Chemistry of bicymantrenyl
3.* Synthesis of polycymantrenyls

A. G. Ginzburg, S. V. Suprunovich, E. V. Vorontsov, and V. I. Sokolov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

Metallation of bicymantrenyl and its equimolar mixture with cymantrene under the action of butyllithium followed by oxidative coupling under the action of $CuCl_2$ results in the formation of quatercymantrenyl and tercymantrenyl, respectively.

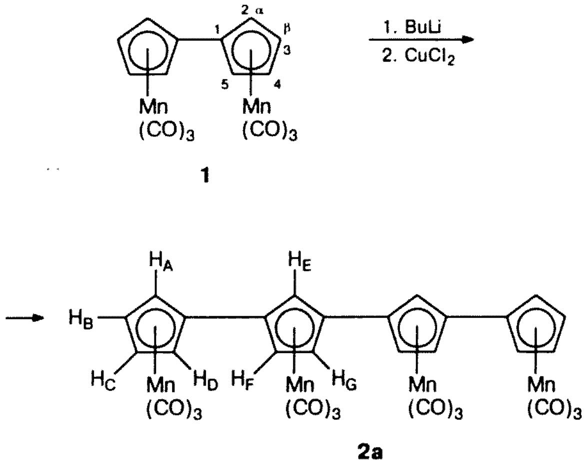
Key words: cymantrene, bicymantrenyl, butyllithium, metallation, oxidative coupling, tercymantrenyl, quatercymantrenyl.

Unlike cymantrene, which has been studied in detail,[2] the chemistry of bicymantrenyl (**1**) has been poorly studied.[3,4] We have shown previously[1] that **1**, like cymantrene, is metallated with butyllithium under mild conditions predominantly at the β-position.

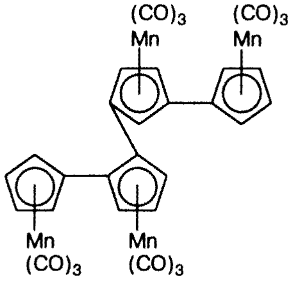
It is known[4] that under the action of $CuCl_2$ cymantrenyllithium is coupled to form compound **1** in high yield.

We performed oxidative coupling of bicymantrenyllithium with $CuCl_2$ and isolated for the first time a compound with a chain of four cymantrenyl units, quatercymantrenyl complex (**2a**) (Scheme 1).

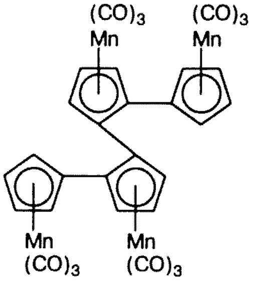
Scheme 1



Since compound **1** is metallated at both positions, the subsequent oxidative coupling could be expected to result in the formation of three dimers of the β,β (**2a**), α,β (**2b**), and α,α (**2c**) type with **2a** predominating.



2b



2c

According to the ^1H NMR data, the reaction product is a mixture of two isomers with **2a** predominating (>90 %). The structure of **2a** is confirmed by the data of X-ray diffraction analysis.*

Complex **2a** can be considered as bicymantrenyl with the substituent at position 3 (in this case, bicymantrenyl). The introduction of any substituent transforms the prochiral system of **1** into the planar-chiral one. Therefore, four C—H groups in each of two terminal rings are diastereotopic, and four different signals should correspond to each of them in the ^1H and ^{13}C NMR spectra (Table 1). In the ^1H NMR spectrum, protons H_A and H_D give two one-proton multiplets in a low field (5.005 and 4.954 ppm, 1 H and 1 H, 5 lines, J = 1.6 Hz); protons H_B and H_C give two one-proton multiplets in higher field (4.802 and 4.757 ppm, 1 H and 1 H, 6 lines, J = 1.6 Hz). The two equivalent protons H_E in the two

---

* For Part 2, see Ref. 1.

* X-ray diffraction analysis was performed by A. I. Yanovskii and F. M. Dolgushin (A. N. Nesmeyanov Institute of Organoelement Compounds of the RAS). The results will be published elsewhere.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 974—976, April, 1996.

