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Synthesis of calix[4]arene alkylamine derivatives as new phase-transfer catalysts for esterification reaction

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ABSTRACT

This study reports the synthesis of calix[4]arene-based phase-transfer catalysts derived from the reaction of 5,17-di-*tert*-butyl-25,27,26,28-tetrahydroxycalix[4]arene with *N*-ethylpiperazine, diallylamine or 4-benzylpiperidine. The catalytic efficiency of the calix[4]arenes alkylamine derivatives was evaluated by carrying out the ester-forming reaction of alkali metal carboxylates (sodium butyrate or sodium caprylate) with *p*-nitrobenzyl bromide. It has been observed that the ester-forming reaction of alkali metal carboxylates with *p*-nitrobenzyl bromide, using the *N*-ethylpiperazine amine derivative of calix[4]arene as a phase-transfer catalyst in dichloromethane at 25 °C, provided the best yields.

1. Introduction

Reaction between two substances located in different phases of a mixture is often inhibited because of the inability of the reagents to come together. An alternative solution to the heterogeneity problem, phase-transfer catalysis (PTC), is introduced here.[1,2]

Nowadays, phase-transfer catalysis has become a favored technique in organic synthesis and is widely used to manufacture pharmaceuticals, agricultural chemicals, perfumes, flavors, dyes, and specialty polymers. Moreover, the applications of phase-transfer catalysis in industry have been extended to the pollution and environmental control processes.[3–7]

Calixarenes can be easily modified and tailored for many applications, such as ionophores in catalysis, heavy metal adsorption agents, alkali metal complexation agents, and chemical sensors.[8–12] Among the functional groups that have been appended are ethers, esters, amides, ketones, alkenes, ammonium species, phosphines, and heterocycles.[13–23] The aromatic-rich nature of calixarenes makes them essentially insoluble in water, which enhances their utility as phase-transfer reagents.

During the past 15 years, calixarenes have received increasing attention due to their utilization in supramolecular chemistry.[24] Some functionalized calixarenes have been developed as new phase-transfer agents for PTC reactions. Shimizu et al.[25,26] prepared *p*-(trimethylammoniomethyl)calix[*n*]arene methyl ethers as catalyst and used the aldol type condensation and Michael addition reactions, alkylation reactions of active methylene compounds with alkyl halides in aqueous NaOH solution.

In this paper, the main focus of this work is the design of new calixarenes bearing alkyl amino groups on their upper rim, and use of the calixarenes as phase-transfer agents in the esterification reaction with *p*-nitrobenzyl bromide and sodium butyrate or sodium caprylate.

2. Results and discussion

2.1. Synthetic routes

The main focus of this work was the design of new calixarene based ionophores that are easily accessible, have effective binding characteristics for a particular set of cations/anions and molecules, and could be useful for multiple applications, such as laboratory, clinical, environmental, and industrial process analyses. To achieve the desired goal, *p*-*tert*-butylcalix[4]arene (**1**) has been chosen as the precursor. A synthesis strategy has been developed to enable its derivatization. Such a synthesis route is depicted in Scheme 1. The syntheses for compounds **1**–**4** are based on previously published procedures.[27,28] The substitution of 5,17-di-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (**4**) at its upper rim (Mannich reaction)[29–31] was conducted in the presence of AcOH in THF with secondary amines (*N*-ethylpiperazine, diallylamine or 4-benzylpiperidine) and formaldehyde to afford the cone conformer **5**–**7** at high yields. The conformational characteristics of calix[4]arenes were conveniently estimated by the splitting pattern of the

