Symmetrical and Asymmetrical Cyclopropenones: Synthesis and Study of Their Chemical Reactivity

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Abstract: Symmetrical and asymmetrical cyclopropenones with diferrocenyl, diaryl and aryl-ferrocenyl substituents were obtained and their chemical behavior was studied. 1-Ethoxy-2,3-diarylcyclopropenylium tetafluoroborate selectively reacts with MeLi, n-BuLi with formation of the 3,3-dialkyl-1,2-diarylcyclopropenes. The structures of 2,3-bis(4-methoxyphenyl) cyclopropenone (10), 2-ferrocenyl-3-(4-methoxyphenyl) cyclopropenone (11), 2-ferrocenyl-3-(naphthalen-1-yl) cyclopropenone (14) and 3,3-dimethyl-1,2-dianysol cyclopropene 19a were confirmed by X-ray crystallographic analysis.

Keywords: Cyclopropenone, ferrocene, cyclopropenium cation, cyclopropene.

The first cyclopropenilium cation, namely triphenylcyclopropenium, was synthesized and described by Breslow and coworkers in 1957 [1], and shortly after that the corresponding diphenylcyclopropenone was obtained [2]. Nowadays, numerous investigations have been carried out with this class of cations [3], and in the last years they were prepared by various routes [3-8].

\[
2\text{C}_6\text{H}_6 + \begin{array}{c} \text{Cl} \\
\text{AlCl}_3 \\
\end{array} \quad \text{1.- 0 oC} \quad \text{H}_2\text{O} \quad + \text{2HCl}
\]

Equation 1.

The diarylcyclopropenone 2 was obtained after hydrolysis of the products of alkylation obtained by the reaction of benzene or benzene derivatives with trichlorocyclopropenium tetrachloroaluminate (1) (Equation 1) [6]. Further study of this reaction showed that it takes place stepwise; at low temperature, a single chlorine atom in the C3Cl3+ ion is replaced, whereas at room temperature, a mixture of mono- and disubstituted products is obtained [6]. Trisubstitution is not normally observed. From the point of view of the mechanism, the reaction shown in equation 1 is a Friedel-Crafts alkylation, involving electrophilic substitution on the carbon of the benzene ring, and generally leads to the formation of symmetrical diarylcyclopropenones. The common reagents for this reaction are aromatic hydrocarbons bearing weakly activating groups (alkyl) or weakly deactivating substituents (halogen).

Diarylcyclopropenone 2 was found to be able to react with several chemical reagents such as amines, hydrazines, alcohols, thiols, organometallics and diazo-compounds [8].

The synthesis of diferrocenylcyclopropenone 3 has been performed in our group [9]. It was found that the reactions of 3 with ethyl- and benzylmagnesium chlorides afforded not only 3,3-diethyl- and 3,3-dibenzyl-1,2-diferrocenylcyclopropanes 4a and 4b, respectively (Equation 2), but also products of nucleophilic opening of the three-membered ring 5a,b and 6a,b. This result was attributed to the presence of two ferrocenyl groups in the structure of the compound 3 making its chemical behavior different from the reported previously for the diaryl cyclopropenones.

\[
\begin{array}{c}
\text{RMgCl} \\
\text{Fc} \\
\text{Fc} \\
\end{array} + \begin{array}{c}
\text{OH} \\
\text{Fc} \\
\text{Fc} \\
\end{array} \quad \text{3} \quad + \quad \begin{array}{c}
\text{RMgCl} \\
\text{Fc} \\
\text{Fc} \\
\end{array} \quad \text{4a, b} \quad \text{5a, b} \quad \text{6a, b}
\]

Equation 2.

In contrast to symmetrical diaryl- or diferrocenyl cyclopropenones, their asymmetrical analogs with the aryl and ferrocenyl substituents in the same molecule have not been synthesized and studied up to now. At the same time, the influence of the ferrocenyl fragment on regio- and stereo-
chemistry of aryl-ferrocenyl cyclopropenones and its chemical properties deserve to be studied.

In the present work, we report the synthesis of symmetrical diaryl and asymmetrical aryl-ferrocenyl cyclopropenones and the behavior of the 1-ethoxy-2,3-diarylcyclopropenium cation in the reactions with organolithium reagents.

