>2</sub> - <sup>c</sup>	a 2.3, b 3.2, c 2.1 <sup>c</sup>	
(CH <sub>3</sub> ) <sub>3</sub> Si-CH <sub>2</sub> -CH <sub>2</sub> - <sup>d</sup>	a 1.92, b 3.08, c 0.59, d -0.25	

<sup>a</sup> Integration indicates ratio of protons a:b:c = 3:2:9. <sup>b</sup> Ref. 18. <sup>c</sup> Ref. 19. <sup>d</sup> Ref. 20.

The <sup>13</sup>C NMR spectra of the silyl ketone and its carbon analog were compared to acetone and its derivatives. Stothers and Lauterbur<sup>20</sup> reported that alkyl substitution at the α-position in acetone produces a small low field shift of the <sup>13</sup>C resonance of the carbonyl carbon which they attributed to a decrease in the number of

possibilities for hyperconjugation. This can be seen from the position of 2-butanone and 4,4-dimethyl-2-pentanone in Table 2. In chloroacetone the +5.3 ppm upfield shift of the carbonyl carbon resonance was attributed to a reduction of the polarization of the  $C^{\delta-}-O^{\delta-}$  bond by the electronegative chloro substituent and an increase in electron density at the carbon atom. Thus, an increase of the polarization of the  $C^{\delta-}-O^{\delta-}$  bond in the silyl ketone with respect to acetone due to a positive inductive effect of the trimethylsilyl group, and, consequently, a shift to lower field would be expected in the absence of intramolecular interaction. Since a shift was not observed, the electron density at the carbonyl carbon was not changed. Thus, the inductive effect of the trimethylsilyl group which would increase the electron density at the carbonyl carbon is balanced by the interaction between silicon and oxygen which should decrease the electron density at the carbonyl carbon. This weak interaction can be envisioned by a consideration of the geometry of the molecule in its most stable configuration. Inspection of molecular models shows that the interaction between the silicon and oxygen in 1-(trimethylsilyl)-2-propanone occurs in an ideal conformation to minimize non-bonded interactions. In fact, rotation about the  $CO-CH_2$  bond in order to prevent coordination causes a strong interaction between the methyl groups on silicon and the methyl group on the carbonyl. Although it might be expected that an interacted conformation would be observed for 4-(trimethylsilyl)-2-butanone because of the formation of a five-membered ring, the energy gained in complex formation may not offset the loss of entropy involved in the loss of free rotation about the carbon-carbon bonds.

Brook<sup>21</sup> reported the infrared spectrum of 1-(triphenylsilyl)acetophenone and noted that the carbonyl stretching frequency was lowered  $31\text{ cm}^{-1}$  from its carbon analog. He attributed this lowering solely to the inductive effect of the triphenylsilyl group; however, it would be far more difficult to ascertain whether an intramolecular interaction contributed to the lowering in this conjugated ketone.

The excessive lowering of the carbonyl frequency coupled with the intensification of the  $n \rightarrow \pi^*$  transition of 1-(trimethylsilyl)-2-propanone suggests that intramolecular interaction between the nonbonding electrons of the ketone oxygen and the  $d$ -orbitals of silicon occurs in this compound, although a direct field effect cannot be completely discounted. This would be the first case where expanded-octet  $\sigma$ -bonding has been observed in a compound where strongly electron withdrawing groups were not present on silicon<sup>22, 23</sup>.

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#### SUMMARY

The infrared spectrum and the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 1-(trimethylsilyl)-2-propanone are reported. The infrared spectrum of this silyl ketone in the gas phase and in non-polar solvents may be interpreted as showing intramolecular interaction

between silicon and the carbonyl group. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra confirm the identity of the silyl ketone and are consistent with this interpretation. The facile decomposition of this compound in hydroxylic solvents and with HCl in non-hydroxylic solvents at room temperature has been observed.

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