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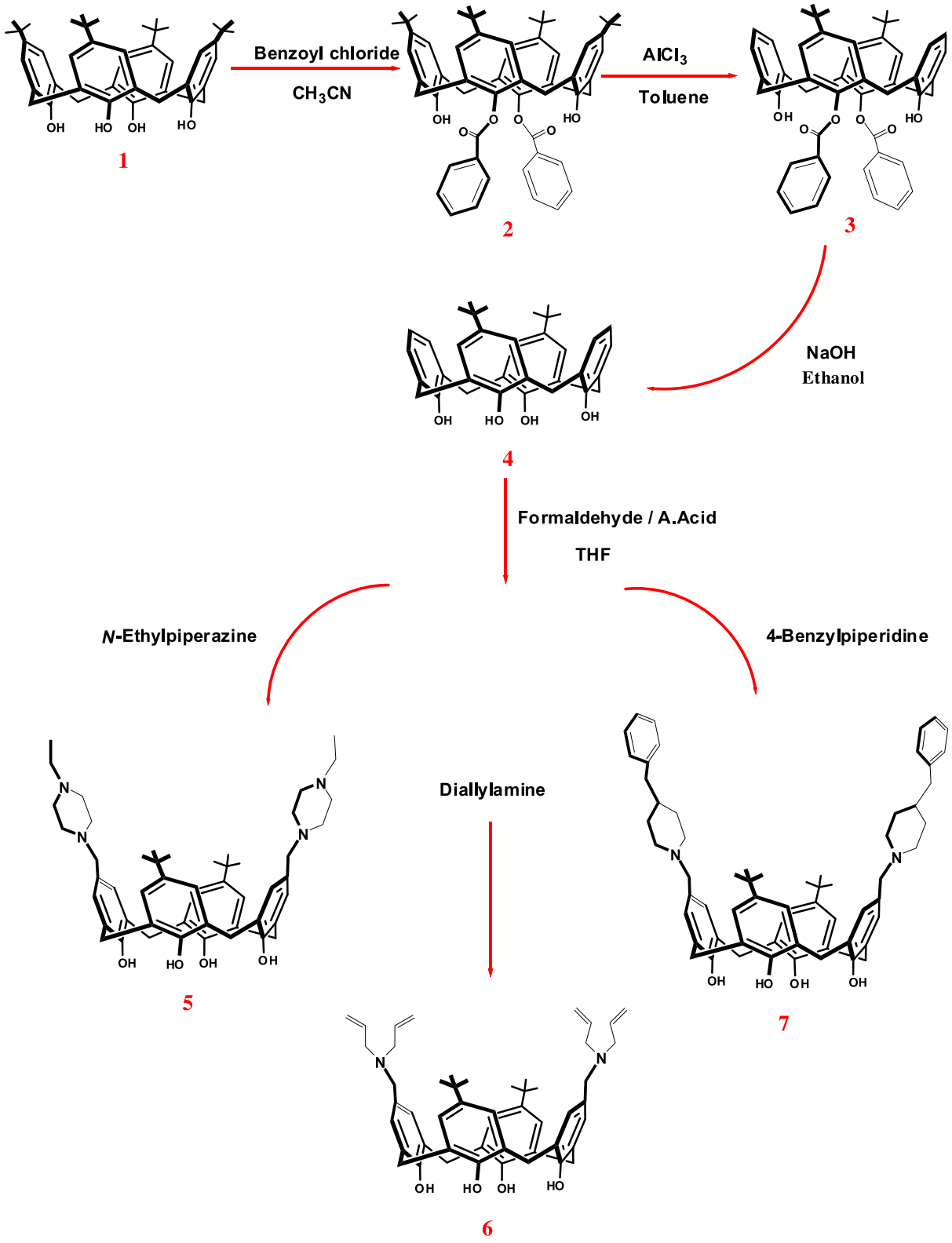
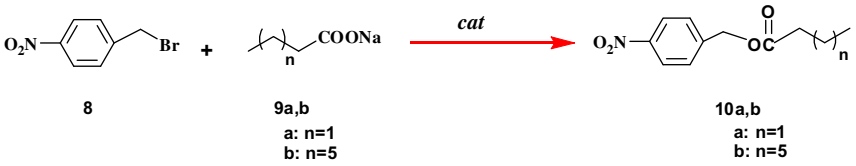


Scheme 1. A schematic representation of the synthesis of calix[4]arene derivatives bearing amino groups on their upper rim (**5**–**7**).

