

PREPARATION AND BASICITY MEASUREMENTS OF FERROCENYL TRIMETHYLSILYL KETONE

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Summary

Ferrocenyl trimethylsilyl ketone, FcCOSiMe_3 (I) has been prepared in good yield by a four step sequence. It exhibits an unusually low carbonyl stretching frequency of 1589 cm^{-1} . MeOD has been used to characterize unequivocally the carbonyl stretching band as well as to estimate the basicity of I. In addition, we have measured the basicity of I in aqueous sulfuric acid solutions.

Introduction

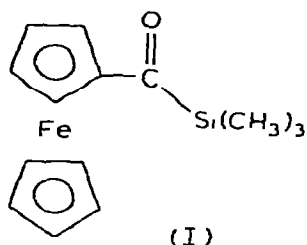
Both the ferrocenyl [1] and the silyl [2] groups are known to perturb the spectroscopic properties of adjacent carbonyl groups. The carbonyl stretching frequency, $\nu(\text{CO})$, for acetylferrocene is 1672 cm^{-1} , while for trimethylsilyl phenyl ketone [3] it is 1618 cm^{-1} . By comparison, $\nu(\text{CO})$ for acetophenone [1] is 1684 cm^{-1} . Consistent with these lowered carbonyl stretching frequencies are basicity measurements of the carbonyl oxygen: the $\text{p}K_{\text{A}}$ of protonated acetylferrocene [4] is -2.80 and that of trimethylsilyl phenyl ketone [5] is -6.49 . It is interesting to note that the ferrocenyl moiety has a very large effect (three to four orders of magnitude: compare $\text{p}K_{\text{A}}$ of -6.15 for acetophenone [6]) on

TABLE I
 CARBONYL STRETCHING FREQUENCIES (cm^{-1}) OF METHYL AND TRIMETHYLSILYL COMPOUNDS

X	$\text{Fc}\overset{\text{O}}{\parallel}\text{CX}^a$	$\text{C}_6\text{H}_5\overset{\text{O}}{\parallel}\text{CX}$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CX}$	$(\text{CH}_3)_3\overset{\text{O}}{\parallel}\text{CCX}$
CH_3	1672	1684 ^b	1715 ^d	1709 ^e
$\text{Si}(\text{CH}_3)_3$	1589	1618 ^c	1645 ^c	1636 ^c
Difference	83	66	70	73

^a This work. ^b Ref. 1. ^c Ref. 2. ^d Ref. 7. ^e Ref. 8.

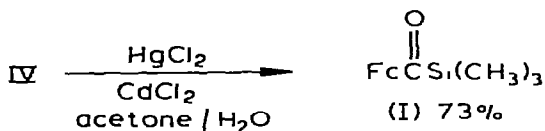
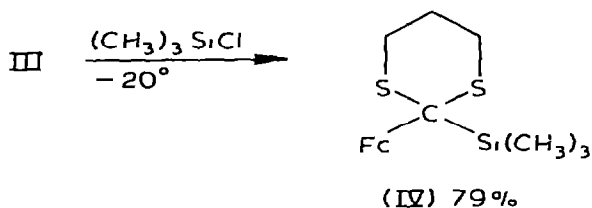
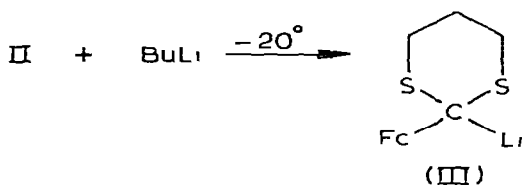
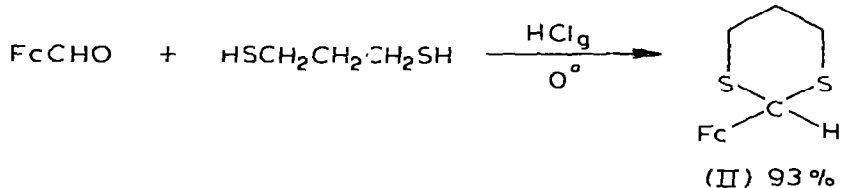
the basicity of adjacent carbonyls while a silyl group does not (compare pK_A of -7.74 for *t*-butyl phenyl ketone [5]); on the other hand, the silyl group has a large effect on $\nu(\text{CO})$ while a ferrocenyl group has a much smaller effect (see Table 1). These facts coupled with recent theoretical activity on the unusual electronic properties of metallocenes [9] and of the Group IV metal carbonyl compounds [10] led us to study ferrocenyl trimethylsilyl ketone (I) a compound containing both of these groups in positions adjacent to the carbonyl function.



