2,3-Diferrocenylcyclopropenone in the reaction with organomagnesium compounds

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The reactions of 2,3-diferrocenylcyclopropenone with ethyl- and benzylmagnesium chlorides afford 3,3-diethyl- and 3,3-dibenzyl-1,2-diferrocenylcyclopropenes along with products of nucleophilic opening of the three-membered ring: α,β-unsaturated and saturated ketones (*cis*-1,2-diferrocenylpent-1-en-3-one and *cis*-1,2-diferrocenyl-4-phenylbut-1-en-3-one, 4,5-diferrocenylheptan-3-one, and 3,4-diferrocenyl-1,5-diphenylpentan-2-one). The products of insertion of intermediate diferrocenyl(vinyl)carbene at one of the σ-bonds of the starting 2,3-diferrocenylcyclopropenone were also isolated: 4-(2-oxo-1-ferrocenylbutyl)- and 4-(2-oxo-3-phenyl-1-ferrocenylpropyl)-2,3,4-triferrocenylcyclobutenones. 3,3-Dibenzyl-1,2-diferrocenylcyclopropene and one of the diastereomers of 4,5-diferrocenylheptan-3-one were studied by X-ray diffraction analysis.

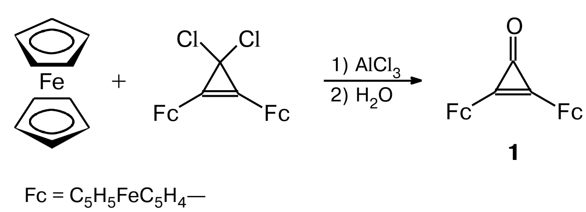
Key words: ferrocene, 2,3-diferrocenylcyclopropenone, 1,2-diferrocenylcyclopropenes, diferrocenyl(vinyl)carbenes, 2,3,4-triferrocenylcyclobutenones.

Compounds of the cyclopropenone series are of interest due to their pseudo-aromatic nature[1,2] and high strain energy, planarity and kinetic lability[1—3] of the cyclopropenone structure, and potential practical applications. 2,3-Diphenylcyclopropenone was the first cyclopropenone derivative described in the literature.[4] Then many works described syntheses and studies of the reactivity of aryl- and alkyl-substituted cyclopropenones and considered the use of these compounds in organic synthesis.[5—10]

Ferrocenyl-substituted analogs of arylcyclopropenones remain unstudied up to date, although 2,3-diferrocenylcyclopropenone (**1**) has been isolated for the first time as early as in 1975 by the alkylation of ferrocene with tetrachlorocyclopropene at low temperature in the presence of $AlCl_3$ in ~7% yield.[11] The main reaction product was the 1,2,3-triferrocenylcyclopropenylium salt. At the same time, the influence of ferrocenyl fragments on regio- and stereochemistry of transformations of ferrocenylcyclopropenones is of doubtless interest. The latter, if accessible, could be the starting substances for syntheses of many useful compounds of the ferrocene series, which combine olefinic fragments with functional groups in the same molecule.

We succeeded in substantial increasing the yield of cyclopropenone **1** (to 90%) by the alkylation of ferrocene with tetrachlorocyclopropene at 20 °C in CH_2Cl_2 using a smaller amount of $AlCl_3$ (Scheme 1).

Scheme 1



In this work, we studied the reactions of cyclopropenone **1** with organomagnesium compounds, *viz.*, ethyl- and benzylmagnesium chlorides (EtMgCl and BnMgCl, respectively).

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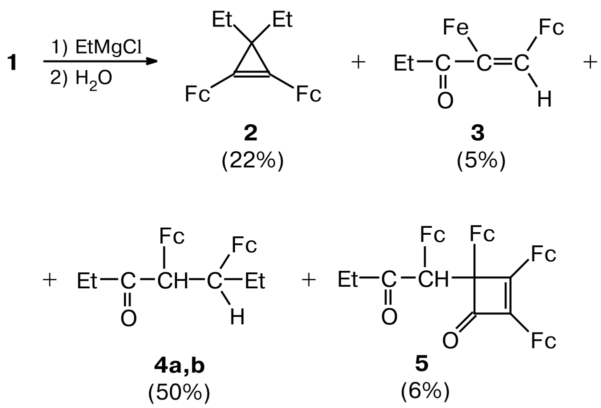
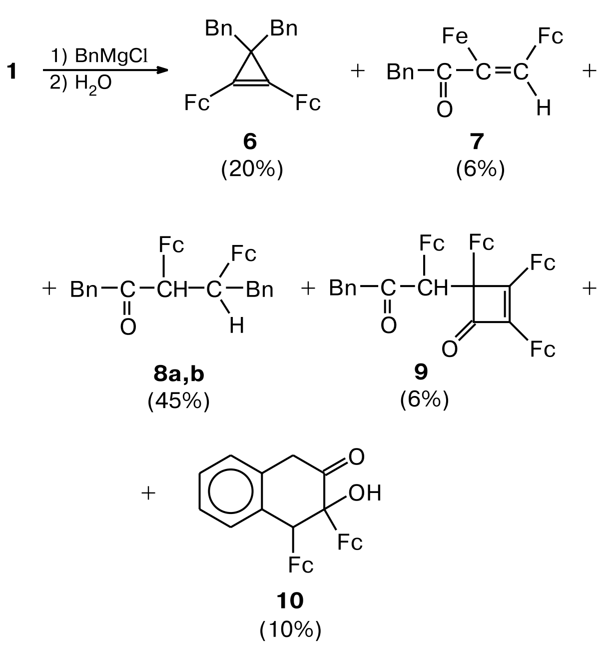
We found that cyclopropenone **1** reacts with excess EtMgCl to yield a mixture of several products, the main of which being 1,2-diferrocenyl-3,3-diethylcyclopropene (**2**), 1,2-diferrocenylpent-1-en-3-one (**3**), 4,5-diferrocenylheptan-3-one (**4**), and 4-(2-oxo-1-ferrocenylbutyl)-2,3,4-triferrocenylcyclobutenone (**5**) (Scheme 2).

Scheme 2



The reaction with BnMgCl occurs similarly to form cyclopropene **6**, α,β-unsaturated ketone **7**, saturated ketone **8**, and cyclobutenone **9**. An unexpected reaction product is 2-hydroxy-3-oxo-1,2-diferrocenyl-1,2,3,4-tetrahydronaphthalene (**10**) (Scheme 3).

