3-Ferrocenyl-3-(1-naphthyl)cyclopropene. Synthesis, structure, and chemical transformations

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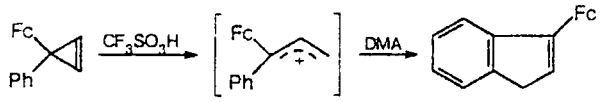
Crystalline 3-ferrocenyl-3-(1-naphthyl)cyclopropene was prepared by dehydrobromination of *Z*- and *E*-2-bromo-1-ferrocenyl-1-(1-naphthyl)-cyclopropanes by Bu^{t}OK in DMSO. The resulting compound and the starting *Z*-monobromocyclopropane were characterized by X-ray diffraction analysis. The obtained cyclopropene reacts with 1,3-diphenylisobenzofuran to give a [4+2]-cycloadduct. The small ring opens upon treatment with HBF_4 etherate to afford isomeric *Z*- and *E*-prop-1-enes and 1-ferrocenyl-3*H*-benzo[*e*]indene. Thermolysis of this cyclopropene results in the formation of 1-ferrocenyl-9*bH*-benzo[*e*]indene. In all cases, opening of the small ring is accompanied by exclusive alkylation of the naphthalene moiety.

Key words: ferrocene, cyclopropane, and cyclopropene derivatives; alkylation, dehydrobromination, three-membered-ring opening, [4+2]-cycloaddition, X-ray diffraction analysis.

Recently[1–3] we reported on the synthesis, structure, and some chemical transformations of crystalline 3-ferrocenyl-3-phenylcyclopropene (**1**). Thus the three-membered ring in compound **1** was easily opened by treatment with superacids to give 3-ferrocenylindene (**2**) as the major product:



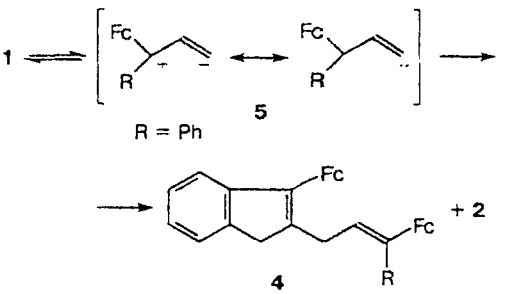
1 **2**

Fc = $C_5H_5FeC_5H_4$, DMA = $PhNMe_2$

The condensation of cyclopropene **1** with 1,3-diphenylisobenzofuran (**3**) also yielded a substantial amount of ferrocenylindene **2**, along with the classical [4+2]-cycloadduct.

In addition, refluxing cyclopropene **1** in toluene in the absence of other reagents gave a product of alkylation of ferrocenylindene **2**, *viz.*, 2-(3-ferrocenyl-3-phenylallyl)-3-ferrocenylindene (**4**).

Evidently, the ferrocenyl derivatives of indene **2** and **4** are formed *via* intermediates of type **5**. In our opinion, the high regioselectivity of the intramolecular alkylation, which involves only the phenyl substituent (rather than the ferrocenyl substituent, as is usually observed for ferrocene derivatives[4,5]), should be attributed to the spatial structure of cyclopropene **1**. It has been assumed[3] that the alkylation is directed at that substituent in position 3 of the small ring that occupies the "non-bisecting" position with respect to this ring; in other words, the plane of the aromatic ring does not lie in the bisecting plane, which passes through the C(3) atom. According to X-ray diffraction data,[2] the ferrocene fragment in compound **1** does occupy the "bisecting" position, whereas the phenyl group is "non-bisecting." Nevertheless, this hypothesis requires additional experimental verification.



In continuation of these studies, we synthesized 3-ferrocenyl-3-(1-naphthyl)cyclopropene (**6**) and studied some of its chemical transformations. Compound **6** is an interesting model object, because it contains two bulky substituents in position 3 of the three-membered ring. Opening of the ring in the case of a "non-bisecting" arrangement of the naphthalene fragment can yield two

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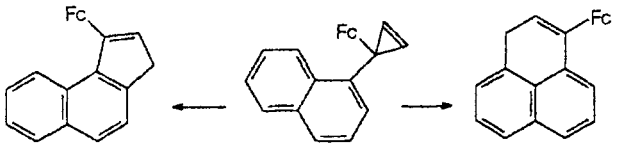
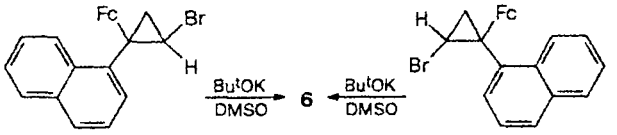
products, namely a compound of type **7** resulting from the alkylation of the naphthalene system in position 2 or *peri*-fused compound **8** formed upon the alkylation in position 8.



7 **6** **8**

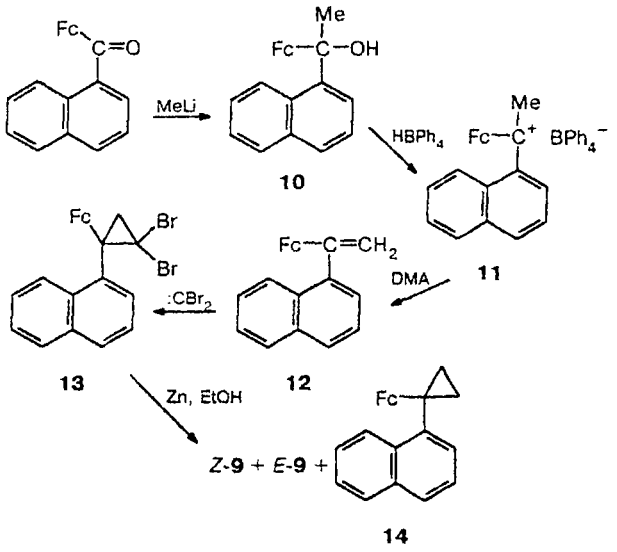
If the ferrocene moiety occupies the "non-bisecting" position, the alkylation should be directed at this substituent.

