

REACTION OF FERROCENYLMETHYL DERIVATIVES OF SILICON AND GERMANIUM WITH METHANOL: SOLVOLYSIS OF THE METAL-CARBON BOND IN THE PRESENCE OF FERRIC IONS

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SUMMARY

Nine ferrocenylmethyl derivatives of silicon and germanium were prepared and found to undergo methanolysis of their C-M (M = Si or Ge) bonds in the presence of ferric ions to give ferrocenylmethyl methyl ether. For this reaction, relative rate studies and polarographic studies of the pertinent ferrocene derivatives were carried out to obtain some insight into the reaction mechanism. The substituted ferricenium ion intermediate which is formed by oxidation with ferric ions can readily undergo nucleophilic attack by methanol on the metal (Si or Ge) atom. The observed higher reactivity of the germanium derivative relative to the silicon congener in this reaction is not that expected for the usual base-catalyzed attack at the metal atom, and may be reasonably interpreted in terms of a possible change in the transition state depending on the nature of the leaving group, *viz.* on the acidity of the corresponding hydrocarbon acid, in the solvolysis of the C-M bond.

INTRODUCTION

In a series of studies on reactions of organosilyl- and organogermeryl-substituted ferrocenes, we previously reported that the M-M (M = Si and/or Ge) bonds adjacent to the ferrocenyl group are readily cleaved in a highly dilute alcohol solution of hydrogen chloride^{1,2} and also in alcohols containing ferric ions³. We proposed a plausible mechanism involving substituted ferricenium ion intermediates produced by an acid-catalyzed autoxidation in the former case or by a redox process between ferrocene derivatives and ferric ions in the latter. It was also suggested that the ferricenium ion thus formed may have a strong electron-withdrawing effect on the adjacent M-M bond, which consequently undergoes ready alcoholysis.

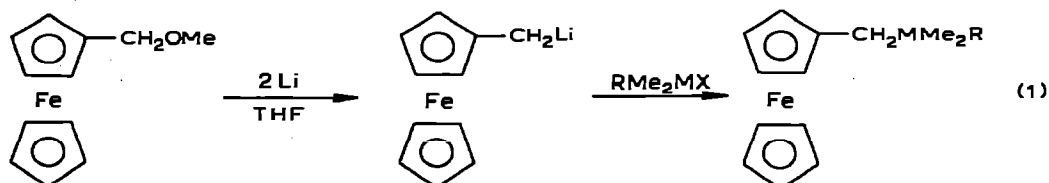
In connection with these studies, it became desirable to examine the reactivity of ferrocenylmethyl-metal (Si or Ge) compounds in both acid-catalyzed solvolysis and oxidation-alcoholysis in the presence of ferric ions, with the aim of elucidating solvolytic behavior of the metal center. We report here an anomalously facile cleavage of a metal-carbon bond of ferrocenylmethyl derivatives of silicon and germanium, which takes place when these compounds are treated with absolute methanol in the presence of ferric ions⁴. We also describe relative rate studies for the oxidation-

alcoholysis and some data on polarographic half-wave potentials of appropriate ferrocene derivatives both measured in order to obtain insight into the mechanism of the reaction.

RESULTS AND DISCUSSION

Preparation of ferrocenylmethyl derivatives of silicon and germanium

All ferrocenylmethyl derivatives of silicon and germanium used here were synthesized by the reaction of appropriate chloro (or alkoxy)silanes or chlorogermanes with ferrocenylmethyl lithium in tetrahydrofuran (THF) [eqn. (1)] as described by Nesmeyanov and co-workers⁵ for the preparation of (ferrocenylmethyl)trimethylsilane (I).



- | | |
|--|-------------------|
| (I) M=Si, R=Me | (VI) M=Si, R=Ph |
| (II) M=Si, R=Et | (VII) M=Si, R=OMe |
| (III) M=Si, R=i-Pr | (VIII) M=Ge, R=Me |
| (IV) M=Si, R=Me ₃ SiCH ₂ | (IX) M=Ge, R=i-Pr |
| (V) M=Si, R=Me ₃ Si | |

Yields, physical properties and elemental analyses for compounds (I)–(IX) are given in Table 1; ¹H NMR data are given in Table 2.

TABLE 1

YIELDS, PHYSICAL PROPERTIES, AND ELEMENTAL ANALYSES OF FERROCENYLMETHYL DERIVATIVES OF SILICON AND GERMANIUM

Compound No.	Formula	Yield (%)	B.p. (°C/mmHg) [m.p. (°C)]	n _D ²⁰	Analysis found (calcd.) (%)	
					C	H
(I)	C ₅ H ₅ FeC ₅ H ₄ CH ₂ SiMe ₃	58.3	118/3 [46–47] ^a			
(II)	C ₅ H ₅ FeC ₅ H ₄ CH ₂ SiMe ₂ Et	26.1	116–118/2	1.5671	62.82 (62.93)	7.99 (7.75)
(III)	C ₅ H ₅ FeC ₅ H ₄ CH ₂ SiMe ₂ i-Pr	43.4	137/3	1.5593	64.10 (63.99)	8.25 (8.06)
(IV)	C ₅ H ₅ FeC ₅ H ₄ CH ₂ SiMe ₂ CH ₂ SiMe ₃	40.1	150–152/2	1.5499	59.41 (59.28)	8.21 (8.19)
(V)	C ₅ H ₅ FeC ₅ H ₄ CH ₂ SiMe ₂ SiMe ₃	23.9	135–137/2.5	1.5619	58.41 (58.16)	7.90 (7.93)
(VI)	C ₅ H ₅ FeC ₅ H ₄ CH ₂ SiMe ₂ Ph	14.5	172–174/2	1.5939	68.50 (68.26)	6.77 (6.63)
(VII)	C ₅ H ₅ FeC ₅ H ₄ CH ₂ SiMe ₂ OMe	22.8	135–137/3	1.5620	59.24 (58.34)	7.41 (6.99)
(VIII)	C ₅ H ₅ FeC ₅ H ₄ CH ₂ GeMe ₃	37.3	114–115/2 [37.5–38.0]		53.32 (53.09)	6.36 (6.36)
(IX)	C ₅ H ₅ FeC ₅ H ₄ CH ₂ GeMe ₂ i-Pr	44.8	130–141/2	1.5732	56.04 (55.74)	7.14 (7.02)

^a Lit.⁵ m.p. 46.5–47.5°.

