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Fragmentation reactions of 1,3,5-triferrocenyl-4-(1-ferrocenylvinyl)-, 1-aryl-4-(1-arylvinyl)-3,5-diferrocenyl-, and 3,5-diaryl-1-ferrocenyl-4-(1-ferrocenylvinyl)cyclohexenes

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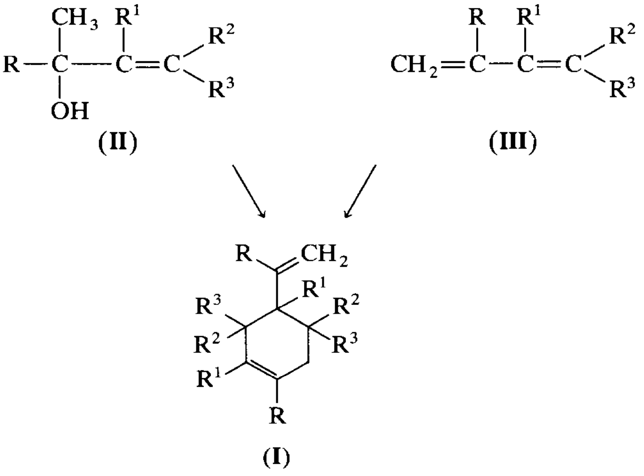
Abstract

Monocyclic ferrocenylsubstituted terpenoids, produced upon proton-induced cyclodimerization of ferrocenyl-1,3-dienes, undergo fragmentation under the action of electrophilic agents (HBF_4, $[PhCHFc]BF_4$, or $[MeOC_6H_4CHCHCHC_6H_4OMe]BF_4$) to give two molecules of methyl-, (2-ferrocenyl-2-phenylethyl)-, or 2,4-bis(p-methoxyphenyl)-3-butenyl-ferrocenylallylium tetrafluoroborates. Treatment of these salts with dimethylaniline yields, depending on their structure, the starting cyclodimers, seven-membered cyclic compounds, dimethylaniline alkylation products, or tricyclic compounds.

1. Introduction

We have recently synthesized ferrocenyl-substituted 4-(1-ferrocenylvinyl)- and 4-(1-arylvinyl)cyclohexenes (**Ia–g**) from ferrocenyl(methyl)allyl alcohols [1] and from ferrocenyl-1,3-butadienes in the presence of acids [2]. Compounds **Ia–g** are the products of acid-catalyzed cyclodimerization of ferrocenyl-1,3-dienes and are quite stable and accessible substances.



$R-C(CH_3)(OH)-C(R^1)=C(R^2)(R^3)$

(II)

$CH_2=C(R)-C(R^1)=C(R^2)(R^3)$

(III)

(I)

a, $R = R^3 = Fc$, $R^1 = R^2 = H$; **b**, $R = R^3 = Fc$, $R^1 = H$, $R^2 = CH_3$; **c**, $R = R^3 = Fc$, $R^1 = CH_3$, $R^2 = H$; **d**, $R = C_6H_5$, $R^1 = R^2 = H$, $R^3 = Fc$; **e**, $R = p\text{-}CH_3OC_6H_4$, $R^1 = R^2 = H$, $R^3 = Fc$; **f**, $R = Fc$, $R^1 = R^2 = H$, $R^3 = C_6H_5$; **g**, $R = Fc$, $R^1 = R^2 = H$, $R^3 = p\text{-}CH_3OC_6H_4$.

Unlike the dimers **Ia–g** and ferrocenyl(methyl)allyl alcohols **IIa–g** the ferrocenyl-1,3-butadienes **IIIa–g** are in most cases rather unstable and they can hardly be employed in organic synthesis [1–3].

In this work we have studied the interaction of cyclodimers **Ia–g** with electrophilic reagents (proton, carbocation).

2. Results and discussion

The action of an excess of HBF_4 on compounds (Ia–g) was found to result in their complete fragmentation into ferrocenyl(methyl)allyl cations isolated quantitatively as solid tetrafluoroborates **IVa–g**. This process is essentially the reverse of the formation of the cyclodimers **Ia–g** since treatment of the salts **IVa–g** with deprotonating nucleophiles (dimethylaniline, pyridine) results, in turn, in regeneration of the starting dimers.