RESULTS AND DISCUSSION

The cyclopropenones 3, 10, 11, 13, 14, 16 and 17 were obtained from tetrachlorocyclopropene 7 and the mixtures of ferrocene-anisole, ferrocene-naphthalene and ferrocene-anthracene in anhydrous CH₂Cl₂ using catalytic amounts of aluminum chloride.

The following signals were observed in the ¹H NMR spectrum of compound 10: one singlet at δ 3.91 for the methoxy groups and two doublets at δ 7.06 and 7.93 for the aryl groups. In the ¹H NMR spectrum of the asymmetrical cyclopropenone (11) were observed the signals of the methoxy group (one singlet at δ 3.90), the ferrocenyl group (three characteristic signals at δ 4.22, 4.59 and 4.89) and the aryl group (two doublets at δ 7.06 and 8.84).

Crystals of 2,3-bis(4-methoxyphenyl) cyclopropenone (10) and 2-ferrocenyl-3-(4-methoxyphenyl) cyclopropenone (11) suitable for X-ray crystallographic studies were obtained by crystallization from hexane. Fig. (1 and 2) show the crystal structures of the compounds 10 and 11.

![Scheme 1. Synthesis of symmetrical and asymmetrical cyclopropenones.](image)

![Fig. (1). Crystal structure of the symmetrical compound (10).](image)
The following signals were observed in the $^1$H NMR spectrum of the compound 13: one doublet assigned to the naphthyl group at $\delta$ 8.94 with a coupling constant $J = 8.5$ Hz due to the proton in the position $7'$, three doublets at $\delta$ 8.38, 8.18 and 7.90, all with coupling constants $J = 7.0$ Hz for the protons in the positions $2'$, $4'$ and $10'$, respectively, and two multiplets at $\delta$ 7.85 and 7.65 due to the protons in the positions $3'$, $8'$, and $10'$. In the $^{13}$C NMR spectrum of this compound, the most important signals observed were at $\delta$ 146 corresponding to the $sp^2$ carbon of the cyclopropene and at $\delta$ 155.5 which is the signal characteristic for the carbonyl group.

In the case of the asymmetrical compound (14), in the $^1$H NMR spectrum were observed the signals of both ferrocenyl (three characteristic signals at $\delta$4.22, 4.59 and 4.89) and naphthyl (at $\delta$ 7.06, 7.84, 7.23-7.42) groups. Crystals of 2-ferrocenyl-3-(naphthalen-1-yl) cyclopropene (14) obtained by crystallization from hexane were studied by X-ray diffraction of monocrystal (Fig. 3).

In $\text{H}^1$ NMR spectrum of compound 16 the following signals assigned to the anthracenyl group were observed: one singlet at $\delta$ 8.86 due to the two protons in the positions $10'$; one doublet at $\delta$ 8.41 with a coupling constant $J = 6.9$ Hz for the protons in the positions $1'$ and $8'$; double of doublets at $\delta$ 8.1 with coupling constants $J = 6.4$ Hz ascribed to the protons in the positions $4'$ and $5'$; one multiplet at $\delta$ 7.4 due to the protons in the positions $3'$, $6'$ and $2'$, $7'$. In the $^{13}$C NMR spectrum of compound 16 were observed the signals characteristic for the anthracene moiety at $\delta$111.3-134.8, the signal due to the $sp^3$ carbons C=C of the cyclopropene ring at $\delta$ 148.1, and the most important signals of the quarternary carbons of the cyclopropene at $\delta$156.7 and the signal characteristic for the carbonyl group at $\delta$ 155.5. For the asymmetrical cyclopropene 17, in the $^1$H NMR spectrum were observed the signals of the ferrocenyl (three characteristic signals at $\delta$4.24, 4.66 and 5.01) and the anthracenyl group (two doublets at $\delta$ 7.06 and 7.84 with coupling constants $J = 7.1$ Hz and $J = 1.3$ Hz, respectively); also two sets of multiplets were observed at $\delta$7.9-8.1 and at$8.32$ due to the protons in the positions $1'$, $4'$, $5'$ and $8'$.

XRD studies of compounds 10, 11 and 14 showed that the presence of two large and heavy substituents in their molecules leads to the distortion of the cyclopropene structure and to enlargement of the internal angles in the positions 2 and 3.

Treatment of diarylcyclopropene with triethylxonium tetrafluoroborate in benzene and precipitation of the resulting product with diethyl ether affords crystalline $1$-ethoxy-2,3-dicyclopropenyltetrafluoroborate 18 (Equation 3).

