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OXIDATION–ALCOHOLYSIS OF ORGANOSILYL- AND ORGANOGERMYL-SUBSTITUTED FERROCENES IN THE PRESENCE OF FERRIC IONS

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SUMMARY

Eleven ferrocene derivatives bearing the M–M (M = Si and/or Ge) substituent bonded directly to the ring have been found to undergo alcoholysis at the M–M linkage in the presence of either ferric chloride or ferricenium tetrachloroferrate. It is suggested that the oxidation–reduction process between the ferrocene derivatives and ferric ions gives rise to the corresponding substituted ferricenium ions, which in turn may readily undergo a nucleophilic attack by alcohol at the adjacent highly polarized M–M bond. The reaction is thus very similar to the acid-catalyzed alcoholysis of these ferrocene derivatives.

INTRODUCTION

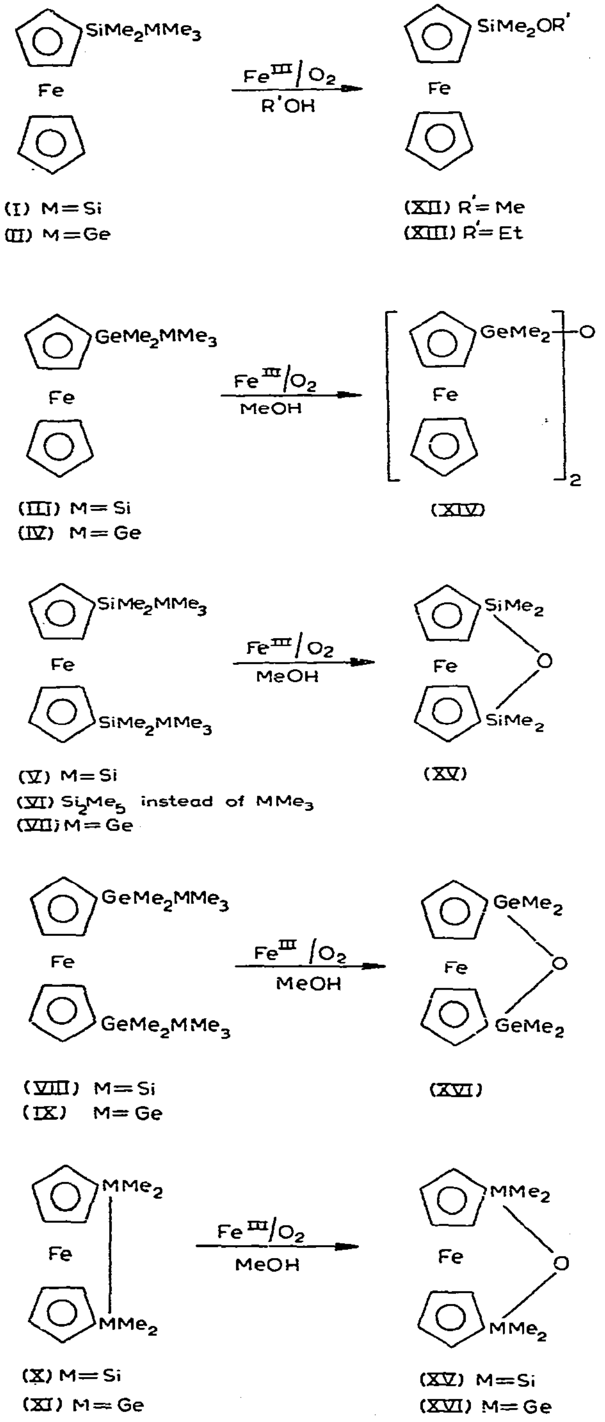
In the preceding paper[1] we showed that M–M (M = Si and/or Ge) bonds adjacent to the ferrocenyl group readily undergo acid-catalyzed alcoholysis under conditions which do not lead to any protodemetalation to form ferrocene. It was suggested that the presence of both oxygen and acid in solvent alcohol is essential for the reaction, and that the substituted ferricenium ion intermediates produced by an acid-catalyzed autoxidation are involved in the course of the reaction. The ferricenium ion thus formed may have a strong electron-withdrawing effect on the adjacent M–M bond, which consequently undergoes ready alcoholysis.