Scheme 3



The structures of compounds **2—10** were established by the data of ^{1}H and ^{13}C NMR spectroscopy (see Experimental).

Table 1. Bond lengths (*d*) and bond (ω) and torsion (α) angles in molecules **4a** and **6**

Bond	*d*/Å
Compound **4a**	
C(11)—C(22)	1.468(7)
C(21)—C(22)	1.567(5)
C(12)—C(13)	1.428(8)
C(1)—C(21)	1.570(7)
C(21)—C(23)	1.539(8)
C(22)—C(25)	1.485(8)
O(1)—C(25)	1.191(6)
C(25)—C(26)	1.469(7)
Compound **6**	
C(11)—C(13)	1.286(3)
C(11)—C(12)	1.499(3)
C(12)—C(13)	1.493(3)
C(1)—C(11)	1.444(3)
C(13)—C(14)	1.444(3)
C(12)—C(24)	1.532(3)
C(12)—C(25)	1.534(3)
Bond angle	**ω/deg**
Compound **4a**	
C(11)—C(22)—C(25)	112.4(5)
C(25)—C(22)—C(21)	110.5(5)
C(22)—C(21)—C(1)	107.4(4)
C(23)—C(21)—C(22)	109.1(5)
O(1)—C(25)—C(22)	120.4(5)
O(1)—C(25)—C(26)	120.9(7)
C(11)—C(22)—C(21)	112.3(4)
C(1)—C(21)—C(23)	112.2(5)
Compound **6**	
C(13)—C(11)—C(12)	64.28(19)
C(13)—C(12)—C(11)	50.90(15)
C(11)—C(13)—C(12)	64.82(19)
C(53)—C(52)—C(51)	50.90(15)
C(52)—C(53)—C(51)	64.14(15)
C(53)—C(51)—C(52)	64.94(19)
C(24)—C(12)—C(11)	120.2(2)
C(24)—C(12)—C(25)	111.4(2)
C(13)—C(12)—C(25)	120.8(2)
C(64)—C(52)—C(65)	111.7(2)
Torsion angle	**α/deg**
Compound **6**	
C(11)—C(12)—C(24)—C(26)	−95.2(3)
C(51)—C(52)—C(65)—C(66)	25.9(4)
C(11)—C(12)—C(25)—C(32)	−33.9(4)
C(51)—C(52)—C(64)—C(72)	−155.4(2)

The spatial configuration of one of cyclopropenes, *viz.*, 3,3-dibenzyl-1,2-diferrocenylcyclopropene **6**, was confirmed by spectral data and X-ray diffraction analysis of single crystals obtained by crystallization from hexane (Tables 1 and 2). The general view of molecule **6** is shown in Fig. 1, *a*. The three-membered ring in structure **6** is an isosceles triangle. The C=C bond length (d = 1.286(3) Å)

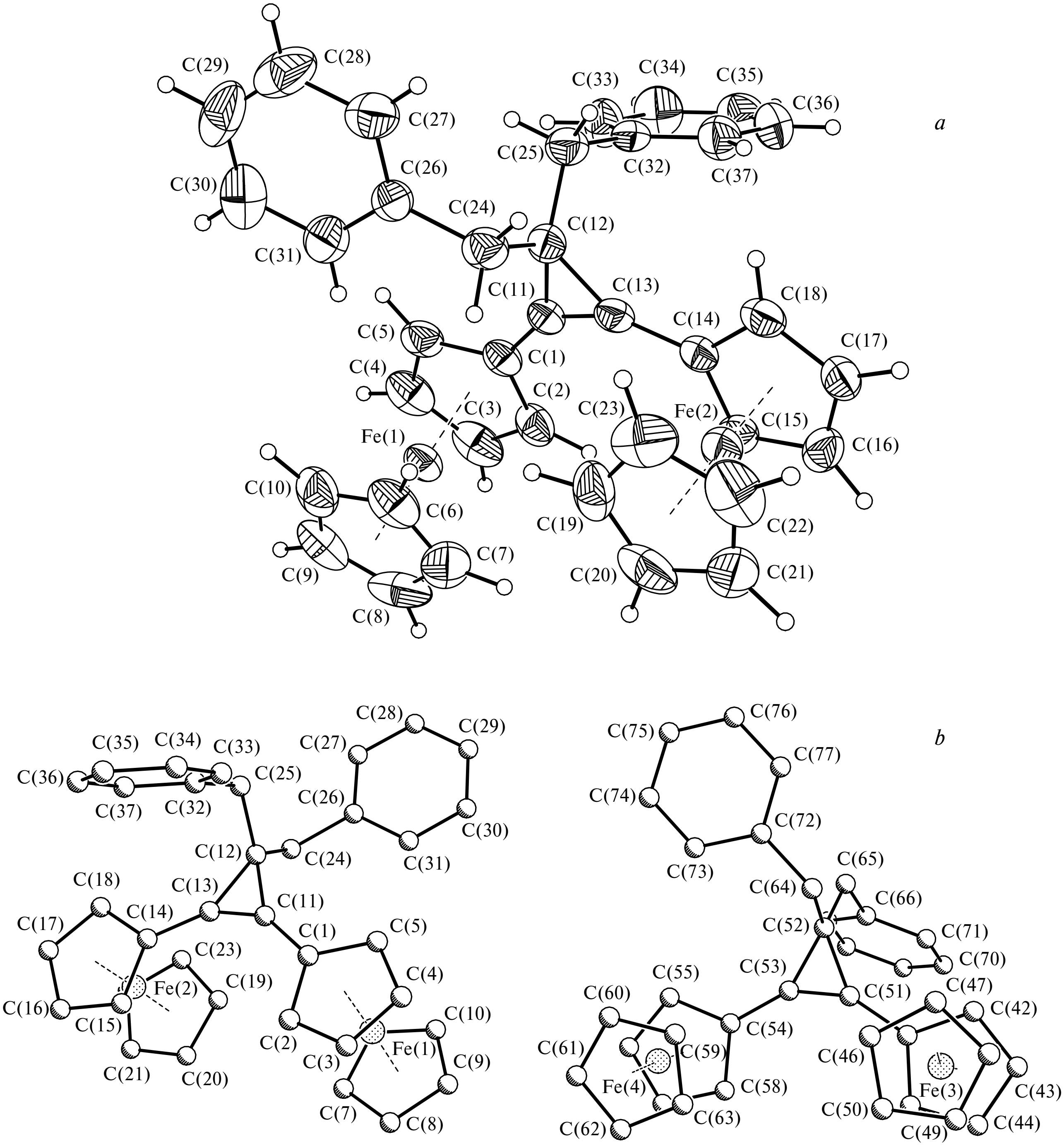


Fig. 1. General view of a 3,3-dibenzyl-1,2-differrocenylcyclopropene (**6**) molecule (*a*) and molecular structures of two independent molecules (*b*).

