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Structure of *Z*- and *E*-2-bromo-1-ferrocenyl-1-phenylcyclopropanes and 3-ferrocenyl-3-phenylcyclopropene and their three-membered ring opening reactions

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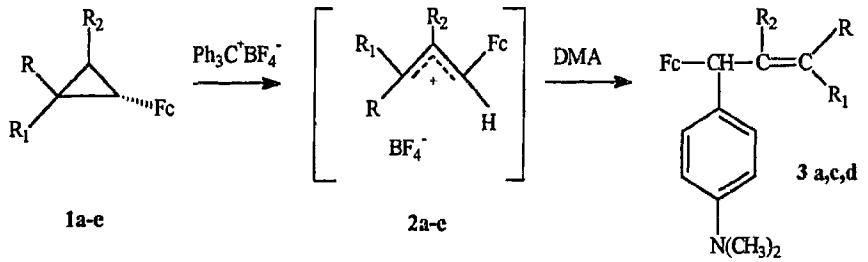
Abstract

The ring-opening reactions in *Z*- and *E*-2-bromo-1-ferrocenyl-1-phenylcyclopropanes and 3-ferrocenyl-3-phenylcyclopropene were studied. It was found that the three-membered ring of the monobromides is opened when treated with $AlCl_3$, while that of cyclopropene is opened when boiled in toluene. X-ray structural data of *E*-2-bromo-1-ferrocenyl-1-phenylcyclopropane and 3-ferrocenyl-3-phenylcyclopropene mono crystals are presented. © 1997 Elsevier Science S.A.

Keywords: Ferrocenylcyclopropene; Dehydrobromination; Opening of the three-membered ring; Carbocations; X-ray diffraction analysis

1. Introduction

It is well known that the introduction of ferrocenyl substituents in three-membered carbocycles (saturated or unsaturated) changes considerably their properties [1–7]. Thus, smooth transformation of 3-aryl-1,2,3-triferrocenylcyclopropenes into the corresponding 3-ferrocenylindenes [1–3] and rearrangement of *Z*-1-aryl-2-ferrocenyl- and *Z*-1,2-diferrocenylcyclopropenes to form the corresponding *E*-isomers [4,5] are documented. Another interesting feature is the formation of linear allylic carbocations containing ferrocenyl substituents through the small cycle ring opening of ferrocenylcyclopropanes **1a–e** when treated with triphenylmethylium tetrafluoroborate [5,6,8]:



1a-e **2a-c**

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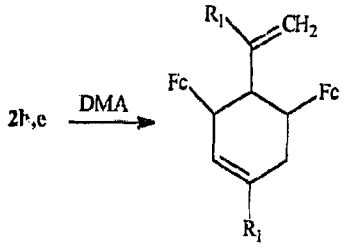
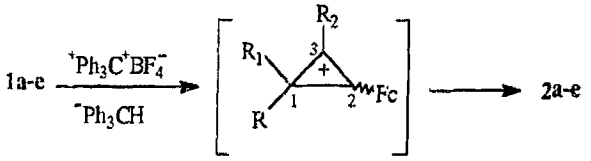


4 b, c

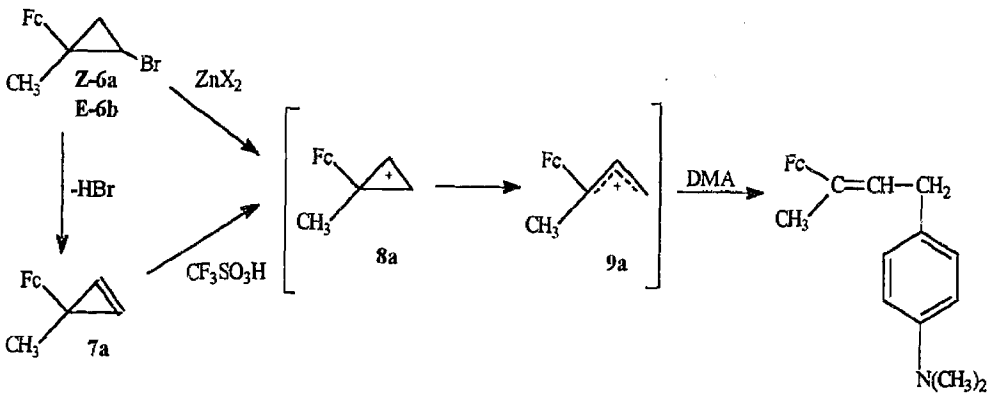
a) R=R_2=H, R_1=Fc [8]; b) R=CH_3, R_1=Fc, R_2=H [5]; c) R=H, R_1=Fc, R_2=CH_3 [5]; d) R=H, R_1=Fc, R_2=Ph [5]; e) R=CH_3, R_1=Ph, R_2=H [6]; Fc=$C_5H_5FeC_5H_4$, DMA=$C_6H_5N(CH_3)_2$.

