TRIORGANOSILICON β-DIKETONATES. ENOL ETHER ISOMERISM AND STEREOCHEMICAL LABILITY

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ABSTRACT

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by Ward T. Collins

A series of triorganosilicon acetylacetonates of the type $R(CH_3)_2Si(acac)$ (R = n-C_4H_9, C_2H_5, CH_2=CH, $CF_3CH_2CH_2$, and C_6H_5), along with $(C_6H_5)_2(CH_3)Si(acac)$, has been prepared by reaction of the appropriate triorganochlorosilane and acetylacetone in the presence of pyridine. The compounds possess open-chain enol ether structures and give rise to configurations in which the uncoordinated carbonyl oxygen atom is positioned both *cis* and *trans* to the siloxy group. Equilibrium values of the *cis* to *trans* ratios in chlorobenzene are dependent on the nature of the substituents on silicon and lie in the range 0.25 - 0.39. The *cis* isomers undergo a rapid intramolecular rearrangement process which interchanges the allylic and acetyl methyl groups on the acetylacetonate moiety. First order rate constants in chlorobenzene solution were determined by nmr line broadening methods, and the results were compared with those reported for $(CH_3)_3Si(acac)$. In the *cis* - $R(CH_3)_2Si(acac)$ series of compounds the lability increases in the order R = n-C_4H_9 < C_2H_5 < CH_3 < CH_2=CH < C_6H_5 < $CF_3CH_2CH_2$. The lability of *cis* - $(C_6H_5)_2(CH_3)Si(acac)$ is comparable to that of *cis* - $(CF_3CH_2CH_2)(CH_3)_2Si(acac)$. The kinetic data are consistent with a

mechanism involving formation of a five-coordinated silicon intermediate.

Trimethylsilyl derivatives of dipivaloylmethane (Hdpm) and hexafluoroacetylacetone (H hfac) have also been prepared and studied briefly. On the basis of infrared and nmr studies, it is suggested that $(CH_3)_3Si$-(dpm) exists almost exclusively as the cis enol ether isomer and undergoes a rapid stereochemical rearrangement which averages the nonequivalent t - C_4H_9 environments on the nmr time scale even at -95°C. On the other hand, $(CH_3)_3Si$(hfac) appears to adopt only the trans enol ether configuration in solution.

TRIORGANOSILICON β-DIKETONATES. ENOL ETHER ISOMERISM AND STEREOCHEMICAL LABILITY

By

Ward T. Thomas Collins

A THESIS

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DEDICATION

To my Parents

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I wish to thank Dow Corning Corporation for their financial assistance and encouragement throughout my graduate studies.

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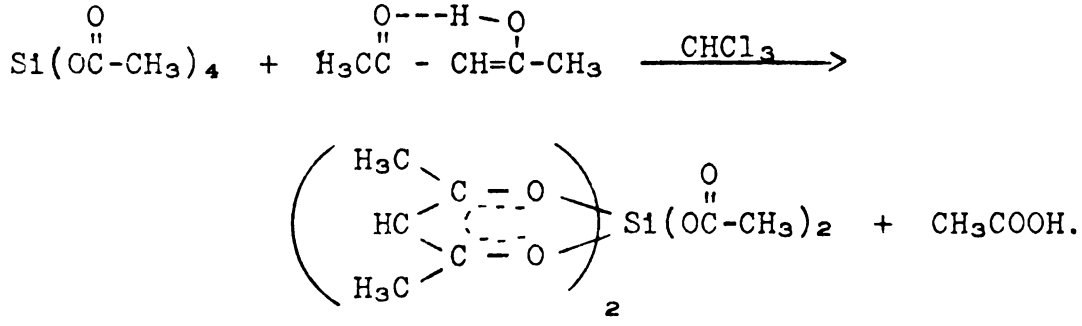
I. INTRODUCTION

The first silicon derivative of acetylacetone was reported by Dilthey[1] in 1903. He found that the product obtained by reaction of $SiCl_4$ and acetylacetone, [H(acac)] had the emperical formula $C_{15}H_{22}O_6Cl_2Si$. Dilthey proposed a siliconium ion containing three chelated acetylacetonate groups and a hydrogen dichloride anion, $[Si(acac)_3][HCl_2]$. A number of other tris(2,4-pentadionato)siliconium salts with other anions were also prepared.

More recently, additional β-ketonate chelate derivatives have been reported. Pike and Luongo[2] found that if organocarboxysilanes are used instead of silicon tetrachloride in the reaction with acetylacetone, then a neutral chelated silane species is produced which contains only two chelated acetylacetonate ligands.

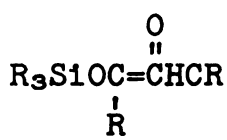


The authors were able to identify both *cis* and *trans* octahedral isomers by nmr spectroscopy. It is of interest to point out that when they carried out the reaction at 0 - 5°, a product with the same empirical formula was obtained. In this case, however, the two

2,4-pentanedionato ligands were believed to be monodentate, producing a tetravalent silicon(IV) derivative. These structural assignments were based solely on infrared spectroscopic analysis which show very characteristic bonds for the chelated and non-chelated derivatives of acetylacetone. A similar compound, $Si(acac)_2Cl_2$, has recently been obtained by Thompson[3] from the reaction of equimolar quantities of acetylacetone and silicon tetrachloride in methylene chloride solution. The compound was insoluble in most organic solvents and only sparingly soluble in chloroform and methylene chloride. The compound rearranges in solution to give $Si(C_5H_7O_2)_3Cl$ and $SiCl_4$. The <u>trans</u>-configuration was assigned to the $Si(acac)_2Cl_2$ compound on the basis of nmr data.

In most of the compounds described so far the β-diketonate is bonded to the metal through both donor oxygens, forming a cyclic chelate structure. In certain silyl-β-diketonates[4-6], however, the ligand is bonded through only one oxygen, resulting in a linear enol ether structure with an uncoordinated carbonyl group.

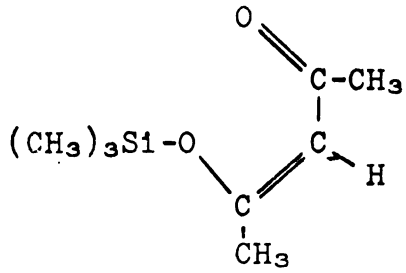
Knoth[4] prepared a series of trialkylsilyl enol ethers (I)



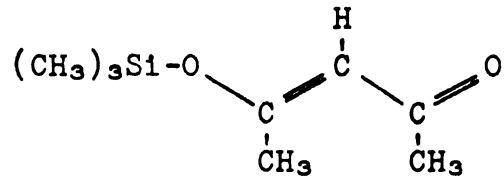
(I)

by reaction of a trialkyl chlorosilane and a β-diketone.

In spite of the favorable geometry of the β-carbonyl oxygen to coordination to silicon, it was shown by infrared spectroscopy that in none of the compounds did the carbonyl oxygen coordinate to form a pentacoordinate silicon(IV) complex. It was further suggested that in the case of $(CH_3)_3Si(acac)$ both cis and trans (II and III) isomers existed in equilibrium.



II
cis



III
trans

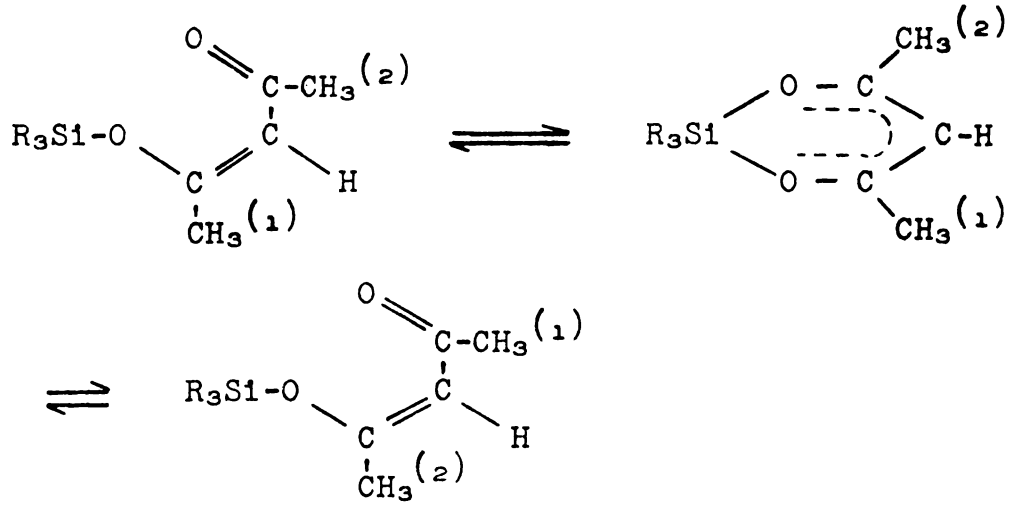
2-(Trimethylsiloxy)-4-ketopentene

The identification of both the cis and trans isomers was based on the coincidence of infrared absorption bands for the compound and the carbonyl stretching frequencies of the cis and trans methyl enol ethers of acetylacetone[7]. It is of interest to point out that the equilibrated methyl enol ether is almost pure trans isomer.

The non-chelated structure of 2-(trimethylsiloxy)-4-ketopentene was confirmed independently in a study by West[8]. This work consisted of preparing a number of acetylacetoxy substituted silanes both chelated and non-chelated, and showing that these two classes of silanes

have very characteristic infrared absorption bands The chelated silicon compounds did not show a carbonyl absorption in the region near 1700 cm^{-1}, but the absorption was shifted to ca. 1555 cm^{-1}. The non-chelated compounds on the other hand showed two strong bonds near 1670 and 1590 cm^{-1}, which are characteristic frequencies for a normal carbonyl stretching vibration and a C=C stretch, respectively.

The presence of cis and trans isomers of $(CH_3)_3$-Si(acac) has recently been confirmed by nuclear magnetic resonance spectroscopy[9]. Howe and Pinnavaia also found that the cis isomer undergoes a novel stereochemical rearrangement process whereby the two methyl groups of the β-diketonate ligand are rapidly exchanging on the silane moiety through a chelated pentacoordinate intermediate or transition state



Values of first order rate constants in chlorobenzene solution gave an Arrhenius activation energy of 13.81 ± 0.64 kcal/mole, and a pre-experimental factor of exp. $(13.052 \pm .538)^{10}$.

The present study is concerned with the preparation and characterization of a series of new silyl enol ethers of acetylacetone. The effect of silicon substituents on the stereochemistry and stereochemical lability of the compounds has been investigated. Silyl enol ethers of other β-diketones have also been prepared in order to assess the effect of the polarity of the terminal groups on the diketonate ligand on the stereochemistry and lability.

II. EXPERIMENTAL

A. Reagents and General Techniques

All of the chlorosilanes were obtained from the Dow Corning Research Department. These silanes were obtained as pure chemicals or were fractionally distilled to a purity of 98% or better, as determined by vapor phase chromatography. The hexane used as a solvent was Fisher Certified A.C.S. Grade solvent. Prior to each reaction the solvent was freshly distilled from CaH_2. Matheson, Coleman and Bell (M.C.B.) dioxane was refluxed over sodium for 24 hours and then was distilled. Pyridine was Baker Analyzed Reagent Grade and was stored over Drierite. M.C.B. white label acetylacetone was freshly redistilled before use. Sodamide was purchased from K and K Laboratories Inc. and was handled in a nitrogen filled glove bag. The reaction flasks were fitted with a reflux condenser and a pressure-compensating addition funnel. The reaction medium was stirred with a magnetic stir-bar. All reactions were run under a dry nitrogen atmosphere to minimize hydrolysis. Reactions which yielded pyridinium chloride or sodium chloride as a by-product were filtered in a closed system under vacuum. All product distillations were conducted *in vacuo* or in a dry nitrogen atmosphere.

B. Preparation of Compounds

1. Triorganosilylacetylacetonates

The triorganosiloxyacetylacetonates were prepared by a procedure reported by West[8]. The following is a general description of the technique used. The exact experimental conditions for the individual compounds are listed in Table I.

A solution of 0.25 moles of pyridine, 0.25 moles of acetylacetone and 100 ml. of hexane was treated with 0.25 moles of a triorganochlorosilane over a 5 to 10 minute period. The solution was refluxed from zero to five hours and then stirred at room temperature for an additional 12 to 24 hours. The reaction medium was vacuum-filtered to remove pyridinium chloride and was continuously evacuated until all of the hexane solvent was removed. The crude products were distilled in a high vacuum or at reduced pressure in a nitrogen atmosphere. The boiling points of the products along with the yields and analytical data are also listed in Table I. The phenyl-substituted siloxyacetylacetonates were not refluxed during their preparation because of apparent slow decomposition at elevated temperatures. Emphasis was placed primarily on obtaining pure compounds and not on maximizing yields.

2. 1,1,1,5,5,5-Hexafluoro-2-trimethylsiloxy-2-pentene-4-one

A solution of 11.7 g. (0.056 moles) hexafluoroacetylacetone and 20 ml. of trimethylchlorosilane was

TABLE I

Synthesis and Analytical Data for Silyl Enol Ethers

Compound	Addition Time	Volume Pyridine	Moles Silane	Moles ACAC	Moles Pyridine	Reflux Time	RT Stir Time	BP	Yield	Analytical Found C	H	Si/F	Analytical Calc'd. C	H	Si/F
$EtMe_2Si(acac)$	10 min	100 ml	0.25 30.7 g	0.25 25.0 g	0.25 19.8 g	5 hrs	19 hrs	80-81° 4 mm	14.7 g 31.6%	58.29	9.56	14.8	58.01	9.74	51.1
$BuMe_2Si(acac)$	5 min	40 ml	0.0614 9.64 g	0.10 10 g	0.10 7.9 g	4.5 hrs	22 hrs	48° 0.01 mm	4.15 g 31.5%	61.85	10.30	13.5	61.63	10.34	13.1
$ViMe_2Si(acac)$	5 min	100 ml	0.25 30.1 g	0.25 25 g	0.25 19.89 g	3 hrs	24 hrs	74-75° 4 mm	12.2 g 26.6%	58.80	8.81	15.2	58.65	8.75	15.2
$ØMe_2Si(acac)$	5 min	100 ml	0.25 42.7 g	0.25 25 g	0.25 19.3 g	0	17 hrs	88-89° 0.02mm	23.7 g 40.5%	66.63	7.68	12.1	66.82	7.74	12.0
$Ø_2MeSi(acac)$	5 min	50 ml	0.125 29.1 g	.125 12.5g	0.125 9.9 g	0	12 hrs	140-146 0.05	17.0 g 23.6%	72.85	6.78	9.20	72.93	6.80	9.48
$nPr_1Me_2Si(acac)$	5 min	100 ml	0.25 47.7 g	0.25 25 g	0.25 19.8 g	2.5 hrs	20 hrs	54° 0.03mm	29.7 g 46.7%	47.27	6.67	12.1 22.1	47.23	6.74	11.0 22.4
$Me_3Si(hfac)$*									6.7 g	34.9 34.8	4.01 4.02	10.9 11.8 40.6	36.0	3.57	10.0 40.7
$Me_3Si(dpm)$*										5.24g 51.2%	66.4 66.0	11.10 11.19	65.6	10.95	10.97

*hfac = hexafluoroacetylacetonate, $CF_3COCHCOCF_3^-$; dpm = dipivaloylmethanate, $(\underline{t}\text{-}C_4H_9)COCHCO(\underline{t}\text{-}C_4H_9)^-$

heated at reflux temperature for eleven days in a dry-nitrogen atmosphere. Gas-liquid chromatographic analysis indicated that approximately 90% of the hexafluoroacetylacetone remaining had undergone silylation. Presumably, some of the free ligand had evaporated through the reflux condenser. The reaction mixture was distilled through a 6 inch vacuum-jacketed Vigreaux column at atmospheric pressure in a closed, dry system to give 6.7 g. (42% yield) of pure enol ether, b.p. 128 - 129°. The compound is a pale yellow liquid.

Anal. Calcd. for $C_8H_{10}F_6O_2Si$: C, 36.0; H, 3.57; F. 40.7; Si, 10.0. Found: C, 34.9; H, 4.01; F, 40.6; Si, 10.9%.

3. 2,2,6,6-Tetramethyl-3-trimethylsiloxy-3-heptene-5-one

No reaction was observed between dipivaloylmethane and trimethylchlorosilane in the presence of pyridine at room temperature. It was necessary to prepare the sodium derivative of the β-diketone and to allow the salt to react with the chlorosilane.

Sodium dipivaloylmethanate was prepared by slowly adding dipivaloylmethane (9.40 g., 0.04 mole) to a slurry of sodamide (1.64 g., 0.04 mole) in 40 ml. of dioxane in a nitrogen atmosphere. The hazy light yellow solution was heated at reflux temperature for 20 minutes to remove as much ammonia as possible. Trimethylchlorosilane (5.90 g., 0.0540 moles) was added dropwise to

the hot solution. During the addition finely divided sodium chloride precipitated from the solution. The reaction mixture was stirred for 10 hours at room temperature and then was heated at reflux temperature for an additional hour. The sodium chloride could not be completely removed by filtration, presumably, because of its fine particle size or slight solubility in dioxane. Consequently it was necessary to remove the dioxane solvent by evacuation, and to dilute the product with hexane before the sodium chloride was completely removed by filtration. The hexane was removed by evacuation and the product was distilled in high vacuum (b.p. 45°/0.04 mm.), producing 5.24 g. (51.2% yield) of colorless liquid.