From this reasoning it follows that all ferricenium ions bearing the M–M substituent bonded directly to the ring should be reactive toward nucleophiles, including solvent alcohol, and this has now been found to be the case. In this paper we report that either ferric chloride or ferricenium tetrachloroferrate in alcohol solution oxidizes several ferrocene derivatives which contain the M–M (M stands for Si and/or Ge throughout this paper) groupings to form the corresponding substituted ferricenium ions and such ions readily undergo alcoholysis at the M–M linkage.

RESULTS AND DISCUSSION

Preparative methods, some physical properties for ferrocene derivatives (I)–(XI) used in the present study were described previously[2].

SCHEME 1


SiMe$_2$MMe$_3$
Fe
Fe^{III}/O$_2$
R'OH
SiMe$_2$OR'
(I) M=Si
(II) M=Ge
(XII) R'=Me
(XIII) R'=Et
GeMe$_2$MMe$_3$
Fe^{III}/O$_2$
MeOH
GeMe$_2$
O
2
(III) M=Si
(IV) M=Ge
(XIV)
SiMe$_2$MMe$_3$
SiMe$_2$
O
(V) M=Si
(VI) Si$_2$Me$_5$ instead of MMe$_3$
(VII) M=Ge
(XV)
GeMe$_2$MMe$_3$
GeMe$_2$
(VIII) M=Si
(IX) M=Ge
(XVI)
MMe$_2$
(X) M=Si
(XI) M=Ge
(XV) M=Si
(XVI) M=Ge

There have been several reports that ferric chloride and ferricenium tetrachloroferrate oxidize ferrocene to give the ferricenium ion[3–5]. These reactions seemed to be suitable for our purpose because alcohols dissolve such oxidizing agents considerably.

Alcoholysis of organosilyl- and organogermyl-substituted ferrocenes in the presence of ferric ions

All the compounds examined, *viz.* (I)–(XI), readily reacted in dry methanol or ethanol at room temperature in the presence of a catalytic amount of anhydrous ferric chloride or ferricenium tetrachloroferrate. The mode of cleavage of the M–M bond in each compound was quite similar to that reported in the preceding paper[1], and summarized in Scheme 1* and Table 1; the latter indicates the reaction conditions employed.

TABLE 1

ALCOHOLYSIS OF ORGANOSILYL- AND ORGANOGERMYL-SUBSTITUTED FERROCENES IN THE PRESENCE OF FERRIC IONS

Compound[a]		*Reaction conditions*				*Product*[a] (%)
No.	(*mmol*)	*Catalyst* (*mmol*)	*Alcohol* (*ml*)	*Temp.*	*Time* (*h*)	
(I)	(0.319)	$FeCl_3$(0.005)	MeOH(5)	[b]	3	(XII)(79.1)
(I)	(0.330)	$FeCl_3$(0.005)	EtOH(5)	[b]	19	(XIII)(92.1)
(I)	(0.375)	$[Fe(C_5H_5)_2]FeCl_4$(0.0099)	MeOH(15)	[b]	40	(XII)(96.3)
(I)	(0.345)	$[Fe(C_5H_5)_2]FeCl_4$(0.0110)	EtOH(15)	[b]	40	(XIII)(78.3)
(II)	(0.252)	$[Fe(C_5H_5)_2]FeCl_4$(0.0890)	MeOH(20)	[b]	19	(XII)(63.2)
(III)	(0.220)	$[Fe(C_5H_5)_2]FeCl_4$(0.0031)	MeOH(15)	[b]	19	(XIV)(92.8)
(IV)	(0.251)	$[Fe(C_5H_5)_2]FeCl_4$(0.0081)	MeOH(20)	[b]	62	(XIV)(87.0)
(V)	(0.317)	$[Fe(C_5H_5)_2]FeCl_4$(0.0096)	MeOH(20)	[c]	1	(XV)(62.5)
(VI)	(0.218)	$[Fe(C_5H_5)_2]FeCl_4$(0.0089)	MeOH(20)	[c]	1	(XV)(76.5)
(VII)	(0.183)	$[Fe(C_5H_5)_2]FeCl_4$(0.0089)	MeOH(20)	[c]	1	(XV)(57.1)
(VIII)	(0.197)	$[Fe(C_5H_5)_2]FeCl_4$(0.0089)	MeOH(20)	[c]	1	(XVI)(69.7)
(IX)	(0.342)	$[Fe(C_5H_5)_2]FeCl_4$(0.0096)	MeOH(20)	[c]	1	(XVI)(70.2)
(X)	(0.368)	$[Fe(C_5H_5)_2]FeCl_4$(0.0081)	MeOH(20)	[b]	43	(XV)(78.4)
(XI)	(0.210)	$[Fe(C_5H_5)_2]FeCl_4$(0.0073)	MeOH(20)	[b]	43	(XVI)(72.2)