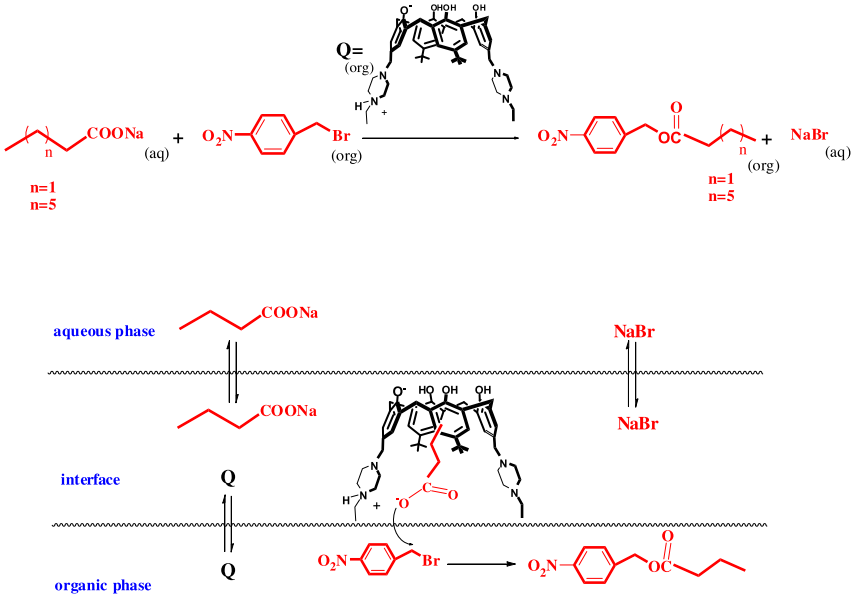
$ArCH_2Ar$ methylene protons in the ^1H NMR spectrum.[24,32] ^1H NMR spectroscopic data showed that compounds **5**–**7** were in the cone conformation. A typical AB pattern was observed for the methylene bridge $ArCH_2Ar$ protons at δ 3.51 and 4.22 ppm (J=12.5 Hz) for **5**, δ 3.50 and 4.24 ppm (J=12.3 Hz) for **6**, and δ 3.50 and 4.25 ppm (J=12.5 Hz) for **7** in ^1H NMR. The high field doublets at δ 3.51 ppm for **5** and δ 3.50 ppm for **6** and **7** were assigned to the equatorial protons of methylene groups, whereas the low field signals at δ 4.22 ppm for **5**, δ 4.24 ppm for **6**, and δ 4.25 ppm for **7** were assigned to the axial protons in the ^1H NMR.

2.2. Ester-forming reactions

Various phase-transfer catalysts were used to compare their catalytic activity. The catalytic activity of calix[4]arenes based alkyl amino groups on their upper rim (**5**, **6**, and **7**) were examined for esterification of *p*-nitrobenzyl bromide and sodium butyrate or sodium caprylate. This synthesis route is depicted in Schemes 2 and 3. Mixtures containing an aqueous solution (5 mL) of sodium butyrate, or sodium caprylate (**9a** or **9b**) solution at a concentration of 0.8 M and 4 mL of a 0.5 M solution of *p*-nitrobenzyl bromide (**8**), and 1 mL of a 5×10^{-2} M solution of calixarene **5**, **6** or **7** in CH_2Cl_2 were vigorously agitated in a stoppered glass tube at 25 °C and 60 °C for a given period of time, usually for 30 h. The results are shown in Table 1. A workup of the resulting mixtures yielded *p*-nitrobenzyl butyrate (**10a**) or *p*-nitrobenzyl caprylate (**10b**) (Scheme 2). The progress of the reaction was followed by monitoring the production of *p*-nitrobenzyl butyrate and *p*-nitrobenzyl caprylate, using HPLC. In the absence of calixarene derivatives, the reaction did not occur appreciably, indicating that **5**, **6**, and **7** serve as catalysts for these esterification reactions. The results are shown in Figs. 1 and 2.



Scheme 2. Synthesis of *p*-nitrobenzyl butyrate and *p*-nitrobenzyl caprylate.



Scheme 3. The proposed mechanism of esterification reaction.

From the data in Table 1, a smaller acceleration effect was observed when calix[4]arene derivative **6** was added to the reaction mixture as a phase-transfer catalyst. In contrast, the addition of the calix[4]arene derivative **5** resulted in an excellent yield of the esterification product, *p*-nitrobenzyl caprylate. It is observed that the catalyst **5** afforded relatively better results than the other catalysts. The percentage of *p*-nitrobenzyl caprylate yield was 80% for catalyst **5**, 47% for **7** and 10% for **6** when the sodium caprylate was used (Fig. 2).

In order to examine the effect of the temperature on the course of the reaction between *p*-nitrobenzyl bromide and sodium butyrate, experiments were carried out at 25 °C and 60 °C. It was found that the reaction rate increased with an increase in temperature.