Anal. Calcd. for $C_{14}H_{22}O_2Si$: C, 65.6; H, 11.0; Si, 11.0. Found: C, 66.2; H, 11.2; Si, 11.6.

4. 2-Trimethylsiloxy-2-pentene-4-one

This compound was also prepared by using the same sodamide technique described for the dipivaloylmethane derivative. Nuclear magnetic resonance spectroscopic analysis of the crude product confirmed that the cis and trans forms of the desired compound are present in their equilibrium ratio and that silylation occurred at an oxygen atom and not at the central carbon atom in the β-diketone.

C. Instrumentation

1. Infrared Spectroscopy

The infrared spectra were obtained with a Perkin-Elmer 521 Spectrometer by using a 0.1 mm path length cell. The following dilutions, solvents and cells were used for the designated infrared regions:

3800 - 3100 cm^{-1}	10% solution in CCl_4, NaCl cell
1300 - 650 cm^{-1}	2% solution in CS_2, NaCl cell
650 - 250 cm^{-1}	10% solution in CCl_4, CsBr cell

2. Proton Magnetic Resonance Spectroscopy

Proton magnetic resonance spectra were obtained with a Varian A56/60D analytical spectrometer operated at 60.000 M Hz. The probe temperature was controlled to ± 0.5° with a Varian Model V-6040 temperature controller. Temperatures were determined by measuring the chemical shift differences between the proton resonances of methanol or ethylene glycol and applying the equations of Van Geet[12]. Magnetic field sweep widths were calibrated by the audio-frequency side band technique. At least three spectral copies were averaged in the determination of line shape parameters and chemical shift values in order to reduce any error caused by variations in the field sweep. All spectra were recorded at a ratio-frequency field strength well below the value necessary to observe the onset of saturation.

The spectrum of $Me_3Si(dpm)$ also was obtained on a Varian HA-100 spectrometer operating at 100 MH_Z.

3. Mass Spectrometry

The mass spectra were obtained with an Associated Electrical Industries MS-12. The following experimental conditions were used to obtain all spectra: inlet temperature (all glass heated) 135 to 138°; source temperature 115 to 180°; accelerating voltage 8 k.v.; trap current 100 microamps; ionizing potential 80 electron volts. Perfluorokerosene was used to calibrate the instrument.

4. Chromatography

Attempts were made to separate the cis and trans isomers of $(CH_3)_3Si(acac)$ on a dual-column F and M Model 810 gas chromatograph equipped with a thermal conductivity detector cell. The column dimension and packings were as follows: 4 ft. x 1/4 in., 10% silmethylene on Chromasorb W; 6 ft. x 1/4 in., FS 1265 fluorosilicone gum on an unknown Chromasorb; 6 ft. x 1/4 in., SE-30 silicone rubber on Chromasorb W. Numerous chromatograms were obtained under isothermal and temperature-programmed column conditions in the temperature range 100 - 300°. In all cases there was no separation of the two isomers. Attempts to separate the isomers on 20 ft. carbowax columns at 150 - 180° with an Aerograph A 90-P3 chromatograph were also unsuccessful.

D. Preparation of Solutions for NMR Study

All solutions used in the nmr studies were prepared in a nitrogen-filled Glove Bag and sealed in nmr tubes which had been previously dried at 150° and cooled

in a calcium sulfate desiccator. Carbon tetrachloride, benzene, and chlorobenzene were dried by refluxing over calcium hydride for at least 48 hours. Despite these precautions to avoid hydrolysis, small amounts (2 - 3%) of free acetylacetone and $(R_3Si)_2O$ could be detected in the nmr spectrum of the solutions after they had aged several days at room temperature. Presumably, these triorganosilicon acetylacetonates undergo slow reaction with hydroxyl groups or strongly bound water on the surface of the glass nmr tubes. The rates of stereochemical rearrangements of the <u>cis</u> isomers, however, showed no dependence on the concentration of hydrolysis products.

III. RESULTS AND DISCUSSION

A. Preparation of Compounds

A series of triorganosilicon enol ethers of acetylacetone of the type $R(CH_3)_2Si(acac)$ (where R = $\underline{n}$-C_4H_9, C_2H_5, $CH_2=CH$, $CF_3CH_2CH_2$ and C_6H_5), along with $(C_6H_5)_2(CH_3)Si(acac)$, has been prepared by reaction of the appropriate triorganochlorosilane and acetylacetone in the presence of pyridine, according to the procedure reported by West[8]

$$R_3SiCl + H(acac) + py \longrightarrow R_3Si(acac) + [py\ H]Cl \quad (1)$$

The previously reported compound $(CH_3)_3Si(acac)$[8,9] was obtained from J. J. Howe[10]. The compounds were obtained as high boiling colorless to pale yellow liquids. All undergo hydrolysis on contact with atmospheric moisture and slow thermal decomposition at elevated temperatures.

Attempts to prepare trimethylsilicon hexafluoroacetylacetonate, $(CH_3)_3Si(hfac)$, and dipivaloylmethanate, $(CH_3)_3Si(dpm)$, by reactions analogous to reaction (1) were unsuccessful. With hexafluoroacetylacetone the reaction mixture yielded only pyridinium hexafluoroacetylacetonate, as identified by infrared spectroscopy. In the case of dipivaloylmethane, no reaction products were observed. However, $(CH_3)_3Si(hfac)$ was obtained by heating at reflux temperature for several days the free ligand in a large excess of $(CH_3)_3SiCl$.

$$(CH_3)_3SiCl + H(hfac) \rightleftharpoons (CH_3)_3Si(hfac) + HCl \quad (2)$$

The equilibrium represented by reaction (2) was displaced to the right by the evolution of gaseous HCl from the reaction mixture. To prepare the dipivaloylmethane derivative it was necessary to first form the sodium salt of the diketone, followed by the reaction of the salt with $(CH_3)_3SiCl$.

$$NaNH_2 + H(dpm) \longrightarrow Na(dpm) + NH_3 \quad (3)$$

$$Na(dpm) + (CH_3)_3SiCl \longrightarrow (CH_3)_3Si(dpm) + NaCl \quad (4)$$

An analogous reaction sequence was also successful for the preparation of $(CH_3)_3Si(acac)$.

B. Mass Spectra

Each of the silyl enol ethers of acetylacetone gave a mass spectral fragmentation pattern consistent with an open chain enol ether structure. In the $R(CH_3)_2Si(acac)$ series silicon containing fragments of the type $R(CH_3)_2Si^+$, $(CH_3)_2Si(acac)^+$ and $R(CH_3)Si(acac)^+$ were generally formed in appreciable amounts. The relative intensities of these ions are collected in Table II along with the intensity of the most abundant organic species. A weak molecular ion peak was observed for the compounds with R = C_2H_5, CH_3, CH_2=CH and $CF_3CH_2CH_2$. The absence of a molecular ion peak for the derivative with R = n - C_4H_9 and C_6H_5 is attributed to the facile loss of n - butyl and methyl groups, respectively, from

Table II. Intensities of Selected Ions in the Mass Spectra of Triorganosilicon Acetylacetonates

Compound	Ion $C_2H_3O^+$ [a]	$R(CH_3)_2Si^+$ [b]	$(CH_3)_2Si(acac)^+$ [c]	$R(CH_3)Si(acac)^+$ [b]
(n-C_4H_9)$(CH_3)_2$Si(acac)	55.6	11.1 (115.0)	100.0[d]	27.0 (199.0)
(C_2H_5)$(CH_3)_2$Si(acac)	45.8	38.4 (87.0)	100.0	51.1 (171.0)
$(CH_3)_3$Si(acac)	74.2	96.8 (73.0)	100.0	----------
(CH_2=CH)$(CH_3)_2$Si(acac)	100.0	94.2 (85.0)	32.5	76.7 (169.0)
($CF_3CH_2CH_2$)$(CH_3)_2$Si(acac)	100.0	1.7 (135.0)	65.2	13.0 (239.0)
(C_6H_5)$(CH_3)_2$Si(acac)	49.7	48.5 (135.0)	59.4	100.0 (219.0)

[a] m/e = 43.0. [b] m/e values are given in parentheses. [c] m/e = 157.0. [d] Ions assigned an intensity of 100.0 represent the most abundant species in each spectrum.

the parent ions. It is noteworthy that $(CF_3CH_2CH_2)$-$(CH_3)_2Si(acac)$ undergoes extensive rearrangement upon electron impact to give ions with mass values corresponding to $(CH_3)_2Si^+F$ and $(CH_3)SiF_2^+$, SiF_3^+ and $(CH_3)Si(acac)F^+$ with intensities of 59.8, 7.6, 93.5 and 14.1 respectively. Some degree of rearrangement probably occurs for the other compounds in the $R(CH_3)_2Si(acac)$ series, because weak to moderately intense peaks were observed in all cases at mass 45, 59 and 75, which correspond to $(CH_3)SiH_2^+$, $(CH_3)_2SiH^+$ and $(CH_3)_2SiOH^+$.

The mass spectrum of $(C_6H_5)_2(CH_3)Si(acac)$ did not contain a molecular ion peak. The fragment $C_2H_3O^+$ was observed as the base ion and $(C_6H_5)CH_3Si(acac)^+$ was the most abundant silicon-containing fragment. Numerous rearrangement fragments were observed in the spectrum, but in all cases their relative intensitites were less than 3.0.

In the spectrum of $(CH_3)_3Si(hfac)$, the base ion was the rearrangement fragment $(CH_3)_2SiF^+$. Another rearrangement fragment present in appreciable abundance was $(CH_3)_2SiOH^+$ with an intensity of 28.3. Intense peaks were also observed for the parent ion minus CF_3 (13.9), CF_3^+ (58.3) and $(CH_3)_3Si^+$ (77.2).

For $(CH_3)_3Si(dpm)$ the mass spectrum showed a very weak parent ion at m/e = 256 with an intensity of 0.3, and a base peak at m/e = 199, which corresponds to the loss of a butyl group from the parent ion. Intense lines

were observed for $(CH_3)_3Si^+$, $C_4H_9^+$, and $(CH_3)_2Si(dpm)^+$ with intensities of 46.3, 26.5 and 23.8, respectively. Silicon-containing rearrangement fragments were found for masses corresponding to $(CH_3)_2SiOH^+$, $(CH_3)_2SiH^+$ and $(CH_3)SiH_2^+$, with intensities of 15.7, 1.4 and 6.8, respectively.

Complete mass spectra for all of silyl enol ethers studied are tabulated in Appendix A.

C. Infrared Spectra

Several of the compounds prepared in this study were investigated by infrared spectroscopy. The C = O and C = C and Si - O stretching frequencies for the silyl enol ethers are summarized in Table III along with the C = O and C = C vibrations of the chelated copper(II) complexes and the enol forms of acetylacetone, hexafluoroacetylacetone, and dipivaloylmethane. Complete spectra are shown in Appexdix B.

Knoth[4] has reported that $(CH_3)_3Si(acac)$ gives rise to two uncoordinated carbonyl stretching frequencies at 1656 and 1683 cm^{-1}, which he assigned to the cis (II) and trans (III) enol ether isomers, respectively. These vibration frequencies were coincident with the carbonyl stretching vibrations of the cis and trans methyl enol ethers of acetylacetone. The less intense, lower energy band at 1656 cm^{-1} was assigned to the cis isomer on the basis that this would be the least favored conformation for steric reasons. The nmr studies reported below

Table III. - Selected Stretching Frequencies (cm^{-1}) for Silyl Enol Ethers and Related Compounds

Compound	ν(C=O)	ν(C=C)	ν(Si-O)
$(n\text{-}C_4H_9)(CH_3)_2Si(acac)$	1685, 1664	1590, 1625	1032
$(C_2H_5)(CH_3)_2Si(acac)$	1682, 1660	1588, 1621	1034
$(CH_3)_3Si(acac)$	1684, 1659	1588, 1625	1032
$[Si(acac)_3][HCl_2]$[a]	1555	?	____
$Cu(acac)_2$[b]	1580	1554	____
H(acac), enol[c]	1620	1620	____
$(CH_3)_3Si(hfac)$	1733	1625	945
$Cu(hfac)_2$[d]	1652	1620	____
H(hfac), enol	1684	1627	____
$(CH_3)_3Si(dpm)$	1676	1625	1100
$Cu(dpm)_2$[e]	1552	1500	____
H(dpm), enol	∿1610	∿1575	____

[a] Ref. 8 [b] Ref. 12 [c] Ref. 15 [d] Ref. 13 [e] Ref. 14.

confirm that the cis isomer is the less abundant form. All of the $R_3Si(acac)$ compounds listed in Table III exhibited two carbonyl stretching frequencies. Following Knoth, we assign the lower energy band to the cis isomer and the higher energy band to the trans isomer. Two C = C stretching vibrations are also observed in the region 1588 - 1625 cm^{-1}. Based on relative intensities, the higher energy C = C band is assigned to the cis isomer. Unlike the acetylacetonate derivatives, $(CH_3)_3$-Si(hfac) and $(CH_3)_3Si(dpm)$ each exhibit only one C = O and one C = C stretching frequency. This result is in agreement with the nmr data presented below which suggest that these two compounds exist almost exclusively as a single isomer. The chelated compounds $[Si(acac)_3]$-$[HCl_2]$, $Cu(acac)_2$, $Cu(hfac)_2$ and $Cu(dpm)_2$ are listed in Table III to illustrate that the C = O and C = C stretching modes occur at much lower energy in the chelates than in the enol ethers. The fact that the carbonyl stretching frequency for the chelated $Cu(hfac)_2$ is at higher frequency than the other chelated compounds results from the electron withdrawing influence of the fluoromethyl groups. This same effect is evident in the spectrum of $(CH_3)_3Si(hfac)$ where the non-chelated carbonyl stretch is shifted to much higher energy than the other diketonate derivatives.

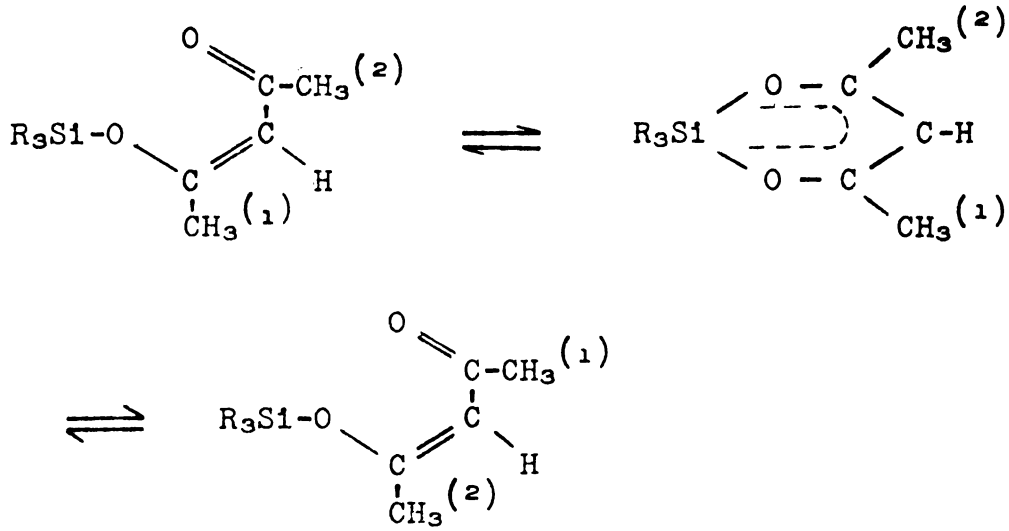
For neat $(CH_3)_3Si(acac)$, West[8] assigned the Si-O stretching vibration at 1020 cm^{-1}. In the $R_3Si(acac)$

compounds investigated here, the vibration was observed at 1032 - 1034 cm^{-1} in CCl_4 solution. The assignment of the Si-O stretching frequency for $(CH_3)_3Si(hfac)$ and $(CH_3)_3Si(dpm)$ is not straightforward because no strong unique bands are observed for these compounds in the 1000 - 1050 region where one normally expects the vibration to occur. In the case of $(CH_3)_3Si(hfac)$, however, there is a strong band at lower frequency, 962 cm^{-1}, which may result from motion of the Si-O group. This assignment is made on the basis of the inductive effect of the terminal CF_3 groups on the diketonate ligand weakening the Si-O bond strength. Similarly, the inductive effect of the terminal t-butyl groups in $(CH_3)_3Si(dpm)$ would be expected to shift the Si-O vibration to higher energy. Thus, the 1,100 cm^{-1} band in $(CH_3)_3Si(dpm)$ is tentatively assigned to the Si-O vibration.

D. Nmr Spectra

The existence of an equilibrium mixture of cis (II) and trans (III) enol ether isomers for $(CH_3)_3Si(acac)$ has been previously confirmed by nmr spectroscopy[9]. Analogous isomers exist for the new silyl derivatives prepared in the present work. The proton nmr spectrum of each trans isomer contains a =CH- multiplet, two acetylacetonate methyl doublets, and a $Si-CH_3$ singlet. Splitting of the acetylacetonate methyl proton lines results from spin-spin coupling between the =CH- proton and both methyl groups. The =CH-, acetylacetonate methyl, and $Si-CH_3$

regions of the nmr spectra of the cis isomers each contain one resonance line. The presence of only one acetylacetonate methyl resonance for the cis isomers is due to rapid intramolecular rearrangement processes which interchange the non-equivalent acetyl and allylic methyl groups on the acetylacetonate moiety. The rearrangement is believed to occur via a penta-coordinated silicon intermediate or transition state[9]. A similar process for the trans isomers is restricted by lack of rotation about the C=C bond. The rates of rearrangement are discussed in detail in Section III D.