Cyclopropene **6** was synthesized using the standard procedure including dehydrobromination of (*Z*)- and (*E*)-2-bromo-1-ferrocenyl-1-(1-naphthyl)cyclopropanes (**9**) by Bu^{t}OK in DMSO:[6]



Z-**9** *E*-**9**

The starting monobromides **9** were synthesized by the following scheme:



10 **11** **13** **12** **14**

It was found that dehydration of alcohol **10** under usual conditions ($POCl_3$ + Py)[2,7] gives alkene **12** in a low yield (32%); therefore, it was prepared by deprotonation of 1-ferrocenyl-1-(1-naphthyl)ethylium tetraphenylborate (**11**, yield 80%) through the action of *N*,*N*-dimethylaniline (DMA). In this case, the yield of alkene **12** was 85%.

The subsequent dibromocyclopropanation of alkene **12** occurred without complications. However, to accomplish the reduction of the resulting dibromide **13** we studied several approaches. Thus the reduction of dibromide **13** by zinc in the presence of Trilon B gave a mixture of monobromides *Z*-**9** and *E*-**9** in a total yield of ~35%. In addition, 1-ferrocenyl-1-(1-naphthyl)cyclopropane (**14**) was isolated as the main reaction product in ~58% yield. Variation of the reduction conditions did not lead to a decrease in the yield of cyclopropane **14**. Nevertheless, despite the formation of a mixture of products, compounds *Z*-**9**, *E*-**9**, and **14** were easily isolated by chromatography on Al_2O_3. The ^1H and ^{13}C NMR spectra of these compounds unambiguously confirmed their structures.

In fact, the ^1H NMR spectrum of bromide *Z*-**9** exhibits two doublets of doublets at δ 1.76 and 2.15 corresponding to the protons of the methylene group (the AB part of an ABM spin system). In the ^1H NMR spectrum of the isomer *E*-**9**, the analogous signals occur at δ 1.92 and 2.08. Thus, *Z*-**9** is characterized by a larger $\Delta\delta_Z = \delta_B - \delta_A = 0.39$ value than isomer *E*-**9** ($\Delta\delta_E$ = 0.16). A similar difference can also be found in the ^1H NMR spectra of *Z*- and *E*-1-alkyl-2-bromo- and 2-bromo-1-ferrocenyl-1-phenylcyclopropanes; apparently, this can be used to determine the geometric configurations of monobromoferrocenylcyclopropanes based only on the data of ^1H NMR spectroscopy (see Refs. 1—3, 6—12).

The reduction of dibromide **13** with ethylmagnesium chloride in the presence of titanium tetra(isopropoxide) proved to occur more selectively yielding only monobromide *Z*-**9**. The use of equimolar quantities of EtMgCl and dibromide **13** makes it possible to avoid the formation of cyclopropane **14**, and the *Z*-isomer of **9** is formed in ~80% yield. The *Z*-configuration of the monobromide **9** was confirmed, in addition to spectroscopy, by X-ray diffraction analysis (Tables 1 and 2). The general view of molecule *Z*-**9** is shown in Fig. 1, and the packing mode of molecules in the crystal is shown in Fig. 2. An interesting feature of the crystal structure of *Z*-**9** is that the unit cell contains two molecules of *Z*-**9** with the bromine atoms located close to each other (Fig. 2).

Subsequently, monobromides **9** were converted into cyclopropene **6**. We found that the *Z*-isomer is dehydrobrominated much more readily than the *E*-isomer. In fact, *Z*-**9** eliminates HBr at 20 °C to give cyclopropene **6** in 70—75% yield, whereas monobromide *E*-**9** eliminates HBr under more drastic conditions (50—60 °C) and gives compound **6** in ~40% yield.

3-Ferrocenyl-3-(1-naphthyl)cyclopropene (**6**) is a yellow crystalline material stable during storage in air. The single crystals of **6** prepared by crystallization from *n*-hexane were studied by X-ray diffraction analysis (see Tables 3, 4). The key fragment in the structure of **6** is the three-membered ring, which is an acute-angled triangle stretched toward the C(11) carbon atom (Fig. 3). The

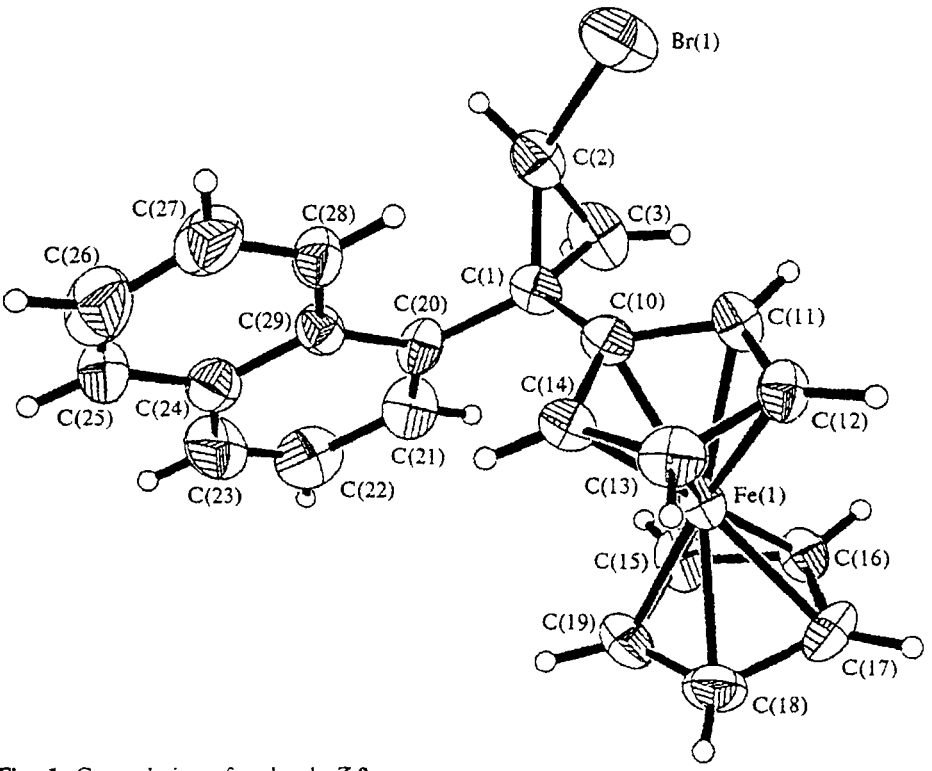


Fig. 1. General view of molecule *Z*-**9**.