The data obtained allow us to assume that the formation of 1,3-diferrocenyl-substituted allylic cations **2a–e** from the corresponding ferrocenylcyclopropanes **1a–e** occurred via an intermediate cyclopropyl cation **5a–e** with a positive charge located at position 3 of the cyclopropane ring and not at positions occupied by the ferrocenyl substituents [5]:



5 a-c

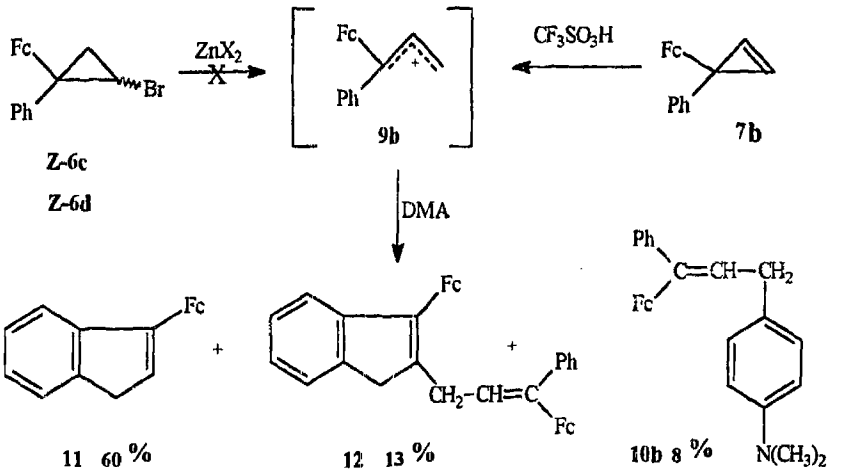
The three-membered ring opening in *Z,E*-2-bromo-ferrocenyl-1-methyl-1-cyclopropane **6a,b** and in 3-methyl-3-ferrocenylcyclopropene **7a** under the action of zinc salts [7] and superacids [6], respectively, indicates unambiguously the localisation of the cationic centre in the intermediate cyclopropyl cation **8a**:



Z,E-10a

The substitution of the methyl group by a phenyl group results in considerable changes in the behaviour of the corresponding compounds **6c,d** and **7b** in similar reactions. For example, 2-bromo-1-ferrocenyl-1-phenylcyclopropanes **6c** and **6d** are stable when treated with zinc salts, while 3-ferrocenyl-3-phenyl-cyclopropene **7b** undergoes ring opening when treated with superacids resulting in the predominant formation of 3-ferrocenylindene **11** together with

the alkylation products, compounds **10b** and **12** [9,10] which form due to the interaction of the 1-ferrocenyl-1-phenylallyl cation **9b** with *N,N*-dimethylaniline and indene:

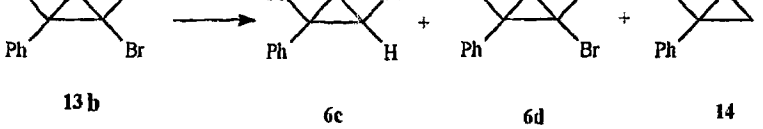


Bearing in mind that ferrocenyl groups, present in the small cycle, exert a pronounced and often highly selective effect, it was of interest to reveal the peculiarities of the electron interaction between the ferrocenyl group and the small cycle, both from the theoretical point of view and in relation to the search for selective reactions of cyclopropanes and cyclopropenes.

2. Results and discussion

In the present paper, we report new data on the chemical properties of *Z*- and *E*-2-bromo-1-ferrocenyl-1-phenylcyclopropanes (**6c** and **6d**, respectively) and 3-ferrocenyl-3-phenylcyclopropene **7b**.

Reduction of 2,2-dibromo-1-ferrocenyl-1-phenylcyclopropane **13b** with zinc in the presence of Trilon B [10] resulted in a mixture of isomeric monobromides (**6c** and **6d** with a yield of about 60%) together with 1-ferrocenyl-1-phenylcyclopropane **14**, formed as a by-product.



Contrary to 2,2-dibromo-1-methyl-1-ferrocenylcyclopropane **13a** [7], the reduction of the dibromide **13b** occurs without ring opening of the three-membered cycle. The reaction products **6c**, **6d**, and **14** can be easily separated by chromatography on alumina. The ^{1}H NMR spectra of the synthesised compounds are given in Section 4.

We carried out X-ray structural analysis of monocrystals of **6d** in order to assign more reliably the isomers **6c** and **6d** to the *Z*- or *E*-type structures.

Fig. 1 shows a general view of the molecule **6d**. Crystal data, data collection, and refinement parametres for the cyclopropane **6d** are listed in Table 1. The X-ray structural analysis data indicate that compound **6d** is the *E*-isomer.

