Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2020, **30**, 352–354

Mendeleev Communications

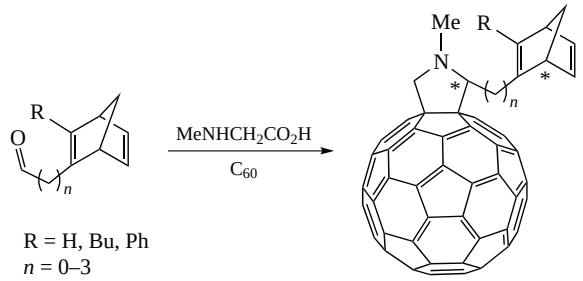
New norbornadiene-tethered fulleropyrrolidines

Arslan R. Akhmetov, Airat R. Tuktarov,* Zarema R. Sadretdinova, Leonard M. Khalilov and Usein M. Dzhemilev

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 450075 Ufa, Russian Federation. Fax: +7 347 284 2750; e-mail: tuktarovar@gmail.com

DOI: 10.1016/j.mencom.2020.05.031

***N*-Methyl-3,4-fulleropyrrolidine–norbornadiene conjugates with or without $(CH_2)_n$ (n = 0–3) spacers were synthesized by the Prato reaction from the corresponding norbornadiene aldehydes. The influence of the spacer length on the diastereomer composition of the conjugates with two chiral centres studied by ^{13}C NMR revealed a pronounced diastereotopic splitting of the fullerene carbon signals relating to four diastereomers in the case when the norbornadiene substituent was directly attached to the pyrrolidine moiety. When norbornadiene moiety was separated from the pyrrolidine one by three methylene units, the diastereotopic difference was lower and some of the signals were grouped.**



Keywords: C_{60} fullerene, azomethine ylides, Prato reaction, [3+2]-cycloaddition, pyrrolidines, norbornadiene, fulleropyrrolidines, quadricyclane.

In 1964, Hammond proposed[1] a solar energy storage system based on the valence isomerization of norbornadiene to quadricyclane in which energy harvesting occurred due to the formation of a metastable structure that could undergo catalytic[2,3] cleavage of strained C–C bonds to release about 110 kJ mol^{-1} of heat.[4] These studies initiated extensive research dealing with applications of this system not only for solar energy harvesting,[5,6] but also as molecular switches and optical waveguides based on them,[7–11] photochromic chemosensors,[12,13] photoswitchable organic magnetic materials,[14–16] rocket fuel additives,[6,17] antitumor agents[18,19] as well as organic synthesis intermediates and polymeric materials.[20,21]

Recently,[22] we obtained energy-rich methanofullerenes by the reaction of C_{60} fullerene with mono- and bis-quadricyclane malonates and showed that retention of the metastable quadricyclane structure in the hybrids molecule can be provided by the separation of quadricyclane and fullerene moieties in a molecule. However, it remained unclear how the mode of chemical bonding of C_{60} fullerene to norbornadiene and quadricyclane affected the stability of the strained ring in the new hybrid molecule. It seemed interesting to study the photochemical isomerization of norbornadiene moieties into quadricyclane ones in the synthesized C_{60} cycloadducts.

