Asian Journal of Chemistry Vol. 22, No. 2 (2010), 1047-1050

Synthesis and Characterization of Mono Hydroxy-*tris*(N,N-diethyl-dithio carbomoyl propoxy ether)-*p*-*tert*-butyl Calix[4]arene as a Macrocyclic Ligand for Constructing of Highly Selective Electrode

MAHSA KIMIA GHALAM
Department of Chemistry, Islamic Azad University, North Tehran Branch, Tehran, Iran
E-mail: mh_kimia@yahoo.com

In this research, the synthesis and characterization of 5,11,17,23-tetra-*tert*-butyl-25-hydroxy-26,27,28-*tris*(3-N,N-diethyl dithio carbamoyle propoxy) Calix[4]arene are described. The compound was synthesized by the coupling of 25-hydroxy-26,27,28-*tris*-(3-bromo propoxy) calix[4]arene and N,N-diethyldithio carbamate sodium salt. This compound can be an effective extractant for transferring some divalent ions from aqueous to an organic phase. Diethyl dithio carbamates are good ligands for making complexes with Ni, Pd and Pt and also the prepared ligand can be used for preparation of ion selective electrode based on capable macrocycle.

Key Words: Calixarene, Ion selective electrode.

INTRODUCTION

Calixarenes have attracted attention because of their potential for forming host-guest complexes in the supramolecular chemistry[1]. They can be easily functionalized both at the phenolic OH groups (lower rim) and after partial removal of tetra-butyl groups, at the *para* position of the phenol rings (upper rim)[2-4]. The vast majority of these modifies calixarenes exist in the cone conformation with a cavity suitable for reception of different ionic and neutral species[5].

Calix[4]arens have attracted considerable interest as building blocks for constructing selective host molecules[6]. Low rim functionalized compounds can be obtained in a multi-steps procedure from suitably substituted precursors[7]. More amount of work using calixarenes as extractants has been focused on the alkali and alkaline earth metals. Dithio carbamate based ligands have an essential role in coordination chemistry[8]. In this paper, the synthesis and characterization of a new dithio carbamate derivative of calix[4]arene is reported, which can be applied as a selective ionophore both in carbamate and calixarene sections.

EXPERIMENTAL

Melting points are taken on a Buchi SMP-20 apparatus. ^{1}H NMR spectra were recorded on a Bruker AM-500 MHZ and 250 MHZ in $CDCl_3$ with Me_4Si as an internal standard. IR spectra were recorded on a Bruker IFS-25 spectrophometer.

Preparation of tetra (*t*-butyl) calix[4]arene (1): A mixture of (20 g, 0.133 mol) of *para-tert*-butyl phenol, (12.4, 1.66 mol) of 37 % formaldehyde solution and (0.24 g, 0.06 mol) of sodium hydroxide and 0.6 mL of water is placed in a three-necked, round-bottomed flask equipped with a mechanical stirrer. The contents of the open flask are allowed to stir for 15 min at room temperature and then heated for 2 h at 100-120 ºC by means of a heater mantle. Stirring is discontinued, the reaction vessel is removed from the heating and the reaction mixture is allowed to cool to room temperature. 200 mL of warm diphenyl ether is added to the flask and the continue the stirring, the process generally require at least 1 h and the contents of the flask heated to 120 ºC for a few minutes and then at refluxed for 3-4 h under a gentle flow of nitrogen. The reaction mixture is cooled to room temperature and the product is precipitated by the addition of 300 mL of ethyl acetate. The resulting mixture is stirred for 15-30 min and allowed to stand for at least 30 min. Filteration yields material that is washed twice with 20 mL portions of ethyl acetate, once with 40 mL of acetic acid, twice with 20 mL portions of water and twice with 10 mL portions of acetone. m.p.: 342-344 ºC, ^{1}H NMR ($CDCl_3$) (δ, ppm): 10.34 (4H, S, OH) 7.05 (8H, S, ArH), 4.25 and 3.51 (8H, 2d, J = 2 Hz, $ArCH_2Ar$), 1.21 [36H, S, $C(CH_3)_3$] IR (KBr, ν_{max}, cm^{-1}): 3451, 2963, 1631, 1482, 1201.