Two double doublets at 1.73 ppm and 1.92 ppm are observed in the ^{1}H NMR spectrum of the **6d** isomer. They are assigned to the protons of the methylene group (AB part of the ABM spin system). The ^{1}H NMR spectrum of the **6c** isomer contains the same type of doublets but at 1.48 ppm and 1.93 ppm. In such a way, the value $\Delta\delta_Z = \delta_B - \delta_A =$ 0.45 ppm, obtained for the *Z*-2-bromo-1-ferrocenyl-1-phenylcyclopropane **6c** isomer is larger than that obtained for the *E*-(**6d**) isomer ($\Delta\delta_E = \delta_B - \delta_A = 0.19$ ppm). Similar differences have been observed also in the ^{1}H NMR spectra of the *Z*- and *E*-isomers of 2-bromo-1-alkyl-1-ferrocenylcyclopropanes [6,7,9,10]. Probably this can be used to determine the geometrical configuration of monobromoferrocenylcyclopropanes.

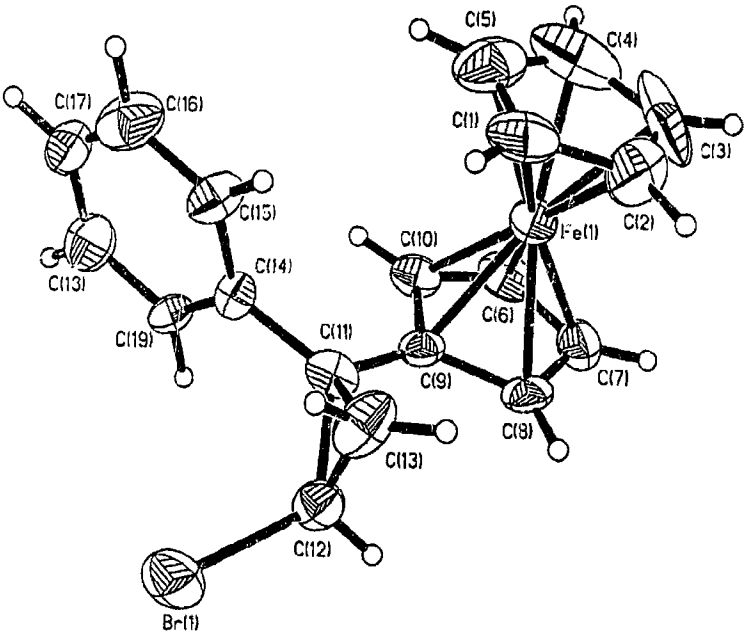
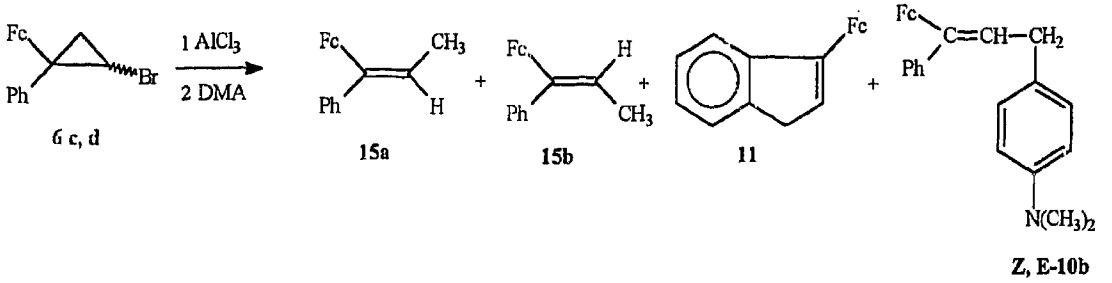


Fig. 1. Crystal structure of **6d**. Selected bond lengths (Å): Br–C_{12} = 1.911(11), C_{11}–C_{12} = 1.486(13), C_{11}–C_{13} = 1.508(15) and C_{12}–C_{13} = 1.464(17); and selected bond angles (°): C_{12}–C_{11}–C_{13} = 58.7(7), C_{11}–C_{12}–C_{13} = 61.5(7) and C_{11}–C_{13}–C_{12} = 60.0(7).

We also found that the monobromides **6c** and **6d** undergo ring opening when treated with $AlCl_3$ in boiling CH_2Cl_2:



3-Ferrocenylindene **11**, *Z*- and *E*-1-ferrocenyl-1-phenylpropenes (**15a** and **15b**), and compound **10b** (the product of alkylation of *N,N*-dimethylaniline at the *para*-position) were isolated by preparative thin-layer chromatography on silica gel. Besides, during the ring opening of *Z*-**6c** a mixture of isomer products is obtained, *E*-**15b** being the prevailing product (~ 70%), while after ring opening of *E*-**6d** the prevailing isomer in the product mixture is *Z*-**15a** (~ 60%).

The structure of compounds **11**, **15a**, **15b**, and **10b** was confirmed by ^{1}H NMR spectral data and elemental analysis (see Section 4).

One can conclude from the ^{1}H NMR spectra that the 3-*p*-dimethylaminophenyl-1-ferrocenyl-1-phenylprop-1-ene **10b** exists as a mixture of *Z*- and *E*-isomers in a ratio of 1:1. We could not separate these two isomers by chromatography.