Results

Compound I was prepared from ferrocenylaldehyde in four steps as outlined in Scheme 1. Yields at each step were excellent; however, several modifica-

SCHEME 1



Fc = ferrocenyl

tions of literature procedures were required. We found that trimethylsilylation of III at 0° did not give acceptable yields of IV upon application of Brook's [11] general procedure. Furthermore, again in contrast to the general published procedures [11], we found it necessary to hydrolyze IV using quite precise conditions. Equimolar quantities of CdCO₃, HgCl₂ and H₂O were added in a two-fold excess over IV. The reaction's progress was monitored by CO₂ evolution. It should be noted that a number of hydrolysis methods were unsuccessful [12-14]. Compounds I, II and IV, prepared for the first time, were characterized by elemental analysis (C and H) and NMR, IR and mass spectroscopy.

Infrared studies

During spectroscopic characterization of I by IR we found that $\nu(\text{CO})$ occurred at very low frequency. Indeed, in Nujol mulls we measured what appeared to be $\nu(\text{CO})$ at 1577 cm⁻¹ while in CCl₄ or C₂Cl₄ the frequency was 1589 cm⁻¹. Because of this low measured frequency we felt it was imperative to unequivocally assign this as the carbonyl stretch. We accomplished this by observing shifts to lower frequency of both the 1589 cm⁻¹ band and the O—D stretch as we added MeOD. Table 2 gives quantitative information for I and acetylferrocene. The simultaneous shifts in $\nu(\text{CO})$ and $\nu(\text{OD})$ are interpreted, in concert with similar observations and interpretations by others [15, 16], in terms of a hydrogen bonding association between the carbonyl oxygen and the OD of MeOD. The $\Delta\nu(\text{OD})$ value (difference between $\nu(\text{OD})$ of pure MeOD and $\nu(\text{OD})$ of MeOD with added base) of acetylferrocene being greater than that of I indicates that acetylferrocene forms a stronger hydrogen bond to MeOD [15] (i.e., more basic behavior). A rough estimate* of the pK_A's would give a value of -3.6 for acetylferrocene and -4.5 for I.

Hammert acidity studies

Because measurements by the infrared technique sometimes give poor pK_A estimates [15], we decided to make an independent measurement on I. We adopted the method of Davis and Geissman [17] to measure the pK_A of acetyl-

TABLE 2

INFRARED STUDY OF I AND ACETYLFERROCENE WITH MeOD

	Solution ^a		
	0.4 M I + 5 M MeOD	0.1 M I + 0.1 M MeOD	0.2 M acetylferrocene + 0.1 M MeOD
$\nu(\text{CO})$ ^b	1589		
$\nu(\text{CO})$ (MeOD) ^c	1576		
$\Delta\nu(\text{CO})$	13		
$\nu(\text{OD})$		2689	2689
$\nu(\text{OD})$ (I) ^d		2594	2583
$\Delta\nu(\text{OD})$		95	106

^a Solutions in tetrachloroethylene. ^b Carbonyl stretching frequency (cm⁻¹) of I. ^c Carbonyl stretching frequency (cm⁻¹) of I with added MeOD. ^d OD stretching frequency (cm⁻¹) of MeOD with added ketone.

