



Synthesis and investigation of catalytic affinities of water-soluble amphiphilic calix[*n*]arene surfactants in the coupling reaction of some heteroaromatic compounds



Serkan Sayin^{a,*}, Mustafa Yilmaz^b

^a Department of Environmental Engineering, Faculty of Engineering, Giresun University, Giresun, 28200, Turkey

^b Department of Chemistry, Selcuk University, Konya, 42075, Turkey

ARTICLE INFO

Article history:

Received 21 April 2016

Received in revised form 9 August 2016

Accepted 23 August 2016

Available online 25 August 2016

Keywords:

Water-soluble calix[*n*]arene

Brønsted acid type catalyst

Alkylation of heteroaromatic compounds

Green chemistry

ABSTRACT

Six water-soluble calix[*n*]arene-based Brønsted acid-type catalysts with amphiphilic groups were successfully synthesized by incorporating sulfonic acid moieties. Their structures were characterized using FTIR, ¹H NMR, ¹³C NMR, APT-NMR, and elemental analysis techniques. Moreover, their catalytic capabilities were evaluated in the coupling reaction of 2-methylfuran and/or *N*-methylindole with some *sec*-alcohols in aqueous media. The association of their surfactant abilities, and the effects of water amount used and reaction durations on the catalytic activities of these amphiphilic calix[*n*]arene derivatives were also investigated. Observations indicated that these amphiphilic calix[*n*]arene catalysts exhibited high catalytic activities in the coupling reactions of 2-methylfuran and *N*-methylindole with some alcohols in water.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Reactions involving carbon–carbon bond formation for arenes and heteroarenes represent a substantial approach for the efficient fabrication of diversely functionalized complex compounds such as dyestuffs, perfumes, flavors, agricultural aids, and pharmaceuticals.^{1–3} In traditional methods, carbon–carbon bond formation is carried out through the reaction between an electrophile (C–X, X=triflate, halide, mesylate, etc.) with a reactive center of arenes or heteroarenes in the presence of a metallic/organometallic reagent.⁴ However, owing to toxicity, a limited number of functional group tolerance, and the poor water-solubility of most metallic/organometallic reagents, developing a reaction for C–C bond construction for arenes/heteroarenes using an alcohol as an electrophile in water is a challenge.^{4–6} To perform this kind of reaction, a water-soluble organic-based catalyst with excellent reusability, which catalyzes the coupling reaction by reducing activation energy, is a requirement in terms of environmental toxicology.

Calixarenes, known as the third generation of supramolecules, represent very useful building blocks in that they possess tunable and different cavity sizes and exhibit versatile applications in

supramolecular chemistry.^{7–10} Because of their easy synthesis, functionalization, and special properties such as having different-sized cavities, including hydrophilic –OH moieties at their lower rim and hydrophobic aromatic subunits along with *tert*-butyl groups, attempts to design and synthesis of new calix[*n*]arene derivatives have been made.^{11–14} It has been reported lately that some of the water-soluble calix[*n*]arene derivatives acting as surfactant-type Brønsted acid catalysts exhibited substantial catalytic abilities for C–C bond formation.^{3a,10,14}

With the goal of translating in aqueous media some organic reactions requiring the usage of a catalyst, in our previous study we have designed *p*-sulfonatocalix[*n*]arenes (*n*=4, 6 and 8) as a catalyst for the alkylation of 2-methylfuran and *N*-methylindole with some alcohols.^{3a} We have preliminarily taken a strategy involving the introduction of hydrophobic groups with different straight alkyl chains to Brønsted acid-type calix[*n*]arene derivatives in order to investigate the effects of amphiphilic groups on the catalytic efficacies of water-soluble calixarenes. Thus, six water-soluble podands, bearing a calix[*n*]arene backbone with various amphiphilic groups at the lower rim, were successfully synthesized. Furthermore, their catalytic activities were evaluated for the first time in the coupling reaction of 4,4'-dimethoxybenzhydrol and/or (*E*)-*trans*-1,3-diphenyl-2-propen-1-ol with 2-methylfuran and/or *N*-methylindole in water without co-solvents.

* Corresponding author. Fax: +90 454 3101749; e-mail address: serkan.sayin@giresun.edu.tr (S. Sayin).