[a] (I) (Pentamethyldisilanyl)ferrocene; (II) [(trimethylgermyl)dimethylsilyl]ferrocene; (III) [(trimethylsilyl)dimethylgermyl]ferrocene; (IV) (pentamethyldigermanyl)ferrocene; (V) 1,1′-bis(pentamethyldisilanyl)ferrocene; (VI) 1,1′-bis(heptamethyltrisilanyl)ferrocene; (VII) 1,1′-bis[(trimethylgermyl)dimethylsilyl]-ferrocene; (VIII) 1,1′-bis[(trimethylsilyl)dimethylgermyl]ferrocene; (IX) 1,1′-bis(pentamethyldigermanyl)-ferrocene; (X) 1,2-(1,1′-ferrocenylene)tetramethyldisilane; (XI) 1,2-(1,1′-ferrocenylene)tetramethyldigermane; (XII) (methoxydimethylsilyl)ferrocene; (XIII) (ethoxydimethylsilyl)ferrocene; (XIV) 1,3-diferrocenyltetramethyldigermoxane; (XV) 1,3-(1,1′-ferrocenylene)tetramethyldisiloxane; (XVI) 1,3-(1,1′-ferrocenylene)tetramethyldigermoxane. [b] At room temperature. [c] At reflux temperature of the reaction mixture.

The effect of oxygen on the cleavage reaction

It was found that the reaction of, for example, (I) catalyzed by ferric chloride (ca. 1.5 mol %) scarcely occurred in methanol which had been carefully freed of oxygen

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* Fe^{III}/O_2 in the scheme stands for the presence of a catalytic amount of Fe^{III} ions under ambient conditions. Rigorous removal of oxygen from the reaction mixture requires stoichiometric amounts of Fe^{III} ions for completion of the reaction (see below).

TABLE 2

METHANOLYSIS OF ORGANOSILYL- AND ORGANOGERMYL-SUBSTITUTED FERROCENES IN THE PRESENCE OF ANHYDROUS FERRIC CHLORIDE UNDER OXYGEN-FREE CONDITIONS[a]

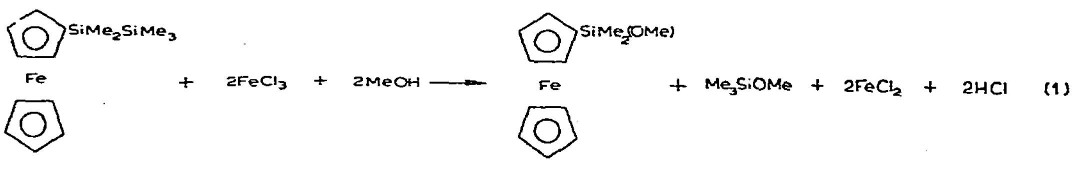
Compound		*$FeCl_3$(mmol)*	*Time(h)*	*Products(%)*
No.	*(mmol)*			
(I)	(0.671)	0.010	234	(I)(75.5)
(I)	(0.375)	[b]	156	(I)(88.1)
(I)	(0.163)	0.167	6.5	(I)(40.3), (XII)(34.9)
(I)	(0.159)	0.320	6.5	(XII)(85.8)
(II)	(0.187)	0.374	42	(XII)(96.1)
(III)	(0.271)	0.542	12	(XIV)(77.9)
(IV)	(0.255)	0.510	12	(XIV)(80.4)
(V)	(0.259)	1.04	12	(XV)(86.8)
(VI)	(0.202)	0.808	12	(XV)(87.8)
(VII)	(0.129)	0.516	12	(XV)(99.3)
(VIII)	(0.196)	0.784	12	(XVI)(70.6)
(IX)	(0.217)	0.870	12	(XVI)(77.1)
(X)	(0.360)	0.722	12	(XV)(76.4)
(XI)	(0.248)	0.496	12	(XVI)(77.4)

[a] Carried out in 10 ml of methanol at room temperature. [b] 0.015 mmol of $[Fe(C_5H_5)_2]FeCl_4$ was used.