^e Value is the same as that reported in ref. 16 for the associated OD stretching frequency.

* Ref. 15, page 256.

TABLE 3
EXPERIMENTAL DETERMINATION OF ΔOD

Silyl ketone I		Acetylferrocene (our measurements)		Acetylferrocene (ref. 4)	
$-H_o$	ΔOD^a	$-H_o$	ΔOD^b	$-H_o$	ΔOD^b
1.27	0.082	1.27	-0.413	1.22	-0.293
1.48	0.102	1.48	-0.377	1.52	-0.297
1.81	0.099	1.81	-0.353	1.81	-0.292
2.24	0.104	2.24	-0.262	2.25	-0.190
2.61	0.216	2.61	-0.120	2.60	-0.004
2.90	0.294	2.90	-0.055	2.84	-0.059
7.72	0.366	3.02	0.063	3.12	0.069
		3.15	0.075	3.32	0.120
		3.24	0.042	3.65	0.163
		3.32	0.031	4.14	0.270
		3.68	0.176	4.43	0.316
		4.14	0.248	4.58	0.302
		4.51	0.297	5.36	0.355
		4.62	0.282	5.60	0.354
				6.06	0.380
				6.55	0.355
				7.75	0.387
				8.88	0.364

^a $\Delta OD = [OD]_{\nu_1} - [OD]_{\nu_2}$ where ν_1 and ν_2 are the wavelengths 262.5 nm and 235 nm in 85.6% H_2SO_4 and in distilled H_2O , respectively. ^b Wavelengths are 260 nm and 227.5 nm in 61.5% H_2SO_4 and distilled H_2O , respectively.

ferrocene and I in aqueous sulfuric acid. In its simplest terms, this method measures pK_A 's at the inflection point of an experimentally obtained plot of ΔOD versus H_o (ΔOD is the difference in the optical density between the ionized BH^+ and unionized B forms of the base whose pK_A is being measured). At the inflection point, $[BH^+] = [B]$ reducing $H_o = \log \frac{[B]}{[BH^+]} + pK_A$ to $H_o = pK_A$. Yates [15] has suggested that a plot of $\log \frac{[B]}{[BH^+]}$ versus $-H_o$ be used to analyze the data presented in Table 3. Such a plot should be linear with a slope characteristic of the class of compounds whose pK_A is being measured. Thus, ketones have slopes

TABLE 4
SLOPE AND pK_A RESULTS FROM PLOTS OF $-H_o$ VERSUS $\log [B]/[BH^+]$

	Silyl ketone I	Acetylferrocene (our measurements)	Acetylferrocene (ref. 4)
Slope ^a	-1.06	-0.75	-0.70
pK_A	-2.76	-2.91	-3.10 ^c
r^b	0.931	0.991	0.967
$\Delta OD (BH^+)$	0.390	0.330	0.375
$\Delta OD (B)$	0.075	-0.450	-0.360

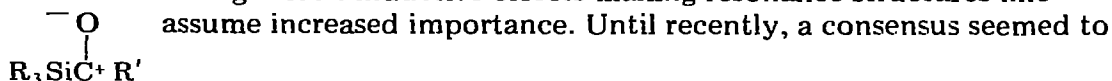
^a $[B]/[BH^+] = (\Delta OD)_{BH^+} - (\Delta OD)/(\Delta OD) - (\Delta OD)_B$ where $\Delta OD (BH^+)$ is the upper limit ΔOD value obtained from sigmoid plots of the data in Table 2. $\Delta OD (B)$ is the lower limit, and ΔOD are the intermediate values. ^b Correlation coefficient for the least square fit of the straight line equation. ^c This value is slightly different from Arnett's reported one [4] because of the different method of obtaining the inflection point.

approximating 0.7, indicative of deviations from normal aniline—anilinium behavior [15, 18] (in which the slope would equal 1.0). In such a plot, the pK_A is the H_o which corresponds to $\log \frac{[B]}{[BH^+]} = 0$. Listed in Table 4 are the results using this treatment for I, acetylferrocene as measured by us, and acetylferrocene using Arnett's [4] reported data.