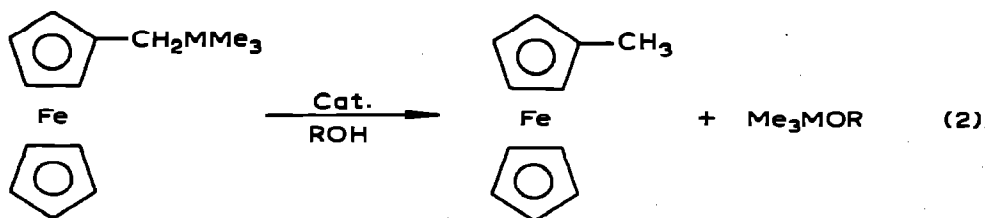
TABLE 2

¹H NMR DATA FOR FERROCENYLMETHYL DERIVATIVES OF SILICON AND GERMANIUM (IN CCl₄)

Compound		Chemical shifts (τ-values) ^a					
No.	Formula	H ^a	H ^b	H ^c	H ^d	H ^e	H ^f
(I)	C ₅ H ₅ ^d FeC ₅ H ₅ ^e CH ₂ ^f Si(CH ₃ ^a) ₃	10.08 (s)	8.33 (s)	6.14 (m)	6.04 (s)		
(II)	C ₅ H ₅ ^d FeC ₅ H ₅ ^e CH ₂ ^f Si(CH ₃ ^a) ₂ (CH ₂ ^b CH ₃ ^c)	10.14 (s)	9.31 (m)	8.31 (s)	6.12 (m)	6.04 (s)	
(III)	C ₅ H ₅ ^d FeC ₅ H ₅ ^e CH ₂ ^f Si(CH ₃ ^a) ₂ [CH ^b (CH ₃ ^c) ₂]	10.15 (s)	9.11 (m)	8.30 (s)	6.11 (bs)	6.01 (s)	
(IV)	C ₅ H ₅ ^d FeC ₅ H ₅ ^e CH ₂ ^f Si(CH ₃ ^a) ₂ CH ₂ ^g Si(CH ₃ ^a) ₃	10.38 (s)	10.08 (s)	10.00 (s)	8.31 (s)	6.11 (m)	6.03 (s)
(V)	C ₅ H ₅ ^d FeC ₅ H ₅ ^e CH ₂ ^f Si(CH ₃ ^a) ₂ Si(CH ₃ ^a) ₃	10.06 (s)	10.05 (s)	8.25 (s)	6.13 (bs)	6.03 (s)	
(VI)	C ₅ H ₅ ^d FeC ₅ H ₅ ^e CH ₂ ^f Si(CH ₃ ^a) ₂ (C ₆ H ₅ ^g)	9.79 (s)	8.08 (s)	6.16 (m)	6.06 (s)	2.79 (bs)	
(VII)	C ₅ H ₅ ^d FeC ₅ H ₅ ^e CH ₂ ^f Si(CH ₃ ^a) ₂ (OCH ₃ ^g)	10.01 (s)	8.40 (s)	6.66 (s)	6.08 (s)	6.06 (s)	
(VIII)	C ₅ H ₅ ^d FeC ₅ H ₅ ^e CH ₂ ^f Ge(CH ₃ ^a) ₃	9.96 (s)	8.15 (s)	6.14 (m)	6.06 (s)		
(IX)	C ₅ H ₅ ^d FeC ₅ H ₅ ^e CH ₂ ^f Ge(CH ₃ ^a) ₂ [CH ^b (CH ₃ ^c) ₂]	9.93 (s)	8.79 (s)	8.04 (s)	6.03 (m)	5.91 (s)	

^a s: singlet, bs: broad singlet, and m: multiplet.*Acid-catalyzed solvolysis of ferrocenylmethyl derivatives of silicon and germanium*

When (ferrocenylmethyl)trimethylsilane (I) was heated either in oxygen-free methanolic solution containing a catalytic amount of hydrogen chloride or in acetic acid, cleavage of the silicon-carbon bond gave methylferrocene, along with trimethylmethoxysilane or trimethylacetoxysilane respectively. Lewis acids, such as aluminum chloride or boron trifluoride, were also effective catalysts for the methanolysis of (I).



(I) M = Si

R = Me, Ac; Cat. = HCl, AlCl₃, BF₃·OEt₂

(VIII) M = Ge

(Ferrocenylmethyl)trimethylgermane (VIII) reacted similarly, giving methylferrocene and trimethylmethoxygermane [eqn. (2)]. The results are summarized in Table 3.

It is likely that initial protonation (in the case of a protic acid catalyst) of the ferrocene derivatives is an essential step in the observed solvolyses, the primary

TABLE 3

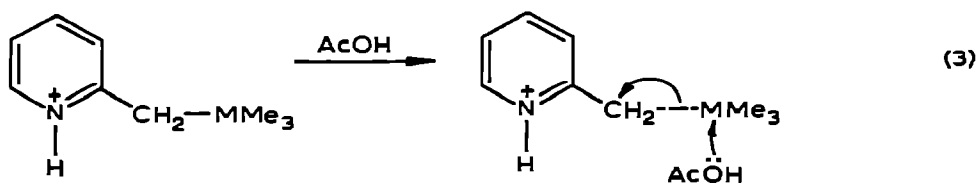
ACID-CATALYZED SOLVOLYSIS OF (FERROCENYLMETHYL)TRIMETHYLSILANE (I) AND -GERMANE (VIII)

Compound		Reaction conditions ^a				Methyl-ferrocene yield ^b (%)
No.	mmole	Catalyst (mmole)	Solvent (ml)	Temp. (°C)	Time (h)	
(I)	0.434	HCl (22.4)	MeOH (10)	140	43	71.3
(I)	0.360	AlCl ₃ (5.40)	MeOH (10)	100	25	74.5
(I)	0.416	BF ₃ ·Et ₂ O ^c	MeOH (10)	80	43	72.5
(I)	0.445		AcOH (10)	140	43	76.5
(VIII)	0.404	HCl (22.4)	MeOH (10)	140	43	74.4
(VIII)	0.338	AlCl ₃ (5.07)	MeOH (10)	100	25	73.4
(VIII)	0.401	BF ₃ ·Et ₂ O ^c	MeOH (10)	80	43	73.7
(VIII)	0.432		AcOH (10)	140	43	73.9