The temperature dependence of the *p*-nitrobenzyl butyrate yield percentage and of the esterification reaction set in motion by catalyst **7** were studied at 60 °C and the results are shown in Figs. 3 and 4.

The main effect on the rate can be attributed to the nature of the anion paired with the quaternary ammonium cation in the organic phase. It has been known that the calixarenes[11] are considerably stronger acids than their monomeric phenolic analogous. The unusual ease with which the first dissociation of the calix[4]arenes occurs is attributed to stabilization of the monoanion relative to the parent species.[31] Semi-empirical calculations[32] indicate that the monoanion is strongly hydrogen bonded to its flanking OH groups which, in turn, are stabilized by a bifurcated hydrogen bond with the fourth OH group. The dissociation of the second proton of the calix[4]arenes, on the other hand, is slightly less facile than that of the corresponding monomeric phenolic analogous. Although calculations indicate that hydrogen bonding still contributes to the stabilization of the dianion, unfavorable electrostatic repulsions appear to be the dominant factor. Thus, a *tert*-amino group of calixarene is protonated with the phenolic group at the interface of two phases in order to yield the ammonium form of calixarene, which remains at the interface due to its highly polar character. The protonated calixarene is complexed with carboxylate anion as an ion pair. In literature Atwood et al.[31] synthesized *p*-[4-(2-hydroxyethyl)-piperidinomethyl]calix[4]arene and single-crystal X-ray diffraction study revealed the presence of a ethyl acetate guest in the cavity. In this complex the arms are directed up from the rim of the calix[4]arene to produce a cavity so deep that the

Table 1
Reaction of alkali metal carboxylates with *p*-nitrobenzyl bromide

Entry	Catalyst	Substrate	Nucleophile	*T*/°C	*t*/h	Yield (%)
1	None	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	25	10	0
2	**5**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	25	10	33
3	**6**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	25	10	Trace
4	**7**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	25	10	3
5	None	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	25	20	0
6	**5**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	25	20	53
7	**6**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	25	20	2
8	**7**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	25	20	23
9	None	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	25	30	0
10	**5**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	25	30	75
11	**6**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	25	30	32
12	**7**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	25	30	55
13	None	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	60	10	0
14	**5**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	60	10	84
15	**7**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	60	10	61
16	None	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	60	20	Trace
17	**5**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	60	20	94
18	**7**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	60	20	65
19	None	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	60	30	Trace
20	**5**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	60	30	99
21	**7**	*p*-NitroBnBr	$CH_3(CH_2)_2COONa$	60	30	90
22	None	*p*-NitroBnBr	$CH_3(CH_2)_6COONa$	25	10	Trace
23	**5**	*p*-NitroBnBr	$CH_3(CH_2)_6COONa$	25	10	28
24	**6**	*p*-NitroBnBr	$CH_3(CH_2)_6COONa$	25	10	2
25	**7**	*p*-NitroBnBr	$CH_3(CH_2)_6COONa$	25	10	8
26	None	*p*-NitroBnBr	$CH_3(CH_2)_6COONa$	25	20	2
27	**5**	*p*-NitroBnBr	$CH_3(CH_2)_6COONa$	25	20	54
28	**6**	*p*-NitroBnBr	$CH_3(CH_2)_6COONa$	25	20	3
29	**7**	*p*-NitroBnBr	$CH_3(CH_2)_6COONa$	25	20	18
30	None	*p*-NitroBnBr	$CH_3(CH_2)_6COONa$	25	30	3
31	**5**	*p*-NitroBnBr	$CH_3(CH_2)_6COONa$	25	30	80
32	**6**	*p*-NitroBnBr	$CH_3(CH_2)_6COONa$	25	30	9
33	**7**	*p*-NitroBnBr	$CH_3(CH_2)_6COONa$	25	30	47