and the value of the ω acute angle at C(12) (50.90(15)°) differ slightly from the corresponding values for 3-aryl-3-ferrocenylcyclopropenes.[12,13] Substituted cyclopentadienyl rings of the ferrocene fragments lie in the plane of the small cycle. The Fe—C bond lengths and geometry of the ferrocene sandwiches are the same as those in related compounds.[12,13] The unit cell of the crystal structure of compound **6** contains two independent differrocenylcyclopropene molecules, whose geometric parameters are the same, except for rotational angles of the phenyl rings about the C_{sp^3}—C_{sp^3} ordinary bonds (see torsion angles in Table 1 and Fig. 1, *b*).

As follows from the data of ^{1}H and ^{13}C NMR spectroscopy, compounds **3** and **7** are formed as one geomet-

Table 2. Crystallographic data and X-ray diffraction parameters for compounds **4a** and **6**

Parameter	**4a**	**6**
Molecular formula	$C_{27}H_{30}Fe_2O$	$C_{37}H_{32}Fe_2$
Molecular weight/g mol^{-1}	482.21	588.33
Temperature/K	291(2)	291(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$	$P\bar{1}$
a/Å	11.0169(8)	10.4144(6)
b/Å	7.8226(5)	10.4124(6)
c/Å	13.1321(9)	27.457(2)
α/deg	90.0	81.120(1)
β/deg	102.3290(10)	80.692(1)
γ/deg	90.0	71.093(1)
V/Å^3	1105.63(13)	2763.0(3)
Z	2	4
d_{calc}/g cm^{-3}	1.448	1.414
Absorption coefficient/mm^{-1}	1.328	1.075
F(000)	504	1224
Radiation	Mo-Kα	Mo-Kα
λ/Å	0.71073	0.71073
Monochromator	Graphite	Graphite
θ/deg	1.59—25.00	2.08—25.00
Total number of reflections	9069	22799
Number of independent reflections with $R(I > 2\sigma(I))$	3864	9737
R_1	0.0390	0.0384
wR_2	0.0749	0.0634
Parameter of absolute structure	0.06(2)	—
R_{int}	0.0351	0.0425
Number of refined parameters	273	703
Weighing scheme	$w = 1/[\sigma^2(F_0^2) + (0.0305P)^2]$, where $P = (F_0^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_0^2) + (0.0190P)^2]$, where $P = (F_0^2 + 2F_c^2)/3$
GOOF (full-matrix least-squares method against F^2)	1.033	0.829
Residual electron density/eÅ^{-3}, ρ_{min}/ρ_{max}	−0.183/0.478	−0.226/0.379

ric isomer, most likely, with *cis*-oriented ferrocene groups,[14,15] and compounds **4** and **8** exist as mixtures of two diastereomeric forms **4a,b** and **8a,b**, respectively, in a ratio of ~3 : 1 (see Experimental). Diastereomeric heptanones **4a** and **4b** were separated by preparative TLC on SiO_2. The spatial structure of isomer **4a** was established by X-ray diffraction analysis of a single crystal isolated by crystallization from hexane (see Tables 1 and 2, Fig. 2). It follows from the X-ray diffraction data that compound **4a** has a structure of 4*R*,5*S*-diferrocenylheptan-3-one. By analogy, we ascribed the *erythro*-configuration to compound **8a**. Spectral identification of ketones **4a,b** and **8a,b** was not difficult, because positions of all signals in the ^{1}H and ^{13}C NMR spectra, their multiplicities, and integral intensities differ distinctly.

Bright violet compounds **5** and **9** were isolated in insignificant amounts (~6%) as one diastereomeric form. Their structures also follow from the data of ^{1}H and ^{13}C NMR spectroscopy. For instance, the ^{1}H NMR spectra of compounds **5** and **9** contain signals of four unsubstituted cyclopentadienyl ferrocene rings along with the corresponding number of signals of protons of the substituted cyclopentadienyl rings, signals of the methyl (in **5**) and methylene (in **9**) groups, and one signal from each methine proton. Each ^{13}C NMR spectrum exhibits four signals of quaternary C atoms of the ferrocene fragments of molecules **5** and **9**, two signals of C atoms of the carbonyl group, and the corresponding number of signals of the quaternary C and C_{ipso} atoms. The mass spectra of compounds **5** and **9** contain peaks of molecular ions with m/z 874 and 936, respectively, which also indicates their dimeric nature and confirms the structure proposed.

The structure of compound **10** was determined from the data of mass spectrometry, IR spectroscopy, and ^{1}H and ^{13}C spectroscopy. The molecule contains the carbonyl and hydroxyl groups, two ferrocene substituents, *ortho*-disubstituted phenyl fragment, and methylene and methine groups.

Thus, the results obtained show that the reaction of 2,3-diferrocenylcyclopropenone **1** with organomagnesium compounds includes three main processes: (1) with retention of the small three-membered ring, (2) with nucleophilic opening of the cyclopropenone ring, and