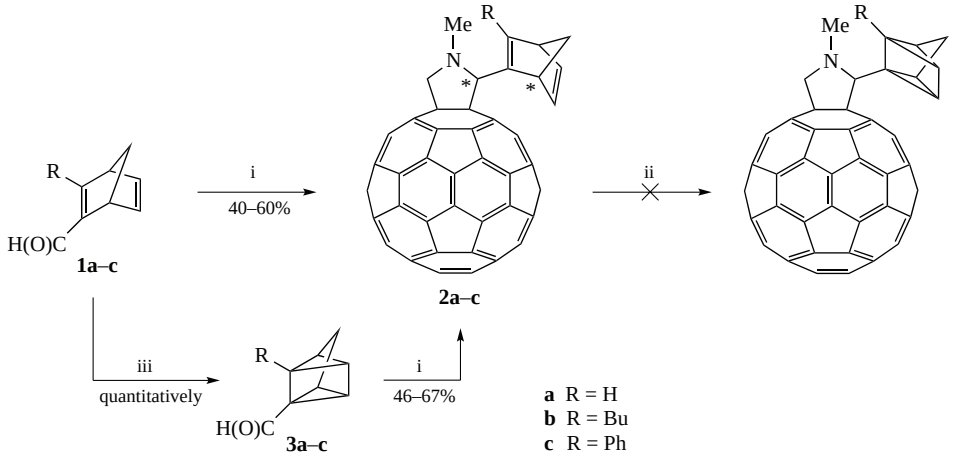
Herein, we performed conjugation of C_{60} fullerene with norbornadienes and quadricyclanes by means of the Prato reaction[23] and studied the photochemical norbornadiene–quadricyclane isomerization within these hybrids.

In the initial stage of our study, C_{60} fullerene was reacted with sarcosine and norbornadiene derivatives **1a–c** in which the aldehyde group was directly linked to the norbornadiene molecule (1 : 5 : 5 molar ratio, respectively) under conditions developed previously (*o*-xylene, 80 °C, 2 h). The synthesis and spectral characteristics of norbornadienes **1a–c** were identical to published data.[22,24,25] The reactions gave mixtures of fulleropyrrolidine diastereomers **2a–c**. Using preparative HPLC, compounds **2a–c** were isolated from the reaction mixture with ~99.9% chromatographic purity (Scheme 1).

The structures of compounds **2a–c** were established by 1D (^1H, ^{13}C) and 2D (HHCOSY, HSQC, HMBC) NMR spectroscopy, MALDI TOF mass spectrometry, and IR and UV spectroscopy. The molecules of compounds **2a–c** contain two chiral centers, namely, C^2 carbon atom of the pyrrolidine ring and C^1 carbon atom of the norbornadiene moiety which are directly linked by a carbon–carbon bond. This would induce a strong diastereotopic splitting of the carbon signals of the fullerene core, by analogy with our previous data.[26]

We attempted to isomerize the norbornadiene moieties of hybrid molecules **2a–c** to quadricyclane ones on exposure to UV radiation. It was found that irradiation of a toluene solution of compounds **2a–c** in the presence of acetophenone as a photosensitizer resulted in formation of a precipitate that could not be analyzed because of low solubility in various solvents (see Scheme 1). Alternatively, formylnorbornadienes **1a–c** were irradiated to give quadricyclane aldehydes **3a–c** in quantitative yields. However, their Prato reaction with C_{60} fullerene (sarcosine, *o*-xylene 80 °C, 2 h) afforded norbornadiene fulleropyrrolidines **2a–c** rather than anticipated quadricyclane ones. This happened despite the reported data indicating that quadricyclanes are thermally stable compounds and, in the absence of catalysts, they undergo reversible conversion to norbornadienes with a half-life of 14 h at 140 °C.[27]

Similar results were obtained in our previous study[22] when we used the Bingel–Hirsch reaction, which may be due, as we assumed, to the proximity of the strained quadricyclane moiety



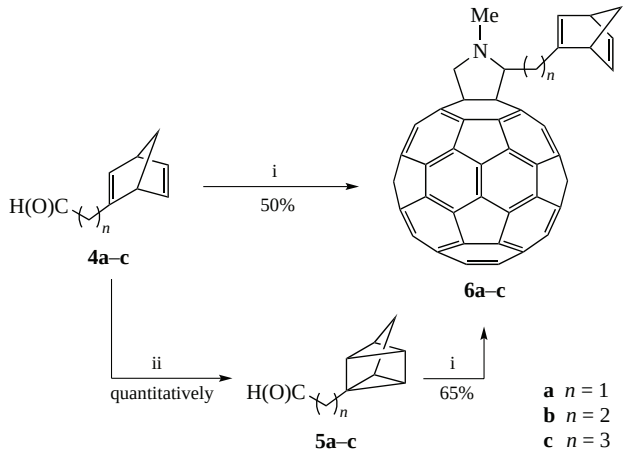
Scheme 1 *Reagents and conditions*: i, $MeNHCH_2CO_2H$, C_{60}, *o*-xylene, 80 °C, 2 h; ii, *hν* (360 nm), toluene, room temperature, 6 h; iii, *hν* (360 nm), Pr^iOH, room temperature, 8 h.