^a Oxygen was removed carefully from the solution. ^b Isolated yield. ^c 1 ml was used.

site of protonation being either the cyclopentadienyl ring or the iron atom⁶. The protonated ferrocenyl group is electron-accepting in contrast with the parent ferrocenyl group which is well known as an electron-donor⁷. Thus once protonation of, for example, (ferrocenylmethyl)trimethylsilane occurs, facile cleavage of the CH₂-SiMe₃ bond follows because the protonated ferrocenylmethyl moiety would be expected to act as a good leaving group and the silicon atom to be very susceptible to the attack of solvent molecules.

It is noteworthy that comparable reactivity for (2-pyridylmethyl)trimethylmetal (Si⁸ and Ge) compounds toward acetic acid was observed⁴, which implies production of a very good leaving group as shown in eqn. (3). In this case, electron deficiency at nitrogen resulting from protonation is obviously responsible for the facile cleavage of the metal-carbon bond.



Methanolysis of ferrocenylmethyl derivatives of silicon and germanium in the presence of ferric chloride or other oxidizing agents

As observed with the ferrocene derivatives bearing M-M (M=Si and/or Ge) groups bonded to the cyclopentadienyl ring³, all compounds examined here, *viz.* (I)-(IX), readily reacted. For example, treatment of (ferrocenylmethyl)trimethylsilane (I) dissolved in dry methanol with anhydrous ferric chloride in a degassed sealed glass tube resulted in an immediate color change of the mixture to greenish blue, indicating the formation of ferricenium ion; after about 40 min, the color faded. From the resultant yellow solution, methoxytrimethylsilane and ferrocenylmethyl methyl

TABLE 4

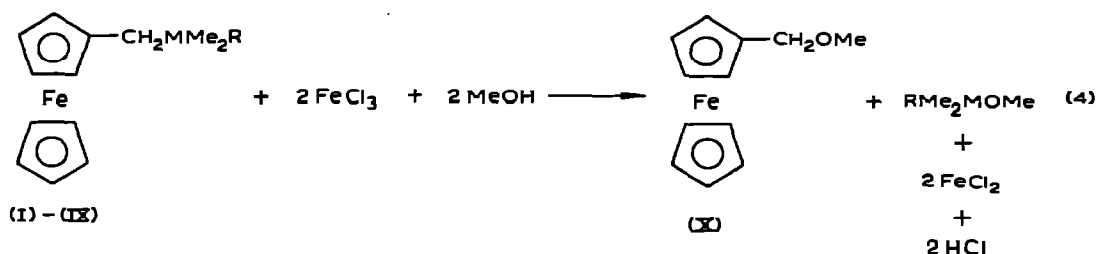
METHANOLYSIS OF FERROCENYLMETHYL DERIVATIVES OF SILICON AND GERMANIUM IN THE PRESENCE OF FERRIC IONS AND OTHER OXIDIZING AGENTS UNDER OXYGEN-FREE CONDITIONS^a

Compound		Reaction conditions		Products ^b (%)
No.	(mmole)	Oxidizing agent (mmole)	Time (h)	
(I)	(0.815)	FeCl ₃ (0.010) ^c	234	(I) (97.7)
(I)	(0.432)	[Fe(C ₅ H ₅) ₂]FeCl ₄ (0.0076) ^c	51	(I) (82.2)
(I)	(0.352)	FeCl ₃ (0.356)	20	(I) (35.8), (X) (36.8)
(I)	(0.371)	FeCl ₃ (0.754)	65	(X) (91.1)
(I)	(0.368)	I ₂ (0.375)	20	(X) (89.0)
(I)	(0.379)	Ce(SO ₄) ₂ · nH ₂ O ^d	20	(X) (75.5)
(I)	(0.397)	Cu(OAc) ₂ · H ₂ O (0.805)	20	(X) (90.1)
(II)	(0.365)	FeCl ₃ (0.730)	35	(X) (74.5)
(III)	(0.347)	FeCl ₃ (0.790)	35	(X) (79.3)
(IV)	(0.267)	FeCl ₃ (0.546)	17	(X) (84.5)
(V)	(0.300)	FeCl ₃ (0.600)	35	(X) (70.6)
(VI)	(0.278)	FeCl ₃ (0.574)	17	(X) (85.2)
(VII)	(0.300)	FeCl ₃ (0.600)	35	(X) (77.2)
(VIII)	(0.347)	FeCl ₃ (0.753)	41	(X) (87.1)
(IX)	(0.342)	FeCl ₃ (0.785)	3	(X) (92.4)

^a Carried out in 10 ml of methanol, at room temperature unless stated otherwise. ^b (X) = ferrocenylmethyl methyl ether. ^c At 90°. ^d 293 mg of ceric sulfate assay minimum 80% was used.

ether (X) were obtained in high yield. It was found that two equivalents of ferric chloride per equivalent of the substrate were essential for complete cleavage when oxygen was rigorously removed from the solution prior to reaction. The results obtained are summarized in Table 4.