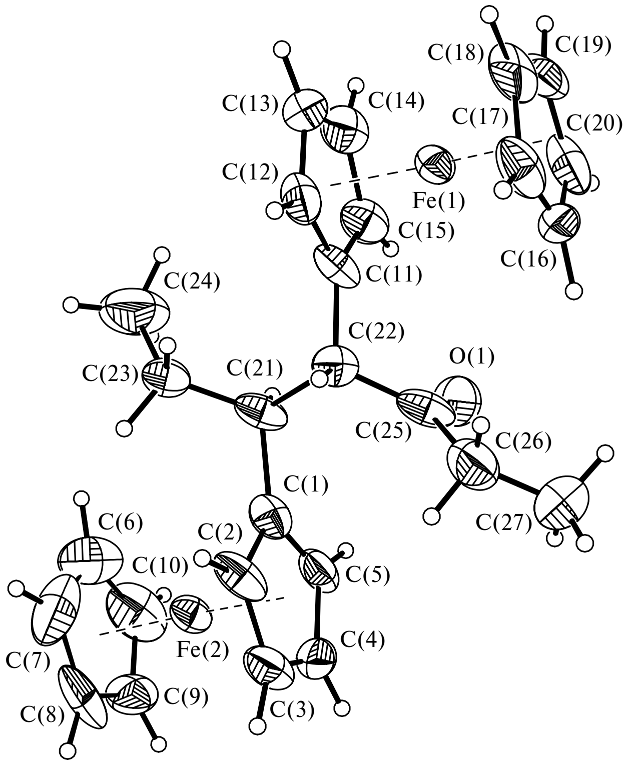
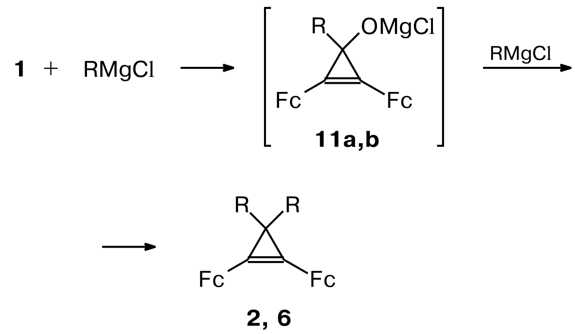


Fig. 2. Molecular structure of *R*,*S*-4,5-diferrocenylheptan-3-one (**4a**).

(3) with subsequent ring closure of cyclopropenone related to ring extension and formation of triferrocenyl-substituted cyclobutenone structures. The second process is prevailing.

3,3-Diethyl- and 3,3-dibenzyl-1,2-diferrocenylcyclopropenes **2** and **6** are formed, most likely, by the interaction of intermediate magnesium alkoxides **11a,b** with the second RMgCl molecule (Scheme 4).

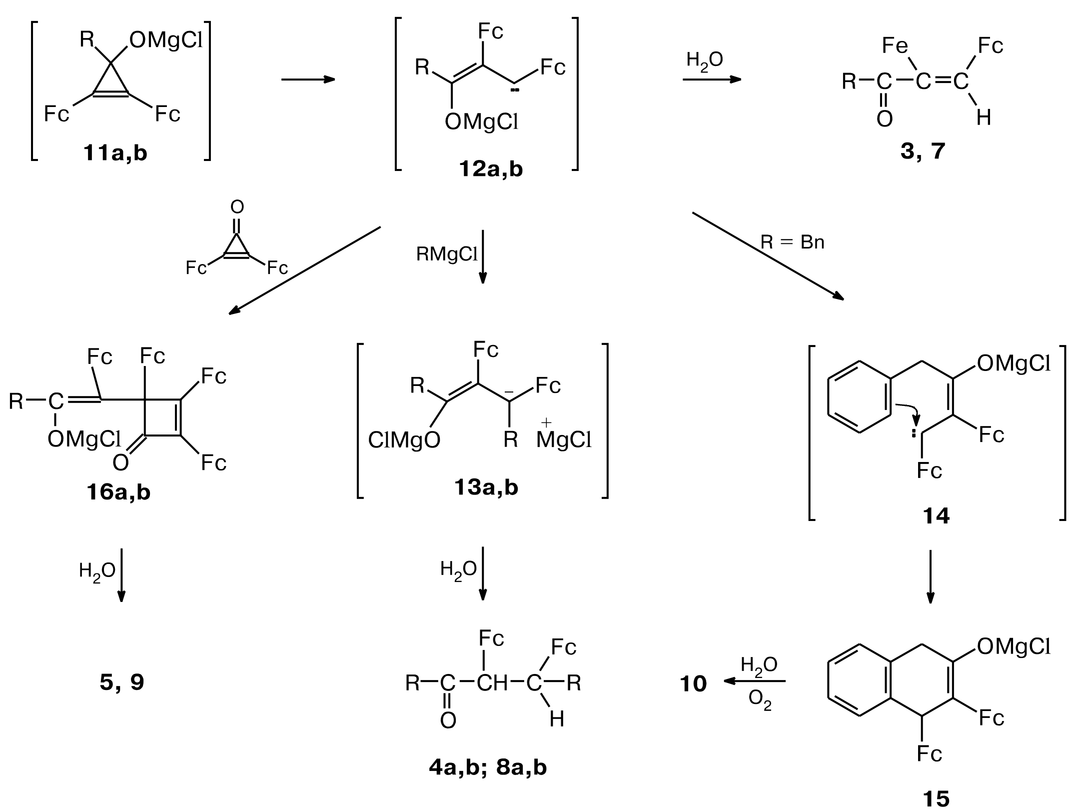
Scheme 4



R = Et (**2**, **11a**); Bn (**6**, **11b**)

Similar processes, resulting in the complete replacement of the carbonyl group by hydrocarbon radicals, have

Scheme 5



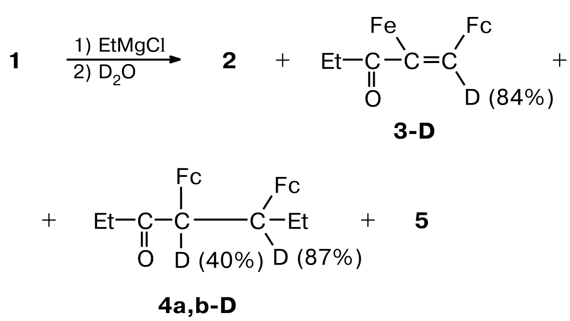
been described previously for the reactions of ferrocenyl ketones with alkylmagnesium iodides.[16,17]

Diferrocenyl ketones **3**, **4a,b**, **7**, and **8a**,**b** were evidently formed due to the small ring closure in **11a,b** followed by the transformation into diferrocenylvinyl carbenoid intermediates **12a,b**. The latter add the second RMgCl molecule and are transformed into vinyl anions **13a,b** (Scheme 5).

The intramolecular alkylation of the phenyl fragment of carbenoid **14** affords enolate **15**. The insertion of carbenoid **12a,b** at one of the σ-bonds of the starting cyclopropenone **1** affords enoxide **16a,b**. The treatment of the reaction mixture with water transforms intermediates **12a,b**, **13a,b**, and enolates **15** (with simultaneous oxidation by air oxygen) and **16a,b** into target compounds **3**, **4a**,**b**, **5**, **7**, **8a**,**b**, **9**, and **10**.