Chemical shifts in carbon tetrachloride for the acetylacetonate and Si-CH_3 protons of the $R_3Si(acac)$ compounds are collected in Table IV; shifts for $(CH_3)_3Si(acac)$ in benzene and as the neat liquid are included for comparison. No significant concentration dependence was observed for $(CH_3)_3Si(acac)$ in carbon tetrachloride over the range 2.0 - 3.0 g/100 ml of solvent.

Table IV

Proton Chemical Shift Data for Cis- and Trans-Triorganosilicon Acetylacetonates [a]

Compound	Solvent	Trans Isomer				Cis Isomer		
		=CH-	$COCH_3$	$=CCH_3$	$SiCH_3$	=CH-	CH_3 [b]	$SiCH_3$
$(n\text{-}C_4H_9)(CH_3)_2Si(acac)$	CCl_4	4.54	7.81	8.00	9.76	4.82	8.03	9.76
$(C_2H_5)(CH_3)_2Si(acac)$	CCl_4	4.53	7.82	8.00	9.76	4.82	8.03	9.76
$(CH_3)_3Si(acac)$	CCl_4	4.53	7.82	8.00	9.74	4.81	8.03	9.74
	C_6H_6 [c]	4.45	7.63	8.10	9.95	4.74	8.22	9.95
	[d]	4.41	7.81	8.00	9.74	4.81	8.01	9.72
$(CH_2{=}CH)(CH_3)_2Si(acac)$	CCl_4	4.50	7.81	8.01	9.69	4.81	8.03	9.67
$(CF_3CH_2CH_2)(CH_3)_2Si(acac)$	CCl_4	4.51	7.80	7.98	9.69	4.64	8.07	9.73
$(C_6H_5)(CH_3)_2Si(acac)$	CCl_4	4.57	7.82	8.09	9.51	4.83	8.09	9.47
$(C_6H_5)_2(CH_3)Si(acac)$	CCl_4	4.53	7.77	8.14	9.26	4.81	8.11	9.22

[a] All shifts reported as τ values; temperature is 40°; concentration is 10 g/100 ml of solvent unless otherwise noted. [b] Time-averaged acetylacetonate methyl resonance. [c] All shifts in benzene are extrapolated to infinite dilution. [d] Neat liquid.

Since some concentration dependence was found in benzene, the shifts in this solvent were extrapolated to infinite dilution. In each trans isomer the magnitude of the coupling between the =CH- and $COCH_3$ protons is approximately 0.6 Hz, and the allylic coupling constant is 0.4 Hz or less. It is to be noted that the relative chemical shifts for the $COCH_3$ and $=CCH_3$ protons of the trans isomers are not in agreement with the empirical "ene-one" rule of Anteunis and Schamp[16] for assigning chemical shifts of similar types of protons in β-diketone enol ethers. However, at least three pieces of evidence can be cited in support of the assignments made here: (1) Replacement of alkyl groups on silicon by phenyl groups leads to 0.09 - 0.14 ppm up-field shifts for the $=CCH_3$ protons, whereas the $COCH_3$ and =CH protons show little or no change in chemical shift. An examination of molecular models of the trans phenylsilyl derivatives reveals that reasonable configurations are possible in which the $=CCH_3$ protons are within the diamagnetic cone of a phenyl group but that configurations which can lead to up-field shifts for the $COCH_3$ protons without also appreciably influencing the chemical shifts of the =CH- protons are unlikely. (2) The up-field shifts for the Si-CH_3 protons of both cis- and trans-$(CH_3)_3Si(acac)$ in benzene solution show that these protons experience the diamagnetic anisotropy of the benzene ring to a greater extent than the internal TMS reference. Apparently, a

stereospecific solvent-solute association results from the interaction of the π electrons on benzene and the siloxy group. Similar stereospecific interactions between benzene and a variety of other types of solute molecules are well known[17]. Such an interaction should be expected to lead to up-field shifts for the $=CCH_3$ protons and to down-field shifts for the $COCH_3$ and =CH- protons, which is indeed the result observed for the trans isomer.

(3) For $(CH_3)_3Si(acac)$ in dichloromethane solution at -40°, where the $COCH_3$ and $=CCH_3$ resonances of the cis isomer are well resolved (see below), the $=CCH_3$ and $COCH_3$ protons of the trans isomer are deshielded by 0.12 ppm and shielded by 0.04 ppm, respectively, relative to the analogous protons of the cis isomer. Deshielding of the $=CCH_3$ protons in the trans isomer is expected, because of the paramagnetic anisotropic effect of the adjacent $COCH_3$ group[18]. Finally, it might be mentioned that for $(CH_3)_3Si(acac)$ at -40°, the magnitude of the allylic coupling is slightly greater in the cis isomer (~ 0.5 Hz) than in the trans isomer (< 0.3 Hz). Under the same conditions, the long-range coupling between the =CH- and $COCH_3$ protons is smaller in the cis isomer (~ 0.0 Hz) than in the trans isomer (~ 0.5 Hz). The relative magnitudes of the allylic coupling are in agreement with the result normally observed for allylic systems, viz., that cisoid coupling is slightly larger than transoid coupling[19]. The coupling constants alone, however, would

not constitute a reliable basis for the chemical shift assignments, because no relationship exists between allylic coupling constants and the stereochemistry of related α,β-unsaturated esters[20].

Several unsuccessful attempts to separate the cis and trans isomers of $(CH_3)_3Si(acac)$ by gas chromatography (cf., Experimental Section) or by vacuum distillation at 68° through a spinning band column suggest that equilibrium is established readily between the two isomers. Facile isomerization is further supported by the fact that a freshly distilled sample contained the same ratio of isomers as a sample that had aged 6 months at room temperature. The aged sample must surely be at equilibrium, because the cis methyl enol ether of acetylacetone is converted to "pure" trans isomer within 8 days at ambient temperature[7]. Thus, solutions of the triorganosilicon acetylacetonates in chlorobenzene were assumed to be at equilibrium after one week at room temperature, and the cis to trans ratios, shown in Table V, were determined by planimetric integration of =CH- nmr lines. With the exception of the phenylsilyl derivatives, the equilibrium amount of cis isomer increases with increasing electron withdrawing ability of the substituents on silicon. This relationship between the cis to trans ratios and the polarity of the silicon substituents suggests that a long-range electrostatic interaction may exist between silicon and the dangling carbonyl oxygen atom in the cis isomers.

Table V

Equilibrium Ratio of *Cis* and *Trans* Enol Ether Isomers for Triorganosilicon Acetylacetonates[a]

Compound	[*cis*]/[*trans*]
(*n*-C_4H_9)$(CH_3)_2$Si(acac)	0.28[b] ± 0.02[c]
(C_2H_5)$(CH_3)_2$Si(acac)	0.29 ± 0.02
$(CH_3)_3$Si(acac)	0.34 ± 0.04
($CF_3CH_2CH_2$)$(CH_3)_2$Si(acac)	0.39 ± 0.03
(CH_2=CH)$(CH_3)_2$Si(acac)	0.38 ± 0.02
(C_6H_5)$(CH_3)_2$Si(acac)	0.31 ± 0.02
$(C_6H_5)_2(CH_3)$Si(acac)	0.25 ± 0.02

a In chlorobenzene solution at room temperature; concentration is 0.60 *m*. b All values are averages of five spectral copies. c Errors are estimated at the 95% confidence level.

Such an interaction would also account, in part, for the enhanced stability of these cis-triorganosilicon acetylacetonates relative to the cis form of the methyl enol ether of acetylacetone. The cis to trans ratios for $(C_6H_5)(CH_3)_2Si(acac)$ and, especially, $(C_6H_5)_2(CH_3)Si(acac)$ are lower than expected on the basis of inductive effects, but steric factors could weaken the long-range silicon-oxygen interaction in the cis isomers of these derivatives.

The nmr data for the trimethylsilyl derivatives of hexafluoroacetylacetone and dipivaloylmethane suggest that these compounds exist almost exclusively as the trans and cis isomers, respectively. A 10% solution of $(CH_3)_3Si(hfac)$ in carbon tetrachloride exhibits a single $(CH_3)_3Si$ resonance (-21.2 Hz) and a single -CH= resonance (-378.3 Hz). The F^{19} -nmr spectrum of this compound showed two sharp lines of equal intensity which were assigned to the two nonequivalent CF_3 groups in the trans isomer. In neither the proton or fluorine nmr spectrum was there evidence for the presence of the cis isomer. The chemical shift difference between the fluorine lines was proportional to the magnetic field strength (442.5 Hz at 100 MHz and 260.0 Hz at 56.4 MHz), which indicates that the two lines are indeed singlets and not an anomalous doublet.

The nmr spectrum of $(CH_3)_3Si(dpm)$ (10% in carbon tetrachloride) showed single $(CH_3)_3Si$, -CH= and t-C_4H_9 resonances at -21.2, -65.3 and -378.3 Hz, respectively.

The existence of one t-C_4H_9 line is attributed to the presence of only the cis isomer which is undergoing a rapid stereochemical rearrangement process similar to that described above for the cis-$R_3Si(acac)$ compounds. A single, sharp t-C_4H_9 line was also observed in a CH_2Cl_2-CS_2 solution at -95°. Apparently, the rearrangement is so facile that the nonequivalent t-C_4H_9 groups cannot be observed on the nmr time scale even at extremely low temperature. The possibility of a stable penta-coordinated silicon species was ruled out by the fact that an uncoordinated C=O stretching vibration is observed in the infrared spectrum (cf., Section III C).

The existence of pure isomers for $(CH_3)_3Si(hfac)$ and $(CH_3)_3Si(dpm)$ is explained, in part, by the long-range interaction between silicon and the dangling oxygen atom proposed above to account for the variation of cis to trans ratio of isomers for the $R_3Si(acac)$ compounds. In $(CH_3)_3Si(hfac)$, the electron withdrawing effect of the CF_3 group apparently decreases the effective negative charge on the uncoordinated oxygen atom and this decrease in charge leads to destabilization of the cis conformation. On the other hand, the inductive effect of the t-C_4H_9 group in $(CH_3)_3Si(dpm)$ should enhance the stability of the cis conformation.

E. Nmr Line Broadening Studies

Gutowsky and Holm[21] have shown that the mean lifetimes, T_A and T_B, of protons exchanging between two

nonequivalent sites can be determined from the nmr line shapes of $\delta\nu$, the frequency separation between the resonance components in absence of exchange, and T_2, the transverse relaxation time, are known. The mean lifetimes are related to the quantity τ by $\tau = \tau_A\tau_B/\tau_A + \tau_B$. Since the two nonequivalent sites in the systems considered here are equally populated, $\tau_A = \tau_B = 2\tau$. In the region of slow exchange $\delta\nu$ for the $R_3Si(acac)$ compounds is temperature dependent, presumably, because of temperature-dependent solvation effects. Since the line widths of both the uncoupled $COCH_3$ resonance in the region of slow exchange and the time-averaged resonance in the region of fast exchange vary with temperature, T_2 is also temperature dependent. The temperature depencence for $\delta\nu$ and T_2 is analogous to the behavior found previously for the non-equivalent methyl protons in chelated metal acetylacetonates[22,23]. Values of $\delta\upsilon$ in the region of exchange were obtained by linear extrapolation of data in the region of slow exchange. Values of T_2 in the region of exchange were obtained from the extrapolated values of the line widths for $(CH_3)_3Si(acac)$, as determined by J. J. Howe[10]. The relaxation times of the $=CCH_3$ protons below coalescense, where they are slightly coupled to the =CH- proton, were assumed to be equal to the relaxation times found for the $COCH_3$ protons.

Values of T in the region of exchange below the coalescense temperature were determined by comparing the observed width at half maximum amplitude of the uncoupled $COCH_3$ resonance with the width calculated from the Gutowsky-Holm equation for various trial values of T. Although the small coupling between the -CH= and $=CCH_3$ protons below coalescense was not included in the calculated spectra, the error generated in the computed values of T is estimated to be only approximately 2%. Above the coalescense temperature T was determined by comparing the observed and computed widths of the time-averaged resonance line.

Using a method similar to those described above, Howe has determined that the following activation parameters for the exchange of methyl groups in cis-$(CH_3)_3Si(acac)$ in chlorobenzene: E_a = 13.8 ± 0.5 kcal/mole, A = exp-(13.05 ± 0.54), $\Delta S^{\ddagger}_{25^\circ}$ = 0.8 ± 2.5, and k_{25° = 851 sec^{-1}. The first order rate constant, k, is related to the quantity T by $k = (2T)^{-1}$. First order rate constants for methyl group exchange in the $R_3Si(acac)$ complexes prepared in this study were determined at selected temperatures in the region of exchange. The exchanged broadened methyl proton resonances for each compound at each selected temperature are illustrated in Figure 1. The nmr line shape parameters are collected in Table VI. The uncertainty in the value of $\delta\nu$ for cis - $(CF_3CH_2CH_2)(CH_3)_2Si(acac)$ is estimated to be ca. ± 2.0 Hz; for the other

Figure 1. Exchange-broaden acetylaceonate methyl proton resonances for cis-triorganosilicon acetylacetonates in chlorobenzene. Dashed lines are the acetylacetonate methyl resonaces of the trans isomer in each equilibrium mixture. Total concentration is 0.60 m.

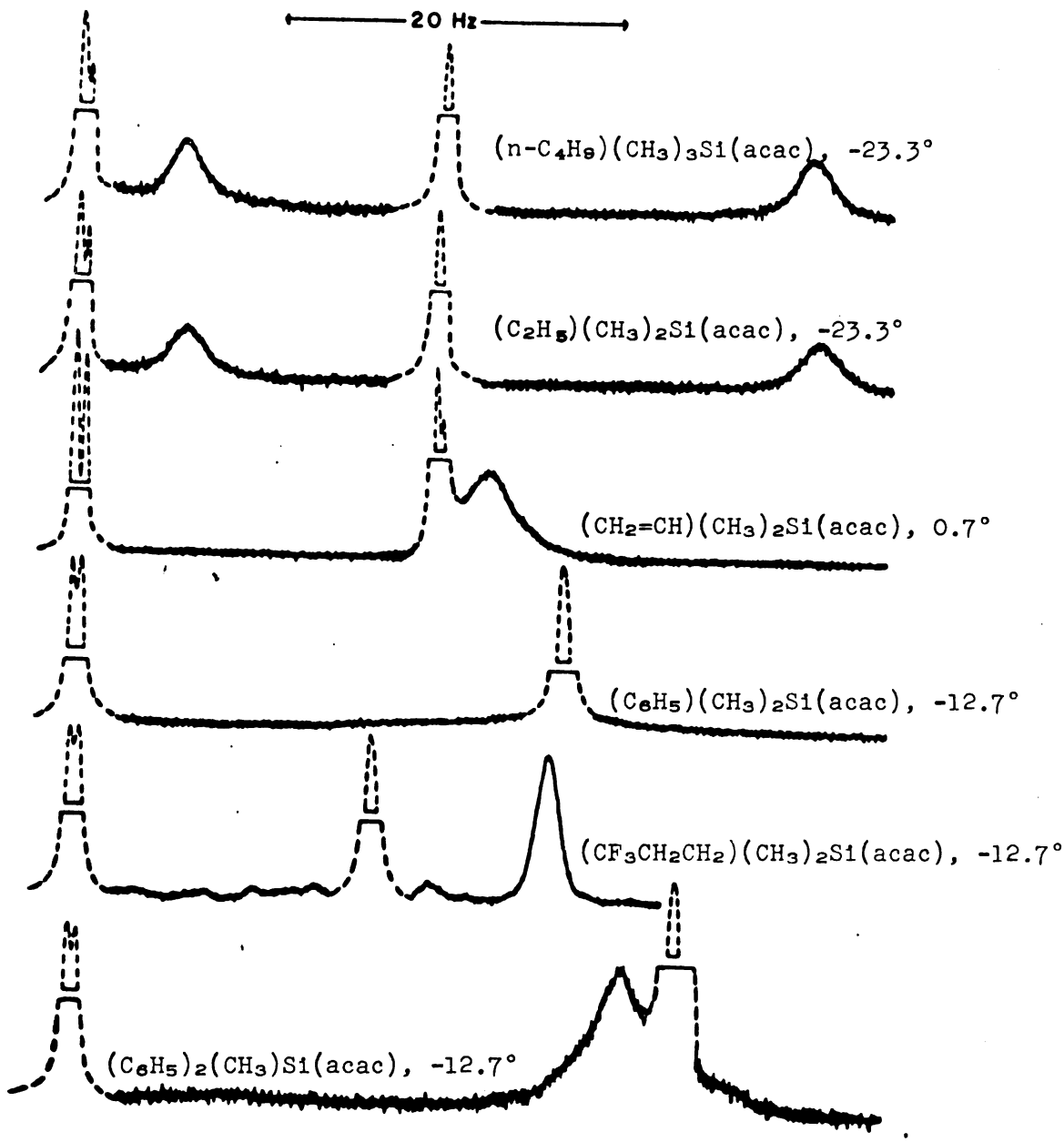

20 Hz
(n-C4H9)(CH3)3Si(acac), -23.3°
(C2H5)(CH3)2Si(acac), -23.3°
(CH2=CH)(CH3)2Si(acac), 0.7°
(C6H5)(CH3)2Si(acac), -12.7°
(CF3CH2CH2)(CH3)2Si(acac), -12.7°
(C6H5)2(CH3)Si(acac), -12.7°

Table VI

Nmr Line Shape Parameters for the Acetylacetonate Methyl Resonances of Cis-Triorganosilicon Acetylacetonates[a]

Compound	Temp., °C	Line Width[b], Hz	δν, Hz
(n-C_4H_9)(CH_3)$_2$Si(acac)	-23.0	2.51[c] ± 0.05[d]	36.76[e]
(C_2H_5)(CH_3)$_2$Si(acac)	-23.0	2.71 ± 0.05	36.86
(CH_2=CH)(CH_3)$_2$Si(acac)	0.7	3.54 ± 0.04	29.92
(C_6H_5)(CH_3)$_2$Si(acac)	-12.7	>10.0	41.40
($CF_3CH_2CH_2$)(CH_3)$_2$Si(acac)	-12.7	1.81 ± 0.02	20.40
(C_6H_5)$_2$(CH_3)Si(acac)	-12.7	3.44 ± 0.04	32.78

a In chlorobenzene solution; concentration is 0.60 m. b Line widths for (n-C_4H_9)Si(acac) and (C_2H_5)(CH_3)$_2$-Si(acac) refer to the $COCH_3$ resonance component below the coalescense temperature; all others are for the time-averaged resonance above coalescence. c Average of at least three spectral copies. d Errors are for one standard deviation. e All values of δν were obtained by linear extrapolation of the temperature dependence of δν in the region of slow exchange.

cis isomers, the uncertainty in $\delta\nu$ is believed to be $\pm$ 1.0 Hz or less.

