Full Paper

Reference Object Identifier - ROI: jbc-01/17-51-8-76 The Digital Object Identifier - DOI: 10.37952/ROI-jbc-01/17-51-8-76 Submitted on August 19, 2017.

Synthesis of the new monomeric fragments for the construction of paracyclophanes

© Dmitry N. Shurpik, and Ivan I. Stoikov*⁺

Organic Chemistry Department. A.M. Butlerov Chemical Institute. Kazan (Volga Region) Federal University. Kremlevskava St., 18. Kazan, 420008. Tatarstan Republic. Russia. Phone: +7 (843) 233-74-62. E-mail: ivan.stoikov@mail.ru

*Supervising author; ⁺Corresponding author

Keywords: Hydroquinone, macrocycles, NMR spectroscopy, pillar[5]arene.

Abstract

In recent years, the pillar [n] arenes (n = 5-10) – paracyclophanes, available in one-pot synthesis macrocycles, containing fragments of 1,4-alkoxybenzene and having a unique column spatial form have attracted special attention. Pillar[n]arenes are able to form inclusion complexes with different linear "guests"-molecules. One of the widely used methods for the synthesis of substituted pillar[5]arenes is the condensation of prefunctionalized derivatives of hydroquinone. However, the number of functional groups, that can be introduced in this way, is limited by the synthetic availability of the monomer units. Thus, the development of accessible methods for the production of substituted hydroquinones opens the possibility of directed design of macrocyclic receptors. In turn, the introduction of amide, ammonium and amino groups into the pillar[5]arene platform will make it possible to obtain new substances with practically significant properties. In this study new monomeric fragments of hydroquinone acting as precursors for the synthesis of the derivatives of pillar[5]arenes have been synthesized. It was shown that the model derivatives enter into the aminolysis reaction and subsequent alkylation under mild conditions. As a result, the target compounds containing amide and ammonium fragments are formed. The method of condensation of monomeric fragments into the target functionalized derivatives of the pillar[5] arene has been developed. Amphiphilic hydroquinone derivatives containing simultaneously ammonium and amide groups were obtained, which opens the possibility of their use as a surfactants. Thus, the development of new approaches to the directed functionalization of the pillar[5]arenes will allow the construction of new compounds with specified physical and chemical properties, such as solubility, optical and mechanical properties, and will also open the possibilities for their further functionalization with high yields.

References

- [1] N.N. Dolgova, M.I. Sorvin, A.A. Yantemirova, I.I. Stoikov, S.V. Belyakova, G.A. Evtugyn, I.S. Antipin, E.E. Stoikova, and H.C. Budnikov. Solid-contact potentiometric sensors based on macrocyclic ligands for the determination of carbonate ions. Butlerov Communications. 2011. Vol.28. No.19. P.59-66. ROI: jbc-02/11-28-19-59
- [2] O.A. Mostovaya, A.V. Galukhin, I.S. Antipin, A.I. Konovalov, and I.I. Stoikov. Supramolecular receptor based on oligoammonium derivative of *p-tert*-buthylthiacalix[4]arene: interaction with nucleic acids. Butlerov Communications. 2011. Vol.28. No.18. P.57-62. ROI: jbc-02/11-28-18-57
- [3] P.L. Padnya, E.A. Andreyko, A.Z. Harisova, Yu.F. Zuev, and I.I. Stoikov. Synthesis of new water soluble *p-tert*-butylthiacalix[4]arene derivatives containing quaternary ammonium fragments. *Butlerov* Communications. 2013. Vol.34. No.5. P.1-10. ROI: jbc-02/13-34-5-1
- [4] A.V. Galukhin, R.V. Nosov, O.A. Mostovaya, and I.I. Stoikov. Synthesis of polycarboxylic dendrimers based on *p-tert*-butylthiacalix[4]arene in 1,3-alternate conformation. Butlerov Communications. 2013. Vol.36. No.10. P.37-42. ROI: jbc-02/13-36-10-37
- [5] A.A. Vavilova, O.A. Mostovaya, R.V. Nosov, A.N. Yagarmina, and I.I. Stoikov. Synthesis and fluorescence properties of 1,3-di- and tetrasubstituted at the lower rim thiacalix [4] arenes containing naphthyl fragments. Butlerov Communications. 2012. Vol.32. No.12. P.1-7. ROI: jbc-02/12-32-12-1
- [6] A.A. Vavilova, M.V. Meleshina, V.V. Gorbachuk, L.S. Yakimova, and I.I. Stoikov. Synthesis of mono- and 1,3-disubstituted at the lower rim thiacalix[4]arenes containing photoswitchable 4-amidoazobenzene fragment. Butlerov Communications. 2012. Vol.31. No.8. P.18-24. ROI: jbc-02/12-31-8-18