It seems that the mechanism of ring opening in the monobromides **6c** and **6d** is similar to that in the isomeric 2-bromo-1-ferrocenyl-1-methylcyclopropanes **6a,b** in the presence of zinc salts [7]:

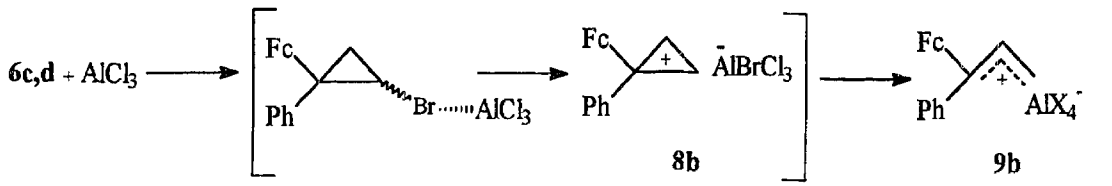


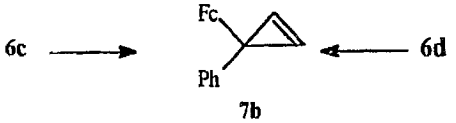
Table 1
Crystal data, data collection, and refinement parametres for compounds **6d** and **7b**

Data	**6d**	**7b**
Empirical formula	$C_{19}H_{17}BrFe$	$C_{19}H_{16}Fe$
Formula weight	381.14	300.14
Color; habit	red; irregular	orange; prism
Crystal size (mm)	0.5×0.4×0.32	0.24×0.14×0.1
Crystal system	orthorhombic	triclinic
Space group	*Pbca*	$P-1$
a (Å)	12.450(6)	8.311(2)
b (Å)	13.733(6)	9.103(2)
c (Å)	18.150(7)	10.296(2)
α (°)		111.71(2)
β (°)		97.60(2)
γ (°)		95.28(2)
V (Å^3)	3103(3)	708.9(2)
Z	8	2
D_{calc} (g cm^{-3})	1.631	1.406
$F(000)$	1536	312
Absorption coefficient (mm^{-1})	3.537	1.049
Radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
Monochromator	graphite	graphite
Temperature	293	293
2θ range	$3 < 2\theta < 50$	$3 < 2\theta < 50$
Index ranges	$0 \le h \le 14$	$0 \le h \le 9$
	$0 \le k \le 16$	$0 \le k \le 9$
	$0 \le l \le 21$	$0 \le l \le 12$
Scan type	ω	ω
Total reflections	2702	2601
Unique reflections	2702	2420
Reflections with $I > 2\sigma(I)$	1308	1861
R_{int}	0.00	0.1997
Solution	Patterson	Direct methods
Refinement method	Full-matrix	Full-matrix
	least squares	least squares
Number of parameters refined	191	182
Hydrogen atoms	Riding model	Riding model
	fixed isotropic U	fixed isotropic U
R (obs. data)	0.0588	0.0529
wR (obs. data)	0.061	0.0616
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$	$w^{-1} = \sigma^2(F) + 0.0008F^2$
Goodness-of-fit	1.17	1.15
min/max residual electron density, e·Å^{-3}	−0.75/0.79	−0.64/0.63

The intermediate ferrocenyl(phenyl)cyclopropyl carbocation **8b** with a positive charge centred at the β-carbon atom of the three-membered cycle, contrary to the α-ferrocenylcyclopropyl cation [11], readily undergoes ring opening to form a ferrocenylallyl carbocation **9b** stabilised by the ferrocenyl substituent [5,6].

Further, the ferrocenylallyl cation **9b** undergoes intramolecular transformation, reduction and alkylates *N,N*-dimethylaniline (as a rule, this involves the least substituted carbenium centre of the allyl cation [5,12]). Earlier, we observed the reduction of similar ferrocenylallyl cations only in the case of a 3-methyl-2,3-(1,2,2-trimethylcyclopenta-1,3-diyl)-1-ferrocenylallyl cation [13,14], which apparently is related to the participation of the iron atom.

The elimination of HBr from **6c** and **6d** upon treatment with *t*-BuOK in DMSO resulted in the formation of 3-ferrocenyl-3-phenylcyclopropene **7b**, which is very stable in crystalline state:



7b

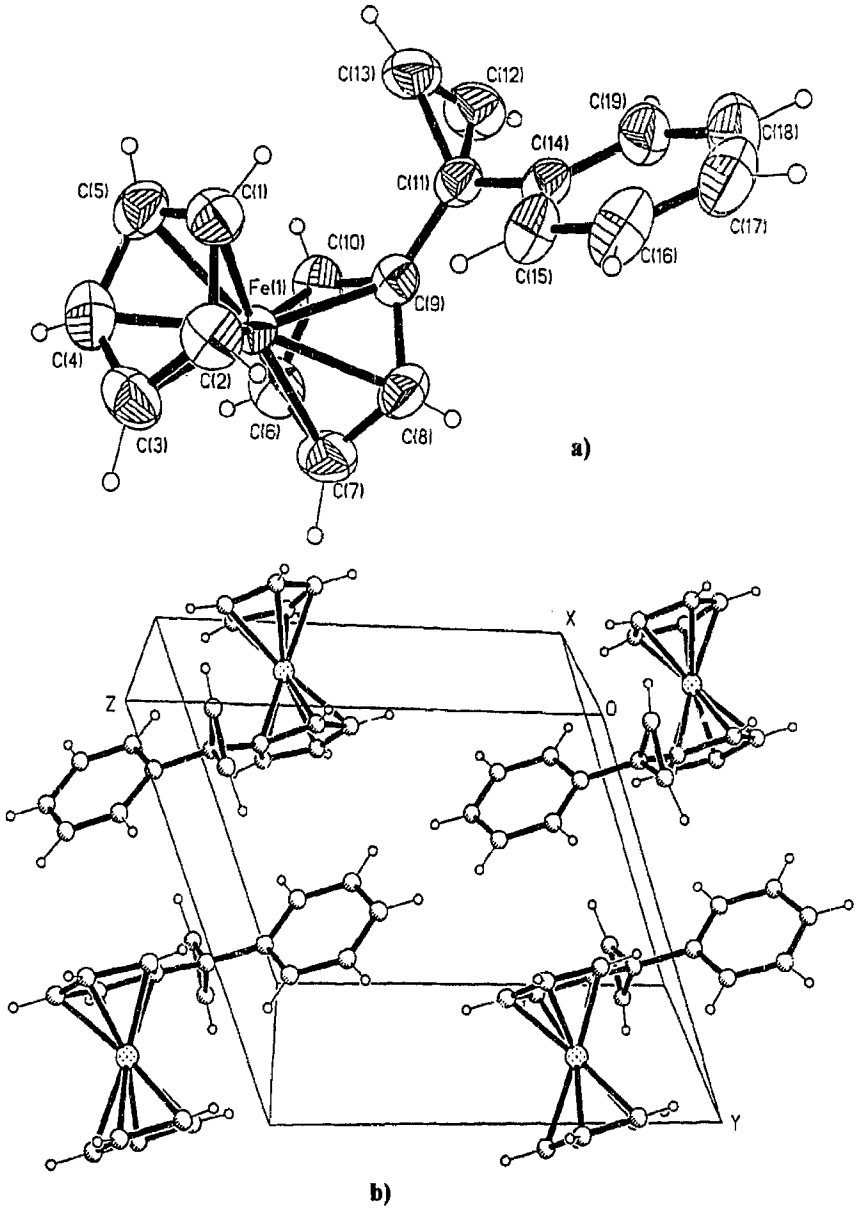
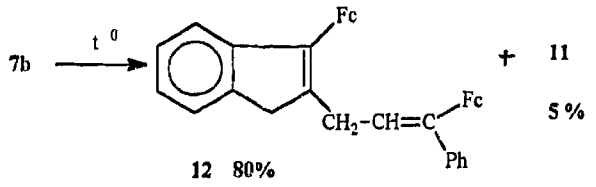


Fig. 2. (a) Crystal structure of **7b**. Selected bond lengths (Å): C_{12}–C_{13} = 1.268(11), C_{11}–C_{13} = 1.507(8), C_{11}–C_{12} = 1.522(7), C_9–C_{11} = 1.487(8) and C_{11}–C_{14} = 1.511(7); and selected bond angles (°): C_{12}–C_{11}–C_{13} = 49.5(4), C_{11}–C_{13}–C_{12} = 65.9(5), C_{13}–C_{12}–C_{11} = 64.7(4) and C_9–C_{11}–C_{14} = 119.1(4). (b) Crystal packing of **7b**.

The structure of **7b** was determined by ^{1}H and ^{13}C NMR spectroscopy (see Section 4). Besides, we were the first to carry out X-ray structural analysis of monocrystals of ferrocenylcyclopropene, which does not have substituents in positions 1 and 2.

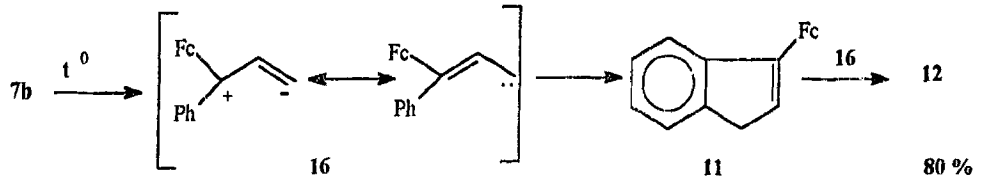
Crystal data, data collection and refinement parametres for the cyclopropene **7b** are listed in Table 1. The spacial position of the three-membered ring (see Fig. 2a) is very important in this structure. The three-membered cycle is an irregular triangle distorted in the direction of the C_{11} carbon atom. The bond length of the double CH=CH bond is 1.268(11) Å and the sharp angle at C_{11} is $\omega = 49.5(4)°$. The position of the ferrocenyl fragment in the molecule **7b** corresponds to the bisector of the angle at C_{11}. The geometry of the ferrocenyl sandwich and bond lengths Fe–C and C–C are not changed by the presence of the three-membered ring.