However, the cyclopropenylium tetrafluoroborate (18) was unstable and its characterization by NMR spectroscopy was not possible.

The action of alkyllithium reagents on difterrocenylcyclopropenyltetrafluoroborate (18), affords the corresponding 1,2,3-substituted cyclopropenes (19a,b) (Equation 4).

The following signals were observed in the $^1$H NMR spectrum of compound 19a: one singlet at $\delta$ 3.62 due to the methyl groups, one singlet at $\delta$ 3.85 for the methoxy groups and two doublets at $\delta$ 6.97 and 7.53 for the protons of the aryl groups.

In the $^1$H NMR spectrum of the 3,3-di-(n-butyl)-1,2-bis(4-methoxyphenyl) cyclopropene 19b were observed: one multiplet at $\delta$ 0.79 due to the methyl groups, two multiplets at $\delta$ 1.19 and 1.81 assigned to the methylene groups, one singlet at $\delta$3.84 due to the methoxy group, and two doublets at $\delta$6.95 and 7.55 due to the aryl groups.

The crystal structure of the 1,2-diaryl-3,3-dimethylcyclopropene (19a) shown in Fig. (4) was established by X-ray
diffraction analysis and is in line with the $^1$H NMR spectroscopy results described above.

**CONCLUSIONS**

The use of electron donating substituents like ferrocene, 4-methoxy-benzene, naphthalene and anthracene in the synthesis of symmetrical or asymmetrical cyclopropenones allows preparation of compounds that are stable for long periods of time. The presence of heavy substituents in the cyclopropenones leads to the distortion of the small cycle. In agreement with our studies, the best yields were obtained with ferrocene. This could be due to its stronger electron-donating properties in comparison with the other aromatic systems studied.

**EXPERIMENTAL SECTION**

**General Information**

Infrared (IR) spectra were recorded on a Nicolet FT-IR Magna 700 Spectrometer. $^1$H- and $^{13}$C- NMR spectra for solutions in CDCl$_3$ were collected on a Varian Unity operating at 300 and 75 MHz, respectively. For both $^1$H and $^{13}$C, chemical shifts are expressed in ppm relative to tetramethylsilane (Me$_4$Si δ 0.00) as the internal standard. Column chromatography was carried out on alumina (Brockmann activity III). Elemental analyses were performed at Galbraith Laboratories, INC. Knoxville, USA. FAB+ mass spectra were taken with a JEOL JMS AX505 HA mass spectrometer. Unit cell parameters and intensities of reflections were measured on a Siemens P4/Pc diffractometer at room temperature.

**General Procedure for the Synthesis of Cyclopropenones**

AlCl$_3$ (0.67 g, 5 mmol) was added by portions to a solution of one of the compounds 8, 12, 15 (23.0 mmol) and ferrocene 9 (23.0 mmol) and tetrachlorocyclopropene (23.0 mmol) in anhydrous CH$_2$Cl$_2$ (200 mL) under continuous stirring for 30 min. The stirring was continued for another 90 min at room temperature, then the mixture was poured in 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$_2$O$_3$ using a hexane-CH$_2$Cl$_2$ (3:1) mixture as eluent.

**Reaction of Tetrachlorocyclopropene 7 with Fc-H and p-CH$_3$O-C$_6$H$_5$**

2,3-diferrocenylcyclopropenone (3)

For spectral data see ref. [10], yield 3.9 g, 9.5 mmol (41.3%).

**2,3-bis(4-methoxyphenyl)cyclopropenone (10)**

For spectral data see ref. [10], yield 3.9 g, 9.5 mmol (41.3%).

**2,3-bis(4-methoxyphenyl)cyclopropenone (10)**

Yield 2.1 g (34.8 %), white powder, m.p. 153-155 °C. FTIR (pellet, KBr, cm$^{-1}$): 511, 754, 830, 1017, 1168, 1256, 1510, 1602, 1846. UV-Vis (CH$_2$Cl$_2$, nm) $\lambda_{max}$: 255, 271, 323, 334, 342. $^1$H NMR (300 MHz, CDCl$_3$), $\delta_H$ (ppm): 3.91 (s, 6H, OCH$_3$), 7.06 (d, 4H, C$_6$H$_4$, $J = 7.1$ Hz), 7.93 (d, 4H, C$_6$H$_4$, $J = 7.3$ Hz). $^{13}$C NMR (75 MHz, CDCl$_3$), $\delta_C$ (ppm): 55.5 (OCH$_3$), 114.7 (Ar), 122.3 (C$_{pao}$), 126.8 (Ar), 160.1 (C$_{ipso}$), 155.2 (C=C), 162.8 (C=O). EM: m/z 267. Calc. for C$_{27}$H$_{27}$O$_3$: C, 76.76; H, 5.28 (%). Found: C, 76.67; H, 5.30.
2-ferrocenyl-3-(4-methoxyphenyl)cyclopropene (11)