It should be noted that for several of the cis derivatives, the temperatures at which accurate line widths could be determined was limited by the acetylacetonate methyl resonance of the trans isomers present in the equilibrium mixtures (cf., Figure 1). In the case of $(C_6H_5)(CH_3)_2Si(acac)$, for example, the time-averaged methyl resonance of the cis isomer at -12.7° is so broad that it is barely detectable above the base line. Above -12.7° the time-averaged line is superimposed on $=CCH_3$ resonance of the trans isomer, and in the region of exchange below coalescence, the $COCH_3$ resonances of the two isomers are nearly superimposed. Therefore, only an upper or lower limit could be determined for the rate constant at -12.7°. The lower limit was estimated from the simplified Gutowsky-Holm equation (cf., equation 6 in ref. 21) and the upper limit was established by assuming the width of the time averaged resonance to be > 10 Hz.

Values of the first-order constants are shown in Table VII, along with calculated values of the Arrhenius activation energies. The errors in the rate constants for cis-$(n\text{-}C_4H_9)(CH_3)_2Si(acac)$ and cis-$(C_2H_5)(CH_3)_2Si(acac)$ are based on the uncertainties in the observed line width of the $COCH_3$ resonance; the estimated error in $\delta\nu$ ($\pm$ 1.0 Hz)

Table VII

Kinetic Data for Acetylacetonate Methyl Group Exchange in Cis-Triorganosilicon Acetylacetonates[a]

Compound	Temp., °C	k, sec^{-1}	E_a, kcal/mol
(n-C_4H_9)$(CH_3)_2$Si(acac)	-23.3	5.35 ± 0.16[b]	14.1
(C_2H_5)$(CH_3)_2$Si(acac)	-23.3	5.96 ± 0.10	14.0
(CH_2=CH)$(CH_3)_2$Si(acac)	0.7	500 ± 30	13.0
(C_6H_5)$(CH_3)_2$Si(acac)	-12.7	> 91.9, < 300	< 13.2, > 12.6
($CF_3CH_2CH_2$)$(CH_3)_2$Si(acac)	-12.7	621 ± 118	12.2
$(C_6H_5)_2(CH_3)$Si(acac)	-12.7	628 ± 38	12.2

a In chlorobenzene solution; total concentration of $(CH_3)_3$Si(acac) is 0.60 m. b Basis for estimates of error are described in the text.

propagates a very small error (<0.05%) in the rate constant. On the other hand, errors in the rate constants for the other cis isomers, which were determined from the widths of the time-averages lines above coalescence, are due mainly to uncertainties in $\delta\nu$. For example, the error generated in the rate constant for cis-$(CH_2{=}CH)(CH_3)_2$-Si(acac) due to the uncertainty in the line width is only 1.0%, whereas the error propagated by an uncertainty of ± 1.0 Hz in $\delta\nu$ is 6.0%. The activation energies shown in Table VII were calculated from the first-order rate constants by assuming that the frequency factor is equal to the value obtained for cis-$(CH_3)_3$Si(acac).

From the data in Table VII it may be concluded that there is a general increase in the rate of acetylacetonate methyl group exchange with increasing polarity of the substituents on silicon. For the cis-$R(CH_3)_2$Si(acac) compounds, the rate increases in the order R = n-C_4H_9 < C_2H_5 < CH_3 < $CH_2{=}CH$, C_6H_5 < $CF_3CH_2CH_2$, and the lability of cis- $(C_6H_5)_2(CH_3)$Si(acac) is comparable to that of $(CF_3CH_2CH_2)(CH_3)_2$Si(acac). The dependence of the rates on the polarity of the silicon substituents is consistent with a mechanism involving formation of a five-coordinated silicon intermediate or transition state. Although several factors contribute to the energy required for such a bond-making activation process, as the electron-withdrawing ability of the substituents is increased, the resulting increase in positive charge on silicon should

facilitate the use of a metal d-orbital in achieving the transition state[24]. Relative to the alkyl-substituted silicon derivatives, the phenylsilyl derivatives are less labile than might be expected on the basis of σ inductive effects alone. However, the phenyl group has a greater steric requirement than the other substituents studied and, also, probably participates in ligand → metal π bonding. Both of these latter factors would tend to lower the rearrangement rate. Since cis-$(C_6H_5)_2(CH_3)Si(acac)$ is more labile than cis-$(C_6H_5)(CH_3)_2Si(acac)$, however, σ inductive effects must play an important role in determining the relative labilities of these derivatives.

A Hammett-Taft reaction constant (ρ^*) of 1.67 at 25° was estimated for the rearrangement of the cis-$R(CH_3)_2Si(acac)$ derivatives in which R is an alkyl group. The Taft substituent constants and extrapolated values of the first order rate constants are give in Table VIII. The plot of log k/k_o vs. σ^* is shown in Figure 2. It is noteworthy that the value of σ^* for $CF_3CH_2CH_2$ has been recently found to be solvent dependent, ranging from 0.32 in water to ca. 1.0 in nonpolar solvents such as hexane. Based on the plot shown in Figure 2, it might be expected that the value of σ^* for $CF_3CH_2CH_2$ in chlorobenzene solution is ca. 0.73.

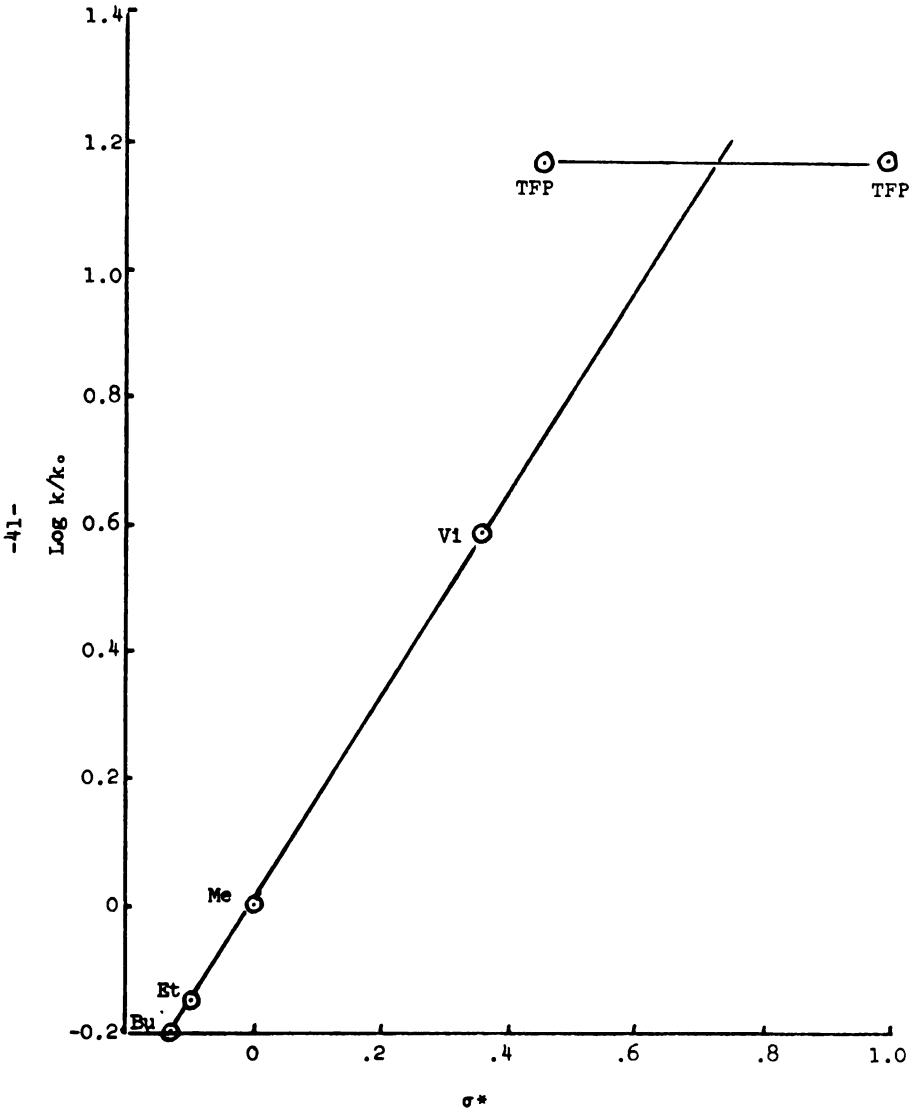
Table VIII

Taft Parameters for Methyl Group Exchange in cis-$R(CH_3)_2Si(acac)$ Derivatives in Chlorobenzene Solution

R	σ^*[a]	$k_{25°}$[b]	log k/k_o
$n\text{-}C_4H_9$	-0.130	513	-0.200
C_2H_5	-0.100	605	-0.148
CH_3	0.00	851(k_o)	0.00
$CH_2 = CH$	0.36[c]	3,275	0.582
$CF_3CH_2CH_2$	0.32-1.00[d]	15,050	1.25

a All values of σ^* were taken from ref. 24 unless otherwise noted. b Values of first order rate constants were calculated from the Arrhenius activation energies given in Table VII and a frequency factor of exp(13.052). c Ref. 25. d Ref. 26.

Figure 2. Log k/k_o *vs.* σ^* plot at 25° for methyl group exchange in *cis*-$R(CH_3)_2Si(acac)$ derivatives in chlorobenzene.



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APPENDIX A

Mass Spectra

NORMALIZED MASS SPECTRUM 214.1383

NAME: 2-(BUTYLDIMETHYLSILOXY)-4-KETOPENTENE-2

EMPIRICAL FORMULA: SIC11H2202

INSTRUMENT: MS-12 SOURCE TEMP: 170 INLET TEMP: 135
ACCEL VOLT: 8 KV TRAP CURNT: 100 MIC AMPS IONIZING POT: 80

MASS	INT	MASS	INT	MASS	INT	MASS	INT	MASS	INT
33.0	0.05	81.0	1.02	129.0	0.71	177.0	0.19		
34.0	0.05	82.0	0.48	130.0	0.22	178.0	0.02		
35.0	0.02	83.0	0.90	131.0	1.21	179.0	0.10		
36.0	0.14	84.0	0.46	132.0	0.48	180.0	0.08		
37.0	0.65	85.0	14.29	133.0	28.57	181.0	0.30		
38.0	1.22	86.0	1.78	134.0	3.17	182.0	0.03		
39.0	6.35	87.0	2.21	135.0	3.17	183.0	0.13		
40.0	1.35	88.0	0.27	136.0	0.44	184.0	0.02		
41.0	0.05	89.0	0.46	137.0	0.78	185.0	0.63		
42.0	1.59	90.0	0.06	138.0	0.10	186.0	0.19		
43.0	55.56	91.0	0.56	139.0	1.08	187.0	0.06		
44.0	3.10	92.0	0.24	140.0	0.22	188.0	0.02		
45.0	6.35	93.0	12.70	141.0	1.73	189.0	9.52		
46.0	0.46	94.0	1.11	142.0	1.29	190.0	2.00		
47.0	3.17	95.0	0.03	143.0	15.87	191.0	0.86		
48.0	0.22	96.0	0.38	144.0	2.06	192.0	0.08		
49.0	0.38	97.0	1.05	145.0	1.56	193.0	0.24		
50.0	0.67	98.0	0.51	146.0	0.21	194.0	0.02		
51.0	0.90	99.0	3.17	147.0	0.30	195.0	0.27		
52.0	0.48	100.0	6.35	148.0	0.02	196.0	0.22		
53.0	1.30	101.0	3.08	149.0	0.21	197.0	4.76		
54.0	0.43	102.0	0.44	150.0	0.48	198.0	1.30		
55.0	1.83	103.0	1.62	151.0	0.16	199.0	26.98		
56.0	1.57	104.0	0.19	152.0	0.25	200.0	3.17		
57.0	1.44	105.0	1.87	153.0	0.17	201.0	1.37		
58.0	3.17	106.0	0.38	154.0	0.13	202.0	0.10		
59.0	36.51	107.0	0.65	155.0	0.44	203.0	0.05		
60.0	3.17	108.0	0.10	156.0	1.70	204.0	0.02		
61.0	7.94	109.0	0.27	157.0	100.00	205.0	0.03		
62.0	0.70	110.0	0.02	158.0	11.11	206.0	0.02		
63.0	1.48	111.0	0.43	159.0	3.17	207.0	0.14		
64.0	0.59	112.0	0.33	160.0	0.48	208.0	0.02		
65.0	1.51	113.0	1.97	161.0	0.10	209.0	0.02		
66.0	2.57	114.0	1.48	162.0	0.02				
67.0	1.21	115.0	11.11	163.0	0.02				
68.0	0.21	116.0	1.71	164.0	0.02				
69.0	1.21	117.0	3.17	165.0	0.27				
70.0	0.35	118.0	0.54	166.0	0.02				
71.0	3.17	119.0	4.76	167.0	0.10				
72.0	1.59	120.0	0.94	168.0	0.06				
73.0	14.29	121.0	1.46	169.0	0.68				
74.0	2.08	122.0	0.38	170.0	0.16				
75.0	26.98	123.0	0.56	171.0	0.30				
76.0	2.14	124.0	2.38	172.0	0.06				
77.0	7.94	125.0	1.27	173.0	0.19				
78.0	1.13	126.0	0.05	174.0	0.02				
79.0	1.59	127.0	4.76	175.0	2.56				
80.0	0.35	128.0	0.87	176.0	0.41				

NORMALIZED MASS SPECTRUM 186.1071

NAME: 2-(DIMETHYLETHYLSILOXY)-4-KETOPENTENE-2

EMPIRICAL FORMULA: SIC9H18O2

INSTRUMENT: MS-12 SOURCE TEMP: 170 INLET TEMP: 135
ACCEL VOLT: 8 KV TRAP CURNT: 100 MIC AMPS IONIZING POT: 80

MASS	INT	MASS	INT	MASS	INT	MASS	INT	MASS	INT
14.0	2.63	67.0	1.19	116.0	1.02	175.0	0.15		
15.0	5.79	68.0	0.24	118.0	0.12	185.0	0.07		
16.0	0.53	69.0	1.18	119.0	0.41	186.0	0.92		
17.0	0.02	70.0	0.36	120.0	0.05	187.0	0.16		
18.0	11.58	71.0	3.16	121.0	0.07	188.0	0.04		
19.0	0.02	72.0	0.75	122.0	0.21	189.0	0.05		
20.0	0.07	73.0	1.58	123.0	0.34				
22.0	0.01	74.0	1.58	124.0	0.13				
24.0	0.09	75.0	30.53	127.0	5.79				
25.0	0.34	76.0	2.11	128.0	0.83				
26.0	1.58	77.0	7.89	130.0	0.20				
27.0	5.26	78.0	0.53	131.0	0.31				
28.0	70.53	79.0	1.05	132.0	0.07				
29.0	2.11	80.0	0.14	133.0	0.53				
30.0	0.23	81.0	0.45	134.0	0.18				
31.0	2.63	82.0	0.42	135.0	0.24				
32.0	12.63	83.0	0.87	137.0	0.13				
33.0	0.11	84.0	0.41	138.0	0.04				
34.0	0.05	85.0	8.42	139.0	1.05				
36.0	0.10	86.0	1.05	140.0	0.23				
37.0	0.42	87.0	38.42	141.0	1.05				
38.0	1.03	88.0	3.16	142.0	1.18				
39.0	5.79	89.0	4.21	143.0	2.63				
40.0	0.53	90.0	0.35	144.0	0.46				
41.0	1.58	91.0	0.64	145.0	0.21				
42.0	2.11	92.0	0.08	147.0	0.24				
43.0	45.79	93.0	2.63	148.0	0.03				
44.0	2.11	94.0	0.27	149.0	0.06				
45.0	12.63	95.0	1.05	151.0	0.10				
46.0	0.82	96.0	0.14	152.0	0.03				
47.0	5.26	97.0	1.05	153.0	0.42				
48.0	0.32	98.0	0.45	154.0	0.07				
49.0	0.39	99.0	5.26	155.0	0.26				
50.0	0.47	100.0	1.58	157.0	100.00				
51.0	0.62	101.0	2.11	158.0	12.63				
52.0	0.30	102.0	0.27	159.0	3.68				
53.0	1.05	103.0	0.34	160.0	0.34				
54.0	0.38	104.0	0.12	161.0	1.11				
55.0	1.05	105.0	0.22	162.0	0.17				
56.0	0.68	106.0	0.08	163.0	0.09				
58.0	5.26	107.0	0.53	165.0	0.04				
59.0	43.68	108.0	0.05	168.0	0.55				
60.0	3.68	109.0	0.26	169.0	0.61				
61.0	12.63	110.0	0.07	170.0	0.55				
62.0	0.53	111.0	0.61	171.0	51.05				
64.0	2.63	112.0	0.27	172.0	6.84				
65.0	0.85	114.0	0.94	173.0	2.11				
66.0	0.45	115.0	6.32	174.0	0.19				