The structure of the tetrafluoroborates **IVa–g** obtained was confirmed by ^1H NMR spectra data (Table 1), their independent synthesis from alcohols **IIa–g** and

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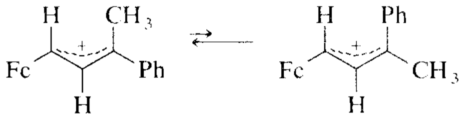
TABLE 1. ^1H NMR spectral data for compounds **IVb–g** and **IXg** [δ, multiplicity, integral intensity, (*J*, Hz)]

Compound	C_5H_5	C_5H_4	CH_3	CH_2	CH	Aromatics
IVb	4.78 s, 10H	5.03–5.65 m, 8H	1.96 s, 6H	–	6.20 s, 1H	–
IVc	4.70 s, 5H; 5.20 s, 5H	5.02–5.17 m, 8H; 2.05 s, 3H	1.97 c, 3H	–	8.66 s, 1H	–
E,E-**IVd**	5.14 s	5.08–6.65 m	2.72 d (0.82)	–	7.00 dd (12.92, 0.82) 8.64 d (12.92)	7.6–8.0 m
E,Z-**IVd**	5.00 s	4.80–6.50 m	2.50 d (1.10)	–	6.64 dd (12.65, 1.10) 8.14 d (12.65)	7.6–8.0 m
IVe	5.08 s, 5H	5.0–6.30 m, 4H	2.56 s, 3H; 4.12 s, 3H	–	7.22 d (13.60); 8.56 d (13.60)	7.32–8.10 m
IVf	4.05 s, 5H	4.48–5.60 m, 4H	1.45 s, 3H	–	6.35 d (15.80); 7.66 d (15.80)	6.60–7 m
IVg	4.16 s, 5H	4.6–5.6 m, 4H	1.4 s, 3H; 3.94 s, 3H	–	6.30 d (15.20); 7.60 d (15.20)	6.2–7.2 m
IXg	4.08 s; 4.06 s; 4.02 s; 3.96 s	4.38–3.90 m	3.76 s; 3.80 s; 3.84 s; 3.98 s	3.0–2.8 m	6.16 d (9.38); 4.40 d (9.38); 3.84 m (CHFc)	7.28–7.75 m

combustion analyses (Table 2). As follows from the data in Table 1, only the cation **IVd** is formed as an equilibrium mixture of two isomers, presumably of (*E,E*)- (major product) and (*E,Z*)-configuration:



(**IVd**-*E,E*) (**IVd**-*E,Z*)

We proposed that replacement of the proton in HBF_4 by a carbocation should not change the essence of the fragmentation process. To test this hypothesis, stable ferrocenyl(phenyl)methylium (**V**) and 1,3-bis(*p*-methoxyphenyl)allylium (**VI**) tetrafluoroborates were assayed.

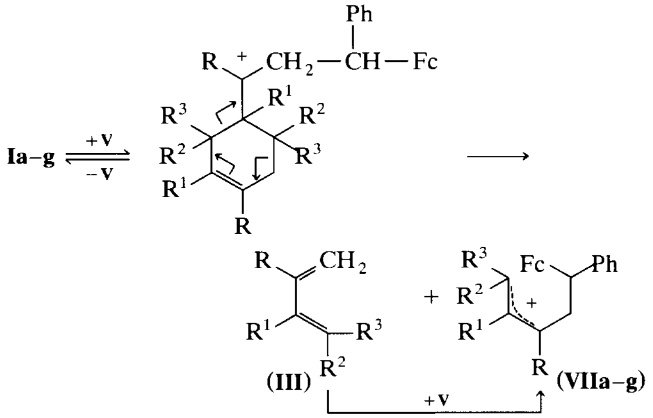
In fact, it turned out that fragmentation of the cyclodimers **Ia–g** under the action of salts **V** and **VI** took place and this could be visually monitored as the change in colour of the reaction mixtures. With no less than a 2-fold excess of the reagents **V** and **VI**, precipitation of the pure, intermediate allylium tetrafluoroborates **VIIa–g** and **VIIIa–g** and recording of their NMR spectra could not be achieved. The reaction mixtures were finally treated with dimethylaniline and the products of the fragmentation processes were isolated by chromatography.

