Brief Communications

Cymantrenyl and styryl derivatives of 1-methyl[60]fullereno[*c*]pyrrolidine: synthesis and electrochemical behavior

N. V. Abramova, S. M. Peregudova, A. O. Emel´yanova, A. P. Pleshkova, and V. I. Sokolov★

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (495) 135 5085. E-mail: stemos@ineos.ac.ru

New cymantrenyl derivatives of 1-methyl[60]fullereno[*c*]pyrrolidine were obtained. According to electrochemical data, the cymantrenyl and phenyl fragments show close electron-donating effects in the presence of the strong acceptor fullerene.

Key words: [60]fullereno[*c*]pyrrolidines, pyrrolidines, manganese complexes, cymantrenes, cyclic voltammetry, the Prato reaction.

Combination of fullerene and metallocene fragments in one molecule can lead to intramolecular transfer of the electron density and impart interesting electrophysical and optical properties to the resulting compound. The best developed method of fullerene modification involves cycloaddition reactions, especially the Prato reaction yielding fullerenopyrrolidines.[1,2] Currently known compounds of this type mainly contain one kind of metallocene, namely, electron-donating ferrocene.[2,3] The synthesis of fullerene derivatives that would be superior in electron-withdrawing effect to fullerene C_{60} itself is of topical interest. Development of these investigations implies introduction into the fullerene molecule of other electron-withdrawing metallocenes, *e.g.*, (cyclopentadienyl)manganese tricarbonyl (cymantrene). Earlier,[4,5] cymantrenyl derivatives of fullerene have been obtained from diazoacetylcymantrene.

Here we carried out the Prato reaction between fullerene C_{60}, sarcosine (**1**), and aldehydes **2a—d** (Scheme 1) and obtained new fullereno[*c*]pyrrolidines containing the cymantrenyl (**3a**), cymantrenylvinyl (**3b**), and styryl substituents (**3c**).

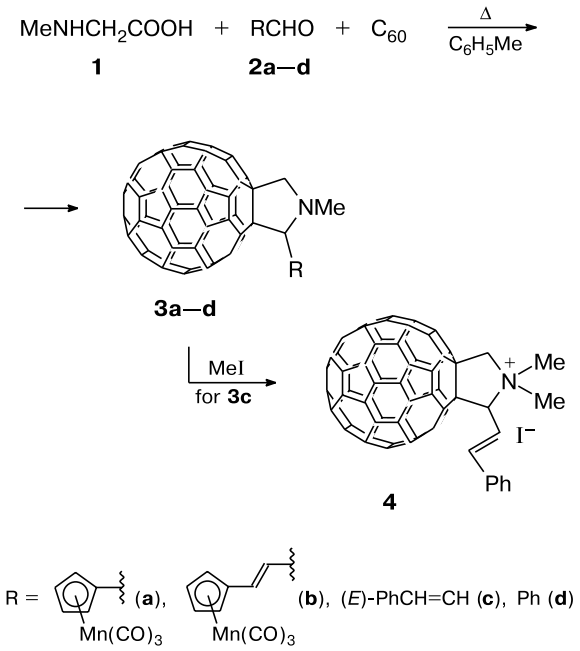
Unlike the rest of the products, 1-methyl-2-styryl[60]fullereno[*c*]pyrrolidine (**3c**) readily produced a quaternary ammonium salt upon heating with MeI in a sealed tube for 15 h.

The ^{1}H NMR spectrum of compound **3a** at 20 °C shows different chemical shifts for all the four protons in the cymantrene residue. This indicates diastereotopism (α—α´, β—β´) resulting from hindered rotation due to the large size of the metallocene group. A similar phenom-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 349—351, February, 2007.

1066-5285/07/5602-0361

Scheme 1



enon takes place in 1-methyl-2-phenyl[60]fullereno[*c*]pyrrolidine (**3d**).[6]

A typical CV curve is shown in Fig. 1 for compound **3b** as an example. According to the presented data, this compound is reduced, like fullerene, in three one-electron steps leading to stable radical anion, dianion, and radical trianion, respectively. We compared the reduction potentials of compounds **3a**—**c** in *o*-dichlorobenzene with those of the known[2] phenyl analog **3d** (Table 1).

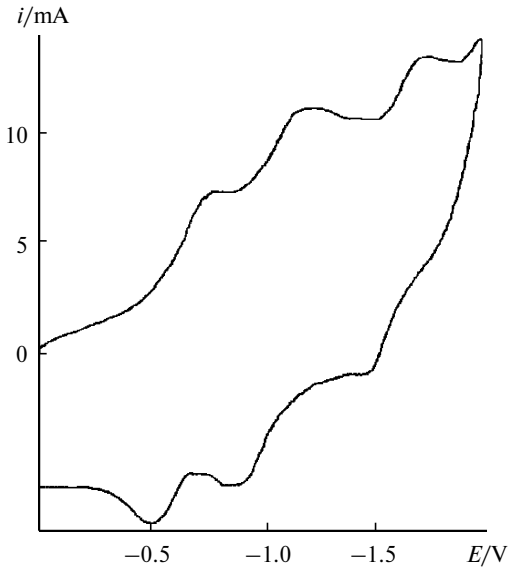


Fig. 1. Cyclic voltammogram of compound **3b** ($C = 1 \cdot 10^{-3}$ mol L^{-1}, *o*-dichlorobenzene, 0.15 *M* Bu_4NPF_6, glassy carbon electrode, scan rate 200 mV s^{-1}).