NORMALIZED MASS SPECTRUM 172.0915

NAME: 2-(TRIMETHYLSILOXY)-4-KETOPENTENE

EMPIRICAL FORMULA: SIC8H1602

INSTRUMENT: MS-12 SOURCE TEMP: 115 INLET TEMP: 138
ACCEL VOLT: 8 KV TRAP CURNT: 100 MIC AMPS IONIZING POT: 80

MASS	INI	MASS	INI	MASS	INI	MASS	INI	MASS	INI
33.0	0.16	79.0	0.81	137.0	0.19				
34.0	0.55	80.0	0.19	139.0	1.74				
36.0	0.26	81.0	0.35	140.0	0.23				
37.0	1.10	82.0	0.32	141.0	1.42				
38.0	2.26	83.0	0.68	142.0	0.32				
39.0	6.45	84.0	0.52	143.0	0.35				
40.0	6.45	85.0	9.68	144.0	0.10				
41.0	5.29	86.0	0.77	147.0	6.45				
42.0	6.29	87.0	1.19	148.0	1.52				
43.0	74.19	88.0	0.13	149.0	0.87				
44.0	6.45	89.0	0.32	155.0	0.26				
45.0	16.13	90.0	0.16	156.0	0.58				
46.0	1.32	91.0	1.68	157.0	100.00				
47.0	6.45	92.0	1.42	158.0	9.68				
48.0	0.68	93.0	4.71	159.0	4.48				
49.0	2.16	94.0	0.35	160.0	0.29				
50.0	1.06	95.0	1.68	172.0	6.45				
51.0	1.35	96.0	0.16	173.0	1.35				
52.0	0.61	97.0	0.90	174.0	0.42				
53.0	1.97	98.0	0.39						
54.0	0.48	99.0	4.77						
55.0	3.16	100.0	5.00						
56.0	0.68	101.0	1.74						
57.0	2.06	102.0	0.23						
58.0	2.26	103.0	0.35						
59.0	4.77	105.0	0.19						
60.0	1.45	108.0	0.26						
61.0	5.29	109.0	0.10						
62.0	1.00	110.0	0.13						
63.0	1.55	111.0	0.39						
64.0	0.32	112.0	0.16						
65.0	1.35	113.0	1.45						
66.0	1.03	114.0	0.35						
67.0	1.23	115.0	6.45						
68.0	0.29	116.0	0.90						
69.0	1.71	117.0	1.61						
70.0	0.61	118.0	0.13						
70.5	0.10	119.0	0.16						
71.0	3.10	123.0	0.23						
71.5	0.19	125.0	0.23						
72.0	3.13	126.0	0.45						
73.0	96.77	127.0	2.97						
74.0	6.45	128.0	0.45						
75.0	35.48	129.0	0.39						
76.0	2.71	130.0	0.42						
77.0	9.68	131.0	0.71						
78.0	1.16	132.0	0.10						
78.5	0.10	133.0	0.35						

NORMALIZED MASS SPECTRUM 184.0915

NAME: 2-(VINYLDIMETHYLSILOXY)-4-KETOPENTENE-2

EMPIRICAL FORMULA: SIC9H1602

INSTRUMENT: MS-12 SOURCE TEMP: 160 INLET TEMP: 135
ACCEL VOLT: 8 KV TRAP CURNT: 100 MIC AMPS IONIZING POT: 80

MASS	INT	MASS	INT	MASS	INT	MASS	INT	MASS	INT
37.0	1.05	86.0	6.67	156.0	3.33				
38.0	1.67	87.0	25.83	157.0	32.50				
39.0	12.50	88.0	1.67	158.0	4.17				
40.0	2.50	89.0	1.67	159.0	1.67				
41.0	5.00	91.0	1.67	165.0	1.10				
42.0	5.83	92.0	0.52	167.0	0.71				
43.0	100.00	93.0	1.67	168.0	0.42				
44.0	3.33	95.0	1.67	169.0	76.67				
45.0	23.33	97.0	0.02	170.0	10.00				
46.0	1.58	98.0	0.74	171.0	8.33				
47.0	7.50	99.0	8.33	172.0	1.21				
48.0	0.50	100.0	0.08	173.0	0.47				
49.0	0.69	101.0	2.50	183.0	1.12				
50.0	1.09	102.0	1.16	184.0	1.67				
51.0	1.33	103.0	1.13						
52.0	0.83	105.0	2.50						
53.0	3.33	107.0	1.09						
54.0	0.77	109.0	1.71						
55.0	5.00	110.0	0.43						
56.0	1.00	111.0	0.03						
57.0	2.50	112.0	0.73						
58.0	5.00	113.0	2.50						
59.0	70.00	114.0	0.77						
60.0	5.00	115.0	4.17						
61.0	25.83	116.0	0.48						
62.0	1.67	117.0	5.83						
63.0	2.50	118.0	0.80						
64.0	4.17	119.0	1.14						
65.0	1.67	120.0	0.49						
66.0	1.11	123.0	1.60						
67.0	2.50	125.0	4.17						
68.0	0.67	126.0	1.37						
69.0	3.33	127.0	9.17						
70.0	1.08	128.0	1.24						
71.0	3.33	129.0	1.88						
72.0	1.82	131.0	0.62						
73.0	4.17	133.0	1.37						
74.0	1.24	135.0	0.58						
75.0	40.83	139.0	5.83						
76.0	3.33	140.0	1.30						
77.0	20.00	141.0	87.50						
78.0	1.67	142.0	12.50						
79.0	1.67	143.0	5.83						
81.0	0.77	144.0	0.93						
82.0	0.74	145.0	0.76						
83.0	3.33	151.0	3.33						
84.0	1.67	152.0	0.59						
85.0	94.17	153.0	0.89						

NORMALIZED MASS SPECTRUM 254.0945

NAME: 2-(TRIFLUOROPROPYLDIMETHYLSILOXY)-4-KETOPENTENE-2

EMPIRICAL FORMULA: SIC10H1702 F3

INSTRUMENT: MS-12 SOURCE TEMP: 160 INLET TEMP: 135
ACCEL VOLT: 8 KV TRAP CURNT: 100 MIC AMPS IONIZING POT: 80

MASS	INT	MASS	INT	MASS	INT	MASS	INT	MASS	INT
33.0	2.17	83.0	1.96	132.0	0.14	185.0	0.23		
34.0	0.08	84.0	0.66	133.0	0.02	186.0	0.03		
36.0	0.24	85.0	93.48	134.0	0.46	187.0	0.07		
37.0	0.64	86.0	3.26	135.0	1.23	219.0	2.17		
38.0	1.65	87.0	2.09	136.0	0.15	220.0	0.42		
39.0	19.57	88.0	0.22	137.0	0.02	221.0	0.15		
41.0	0.03	89.0	0.88	138.0	0.39	223.0	0.15		
42.0	0.02	90.0	0.26	139.0	1.50	224.0	0.03		
43.0	100.00	91.0	0.78	140.0	0.22	225.0	0.11		
44.0	3.26	92.0	0.13	141.0	1.48	235.0	0.93		
45.0	8.70	93.0	2.21	142.0	0.48	236.0	0.42		
46.0	0.62	94.0	0.20	143.0	0.26	237.0	0.13		
47.0	9.78	95.0	2.00	144.0	0.28	238.0	0.17		
48.0	0.74	96.0	0.67	145.0	0.50	239.0	13.04		
49.0	5.43	97.0	1.13	146.0	0.11	240.0	2.25		
50.0	1.18	98.0	0.73	147.0	0.16	241.0	0.67		
51.0	2.17	99.0	3.26	148.0	0.02	242.0	0.04		
52.0	0.65	100.0	0.03	149.0	0.05	254.0	4.35		
53.0	2.17	102.0	0.25	150.0	0.02	255.0	0.89		
54.0	0.82	103.0	1.26	151.0	3.26	256.0	0.25		
55.0	0.02	104.0	0.16	152.0	0.70				
56.0	0.59	105.0	1.60	153.0	0.57				
57.0	2.17	106.0	0.16	154.0	0.26				
58.0	4.35	107.0	0.29	155.0	1.72				
59.0	75.00	108.0	0.10	156.0	0.84				
60.0	2.17	109.0	0.84	157.0	65.22				
61.0	2.17	110.0	0.12	158.0	7.61				
62.0	1.38	111.0	0.57	159.0	0.02				
63.0	0.03	112.0	0.23	160.0	0.86				
64.0	0.96	113.0	1.11	161.0	14.13				
65.0	1.41	114.0	0.50	162.0	2.07				
66.0	0.51	115.0	0.03	163.0	0.71				
67.0	1.76	116.0	0.52	164.0	0.04				
68.0	0.38	117.0	1.32	165.0	0.78				
69.0	2.17	118.0	0.25	166.0	0.08				
70.0	0.35	119.0	0.87	167.0	0.05				
71.0	3.26	120.0	0.13	169.0	0.39				
72.0	1.04	121.0	0.59	170.0	0.09				
73.0	2.17	122.0	0.07	171.0	0.13				
74.0	1.02	123.0	0.43	172.0	0.04				
75.0	23.91	124.0	0.07	173.0	0.27				
76.0	2.17	125.0	0.74	174.0	0.03				
77.0	59.78	126.0	0.43	175.0	0.18				
78.0	9.78	127.0	0.03	176.0	0.03				
79.0	10.87	128.0	0.53	177.0	0.48				
80.0	0.88	129.0	0.39	178.0	0.05				
81.0	7.61	130.0	0.09	179.0	0.07				
82.0	1.15	131.0	0.66	181.0	0.04				

NORMALIZED MASS SPECTRUM 234.1071

NAME: 2(PHENYLDIMETHYLSILOXY)-4-KETOPENTENE

EMPIRICAL FORMULA: SIC13H1802

INSTRUMENT: MS-12 SOURCE TEMP: 170 INLET TEMP: 135
ACCEL VOLT: 8 KV TRAP CURNT: 100 MIC AMPS IONIZING POT: 80

MASS	INT	MASS	INT	MASS	INT	MASS	INT	MASS	INT
33.0	0.06	77.0	10.30	111.0	1.02	153.0	0.77	201.0	4.85
34.0	0.23	77.5	1.67	112.0	0.42	154.0	2.33	202.0	2.41
35.0	0.06	78.0	5.45	112.5	0.20	155.0	15.76	203.0	1.48
36.0	0.70	78.5	0.59	113.0	3.20	156.0	4.85	204.0	0.45
37.0	1.83	79.0	1.82	114.0	0.74	157.0	59.39	205.0	0.26
38.0	1.21	80.0	0.73	115.0	2.42	158.0	7.88	206.0	0.06
39.0	6.06	81.0	1.21	116.0	1.74	159.0	6.06	207.0	0.48
40.0	1.21	82.0	1.73	117.0	1.82	160.0	1.86	208.0	0.17
41.0	3.03	83.0	1.21	118.0	1.20	161.0	3.64	212.0	0.05
42.0	2.42	84.0	1.76	119.0	5.45	162.0	1.61	213.0	0.14
43.0	49.70	85.0	12.12	120.0	1.21	163.0	1.94	214.0	0.08
44.0	3.03	86.0	1.70	120.5	0.14	164.0	0.39	215.0	2.83
45.0	9.09	87.0	2.27	121.0	1.82	165.0	1.67	216.0	0.86
46.0	1.24	87.5	0.09	122.0	0.83	166.0	0.30	217.0	0.58
47.0	1.82	88.0	0.53	123.0	2.95	167.0	0.30	218.0	0.88
48.0	0.44	89.0	4.24	124.0	0.38	168.0	0.06	219.0	100.00
49.0	1.18	89.5	2.03	125.0	0.70	169.0	0.64	220.0	18.18
50.0	2.42	90.0	1.62	126.0	1.45	170.0	2.42	221.0	4.85
51.0	4.24	90.5	0.21	127.0	2.42	171.0	1.27	222.0	1.55
52.0	1.21	91.0	10.30	128.0	3.64	172.0	2.68	223.0	0.15
53.0	3.64	92.0	1.21	128.5	1.42	173.0	1.42	225.0	0.39
54.0	1.23	93.0	3.03	129.0	2.33	174.0	0.35	226.0	0.05
55.0	1.82	94.0	1.42	129.5	0.08	175.0	1.82		
56.0	0.52	94.5	0.06	130.0	0.47	176.0	0.94		
57.0	1.82	95.0	1.21	131.0	2.95	177.0	2.73		
58.0	1.21	95.5	0.09	132.0	0.73	178.0	0.83		
59.0	2.42	96.0	0.61	133.0	1.21	179.0	2.99		
60.0	1.18	97.0	1.80	134.0	2.35	180.0	0.68		
61.0	1.21	97.5	0.21	135.0	48.48	181.0	0.97		
62.0	1.30	98.0	0.82	135.5	1.56	182.0	0.18		
63.0	3.03	99.0	3.03	136.0	6.67	183.0	1.06		
64.0	0.97	100.0	7.27	136.5	0.20	184.0	0.59		
65.0	2.42	100.5	0.12	137.0	15.15	185.0	0.77		
66.0	1.80	101.0	3.09	138.0	1.82	186.0	0.20		
67.0	1.82	101.5	0.09	139.0	4.24	187.0	0.20		
67.5	0.29	102.0	6.67	140.0	1.74	188.0	0.15		
68.0	0.85	102.5	2.71	141.0	6.67	189.0	0.45		
68.5	0.61	103.0	1.21	142.0	1.21	190.0	0.70		
69.0	1.21	103.5	0.11	143.0	3.64	191.0	1.82		
69.5	0.32	104.0	0.94	143.5	0.11	192.0	1.05		
70.0	0.59	105.0	7.88	144.0	1.29	193.0	9.09		
70.5	0.26	106.0	2.94	144.0	0.29	194.0	1.82		
71.0	1.32	107.0	6.06	147.0	1.11	195.0	1.82		
72.0	2.50	108.0	2.09	148.0	0.26	196.0	0.77		
73.0	3.02	109.0	1.21	149.0	0.62	197.0	2.24		
74.0	2.50	109.5	1.21	150.0	0.17	198.0	0.44		
75.0	8.48	110.0	1.17	151.0	1.18	199.0	0.67		
76.0	1.21	110.5	0.17	152.0	2.64	200.0	0.17		