Thus, addition of ferrocenyl(phenyl)methylium te-

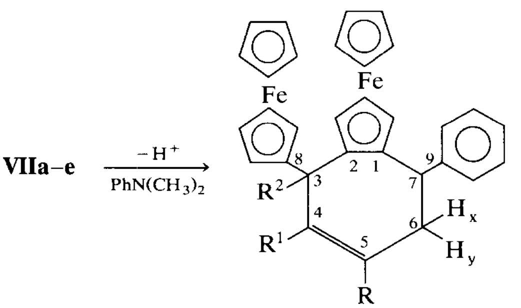
TABLE 2. Melting points, yields, and elemental analysis data for compounds synthesized

Compound	M.p., °C	Yield, %	Found			Molecular Formula	Calculated		
			C	H	Fe		C	H	Fe
IVb	dec.	91	57.43	4.65	21.51	$C_{25}H_{25}BF_4Fe$	57.30	4.81	21.32
IVc	dec.	93	57.24	4.90	21.46	$C_{25}H_{25}BF_4Fe$	57.30	4.81	21.32
IVd	dec.	90	60.01	4.83	14.02	$C_{20}H_{19}BF_4Fe$	59.75	4.76	13.93
IVe	dec.	92	58.56	4.78	17.80	$C_{21}H_{21}BF_4FeO$	58.35	4.90	17.58
IVf	dec.	91	59.53	5.04	13.76	$C_{20}H_{19}BF_4Fe$	59.75	4.76	13.93
IVg	dec.	90	58.27	4.95	17.41	$C_{21}H_{21}BF_4FeO$	58.35	4.90	17.58
IXa	221–222	74	70.69	5.43	23.91	$C_{41}H_{36}Fe_3$	70.72	5.21	24.07
IXb	217–218	70	70.83	5.31	23.28	$C_{42}H_{38}Fe_3$	71.02	5.38	23.59
IXc	224–225	71	71.20	5.25	23.81	$C_{42}H_{38}Fe_3$	71.02	5.38	23.59
IXg	107–109	57	74.52	6.30	14.87	$C_{46}H_{45}Fe_2NO$	74.70	6.13	15.10
Xa	179–180	72	72.85	5.78	16.71	$C_{41}H_{38}Fe_2O_2$	73.01	5.68	16.56
Xb	193–194	69	73.47	5.74	15.98	$C_{42}H_{40}Fe_2O_2$	73.27	5.85	16.23
Xc	197–198	75	73.30	6.01	16.38	$C_{42}H_{40}Fe_2O_2$	73.27	5.85	16.23
Xd	171–172	64	78.56	5.84	9.77	$C_{37}H_{34}FeO_2$	78.44	6.05	9.86
Xe	166–167	67	76.63	5.91	9.29	$C_{38}H_{36}FeO_3$	76.51	6.08	9.36

trafluoroborate (**V**) to the terminal methylene group of the dimers **Ia–g** brings about their fragmentation. As a result, two molecules of ferrocenyl(phenyl)allylium tetrafluoroborates (**VIIa–g**) are produced from each molecule of the cyclodimers **Ia–g**:

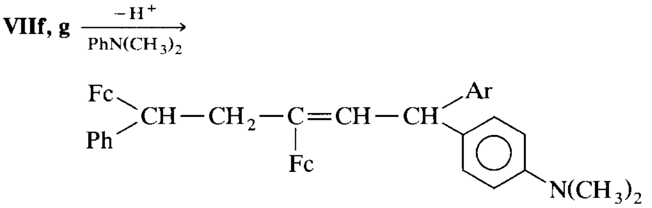


Treatment of the salts **VIIa–g** with dimethylaniline affords final products, whose structure depends on the position of the ferrocenyl substituent in the starting dimers. Seven-membered cyclic compounds **IXa–e** are obtained in good yields from the cyclodimers **Ia–e** due to intramolecular homoannular alkylation of the ferrocene moieties in the cations **VIIa–e**:



(IXa–e)

Allyl cations **VIIf, g** obtainable from the dimers **If, g** alkylate dimethylaniline at the *para*-position to give compounds **IXf, g** under the same conditions:

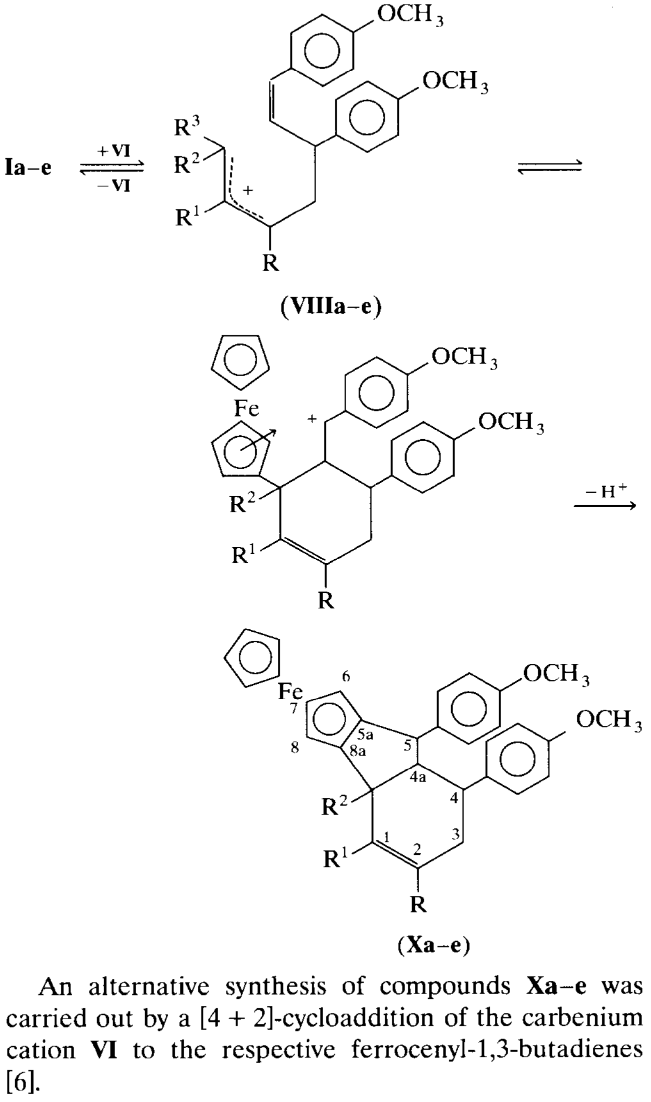


(IXf, g)

Compounds **IXa–e** and **IXf, g** were also synthesized from the respective ferrocenyl-1,3-dienes and the tetrafluoroborate (**V**) (freshly isolated).

Intramolecular alkylation of ferrocene in allyl cations **VIIa–e** is thought to be the consequence of enhanced electrophilicity of a C(1) centre in the cations **VIIa–e** where the positive charge is to greater extent localized on the α-carbon, with respect to the ferrocenyl group, as compared to the cations **VIIf** and **VIIg** [4,5].

Interaction of 1,3-bis(*p*-methoxyphenyl)allylium tetrafluoroborate (**VI**) with cyclodimers **Ia–e** under the same conditions gives rise to tricyclic systems **Xa–e**. This follows the similar pathway, *viz*., fragmentation of the dimers, production of two intermediate allyl cations of green (**VIIIa–c**) and brown (**VIIId, e**) colour, and intramolecular alkylation of the ferrocenyl nucleus by a carbenium centre of a cyclohexene intermediate:



(Xa–e)

An alternative synthesis of compounds **Xa–e** was carried out by a [4 + 2]-cycloaddition of the carbenium cation **VI** to the respective ferrocenyl-1,3-butadienes [6].