Table 1. Reduction potentials $E_{1/2}$ of compounds C_{60} and **3a**—**d** in *o*-dichlorobenzene *vs.* the saturated calomel electrode

Compound	$-E_{1/2}$/V	Compound	$-E_{1/2}$/V
C_{60}	0.56, 1.00, 1.45	**3c**	0.80, 1.19, 1.74
3a	0.83, 1.23, 1.78	**3d**	0.82, 1.22, 1.78
3b	0.79, 1.16, 1.69		

When a molecular system combines fullerene with a moderate acceptor (phenyl) or a strong acceptor (cymantrenyl), the difference between their electronic effects is canceled. For instance, the reduction potentials of compounds **3a** and **3d** are close to each other: both the phenyl and cymantrenyl fragments act as electron donors toward C_{60}. The presence of a double bond (as in compounds **3b,c**) slightly weakens the electronic effect.

Experimental

^{1}H NMR spectra were recorded on a Bruker 400 HX spectrometer in $CDCl_3$, DMSO-d_6, or C_6D_6. Electrochemical CV studies were performed on a PI-50-1 potentiostat in *o*-dichlorobenzene solution with a glassy carbon electrode (section area 2 mm^2) and 0.15 *M* Bu_4NPF_6 as a supporting electrolyte; potentials were measured versus a saturated calomel electrode. MALDI-TOF mass spectra (positive-ion reflectron mode, reflectron voltage 20 mV, anthracene-1,8,9-triol matrix) were recorded on a Reflex-III mass spectrometer (Bruker Daltonics). Samples were prepared by dissolving an analyte compound in $CHCl_3$ ($C = 10^{-4}$—10^{-6} mol L^{-1}) and mixed in the ratio 1 : 1 with a matrix solution (20 mg mL^{-1}) in $CHCl_3$.

Fullerene C_{60} (99.9% purity) was manufactured at the G. A. Razuvaev Institute of Organometallic Chemistry (Nizhny Novgorod). Cymantrenecarbaldehyde (**2a**) was prepared according to an earlier described procedure.[7]

3-Cymantrenylprop-2-enal (2b). A mixture of cymantrenecarbaldehyde (**2a**) (0.478 g, 2.06 mmol) and 1 *M* NaOH (50 mL) was heated to 80 °C. Then acetaldehyde (0.139 mL, 2.47 mmol) was gradually added dropwise. The reaction mixture was refluxed for 2.5 h. The product was isolated by column chromatography on SiO_2 eluted with hexane—benzene (1 : 1). The yield was 24%. ^{1}H NMR ($CDCl_3$), δ: 4.90—5.60 (m, 4 H, C_5H_4); 6.30—7.20 (m, 2 H, CH=CH); 9.60 (br.s, 1 H, CHO).

2-Cymantrenyl-1-methyl[60]fullereno[*c*]pyrrolidine (3a). A mixture of fullerene C_{60} (0.1 g, 0.138 mmol), cymantrenecarbaldehyde (**2a**) (0.039 g, 0.221 mmol), and sarcosine (**1**) (0.037 g, 0.414 mmol) was refluxed in toluene (100 mL) under argon for 2 h. Column chromatography on SiO_2 eluted with hexane—toluene (1 : 1) gave compound **3a** in 40% yield. Found (%): C, 86.79; H, 1.07; N, 1.37. $C_{71}H_{10}MnNO_3$. Calculated (%): C, 87.04; H, 1.09; N, 1.49. IR, ν/cm^{-1}: 2035, 1955 (CO). MS, *m/z*: 896 $[M - 3\,CO]^+$. ^{1}H NMR ($CDCl_3$), δ: 3.14 (s, 3 H, NMe); 4.27 (d, 1 H, CH_2, $J = 9.2$ Hz); 4.55, 4.95, 4.97, 5.50 (all m, 1 H each, C_5H_4); 4.75 (1 H, C<u>H</u>Cp); 4.90 (d, 1 H, CH_2, $J = 9.2$ Hz). ^{13}C NMR ($CDCl_3$), δ: 224.76 (CO); 155.74, 153.58, 152.67, 152.23, 146.42, 146.35,

146.28, 146.16, 146.03, 145.39, 145.25, 143.11, 142.79, 142.68, 142.19, 142.16, 142.03, 141.86, 141.73, 141.62, 140.36, 140.31, 139.73, 139.22, 136.91, 136.39, 135.56 (atoms of the fullerene cage, which are not bound to the pyrrolidine fragment); 102.3 (quaternary C atom of Cp); 87.09, 86.20 (sp^3-hybridized C atoms of the fullerene cage); 79.43, 71.10, 67.91, 41.19, 29.71 (NMe).