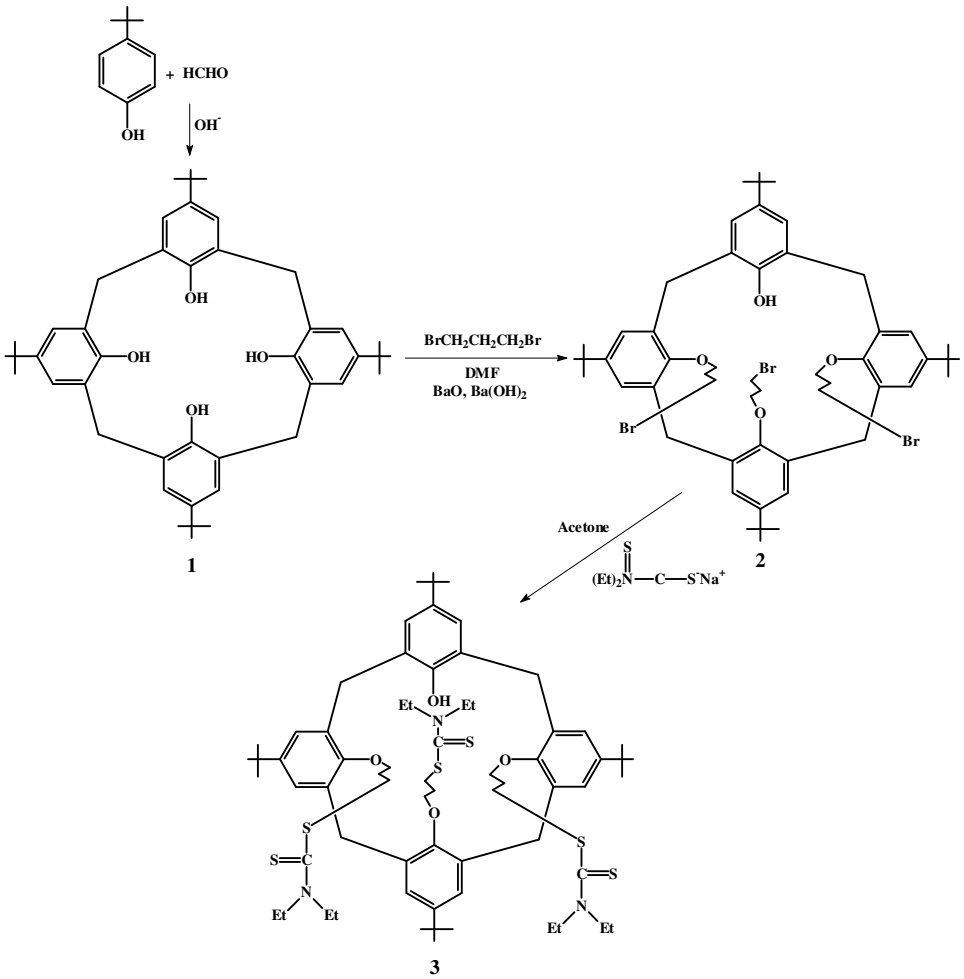
Preparation of 26,27,28-*tris*-(3-bromopropoxy)-25-hydroxy-5,11,17,23-tetra-*tert*-butyl calix[4]arene: A mixture of **1** (1.97 g, 3.04 mmol), dibromo propane (4.65 mL, 45.6 mmol), $Ba(OH)_2$ (19.65 mmol) and BaO (20.55 mmol) in DMF (39.4 mL) was stirred magnetically at room temperature for 3 h. After completion of the reaction (monitored by TLC), the reaction mixture was treated with water and then extracted by dichloro methane. The organic layer was separated, dried over magnesium sulfate and concentrated. Remaining viscous mass was purified by column chromatography (silica gel/CH_2Cl_2: *n*-hexane, 1:4). Yield, 25 %, m.p.: Oily viscous, ^{1}H NMR ($CDCl_3$, 500 MHz); (δ, ppm): 7.22 (2H, S, ArH), 7.13 (2H, S, ArH), 6.57 (2H, S, ArH), 6.56 (2H, S, ArH) 5.03 (H, S, OH), 3.27, 4.34 (4H, 2d, *J* = 15 Hz, $ArCH_2Ar$), 3.24, 4.31 (4H, 2d, *J* = 15 Hz, $ArCH_2Ar$), 4.08 (2H, t, CH_2), 3.98 (4H, m, CH_2), 3.78 (4H, m, CH_2), 3.71, 3.35 (2H, t, CH_2), 2.9 (2H, m, CH_2), 2.57 (2H, m, CH_2), 2.4 (2H, m, CH_2), 1.38 (18H, S, CH_3), 0.87 (18H, S, CH_3); IR (KBr, ν_{max}, cm^{-1}): 3454, 2963, 1639, 1482, 1362, 1261, 1199, 1021.