to electron-deficient C_{60} in the hybrid molecule. Therein,[22] we also demonstrated that separation of quadricyclane moiety from the fullerene core increased its stability. In view of that fact we assumed that if fullerene is reacted with quadricyclanes with bearing remote aldehyde group, the target quadricyclane hybrids could be accessed. For this purpose, known[28,29] norbornadiene alkanals **4a–c** with $(CH_2)_n$ linkers were converted into their quadricyclane isomers **5a–c** (Scheme 2).

However, the Prato reaction of quadricyclane alkanals **5a–c** afforded fulleropyrrolidines **6a–c** with isomerized norbornadiene moieties (see Scheme 2). Obviously, the same products are formed in the Prato reaction from norbornadiene alkanals **4a–c**. It still remains intriguing why quadricyclane aldehydes **5a–c** would easily undergo skeletal isomerization with the C–C bond cleavage in the course of the Prato reaction. In our opinion, such a cyclopropane ring opening might be caused by the presence of sarcosine in the reaction mixture since its carboxyl group could induce acid-promoted skeletal isomerization of quadricyclane (*cf.* ref. 30).

Analysis of ^{13}C NMR spectra of synthesized fulleropyrrolidines **6a–c** showed that when chiral centers in the latter are removed by one, two, and three methylene units, the diastereotopic differences decrease, some of the signals are grouped in the region of 154.35–154.52 ppm instead of a wider range of chemical shifts, 154.0–154.8 ppm, in contrast to compounds **2a–c**, in which the norbornadiene fragment is directly linked to the pyrrolidine ring.

To conclude, employing the Prato reaction we synthesized new fulleropyrrolidines containing norbornadiene molecules



Scheme 2 *Reagents and conditions*: i, $MeNHCH_2CO_2H$, C_{60}, *o*-xylene, 80 °C, 2 h; ii, *hν* (360 nm), Pr^iOH, room temperature, 8 h.

covalently bound to the pyrrolidine core either directly or through one, two, or three methylene units. The influence of the spacer length on the diastereotopic splitting in the conjugates was assessed by ^{13}C NMR. The Prato reaction between C_{60} fullerene and quadricyclane aldehydes affords the corresponding norbornadiene derivatives.

This work was supported by the Russian Foundation for Basic Research (grant no. 17-03-00120). The structural studies were performed with the financial support of the Russian Ministry of Education and Science (project no. 2019-05-595-000-058) on a unique equipment at the 'Agidel' Collective Usage Center (Ufa Federal Research Center, Russian Academy of Sciences).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.031.