The scheme proposed is favored by the isolation of deuterated ketones **3-D** and **4a,b-D** upon decomposition of the reaction mixture of diferrocenylcyclopropenone and EtMgCl with heavy water D_2O (Scheme 6).

Scheme 6



The deuterium content in position 4 of saturated ketone **4a,b-D** decreased, most probably, due to isotope exchange during chromatography on a column with Al_2O_3.

Experimental

Solvents were dried by standard procedures and distilled before use. Fixed-bed SiO_2 plates and Al_2O_3 (activity grade III according to Brockmann) were used for chromatography. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova spectrometer (300 and 75 MHz, respectively) for solutions in $CDCl_3$ using Me_4Si as internal standard.

IR spectra were recorded on a Specord IR-75 spectrometer (KBr pellets). Molecular weights were determined on a Varian-MAT CH-6 mass spectrometer (EI, 70 eV) .

The following reagents available from Aldrich were used: ferrocene, 98%; tetrachlorocyclopropene, 98%; aluminum chloride 99.99%; ethylmagnesium chloride, 2.0 *M* solution in Et_2O; and benzylmagnesium chloride, 1.0 *M* solution in Et_2O.

2,3-Diferrocenylcyclopropenone (1). $AlCl_3$ (0.67 g, 0.005 mol) was added by portions with stirring to a solution of ferrocene (5.6 g, 0.03 mol) and tetrachlorocyclopropene (3.6 g, 0.02 mol) in anhydrous CH_2Cl_2 (200 mL). Stirring was continued for 1 h at 20 °C, and then the mixture was poured in a cold water (200 mL). The organic layer was separated, washed with water (2×50 mL), and dried with $MgSO_4$. After the solvent was distilled off *in vacuo*, the residue was chromatographed on Al_2O_3 using a hexane—CH_2Cl_2 (3 : 1) mixture as eluant. Compound **1** was obtained as orange crystals in 92% yield (5.8 g), m.p. 182—183 °C (*cf.* Ref. 11: m.p. 181 °C (with decomp.)). Found (%): C, 65.71; H, 4.09; Fe, 26.54. $C_{23}H_{18}Fe_2O$. Calculated (%): C, 65.58; H, 4.28; Fe, 26.36. IR, ν/cm^{-1}: 729, 821, 850, 887, 1003, 1100, 1109, 1480, 1602, 1825, 1850, 2917, 3100. ^{1}H NMR, δ: 4.25 (s, 10 H, 2 C_5H_5); 4.58, 4.84 (both m, 4 H each, C_5H_4). ^{13}C NMR, δ: 65.16 (2 C_{ipso}Fc); 70.0 (2 C_5H_5); 70.9, 71.93 (2 C_5H_4); 144.9 (2 C); 152.3 (C=O).

Reaction of cyclopropenone 1 with EtMgCl. A 2 *M* solution of EtMgCl in Et_2O (8 mL, 16 mmol) was added dropwise to a solution of compound **1** (0.84 g, 2 mmol) in anhydrous benzene (100 mL). The mixture was stirred for 3 h at 20 °C, and then water (100 mL) was added. The organic layer was separated and washed with water, and benzene was distilled off *in vacuo*. The residue was chromatographed on a column with Al_2O_3 using a hexane—diethyl ether (3 : 1) mixture as eluant. Products **2—5** were isolated.

1,2-Diferrocenyl-3,3-diethylcyclopropene (2), 22% yield (0.20 g), orange crystals, m.p. 168—169 °C. Found (%): C, 69.74; H, 6.21; Fe, 23.87. $C_{27}H_{28}Fe_2$. Calculated (%): C, 69.86; H, 6.08; Fe, 24.06. IR, ν/cm^{-1}: 721, 824, 1004, 1120, 1267, 1464, 1609, 1643, 2859, 2920, 3095. ^{1}H NMR, δ: 0.98 (t, 6 H, 2 Me, *J* = 7.5 Hz); 1.70 (q, 4 H, 2 CH_2, *J* = 7.5 Hz); 4.15 (s, 10 H, 2 C_5H_5); 4.33, 4.46 (both m, 4 H each, C_5H_4). ^{13}C NMR, δ: 12.5 (2 Me); 29.5 (2 CH_2); 32.2 (C); 68.6, 68.9 (2 C_5H_4); 69.3 (2 C_5H_5); 75.2 (2 C_{ipso}Fc); 117.0 (2 C). MS, *m/z* 464 [M]$^+$.

***cis*-1,2-Diferrocenylpent-1-en-3-one (3),** 5% yield (0.046 g), red powder, m.p. 146—147 °C. Found (%): C, 66.69; H, 5.22; Fe, 24.89. $C_{25}H_{24}Fe_2O$. Calculated (%): C, 66.41; H, 5.35; Fe, 24.70. IR, ν/cm^{-1}: 812, 1009, 1110, 1276, 1484, 1641, 1668, 1723, 2859, 2920, 3095. ^{1}H NMR, δ: 1.21 (t, 3 H, Me, *J* = 7.0 Hz); 3.48 (q, 2 H, CH_2, *J* = 7.0 Hz); 4.11, 4.13, 4.23, 4.31, 4.37, 4.44 (all m, 2 H each, C_5H_4); 6.72 (s, 1 H, CH=). ^{13}C NMR, δ: 14.6 (CH_3); 39.3 (CH_2); 67.8, 69.9, 70.8, 71.0 (2 C_5H_4); 69.1, 69.7 (2 C_5H_5); 78.4, 78.7 (2 C_{ipso}Fc); 136.0 (C); 136.6 (CH=); 198.4 (C=O). MS, *m/z* 453 [M]$^+$.

4,5-Diferrocenylheptan-3-one (4), 50% yield (0.45 g), orange oil, a mixture of two isomers **4a** and **4b** in a ratio of ~3 : 1 (according to the data of ^{1}H NMR spectroscopy). The isomers were separated by TLC on fixed-bed SiO_2 plates (hexane—diethyl ether (4 : 1)).