Preparation of 25-hydroxy, 26,27,28-(3-N,N-diethyl-dithio-carbamoyl propoxy)-5,11,17,23-tetra-*t*-butyl calix[4]arene: To a solution of (0.256 g, 0.204 mmol) of **2** in 29.5 mL acetone was added (0.85 g, 3.8 mmol) N,N-dithio carbamate sodium salt and put at reflux condition for 6 h. The solvent was evaporated by rotary evaporator and 30 mL water was added to the remaining crude and immediately was extracted with dichloromethane. The organic layer was seprated, dried over magnesium sulfate and evaporated, compound **3** was purified by column chromatography (silica gel/CH_2Cl_2; *n*-hexane, 1:4). Yield, 20 %, m.p.: Oily viscous, ^{1}H NMR ($CDCl_3$, 250 MHz); (δ, ppm): 7.07 (2H, S, ArH), 6.99 (2H, S, ArH), 6.43 (4H, S, ArH), 5.23 (1H, S, OH), 3.16, 4.20 (4H, 2d, *J* = 7.5 Hz, $ArCH_2Ar$), 3.19, 4.23 (4H,

2d, J = 7.5 Hz, $ArCH_2Ar$), 3.94 (8H, m, CH_2), 3.87 (4H, t, CH_2), 3.72 (6H, m, CH_2), 3.47 (6H, m, CH_2), 2.53 (2H, m, CH_2), 2.26 (4H, m, CH_2), 1.22 (9H, S, CH_3), 1.19 (9H, S, CH_3), 0.78 (18H, S, CH_3); IR (KBr, ν_{max}, cm^{-1}): 3449, 2962, 1733, 1638, 1482, 1415, 1360, 1271, 1205.

RESULTS AND DISCUSSION

In order to use calixarenes as extractants for 'soft' metals, it is necessary to incorporate 'soft' donor ligating atoms on the lower rim positions. We have accomplished such a goal by first synthesizing 26,27,28-(3-bromo propoxy-25-hydroxy-5,11,17,23-tetra-*tert*-butyl calix[4]arene (**2**) as a precursor to such compounds. Compound **2** has been characterized by a combination of spectroscopic techniques. A perspective view of the compound is shown in **Scheme-I**. The molecule adopts the 'full con' conformation.



1 **2** **3**

Scheme-I

Compound **2** has been converted into 25-hydroxy-26,27,28(3-N,N-diethyl dithiocarbamoyl propoxy)-5,11,17,23-tetra-*tert*-butyl calix[4]arene (**3**) by reaction with NaSC-(S)-Net2. The overall route chosen to synthesize **3** is shown in **Scheme-I**.

For synthesis of considering molecule **3**, cone conformation of mono hydroxy tris (bromo propoxy)-calix[4]arene **2**, as a key intermediate has been reacted with N,N-diethyl dithio carbamate in acetone. **Scheme-I** shows the synthetic strategy of target molecule **3**. ^{1}H NMR spectra of compounds **2** and **3** in bridge methylene of calixarene zone (3.1-4.34 ppm) show 2d-2d according to symmetry of these molecules.

The different between these 2d-2d signals are more than 1 ppm ($\Delta\delta > 1$ ppm) and so establish the cone conformation of calixarene in all of derivatives. Free phenolic rings in compound **2** let us for substituting of 1,3-dibromopropane in a quantitative and selective reaction.

The free phenolic rings and also dithio carbamate sections can be afforded the best form for complexing of **3** with some soft transition metals, the complexation behaviour of **3** is under study in our research group.

REFERENCES

1. C.D. Gutsche, Calixarenes, Cambridge: Royal Society of Chemistry, ISBN 085185385x (1989).
2. C.D. Gutsche, Calixarenes, Revisited, The Royal Society of Chemistry, Cambridge (1998).
3. J. Vicens and V. Boehmer, Calixarenes: A Versatile Class of Macrocyclic Compounds, Kluver Academic, Boston (1991).
4. J.D. Van Loon, A. Arduini, L. Coppi, W. Verboom, A. Ponchi, R. Ungaro, S. Harkema and D.N. Reinhoudt, *J. Org. Chem*., **55**, 5639 (1990).
5. Y. Morzherin, D.M. Rudkevich, W. Verboom and D.N. Reinhoudt, *J. Org. Chem*., **58**, 7602 (1993).
6. C.D. Gutsche and J.A. Levine, *J. Am. Chem. Soc*., **104**, 2652 (1982).
7. E.B. Merkushev, *Synthesis*, 923 (1988).
8. A.T. Yordanov, J.T. Mague and D.M. Roundhill, *Inorg. Chim. Acta*, **240**, 441 (1995).

(*Received*: 3 December 2008; *Accepted*: 12 October 2009) AJC-7945