Yield 1.22 g (15.2 %), orange powder, m.p. 120-121 °C. FTIR (pellet, KBr, cm⁻¹): 512, 756, 833, 1019, 1178, 1286, 1521, 1602, 1846. UV-Vis (CH₂Cl₂, nm) λmax: 225, 261, 334, 348. 1H NMR (300 MHz, CDCl₃, δH ppm): 3.90 (s, 3H, OCH₃), 4.22 (s, 5H, CH₃), 4.59 (s, 2H, CH₂), 4.89 (s, 2H, CH₂), 7.06 (d, 2H, CH₃, J= 7.1 Hz), 7.84 (d, 2H, CH₃, J= 7.6 Hz). 13C NMR (75 MHz, CDCl₃, δC ppm): 55.5 (CH₃), 64.6 (Fc ipso), 70.7 (C 5H₅), 71.5 (C 5H₅), 72.2 (C 5H₅), 114.7 (C), 117.8 (Ar), 127.6 (Ar), 129.7 (Ar), 130.1 (Ar), 132.2 (Ar), 133.8 (Ar). EM: m/z 344. Calc. for C₂₃H₁₆FeO: C, 75.82; H, 4.43 (%). Found: C, 75.81; H, 4.38 (%).

Reaction of tetrachlorocyclopropene 7 with Fe-H and C₁₀H₈

Diferrocenyl cyclopropene (3)

Yield 1.2 g, 2.85 mmol (19.1 %).

2,3-bis(naphthalen-1-yl)cyclopropenone (13)

Yield 1.2 g, 2.85 mmol (19.1 %).

Diferrocenyl cyclopropene (3)

Yield 1.2 g, 2.85 mmol (19.1 %).

2,3-bis(anthracen-9-yl)cyclopropenone (16)

Yield 1.6 g (16.5 %).

Diferrocenylcyclopropene (3)

Yield 1.6 g (16.5 %).

2,3-bis(anthracen-9-yl)cyclopropenone (16)

Yield 0.98 g (10.5 %), white powder, m.p. 169-170 °C. FTIR (pellet, KBr, cm⁻¹): 522, 839, 852, 1049, 1168, 1275, 1571, 1882, 1896. UV-Vis (CH₂Cl₂, nm) λmax: 215, 261, 334, 348. 1H NMR (300 MHz, CDCl₃, δH ppm): 8.66 (s, 2H, Ar), 8.41 (d, 4H, Ar, J= 6.9 Hz), 8.10 (d, 4H, Ar, J= 6.4 Hz), 7.4 (m, 8H, Ar). 13C NMR (75 MHz, CDCl₃, δC ppm): 111.3 (Ar), 125.2 (Ar), 126.9 (Ar), 127.8 (Ar), 128.9 (Ar), 128.6, 130.1 (Ar), 132.2 (Ar), 133.8 (Ar). EM: m/z 344. Calc. for C₂₃H₁₆FeO: C, 90.17; H, 4.61 (%). Found: C, 90.18; H, 4.59.

1-ethoxy-2,3-bis(4-methoxyphenyl)cyclopentenium fluoroborate (18)

A solution of the triethyloxonium tetrafluoroborate in CH₂Cl₂ (1M, 5.14 ml, 5.14 mmol) was added under stirring to a solution of 2,3-bis(4-methoxyphenyl)cyclopropenone (10) (1.33 g, 5.0 mmol) in benzene (50 ml). The mixture was kept at room temperature for 3 h, then dry diethyl ether (100 ml) was added. The formed precipitate was filtered off, washed on a filter with several portions of dry ether, and dried in a vacuum desiccator to give 1-ethoxy-2,3-bis(4-methoxyphenyl)cyclopentenium fluoroborate (18) as a white powder, yield 1.73 g (91 %).