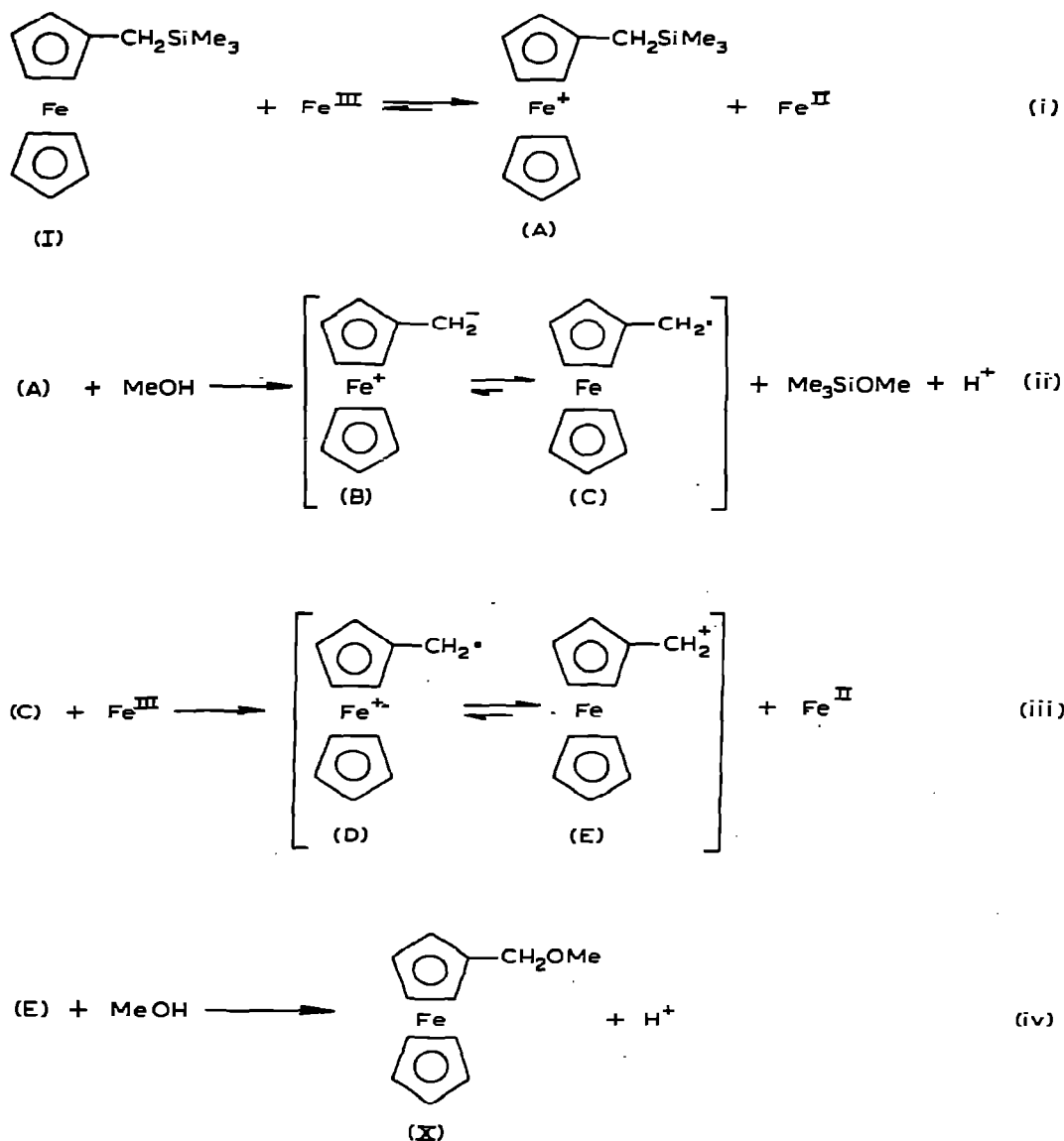
An apparent stoichiometry for the reaction is shown in eqn. (4).



When the same reactions were carried out under ambient conditions, only a catalytic quantity of ferric chloride was required. Previously, we discussed³ the very ready participation of oxygen in Fe^{II} ⇌ Fe^{III} oxidation-reduction process, therefore, the oxygen present in the reaction mixture must play an important role in reoxidizing Fe^{II} to Fe^{III}, the latter then oxidizes ferrocene derivatives.

Furthermore, the analogous methanolysis of compound (I) was found to take place quantitatively in the presence of oxidizing agents such as iodine and ceric and cupric ions, which are known to oxidize ferrocene to ferricenium ion (Table 4)⁹⁻¹¹.

SCHEME 1

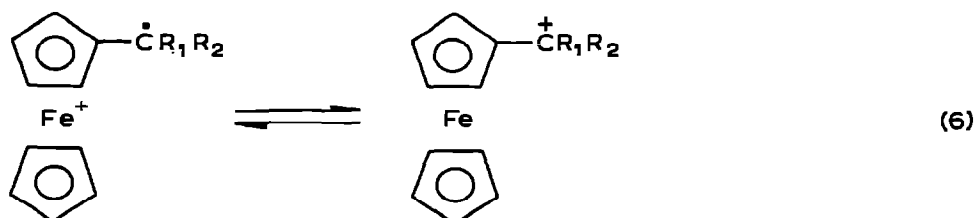
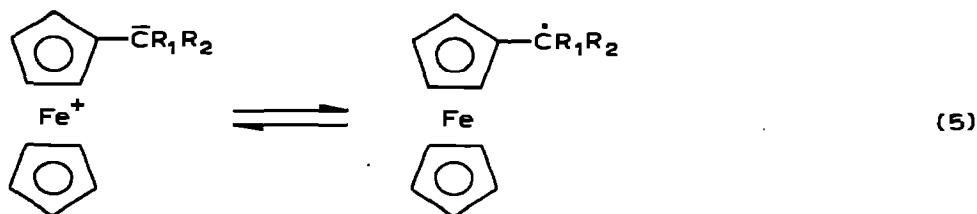


As briefly described in a recent communication⁴, the reaction may be best formulated as proceeding in the sequence depicted by Scheme 1, exemplified by compound (I).

Step (i) involves reversible oxidation-reduction, which is generally recognized in the chemistry of ferrocene^{1,2}, and is known to be very fast^{13,14}. The resulting substituted ferricenium ion (A) may undergo methanolysis at the adjacent highly polarized silicon-carbon bond in a subsequent, probably rate-determining, step (ii); here the strongly electron-withdrawing effect of the ferricenium ion^{1,5} renders (B) a good leaving

group. The ferrocenylmethyl radical (C), presumably formed by a concomitant intramolecular redox process, would then be rapidly oxidized by a second mole of ferric ion ether to ferricenylmethyl radical (D) or to ferrocenylcarbonium ion (E) [step (iii)]. It is well established that ferrocenylcarbonium ions are very stable¹⁶. Finally, the product, ferrocenylmethyl methyl ether (X) is certainly formed from the carbonium ion (E) in methanol solution.

