

CYCLOPROPANES WITH A FERROCENYL GROUP

A.N. NESMEYANOV, E.I. KLIMOVA, Yu.T. STRUCHKOV, V.G. ANDRIANOV,
 V.N. POSTNOV and V.A. SAZONOVA *

Moscow State University, Chemistry Department, Moscow (U.S.S.R.)

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Summary

1-Ferrocenyl-2-arylcyclopropanes have been synthesized by catalytic thermolysis of ferrocenylpyrazolines. An X-ray diffraction study of *trans*-1-ferrocenyl-2-*p*-methoxyphenylcyclopropane isolated in an individual form was carried out.

In the chemistry of ferrocene a number of cyclopropanes with ferrocenyl substituents are known [1–7], yet the synthesis of ferrocenylcyclopropanes from their corresponding pyrazolines is more advantageous [8].

In the present paper it is shown that catalytic thermolysis [9] of isomeric ferrocenylpyrazolines gives a mixture of *cis*- and *trans*-1-ferrocenyl-2-arylcyclopropanes (Scheme 1).

The formation of a mixture of approximately equal amounts of III and IV is indicated by the doublet character of OCH₃ proton signals and the doubled number of signals of protons of *p*-substituted phenyl rings in the PMR spectrum of a freshly prepared sample.

The mixture of cyclopropanes cannot be separated chromatographically on Al₂O₃ or SiO₂, however, crystallization from dilute alcohol solutions gives only

Scheme 1

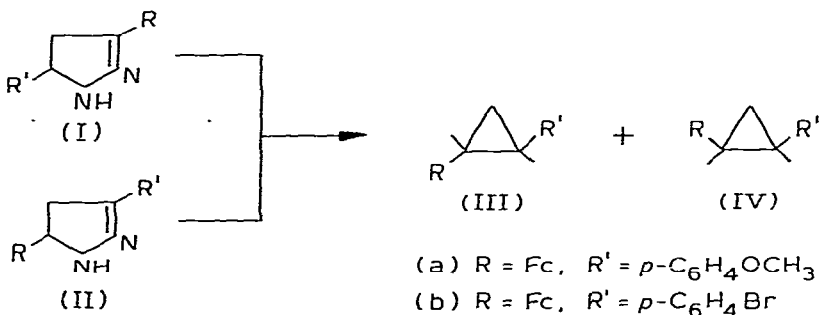
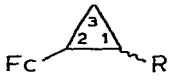


TABLE 1
 ^{13}C NMR PARAMETERS OF *cis*- AND *trans*-CYCLOPROPANES AND PURE *trans* ISOMERS

 cyclopropanes	$\delta(\text{C}(2))$	$\delta(\text{C}(1))$	$\delta(\text{C}(3))$
IIIa + IVa	26.8 24.1	22.4 18.9	18.3 11.8
IIIa	26.8	22.4	18.3
IIIb + IVb	27.1 24.3	23.3 19.4	18.8 11.8
IIIb	27.2	23.4	18.8
<i>trans</i> -1,2-Diphenylcyclopropane [10]	27.7	27.7	17.9
<i>cis</i> -1,2-Diphenylcyclopropane [10]	24.2	24.2	10.8

needles of the pure *trans* form without formation of any by-products.

Table 1 gives data on ^{13}C NMR spectra for the fresh mixture of *cis*- and *trans*-cyclopropanes and pure *trans* isomers.

It can be assumed that in the ^{13}C NMR spectra of the ferrocene series signals due to the unsubstituted carbon atom of a *trans*-cyclopropane derivative will be observed further downfield than that of a *cis* isomer [10].

To determine unambiguously the mutual arrangement of substituents in the cyclopropane nucleus we have undertaken an X-ray diffraction study of 1-ferrocenyl-2-*p*-methoxyphenylcyclopropane $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{C}_3\text{H}_4\text{C}_6\text{H}_4\text{OCH}_3$ (IIIa).