We found that 3-ferrocenyl-3-phenylcyclopropene **7b**, when boiled in toluene, forms 2-(3-ferrocenyl-3-phenylallyl)-3-ferrocenylindene **12** with a high yield and 3-ferrocenylindene **11** as a by-product (~ 5%).



The structure of compounds **11** and **12** is confirmed by ^{1}H NMR spectra and elemental analysis (see Section 4). The ^{1}H NMR spectral data indicate that compound **12** exists as a ~ 5:1 mixture of *Z*-(**12a**) and *E*-(**12b**) isomers. Recrystallisation from hexane gave pure *Z*-isomer **12a**.

Obviously, the formation of **12a,b** from the cyclopropene **7b** is caused by thermal heterolysis of one of the σ C–C bonds [1–3,15]. One of the possible mechanisms is shown below and includes the formation of an intermediate **16** with its selective cyclisation exclusively at the phenyl nucleus. Then alkylation of the intermediate 3-ferrocenylindene **11** takes place:



Contrary to the thermal ring opening in **7b**, the protonation of **7b** with superacids gives indene **11** as a major product (~ 60%) and the reaction proceeds through the formation of 1-phenyl-1-ferrocenylallyl cation **9b** [9,10].

3. Conclusion

The results presented in this paper and results reported earlier [9,10] allow to conclude that a regioselective intramolecular transformation in 3-ferrocenyl-3-phenylcyclopropene **7b** takes place. When the small cycle is opened, although the reaction conditions might be different, alkylation of the phenyl group is always observed. We did not observe intramolecular cyclisation in the ferrocenyl fragment, although similar intramolecular alkylation of the γ-ferrocenyl group (relative to the cation or carbenium centre) is well known [1–3,16–18].

In our opinion, this regioselectivity of the intramolecular transformation of **7b** is related to the geometry of the molecule and basically to the spacial orientation of the aryl and of the ferrocenyl substituents relative to the three-membered ring. For example, the C_5H_4 group in the ferrocenyl fragment lies in one and the same plane with the bisector of the C_{12}-C_{11}-C_{13} angle in the cyclopropene ring. In the same time, the phenyl group lies in a plane perpendicular to the above-mentioned plane. During the opening of the cyclopropene ring, the electronodeficient end of the formed intermediates **9b** and **16** is situated very near to the *ortho*-carbon atom of the phenyl substituent. This is responsible for the regioselectivity of alkylation.

4. Experimental

The solvents were dried by standard methods and distilled prior to use. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University. ^{1}H and ^{13}C NMR spectra were registered in $CDCl_3$ on a 'Gemini 200 Varian' spectrometre at 200 MHz using Me_4Si as the internal standard. FAB$^+$ MS was recorded on a 'JEOL AX-505' spectrometre. The parametres of the unit cell and the X-ray diffraction intensities were recorded on 'Siemens P4' for **6d** and for **7b** on 'Siemens P4/PC' spectrometres.

4.1. 2,2-Dibromo-1-ferrocenyl-1-phenylcyclopropane 13b

The dibromide **13b** was prepared from 1-ferrocenyl-1-phenyl-ethylene with a 73% yield as orange crystals [16]. FAB^+ MS, m/z 460 (M^+). Calcd. $C_{19}H_{16}Br_2Fe$ (M^+) 460.17.

4.2. Reduction of the dibromide 13b

The dibromide **13b** was reduced by zinc powder in aqueous ethanol in the presence of Trilon B following a known procedure [17]. The preparative TLC of the reaction mixture on silica gel (using hexane as eluent) gave:

1-ferrocenyl-1-phenylcyclopropane **14** (yield 24%), R_f 0.75, orange crystals, m.p. 89°C. FAB^+ MS, m/z 302 (M^+). Calcd. $C_{19}H_{18}Fe$ (M^+) 302.18;

Z-2-bromo-1-ferrocenyl-1-phenylcyclopropane **6c** (yield 31%), R_f 0.63, orange needles, m.p. 103–104°C, ^1H NMR: $\delta = 1.48$ (dd, 1H, CH_2, $J_{gem} = 6.65$ Hz, $J_{trans} = 5.16$ Hz, $J_{cis} = 8.0$ Hz); 1.93 (dd, 1H, CH_2, $J_{gem} = 6.65$ Hz, $J_{trans} = 5.16$ Hz, $J_{cis} = 8.16$ Hz); 3.44 (dd, 1H, CH, $J = 5.16$, 8.16 Hz); 4.0 (s, 5H, C_5H_5); 3.88 (m, 1H, C_5H_4); 4.10 (m, 2H, C_5H_4); 4.14 (m, 1H, C_5H_4); 7.29–7.49 (m, 5H, C_6H_5); ^{13}C NMR: $\delta = 68.70$ (C_5H_5); 69.06, 67.97, 66.68 (C_5H_4); 90.96 (C_9, see numbering on Fig. 1); 30.72 (C_{11}); 32.65 (C_{12}); 22.85 (C_{13}); 131.08 (C_{14}); 129.85, 128.21, 127.13 (C_6H_5). Anal. Calcd. for $C_{19}H_{17}BrFe$: C, 59.88; H, 4.50; Fe, 14.66; Br, 20.96. Found: C, 60.04; H, 4.27; Fe, 14.66; Br, 20.69;