Compound **4a**, 30% yield (0.27 g), R_f 0.68, orange crystals, m.p. 176—177 °C. Found (%): C, 67.41; H, 6.09; Fe, 23.31. $C_{27}H_{30}Fe_2O$. Calculated (%): C, 67.25; H, 6.27; Fe, 23.16. IR, ν/cm^{-1}: 762, 815, 998, 1102, 1145, 1250, 1435, 1520, 1709, 2931, 3089. ^{1}H NMR, δ: 0.75 (t, 3 H, Me, *J* = 7.5 Hz): 0.92 (t, 3 H, Me, *J* = 7.2 Hz); 1.80 (m, 2 H, CH_2); 2.41 (q, 2 H, CH_2, *J* = 7.2 Hz); 2.46 (m, 1 H, CH); 3.22 (d, 1 H, CH, *J* = 9.0 Hz); 3.85 (m, 1 H, C_5H_4); 3.92 (m, 2 H, C_5H_4); 3.99 (s, 5 H, C_5H_5); 4.02 (m, 1 H, C_5H_4); 4.06 (s, 5 H, C_5H_5); 4.09 (m, 2 H, C_5H_4); 4.16, 4.36 (both m, 1 H each, C_5H_4). ^{13}C NMR, δ: 6.9, 12.5 (2 Me); 26.5, 38.3 (2 CH_2); 46.0, 58.4 (2 CH); 66.3, 66.6, 66.9, 67.5, 68.3, 68.6, 69.3, 69.7 (2 C_5H_4); 68.4, 68.4 (2 C_5H_5); 84.1, 93.5 (2 C_{ipso}Fc); 210.95 (C=O). MS, *m/z* 482 [M]$^+$.

Compound **4b**, 10% yield, (0.10 g), orange powder, m.p. 164—165 °C. IR, ν/cm^{-1}: 768, 824, 1004, 1100, 1125, 1231, 1425, 1512, 1689, 2919, 3086. ^{1}H NMR, δ: 0.94 (t, 3 H, Me, *J* = 7.3 Hz); 1.05 (t, 3 H, Me, *J* = 7.5 Hz); 1.88 (m, 2 H, CH_2); 2.45 (q, 2 H, CH_2, *J* = 7.5 Hz); 2.49 (m, 1 H, CH); 3.56 (d, 1 H, CH, *J* = 5.1 Hz); 3.67, 3.76, 3.79, 3.94 (all m, 1 H each, C_5H_4); 3.97, 4.04 (both s, 5 H each, C_5H_5); 4.03, 4.08 (both, 2 H each, C_5H_4). ^{13}C NMR, δ: 8.4, 13.6 (2 Me); 24.7, 37.3 (2 CH_2); 46.1, 56.6 (2 CH); 66.7, 67.0, 68.0, 68.7 (2 C); 68.9, 69.6, 69.7 (2 C_5H_4); 68.4, 68.5 (2 C_5H_5); 91.3, 94.0 (2 C_{ipso}Fc); 210.1 (C=O). MS, *m/z* 482 [M]$^+$.

4-(1-Ferrocenyl-2-oxobutyl)-2,3,4-triferrocenylcyclobutenone (5), 6% yield (6%), violet powder, m.p. 289—292 °C (with decomp.). Found (%): C, 66.19; H, 4.71; Fe, 25.77. $C_{48}H_{42}Fe_4O_2$. Calculated (%): C, 65.94; H, 4.84; Fe, 25.56. ^{1}H NMR (δ: 1.28 (t, 3 H, Me, *J* = 7.2 Hz); 2.92 (q, 2 H, CH_2, *J* = 7.2 Hz); 3.48 (s, 1 H, CH); 3.92, 3.96 (both m, 1 H each, C_5H_4); 4.06 (s, 5 H, C_5H_5); 4.10 (m, 2 H, C_5H_4); 4.11, 4.18, 4.23 (all s, 5 H each, C_5H_5); 4.25, 4.36, 4.41, 4.41 (all m, 2 H each, C_5H_4); 4.46 (m, 1 H, C_5H_4); 4.51 (m, 2 H, C_5H_4); 4.91 (m, 1 H, C_5H_4). ^{13}C NMR, δ: 16.5 (CH_3); 48.0 (CH_2); 58.9 (CH); 66.9, 67.4, 67.4 (2 C); 67.5, 68.4, 68.6, 68.9 (2 C); 69.1, 69.2, 69.5, 70.5, 70.6, 70.9, 71.5 (4 C_5H_4); 69.0, 69.2, 69.4, 69.9 (4 C_5H_5); 73.0, 73.3, 80.3, 89.7 (4 C_{ipso}Fc); 140.1, 167.0, 185.7 (3 C); 198.9, 206.2 (2 C=O). MS, *m/z* 874 [M]$^+$.

Decomposition of the reaction mixture with D_2O. The reaction was carried out similarly to the procedure described above, and D_2O (100 mL) was added to decompose the reaction mixture. Compounds **2—5** were obtained after chromatography on a column with Al_2O_3, hexane—diethyl ether (3 : 1) mixture as eluant).

Cyclopropene **2**, 20% yield, 0.18 g, orange crystals, m.p. 169 °C.

Compound **3-D**, 5.5% yield (0.05 g), red powder, m.p. 146 °C. ^{1}H NMR, δ: 1.20 (t, 3 H, Me, *J* = 7.0 Hz); 3.46 (q, 2 H, CH_2, *J* = 7.0 Hz); 4.10, 4.13 (both s, 5 H each, C_5H_5); 4.24, 4.32, 4.38, 4.43 (all m, 2 H each, C_5H_4); 6.72 (s, 0.16 H, CH=). MS, *m/z* 454 [M]$^+$.

Compounds **4a,b-D**, 56% yield (0.51 g), orange oil, mixture of isomers **4a-D** and **4b-D** in a ratio of ~3 : 1 (according to the data of ^{1}H NMR spectroscopy). MS, *m/z*: 483, 484 [M]$^+$.

Compound **4a-D**. ^{1}H NMR, δ: 0.76 (t, 3 H, Me, *J* = 7.3 Hz); 0.92 (t, 3 H, Me, *J* = 7.2 Hz); 1.81 (q, 2 H, CH_2, *J* = 7.3 Hz); 2.41 (q, 2 H, CH_2, *J* = 7.2 Hz); 2.46 (m, 0.13 H, CH); 3.22 (s, 0.6 H, CH); 3.85 (m, 1 H, C_5H_4); 3.92 (m, 2 H, C_5H_4); 3.99 (s, 5 H, C_5H_5); 4.02 (m, 1 H, C_5H_4); 4.06 (s, 5 H, C_5H_5); 4.09 (m, 2 H, C_5H_4); 4.16, 4.36 (both m, 1 H each, C_5H_4).