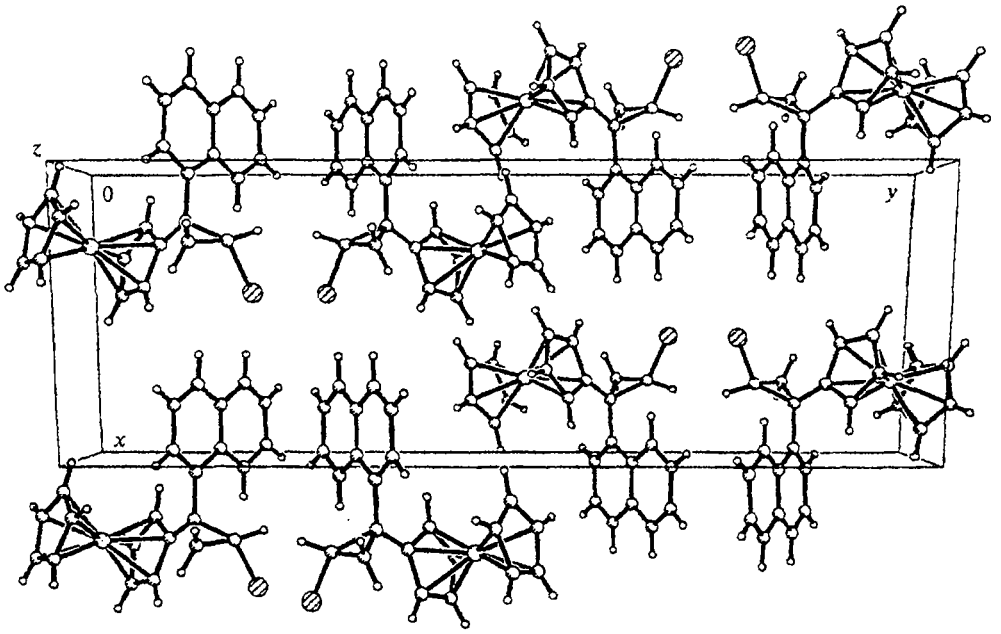


Fig. 2. Packing mode of molecules of compound *Z*-**9**.

angles of rotation of the plane of the cyclopentadienyl ring in molecule **6** correspond to its "bisecting" position with respect to the cyclopropene ring, while those of the naphthalene ring correspond to its "non-bisecting" position (Fig. 4). The Fe–C and C–C bond lengths and also the geometry of the ferrocene sandwich are normal.[5]

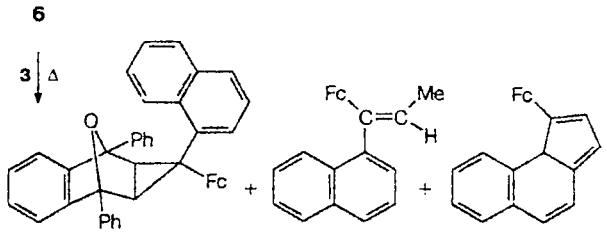
Cyclopropene **6** reacts with 1,3-diphenylisobenzofuran (**3**) upon refluxing in toluene to give [4+2]-cycloadduct

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal factors of molecule *Z*-**9** ($\times 10^3/Å^2$)

Atom	*x*	*y*	*z*	U_{eq}
Fe(1)	2709(2)	4703(1)	2068(2)	27(1)
C(10)	2607(11)	3937(4)	1917(17)	32(4)
C(11)	4048(10)	4107(4)	2430(16)	32(4)
C(12)	4323(11)	4425(4)	952(17)	34(4)
C(13)	3047(12)	4455(4)	−545(17)	38(4)
C(14)	2009(11)	4169(4)	87(15)	30(4)
C(15)	1757(12)	4925(5)	4263(17)	40(4)
C(16)	3157(11)	5127(4)	4552(18)	33(4)
C(17)	3239(13)	5412(4)	2944(19)	41(5)
C(18)	1887(13)	5399(4)	1616(20)	45(5)
C(19)	988(12)	5098(4)	2456(18)	40(4)
Br(1)	4241(2)	2872(1)	3014(3)	67(1)
C(1)	1885(11)	3604(4)	3046(15)	30(4)
C(2)	2551(12)	3115(5)	3761(19)	42(4)
C(3)	2597(13)	3503(5)	5152(18)	47(5)
C(20)	285(12)	3589(4)	2445(17)	33(4)
C(21)	−503(13)	3794(5)	3681(19)	45(5)
C(22)	−2009(15)	3785(5)	3144(24)	57(6)
C(23)	−2680(14)	3570(5)	1494(23)	57(6)
C(24)	−1916(12)	3353(4)	187(19)	41(5)
C(25)	−2626(14)	3121(5)	−1582(21)	55(6)
C(26)	−1890(18)	2921(5)	−2808(23)	66(6)
C(27)	−406(16)	2905(5)	−2309(22)	58(6)
C(28)	314(12)	3124(4)	−639(18)	39(4)
C(29)	−408(11)	3352(4)	711(18)	34(4)

Table 2. Main geometric parameters of molecule *Z*-**9**

Bond	*d*/Å	Angle	ω/deg
C(10)—C(1)	1.472(17)	C(10)—C(1)—C(2)	120.0(10)
C(1)—C(2)	1.513(17)	C(2)—C(1)—C(3)	56.4(8)
C(1)—C(20)	1.514(15)	C(2)—C(1)—C(20)	113.9(9)
Br(1)—C(2)	1.935(13)	Br(1)—C(2)—C(1)	122.2(9)
C(1)—C(3)	1.510(15)	C(1)—C(2)—C(3)	61.7(8)
C(2)—C(3)	1.429(19)	C(1)—C(3)—C(2)	61.9(8)
C(20)—C(21)	1.386(19)	Br(1)—C(2)—C(3)	122.1(8)
C(10)—C(14)	1.432(15)	C(3)—C(1)—C(20)	119.4(10)



	15	**16a**	**17**
110 °C	65%	12%	—
140 °C	50%	7%	20%

15 and *Z*-1-ferrocenyl-1-(1-naphthyl)prop-1-ene (**16a**) resulting from intramolecular isomerization.

