# Chemistry of bicymantrenyl

## 2.* Metallation with butyllithium

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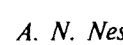
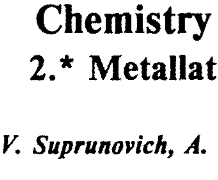
Bicymantrenyl, $(CO)_3MnC_5H_4C_5H_4Mn(CO)_3$, can be metallated with butyllithium in THF at −60 °C into Cp rings. Quenching with electrophiles ($D_2O$, $I_2$, $CO_2$, and DMF) results in the formation of the corresponding bicymantrenyl derivatives with substituents predominantly at β-positions.

**Key words:** bicymantrenyl, butyllithium, metallation, manganese complexes, cyclopentadienyl, carbonyl.

The chemistry of bicymantrenyl (**1**) is poorly studied.[2,3] Recently we have studied its acylation.[1] In the present work, the reaction of **1** with BuLi is studied.



**1—3, 5, 6**



**4**

R = H (**1**); Et (**2**); CHO (**3**); COOH (**5**); COCl (**6**)

Similarly to cyclopentadienylmanganesetricarbonyl (cymantrene), complex **1** is readily metallated into Cp rings under the action of BuLi in THF at −60 to −70 °C. Depending on the amount of BuLi, either a monolithium derivative or a mixture of mono- and polylithium derivatives are formed. The metallation of **1** by four- to fivefold excess of BuLi followed by quenching with $D_2O$ results in a mixture of isotopomers of **1** containing from one to four deuterium atoms (peaks with *m/z* from 407 to 410 are observed in the mass spectrum in the region of the molecular ion). The metallation of **1** with BuLi occurs at both α- and (predominantly) β-positions. The $^1H$ NMR data show that the β/α ratio of deuterio-substituted derivatives is 3—4.

The complex with the Et-substituent at the β-position (**2**) obtained previously[1] is metallated nonselectively as well; all seven H atoms of the $C_5H_4—C_5H_3$ fragment are involved. According to $^1H$ NMR spectral data, the D atoms were present mostly at the β-positions, and the smallest amount at the α-positions of the nonsubstituted ring following metallation with BuLi and quenching with $D_2O$. The amount of D atoms in the $C_5H_3$ ring is intermediate. It is known that the metallation of methylcyclopentadienylmanganesetricarbonyl is also nonselective.[4]

When Li derivatives are quenched with other electrophiles, mixtures of mono- and polysubstituted derivatives, whose ratio depends on the amount of BuLi, are also formed. After treatment with iodine, a mixture of mono- and diiodobicymantrenyl is obtained. The action of DMF followed by hydrolysis gives a mixture of aldehydes, from which β-aldehyde (**3**) and α-aldehyde (**4**) were isolated in a ratio of ~10 : 1. The mass spectra of aldehydes **3** and **4** are similar, but their $^1H$ NMR spectra differ strongly. For aldehyde **3**, the three protons of the substituted ring give three signals in lower field with δ: 5.621 (t, 1 H, *J* = 1.7 Hz); 5.488 (dd, 1 H, *J* = 1.7 and 3.0 Hz); 5.089 (dd, 1 H, *J* = 1.7 and 3.0 Hz). The four protons of the nonsubstituted ring manifest themselves as two multiplets, each of them consisting of 10 lines at δ 5.028 (2 H, α-position) and 4.807 (2 H, β-position). The proton of the CHO group gives the signal at δ 9.597 (s).

In the $^1H$ NMR spectrum of aldehyde **4**, the three signals with δ 5.456 (dd, 1 H, *J* = 1.8 and 3.0 Hz), 5.153 (t with the broadened central line, 1 H, *J* = 1.8 and 3.0 Hz), and 4.882 (t, 1 H, *J* = 3.0 Hz) correspond to the three protons of the substituted ring. Unlike compound **3**, in the spectrum of **4**, the protons of the nonsubstituted $C_5H_4$ ring give not two, but three separate signals. The signal at 4.818 ppm (two partially overlapped sets of triplet of doublets, 10 individual lines of the theoretical number 12 are resolved, 2 H, *J* = 1.8 and 2.9 Hz) correspond to two protons at the β'-positions. Two protons at the α'-positions, one of

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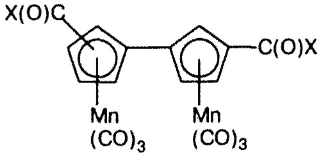
which is much closer to the CHO substituent than another, give two signals due to the diastereotopic nonequivalence: δ 5.571 (5 lines, 1 H, $J$ = 1.9 and 2.6 Hz) and 5.063 (5 lines, 1 H, $J$ = 1.9 and 2.6 Hz). The singlet at 9.772 ppm corresponds to the CHO proton.