Crystals of IIIa are monoclinic, a 15.495(1), b 12.2365(9), c 8.3197(6) Å, $\beta = 94.39(1)^\circ$, V 1572.9 Å³, mol. wt. 332.2, d_{exp} 1.39, d_{calc} 1.40 g cm⁻³ for $Z = 4$, space group $P2_1/C$. Intensities of 1496 reflections with $I \geq 2\sigma(I)$ were measured with an automatic Hilger—Watts diffractometer without absorption correction ($\lambda(\text{Cu-K}\alpha)$, graphite monochromator, $\theta/2\theta$ scan).

The structure was solved by the standard heavy atom method and refined by the full-matrix isotropic (anisotropic for Fe atom) least squares, $R = 0.056$. Atomic coordinates and temperature factors are given in Table 2, bond lengths and bond angles in Tables 3 and 4.

According to X-ray structure results, the mutual orientation of substituents in the cyclopropane nucleus (Fig. 1) corresponds to the *trans* configuration, since the torsional angle around the C(11)—C(12) bond is 140.2° . Such a configuration seems to be the most favourable with respect to both intra- and intermolecular steric interactions.

The geometry of the ferrocenyl nucleus is unexceptional, i.e., cyclopentadienyl rings are planar with an average C—C bond length of 1.41 Å, while the average Fe—C distance of 2.04 Å is very close to that found in ferrocene and its derivatives. The sandwich conformation is closer to the eclipsed one, the angle of relative ring rotation being 9.1° (Fig. 2). The dihedral angle between ring planes is 3.6° .

The *p*-methoxyphenyl fragment is planar with normal C—C and C—O bond lengths. The coplanarity of the methoxy substituent and phenyl ring causes a

TABLE 2

ATOMIC COORDINATES ($\times 10^4$) AND ISOTROPIC TEMPERATURE FACTORS B_{iso}

Atom	X	Y	Z	B_{iso} (\AA^2)
Fe	1299(1)	51(1)	2657(2)	^a
O	5837(5)	-1421(6)	-4387(9)	5.8(2)
C(1)	1014(7)	1660(9)	2273(13)	5.0(3)
C(2)	493(7)	1241(9)	3446(14)	5.6(3)
C(3)	1036(8)	846(10)	4710(14)	5.8(3)
C(4)	1884(7)	999(9)	4409(15)	5.9(3)
C(5)	1902(7)	1516(10)	2895(14)	5.7(3)
C(6)	1010(7)	788(9)	561(12)	4.4(2)
C(7)	601(7)	-1278(9)	1833(13)	4.7(2)
C(8)	1229(7)	-1593(9)	3036(14)	5.3(3)
C(9)	2061(7)	-1284(9)	2499(14)	5.0(3)
C(10)	1917(7)	-787(8)	971(12)	4.1(2)
C(11)	2586(6)	-338(8)	1(12)	4.1(2)
C(12)	2380(7)	488(9)	-1253(14)	5.5(3)
C(13)	2630(6)	-656(9)	-1763(13)	4.5(2)
C(14)	3451(6)	-852(8)	-2470(12)	3.9(2)
C(15)	4217(7)	-292(8)	-1990(13)	4.8(3)
C(16)	4979(7)	-468(8)	-2667(13)	4.7(2)
C(17)	5027(6)	-1284(8)	-3845(12)	4.2(2)
C(18)	4287(6)	-1846(8)	-4328(13)	4.5(2)
C(19)	3535(6)	-1629(8)	-3666(12)	4.4(2)
C(20)	5910(7)	-2195(10)	-5619(15)	6.2(3)

^a Parameters of anisotropic temperature factor ($\times 10^2$) for the Fe atom in the form $T = \exp[-1/4(B_{11}hka^{*2} + \dots + 2B_{23}klb^*c^*)]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	453(8)	299(6)	423(7)	-15(9)	48(5)	-19(8)

distortion of the exocyclic angles C(16)C(17)O [$114.5(9)^\circ$] and C(18)C(17)O [$127.3(9)^\circ$] due to steric repulsion between the methyl group and the *ortho*-carbon atom C(18).

Some distortion of the local symmetry D_{3h} of the cyclopropane nucleus is to be noted as the C—C bond lengths in the threemembered cycle are not equal.