Compound **4b-D**. ^{1}H NMR, δ: 0.95 (t, 3 H, Me, *J* = 7.2 Hz); 1.04 (t, 3 H, Me, *J* = 7.5 Hz); 1.89 (q, 2 H, CH_2, *J* = 7.2 Hz); 2.44 (q, 2 H, CH_2, *J* = 7.5 Hz); 2.49 (m, 0.12 H, CH); 3.56 (s, 0.55 H, CH); 3.67, 3.76, 3.79, 3.94 (all m, 1 H each, C_5H_4); 3.97 (s, 5 H, C_5H_5); 4.03 (m, 2 H, C_5H_4); 4.04 (s, 5 H, C_5H_5); 4.07 (m, 2 H, C_5H_4).

Compound **5**, 5% yield (0.05 g), violet powder, m.p. 289—291 °C (with decomp.). MS, *m/z* 874 [M]$^+$.

Reaction of cyclopropenone 1 with BnMgBr. Compounds **6—10** were synthesized similarly from compound **1** (0.84 g, 2 mmol) in anhydrous benzene (100 mL) and a 1 *M* solution of BnMgCl in Et_2O (16.0 mL) after the respective treatment and chromatography on Al_2O_3 (hexane—diethyl ether (2 : 1) as eluant).

3,3-Dibenzyl-1,2-diferrocenylcyclopropene (6), 20% yield (0.24 g), orange crystals, m.p. 112—113 °C. Found (%): C, 75.39; H, 5.67; Fe, 19.20. $C_{37}H_{32}Fe_2$. Calculated (%): C, 75.53; H, 5.48; Fe, 18.99. IR, ν/cm^{-1}: 718, 821, 1003, 1105, 1258, 1470, 1589, 1623, 1645, 2883, 2936, 3085. ^{1}H NMR, δ: 2.96 (s, 4 H, 2 CH_2); 4.10 (s, 10 H, 2 C_5H_5); 4.33, 4.39 (both m, 4 H each, C_5H_4); 7.15—7.29 (m, 10 H, 2 C_6H_5). ^{13}C NMR, δ: 33.3 (C); 43.9 (2 CH_2); 68.9, 69.0 (2 C_5H_4); 69.3 (2 C_5H_5); 74.4 (2 C_{ipso}Fc); 117.7 (2 C); 125.7, 127.9, 129.9 (2 C_6H_5); 140.9 (2 C_{ipso}). MS, *m/z* 588 [M]$^+$.

***cis*-4-Phenyl-1,2-diferrocenylbut-1-en-3-one (7)**, 6% yield (0.077 g), red powder, m.p. 161—162 °C. Found (%): C, 69.88; H, 5.28; Fe, 21.93. $C_{30}H_{26}Fe_2O$. Calculated (%): C, 70.07; H, 5.10; Fe, 21.72. IR, ν/cm^{-1}: 815, 1003, 1106, 1265, 1467, 1620, 1648, 1665, 1715, 2853, 2918, 3095. ^{1}H NMR, δ: 3.01 (s, 2 H, CH_2); 4.08, 4.15 (both s, 5 H each, C_5H_5); 4.28, 4.33, 4.37, 4.49 (all m, 2 H each, C_5H_4); 6.86 (s, 1 H, CH=). ^{13}C NMR, δ: 42.3 (CH_2); 67.8, 68.8, 70.5, 70.6 (2 C_5H_4); 69.3, 69.7 (2 C_5H_5); 81.2, 82.6 (2 C_{ipso}Fc); 126.5, 128.5, 130.9 (C_6H_5); 137.2 (C); 138.2 (CH=); 140.6 (C_{ipso}); 199.1 (C=O). MS, *m/z* 514 [M]$^+$.

1,5-Diphenyl-3,4-diferrocenylpent-3-en-2-one (8), 45% yield (0.54 g), orange powder, m.p. 183—188 °C, mixture of two diastereomers **8a** and **8b** in a ratio of ~3 : 1 (data of the ^{1}H NMR spectroscopy). Found (%): C, 73.41; H, 5.39; Fe, 18.31. $C_{37}H_{34}Fe_2O$. Calculated (%): C, 73.29; H, 5.65; Fe, 18.42. IR, ν/cm^{-1}: 767, 823, 1021, 1110, 1233, 1448, 1525, 1536, 1654, 1710, 2921, 3098. MS, *m/z* 606 [M]$^+$.

Compound **8a**. ^{1}H NMR, δ: 2.61 (m, 1 H, CH); 3.15 (d, 2 H, CH_2, *J* = 6.3 Hz); 3.23 (s, 2 H, CH_2), 3.54 (d, 1 H, CH, *J* = 8.4 Hz); 4.05 (m, 1 H, C_5H_4); 4.09 (s, 5 H, C_5H_5); 4.12 (m, 2 H, C_5H_4); 4.14 (s, 5 H, C_5H_5); 4.15 (m, 1 H, C_5H_4); 4.18 (m, 2 H, C_5H_4); 4.21, 4.46 (both m, 1 H each, C_5H_4); 6.89—7.54 (m, 10 H, 2 C_6H_5).

Compound **8b**. ^{1}H NMR, δ: 2.68 (m, 1 H, CH); 3.10 (d, 2 H, CH_2, *J* = 6.6 Hz); 3.30 (s, 2 H, CH_2); 3.41 (d, 1 H, CH, *J* = 8.7 Hz); 3.95 (m, 1 H, C_5H_4); 4.00 (s, 5 H, C_5H_5); 4.02 (m, 2 H, C_5H_4); 4.10 (s, 5 H, C_5H_5); 4.13 (m, 1 H, C_5H_4); 4.15 (m, 2 H, C_5H_4); 4.17, 4.32 (both m, 1 H each, C_5H_4); 7.04—7.63 (m, 10 H, 2 C_6H_5).