1066-5285/96/4504-0930 $15.00 © 1996 Plenum Publishing Corporation

Table 1. ^{1}H and ^{13}C NMR spectra of compounds **2** and **3**

Compound	^{1}H NMR (δ)				^{13}C NMR (δ)		
	H_A, H_D	H_B, H_C	H_E*	H_F, H_G*	CH	*ipso*-C atoms	$Mn(CO)_3$
2	5.005; 4.954	4.802; 4.757	5.166 t (5.125 t)	4.934 d (4.973 d)	82.532; 82.012; 81.019; 80.732; 80.137; 79.756; 78.645	95.272; 94.447; 94.159	223.98; 223.53 (1:1)**
3	4.890; 4.860	4.684; 4.648	5.042 t	4.849 d	82.462; 81.912; 81.133; 80.831; 80.745; 78.993 (C—H_E)	94.833; 94.545	224.00; 223.80 (2:1)**

* In the case of compound **2**, the δ values for **2a** are given, and those for **2b** are given in parentheses.
** The ratio of intensities of signals is given in parentheses.

central rings are manifested as a triplet in low field (5.166 ppm, J = 1.8 Hz). Protons H_F and H_G should theoretically give different signals; however, this nonequivalence could not be observed at 400 MHz, and they give one signal, a doublet at 4.934 ppm (J = 1.8 Hz).

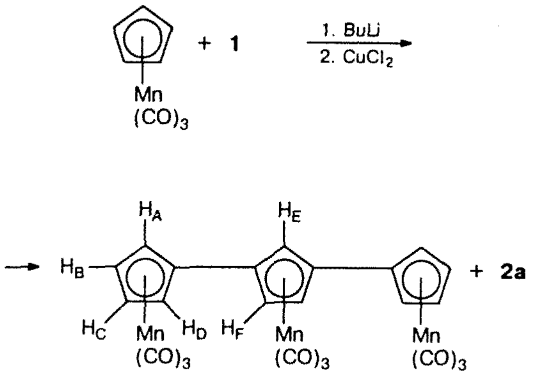
In addition to complex **2a**, the compound obtained contains a small amount (5—8 %) of the other isomer (seemingly, **2b**), whose protons appear in the spectrum as a triplet at 5.125 ppm and a doublet at 4.973 ppm, J = 1.8 Hz. The other protons of this isomer likely give signals that are masked by the more intense signals of the corresponding protons of isomer **2a** in the region 4.9—5.0 ppm. An attempt to separate the isomers by chromatography was unsuccessful.

Metallation of an equimolar mixture of cymantrene and bicymantrenyl **1** followed by subsequent oxidative coupling with $CuCl_2$ gave a mixture of products containing unchanged cymantrene and bicymantrenyl **1** and coupling products, tercymantrenyl (**3**) and complex **2a** (Scheme 2). The ^{1}H NMR spectrum of compound **3** is similar to that of **2a** and differs only in the ratio of intensities of signals. The structures of compounds **2a** and **3** are confirmed by mass spectrometry (see Experimental) and ^{13}C NMR spectroscopy (see Table 1). In the ^{13}C NMR spectrum of tercymantrenyl **3**, the 10 carbon atoms bound to hydrogen atoms H_A—H_D and H_F give five signals due to their mutual equivalence. The signal in higher field with a halved intensity corresponds to the carbon atom C—H_E. Four *ipso*-C atoms, which are mutually equivalent, give two signals in lower field, and C atoms of CO groups, as expected, give two signals with ratio of intensities ~2 : 1.

The ^{13}C NMR spectrum of complex **2a** is similar, but is more complicated: the 14 mutually equivalent C atoms of C—H bonds give seven signals with close intensities in the region 83—78 ppm, and the six *ipso*-C atoms exhibit three signals in the region 94—95 ppm. It is noteworthy that the C atoms bound to the H_E, H_F, and H_G atoms are manifested as individual signals in the ^{13}C NMR spectra. Two signals with equal intensities correspond to the C atoms of the CO groups in complex **2a**.

Preliminary data show that quatercymantrenyl **2a** enters reactions typical of cymantrene, in particular, acetylation and metallation with butyllithium. The acetylation of compound **2a** with AcCl + $AlCl_3$ in CH_2Cl_2 gave a mixture of several monoacetyl isomers and a diacetyl derivative.