E-2-Bromo-1-ferrocenyl-1-phenylcyclopropane **6d** (yield 28%), R_f 0.56, orange crystals, m.p. 85–86°C, ^1H NMR: $\delta = 1.73$ (dd, 1H, CH_2, $J_{gem} = 6.4$ Hz, $J_{trans} = 5.0$ Hz, $J_{cis} = 8.0$ Hz); 1.92 (dd, 1H, CH_2, $J_{gem} = 6.4$ Hz, $J_{trans} = 5.0$ Hz, $J_{cis} = 8.0$ Hz); 3.37 (dd, 1H, CH, $J = 5.0$, 8.0 Hz); 4.13 (s, 5H, C_5H_5); 3.80 (m, 2H, C_5H_4); 4.05 (m, 2H, C_5H_4); 7.32–7.50 (m, 5H, C_6H_5); ^{13}C NMR: $\delta = 68.70$ (C_5H_5); 69.50, 67.61, 67.58, 66.00 (C_5H_4); 92.01 (C_9); 30.98 (C_{11}); 29.95 (C_{12}); 25.13 (C_{13}); 138.81 (C_{14}); 129.71, 128.80, 127.90 (C_6H_5). Anal. Calcd. for $C_{19}H_{17}BrFe$: C, 59.88; H, 4.50; Fe, 14.66; Br, 20.96. Found: C, 59.65; H, 4.70; Fe, 14.83; Br, 21.24.

4.3. 3-Ferrocenyl-3-phenylcyclopropene 7b

A total of 0.38 g (1 mmol) of bromide **6c** or **6d** was added to a mixture of 20 ml dry DMSO and 0.17 g (1.5 mmol) *t*-BuOK. The reaction mixture was stirred in an argon atmosphere for 12 h at 20°C and then 100 ml of benzene and 50 ml of water were added. The organic layer was separated and washed with water. The solvent was removed in vacuo and the residue was chromatographed on Al_2O_3 in hexane. Compound **7b** (yellow crystals, yield 73% from **6c** and 70% from **6d**) was isolated. M.p. 69°C; ^1H NMR: $\delta = 4.16$ (s, 5H, C_5H_5); 3.89 (m, 2H, C_5H_4); 4.05 (m, 2H, C_5H_4); 7.32 (s, 2H, CH=CH); 7.20–7.41 (m, 5H, C_6H_5). ^{13}C NMR: $\delta = 68.10$ (C_5H_5); 67.90, 67.14 (C_5H_4); 97.42 (C_9); 19.81 (C_{11}); 112.84 (C_{12}, C_{13}); 146.46 (C_{14}); 126.07, 127.92, 125.84 (C_6H_5). Anal. Calcd. for $C_{19}H_{16}Fe$: C, 76.02; H, 5.37; Fe, 18.61. Found: C, 75.89; H, 5.42; Fe, 18.83.

4.4. Thermal treatment of 3-ferrocenyl-3-phenylcyclopropene 7b

A solution of 0.30 g (1 mmol) of **7b** in 50 ml of toluene was boiled in an argon atmosphere for 10 h. After evaporation of the solvent in vacuo, the residue was subjected to preparative TLC on SiO_2 (hexane–benzene, 6:1) to give:

3-Ferrocenylindene **11**, 0.15 g (5%), R_f 0.85. m.p. 92–93°C. ^1H NMR: $\delta = 3.38$ (d, 2H, CH_2, $J = 2.3$ Hz); 4.13 (s, 1H, C_5H_5); 4.33 (m, 2H, C_5H_4); 4.63 (m, 2H, C_5H_4); 6.52 (m, 1H, $J = 2.3$ Hz); 7.26–7.93 (m, 4H, C_6H_4). ^{13}C NMR: $\delta = 69.18$ (C_5H_5); 68.43, 67.09 (C_5H_4); 80.73 (C_9Fe); 120.94 (C_2); 38.06 (C_1); 144.94, 144.15, 141.45 (C_3, C_8, C_9); 128.69, 126.00, 124.55, 123.87 (C_6H_4). FAB^+ MS, m/z 300 (M^+). Calcd. $C_{19}H_{16}Fe$ (M^+) 300.17;