4-(3-Phenyl-1-ferrocenyl-2-oxopropyl)-2,3,4-triferrocenylcyclobutenone (9), 6% yield (0.053 g), violet powder, m.p. 312—315 °C (with decomp.). Found (%): C, 68.21; H, 4.91; Fe, 23.65. $C_{53}H_{44}Fe_4O_2$. Calculated (%): C, 67.98; H, 4.74; Fe, 23.86. ^{1}H NMR, δ: 3.23 (s, 2 H, CH_2); 3.52 (s, 1 H, CH); 4.02, 4.07 (both m, 1 H each, C_5H_4); 4.09 (s, 5 H, C_5H_5); 4.13 (m, 2 H, C_5H_4); 4.14, 4.26 (both s, 5 H each, C_5H_5); 4.29 (m, 2 H, C_5H_4); 4.39 (s, 5 H, C_5H_5); 4.40, 4.52, 4.54 (all m, 2 H each, C_5H_4); 4.56 (m, 1 H, C_5H_4); 4.61 (m, 2 H, C_5H_4); 4.99 (m, 1 H, C_5H_4); 7.09—7.45 (m, 5 H, C_6H_5). ^{13}C NMR, δ: 47.4 (CH_2); 57.7 (CH); 67.2, 67.4, 67.6 (2 C); 67.7, 68.7, 68.8, 69.0 (2 C); 69.2, 69.3, 69.6, 70.5, 70.6, 71.0, 71.6 (4 C_5H_4); 69.1, 69.2, 69.5, 69.9 (4 C_5H_5); 73.3, 73.5, 80.6, 89.9 (4 C_{ipso}Fc); 128.3, 129.5, 134.3 (C_6H_5); 139.2 (C_{ipso}); 140.3, 159.9, 175.6 (3 C); 194.3, 209.1 (2 C=O). MS, *m/z* 936 [M]$^+$.

2-Hydroxy-3-oxo-1,2-diferrocenyl-1,2,3,4-tetrahydronaphthalene (10), 10% yield (0.10 g), orange powder, m.p. 159—160 °C Found (%): C, 67.78; H, 5.13; Fe, 21.29. $C_{30}H_{26}Fe_2O_2$. Calculated (%): C, 67.95; H, 4.94; Fe, 21.06. IR, ν/cm^{-1}: 823, 1013, 1100, 1256, 1464, 1625, 1661, 1718, 2879, 2905, 3095, 3368—3459. ^{1}H NMR, δ: 3.14 (s, 2 H, CH_2); 3. 63 (s, 1 H, CH); 4.08 (s, 5 H, C_5H_5); 4.12 (m, 2 H, C_5H_4); 4.21 (s, 5 H, C_5H_5); 4.23, 4.27, 4.34 (all m, 2 H each, C_5H_4); 5.03 (br.s, 1 H, OH); 6.98—7.35 (m, 4 H, C_6H_4). ^{13}C NMR, δ: 41.1 (CH_2); 67.5, 68.9, 70.4, 70.5 (2 C_5H_4); 69.3, 69.7 (2 C_5H_5); 70.2 (C); 78.9, 80.7 (2 C_{ipso}Fc); 127.8, 129.3, 129.8, 134.3 (C_6H_4); 136.5, 144.8 (2 C_{ipso}); 210.1 (C=O). MS, m/z 530 $[M]^+$.

X-ray diffraction analysis of compounds 4a and 6. Unit cell parameters and intensities of reflections were measured on a Bruker Smart Apex CCD diffractometer at 291 K. The structures were solved by the direct method and refined by the least-squares method in the full-matrix anisotropic approximation for non-hydrogen atoms. All H atoms were revealed from the difference series and refined isotropically. The coordinates of atoms were deposited with the Cambridge Structural Database. The crystallographic data, parameters of X-ray diffraction experiment, and refinement parameters are presented in Table 2.

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References

1. A. Greenberg, R. P. T. Tomkins, M. Dobrovolny, and J. F. Liebman, *J. Am. Chem. Soc.*, 1983, **105**, 6855
2. P. H. M. Budzelaar, E. Kraka, D. Cremer, and P. v. R. Schleyer, *J. Am. Chem. Soc.,* 1986, **108**, 561.
3. H. Dahn and M.-N. Ung-Truong, *Helv. Chim. Acta*, 1987, **70**, 2130.
4. R. Breslow, R. Haynie, and J. Mirra, *J. Am. Chem. Soc.*, 1959, **81**, 247.
5. I. Agranat and S. Kohen, *Bull. Chem. Soc. Jpn*, 1974, **47**, 723.
6. H. Tsukada, H. Shimanouchi, and Y. Sasada, *Tetrahedron Lett.*, 1973, 2455.
7. Y. Veprek-Bilinski, K. Natasimhan, and A. S. Dreiding, *Helv. Chim. Acta*, 1978, **61**, 3018.
8. M. Takahashi, N. Inaba, H. Kirihara, and S. Watanabe, *Bull. Chem. Soc. Jpn*, 1978, **51**, 3312.
9. T. Eicher and M. Urban, *Chem. Ber.*, 1980, **113**, 408.
10. M. Takahashi and S. Watanabe, *Chem. Lett.*, 1979, 1213.
11. I. Agranat, E. Aharon-Shalom, A. J. Fry, R. L. Krieger, and W. O. Krug, *Tetrahedron*, 1979, **35**, 733.
12. E. I. Klimova, T. Klimova Berestneva, L. Ruiz Ramirez, M. Martinez Garcia, C. Alvarez Toledano, P. G. Espinosa, and R. A. Toscano, *J. Organomet. Chem.*, 1997, **545—546**, 191.
13. E. I. Klimova, M. Martinez Garcia, T. Klimova, C. Alvarez Toledano, R. A. Toscano, R. Moreno Esparza, and L. Ruiz Ramirez, *J. Organomet. Chem.*, 1998, **566**, 175.
14. W. G. Young, S. U. Sharman, and S. Winstein, *J. Am. Chem. Soc.*, 1960, **82**, 1376.
15. E. I. Klimova, T. Klimova Berestneva, L. Ruiz Ramirez, A. Cinquantini, M. Corsini, P. Zanello, S. Hernandez Ortega, and M. Martinez Garcia, *Eur. J. Org. Chem.,* 2003, 4265.
16. D. B. Werz, R. Gleiter, and F. Rominger, *Eur. J. Org. Chem.,* 2003, 151
17. G. A. Olah and M. Mayer, *J. Am. Chem. Soc.*, 1975, **97**, 1539.

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