We have experienced some experimental difficulties with ketone I which have limited the number of measurements we could make. There is an absorption band in the dilute acid spectrum of I at 255 nm which at higher acid concentrations become poorly defined. This band is obtained reversibly, but not instantaneously. Its appearance makes high acidity measurements less certain. Further, we note that I has a very narrow range of ΔOD values when compared with acetylferrocene, again leading to difficulties in obtaining highly accurate data. We believe that the 255 nm band contributes to the higher than normal slope for ketone I (1.06 vs. 0.7 for most ketones). Thus our pK_A value for I of -2.8 is probably in error by 0.2-0.3 pK units [18]. We believe a value of -3.0 to -3.1 is more realistic and point out that such values are quite similar to those for acetylferrocene.

Discussion

Since the discovery of α -silyl ketones and the realization that they possessed unusual spectroscopic properties, numerous explanations have been offered for these properties [2]. They ranged from $d_\pi - p_\pi$ interactions with vacant $3d$ silicon orbitals to strong silicon inductive effects making resonance structures like



be forming favoring the inductive effect explanation [2]. The lines of argument favoring this view are: (1) the enhanced basicity of α -silyl ketones measured by both IR and Hammett acidity methods [5] (2) the lack of effect on the spectroscopic properties when strong $d_\pi - p_\pi$ bonding substituents are directly bonded to silicon [19], and (3) extended Hückel calculations in which d orbital parameters have little effect [20].

Recently, however, perturbation theory calculations [10] and both spectroscopic and electrochemical measurements [21] have reopened this question. The calculations suggest not only that $d_\pi - p_\pi$ contributions to lowered $\nu(\text{CO})$ outweigh inductive effects, but that such a view is also consistent with basicity studies [5] just mentioned. Bock and co-workers [21] have interpreted ionization potential, charge transfer complex, polarographic and electronic spectral data to be consistent with not only important inductive effect contributions by silicon in the groundstate, but also additional $d_\pi - p_\pi$ contributions.

While explanations for the spectroscopic and chemical behavior of α -silyl ketones will remain controversial for some time, many of the controversies regarding the interaction of metallocenyl groups at electron deficient sites have disappeared with the recent work of Traylor [9]. He proposes that such electron deficient centers are stabilized by $\sigma - \pi$ conjugation through a vertical stabilization process [9]. Such conjugation is a phenomenon capable of explaining a wide variety of experiments in not only metallocene chemistry, but also in other areas of organometallic chemistry [9].

We have carried out the experiments described earlier to ascertain what the effect of two highly perturbing groups would be on a carbonyl group. Our pK_A value (-3.0 to -3.1) for I is within $0.3 pK_A$ units of the reported [4] value for acetylferrocene. Yet its carbonyl stretching frequency (1589 cm^{-1}) is among the lowest known*. Since the basicity of I is 3 to 4 orders of magnitude greater than that of other reported silyl ketones, it is clear that the ferrocenyl group exercises the dominant basicity enhancing effect. On the other hand it is quite difficult to assess the effect of the trimethylsilyl group because (1) of the uncertainties of our pK_A measurements and (2) the effect is quite small. In contrast with the pK_A measurements, the carbonyl stretching frequency appears to be dominated by the silyl substituent. Reference to Table 1 indicates that the replacement of CH_3 by $\text{Si}(\text{CH}_3)_3$ in FcCOX , $\text{C}_6\text{H}_5\text{COX}$, CH_3COX and $(\text{CH}_3)_3\text{CCOX}$ leads to lowered $\Delta\nu(\text{CO})$ values of 83, 66, 70, and 73 cm^{-1} . The values for $\text{C}_6\text{H}_5\text{COX}$ and CH_3COX can be considered "normal" shift changes. We note that the 73 cm^{-1} shift for the tertiary butyl compounds is consistent with slightly enhanced lowering of the $\nu(\text{CO})$ for $(\text{CH}_3)_3\text{CCOSi}(\text{CH}_3)_3$ caused by steric effects. Such effects are well known; in fact, Taft's steric parameter, E_s , has been linearly correlated [23] with $\nu(\text{CO})$. We believe the larger 83 cm^{-1} change in going from acetylferrocene to I is consistent with a greater steric effect (the ferrocenyl group [24] has been shown to be unusually bulky).