The structures of the compounds obtained were established on the basis of NMR spectra with the use of homonuclear double resonance. Chemical shift values and spin coupling constants of aliphatic protons in compounds **IXa–e** accord with the structures proposed; ^{13}C NMR spectra give additional information (Table 4). The presence in the spectra of three signals for

TABLE 3. ^{1}H NMR spectral data for compounds **Xa–e** [δ, multiplicity, (J, Hz)]

Hydrogen No. or group	Compound				
	Xa	**Xb**	**Xc**	**Xd**	**Xe**
1	5.72 bs; 6.41 bd (2.8)	5.70 bs	–	6.73 bd (4.80)	6.64 bd (4.90)
4a	3.34 bd (10.0)	3.36 bd (10.05)	3.40 bd (10.00)	3.36 bd (10.05)	3.30 bd (10.01)
4	3.38 m (–)	3.40 m (–)	3.38 m (–)	3.36 m (–)	3.44 m (–)
3x	2.76 m ($J_{3x} = J_{3y}$)	2.75 m (17.6)	2.74 m (17.0)	2.82 bdd (14.6)	2.78 bdd (14.8)
3y	2.85 m (16.98)	2.82 m	2.86 m	3.12 bt (14.6)	3.08 bt (14.8)
5	3.78 d (10.00)	3.76 d (10.05)	3.70 d (10.00)	3.76 d (10.05)	3.75 d (10.01)
6	3.71 bd 2.0)	3.70 bd (2.0)	3.66 d (2.1)	3.72 bd (2.0)	3.70 bd (2.05)
7	4.05 t (2.0)	4.03 t (2.0)	4.03 t (2.1)	4.05 t (2.0)	4.05 t (2.05)
8	3.94 bd (2.0)	3.92 bd (2.0)	3.94 bd (2.1)	3.95 bd (2.0)	3.96 bd (2.05)
C_5H_5	4.10 s, 3.51 s	4.12 s, 3.48 s	4.10 s, 3.50 s	4.12 s, 3.64 s	4.12 s, 3.60 s
CH_3	–	1.14 s	2.13 s	–	–
CH_3O	3.91 s, 3.82 s	3.90 s, 3.83 s	3.92 s, 3.70 s	3.95 s, 3.90 s	3.90 s, 3.81 s
Aromatics	7.53–6.81 m	7.50–6.75 m	7.56–6.70 m	7.68–6.45 m	7.63–6.65 m

quaternary carbon atoms of ferrocene fragments in compounds **IXd** and **IXe**, and of four signals for quaternary carbon atoms in **IXa–c**, together with the presence of signals due to unsubstituted ferrocene nuclei, point unambiguously to the cyclic character of the products and homoannular cycle closure. Attribution of signals to quaternary carbon atoms, CH, CH_2, and CH_3-groups was made with the use of off-resonance spectra. Signals for C(3) and C(7) were assigned on the basis of differences in half-widths of the respective multiplets in monoresonance spectra. As follows from ^{1}H NMR spectral data for compounds **IXf** and **IXg** (Table 1), they exists as mixtures of diastereomers (*ca.* 2:3), whose signals overlap and sometimes coincide.

^{1}H NMR spectra of compounds **Xa–e** reveal a doublet of doublets which is ascribed to H(3), J *ca.* 2.3 and 0.8–0.5 Hz, and a triplet for H(2), J *ca.* 2.2–2.3 Hz. This only could be in 1,2-di-substituted ferrocene. The spin coupling constant values for protons of a six-membered cycle correspond to the structure proposed (Table 3).

Noteworthy in the reactions studied is the high stereoselectivity of formation of isomers of compounds **IXa–e** and **Xa–e**. Despite the presence therein of several chiral centres and a chiral 1,2-Fc moiety, compounds **IXa–e** and **Xa–e** were isolated in a single diastereomeric form. High stereoselectivity of the process is probably explained by conformational stability of α-ferrocenylcarbocations [7].