In Scheme 1, we assumed two intramolecular redox processes generally expressed by eqns. (5) and (6) which seem to be potentially characteristic of the ferrocenylmethyl system. Several studies¹⁷⁻²¹ of the latter process have been reported and the position of the equilibrium depends on the substituents R_1 and R_2 . With both R_1 and R_2 as hydrogens in Scheme 1, the equilibrium appears to lie far on the carbonium ion side. On the other hand, none of the examples of the former process, *viz.* eqn. (5), has been reported to date. The process may now be postulated on the basis of the fact that no traces of methylferrocene were detected in the products.



Although any radical (C) once formed, if wholly free, would give a coupling product, *e.g.* 1,2-diferrocenylethane, we could not detect such a product in the reaction mixture. This probably implies that some intimate counter ions such as Fe_2Cl_6^- are formed in step (i), which are responsible for rapid oxidation of the resultant radical (C) in step (iii). In fact, if a suitable carbonium ion is employed for the oxidation of [α -(trimethylsilyl)benzyl]ferrocene, 1,2-diferrocenyl-1,2-diphenylethane is obtained as a result of the coupling of free ferrocenylphenylmethyl radicals²².

Relative reactivity studies of methanolysis of ferrocenylmethyl derivatives of silicon and germanium in the presence of anhydrous ferric chloride

In order to obtain further information concerning the cleavage mechanism of the M-C (M = Si or Ge) bond as exemplified by Scheme 1, the relative rates of methanolysis of a series of ferrocenylmethyl derivatives of silicon and germanium, (I)-(IX), were measured by a competitive reaction technique taking the relative reactivity of compound (I) as unity. The results are listed in Table 5.

Since step (i) in Scheme 1 is rapid and reversible, the apparent relative rates might be affected to a rather significant extent by the ratio of the equilibrium constants for such a process. The contribution of the equilibrium constants to the overall relative rates may be reasonably estimated from the oxidation potentials of the specifically-substituted ferrocenes, which depend upon electronic effects of the substituent as described below. The net relative rates of step (ii) may thus be reasonably estimated by dividing the overall relative rate k_{rel} by the equilibrium constant K_{rel} in eqn. (8). Values thus obtained of $k_{(ii)rel}$ for compounds (I), (III), (V), (VI), (VII), and (VIII) are listed in Table 5.

Summarizing the results in Tables 5 and 6, we conclude that the net relative reactivities of this reaction cannot be correlated with oxidation potentials of the com-

TABLE 5

RELATIVE RATE CONSTANTS OF METHANOLYSIS OF FERROCENYLMETHYL DERIVATIVES OF SILICON AND GERMANIUM IN THE PRESENCE OF ANHYDROUS FERRIC CHLORIDE

Compound No.	k_{rel}^a	$k_{(ii)rel}^a$
(I)	1.0	1.0
(II)	0.27	
(III)	0.032	0.025
(IV)	0.13	
(V)	1.3	0.87
(VI)	2.8	8.7
(VII)	2.0	3.1
(VIII)	30	11
(IX)	2.0	

^a $k_{rel} = K_{rel} \times k_{(ii)rel}$ (for K_{rel} see Table 6).

TABLE 6

POLAROGRAPHIC HALF-WAVE POTENTIALS OF MONOSUBSTITUTED FERROCENES AT ROOM TEMPERATURE IN ACETONITRILE vs. SATURATED CALOMEL ELECTRODE

Substituent	$E_{1/2}$ (eV)	$\Delta E_{1/2}$ (eV)	K_{rel}	σ_p
CH_2GeMe_3	0.206	-0.141	2.7	
$\text{CH}_2\text{SiMe}_2\text{SiMe}_3$	0.221	-0.126	1.5	
$\text{CH}_2\text{SiMe}_2\text{CH}(\text{CH}_3)_2$	0.224	-0.123	1.3	
CH_2SiMe_3	0.231	-0.116	1.0	-0.29 ^a
$\text{CH}_2\text{SiMe}_2\text{OCH}_3$	0.242	-0.105	0.65	
$\text{CH}_2\text{SiMe}_2\text{C}_6\text{H}_5$	0.260	-0.087	0.32	
CH_2CH_3	0.287	-0.060		-0.151 ^b
CH_3	0.290	-0.057		-0.170 ^b
H	0.347	0.000		0.000 ^b
SiMe_3	0.354	0.007		-0.07 ^b
COCH_3	0.600	0.253		0.502 ^b

^a From ref. 37 (a). ^b From ref. 39.

pounds concerned. Furthermore, electron-withdrawing substituents such as phenyl and methoxy groups on silicon even slightly enhance the reactivity of compounds (VI) and (VII), while fairly bulky substituents such as ethyl, isopropyl and (trimethylsilyl)methyl groups on silicon and germanium markedly decrease the reactivity of compounds (II), (III), (IV), and (IX). The observations seem to be consistent with the reaction sequence shown in Scheme 1 which involves rate-determining nucleophilic attack by oxygen of the solvent methanol on the metal.

Mechanism of the anomalous solvolysis of the metal-carbon bonds

In addition to the observations described above, it is noteworthy that the germanium compounds (VIII) and (IX) undergo cleavage much faster than the silicon analogs (I) and (III), respectively. The order of reactivity for each pair of silicon and germanium compounds is not that expected for a usual base-initiated attack at the metal atom²³. Although the reasons for the reversed relative reactivity order ($\text{Ge} > \text{Si}$) are not fully understood at the moment, dependence of the rate constant for base-catalyzed cleavage of R-MMe_3 upon the acidity of the corresponding hydrocarbon acid $\text{R-H}^{23,24}$ is highly suggestive. If R is a very good leaving group or R-H is a strong acid, then even with a weak nucleophile reaction can take place, in which the formation of a pentacoordinate intermediate $[\text{RMMe}_3(\text{nucleophile})]$ is the limiting step, followed by fast cleavage of the R-M bond. A germanium compound would be more capable of forming such a complex than a silicon compound²⁵, especially in case of a compound having an electron deficient center in the leaving group such as $\text{Fc}^+\text{CH}_2\text{-MMe}_3$ ($\text{Fc}^+ = \text{ferricenyl}$) and $2\text{-(Me}_3\text{MCH}_2)\text{C}_5\text{H}_4\text{NH}^+$ [eqn. (3)]. It may be said that the transition state is reactant-like. Therefore, in general a decrease in metal-carbon bond strength in going from silicon to germanium should also be responsible for the higher reactivity of germanium compound compared with the silicon congener toward nucleophilic attack on the metal atom.