2. Results and discussion

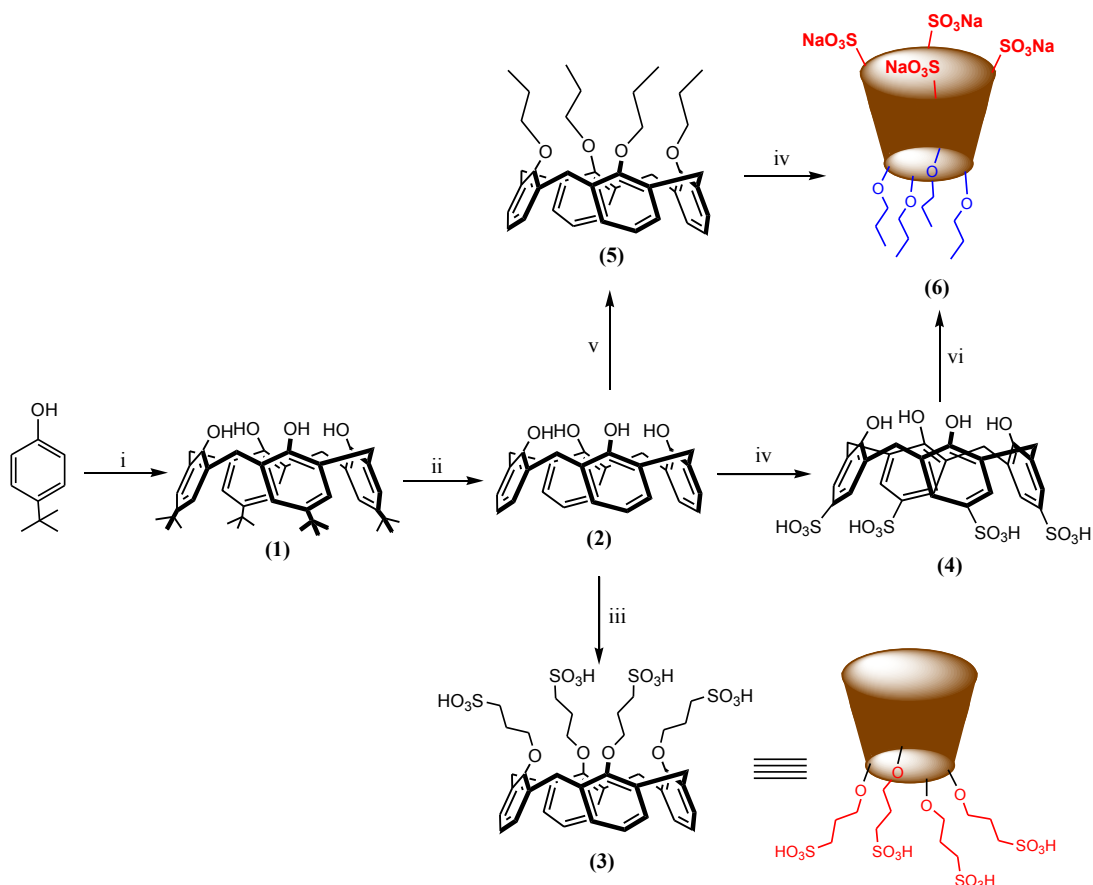
2.1. Synthesis and characterizations of water-soluble calix[*n*]arene derivatives