References

1 G. S. Hammond, P. Wyatt, C. D. De Boer and N. J. Turro, *J. Am. Chem. Soc*., 1964, **86**, 2532.
2 V. A. Bren, A. D. Dubonosov, V. I. Minkin and V. A. Chernoivanov, *Russ. Chem. Rev*., 1991, **60**, 451 (*Usp. Khim*., 1991, **60**, 913).
3 A. D. Dubonosov, V. A. Bren and V. A. Chernoivanov, *Russ. Chem. Rev*., 2002, **71**, 917 (*Usp. Khim*., 2002, **71**, 1040).
4 K. B. Wiberg and H. A. Connon, *J. Am. Chem. Soc*., 1976, **98**, 5411.
5 E. E. Bonfantini and D. L. Officer, *J. Chem. Soc., Chem. Commun*., 1994, **12**, 1445.
6 P. Lainé, V. Marvaud, A. Gourdon, J.-P. Launay, R. Argazzi and C.-A. Bignozzi, *Inorg. Chem*., 1996, **35,** 711.
7 S. Fraysse, C. Coudret and J.-P. Launay, *Eur. J. Inorg. Chem*., 2000, 1581.
8 S. Morino, T. Watanabe, Y. Magaya, T. Yamashita, K. Horie and T. Nishikubo, *J. Photopolym. Sci. Technol*., 1994, **7**, 121.
9 S. Takahashi, K. Samata, H. Muta, S. Machida and K. Horie, *Appl. Phys. Lett*., 2001, **78**, 13.
10 R. Herges and W. Reif, *Liebigs Ann. Chem*., 1996, 761.
11 F. Starck, P. G. Jones and R. Herges, *Eur. J. Org. Chem*., 1998, 2533.
12 S. Nakatsuji, S. Takeuchi, T. Ojima, Y. Ogawa, H. Akutsu and J. I. Yamada, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, 2001, **356**, 23.
13 S. Takeuchi, Y. Ogawa, A. Naito, K. Sudo, N. Yasuoka, H. Akutsu, J. I. Yamada and S. Nakatsuji, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, 2000, **345**, 167.
14 S. Nakatsuji, Y. Ogawa, S. Takeuchi, H. Akutsu, J. I. Yamada, A. Naito, K. Sudo and N. Yasuoka, *J. Chem. Soc., Perkin Trans. 2*, 2000, 1969.
15 M. E. Wright, G. D. Allred, R. B. Wardle and L. F. Cannizzo, *J. Org. Chem*., 1993, **58**, 4122.
16 Y. Kunugi, K. Takimiya, N. O. Negishi, T. Otsubo and Y. Aso, *J. Mater. Chem.*, 2004, **14**, 2840.
17 K. Matsumoto, K. Hashimoto, M. Kato, Y. Uetani, S. Hayase, M. Kawatsura and T. Itoh, *J. Mater. Chem*., 2010, **20**, 9226.

18 M. Carini, L. Dordevic and T. Da Ros, in *Handbook of Carbon Nano Materials*, eds. F. D'Souza and K. M. Kadish, World Scientific, 2012, ch. 1, pp. 1–48.
19 E. Castro, A. Hernandez Garcia, G. Zavala and L. Echegoyen, *J. Mater. Chem. B*, 2017, **5**, 6523.
20 V. R. Flid, M. L. Gringolts, R. S. Shamsiev and E. Sh. Finkelshtein, *Russ. Chem. Rev*., 2018, **87**, 1169.
21 S. A. Durakov, R. S. Shamsiev, V. R. Flid and A. E. Gekhman, *Russ. Chem. Bull., Int. Ed*., 2018, **67**, 2234 (*Izv. Akad. Nauk, Ser. Khim*., 2018, 2234).
22 A. R. Tuktarov, A. R. Akhmetov, A. A. Khuzin and U. M. Dzhemilev, *J. Org. Chem*., 2018, **83**, 4160.
23 M. Maggini, G. Scorrano and M. Prato, *J. Am. Chem. Soc*., 1993, **115**, 9798.
24 C. Tanyeli, G. Çelikel and I. M. Akhmedov, *Tetrahedron: Asymmetry*, 2001, **12**, 2305.
25 H. Yamamoto, K. Ishihara, S. Kondo and H. Kurihara, *J. Org. Chem*., 1997, **62**, 3026.
26 A. R. Tulyabaev, A. R. Tuktarov and L. M. Khalilov, *Magn. Reson. Chem*., 2014, **52**, 3.
27 E. E. Bonfantini and D. L. Officer, *J. Chem. Soc., Chem. Commun*., 1994, 1445.
28 G. K. Tranmer and W. Tam, *J. Org. Chem*., 2001, **66**, 5113.
29 M. Laurens, L. G. Edwards, W. Tam and A. J. Lough, *J. Am. Chem. Soc*., 1995, **117**, 10276.
30 V. A. Petrov and N. V. Vasil'ev, *Curr. Org. Synth.*, 2006, **3**, 215.

Received: 6th September 2019; Com. 19/6026