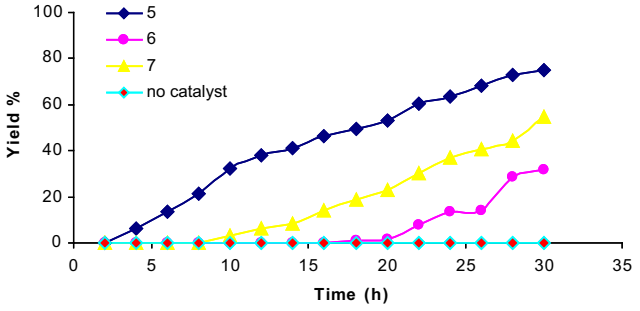


Fig. 1. Effect of PTC type on the formation of *p*-nitrobenzyl butyrate. Aqueous phase (5.0 mL) contains sodium butyrate (0.8 M), whereas organic phase (CH_2Cl_2, 5.0 mL) contains *p*-nitrobenzyl bromide (0.50 M) and catalyst (0.050 M). Temperature 25 °C.

ethyl acetate guest molecule is completely enshrouded. The sufficiently lipophilic Q then moves into the organic phase to react with *p*-nitrobenzyl bromide and thus yield the ester. After the reaction, calixarene is regenerated and enters the next catalytic cycle.

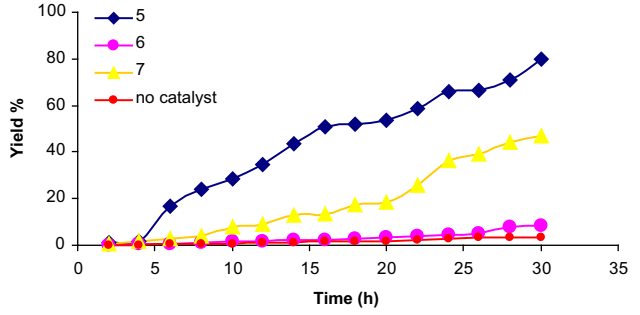


Fig. 2. Effect of PTC type on the formation of *p*-nitrobenzyl caprylate. Aqueous phase (5.0 mL) contains sodium caprylate (0.8 M) whereas organic phase (CH_2Cl_2, 5.0 mL) contains *p*-nitrobenzyl bromide (0.50 M) and catalyst (0.050 M). Temperature 25 °C.

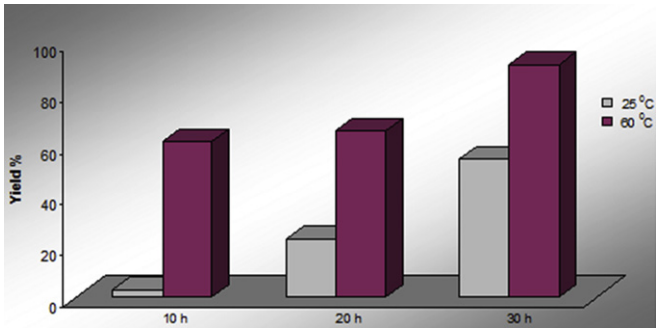


Fig. 3. Effect of reaction temperature on the esterification of *p*-nitrobenzyl bromide with sodium butyrate with catalyst **5**.

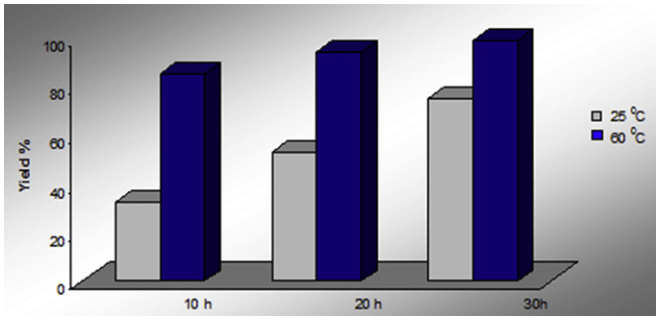
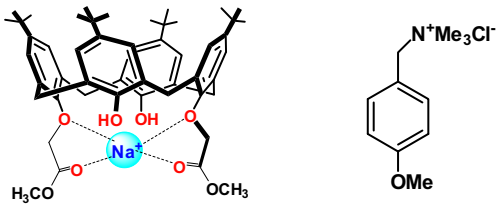


Fig. 4. Effect of reaction temperature on the esterification of *p*-nitrobenzyl bromide with sodium butyrate with catalyst **7**.