(*E*)-2-Cymantrenylethenyl-1-methyl[60]fullereno[*c*]pyrrolidine (3b). A mixture of fullerene C_{60} (0.1 g, 0.138 mmol), 3-cymantrenylprop-2-enal (**2b**) (0.043 g, 0.221 mmol), and sarcosine (**1**) (0.037 g, 0.414 mmol) was refluxed in toluene (100 mL) under argon for 10 h. The course of the reaction was monitored by TLC with hexane—toluene (1 : 1) as an eluent. The product was isolated by column chromatography on SiO_2 eluted with hexane—toluene (1 : 1). The yield of compound **3b** was 43 mg (31%). Found (%): C, 84.67; H, 1.57; N, 1.26. $C_{73}H_{12}MnNO_3$. Calculated (%): C, 87.17; H, 1.20; N, 1.39. ^{1}H NMR (C_6D_6), δ: 2.93 (s, 3 H, NMe); 4.10—4.18, 4.32—4.40 (both m, 1 H each, C_5H_4); 4.67—4.95 (m, 4 H, 2 H from C_5H_4 + 2 H from CH_2); 5.05 (s, 1 H, CH); 6.45—6.55, 6.58—6.70 (both m, 1 H each, CH=CH).

1-Methyl-(*E*)-2-phenylethenyl[60]fullereno[*c*]pyrrolidine (3c). A mixture of fullerene C_{60} (0.1 g, 0.138 mmol), cinnamaldehyde (0.03 g, 0.221 mmol), and sarcosine (**1**) (0.037 g, 0.414 mmol) was refluxed in toluene (100 mL) under argon for 10 h. The course of the reaction was monitored by TLC with hexane—toluene (1 : 1) as an eluent. The product was isolated by column chromatography on SiO_2 eluted with hexane—toluene (1 : 1). The yield of compound **3c** was 36 mg (30%). ^{1}H NMR ($CDCl_3$), δ: 2.68 (s, 3 H, NMe); 3.82 (d, 1 H, CH_2, J = 9.2 Hz); 4.33 (d, 1 H, CHC=, J = 8.7 Hz); 4.52 (d, 1 H, CH_2, J = 9.2 Hz); 6.88 (dd, 1 H, =C<u>H</u>CH, J = 15.8 Hz, J = 9.2 Hz); 7.00 (d, 1 H, =C<u>H</u>Ph, J = 15.8 Hz); 7.08—7.18 (m, 5 H, Ph). MALDI-TOF MS, m/z: 878 $[M]^+$.

***N*,*N*-Dimethyl-(*E*)-2-phenylethenyl[60]fullereno[*c*]pyrrolidinium iodide (4).** A mixture of compound **3c** (18 mg) and MeI (6 mL) was heated in a sealed tube on a water bath (70—80 °C) for 15 h. The precipitate that formed was washed with toluene and hexane. The yield of compound **4** was 9.3 mg (47%). Found (%): C, 81.36; H, 2.73; N, 1.41. $C_{72}H_{16}IN$. Calculated (%): C, 84.63; H, 1.58; N, 1.37. ^{1}H NMR (DMSO-d_6), δ: 3.68, 4.23 (both s, 3 H each, NMe); 5.74 (d, 1 H, CH_2, J = 8.5 Hz); 5.93 (d, 1 H, CHC=, J = 8.5 Hz); 6.53 (d, 1 H, CH_2, J = 8.5 Hz); 7.16 (dd, 1 H, =CH, J = 13.0 Hz, J = 7.5 Hz); 7.38—7.43 (m, 4 H, =CH, Ph); 7.78 (d, 2 H, Ph, J = 8.5 Hz).

This work was financially supported by the Division of Chemistry and Materials Sciences of the Russian Academy of Sciences (Program No. 1) and the Federal Science Agency (Contract No. 02.434.11.2023).

References

1. M. Prato and M. Maggini, *Acc. Chem. Res.*, 1998, **31**, 519.
2. D. M. Guldi, M. Maggini, G. Scorrano, and M. Prato, *J. Am. Chem. Soc.*, 1997, **119**, 974.
3. V. I. Sokolov, N. V. Abramova, N. S. Khrushcheva, and S. M. Peregudova, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 2616 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2764].
4. M. N. Nefedova, T. V. Mukha, and V. I. Sokolov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1615 [*Russ. Chem. Bull.*, 1999, **48** (Engl. Transl.)].
5. R. Pellicciari, B. Natalini, T. V. Potolokova, M. Marinozzi, M. N. Nefedova, A. S. Peregudov, and V. I. Sokolov, *Synth. Commun.*, 2003, **33**, 903.
6. P. de la Cruz, A. de la Hoz, L. M. Font, F. Langa, and M. C. Perez-Rodriguez, *Tetrahedron Lett.*, 1998, **39**, 6053.
7. N. M. Loim, N. A. Abramova, Z. N. Parnes, and D. N. Kursanov, *J. Organomet. Chem.*, 1979, **168**, 33.

Received August 9, 2006;
in revised form December 19, 2006