3-Ferrocenyl-2-(3-ferrocenyl-3-phenylallyl)indenes **12a** and **12b** (~5:1), 0.25 g (80%), R_f 0.52, m.p. 127–128°C. Pure *Z*-isomer **12a** was obtained after recrystallisation from hexane: m.p. 140–141°C; ^1H NMR **12a**: $\delta = 3.27$ (d, 2H, CH_2, $J = 7.2$ Hz); 3.37 (s, 2H, CH_2); 4.12 (s, 5H, C_5H_5); 4.10 (s, 5H, C_5H_5); 4.10–4.13 (m, 2H, C_5H_4); 4.16 (m, 2H, C_5H_4); 4.31 (m, 2H, C_5H_4); 4.47 (m, 2H, C_5H_4); 6.0 (t, 1H, CH, $J = 7.2$ Hz); ^1H NMR **12b**: $\delta = 3.49$ (d, 2H, CH_2, $J = 7.2$ Hz); 3.53 (s, 2H, CH_2); 4.17 (s, 5H, C_5H_5); 4.18 (s, 5H, C_5H_5); 4.22 (m, 2H, C_5H_4); 4.28 (m, 2H, C_5H_4); 4.37 (m, 2H, C_5H_4); 4.61 (m, 2H, C_5H_4); 5.70 (t, 1H, CH, $J = 7.2$ Hz). Anal. Calcd. for $C_{38}H_{32}Fe_2$ **12a,b**: C, 76.02; H, 5.37; Fe, 18.61. Found for **12a,b**: C, 76.24; H, 5.53; Fe, 18.37. Found for **12a**: C, 75.87; H, 5.37; Fe, 18.46.

4.5. Interaction of 6c,d with $AlCl_3$

A total of 0.16 g (1.2 mmol) of $AlCl_3$ was added to a solution of 0.38 g (1 mmol) of **6c** in 30 ml of CH_2Cl_2. The reaction mixture was boiled under reflux in an inert atmosphere for 3 h with stirring. Then the mixture was cooled to ambient temperature and 2 ml of *N,N*-dimethylanyline was added. After 1 h, 100 ml of benzene was added, the reaction mixture was washed with water, 1% HCl, and again with water. The solvent was removed in vacuo, and residue was subjected to preparative TLC on SiO_2 (hexane–benzene, 10:1) to give:

Z-1-ferrocenyl-1-phenylpropene-1 **15a**, 0.046 g (yield 15.5%); R_f 0.90, orange oil [15], ^{1}H NMR: $\delta = 1.53$ (d, 3H, CH_3, $J = 7.0$ Hz); 4.07 (s, 5H, C_5H_5); 4.0–4.3 (m, 4H, C_5H_4); 6.05 (q, 1H, CH, $J = 7.0$ Hz). Anal. Calcd. for $C_{19}H_{18}Fe$: C, 75.51; H, 6.00; Fe, 18.49. Found: C, 75.68; H, 5.91; Fe, 18.70;

E-1-ferrocenyl-1-phenylpropene-1 **15b**, 0.109 g (yield 37%); R_f 0.86, orange oil [15], ^{1}H NMR: $\delta = 2.07$ (d, 3H, CH_3, $J = 7.2$ Hz); 4.15 (s, 5H, C_5H_5); 4.0–4.3 (m, 4H, C_5H_4); 5.69 (q, 1H, CH, $J = 7.2$ Hz). Anal. Calcd. for $C_{19}H_{18}Fe$: C, 75.51; H, 6.00; Fe, 18.49. Found: C, 75.42; H, 6.21; Fe, 18.33;

3-Ferrocenylindene **11**, 0.02 g (yield 6.7%); R_f 0.82, m.p. 92°C (lit. 92–93°C [9,10]). FAB$^+$ MS, m/z 300 (M^+). Calcd. $C_{19}H_{16}Fe$ (M^+) 300.17;

3-*p*-Dimethylaminophenyl-1-ferrocenyl-1-phenyl-1-propene **10b** as a mixture of *Z*- and *E*-isomers (~ 1:1); 0.043 g (10%); R_f 0.21, orange oil, ^{1}H NMR: $\delta = 3.16$ (d, 2H, CH_2, $J = 6.8$ Hz); 3.30 (d, 2H, CH_2, $J = 6.8$ Hz); 2.85 (s, 6H, CH_3); 3.0 (s, 6H, CH_3); 3.70 (s, 5H, C_5H_5); 4.07 (s, 5H, C_5H_5); 3.70–4.15 (m, 8H, C_5H_4); 6.07 (t, 1H, CH, $J = 6.8$ Hz); 6.81 (t, 1H, CH, $J = 6.8$ Hz); 6.85–7.80 (m, 18H, C_6H_5, C_6H_4). Anal. Calcd. for $C_{27}H_{27}FeN$: C, 76.96; H, 6.46; Fe, 13.26; N, 3.32. Found: C, 77.07; H, 6.30; Fe, 13.41; N, 3.20.

In a similar way, **6d** (0.38 g) gave 0.085 g (28.1%) of **15a**; 0.055 g (18.3%) of **15b**; 0.03 g (10%) of **11**, and 0.047 g (11%) of *Z,E*-**10b**.

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