TABLE 3

BOND LENGTHS d (\AA)

Bond	d	Bond	d	Bond	d
Fe—C(1)	2.037(11)	C(2)—C(3)	1.38(2)	C(12)—C(13)	1.52(1)
Fe—C(2)	2.057(11)	C(3)—C(4)	1.37(2)	C(13)—C(11)	1.52(1)
Fe—C(3)	2.034(12)	C(4)—C(5)	1.41(2)	C(13)—C(14)	1.46(1)
Fe—C(4)	2.022(12)	C(5)—C(1)	1.44(2)	C(14)—C(15)	1.40(1)
Fe—C(5)	2.024(12)	C(6)—C(7)	1.41(1)	C(15)—C(16)	1.37(1)
Fe—C(6)	2.043(10)	C(7)—C(8)	1.40(1)	C(16)—C(17)	1.41(1)
Fe—C(7)	2.042(11)	C(8)—C(9)	1.45(1)	C(17)—C(18)	1.37(1)
Fe—C(8)	2.041(11)	C(9)—C(10)	1.41(1)	C(18)—C(19)	1.35(1)
Fe—C(9)	2.026(11)	C(10)—C(6)	1.42(1)	C(19)—C(14)	1.39(1)
Fe—C(10)	2.036(10)	C(10)—C(11)	1.47(1)	C(17)—O	1.38(1)
C(1)—C(2)	1.41(2)	C(11)—C(12)	1.47(1)	O—C(20)	1.41(1)

TABLE 4
BOND ANGLES $\omega(^{\circ})$

Angle	ω	Angle	ω	Angle	ω
C(1)—C(2)—C(3)	107.9(1.0)	C(6)—C(10)—C(11)	126.6(9)	C(13)—C(14)—C(15)	122.1(9)
C(2)—C(3)—C(4)	110.4(1.0)	C(9)—C(10)—C(11)	125.9(9)	C(14)—C(15)—C(16)	123.1(1.0)
C(3)—C(4)—C(5)	108.0(1.0)	C(10)—C(11)—C(12)	121.5(9)	C(15)—C(16)—C(17)	119.6(1.0)
C(4)—C(5)—C(1)	107.0(1.0)	C(10)—C(11)—C(13)	121.2(9)	C(16)—C(17)—C(18)	118.2(9)
C(5)—C(1)—C(2)	106.7(1.0)	C(11)—C(12)—C(13)	61.3(7)	C(17)—C(18)—C(19)	120.6(1.0)
C(6)—C(7)—C(8)	109.1(9)	C(12)—C(13)—C(11)	57.7(7)	C(18)—C(19)—C(14)	123.8(9)
C(7)—C(8)—C(9)	107.2(9)	C(13)—C(11)—C(12)	61.0(7)	C(19)—C(14)—C(15)	114.6(9)
C(8)—C(9)—C(10)	108.0(9)	C(11)—C(13)—C(14)	122.2(9)	C(16)—C(17)—O	114.5(9)
C(9)—C(10)—C(6)	107.5(9)	C(12)—C(13)—C(14)	120.8(9)	C(18)—C(17)—O	127.3(9)
C(10)—C(6)—C(7)	108.3(9)	C(13)—C(14)—C(19)	123.3(9)	C(17)—O—C(20)	116.6(8)

Two bonds, C(13)—C(11) and C(12)—C(13), are very similar in length to that in cyclopropane (1.5096 Å) [11], while the third one, C(11)—C(12), is somewhat shorter. A similar effect has already been observed for a number of substituted cyclopropanes [12] with substituents capable of π -conjugation and suitably oriented to the plane of the threemembered cycle [13,14].