On the other hand, if R is a poor leaving group or R-H is a weak acid, then with a strong nucleophile, the mechanism will involve the rapid and reversible formation of the pentacoordinate complex followed by slow cleavage of the R-M bond. In general, a silicon compound undergoes base-catalyzed alcoholysis (or hydrolysis) much faster than a germanium analog, presumably, partly because the Si-O bond energy is much larger than the Ge-O bond energy²⁶ in the resulting $\text{Me}_3\text{M-OR}'$ compounds. In other words, the transition state would be product-like. The latter type of reaction is usually encountered and many rate studies have been carried out to date. For example, (*m*-chlorobenzyl)trimethylsilane was found by Eaborn *et al.*²⁷ to be 10^3 times more reactive in the alkali cleavage than the germanium congener. They attributed the observed difference in reactivity to increased nuclear shielding on the germanium atom. Recently, Roberts *et al.*²⁸ have discussed the rates of cleavage of cinnamyl and benzyl derivatives of silicon, germanium, and tin in strongly basic media, while it seems to remain ambiguous to distinguish two-step mechanism from single step one in nucleophilic substitution at the metal atom²⁴. However, little has been known so far about solvolysis of Group IVB compounds having a good leaving group.

Polarographic studies on the oxidation of ferrocenylmethyl derivatives of silicon and germanium

We have examined the effect of substituents on the oxidation potentials of the

ferrocenylmethyl silicon and germanium compounds, since the oxidation potentials may well be correlated with the magnitudes of equilibrium constants of step (i) in Scheme 1.

It has been amply demonstrated that the titrimetric^{29,30}, polarographic³¹, and chronopotentiometric³²⁻³⁵ oxidation potentials of substituted ferrocenes depend on the electronic effects of the substituent groups and exhibit a best correlation with their Hammett's σ_p constants.

Thus, we have measured polarographic half-wave oxidation potentials of several ferrocenylmethyl derivatives of silicon and germanium [(I), (III), (V), (VI), (VII), and (VIII)] in acetonitrile as well as some other ferrocene derivatives, the substituent constants of which are known.

Polarographic half-wave oxidation potentials at room temperature, $E_{1/2}$, vs. the saturated calomel electrode for ferrocene derivatives determined in the present study and the differences in the magnitude between each derivative and ferrocene itself, $\Delta E_{1/2}$, are given in Table 6. Since absolute values of these potentials ($E_{1/2}$) may vary with variations in any junction potentials or due to traces of moisture in the solvent^{34,36}, $\Delta E_{1/2}$ was generally used in the correlations. Some data in Table 6 for which σ_p constants are known were used to establish the regression line in Fig. 1. The regression line established by the least-squares method and expressed by eqn. (7), had a correlation coefficient of 0.995 and a standard deviation of $\Delta E_{1/2}$ of 0.012 eV from the regression line.

$$\Delta E_{1/2} = 0.464 \sigma_p + 0.018 \text{ (eV)} \quad (7)$$

The correlation is fairly good and eqn. (7) is tolerably in accord with chronopotentiometric quarter-wave potentials* reported for substituted ferrocenes relative to that for ferrocene ($\Delta E_{1/2}$).

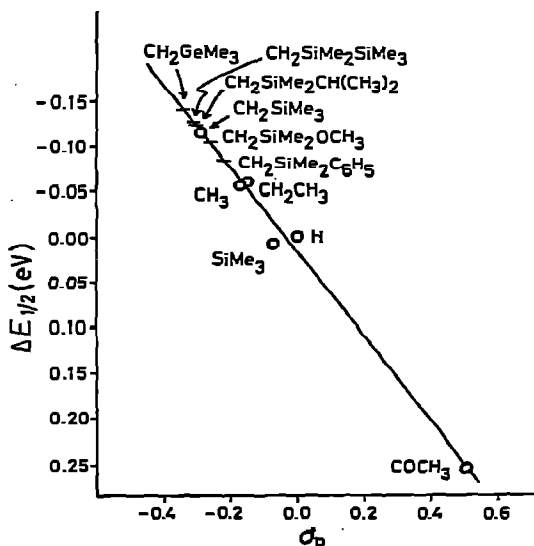


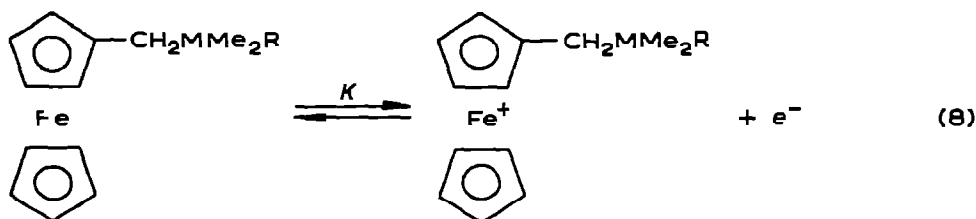
Fig. 1. Relationship between $\Delta E_{1/2}$ of monosubstituted ferrocenes and Hammett's σ_p constants.

* $\Delta E_{1/4} = 0.450 \sigma_p + 0.022 \text{ eV}$ (ref. 34) and $\Delta E_{1/4} = 0.431 \sigma_p + 0.026 \text{ eV}$ (ref. 33).

Attempts to correlate $\Delta E_{\frac{1}{2}}$ with Hammett's σ_m , Taft's σ^* or Brown's σ^+ constants were unsuccessful as previously reported^{30,31,33,34}.