3,3-dimethyl-1,2-bis(4-methoxyphenyl)cyclopentenone (19a)

A solution of methyliithium in diethyl ether (1.6 M, 4.5 ml) was added with stirring in an inert atmosphere to a solution of (18) (0.27 g, 0.71 mmol) in dry benzene (200 ml). The mixture was stirred for 3 h at room temperature, and then water (100 ml) was added. The organic layer was separated, washed with water (250 ml), the solvent was removed in vacuum, and the residue was chromatographed on alumina (hexane-diehtyl ether) ether). 3:1 to give dimethylichloropropene (19a) as a white powder, yield 0.042 g, 0.15 mmol (21 %), m.p. 122-124 °C. FTIR (pellet, KBr, cm⁻¹): 511, 754, 830, 1033, 1219, 1510, 1604, 1846, 961. UV-Vis (CH₂Cl₂, nm) λmax: 240, 264, 332, 345, 351. 1H NMR (300 MHz, CDCl₃, δH ppm): 1.62 (s, 6H, CH₃), 3.85 (s, 6H, OCH₃), 6.96 (d, 4H, CH₃, J= 7.2 Hz), 7.53 (d, 4H, CH₃, J= 7.2 Hz). 13C NMR (75 MHz, CDCl₃, δC ppm): 24.6 (CH₃) 30.2 (C), 55.3 (OCH₃) 114.3 (C = cyclopentenone), 130.3 (Ar) 130.7 (Cipso), 131.0 (Ar). EM: m/z 280 [M⁺] Calc. for C₂₀H₁₄O₂: C, 81.40; H, 7.19 (%). Found: C, 81.42; H, 7.19.

3,3-di-(n-butyl)-1,2-bis(4-methoxyphenyl)cyclopropene (19b)

A 2.5 M solution of methylolithium in hexanes (8.0 ml) was added with stirring in an inert atmosphere to a solution of (17) (1.39 g, 5.0 mmol) in dry benzene (200 ml). The mixture was stirred for 3 h at room temperature and then water (100 ml) was added. The organic layer was separated, washed with water (250 ml), the solvent was removed in vacuum, and the residue was chromatographed on alumina (hexane-diehtyl ether, 3:1) to give dimethylichloropropene (19b), as a white powder, yield (1.5 g, 4.12 mmol, 82 %), m.p. 48-49 °C. FTIR (pellet, KBr, cm⁻¹): 511, 754, 820,
1030, 1246, 1509, 1603, 1846, 921. UV-Vis (CH₂Cl₂, nm) λ_max: 240, 265, 335, 348, 354. ¹H NMR (300 MHz, CDCl₃), δH (ppm): 3.62 (s, 6H, CH₃), 0.795 (m, 6H, CH₃), 1.19 (m, 8H, CH₂), 1.81 (m, 4H, CH₂), 3.84 (s, 3H, OCH₃), 6.95 (d, 4H, C₆H₄, J = 6.9 Hz), 7.55 (d, 4H, C₆H₄, J = 6.9 Hz), 13C NMR (75 MHz, CDCl₃), δC (ppm): 14.1 (CH₃), 23.2 (CH₂), 36.7 (CH₂), 55.3 (OCH₃), 114.1 (C=, cyclopropene), 118.4 (Cipso), 124.2 (Ar), 130.2 (Ar), 159.1 (Cipso). EM: m/z 364 [M]⁺ Calc. for C₂₅H₃₂O₂: C, 82.37; H, 8.83.

X-Ray Crystallography

A suitable crystal of compound 10, 11, 14 and 19a (obtained by crystallization from hexane at room temperature) was rolled in epoxy resin and mounted on a glass fiber. Bruker Apex AXS CCD area detector X-Ray diffractometer was the instrument used for the determination. The data were first reduced and corrected for absorption using psi-scans, and then solved using the program SHELL-XS. All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were refined at calculated positions with thermal parameters constrained to the carbon atom on which they were attached.

SUPPLEMENTARY MATERIALS

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 684321 for the 2,3-bis(4-methoxyphenyl)cyclopropene 10, CCDC No. 684322 for the 2-ferrocenyl-3-(4-methoxyphenyl) cyclopropene 11, CCDC No. 684323 for the 2-ferrocenyl-3-(naphthalen-1-yl) cyclopropene 14 and CCDC No. 684324 for the 3,3-dimethyl-1,2-bis(4-methoxyphenyl) cyclopropene 19a.

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REFERENCES