Scheme 2



3

Experimental

All experiments were carried out in an argon atmosphere. Bicymantrenyl **1** was obtained by the known procedure.[4] THF was distilled from sodiumbenzophenoneketyl prior to use. ^{1}H NMR spectra were recorded in $CDCl_3$ relative to $SiMe_4$ on Bruker WP-200-SY (200 MHz) and Bruker-AMX-400 (400 MHz) spectrometers. IR spectra were recorded on a UR-20 spectrometer. Mass spectra were recorded on a Kratos-MS-890 instrument (EI, 70 eV).

Quatercymantrenyl (2). A 2.2 M solution of butyllithium (2.5 mL, 5.5 mmol) in hexane was added dropwise to a solution of compound **1** (2.04 g, 5 mmol) in THF (40 mL) at −60 to −65 °C. After 2 h, anhydrous $CuCl_2$ (2.6 g, 19 mmol) was added. The mixture was stirred for 3 h at −65 °C, allowed to warm to ~20 °C, and quenched with 5 % HCl. The reaction products were extracted with CH_2Cl_2. The extract was washed with 5 % HCl and water, dried, and concentrated. The residue was chromatographed on a column with Al_2O_3 (benzene—light petroleum (1 : 1) as the eluent) to isolate unchanged compound **1**, a small amount of a mixture of **1** and **2** (0.12 g), and complex **2** (0.57 g, 29 %) as yellow crystals with m.p. 211—218 °C (from a 1 : 3 toluene—light petroleum mixture). The analytical sample has m.p. 217—219 °C. Found (%): C, 47.56;

H, 1.73. $C_{32}H_{14}Mn_4O_{12}$. Calculated (%): C, 47.41; H, 1.73. IR spectrum (CH_2Cl_2), νCO/cm^{-1}: 1950 b, 2025, 2030 sh. Mass spectrum, *m/z*: 810 $[M]^+$, 726 [M−3 CO], 614 [M−7 CO], 558 [M−9 CO], 530 [M−10 CO], 474 [M−12 CO] as well as ions with *m/z* 419, 364, 309, and 264 corresponding to the [M−12 CO−*n* Mn] fragments, where *n* = 1 to 4.

Tercymantrenyl (3). The procedure described above when applied to compound **1** (0.92 g, 2.3 mmol) and cymantrene (0.46 g, 2.3 mmol) gave after chromatography on a column with Al_2O_3 (benzene—light petroleum (1 : 2) as the eluent) unchanged cymantrene (0.07 g, 15 %) and **1** (0.18 g, 16 %), tercymantrenyl **3** (0.20 g, 14 %), and complex **2** (0.37 g, 20 %). Complex **3** consists of yellow crystals, m.p. 156—158 °C (from toluene—heptane, 1 : 3). Found (%): C, 47.62; H, 1.80. $C_{24}H_{11}Mn_3O_9$. Calculated (%): C, 47.37; H, 1.81. IR spectrum (CH_2Cl_2), νCO/cm^{-1}: 1950 b, 2025, 2030 sh. Mass spectrum, *m/z*: 608 $[M]^+$, 524 [M−3 CO], 440 [M−6 CO], 412 [M−7 CO], 356 [M−9 CO] as well as ions with *m/z* 301, 246, and 191 corresponding to the [M−9 CO−*n* Mn] fragments, where *n* = 1 to 3.

The authors are grateful to Yu. I. Lyakhovetskii and D. V. Zverev (A. N. Nesmeyanov Institute of Organoelement Compounds of the RAS) for recording the mass spectra.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32644).

References

1. S. V. Suprunovich, A. G. Ginzburg, and V. I. Sokolov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 971 [*Russ. Chem. Bull.*, 1996, **45**, 927 (Engl. Transl.)].
2. A. G. Ginzburg, *Usp. Khim.*, 1993, **62**, 1098 [*Russ. Chem. Rev.*, 1993, **62**, 1025 (Engl. Transl.)].
3. R. F. Covar and M. D. Rauch, *J. Org. Chem.*, 1973, **38**, 1918.
4. W. A. Herrmann, D. Andrejewski, and E. Herdtweck, *J. Organomet. Chem.*, 1987, **319**, 183.

Received July 28, 1995;
in revised form November 17, 1995