NORMALIZED MASS SPECTRUM 296.1226

NAME: 2-(METHYLDIPHENYLSILOXY)-4-KETOPENTENE

EMPIRICAL FORMULA: $SIC_{18}H_{20}O_2$

INSTRUMENT: MS-12 SOURCE TEMP: 180 INLET TEMP: 138
ACCEL VOLT: 8 KV TRAP CURNT: 100 MIC AMPS IONIZING POT: 80

MASS	INT	MASS	INT	MASS	INT	MASS	INT	MASS	INT
33.0	0.06	81.0	0.31	129.0	0.59	177.0	0.12	225.0	0.44
34.0	0.20	82.0	0.25	130.0	0.09	178.0	0.19	226.0	0.15
35.0	0.04	83.0	0.08	131.0	0.19	179.0	0.78	227.0	0.35
36.0	0.41	84.0	0.60	132.0	0.02	180.0	0.89	228.0	0.06
37.0	1.29	85.0	35.29	133.0	0.42	181.0	2.35	229.0	0.01
38.0	2.35	86.0	1.73	134.0	0.05	182.0	0.54	230.0	0.01
39.0	7.06	87.0	0.45	135.0	0.74	183.0	0.36	231.0	0.02
40.0	0.02	88.0	0.07	136.0	0.11	184.0	0.06	232.0	0.05
41.0	0.06	89.0	0.46	137.0	2.11	185.0	0.09	233.0	1.11
42.0	5.88	90.0	0.13	138.0	0.24	186.0	0.01	234.0	2.31
43.0	100.00	91.0	3.53	139.0	1.61	187.0	0.02	235.0	0.39
44.0	2.35	92.0	0.74	140.0	0.46	188.0	0.01	236.0	0.07
45.0	2.26	93.0	1.29	141.0	1.01	189.0	0.07	237.0	0.09
46.0	0.08	94.0	0.16	142.0	1.12	190.0	0.01	238.0	0.01
47.0	1.39	95.0	0.35	143.0	0.61	191.0	0.09	239.0	0.14
48.0	0.12	96.0	0.07	144.0	0.08	192.0	0.04	240.0	0.02
49.0	0.41	97.0	0.18	145.0	0.22	193.0	0.61	241.0	0.48
50.0	1.82	98.0	1.45	146.0	0.01	194.0	0.12	242.0	0.12
51.0	2.35	99.0	0.49	147.0	0.59	195.0	1.39	243.0	0.02
52.0	0.92	100.0	23.53	148.0	0.08	196.0	0.34	263.0	0.16
53.0	2.29	101.0	1.54	149.0	0.14	197.0	4.71	264.0	0.02
54.0	0.24	102.0	0.38	150.0	0.06	198.0	1.14	265.0	0.01
55.0	1.93	103.0	0.80	151.0	0.32	199.0	1.85	271.0	0.42
56.0	0.16	104.0	0.18	152.0	1.13	200.0	0.32	272.0	0.11
57.0	0.81	105.0	2.35	153.0	0.69	201.0	2.35	273.0	0.04
58.0	2.35	106.0	0.38	154.0	1.40	202.0	0.60	275.0	0.87
59.0	1.14	107.0	0.24	155.0	2.35	203.0	0.60	276.0	0.20
60.0	0.14	108.0	0.08	156.0	0.54	204.0	0.12	277.0	0.06
61.0	0.51	109.0	0.06	157.0	2.40	205.0	0.39	281.0	0.02
62.0	0.34	110.0	0.01	158.0	0.31	206.0	0.05	282.0	0.75
63.0	0.04	111.0	0.04	159.0	0.38	207.0	0.09	283.0	0.19
64.0	0.28	112.0	0.02	160.0	0.06	208.0	0.01	291.0	0.46
65.0	1.73	113.0	0.13	161.0	0.54	209.0	0.06	292.0	0.09
66.0	0.35	114.0	0.05	162.0	0.07	210.0	0.01	293.0	0.01
67.0	0.87	115.0	0.76	163.0	0.15	211.0	0.04	294.0	0.01
68.0	0.13	116.0	0.19	164.0	0.07	212.0	0.01	295.0	0.01
69.0	1.46	117.0	0.53	165.0	1.27	213.0	0.16	296.0	0.01
70.0	0.08	118.0	0.09	166.0	0.24	214.0	0.13		
71.0	0.27	119.0	1.35	167.0	0.31	215.0	0.51		
72.0	2.35	120.0	0.31	168.0	0.04	216.0	1.14		
73.0	0.89	121.0	0.61	169.0	0.13	217.0	18.82		
74.0	0.46	122.0	0.08	170.0	0.13	218.0	3.53		
75.0	1.25	123.0	0.21	171.0	0.07	219.0	24.71		
76.0	0.45	124.0	0.04	172.0	0.09	220.0	3.53		
77.0	2.35	125.0	0.07	173.0	0.05	221.0	1.26		
78.0	0.01	126.0	0.13	174.0	0.01	222.0	0.13		
79.0	1.14	127.0	1.00	175.0	0.69	223.0	0.29		
80.0	0.12	128.0	0.61	176.0	0.11	224.0	0.08		

7

NORMALIZED MASS SPECTRUM 280.0349

NAME: 1,1,1,5,5,5-HEXAFLORO-2-TRIMETHYLSILOXY-4-KETOPENTENE-2

EMPIRICAL FORMULA: SIC8H1002F6

INSTRUMENT: MS-12 SOURCE TEMP: 160 INLET TEMP: 135
ACCEL VOLT: 8 KV TRAP CURNT: 100 MIC AMPS IONIZING POT: 80

MASS	INI	MASS	INI	MASS	INI	MASS	INI	MASS	INI
33.0	0.17	82.0	0.59	130.0	0.08	194.0	0.07		
34.0	0.21	83.0	0.53	131.0	0.29	195.0	0.28		
36.0	0.13	84.0	0.24	132.0	0.07	196.0	2.22		
37.0	0.42	85.0	2.78	133.0	0.16	197.0	0.86		
38.0	0.44	86.0	0.27	135.0	0.44	198.0	0.18		
39.0	2.78	87.0	2.78	136.0	0.19	199.0	0.66		
40.0	3.33	88.0	0.35	137.0	0.45	200.0	1.03		
41.0	1.67	89.0	1.13	138.0	0.09	201.0	1.14		
42.0	2.78	90.0	0.23	139.0	1.67	202.0	0.20		
43.0	17.22	91.0	13.33	140.0	0.13	203.0	0.07		
44.0	5.56	92.0	0.67	141.0	0.44	207.0	0.08		
45.0	13.89	93.0	5.00	142.0	0.06	208.0	0.08		
46.0	1.10	94.0	0.62	143.0	0.51	209.0	0.09		
47.0	11.67	95.0	1.67	144.0	0.08	210.0	0.05		
48.0	0.82	96.0	0.19	145.0	2.22	211.0	13.89		
49.0	10.56	97.0	0.80	146.0	0.26	212.0	1.67		
50.0	1.26	98.0	0.36	147.0	3.33	213.0	0.69		
51.0	1.19	99.0	0.39	148.0	0.64	214.0	0.35		
52.0	0.30	100.0	1.67	149.0	1.15	215.0	8.89		
53.0	9.44	101.0	0.57	150.0	0.21	216.0	1.67		
54.0	0.73	102.0	0.31	151.0	0.29	217.0	1.67		
55.0	2.78	103.0	2.22	152.0	0.17	218.0	0.25		
56.0	1.10	104.0	0.24	153.0	0.56	219.0	0.66		
57.0	1.67	105.0	0.47	154.0	0.23	220.0	0.11		
58.0	1.67	106.0	0.18	155.0	0.38	221.0	0.06		
59.0	1.67	107.0	0.49	156.0	0.08	225.0	0.08		
60.0	0.33	108.0	0.54	157.0	1.67	231.0	0.11		
61.0	0.74	109.0	0.52	158.0	0.24	232.0	0.38		
62.0	1.09	110.0	0.26	159.0	0.24	233.0	0.07		
63.0	10.00	111.0	0.19	163.0	0.09	234.0	0.13		
64.0	0.83	112.0	0.04	164.0	0.06	241.0	0.12		
65.0	1.10	113.0	0.38	165.0	0.37	246.0	0.53		
66.0	0.76	114.0	0.05	166.0	0.07	247.0	0.08		
67.0	1.16	115.0	1.14	167.0	0.27	250.0	0.61		
68.0	0.37	116.0	0.14	169.0	11.67	251.0	0.08		
69.0	58.33	117.0	0.64	170.0	0.68	261.0	0.05		
70.0	2.22	118.0	0.25	171.0	0.12	263.0	0.06		
71.0	1.67	119.0	11.11	172.0	0.22	265.0	81.67		
72.0	4.44	120.0	0.62	179.0	0.10	266.0	11.67		
73.0	77.22	121.0	0.45	180.0	0.06	267.0	3.89		
74.0	6.67	122.0	0.76	181.0	0.24	268.0	0.29		
75.0	28.33	123.0	0.28	182.0	0.13	271.0	0.56		
76.0	2.78	124.0	0.07	183.0	0.06	272.0	0.13		
77.0	100.00	125.0	0.21	184.0	0.09	273.0	0.06		
78.0	6.67	126.0	0.04	185.0	0.11	275.0	0.06		
79.0	3.89	127.0	1.12	186.0	0.21	278.0	0.06		
80.0	0.47	128.0	0.18	192.0	0.07				
81.0	8.33	129.0	0.27	193.0	0.33				

NORMALIZED MASS SPECTRUM 256.1851

NAME: 2,2,6,6-TETRAMETHYL-3-TRIMETHYLSILOXY-5-KETOHEPTENE-3

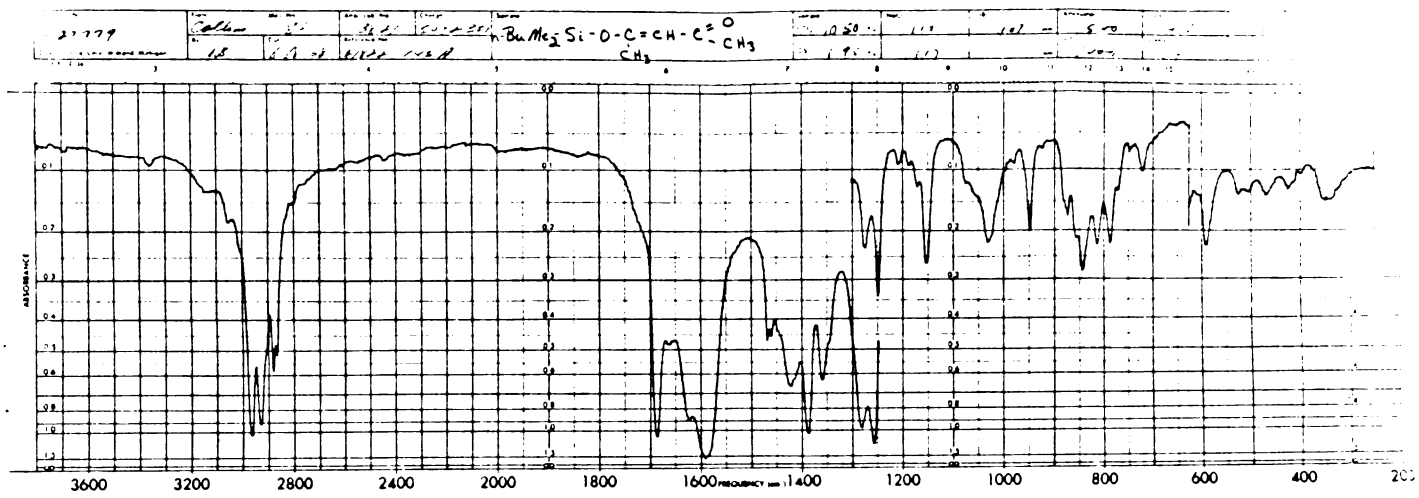
EMPIRICAL FORMULA: SIC14 H2802

INSTRUMENT: MS-12 SOURCE TEMP: 170 INLET TEMP: 135
ACCEL VOLT: 8 KV TRAP CURNT: 100 MIC AMPS IONIZING POT: 80

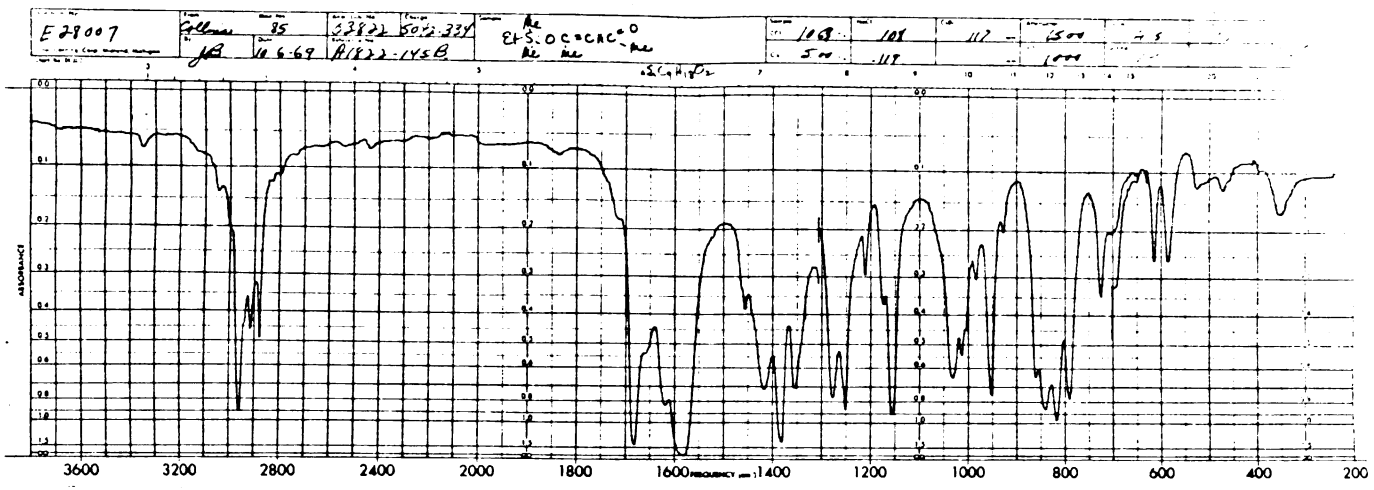
MASS	INT	MASS	INT	MASS	INT	MASS	INT	MASS	INT
12.0	0.11	65.0	0.67	113.0	0.75	163.0	0.05	217.0	0.83
13.0	0.10	66.0	0.50	114.0	0.20	164.0	0.01	218.0	0.18
14.0	2.04	67.0	1.51	115.0	0.49	165.0	0.31	219.0	1.36
15.0	1.36	68.0	0.15	116.0	0.10	166.0	0.09	220.0	0.40
16.0	0.85	69.0	1.37	117.0	0.31	167.0	0.45	221.0	0.13
17.0	1.14	70.0	0.60	118.0	0.04	168.0	0.19	222.0	0.01
18.0	0.04	71.0	0.52	119.0	0.48	169.0	1.12	223.0	0.09
20.0	0.06	72.0	1.36	120.0	0.07	170.0	0.35	224.0	0.06
22.0	0.01	73.0	46.26	121.0	0.17	171.0	0.26	225.0	1.33
24.0	0.03	74.0	3.40	122.0	0.06	172.0	0.08	226.0	2.04
25.0	0.14	75.0	15.65	123.0	0.73	173.0	0.02	227.0	0.54
26.0	0.82	76.0	1.36	124.0	0.10	175.0	0.09	228.0	0.13
27.0	1.36	77.0	1.36	125.0	2.04	176.0	0.01	230.0	0.01
28.0	65.99	78.0	0.56	126.0	0.28	177.0	0.04	232.0	0.16
29.0	6.12	79.0	0.80	127.0	0.03	178.0	0.03	233.0	0.03
30.0	0.14	80.0	0.14	128.0	0.42	179.0	0.12	234.0	0.07
31.0	0.33	81.0	4.08	129.0	0.18	180.0	0.10	236.0	0.01
32.0	10.88	82.0	0.44	130.0	0.04	181.0	0.73	238.0	0.01
34.0	0.03	83.0	0.93	131.0	0.16	182.0	0.19	239.0	0.10
36.0	0.05	84.0	0.20	132.0	0.02	183.0	0.01	240.0	0.05
37.0	0.20	85.0	2.04	133.0	0.32	184.0	0.01	241.0	23.81
38.0	0.36	86.0	0.22	134.0	0.05	185.0	1.18	242.0	4.08
39.0	3.40	87.0	0.28	135.0	0.16	186.0	0.19	243.0	0.80
40.0	0.90	88.0	0.03	136.0	0.07	187.0	0.05	244.0	0.14
41.0	11.56	89.0	0.43	137.0	0.87	189.0	0.03	255.0	0.14
42.0	1.11	90.0	0.07	138.0	0.12	191.0	0.02	256.0	0.34
43.0	8.16	91.0	0.97	139.0	0.55	193.0	0.15	257.0	0.07
44.0	0.68	92.0	0.19	140.0	0.15	194.0	0.05		
45.0	6.80	93.0	0.39	141.0	1.36	195.0	1.31		
46.0	0.49	94.0	0.07	142.0	0.52	196.0	0.44		
47.0	1.51	95.0	0.54	143.0	0.46	197.0	0.99		
48.0	0.09	96.0	0.10	144.0	0.10	198.0	0.29		
49.0	0.16	97.0	0.52	145.0	0.07	199.0	100.00		
50.0	0.46	98.0	0.27	147.0	1.36	200.0	15.65		
51.0	0.80	99.0	2.72	148.0	0.34	201.0	4.76		
52.0	0.35	100.0	1.18	149.0	0.24	202.0	0.54		
53.0	1.18	101.0	0.50	150.0	0.04	203.0	0.10		
54.0	0.22	102.0	0.07	151.0	0.20	205.0	0.05		
55.0	1.36	103.0	0.19	152.0	0.12	207.0	0.04		
56.0	1.08	104.0	0.06	153.0	0.28	208.0	0.02		
57.0	26.53	105.0	0.54	154.0	0.15	209.0	0.41		
58.0	1.37	106.0	0.07	155.0	0.68	210.0	0.42		
59.0	1.36	107.0	0.29	156.0	0.35	211.0	2.72		
60.0	0.42	108.0	0.07	157.0	0.90	212.0	0.85		
61.0	0.01	109.0	6.80	158.0	0.12	213.0	1.09		
62.0	0.18	110.0	0.74	159.0	0.28	214.0	0.20		
63.0	0.33	111.0	0.73	160.0	0.03	215.0	0.05		
64.0	0.12	112.0	0.14	161.0	0.07	216.0	0.15		