We conclude that ketone I, despite difficulties we have had in obtaining an exact basicity measurement, has several interesting characteristics: (1) its ferrocenyl group appears to dominate its basicity, (2) its silyl group has little, if any, measurable effect on basicity, and (3) the carbonyl stretching frequency of I is dominated by steric factors.

Experimental

All reactions were carried out under an atmosphere of prepurified nitrogen. Elemental analyses were performed by Huffman Laboratories (Wheatridge, Colorado). IR spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. Silver chloride plates were used in the MeOD study. Band intensities were recorded as very strong (vs), strong (s), medium (m), weak (w), and shoulder (sh). The NMR spectra were recorded using a JEOL C 60 HL high resolution spectrometer. All chemical shifts are expressed in δ units (ppm) downfield from tetramethylsilane. Mass spectra were recorded using a Varian CH-5 mass spectrometer. The UV spectra were recorded on a Beckman Acta V spectrophotometer. Boiling points were recorded at prevailing pressure ($\sim 640 \text{ mm}$) unless otherwise indicated. Boiling and melting points are uncorrected.

The pK_A measurements were carried out using the methods of Stewart and Yates [6] and Davis and Geissmann [17].

Preparation of 2-ferrocenyl-1,3-dithiane (II)

Into a 500 ml 3-neck flask equipped with a gas inlet tube and a mechanical stirrer was charged 30.0 g (0.14 mole) of ferrocenecarboxaldehyde (Arapahoe

* Brook [22] has prepared several ketones [e.g., $(\text{C}_6\text{H}_5)_3\text{SiCOSi}(\text{C}_6\text{H}_5)_3$] whose $\nu(\text{CO})$ is approximately 1560 cm^{-1} .

Chemical Co.), 15 ml (0.15 mole) of 1,3-propanedithiol (Aldrich), and 250 ml of benzene. After cooling to 0°, hydrogen chloride was bubbled slowly into the reaction. A precipitate was formed within a few minutes; addition of HCl (g) was continued for four hours. After addition of 250 ml of benzene, the mixture was washed with 1 M NaOH and saturated NaCl. The benzene layer was separated and dried over MgSO₄. Removal of solvent by rotary evaporation yielded 39.7 g (93%) of a yellow crystalline material (m.p. 110-112°).

The crude product was suitable for further synthetic work. An analytical sample was prepared by slurring 0.5 g in 75 ml of hexane followed by gravity filtration. Brilliant orange-yellow needles (m.p. 110-110.5°) precipitated from the cooled filtrate. (Found: C, 55.01; H, 5.42. C₁₄H₁₆FeS₂ calcd.: C, 55.27; H, 5.30%.)

The IR spectrum (CCl₄ and nujol) had principal bands at 3104 m, 2952 s, 2901 s, 1424 s, 1292 s, 1107 s, 1003 s, 815 s, and 776 s cm⁻¹. The NMR spectrum (CDCl₃) consisted of peaks at 1.99 (m) 2H, 2.95 (m) 4H, 4.24 singlet superimposed on multiplet 9H, and 4.97 (s) 1H. The mass spectrum showed principal *m/e* (intensity) peaks at: 306 (11), 305 (21), molecular ion 304 (100), 230 (71), 204 (18), 186 (37), 165 (26), 121 (67), and 56 (30).