Thus the ease of fragmentation of cyclodimers of terpenoid character with ferrocenyl substituents under the action of electrophilic reagents makes possible, on the one hand, their wide synthetic applicability in place of unstable ferrocenyl-1,3-butadienes and, on the other

TABLE 4. NMR spectral data for compounds **IXa, IXb**, and **IXc** [$\delta(^1H)$, multiplicity, J, Hz), $\delta(^{13}C)$]

Carbon No. or group	Compound **IXa**	Compound **IXb**	Compound **IXc**
3	4.50 d (5.1), 37.10	– – 36.93	4.55 d (5.0), 37.0
4	6.64 bd (5.1), 134.40	6.58 s (–), 134.20	–, 134.4
6x	3.16 t (13.6), 38.23	3.12 bt (13.45), 38.24	3.20 bt (13.5), 38.2
6x	3.16 d (1.4)		
6y	2.90 bdd (13.5, 3.6)	2.78 bdd (13.45, 3.7)	2.83 bd (13.5, 3.6)
7	4.32 dd (13.5, 3.4), 44.42	4.30 dd (13.45, 3.70), 44.36	4.30 dd (13.5, 3.6), 44.4
C_5H_5	4.40 s (–), 69.20; 4.13 s (–), 68.91; 3.96 s (–), 68.60	4.21 s (–), 69.23; 4.10 s (–), 68.90; 3.86 s (–), 68.42	4.20 s (–), 69.2 4.08 s (–), 68 3.90 s (–), 68
$C_5H_4 + C_5H_3$	4.40–3.36 m (–), 69.98–63.56	4.45–3.40 m (–), 69.90–63.52	4.42–3.50 m (–), 69.9, 63.6
CH_3	– (–) –	0.96 s (–), 38.90	2.00 s (–), 20.9
C_6H_5	7.70–7.10 m (–), 142.8; 128.3; 125.42; 126.0	7.56–7.2 m (–), 142.92; 128.4; 125.50; 126.01	7.60–7.15 m (–), 143.1; 128.8; 125.4; 126.6
1, 2, 8, 9	– (–) 91.15; 90.20; 87.73; 93.50	– (–) 91.13; 90.18; 87.84; 93.48	– (–), 91; 90.2; 87; 93
5	– (–) 142.80	– (–) 142.92	– (–), 143.1

hand, points unambiguously to a stepwise mechanism of cationic cycloaddition in ferrocenylbutadiene series, this hypothesis and indirect evidence in its favour being advanced in our previous papers [1–3,5,6].

3. Experimental section

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker WM-250 and CXP-200 instruments in $CDCl_3$ with TMS as an internal standard.

Solutions of cyclodimers **Ia–g** in minimal amounts of dry dichloromethane were treated with 40% HBF_4 in acetic anhydride at room temperature and solid salts were isolated conventionally [1].

Interaction of cyclodimers **Ia–g** with ferrocenyl (phenyl)methylium tetrafluoroborate (**V**) [5] was performed by boiling 0.5 mmol of dimers **Ia–g** with 1.5 mmol of the salt **V** in dichloromethane. After 1 h dimethylaniline was added directly to the reaction mixture. Reaction products **IXa–g** were isolated by thin-layer chromatography on silica gel in a solvent system (light petroleum–benzene–ether 1 : 1 : 1).

The reaction of the cation **VI** [8] with **Ia–e** was carried out in an analogous manner; boiling in dichloromethane for 30 min, addition of dimethylaniline, isolation of the products **Xa–e** by chromatography.

Authentic samples of compounds **IXa–g** and **Xa–e** were synthesized from diferrocenyl- and arylferrocenyl-1,3-butadienes **IIIa–g** and the cations **V** and **VI**, respectively, in dichloromethane at 20°C [5,6]. Authentic samples of **IVb–g** were prepared from ferrocenyl(methyl) allyl alcohols **IIb–g** and HBF_4 as described [1].

NMR spectral data of compounds obtained in this work are listed in Tables 1, 3 and 4; their melting points, yields, and elemental analysis data are listed in Table 2.

Compounds **IVa, IXd, IXe**, and **IXf** exhibited properties which coincided with the literature data [1,5].

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