(see Table 2). Therefore, the oxygen present in the reaction mixture must play an important role in reoxidizing Fe^{II} species to Fe^{III}, the latter oxidizing ferrocene derivatives which contain the M–M groupings to form the substituted ferricenium ions. Although very ready participation of oxygen in the $Fe^{II} \rightleftarrows Fe^{III}$ oxidation–reduction process has not been fully verified here*, this may underlie the requirement of only a catalytic amount of Fe^{III} salt as the oxidizing agent for the present reaction under ambient conditions.

Methanolysis of organosilyl- and organogermyl-substituted ferrocenes in the presence of stoichiometric amounts of anhydrous ferric chloride in oxygen-free solution

The stoichiometric reaction of (I) with ferric chloride in methanol solution was carried out with rigorous exclusion of oxygen from the solution. It was found that two equivalents of ferric chloride for each molecule of the substrate (I) were essential for completion of the reaction (see Table 2). A plausible stoichiometry for the reaction may thus be represented by eqn. (1).



(I) (XII) (1)

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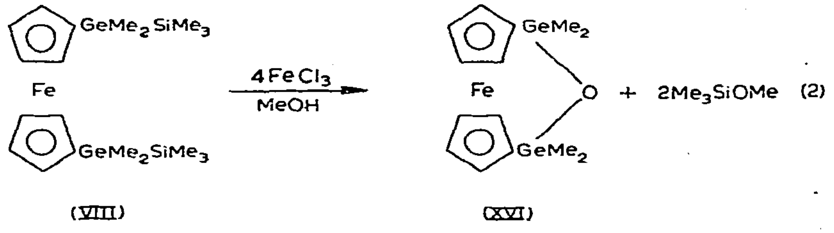
* Fe^{II} ions are readily autoxidized in aqueous or alcoholic solution.

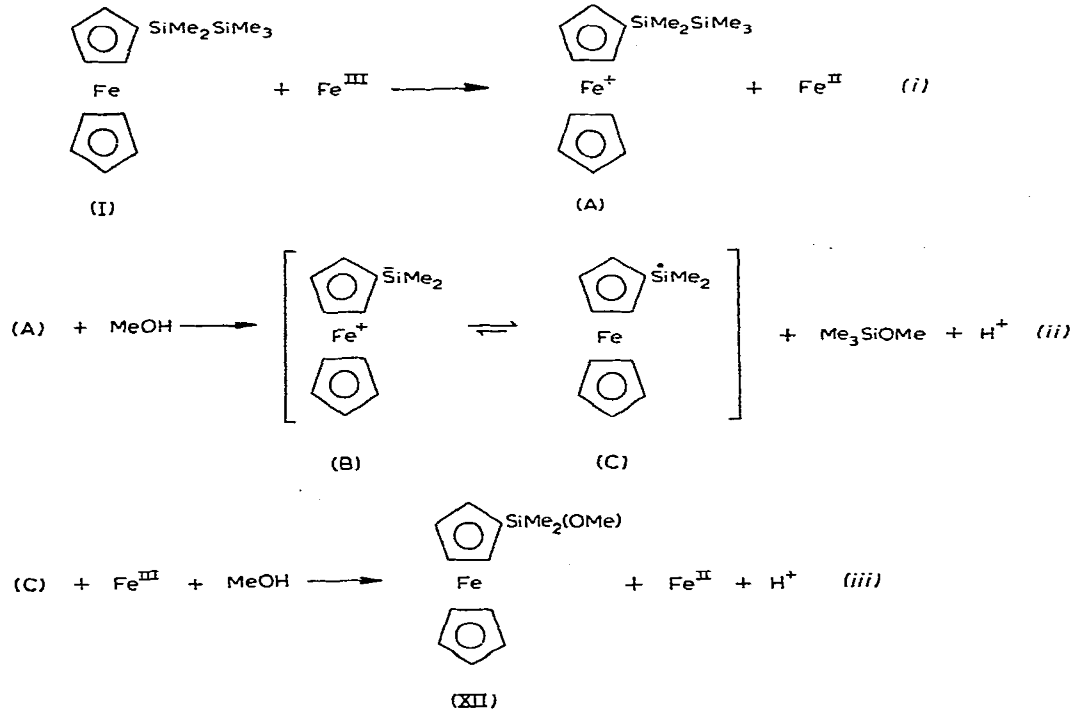
Compounds (II)–(XI) reacted similarly with stoichiometric amounts of anhydrous ferric chloride in degassed methanol solution.