In the molecule studied here the dihedral angle between planes of cyclopropane and phenyl rings is 89.3° , i.e., these rings are almost orthogonal, which

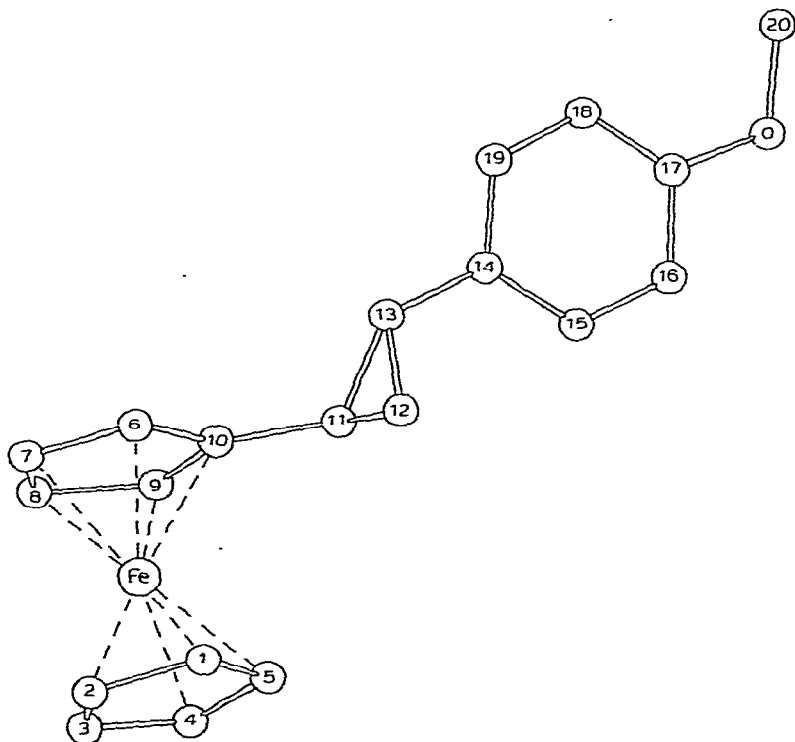


Fig. 1. The molecular geometry of IIIa.

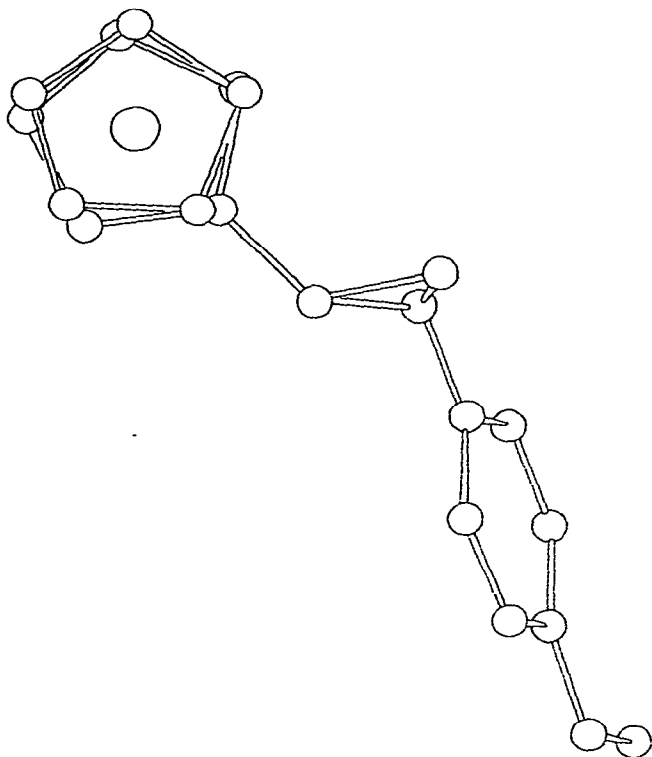


Fig. 2. The ferrocenyl sandwich conformation in IIIa.

favours such π -interaction when the C(13)—C(11) and C(13)—C(12) bonds are weakened.

The cause of the unusual readiness of 1-ferrocenyl-2-arylcyclopropanes to undergo *cis-trans* isomerisation is under study.