With the aim of developing new water-soluble organic-based catalysts, a large number of studies have been published in the last few decades.^{3a,10,14–17} In our previous study, catalytic capabilities of *p*-sulfonatocalix[*n*]arenes (*n*=4, 6 or 8) were evaluated in the coupling reactions of some electron-rich arenes with *sec*-alcohols in water.^{3a} Inspired by our results,^{3a} in this study we investigated the effects of hydrophobic groups of amphiphilic calix[*n*]arene derivatives. For this purpose, six water-soluble podands, including calix[*n*]arene backbones bearing different lipophilic subunits, were synthesized and characterized in order to investigate their catalytic efficiencies in the coupling reactions for 4,4'-dimethoxybenzhydrol and/or (*E*)-*trans*-1,3-diphenyl-2-propen-1-ol with 2-methylfuran and/or *N*-methylindole in water without co-solvents. Thus, *p*-*tert*-butylcalix[4]arene (**1**), calix[4]arene (**2**), calix[4]aryloxy-25,26,27,28-tetrakis(propane-3-sulfonic acid) (**3**), calix[4]arene-*p*-sulfonate (**4**), 25,26,27,28-tetrakis(propoxy)calix[4]arene (**5**), 5,11,17,23-tetrakisulfonato-25,26,27,28-tetrakis(propoxy)calix[4]arene (**6**), *p*-*tert*-butylcalix[6]arene (**7**), calix[6]arene (**8**), calix[6]arene-*p*-sulfonate (**9**), 5,11,17,23,29,35-hexasulfonato-37,38,39,40,41,42-hexakis(dodecyloxy)calix[6]arene (**11**), *p*-*tert*-butylcalix[8]arene (**12**), calix[8]arene (**13**), calix[8]arene-*p*-sulfonate (**14**), 5,11,17,23,29,35,41,47-octasulfonato-49,50,51,52,53,54,55,56-octakis(dodecyloxy)calix[8]arene (**16**) were synthesized according to literature procedures^{15,18–22} (Schemes 1–3). FTIR, ¹H NMR, ¹³C NMR spectroscopy and elemental analysis techniques were performed to characterize the

structures of the synthesized compounds. However, 5,11,17,23,29,35-hexasulfonato-37,38,39,40,41,42-hexakis(propoxy)calix[6]arene (**10**) and 5,11,17,23,29,35,41,47-octasulfonato-49,50,51,52,53,54,55,56-octakis(propoxy)calix[8]arene (**15**) were synthesized for the first time (Schemes 2 and 3). Typically, an aqueous solution of calix[6]arene-*p*-hexasulfonate (**9**) was treated with propyl bromide and NaOH in DMSO, affording amphiphilic *p*-sulfonatocalix[6]arene **10**, concurrently appended with the hydrophobic propyl chains at the lower rim of *p*-sulfonatocalix[6]arene with a yield of 58% (Scheme 2). An FTIR spectrum of **10** confirmed the existence of sulfonate groups in which characteristic peaks for the stretching vibrations of S–O, the symmetric and asymmetric vibrations of the SO₂ bands of derivative **10**, appeared at 861, 1050, 1163, and 1111 cm⁻¹, respectively (see Supplementary data).

The ¹H NMR spectrum of amphiphilic *p*-sulfonatocalix[6]arene **10** showed that the hydrophobic subunits were successfully attached to the *p*-sulfonatocalix[6]arene, which resonances at 0.88–1.27 (18H), 1.62–2.01 (12H), and 4.25–4.61 (12H) ppm for the protons of the –CH₃, –CH₂, and –OCH₂ groups, respectively (see Supplementary data). The APT-¹³C NMR spectrum of derivative **10** clearly showed that the peaks at the positive region belonging to the –CH₃ and –CH groups appeared at 9.81 and 124.99–125.77 ppm (Fig. 1).

The substitution of calix[8]arene-*p*-sulfonate (**14**) at the lower rim was conducted with propyl bromide and NaOH in a mixture of H₂O/DMSO to afford 5,11,17,23,29,35,41,47-octasulfonato-49,50,51,52,53,54,55,56-octakis(propoxy)calix[8]arene (**15**) with a yield of 48% (see Scheme 3). The structure of amphiphilic *p*-sulfonatocalix[8]arene **14** was confirmed not only by the appearance of notably characteristic IR peaks at 1175, 1050, and 879 cm⁻¹ for the asymmetric and symmetric vibrations of the SO₂ bands, and the



Scheme 1. Synthesis of Brønsted acid-type calix[4]arene derivatives. Reaction conditions; i) HCHO, NaOH; ii) AlCl₃, phenol; iii) 1,3-propanesultone, NaH; iv) H₂SO₄; v) propyl iodide, NaH; vi) propyl bromide, NaOH.

Download English Version:

<https://daneshyari.com/en/article/5212882>

Download Persian Version:

<https://daneshyari.com/article/5212882>

[Daneshyari.com](https://daneshyari.com)