The resulting substituted ferricenium ions underwent cleavage of the M–M bond by nucleophilic attack of solvent methanol, leading in each case to the same products as are indicated in Scheme 1. All the results are summarized in Table 2. It should be noted that two equivalents of ferric chloride were always required for cleavage of each M–M linkage in a given compound, *e.g.*,



Therefore, the reaction in the present study may be best formulated as proceeding in the sequence of steps depicted by Scheme 2, in which compound (I) is taken as an example:

SCHEME 2



Step (*i*) involves the reversible oxidation–reduction process, which is well recognized in the chemistry of ferrocene[4] in general, and known to be very fast[5,6]. The resulting substituted ferricenium ion (A) may undergo methanolysis at the adjacent highly polarized silicon–silicon bond in a subsequent, probably rate-determining, step (*ii*); here, a strongly electron-withdrawing effect of the ferricenyl group, which has been well established by Gubin and Lubovich[7], must play an important role by rendering the system (B) as a good leaving group. The ferrocenylsilyl radical (C) presumably formed by the concomitant intramolecular redox process would be then rapidly oxidized* by a second mole of ferric ions to give (methoxydimethylsilyl)ferrocene (XII) in methanol solution [step (*iii*)]. A similar intramolecular redox process involving α-ferrocenylcarbonium ions has already been postulated by several authors[8–11].

Recently, we have reported 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 chloride. This is very similar to the M–M cleavage in the present study, and may be best explained in terms of the redox process of ferrocenylmethyl radicals with ferric ions to give the observed ferrocenylmethyl methyl ether[12].

EXPERIMENTAL

Alcoholysis of organosilyl- and organogermyl-substituted ferrocenes in the presence of ferric ions

The following is typical of the procedure used. A solution of 119 mg (0.375 mmol) of (pentamethyldisilanyl)ferrocene (I) and 3.8 mg (0.0099 mmol) of ferricenium tetrachloroferrate in 15 ml of absolute methanol was allowed to stand at room temperature for 40 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 distilled under reduced pressure to give 99.0 mg (96.3% yield) of (XIII). Its IR and NMR spectra were superimposable on those of an authentic sample.

All the results, together with the conditions under which reactions of compounds (I)–(XI) were carried out, are summarized in Table 1.

Methanolysis of organosilyl- and organogermyl-substituted ferrocenes in the presence of anhydrous ferric chloride under oxygen-free conditions

The following describes a typical procedure. In a two-limbed glass tube were placed separately two solutions of 50.3 mg (0.159 mmol) of (I) in 5 ml of absolute methanol and 51.9 mg (0.320 mmol) of anhydrous ferric chloride in 5 ml of absolute methanol, and the solutions were degassed several times by repeated freezing and melting under vacuum. The tube was then sealed under vacuum and the two solutions were mixed at room temperature. The mixture immediately turned greenish blue, indicating formation of ferricenium ion. It was allowed to stand at room temperature for 6.5 h. After work-up in the same way as above, there was obtained 37.4 mg (85.8% yield) of (XIII).

All the results, together with reaction conditions for compounds (I)–(XI), are summarized in Table 2.

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* The oxidation probably involves an intermolecular $Fe^{II} \rightleftharpoons Fe^{III}$ redox process, though there may be a direct oxidation of the silyl radical by ferric ions.

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

Compound (I) (0.100 mmol) and anhydrous ferric chloride (0.180 mmol) 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, but tests with potassium ferricyanide showed that Fe^{II} ions were present.

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