APPENDIX B

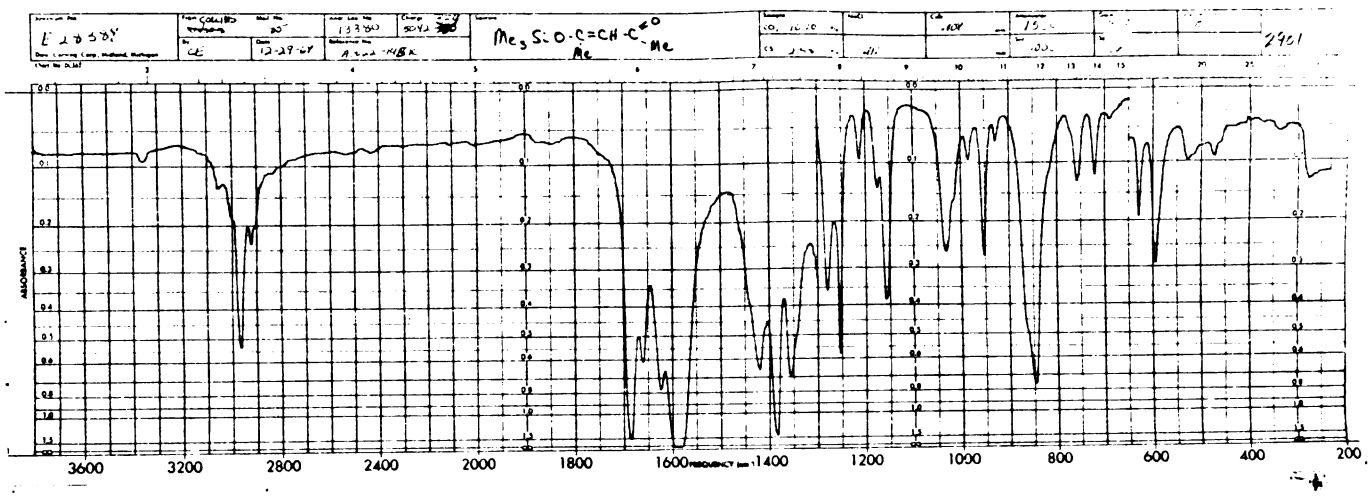
Infrared Spectra



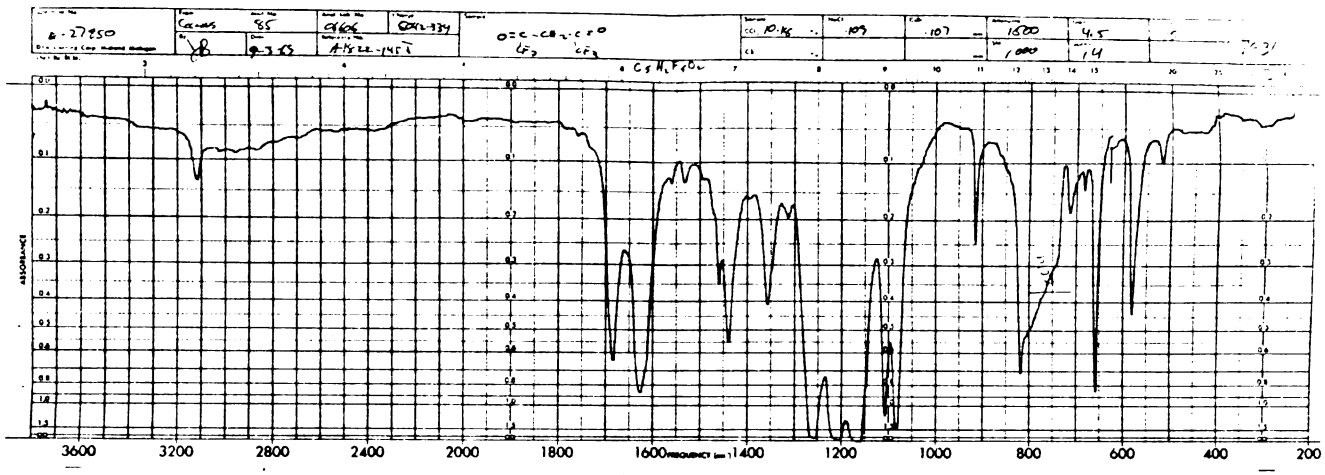
$(\underline{n} - C_4H_9)(CH_3)_2Si(acac)$



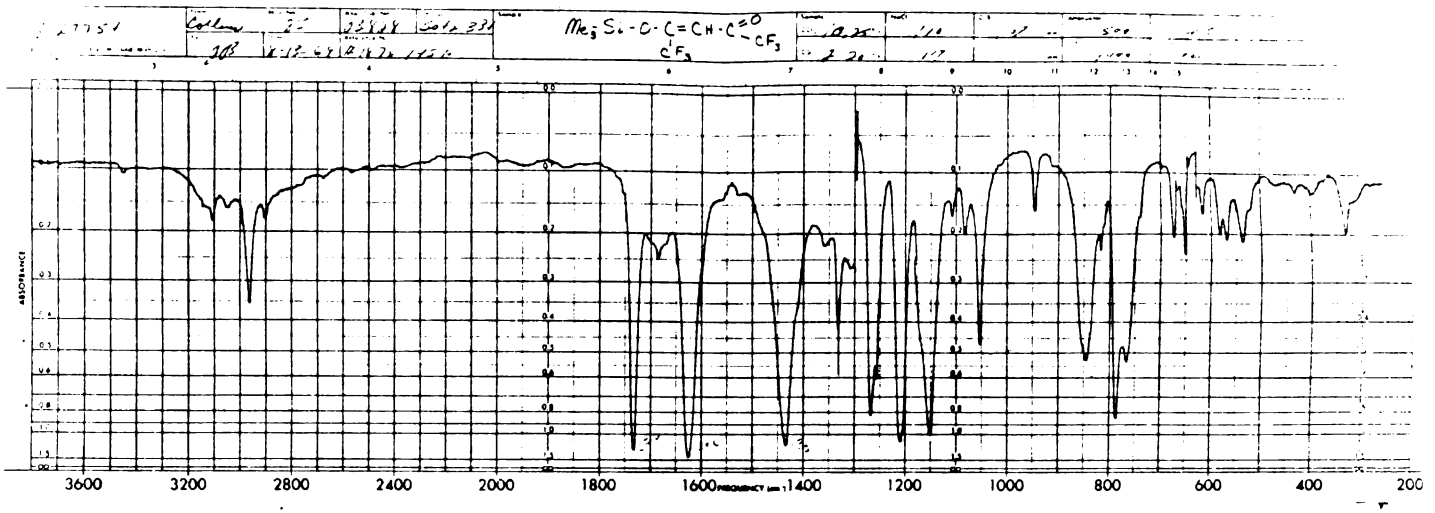
$(C_2H_5)(CH_3)_2Si(acac)$


Me3Si-O-C=CH-C-Me
Me
2901
ABSORBANCE
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
200

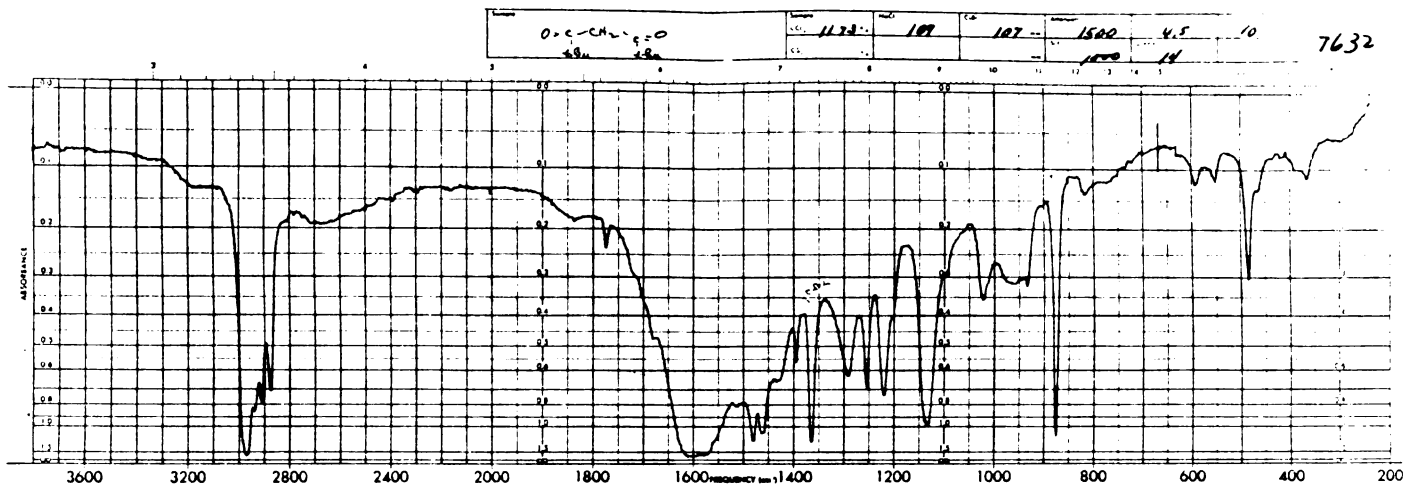
$(CH_3)_3Si(acac)$


3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
200

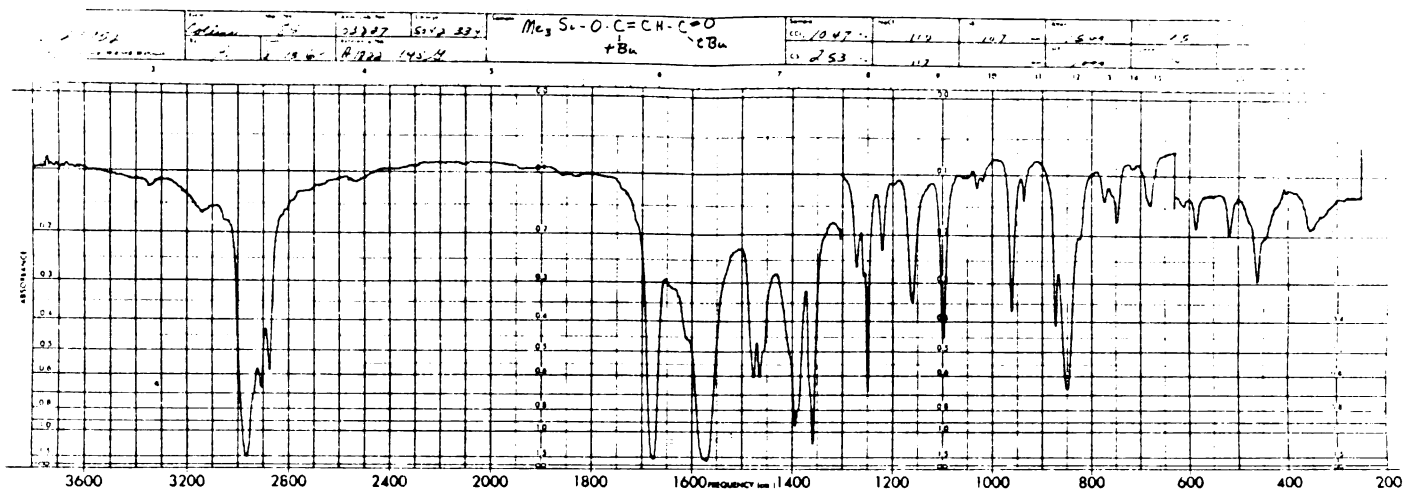
H(hfac)


3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
200

$(CH_3)_3Si(hfac)$


7632
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
200

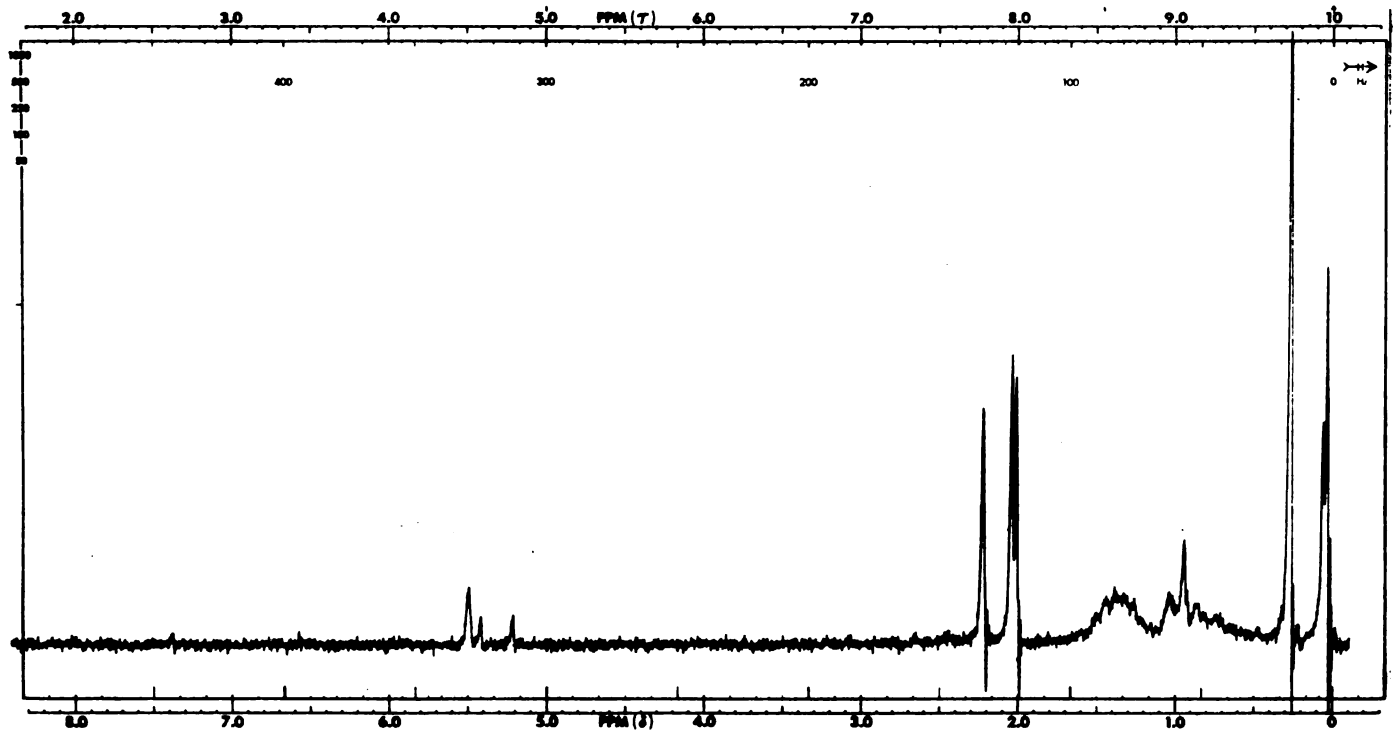
H(dpm)


Me3 Si-O-C=CH-C=O
+Bu
tBu
3600
3200
2600
2400
2000
1800
1600
1400
1200
1000
800
600
400
200

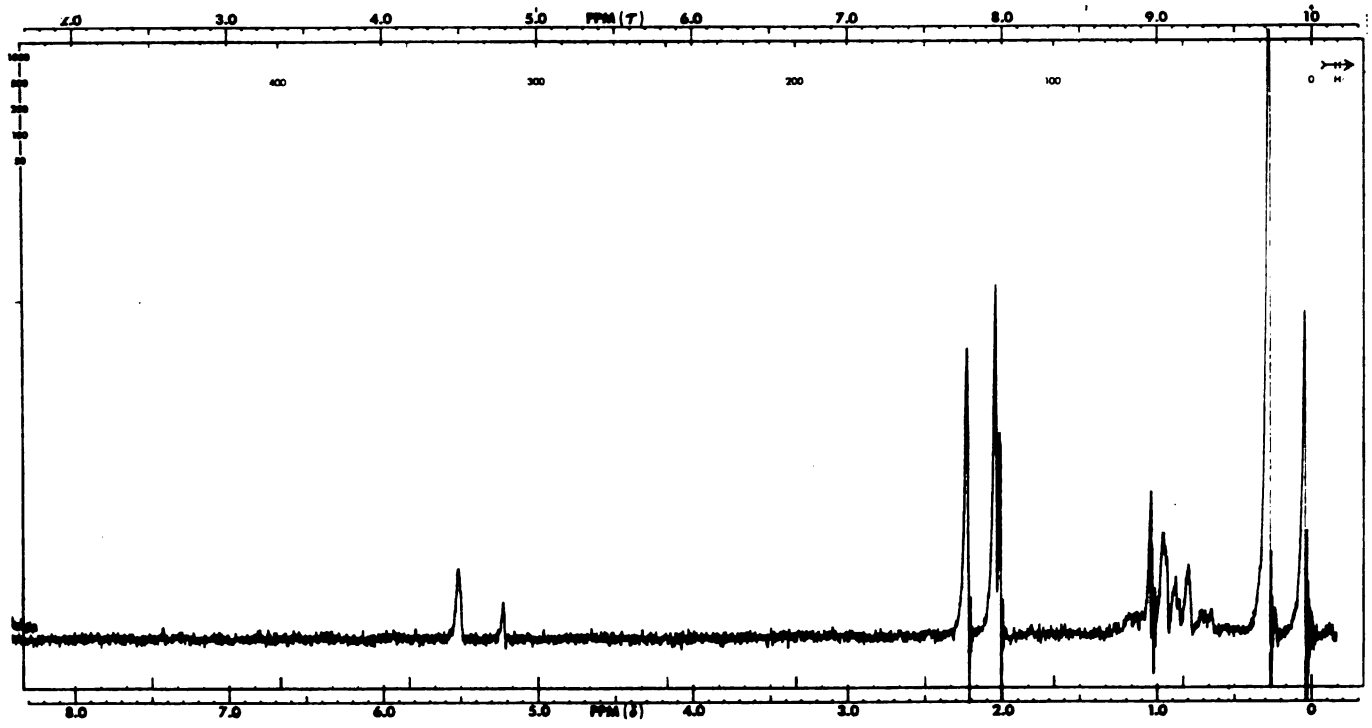
$(CH_3)_3Si$(dpm)

