

SYNTHESIS OF POLY-5,7-DIALLYL-25,26,27,28-TETRAHYDROXYCALIX[4]ARENE

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ABSTRACT

The synthesis of poly-5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene were performed in experimental series as follows: (1) Cyclotetramerization of *p*-*t*-butylphenol with NaOH and paraformaldehyde to *p*-butylcalix[4]arene, (2) Debutylation of *p*-butylcalix[4]arene using AlCl₃ and phenol to tetrahydroxycalix[4]arene, (3) Allylation reaction using allylbromide to diallyloxy-dihydroxycalix[4]arene, (4) Claisen rearrangement reaction, (5) Cationic polymerization to diallylcalix[4]arenes. All of the synthesized products were analyzed by means of IR spectrometer and ¹H-NMR spectrometer. The result of 25,27-diallyloxy-26,28-dihydroxycalix[4]arene synthesis was white crystals having m.p. 205-207 °C in 80.95% yield. The synthesis of 5,7-diallyl-25,26,27,28-tetrahydroxy-calix[4]arene gave light yellow crystals having m.p. 214-216 °C in 78.67% yield. The polymerization gave poly(5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene) having m.p. 338-340 °C, in 60% yield. Its estimated has a relative molecular weight of 18,738 g/mol with the number of unit repetition about 37 monomer units.

Keywords: Diallylation, polymerization, Poly-5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene

INTRODUCTION

Calixarenes are belonging to macrocyclic molecules for example crown ether and cyclodextrin [1]. These compounds have active groups arranged in unique molecular geometry in the form of vase or pot in which can be used as host of cation, anion, and neutral molecule [2]. Calixarenes in water system can also be utilized as a surfactant and acid catalyst [3].

Based on its characteristic structure and its function of calixarenes structures, this compound has many great attentions in supramolecular chemistry especially for the synthesis of its derivative. Haverlock et al. [4] had been synthesized calix[4]arene-bis(benzocrown-6) which was reported having transport ability for Francium ion. Synthesis of 5,17-bis[(4-nitrophenyl)(azo)phenyl]-26,28-bis(1-propyloxy)-25,27-calix[4] monocrown-6 was synthesized and was reported able to trap metal cation i.e. Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Ag⁺, Mg²⁺, Ca²⁺, dan Sr²⁺ [5].

Functionalized calixarenes have previously been prepared by the direct substitution route [6] and the *p*-Claisen rearrangement route [7-8]; the present work adds another procedure for introducing various groups onto the *p*-position of the calixarene framework. *p*-*tert*-Butylcalix[4]arene (Fig. 1 (1)) can be prepared in good yield by the base-induced condensation of *tert*-butylphenol and formaldehyde [9]. Aluminum chloride-

catalyzed removal of the *tert*-butyl groups proceeds in excellent yield [7-8].

Monoalkylation of calix[4]arenes to the corresponding monoalkyl ethers **2** (Fig. 1) can be performed directly by reaction with an excess of alkylating agent in the presence of 1.2 equivalents of a weak base (CsF) in *N,N*-dimethylformamide (DMF) [10], as an alternative for the selective dealkylation of di- or tetraalkylated calix[4]arenes with Me₃SiI [11]. A stronger base like K₂CO₃ in acetonitrile gave not only the monoalkyl ethers (**2**) but also the 1,3-dialkyl ethers (**3**) (Fig. 1). Selective alkylation of two diametrically located phenol rings is possible in good yields by reacting calix[4]arenes with 2 equivalents of alkylating agent in acetonitrile, in the presence of 1 equivalent of K₂CO₃ [12-13]. All the products (**3**) are obtained in the cone conformation and further alkylation does not take place. Alkylation of calix[4]arenes with an excess of NaH in DMF and 2.2 equivalents of alkylating agent leads to the 1,2-dialkoxycalix[4]arenes (Fig. 2 (**4**)) (in the cone conformation) in acceptable yields, besides tetrasubstituted calix[4]arenes and starting material [14]. Among the upper rim functionalized methods, Gutsche and his coworker reported that the allyl group could be introduced by the Claisen rearrangement route (**5**) [8].