Preparation of 2-ferrocenyl-2-lithio-1,3-dithiane (III)

Into a thoroughly dry 1 liter 3-neck flask fitted with a nitrogen inlet, mechanical stirrer, and addition funnel was charged 15.0 g (49 mmole) of 2-ferrocenyl-1,3-dithiane and 120 ml THF (freshly distilled from LiAlH₄). The solution was maintained between -20 and -30° as 21.0 g (52 mmole) 1.6 M *n*-butyllithium was added. The addition period was 10-15 minutes after which the reaction mixture was stirred at -30° for about 10 h. Compound III was used *in situ* in the following reaction.

Preparation of 2-ferrocenyl-2-trimethylsilyl-1,3-dithiane (IV)

To the stirred solution prepared above and maintained between -20 and -30° was added trimethylchlorosilane (6.2 g; 57 mmole) over 5 minutes. A precipitate formed immediately. The bright orange reaction mixture was stirred an additional hour at -20 to -30°. The precipitated product was isolated by low temperature suction filtration. It was washed with cold THF and subsequently air dried (14.6 g; 79%; m.p. 161-163°).

An analytical sample was prepared by repeated recrystallization of 0.5 g in 500 ml petroleum ether (m.p. 161-162°). (Found: C, 54.21; H, 6.39. C₁₇H₂₄FeSiS₂ calcd.: C, 54.24; H, 6.43%.)

The IR spectrum (CCl₄ and nujol) had principal bands at 3106 m, 2960 m, 2927 m, 2900 m, 1233 s, 1105 m, 1002 s, 885 s, 854 s, 838 s, and 824 s cm⁻¹. The NMR spectrum (CDCl₃) consisted of peaks at -0.03 (s) 9H, 2.12 (m) 2H, 3.04 (m) 4H, and 4.19 (m) 9H prominent singlet within multiplet. The mass spectrum showed principal *m/e* (intensity) peaks at: 378 (10), molecular ion 377 (14), 376 (48), 303 (62), 271 (26), 229 (71), 121 (29), and 73 (100).

Preparation of ferrocenyl trimethylsilyl ketone (I)

Into a 50 ml 3-neck flask equipped with reflux condenser, addition funnel, magnetic stirring bar and nitrogen inlet tube was charged 3.6 g (13 mmole) of

mercuric chloride. About 10 ml of acetone and 0.24 ml of distilled water were added to dissolve the mercuric chloride before 2.3 g (13 mmole) of cadmium chloride was added. Finally, 3 ml of acetone were used to rinse the flask. The resulting slurry was heated to reflux as 1.0 g (27 mmole) of 2-ferrocenyl-2-trimethylsilyl-1,3-dithiane in 20 ml of THF was added. The addition was carried out such that a brisk reflux was maintained. Evolution of CO₂ was monitored and heating was maintained for 15 minutes after the final addition. No more CO₂ evolved at this time. The reaction mixture was filtered through a sintered glass filter and rinsed with acetone. Removal of solvent from the filtrate by rotary evaporation gave 0.56 g (73%) of dark red crystalline I with m.p. 93-95°.

Analytically pure material (m.p. 95-96°) was prepared by recrystallization from mixed hexanes (Found: C, 59.00; H, 6.35. C₁₄H₁₈FeSiO calcd.: C, 58.75; H, 6.34%).

The IR spectrum (CCl₄ and nujol) had principal bands 3104 w, 2965 m, 2901 w, 1577 vs, 1245 vs, 844 s, 819 s, and 810 s cm⁻¹. The NMR spectrum (CDCl₃) consisted of peaks at 0.32 (s) 9H, 4.17 (s) 5H, 4.52 (t) 2H, and 4.98 (t) 2H. The mass spectrum showed principal *m/e* (intensity) peaks at: 287 (16), molecular ion 288 (65), 243 (34), 213 (35), 212 (100), 195 (41), 185 (20), and 129 (32).

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