Monometallation of complex **1** followed by quenching with $CO_2$ results in the formation of β-monocarboxylic acid (**5**). The treatment of this acid with $PCl_5$ gives acid chloride (**6**). When >2 equiv. of BuLi are used, a mixture of dicarboxylic acids (**7**) is obtained. A mixture of acid dichlorides (**8**) is formed from **7** under the action of $PCl_5$.



**7, 8**

X = OH (**7**); Cl (**8**)

Carboxylic acids and acid chlorides, derivatives of **1**, exhibit characteristic bands in the IR spectra in the νCO region (Table 1). The positions and intensities of these bands are similar to or coincide with those of the corresponding bands for cymantrenyl analogs. In the IR spectrum of acid chloride **6**, different νCO bands correspond to two fragments of $Mn(CO)_3$: the bands at 1950 sh, 1954, and 2029 $cm^{-1}$ correspond to the $(CO)_3MnC_5H_4$ fragment, and those at 1964, 1972, and 2041 $cm^{-1}$ correspond to the $(CO)_3MnC_5H_3C(O)Cl$ fragment with the strong electron-acceptor substituent. The latter bands are shifted to the region of higher wave numbers and coincide with the bands in the spectrum of acid chloride $(CO)MnC_5H_4C(O)Cl$. The $^1H$ NMR spectrum of acyl chloride **6** resembles that of aldehyde **3** very much. The IR spectrum of a mixture of acid dichlorides **8** contains only one set of bands at 1969/1978 and 2039/2051 $cm^{-1}$, which are even more shifted to the region of higher wave numbers than those of acid chloride **6**. It follows from the data of IR and $^1H$ NMR spectroscopy that COCl substituents in acid dichlorides **8** are located in different Cp rings.

The synthesis of key compounds of the bicymantrenyl series such as ketones[1] and aldehydes **3** and **4** described above, carboxylic acid **5**, and acid chloride **6** opens up the possibility for developing the synthetic chemistry of **1**, similar to the chemistry of cymantrene derivatives.[5] When 1.0 to 1.2 equiv. of BuLi are used, some **1** is recovered, but the metallation occurs almost completely at the β-positions. α-Derivatives formed in minor amounts can be separated in the workup (chromatography, recrystallization). To the contrary, when 1.5 to 2 equiv. or larger excess of BuLi are used, mixtures that are difficult to separate, containing mono- and polysubstituted derivatives, are formed.

All monosubstituted derivatives of **1** independent of the position of the substituent (α- or β-) are planar-chiral. Therefore, the seven CH groups are diastereotopic, and the protons of the $C_5H_4C_5H_3$ fragment give, as a rule, from five to seven different signals in the $^1H$ NMR spectra.

## Experimental

Bicymantrenyl **1** was obtained by the known procedure.[3] All experiments were carried out in an argon atmosphere. THF was distilled over sodiumbenzophenoneketyl prior to use. $^1H$ NMR spectra were recorded on Bruker WP-200-SY and Bruker-AMX-400 instruments in $CDCl_3$. IR spectra were recorded on a UR-20 instrument. Mass spectra were obtained on a Kratos-MS-890 instrument (70 eV).

**Deuteration of 1.** A calculated amount of a 1.6 $M$ solution of BuLi in hexane was added at −60 to −65 °C to a solution of **1** (0.406 g, 1 mmol) in THF (30 mL). The mixture was stirred on a magnetic stirrer for 1.5—2 h at −60 °C, then $D_2O$ was added, and the mixture was allowed to warm to ~20 °C for 1 h. Dilute HCl was added to the reaction mixture, and the products were extracted with $CH_2Cl_2$. The extract was concentrated, the residue was chromatographed on a column with $Al_2O_3$ (petroleum ether—benzene (2 : 1) as the eluent), and deuterated **1** (yield >90 %) was isolated. To determine the number of deuterium atoms at each position of the ring, mixtures of known amounts of isolated **1** and hexamethylbenzene ($C_6Me_6$, singlet at δ 2.150, internal standard) were