SYNTHESIS OF THE NEW MONOMERIC FRAGMENTS FOR THE CONSTRUCTION OF PARACYCLOPHANES 76-83

- [7] M.P. Kutyreva, A.R. Mukhametzyanova, N.A. Ulakhovich, V.V. Gorbachuk, L.S. Yakimova, and I.I. Stoikov. Silica nanoparticles modified by amine groups and zinc as precursors foranti-candida drugs. *Butlerov Communications.* 2012. Vol.31. No.7. P.65-72. ROI: jbc-02/12-31-7-65
- [8] A.A. Vavilova, O.A. Mostovaya, R.V. Nosov, A.N. Yagarmina, and I.I. Stoikov. Fluorescent probes for fluoride ion based on 1,3-disubstituted at the lower rim thiacalix[4]arenes containing anthraquinone fragments. *Butlerov Communications*. 2012. Vol.29. No.2. P.8-12. ROI: jbc-02/12-29-2-8
- [9] V.V. Gorbachuk, A.A. Vavilova, M.V. Meleshina, L.S. Yakimova, and I.I. Stoikov. Synthesis of organotrialkoxysilanes and preparation of hybrid organosilicate based nanoparticles. *Butlerov Communications.* 2012. Vol.29. No.2. P.1-7. ROI: jbc-02/12-29-2-1
- [10] P.L. Padnya, E.A. Yushkova, A.Z. Harisova, O.A. Mostovaya, Yu.F. Zuev, and I.I. Stoikov. Synthesis of *p-tert*-butyl thiacalix[4]arene tetrasubstituted at the lower rim by oxazoline groups in *1,3-alternate* conformation: dramatical effect of macrocyclic platform. *Butlerov Communications*. 2012. Vol.31. No.9. P.36-42. ROI: jbc-02/12-31-9-36
- [11] E.A. Arkhipova, L.B. Magomedova, A.B. Konov, P.L. Padnya, I.I.Stoikov, B.I. Khairutdinov, and Yu.F. Zuev. A pulsed field gradient NMR diffusion investigation of water-soluble *p-tert*-butylthiacalix[4]arene derivatives. *Butlerov Communications*. 2015. Vol.42. No.4. P.138-142. DOI: 10.37952/ROI-jbc-01/15-42-4-138
- [12] I.I. Stoikov, E.A. Andreyko, and P.L. Padnya. Amphiphilic thiacalixarenes in supramolecular systems. *Butlerov Communications*. **2015**. Vol.42. No.4. P.130-137. DOI: 10.37952/ROI-jbc-01/15-42-4-130
- [13] T. Ogoshi, S. Kanai, S. Fujinami, T.A. Yamagishi, Y. Nakamoto. Para-Bridged symmetrical pillar[5]arenes: their Lewis acid catalyzed synthesis and host–guest property. J. Am. Chem. Soc. 2008. Vol.130. No.15. P.5022-5023.
- [14] D. Cao, H. Meier. Pillar[n]arenes a novel, highly promising class of macrocyclic host molecules. *Asian J. Org. Chem.* **2014**. Vol.3. No.3. P.244-262.
- [15] Z.G. Zhao, X.L. Liu, Z.C. Shi, & Y. Chen. Microwave-assisted synthesis of novel aryloxyacetyl hydrazones molecular tweezers under solvent-free conditions. *Journal of Chemical Research.* 2010. Vol.34. P.208-210.