The ^1H and ^{13}C NMR spectra of adduct **15** correspond to a single structural isomer, which implies stereospecific [4+2]-cycloaddition. By analogy with the adduct obtained by the reaction of **3** with cyclopropene **1** (see Ref. 2), compound **15** was identified as *exo*-3-ferrocenyl-3-(1-naphthyl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene with the *syn*-arranged naphthalene fragment. Tentative X-ray diffraction data for the single crystals of adduct **15** confirm the proposed structure.

When the reaction of **6** with **3** was conducted at a higher temperature (refluxing in *m*-xylene), the yields of both adduct **15** and propene **16a** decreased. In addition,

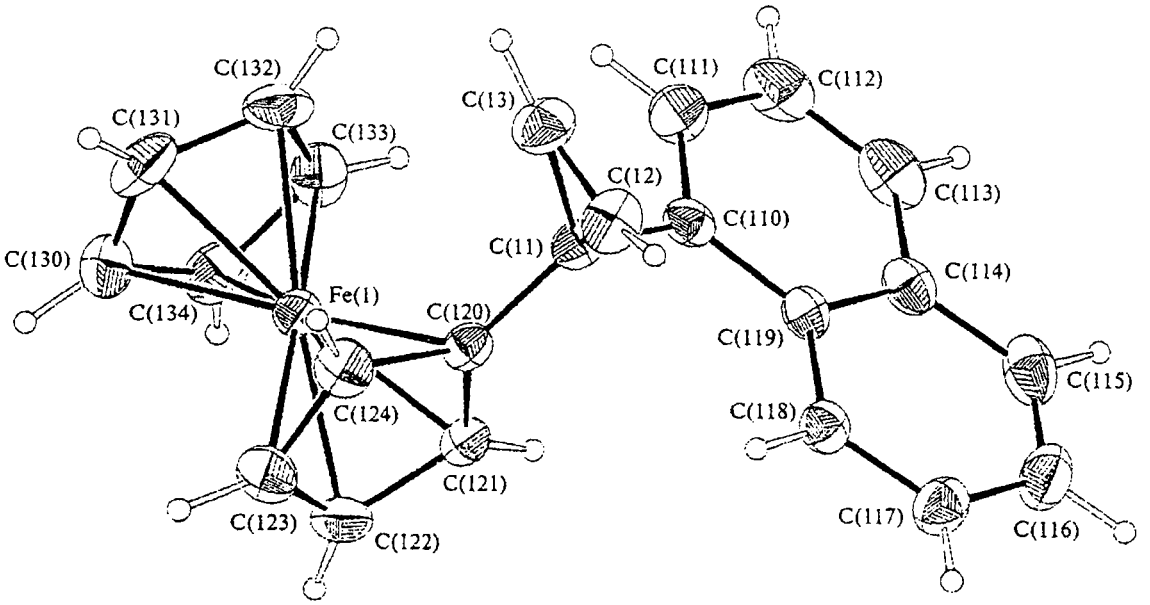


Fig. 3. General view of molecule **6**.

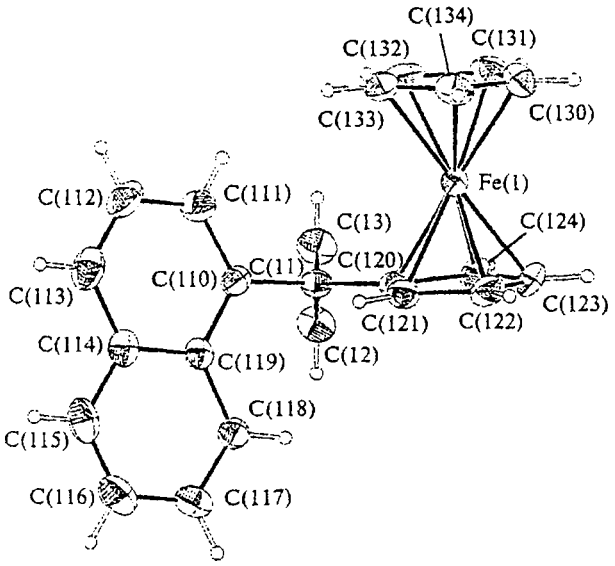


Fig. 4. One of the projections of molecule **6**.

Table 3. Atomic coordinates ($\times 10^4$) and isotropic thermal factors of molecule **6** ($\times 10^3/Å^2$)

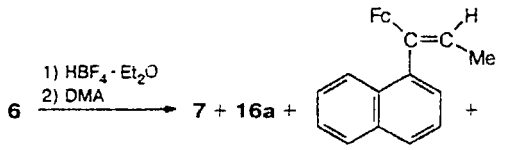
Atom	*x*	*y*	*z*	U_{eq}
Fe(1)	721(1)	3725(1)	1342(1)	40(1)
C(11)	405(5)	2232(2)	−213(2)	41(1)
C(12)	−354(7)	1239(3)	−360(3)	57(1)
C(13)	1121(7)	1384(3)	198(3)	60(1)
C(110)	1367(5)	2672(3)	−851(3)	41(1)
C(111)	3217(6)	2916(3)	−615(3)	56(1)
C(112)	4173(7)	3328(3)	−1183(4)	68(1)
C(113)	3269(7)	3477(3)	−1997(4)	67(1)
C(114)	1366(6)	3219(3)	−2277(3)	47(1)
C(115)	418(8)	3318(3)	−3135(3)	63(1)
C(116)	−1397(8)	3069(3)	−3398(3)	67(1)
C(117)	−2380(7)	2708(3)	−2815(3)	57(1)
C(118)	−1515(6)	2594(3)	−1987(3)	45(1)
C(119)	389(6)	2830(2)	−1692(2)	39(1)
C(120)	−504(5)	2871(3)	275(2)	38(1)
C(121)	−816(6)	3808(3)	119(2)	44(1)
C(122)	−1737(6)	4153(3)	735(3)	57(1)
C(123)	−2008(6)	3434(4)	1268(3)	62(1)
C(124)	−1243(6)	2646(3)	997(3)	52(1)
C(130)	1885(7)	4378(4)	2513(3)	64(1)
C(131)	2404(7)	3483(4)	2481(3)	68(2)
C(132)	3314(6)	3393(4)	1795(3)	65(2)
C(133)	3363(6)	4249(3)	1429(3)	59(1)
C(134)	2468(6)	4844(3)	1869(3)	60(1)