**Table 1.** Frequencies νCO in the IR spectra of carboxylic acids and acid chlorides

| Compound (fragment) | Solvent | νCO/$cm^{-1}$ | |
|---|---|---|---|
| | | $Mn(CO)_3$ | Substituent |
| $(CO)_3MnC_5H_4COOH$ | $CH_2Cl_2$ | 1955 b, 2035 | 1695, 1740 |
| Acid **5** | $CH_2Cl_2$ | 1955 b, 2025, 2035 sh | 1695, 1740 |
| Acid **7** | $CH_2Cl_2$ | 1950—1960, 2025, 2030 sh | 1695, 1725, 1740 sh |
| $(CO)_3MnC_5H_4C(O)Cl$ | Light petroleum | 1966, 1972, 2043 | 1775 |
| Acid chloride **6** ($C_5H_4Mn(CO)_3$) | Light petroleum | 1950 sh, 1954, 2029 | 1754, 1769 sh, 1780 |
| Acid chloride **6** ($C_5H_3Mn(CO)_3$) | Light petroleum | 1964, 1972, 2041 | |
| Acid chlorides **8** | Light petroleum | 1969, 1978, 2039, 2051 sh | 1756, 1769 sh, 1782 |

prepared by weighing on analytical balances. The $^1$H NMR spectrum of the mixture was recorded, and the amount of hydrogen at each of the positions was determined by integration. The $^1$H NMR spectrum of the initial **1** contains two triplets at δ 4.957 (α-H) and 4.750 (β-H) of equal intensity.

**Metallation of 2.** Complex **2** was obtained by the known procedure.[1] It was deuterated under the same conditions as compound **1**.

**Iodo- and diiodobicymantrenyl.** A 1.6 *M* solution of BuLi in hexane (3.2 mL) was added dropwise to a solution of **1** (1.01 g, 2.5 mmol) in 60 mL of THF at −65 °C and kept for 1 h. Then a solution of iodine (1.27 g, 5 mmol) in 20 mL of THF was added dropwise for 40 min. The reaction mixture was allowed to warm to ~20 °C and then poured into a solution of sodium thiosulfate to remove excess iodine. After extraction with $CH_2Cl_2$, a mixture of compounds was isolated from the organic layer. The mixture was chromatographed on $Al_2O_3$. Benzene eluted initial compound **1** (0.16 g, 16 %) and a mixture of mono- and diiodobicymantrenyl (1.15 g), which could not be separated by column chromatography nor by TLC. After recrystallization from light petroleum, m.p. was 107—114 °C. Found (%): C, 30.27; H, 1.10; I, 36.30. Monoiodobicymantrenyl. $C_{16}H_7IMn_2O_6$. Calculated (%): C, 36.09; H, 1.30; I, 23.87. Diiodobicymantrenyl. $C_{16}H_6I_2Mn_2O_6$. Calculated (%): C, 29.18; H, 0.91; I, 38.60. The mass spectrum of the mixture contains peaks of molecular ions with *m/z* 532 and 658 corresponding to mono- and diiodo-derivatives, respectively, and fragmentation ions of the M−3 CO, M−6 CO, and other types.

**Bicymantrenylcarbaldehydes (3 and 4).** DMF (2 mL, 26 mmol) was added to a solution of a Li derivative obtained from compound **1** (4.06 g, 10 mmol) in 100 mL of THF and a 2.2 *M* solution of BuLi in hexane (4.7 mL) at −60 °C. Cooling was discontinued after 2 h, and the mixture was quenched with 20 % $H_3PO_4$ (10 mL) and poured into water after warming to ~20 °C. The mixture was extracted with $CH_2Cl_2$, the extract was dried, and the solvent was removed to give a residue of 4.10 g. Repeated chromatography on a column with silica gel (100—200 mesh, 40×3 cm) using benzene—light petroleum (1 : 1 to 1 : 3) mixtures as the eluents gave the initial compound **1** (0.73 g, 17 %), aldehyde **4** (0.14 g, 3 %), and aldehyde **3** (1.39 g, 32 %).

Aldehyde **3**, orange crystals with m.p. 138—139 °C (from light petroleum). Found (%): C, 46.99; H, 1.79. $C_{17}H_8Mn_2O_7$. Calculated (%): C, 47.00; H, 1.84. Aldehyde **4**, orange crystals with m.p. 94—95 °C. Found (%): C, 47.26; H, 1.76. $C_{17}H_8Mn_2O_7$. Calculated (%): C, 47.00; H, 1.84. Both isomers give the same IR spectra, ν/cm$^{-1}$: 1690—1695 (C(=O)H); 1962 b, 2027, 2039 sh (Mn—CO). Mass spectra of compounds **3** and **4** contain the same sets of peaks, *m/z*: 434 [M]$^+$, 350 [M−3 CO], 266 [M−6 CO], 238 [M−7 CO], 211 [M−6 CO−Mn], 156 [M−6 CO−2 Mn], and 128 [M−7 CO−2 Mn].