Experimental

cis- and trans-1-Ferrocenyl-2-p-methoxyphenylcyclopropanes (IIIa + IVa)

(a). A well ground mixture of 0.72 g of 3-*p*-methoxyphenyl-5-ferrocenyl-2-pyrazoline (IIa), 0.1 g of solid NaOH/Ag and 0.01 g of platinated (10%) coal was heated intensively until nitrogen evolution ceased. On cooling the mixture the reaction product was extracted with benzene and chromatographed on Al₂O₃ with benzene petroleum ether (1/1). 0.60 g (90% of the theoretical yield) of a mixture of cyclopropanes with melting point 50°C (recrystallized from alcohol) was obtained. (Found: C, 72.32; H, 6.17; Fe, 16.88. C₂₀H₂₀FeO calcd.: C, 72.30; H, 6.07; Fe, 16.81%.)

(b). Similarly, 0.36 g of 3-ferrocenyl-5-*p*-methoxyphenyl-2-pyrazoline (Ia) yielded 0.28 g (86% of the theoretical yield) of a mixture of cyclopropanes with melting point 50–51°C (recrystallised from alcohol). PMR spectrum of IIIa + IVa: δ 1.27, 2.1 (m 4H, C₃H₄), 3.68 and 3.77 (s, 3H, CH₃O), 4.03 (s, 4H, C₅H₄), 4.1 and 4.14 (s, 5H, C₅H₅), 7.0 (m, 4H, —C₆H₄—) ppm.

trans-1-Ferrocenyl-2-p-methoxyphenylcyclopropane (IIIa)

0.3 g of the cyclopropane mixture (IIIa + IVa) was dissolved with heating, in 10 ml of ethanol. The solution was left to stand at room temperature for several days. *trans-1-Ferrocenyl-2-p-methoxyphenylcyclopropane* precipitated as long orange needles. 0.25 g (83%) of the *trans* isomer was obtained, m.p. 59–60°C. Pure *trans* isomer was also isolated from the mother liquid on evaporation.

(Found: C, 72.28; H, 6.10; Fe, 16.90. C₂₀H₂₀FeO calcd.: C, 72.30; H, 6.07; Fe, 16.81%.) PMR spectrum of IIIa: δ 1.18 and 1.83 (m, 4H, C₃H₄), 3.7 (s, 3H, CH₃O), 4.0 (s, 4H, C₅H₄), 4.07 (s, 5H, C₅H₅) 6.70 and 7.00 (d, 4H, C₆H₄) ppm.

cis- and *trans-1-Ferrocenyl-2-p-bromophenylcyclopropanes* (IIIb, IVb) were obtained similarly.

(a) 0.65 g (85%) of the cyclopropane mixture with a melting point 68–69°C (recrystallised from alcohol) was obtained from 0.8 g of 3-*p*-bromophenyl-6-ferrocenyl-2-pyrazoline (IIb). (Found: C, 59.78; H, 4.52; Fe, 14.65; Br, 20.81. C₁₉H₁₇FeBr calcd.: C, 59.88; H, 4.50; Fe, 14.66; Br, 20.96%.)

(b) 0.31 g (81%) of the cyclopropane mixture with a melting point 70°C (recrystallised from alcohol) was obtained from 0.4 g of 3-ferrocenyl-5-*p*-bromophenyl-2-pyrazoline (Ib). PMR spectrum of IIIb + IVb; δ 1.21 and 2.16 (m, 4H, C₃H₄), 3.87 (s, 4H, C₅H₄), 4.01 and 4.08 (s, 5H, C₅H₅), 7.00 (m, 4H, C₆H₄) ppm.

trans-1-Ferrocenyl-2-p-bromophenylcyclopropane (IIIb)

Obtained similarly. 0.4 g of the IIIb + IVb mixture gave 0.33 g (80%) of the *trans* isomer of IIIb, m.p. 77°C. (Found: C, 59.90; H, 4.48; Fe, 14.70; Br, 20.85. C₁₉H₁₇FeBr calcd.: C, 59.88; H, 4.50; Fe, 14.66; Br, 20.96%.) PMR spectrum of IIIb: δ 1.20 and 1.83 (m, 4H, C₃H₄), 3.98 (s, 4H, C₅H₄), 4.05 (s, 5H, C₅H₅), 6.83 and 7.32 (d, 4H, C₆H₄) ppm.

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