Table 4. Main geometric parameters of molecule **6**

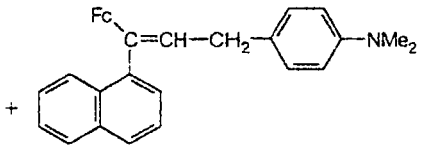
Bond	*d*/Å	Angle	ω/deg
C(11)—C(12)	1.504(5)	C(120)—C(11)—C(13)	119.1(3)
C(11)—C(13)	1.500(5)	C(120)—C(11)—C(12)	118.3(3)
C(11)—C(120)	1.491(5)	C(13)—C(11)—C(12)	49.4(2)
C(11)—C(110)	1.510(5)	C(13)—C(11)—C(110)	118.4(4)
C(12)—C(13)	1.255(6)	C(12)—C(11)—C(110)	119.9(3)
C(12)—H(12)	0.93	C(13)—C(12)—C(11)	65.1(3)
C(13)—H(13)	0.93	C(12)—C(13)—C(11)	65.5(3)

a new compound was isolated from the reaction mixture; based on the ^{1}H NMR spectra, this compound was identified as 1-ferrocenyl-9b*H*-benzo[*e*]indene (**17**).

After that, we showed that the three-membered ring in cyclopropene **6** is readily opened upon treatment with HBF_4 etherate. After treatment with DMA, the following products were isolated from the reaction mixture by preparative TLC: *Z*-**16a** and *E*-1-ferrocenyl-1-(1-naphthyl)prop-1-ene (**16b**) (~5 : 1, according to ^{1}H NMR spectra), 1-ferrocenyl-3*H*-benzo[*e*]indene (**7**), and *N*,*N*-dimethyl-4-(3-ferrocenyl-3-(1-naphthyl)prop-2-enyl)phenylamine (**18a**,**b**) as a mixture of *Z*- and *E*-isomers (~4 : 1).

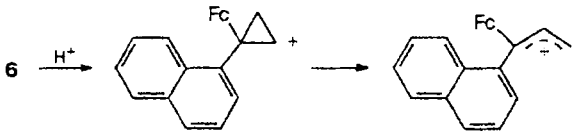


16b



18a,b

Apparently, protonation of cyclopropene **6** results in the intermediate formation of cyclopropyl carbocation **19**, which is readily converted into ferrocenylallyl carbocation **20**, stabilized by the ferrocenyl substituent.[1—3]



19 **20**

After that, cation **20** intramolecularly alkylates the ("non-bisecting") naphthalene substituent and intermolecularly alkylates DMA through the least substituted cationic center[8,9] or undergoes reduction. Previously we observed similar reduction of ferrocenylallyl cations for the 1-ferrocenyl-1-phenylallyl cation[3] and 3-ferrocenylmethylene-1,2,7,7-tetramethylbicyclo[2.2.1]hept-2-yl cation;[10,11] evidently, this reaction occurs with participation of the iron atom.[12]

The formation of compounds **16a** and **17** during the thermolysis of **6** occurs apparently as a result of heterolysis of one of the σ-bonds in the small ring[3,13] followed by transformations of intermediates of type **5** (R = 1-naphthyl), which are similar to the reactions of ferrocenylallyl carbocation **20**.

However, reduction of intermediate **5** (R = 1-naphthyl), unlike that of cation **20**, is stereospecific and gives

Z-alkene **16a**, while its intramolecular transformation affords 9*bH*-benzo[*e*]indene **17**, whose structure differs from that of 3*H*-benzo[*e*]indene **7**.

Thus, the results presented here together with those obtained previously indicate that the intramolecular transformations of 3-aryl-3-ferrocenylcyclopropenes **1** and **6** are regioselective. In all cases when the small ring is cleaved, the alkylation involves the aryl substituents, which occupy a "non-bisecting" position in the initial cyclopropenes. We detected no products of intramolecular cyclization at the ferrocene fragment, although intramolecular alkylation of the γ-ferrocenyl group (with respect to a cationic or carbenoid center) is well known.[4,5] We attribute this result to the "bisecting" arrangement of the cyclopentadienyl ring of ferrocene in the 3-aryl-3-ferrocenylcyclopropenes.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker CXP-200 spectrometer (200 and 50 MHz) for solutions in $CDCl_3$ using tetramethylsilane as the internal standard. Column chromatography was carried out using Al_2O_3 of Brockmann activity III. The results of elemental analysis of the resulting compounds are listed in Table 5.

1-Ferrocenyl-(1-naphthyl)ethanol (10). An ethereal solution of methyllithium (30 mmol) was added with stirring to a solution of ferrocenyl 1-naphthyl ketone (3.4 g, 10 mmol) in 100 mL of anhydrous benzene. The mixture was stirred for an additional 1 h and treated with a 5% solution of NaOH. The organic layer was separated, washed with water, and dried with Na_2SO_4. After evaporation of the solvent *in vacuo*, the residue was recrystallized from ethanol to give 2.78 g (78%) of alcohol **10**, yellow crystals, m.p. 105—106 °C. ^1H NMR, δ: 2.08 (s, 3 H, CH_3); 3.29 (s, 1 H, OH); 4.17 (m, 1 H, C_5H_4); 4.25 (m, 1 H, C_5H_4); 4.33 (s, 5 H, C_5H_5); 4.36 (m, 1 H, C_5H_4); 4.49 (m, 1 H, C_5H_4); 7.27, 7.45, 7.80, 8.70 (all m, 7 H, $C_{10}H_7$).