The $\Delta E_{\frac{1}{2}}$ values for the (organometal)methyl groups whose σ_p constants are not available are represented in Fig. 1 by short horizontal lines across the regression line. The electron-donating feature of the metalmethyl groups including silicon, germanium, tin, lead, and mercury relative to the parent methyl group has been amply demonstrated (see *e.g.* ref. 37) and interpreted in terms of σ - π conjugation. In agreement with these results, all metalmethyl groups studied here exhibit a larger electron-donating effect relative to methyl. It was confirmed that trimethylgermylmethyl group is more electron-donating than trimethylsilylmethyl, and that within the silicon compounds, the presence of an electron-withdrawing group such as phenyl or methoxy on the silicon atom slightly enhances oxidation potentials as expected, while the presence of a bulky group such as isopropyl or trimethylsilyl on silicon decrease the oxidation potentials only slightly, reflecting an electron-donating effect of these groups.

In connection with the relative rate study on the cleavage of the metal-carbon bonds of ferrocenylmethyl derivatives of silicon and germanium, we have estimated approximate equilibrium constants for the pertinent ferrocenyl derivatives in eqn. (8). Assuming that $\Delta E_{\frac{1}{2}} = \Delta E^0$, $\log K_A/K_B$ can be obtained by dividing $[(-\Delta E_{\frac{1}{2}A}) - (-\Delta E_{\frac{1}{2}B})]$ by 0.059 (ref. 34). Thus, K_{rel} values calculated for compounds (I), (III), (V), (VI), and (VIII) are listed in Table 6.



EXPERIMENTAL

All boiling and melting points are uncorrected. Reactions using organolithium and organomagnesium compounds were carried out in an oxygen-free dry nitrogen atmosphere. IR spectra were recorded on a Hitachi EPI G3 grating spectrophotometer. NMR spectra were obtained on a Varian T60 spectrometer in carbon tetrachloride solution with cyclohexane or TMS as an internal standard and the data are given in τ -values.

All silanes and germanes except for isopropyl dimethylchlorogermane employed for the preparation of ferrocenylmethyl derivatives of silicon and germanium are known and were prepared by standard methods.

Isopropyl dimethylchlorogermane

An isopropylmagnesium chloride solution was prepared from 4.5 g (0.185 g-atom) of magnesium and 14.1 g (0.180 mole) of isopropyl chloride in 200 ml of THF over a period of 1 h. The Grignard reagent was added slowly to a solution of 30 g (0.172 mole) of dimethyldichlorogermane in 50 ml of THF and the reaction mixture was stirred at room temperature for 2 h and heated at reflux for an additional 2 h.

After removal of most of the THF by distillation, the remaining solid was filtered by using 300 ml of benzene. The filtrate was fractionally distilled to give 12.0 g (38.5% yield) of isopropylidimethylchlorogermane, b.p. 140–141°, n_D^{20} 1.4484. (Found: C, 33.26; H, 7.39. $C_5H_{13}ClGe$ calcd.: C, 33.14; H, 7.23%.) NMR: 9.39 (s, $GeCH_3$) and 8.99 [m, $GeCH(CH_3)_2$].

Ferrocenylmethyl derivatives of silicon and germanium

The following detailed description of the synthesis of compound (III) is typical of the procedure.

A red ferrocenylmethyl lithium solution, prepared from 5.0 g (0.022 mole) of ferrocenylmethyl methyl ether⁵ and 3.0 g (0.43 g-atom) of lithium in 200 ml of THF at -10 to -5° over a period of 4 h, was added to a solution of 3.4 g (0.025 mole) of isopropylidimethylchlorosilane in 50 ml of THF with cooling in an ice bath over a 20-min period. The mixture was stirred at room temperature for 1 h and then hydrolyzed with cooling. The resulting organic layer was separated and the aqueous phase was extracted twice with ca. 100-ml portions of ether. The combined organic layer was dried over anhydrous sodium sulfate. After removal of the solvents, fractional distillation under reduced pressure gave 1.3 g of (ferrocenylmethyl)isopropylidimethylsilane (III). Its IR spectrum exhibited bands near 1000 and 1106 cm^{-1} characteristic of an unsubstituted cyclopentadienyl ring and at 1255 cm^{-1} typical for the $SiCH_3$ grouping.

Yields, some physical properties and analytical data for compounds (I)–(IX) so synthesized are summarized in Table 1; 1H NMR data are given in Table 2.

Acid-catalyzed solvolysis of (ferrocenylmethyl)trimethylsilane (I) and -germane (VIII)

The following is typical of the procedure used. A glass ampoule was charged with 98.0 mg (0.360 mmole) of (ferrocenylmethyl)trimethylsilane (I), 7.8 mg (5.40 mmoles) of anhydrous aluminum chloride, and 10 ml of absolute methanol, and the solution was degassed by several freeze-thawings under reduced pressure. The ampoule was then sealed *in vacuo* and heated at 100° for 25 h. The solution was then added to water (50 ml) and the mixture was extracted twice with 30-ml portions of petroleum ether. The extracts were dried over sodium sulfate. After evaporation of the solvent, the residue was chromatographed through an alumina column (1 × 15 cm) using petroleum ether as an eluant to give 53.0 mg (74.5% yield) of methylferrocene, m.p. 36–37° (lit.³⁸ m.p. 35.5–36.5°). Its IR and NMR spectra were superimposable on those of an authentic sample.

All the results for compounds (I) and (VIII) are summarized in Table 3.

Methanolysis of ferrocenylmethyl derivatives of silicon and germanium in the presence of anhydrous ferric chloride and other oxidizing agents under oxygen-free conditions

The following procedure is typical. In a two-limbed glass tube were placed separately two solutions, one consisting of 101 mg (0.371 mmole) of (I) in 5 ml of absolute methanol, and the other of 122 mg (0.754 mmole) of anhydrous ferric chloride in 5 ml of absolute methanol. The solutions were degassed by several freeze-thawings *in vacuo*, and the tube was then sealed with evacuation. Upon mixing the two solutions at room temperature, an immediate greenish blue color developed, indicating formation of ferricenium ion and then the color faded in about 40 min. After standing at room temperature for 65 h, the resulting orange-yellow solution was then added to

water (50 ml) and the mixture was extracted twice with 30-ml portions of petroleum ether. The extracts were dried over sodium sulfate. After evaporation of the solvent, the residue was chromatographed through an alumina column (1 × 15 cm) using ether as eluant to give 77.8 mg (91.1 % yield) of ferrocenylmethyl methyl ether (X)⁵ whose IR and NMR spectra were superimposable upon those of an authentic sample.