To clarify the phenomena, similar experiments were performed on compound **11** (Scheme 4). From the results, it has been observed that the diester derivative of calix[4]arene (**11**), which has a cone conformation, is a good extractant for Na^+ ion, but a poor catalyst for the reaction. On the other hand, Et_3N was used as phase-transfer agent in the ester-forming reaction, however, the results showed that Et_3N was poor catalyst. In literature Shimizu et al.[26] synthesized noncyclic monomeric analog of macrocyclic calixarene (**12**) (Scheme 4) to understand the effective role of the macrocyclic scaffold of calixarenes as a phase-transfer catalyst. The results showed that no acceleration effect is observed when the noncyclic monomeric analog is added to the reaction mixture. It has been concluded that the protonated form of calixarene and the guest inclusion in the calixarene cavity plays a key role in the catalytic process.



11 **12**

Scheme 4. Proposed interactions of the compound **11** with Na^+ and previously synthesized compound **12**.

3. Conclusions

In summary, we have synthesized three new upper rim-substituted calix[4]arene alkylamine derivatives, and have used calixarenes as phase-transfer agents in the esterification reaction with *p*-nitrobenzyl bromide and sodium butyrate or sodium caprylate. In the absence of calixarene derivatives, the reaction did not

occur appreciably, indicating that **5**, **6**, and **7** serve as catalysts for these esterification reactions. It is observed that catalyst **5** afforded relatively better results than the other catalysts.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded with a Varian 400 MHz spectrometer in $CDCl_3$. FT-IR spectra was recorded with a Perkin–Elmer spectrum 100. Elemental analyses were performed on a Leco CHNS-932 analyzer. High-performance liquid chromatography (HPLC) Agilent 1200 Series were carried out using a 1200 model quaternary pump, a G1315B model Diode Array and Multiple Wavelength UV–vis detector, a 1200 model Standard and preparative autosampler, a G1316A model thermostated column compartment, a 1200 model vacuum degasser, and an Agilent Chemstation B.02.01-SR2 Tatch data processor. All analytes used in this study were of analytical grade and were obtained from Sigma–Aldrich and Merck. All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli Q Plus water purification system. The yield of product was determined by HPLC (Agilent 1200 Series) analysis by using Zorbax SIL (4.6×250 mm) column at the temperature of 25 °C. Column Zorbax SIL was purchased from Agilent technology. In the analysis, hexane/chloroform (2:8 v/v) was used as the mobile phase at the flow rate of 1 mL/min; and UV detection was done at 254 nm. HPLC grade *n*-hexane and chloroform were purchased from Merck.

4.2. Catalytic application

The phase-transfer catalysis was carried out between water (5 mL, [sodium butyrate and sodium caprylate]=0.8 M) and dichloromethane (5 mL, [catalyst]=5.0×10^{-2} M, [*p*-nitrobenzyl bromide]=0.50 M). We here tested compounds **5**, **6**, and **7** as phase-transfer catalysts. The aliquot was withdrawn from the organic phase and subjected to HPLC analysis (column Zorbax SIL, mobile phase hexane/chloroform=2:8 v/v). The concentration of yielded *p*-nitrobenzyl butyrate and caprylate was determined from the calibration curve made separately using the authentic sample.

4.3. Synthesis

4.3.1. Calix[4]arene derivatives. Calixarenes have been widely used as three-dimensional building blocks for the construction of artificial molecular receptors capable of recognizing neutral molecules, cations, and more recently anions.[33] Thus, having chosen the *p*-*tert*-butylcalix[4]arene as the basis for derivatives, a synthetic scheme had to be developed to enable the derivatization of the molecule. Such a synthetic route is shown in Scheme 1.

The syntheses of compounds **1**–**4** (Scheme 1) were based on the previously published procedures.[27,28] The following general procedure[29–31] was adopted to transform calix[4]arene (**4**) into the corresponding alkylamine derivatives **5**, **6**, and **7**.

4.3.2. General procedure (Mannich reactions). To a solution of compound **4** (10 mmol) in 90 mL of THF/DMF were added 11 mL of acetic acid, the secondary amine (*N*-Ethylpiperazine, diallylamine or 4-benzylpiperidine) (50 mmol), and 37% aqueous formaldehyde (50 mmol) and the reaction mixture was stirred for 24 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in 75 mL of water. The aqueous solution was extracted twice with 50 mL of diethyl ether and then neutralized with 10% aqueous K_2CO_3 solution. The precipitate that formed was removed by suction filtration. The product was dried in vacuo and recrystallized from chloroform.