**Bicymantrenylcarboxylic acid (5).** Excess of crushed solid $CO_2$ was added at −60 °C to a THF (40 mL) solution of a Li derivative obtained from compound **1** (1.02 g, 2.5 mmol) and a 1.6 *M* solution of BuLi in hexane (1.8 mL, 2.8 mmol). The mixture was kept for 30 min. Then cooling was discontinued, and the mixture was warmed to 20 °C and poured into a 2 % solution of KOH (100 mL). The initial compound **1** (0.28 g, 27 %) was isolated from the organic layer by extraction with benzene. The aqueous layer was filtered, and the filtrate was acidified with 10 % HCl to give a light-yellow voluminous precipitate of acid **5**. The precipitate was thoroughly washed with ice water to the neutral reaction and dried. Acid **5** (0.35 g, 34 % calculated for the consumed compound **1**) was obtained, decomp.p. >250 °C. Found (%): C, 46.30; H, 1.83. $C_{17}H_8Mn_2O_8$. Calculated (%): C, 45.33; H, 1.79.

**Bicymantrenylcarboxylic acid chloride (6).** A solution of acid **5** (0.49 g, 1.1 mmol) and $PCl_5$ (0.27 g, 1.3 mmol) in benzene (10 mL) was stirred for 12 h. The dark-green solution was filtered, concentrated, and kept *in vacuo*. The residue was recrystallized from light petroleum (b.p. 85—100 °C). Yellow crystals (0.13 g, 25 %) with m.p. 116—120 °C were obtained. Found (%): C, 44.07; H, 1.74; Cl, 7.33. $C_{17}H_7ClMn_2O_7$. Calculated (%): C, 43.54; H, 1.49; Cl, 7.58. For the IR spectrum, see Table 1. $^1$H NMR spectrum, δ: 5.710 (t, 1 H, *J* = 1.7 Hz); 5.634 and 5.091 (both dd, 1 H and 1 H, $C_5H_3$ ring, *J* = 1.7 and 3.0 Hz); 5.022 and 4.821 (2 m, 2 H and 2 H, $C_5H_4$). Mass spectrum contains ions with *m/z* 468 and 470 [M]$^+$, a fragmentation ion 433 [M−Cl], and fragmentation ions of the M−3 CO (384, 386), M−6 CO (300, 302), and M−3 COCl (349) types.

**Bicymantrenyldicarboxylic acid (7) (mixture of isomers).** Excess of crushed solid $CO_2$ was added at −60 °C to a THF (60 mL) solution of a Li derivative obtained from compound **1** (1.04 g, 2.6 mmol) and a 2.2 *M* solution of BuLi in hexane (2.5 mL). After workup similar to that for the synthesis of compound **5**, yellow crystals of acids **7** (0.62 g, 50 %) were obtained. Upon heating the compound decomposes without melting at a temperature higher than 230—240 °C. Found (%): C, 43.83; H, 1.41. $C_{18}H_8Mn_2O_{10}$. Calculated (%): C, 43.72; H, 1.62.

**Bicymantrenyldicarboxylic acid dichloride (mixture of isomers).** A solution of compound **7** (0.62 g, 1.3 mmol) and $PCl_5$ (0.62 g, 3.0 mmol) in anhydrous benzene (15 mL) was stirred for 6 h and worked up as in the synthesis of compound **6** to obtain yellow crystals (0.24 g, 36 %) with m.p. 115—137 °C. The mass spectrum contains a set of molecular ions with *m/z* 530, 531, 532, 533, and 534, and the ratio of intensities is close to the calculated one for a molecule with a molecular formula $C_{18}H_6Cl_2Mn_2O_8$. $^1$H NMR spectrum, δ: 5.818 and 5.763 (2 t, total intensity ~2 H, *J* = 1.7 Hz); 5.668 and 5.141 (both m, ~2 H and 2 H).

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## References

1. A. G. Ginzburg, S. V. Suprunovich, and V. I. Sokolov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2017 [*Russ. Chem. Bull.*, 1995, **44**, 1947 (Engl. Transl.)].
2. R. F. Kovar and M. D. Rausch, *J. Org. Chem.*, 1973, **38**, 1918.
3. W. A. Herrmann, D. Andrejewski, and E. Herdtweck, *J. Organomet. Chem.*, 1987, **319**, 183.
4. D. N. Kursanov, N. M. Loim, M. V. Laryukova, E. F. Mullakhmetova, and Z. N. Parnes, *Dokl. Akad. Nauk SSSR*, 1984, **277**, 878 [*Dokl. Chem.*, 1984, **277** (Engl. Transl.)].
5. A. G. Ginzburg, *Usp. Khim.*, 1993, **62**, 1098 [*Russ. Chem. Rev.*, 1993, **62**, 1025 (Engl. Transl.)].

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