Table 5. Data of elemental analyses of the compounds synthesized

Compound	Found / Calculated (%)				Molecular formula
	C	H	Fe	Br or N	
6	78.98 78.87	5.26 5.18	15.73 15.95	—	$C_{23}H_{18}Fe$
7	78.98 78.87	5.34 5.18	16.11 15.95	—	$C_{23}H_{18}Fe$
***Z*-9**	63.85 64.07	4.58 4.44	13.07 12.95	18.68 18.54	$C_{23}H_{19}BrFe$
***E*-9**	63.92 64.07	4.32 4.44	12.74 12.95	18.35 18.54	$C_{23}H_{19}BrFe$
13	54.25 54.16	3.49 3.56	11.04 10.95	31.60 31.33	$C_{23}H_{18}Br_2Fe$
14	78.35 78.43	5.94 5.72	15.63 15.85	—	$C_{23}H_{20}Fe$
10	73.98 74.17	5.73 5.66	15.51 15.68	—	$C_{22}H_{20}FeO$
11	78.24 78.12	5.27 5.36	16.63 16.51	—	$C_{22}H_{18}Fe$
15	83.63 83.22	5.04 5.20	8.74 9.00	—	$C_{43}H_{32}FeO$
16a,b (~5 : 1)	78.23 78.43	5.88 5.72	15.68 15.85	—	$C_{23}H_{20}Fe$
17	78.64 78.87	5.27 5.18	15.73 15.95	—	$C_{23}H_{18}Fe$
18a,b (~4 : 1)	78.76 78.98	6.44 6.20	11.71 11.85	2.68 1.97	$C_{31}H_{29}FeN$

A. Phosphorus oxychloride (2 mL) was added dropwise to a solution of alcohol **10** (1.8 g, 5 mmol) in 70 mL of anhydrous pyridine, and the mixture was stirred for 3 h at 20 °C and diluted with water. The resulting alkene was extracted with benzene. After evaporation of the solvent *in vacuo*, the residue was purified by column chromatography (using hexane as the eluent) to give 0.54 g (32%) of alkene **12**, yellow crystals, m.p. 84—85 °C. ^1H NMR, δ: 4.12 (s, 5 H, C_5H_5); 4.21 (m, 4 H, C_5H_4); 5.22 (d, 1 H, CH_2, J = 1.7 Hz); 5.85 (d, 1 H, CH_2, J = 1.7 Hz); 7.35—7.65, 7.80—8.00 (m, 7 H, $C_{10}H_7$). ^{13}C NMR, δ: 68.5 (C_5H_4); 69.6 (C_5H_5); 86.0 (C_{ipso}, Fe); 112.8 (CH_2=); 125.2, 125.6, 126.0, 126.5, 127.5, 128.0 (CH); 131.9, 133.5, 140.0, 146.3 (C).

B. $NaBPh_4$ (2.4 g, 7 mmol) was added to a solution of alcohol **10** (1.8 g, 5 mmol) in 30 mL of glacial acetic acid. The mixture was stirred for 1 h at 10 °C, and the brown precipitate of salt **11** was filtered off and washed with anhydrous ether and anhydrous hexane. The yield of tetraphenylborate **11** was 2.64 g (80%).

N,N-Dimethylaniline (2 mL) was added to salt **11** (2.2 g, 3.3 mmol), the mixture was thoroughly triturated until a pale yellow paste formed, and anhydrous benzene (100 mL) was added. An hour later, the benzene solution was washed with water, 1% HCl, and again with water. Evaporation of the solvent followed by chromatography gave 0.96 g (85%) of alkene **12**, m.p. 85 °C.

2,2-Dibromo-1-ferrocenyl-1-(1-naphthyl)cyclopropane (13). Dibromocyclopropane **13** was prepared from alkene **12** by a known procedure,[14] yield 75%, orange crystals, m.p. 141—142 °C. ^1H NMR, δ: 2.46 (d, 1 H, CH_2, J = 8.0 Hz); 2.55 (d, 1 H, CH_2, J = 8.0 Hz); 3.63 (m, 1 H, C_5H_4); 3.95 (s, 5 H, C_5H_5); 3.98 (m, 1 H, C_5H_4); 4.15 (m, 1 H, C_5H_4); 4.27 (m, 1 H, C_5H_4); 7.53, 7.94, 8.05 (both m, 7 H, $C_{10}H_7$). ^{13}C NMR, δ: 35.6 (CH_2); 38.6 (C); 68.8 (C_5H_5); 67.0, 68.1, 69.0, 71.2 (C_5H_4); 89.7 (C_{ipso}, Fe); 125.1, 125.8, 126.0, 127.4, 127.5, 128.3, 128.4 (CH); 129.4, 133.7, 138.8 (C).

Reduction of dibromide 13. ***A.*** Dibromide **13** was reduced by Zn dust in aqueous ethanol in the presence of Trilon B, as described previously.[15] Preparative TLC on silica gel (with hexane as the eluent) gave the products described below.

1-Ferrocenyl-1-(1-naphthyl)cyclopropane (14), yield 58%, R_f 0.76, yellow crystals, m.p. 118—119 °C. ^1H NMR, δ: 1.35 (m, 2 H, CH_2); 1.38 (m, 2 H, CH_2); 3.71 (m, 2 H, C_5H_4); 3.93 (m, 2 H, C_5H_4); 4.11 (s, 5 H, C_5H_5); 7.40—8.26 (m, 7 H, $C_{10}H_7$). ^{13}C NMR, δ: 19.4 (CH_2); 19.4 (CH_2); 37.2 (C); 66.6 (C_5H_4); 68.5 (C_5H_5); 69.6 (C_{ipso}, Fe); 125.3, 125.4, 125.4, 125.9, 127.4, 127.9, 128.4 (CH); 133.1, 133.8, 140.8 (C).

***Z*-2-Bromo-1-ferrocenyl-1-(1-naphthyl)cyclopropane (*Z*-9)**, yield 17%, R_f 0.67, orange crystals, m.p. 108—109 °C. ^1H NMR, δ: 1.76 (dd, 1 H, CH_2, J = 5.7, 6.6 Hz); 2.15 (dd, 1 H, CH_2, J = 6.6, 8.4 Hz); 3.53 (dd, 1 H, CH, J = 5.7, 8.4 Hz); 3.55 (m, 1 H, C_5H_4); 3.98 (m, 1 H, C_5H_4); 4.08 (s, 5 H, C_5H_5); 4.20 (m, 1 H, C_5H_4); 4.35 (m, 1 H, C_5H_4); 7.46—8.02 (m, 7 H, $C_{10}H_7$).