4.3.3. 5,17,Di-tert-butyl-11,23-bis[(N-ethylpiperazine)methyl]-25,26,27,28-tetrahydroxycalix[4]arene. Compound **5** was obtained in 85% yield as a pink solid; mp 140 °C; IR (KBr disk): 3168, 2951, 2806, 1662, 1481, 1163, 872, 790 cm^{-1}; ^{1}H NMR ($CHCl_3$): δ=1.02 (t, 6H, CH_2CH_3), 1.18 (s, 18H, ^{t}Bu), 2.35 (m, 20H, NCH_2), 3.24 (s, 4H, $ArCH_2N$), 3.51 (d, 4H, *J*=12.5 Hz, $ArCH_2Ar$), 4.22 (d, 4H, *J*=12.5 Hz, $ArCH_2Ar$), 6.92 (s, 4H, Ar), 7.08 (s, 4H, Ar). ^{13}C NMR ($CDCl_3$): δ (ppm): 12.17, 31.71, 32.42, 34.29, 52.52, 53.02, 53.31, 62.83, 126.12, 127.80, 128.40, 129.92, 131.65. Anal. Calcd for $C_{50}H_{68}O_4N_4$: C, 75.94; H, 8.86; N, 7.08%. Found: C, 75.89; H, 8.89; N, 7.15%.

4.3.4. 5,17,Di-tert-butyl-11,23-bis[(diallyl) methyl]-25,26,27,28-tetrahydroxycalix[4]arene. Compound **6** was obtained in 70% yield as white solid; mp 170 °C; IR (KBr disk): 3172, 2954, 1657, 1482, 1199, 1091, 816, 782 cm^{-1}; ^{1}H NMR ($CHCl_3$): δ=1.22 (s, 18H, ^{t}Bu), 3.02 (d, 8H, NCH_2CH=), 3.34 (s, 4H, $ArCH_2N$), 3.50 (d, 4H, *J*=12.3 Hz, $ArCH_2Ar$), 4.24 (d, 4H, *J*=12.3 Hz, $ArCH_2Ar$), 5.13 (m, 8H, CH_2=), 5.82 (m, 4H, CH=CH_2), 6.99 (s, 4H, Ar), 7.06 (s, 4H, Ar). ^{13}C NMR ($CDCl_3$): δ (ppm): 31.9, 32.5, 34.54, 56.52, 57.55, 117.58, 126.16, 127.78, 128.37, 129.78, 136.17, 144.78, 146.96, 147.77. Anal. Calcd for $C_{50}H_{62}O_4N_2$: C, 79.57; H, 8.22; N, 3.71%. Found: C, 79.83; H, 8.35; N, 3.93%.

4.3.5. 5,17,Di-tert-butyl-11,23-bis[(4-benzylpiperidine) methyl]-25,26,27,28-tetrahydroxycalix[4]arene. Compound **7** was obtained in 80% yield as white solid; mp 135 °C; IR (KBr disk): 3242, 2921, 1659, 1453, 1301, 745, 699 cm^{-1}; ^{1}H NMR ($CHCl_3$): δ=1.23 (s, 18H, ^{t}Bu), 1.36 (m, 4H, NCH_2CH_2), 1.51 (m, 2H, CH), 1.6 (m, 4H, NCH_2CH_2), 1.85 (m, 4H, NCH_2CH_2), 2.54 (d, 4H, $CHCH_2Ar$), 2.87 (m, 4H, NCH_2CH_2), 3.3 (s, 4H, $ArCH_2N$), 3.50 (d, 4H, *J*=12.5 Hz, $ArCH_2Ar$), 4.25 (d, 4H, *J*=12.5 Hz, $ArCH_2Ar$), 6.97 (s, 4H, Ar), 7.07 (s, 4H, Ar), 7.13–7.3 (m, 10H, Ar). ^{13}C NMR ($CDCl_3$): δ (ppm): 31.7, 32.15, 32.46, 34.27, 37.9, 43.01, 53.08, 62.8, 125.99, 126.1, 127.87, 128.36, 128.50, 129.39, 130.01, 140.8, 144.58, 147.14, 148.39. Anal. Calcd for $C_{62}H_{74}O_4N_2$: C, 81.75; H, 8.13; N, 3.07%. Found: C, 81.49; H, 8.3; N, 3.13%.

Acknowledgements

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