All the results, and reaction conditions for compounds (I)–(IX) are summarized in Table 4.

Qualitative tests for Fe^{II} and Fe^{III} ions

Compound (I) (0.166 mmole) and anhydrous ferric chloride (0.266 mmole) were allowed to react in oxygen-free methanol in the same way as described above. The resulting reaction mixture was hydrolyzed and extracted with petroleum ether. Tests of the separated aqueous layer with potassium ferrocyanide and thiocyanate indicated the virtual absence of Fe^{III} ions, whereas tests with potassium ferricyanide showed that Fe^{II} ions were present.

Alcoholysis of ferrocenylmethyl derivatives of silicon and germanium in the presence of catalytic amounts of ferric ions under ambient conditions

The following is typical of the procedure used. A solution of 106 mg (0.530 mmole) of (I) in 10 ml of absolute ethanol containing anhydrous ferric chloride (10⁻³ mmole) was heated under reflux for 10 h. After work-up in the same way as above, 85.2 mg (89 % yield) of ferrocenylmethyl ethyl ether⁵ was obtained, whose IR and NMR spectra were superimposable upon those of an authentic sample.

Measurements of relative rates of methanolysis of ferrocenylmethyl derivatives of silicon and germanium in the presence of anhydrous ferric chloride

In a two-limbed glass tube were placed separately two solutions, one consisting of two different ferrocene derivatives (A) and (B) accurately weighed (ca. 0.1 mmole) and an internal standard (cetane, octadecane, or eicosane) in 5 ml of a dry methanol/benzene (4/1) mixture, the other containing anhydrous ferric chloride accurately weighed (ca. 0.07 mmole) in 5 ml of absolute methanol. The solutions were degassed by several freeze-thawings *in vacuo*. The tube was then sealed with evacuation and the two solutions were mixed at room temperature. The mixture which immediately turned greenish blue indicating formation of ferricenium ion was allowed to stand at room temperature. After completion of the reaction, indicated by a change to orange-yellow, the solution was added to water (50 ml) and the mixture was extracted twice with 30 ml portions of petroleum ether. The extracts were dried over sodium sulfate. After evaporation of the solvents, the residue was analyzed by GLC (30 % Apiezon L on Celite, 280°). The ratio of rate constants for the reaction was calculated by the usual expression:

$$k_A/k_B = \frac{\log(\text{initial moles of A/final moles of A})}{\log(\text{initial moles of B/final moles of B})}$$

The average result was taken from two runs for each ferrocene derivative relative to compound (I) as unity.

All the results for compounds (I)–(IX) are listed in Table 5.

(2-Pyridylmethyl)trimethylsilane and -germane

(2-Pyridylmethyl)trimethylsilane and -germane were prepared by the method described below, although different procedures have been reported in the literature^{8,40}.

A solution of (2-pyridylmethyl)lithium prepared from α -picoline (12.0 g, 0.129 mole) in THF (50 ml) and *n*-butyllithium (0.130 mole) in hexane (108 ml) was added dropwise to trimethylchlorosilane (16.0 g, 0.147 mole) in THF (50 ml) with ice-cooling. The mixture was stirred at room temperature for 10 min and then hydrolyzed. After work-up, fractional distillation gave 11.1 g (52.1% yield) of (2-pyridylmethyl)trimethylsilane, b.p. 82–84°/15 mmHg (lit.⁸ b.p. 191–192°), n_D^{20} 1.4899 (lit.⁸ n_D^{25} 1.4866).

In contrast to the method described above, when addition of the reagent was reversed, considerable amounts of the disilylated picoline were formed as described in the literature⁸.

Similarly, (2-pyridylmethyl)trimethylgermane (b.p. 94–95°/15 mmHg, n_D^{20} 1.5073) was prepared in 39.6% yield from trimethylchlorogermane.

Acetolysis of (2-pyridylmethyl)trimethylsilane and -germane

A sample (1 mmole) of either (2-pyridylmethyl)trimethylsilane or -germane was dissolved in 3 ml of 0.67 *M* acetone solution of acetic acid. The mixture was rapidly shaken and allowed to stand at $23 \pm 1^\circ$ for a given period. Two ml of 3 *M* aqueous sodium hydroxide solution followed by water (30 ml) were then added with ice-cooling. The mixture was extracted twice with 30 ml portions of ether and the extracts were dried over sodium sulfate. After evaporation of the solvent, the resulting residue was dissolved in carbon tetrachloride. The solution was analyzed for the methylene protons of the starting substance and the methyl protons of α -picoline produced during the reaction by ¹H NMR spectroscopy.

Structure proof of the reaction product was based on the fact that the ¹H NMR spectrum of the product from a run carried out for 10 h was superimposable on that of an authentic sample of α -picoline.

According to the method described above, the following approximate pseudo-first-order rate constants for (2-pyridylmethyl)trimethylsilane and -germane were obtained at $23 \pm 1^\circ$ by two point kinetics: (2-Me₃SiCH₂)C₅H₅N 5.6×10^{-4} ; (2-Me₃GeCH₂)C₅H₄N 7.2×10^{-4} sec⁻¹.

Measurements of polarographic half-wave oxidation potentials of ferrocenylmethyl derivatives of silicon and germanium

Polarograms of ferrocenylmethyl derivatives of silicon and germanium were recorded on a Yanaco P8A polarograph with a compensation circuit of liquid junction potentials. A three-electrode system with a large platinum foil electrode which served as a shielded electrode, a platinum wire, the working electrode, rotated at 900 cycles per min, and a saturated calomel reference electrode was utilized.

Measurements were carried out at room temperature on solutions of ferrocene derivatives (10^{-3} *M*) in acetonitrile containing lithium perchlorate (0.2 *M*) as a supporting electrolyte. Acetonitrile was distilled before use from phosphorus pentoxide under nitrogen. Lithium perchlorate was prepared by heating LiClO₄ · 3H₂O at 150° for 20 h under reduced pressure.

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