***E*-2-Bromo-1-ferrocenyl-1-(1-naphthyl)cyclopropane (*E*-9)**, yield 9%, R_f 0.59, orange crystals, m.p. 94—95 °C.

^{1}H NMR, δ: 1.92 (dd, 1 H, CH_2, J = 4.8 Hz, J = 7.4 Hz); 2.08 (dd, 1 H, CH_2, J = 6.8, 7.4 Hz); 3.53 (dd, 1 H, CH, J = 4.8, 7.4 Hz); 3.87 (m, 1 H, C_5H_4); 3.96 (m, 1 H, C_5H_4); 4.08 (s, 5 H, C_5H_5); 4.14 (m, 1 H, C_5H_4); 4.26 (m, 1 H, C_5H_4); 7.39—8.04 (m, 7 H, $C_{10}H_7$).

B. An ethereal solution of EtMgCl (3.2 mmol) and several drops of titanium tetraisopropoxide were added with stirring to a solution of dibromide **13** (1.53 g, 3 mmol) in 50 mL of anhydrous ether. The mixture was stirred at ~20 °C until its dark brown color changed to yellow; after that, water (50 mL) was added. The organic layer was separated, the solvent was evaporated *in vacuo*, and the residue was chromatographed on silica gel (using hexane as the eluent) to give 1.04 g (80%) of monobromide *Z*-**9**, m.p. 108—109 °C.

3-Ferrocenyl-3-(1-naphthyl)cyclopropene (6). A mixture of monobromide *Z*-**9** (1.3 g, 3 mmol) and Bu^{t}OK (4 mmol) in 30 mL of DMSO was stirred at 20 °C for 10 h in an atmosphere of dry argon. Then the reaction mixture was partitioned between benzene (100 mL) and water (50 mL), and the organic layer was separated and washed with water. After evaporation of the solvent, the residue was chromatographed on Al_2O_3 (using hexane as the eluent) to give 0.83 g (72%) of cyclopropene **6**, yellow crystals, m.p. 123—124 °C.

The reaction of *E*-**9** (1.3 g, 3 mmol) carried out in a similar way (50—60 °C, 10 h) gave 0.42 g (40%) of compound **6**, m.p. 123—124 °C. ^{1}H NMR, δ: 3.74 (m, 2 H, C_5H_4); 3.96 (m, 2 H, C_5H_4); 4.15 (s, 5 H, C_5H_5); 7.51 (s, 2 H, CH=CH); 7.38—7.58, 7.70—7.80, 8.10—8.20 (all m, 7 H, $C_{10}H_7$). ^{13}C NMR, δ: 26.3 (C); 67.1 (C_5H_4); 67.9 (C_5H_4); 68.1 (C_5H_5); 98.7 (C_{ipso}, Fc); 113.5 (CH=CH); 125.4, 125.5, 125.5, 125.6, 125.9, 127.0, 128.5 (CH); 132.0, 134.0, 143.1 (C).

Reaction of cyclopropene 6 with 1,3-diphenylisobenzofuran (3). *A*. A mixture of cyclopropene **6** (0.35 g, 1 mmol) and compound **3** (0.56 g, 2 mmol) was refluxed in 50 mL of toluene for 4 h until the starting cyclopropene **6** was entirely consumed (TLC monitoring). After evaporation of the solvent *in vacuo*, the residue was chromatographed on silica gel (using a 2 : 1 hexane—benzene as the eluent) to give 0.042 g (12%) of *Z*-1-ferrocenyl-1-(1-naphthyl)prop-1-ene (**16a**) and 0.41 g (65%) of *exo*-3-ferrocenyl-3-(1-naphthyl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (**15**).

Compound **16a**, R_f 0.78, yellow crystals, m.p. 124—125 °C. ^{1}H NMR, δ: 1.42 (d, 3 H, CH_3, J = 6.9 Hz); 3.74 (m, 1 H, C_5H_4); 4.02 (m, 1 H, C_5H_4); 4.08 (s, 5 H, C_5H_5); 4.19 (m, 1 H, C_5H_4); 4.41 (m, 1 H, C_5H_4); 6.32 (q, 1 H, CH=, J = 6.9 Hz); 7.31—7.60, 7.75—7.90 (all m, 7 H, $C_{10}H_7$). ^{13}C NMR, δ: 29.7 (CH_3); 64.8, 67.9, 68.1 (C_5H_4); 69.3 (C_5H_5); 87.1 (C_{ipso}, Fc); 122.1 (CH=); 125.3, 125.6, 125.7, 126.2, 126.7, 127.1, 128.1 (C); 128.2 (CH); 133.6, 137.0, 140.1 (C).

Compound **15**, R_f 0.36, yellow needles, m.p. 266—267 °C. ^{1}H NMR, δ: 2.55 (d, 1 H, CH, J = 7.2 Hz); 2.75 (d, 1 H, CH, J = 7.2 Hz); 3.12 (br.s, 1 H, C_5H_4); 3.74 (br.s, 1 H, C_5H_4); 3.96 (br.s, 1 H, C_5H_4); 4.01 (br.s, 1 H, C_5H_4); 4.05 (s, 5 H, C_5H_5); 6.45, 6.80, 6.92—7.15, 7.31—7.40, 7.46—7.65 (all m, 21 H, Ar). ^{13}C NMR, δ: 41.9 (CH); 45.4 (C); 47.8 (CH); 63.9, 66.6, 67.3, 69.6 (C_5H_4); 68.8 (C_5H_5); 88.5, 88.5 (C); 95.9 (C_{ipso}, Fc); 118.98, 119.04, 123.4, 124.4, 125.0, 126.1, 126.3, 126.7, 126.9, 127.6, 127.7, 128.3 (CH); 132.1, 133.0, 134.8, 136.2, 138.1, 149.6, 150.4 (C).

