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Total oxidation of decahydroxypillar[5]arene with copper(II) and iron(III) nitrates

© **Vladimir V. Gorbachuk**, **Anna R. Marysheva**, and **Ivan I. Stoykov***[+]
Department of Organic Chemistry. A.M. Butlerov Institute of Chemistry. Kazan Federal University. Kremlevskaya St., 18. Kazan, 420008. Tatarstan Republic. Russia.
Phone: +7 (843) 233-74-62. E-mail: ivan.stoikov@mail.ru

*Supervising author; [+]Corresponding author

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Abstract

Pillar[n]arenes are suitable synthetic platforms for synthesis of functionalized *p*-cyclophanes, versatile building blocks for creating supramolecular polymers and (pseudo)rotaxanes. The presence of hydroquinone fragments in unsubstituted pillar[*n*]arene derivatives opens wide opportunities for their application in electrochemical sensors and for their use as reducing agents for synthesis of hybrid materials. Macrocyclic cavity plays the key role in molecular recognition, supramolecular self-assembly of pillararenes, and therefore possibility of switching electron donor properties of aromatic moieties, forming macrocyclic cavity presents specific interest. Synthesis of pillar[*n*]quinones is non-trivial goal, usually, it requires expensive reagents (cerium(IV) ammonium nitrate). As an oxidized compound alkoxy-derivatives of pillararenes are used. While possibility of red-ox transitions of decahydroxypillar[5]arene are well known, to the date in literature there are no examples of total oxidation of decahydroxypillar[5]arene. We have studied interaction of decahydroxy-pillar[5]arene with a row of inorganic oxidants: catalytic oxidation with air oxygen in presence of copper(II) and iron(III) nitrates, and oxidation with ammonium persulfate. In order to find the optimal conditions for oxidation of pillar[5]arene the series of solvents were tried (proton donor alcohols and acetic acid, proton acceptor dimethylformamide and dimethylsulfoxide). It was established that using glacial acetic acid as a solvent with ultrasonication leads to total oxidation of pillar[5]arene to pillar[5]quinone. This fact is explained by strong proton-donor properties of glacial acetic acid, to prevent formation of insoluble quinhydrone complexes of pillar[5]arene oxidation products. Using ammonium persulfate does not lead to the product of total oxidation.

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