APPENDIX C

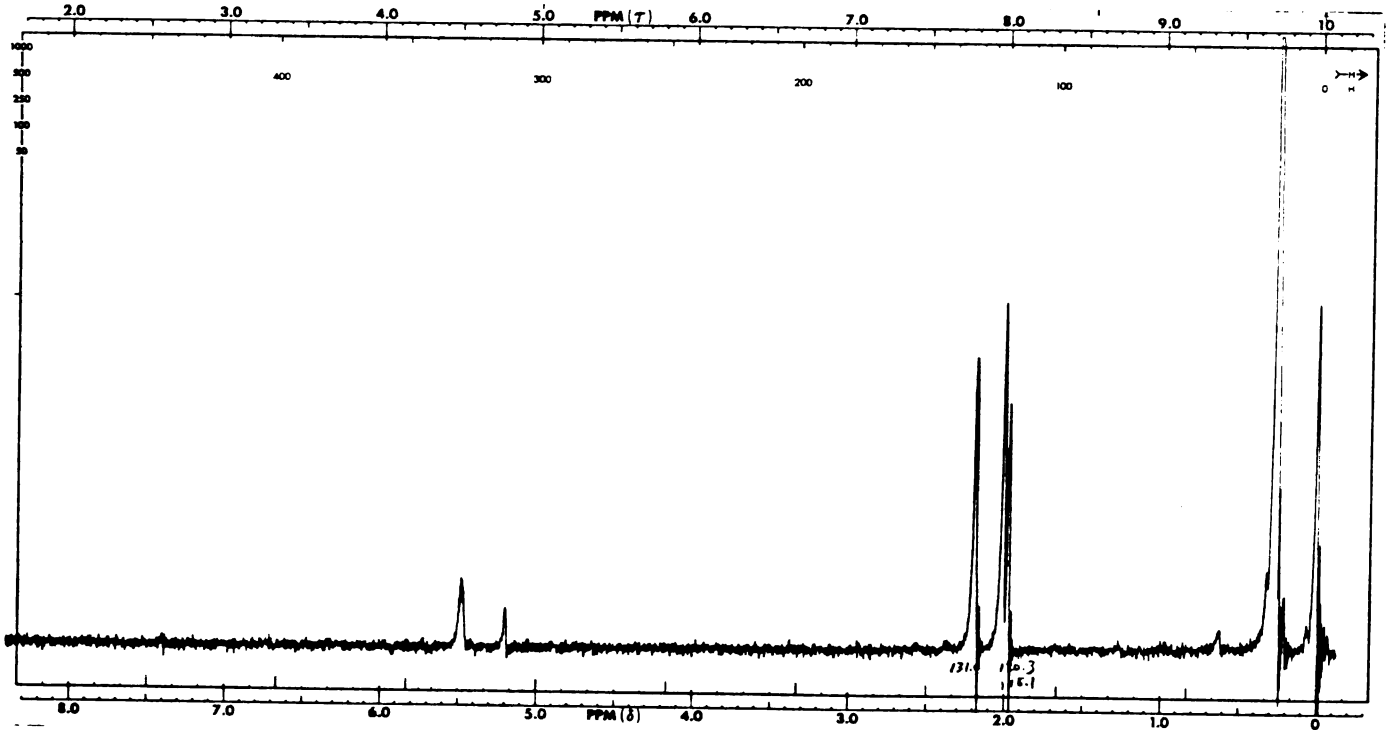
Proton Nmr Spectra



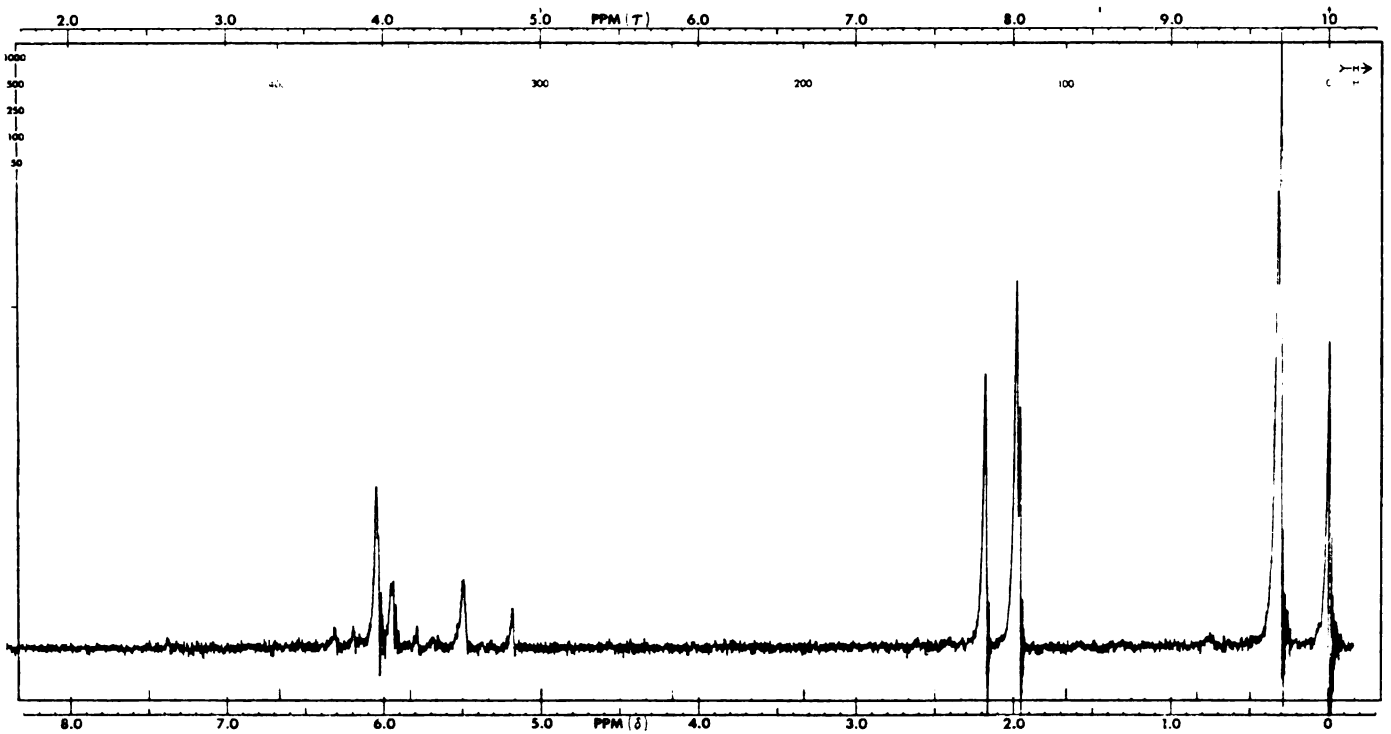
($\underline{n}$ - C_4H_9)$(CH_3)_2$Si(acac) in CCl_4 (10.0 g/100 ml.)



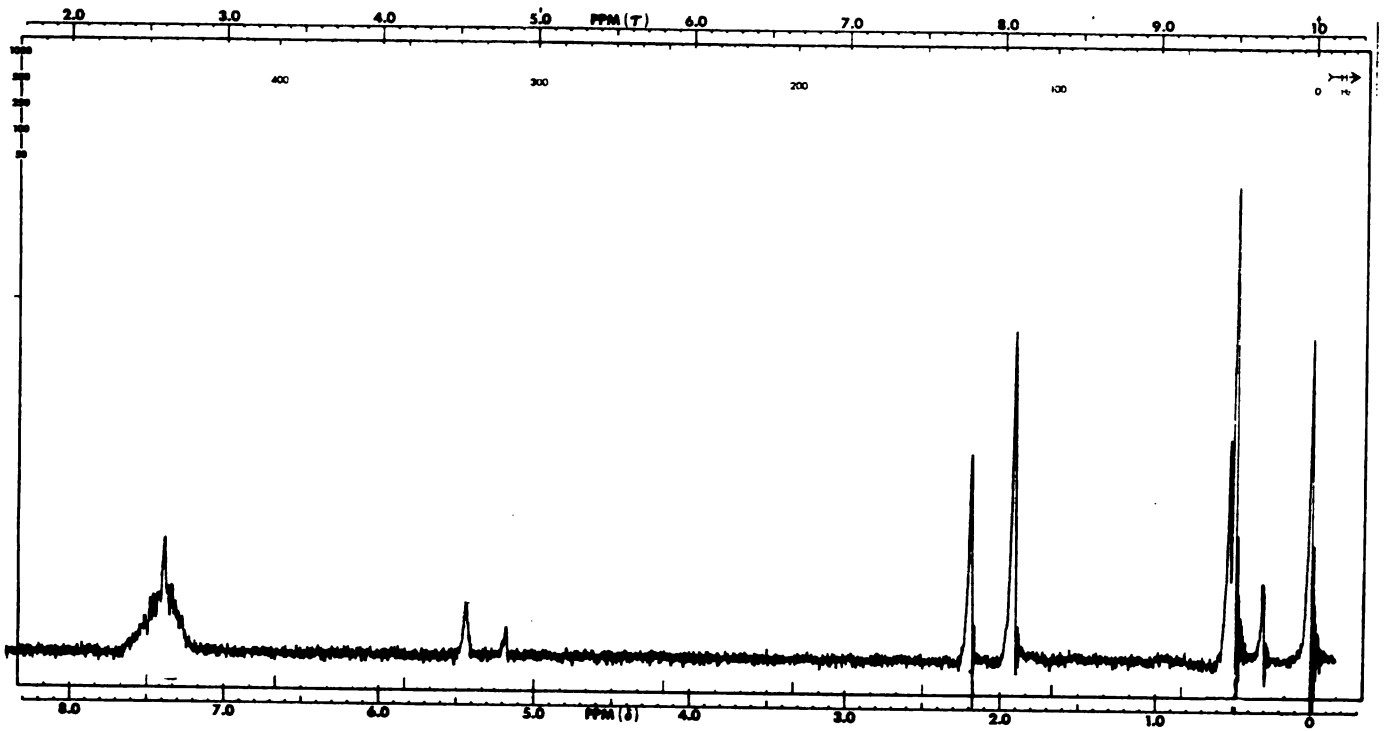
$(C_2H_5)(CH_3)_2Si(acac)$ in CCl_4 (10.0 g/100 ml.)



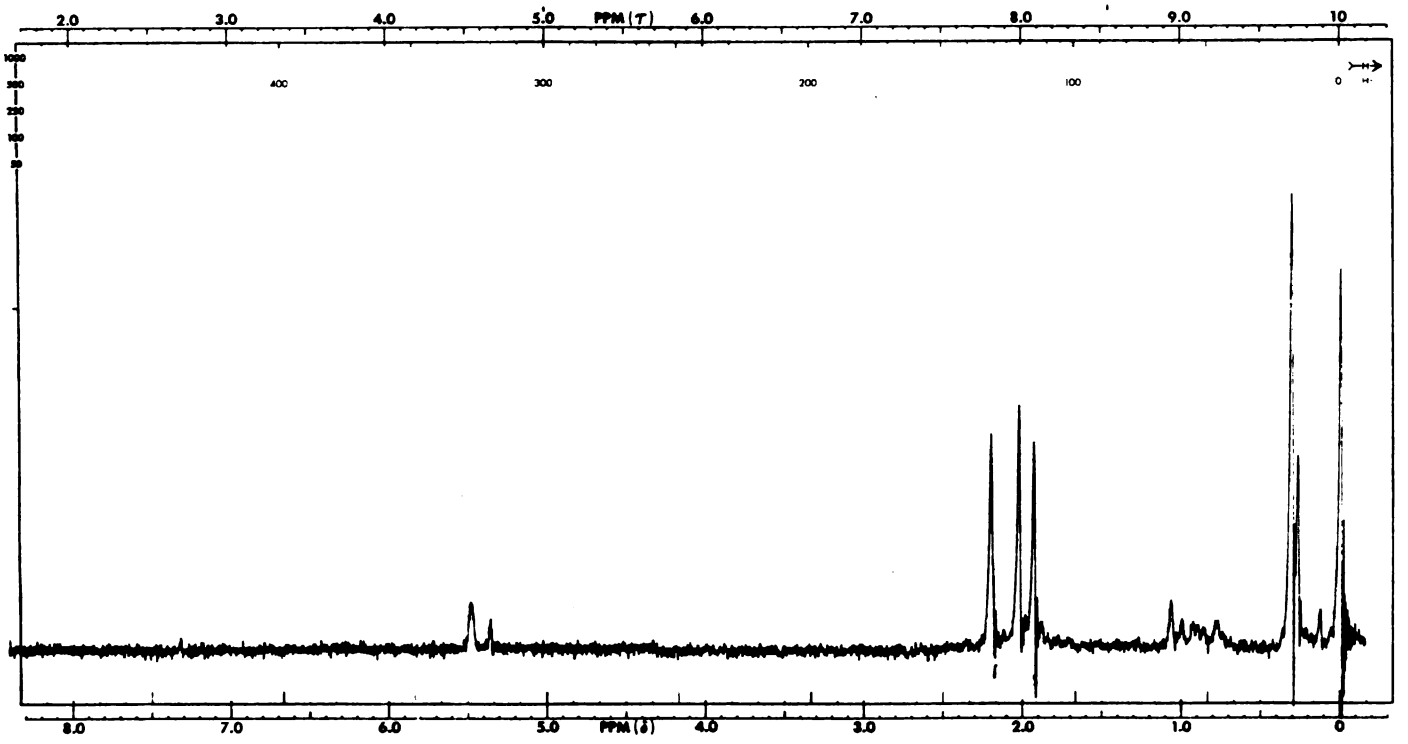
$(CH_3)_3Si(acac)$ in CCl_4 (10.0 g/100 ml.)



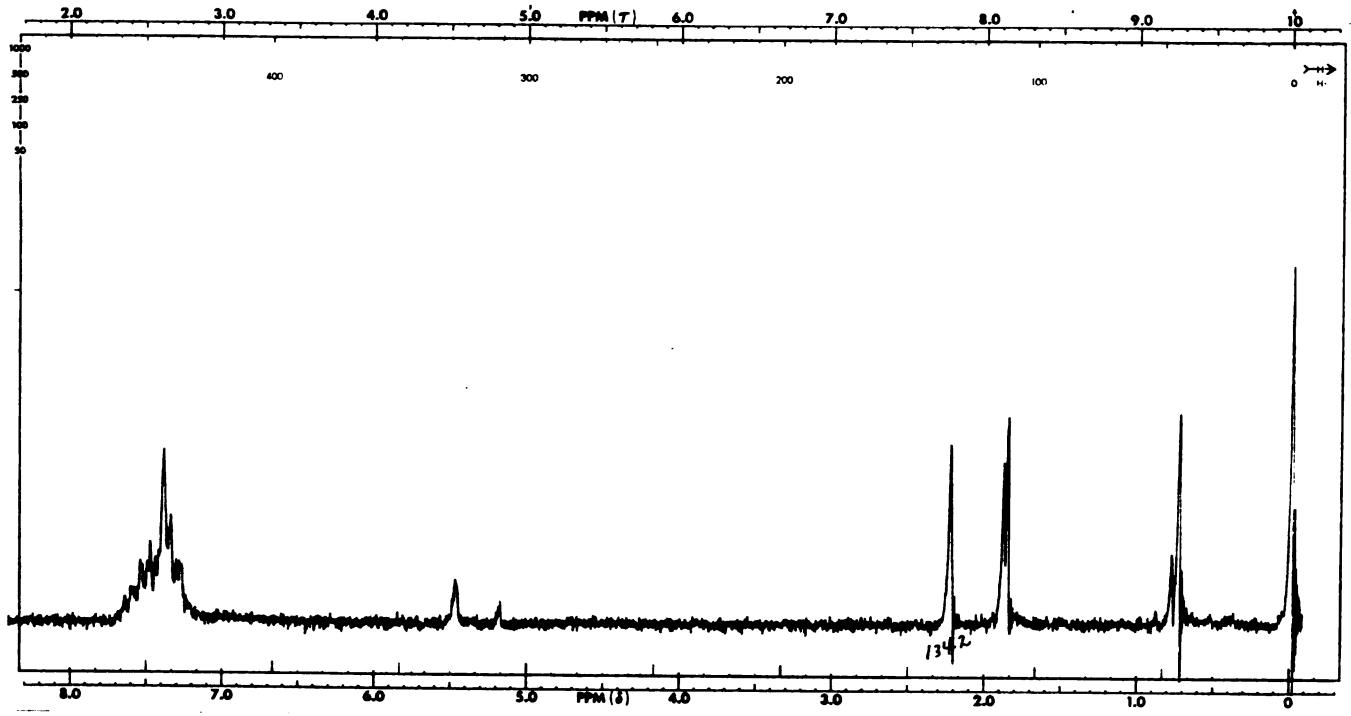
$(CH_2 = CH)(CH_3)Si(acac)$ in CCl_4 (10.0 g/100 ml.)



$(C_6H_5)(CH_3)_2Si(acac)$ in CCl_4 (10.0 g/100 ml.)



$(CF_3CH_2CH_2)(CH_3)_2Si(acac)$ in CCl_4 (10.0 g/100 ml.)



$(C_6H_5)_2(CH_3)Si(acac)$ in CCl_4 (10.0 g/100 ml.)