Similarly, refluxing of **6** (0.35 g) and **3** (0.56 g) in *m*-xylene (4 h) gave 0.024 g (7%) of *Z*-alkene **16a**, m.p. 124—125 °C, 0.32 g (50%) of adduct **15**, m.p. 265—267 °C, and 0.07 g (20%) of 1-ferrocenyl-9*bH*-benzo[*e*]indene (**17**), R_f 0.29, pale yellow crystals, m.p. 121—122 °C. ^{1}H NMR, δ: 2.48 (s, 1 H, CH); 4.01 (m, 1 H, C_5H_4); 4.06 (m, 1 H, C_5H_4); 4.18 (s, 5 H, C_5H_5); 4.20 (m, 1 H, C_5H_4); 4.72 (br.s, 1 H, C_5H_4); 6.75 (d, 1 H, J = 5.7 Hz); 6.81 (d, 1 H, J = 5.7 Hz); 7.33—7.46, 7.75—7.81, 8.31—8.34 (all m, $C_{10}H_6$).

Table 6. Crystallographic data for cyclopropene **6** and monobromide *Z*-**9**

Parameter	Compound **6**	Compound *Z*-**9**
Molecular formula	$C_{23}H_{18}Fe$	$C_{23}H_{19}BrFe$
Molecular weight	350.23	431.10
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	7.508(1)	9.668(3)
b/Å	14.563(2)	27.143(4)
c/Å	15.995(2)	6.992(10)
α/deg	92.140(10)	—
β/deg	102.950(10)	102.45(2)
γ/deg	94.00(10)	—
V/Å^3	1696.7(4)	1790.1(7)
Z	2	4
Calculated density/g cm^{-3}	1.355	1.600
Absorption coefficient/mm^{-1}	0.887	3.076
F(000)	712	872
Radiation	Mo-Kα, highly oriented graphite crystal	
λ/Å	0.71073	0.71073
2θ-region/deg	3.74 < 2θ < 50.00	2.0 < 2θ < 50.00
Scan mode	θ/2θ	2θ − ω
Total number of reflections	7445	4351
Number of independent reflections	5954	3158
R_{int}	0.0289	0.0494
Number of variables in the refinement	222	226
Weighting scheme	$w^{-1} = \sigma^2(F) + kF^2$	
	k = 0.0008	k = 0.0050
Quality factor	0.984	0.95
Residual electron density, min/max/e · Å^{-3}	−0.263/0.227	−1.28/0.95
Temperature/K	293	293

Reaction of cyclopropene 6 with HBF_4 etherate. $HBF_4 \cdot Et_2O$ (2 mL) was added to a solution of cyclopropene **6** (0.18 g, 0.5 mmol) in 25 mL of anhydrous ether. The resulting brown mixture was stirred under argon for 1 h, then 2 mL of DMA was added, and the mixture was again stirred for 1 h. Then water (100 mL) and benzene (50 mL) were added to the reaction mixture, the organic layer was separated and washed several times with 1% HCl and with water, and the solvent was evaporated *in vacuo*. Preparative TLC (on silica

gel using hexane as the eluent) gave 0.09 g (50%) of propene **16** as a mixture of *Z*- and *E*-isomers (**16a** : **16b** ~5 : 1), 0.041 g (17%) of *Z*- and *E*-*N*,*N*-dimethyl-4-[3-ferrocenyl-3-(1-naphthyl)prop-2-enyl]phenylamines (**18a,b**), and 0.027 g (15%) of 1-ferrocenyl-3*H*-benzo[*e*]indene (**7**).

Compound **16a,b**, R_f 0.75 (hexane—benzene, 2 : 1); yellow crystals, m.p. 84—86 °C. ^{1}H NMR for **16b**, δ: 2.17 (d, 3 H, CH_3, J = 7.2 Hz); 3.85 (m, 1 H, C_5H_4); 4.03 (m, 1 H, C_5H_4); 4.07 (s, 5 H, C_5H_5); 4.09 (m, 1 H, C_5H_4); 4.40 (m, 1 H, C_5H_4); 5.74 (q, 1 H, CH=, J = 7.2); 7.34—7.98 (m, 7 H, $C_{10}H_7$).

Compound **18a,b**, R_f 0.42, brown oil. ^{1}H NMR, δ: 2.84 (s, 6 H, CH_3); 2.89 (s, 6 H, CH_3); 2.94 (d, 2 H, J = 6.7 Hz); 2.98 (d, 2 H, J = 6.6 Hz); 4.06 (s, 5 H, C_5H_5); 4.08 (s, 5 H, C_5H_5); 4.19 (m, 2 H, C_5H_4); 4.23 (m, 2 H, C_5H_4); 4.17 (m, 1 H, C_5H_4); 4.26 (m, 1 H, C_5H_4); 4.31 (m, 2 H, C_5H_4); 6.68 (t, 1 H, J = 6.7 Hz); 6.92 (t, 1 H, J = 6.6 Hz); 7.35—7.60, 7.68—7.75, 7.82—7.93 (all m, 11 H, Ar).

Compound **7**, R_f 0.35, yellow crystals, m.p. 136—137 °C. ^{1}H NMR, δ: 3.85 (dd, 2 H, J = 1.2 Hz, J = 6.9 Hz); 3.72 (m, 1 H, C_5H_4); 4.08 (m, 1 H, C_5H_4); 4.10 (s, 5 H, C_5H_5); 4.25 (m, 1 H, C_5H_4); 4.52 (m, 1 H, C_5H_4); 6.43 (t, 1 H, J = 6.9 Hz); 7.15—7.60, 7.75—7.93 (all m, $C_{10}H_6$).

X-ray diffraction study of compounds 6 and *Z*-9. Unit cell parameters and the intensities of reflections were measured on a Siemens P4/PC diffractometer for compound **6** and on a Siemens P4 diffractometer for compound *Z*-**9**. The structures were solved by the direct method and refined by the least-squares method in the full-matrix anisotropic approximation for nonhydrogen atoms. All the hydrogen atoms were revealed from the difference series and refined isotropically. The crystallographic data and the parameters of the X-ray diffraction experiment and refinement are listed in Table 6.

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