It has been mentioned that the ability of calixarenes to function as host molecules, extractant, adsorbent, and complexing agent are due to the presence

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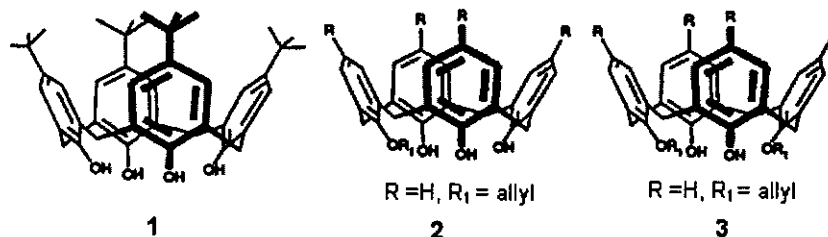


Fig 1. Structures of (1) *p*-*t*-butylcalix[4]arene, (2) monoallyloxycalix[4]arene, (3) 1,3-diallyloxycalix[4]arene

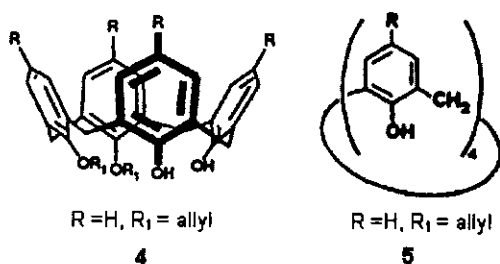


Fig 2. structures of 1,2-diallyloxycalix[4]arene (4) and diallylcalix[4]arene (5)

of cavity and donor atoms in the molecule. Accordingly, it could be expected that such functions would be greatly enhanced when the molecule does exist in a polymeric state. This occurs as the total volume of the cavity and the number of donor atoms in calixarene polymeric materials would be exponentially multiplied compared to those of calixarene monomer. This is the reason why we are interested to synthesize polypropylcalix[4]arene polymers. Based on this phenomenon, this research was carried out to synthesize calix[4]arene polymers having two allyl groups. Due to the existence of the two allyl groups, cross link reaction between calix[4]arene was taken place. This makes the molecules immobile and it can be predicted that the adsorption process for heavy metal cation will be higher.

EXPERIMENTAL SECTION

Materials

Most of organic compounds utilized in this research were commercial products of high purity purchased from Merck, and used as such without any further purification.

Instrumentation

Structure identifications were performed using infra red spectrometer (IR Shimadzu 8201 PC) and $^1\text{H-NMR}$ spectra were recorded at room temperature on JEOL-MY500 spectrometer. The relative molecular weight a polymer could be determined using Ubbelohde viscometer.

Procedure

Synthesis of *p*-*t*-butylcalix[4]arene

p-*t*-butyl-calix[4]arene was prepared according reported to procedures reported previously [15]. Recrystallization from CH_3Cl and CH_3OH afforded 57.83% of a white crystal: m.p 343-345 °C (literature 344-346 °C); FTIR ($\text{KBr}/\text{cm}^{-1}$) ν_{OH} 3178.5, $\nu_{\text{C=C}}$ 3024 and 1604.7, ν_{CH_2} 1456.8, ν_{CH_3} 1361.7.

Synthesis of 25,26,27,28-tetrahydroxycalix[4]arene

Powdered agregat of *p*-*t*-butylcalix[4]arene (13.3 g; 20 mmol) was dissolved in 125 mL toluene in a three neck round bottom flask equipped with a nitrogen flow pipe. In the mixture was added 9.02 g (96 mmol) powdered phenol and 14 g (105 mmol) AlCl_3 anhydrous. The mixture was stirred at room temperature for 1 h under slow nitrogen atmosphere. The mixture was cooled at ice bath and 250 mL HCl 0.2 N solution was added to be followed by stirring for 30 min. Organic layer was collected. The excess of toluene was evaporated and methanol was added until a solid was formed. Recrystallization from CH_3Cl and CH_3OH afforded 6.16 g (72.64%) of a white crystal: m.p 310-312.5 °C; FTIR ($\text{KBr}/\text{cm}^{-1}$) ν_{OH} 3159, $\nu_{\text{C=C}}$ 1593.1 and ν_{CH_2} 1456.8.

Synthesis of 25,27-diallyloxy-26,28-dihydroxycalix[4]arene

25,26,27,28-tetrahydroxycalix[4]arene (1.06 g, 2.5 mmol) was dissolved in acetonitrile. K_2CO_3 (0.34 g, 3 mmol) and allylbromide (0.67 g, 5.6 mmol) were then added. The mixture was refluxed for 24 h under nitrogen atmosphere (the reaction was monitored using TLC until the starting material spot disappear). The solvent was removed, the residu was dissolved in chloroform and washed with diluted HCl, and solvent was then removed. The product was recrystallized from CH_3Cl and CH_3OH afforded 1.02 g (80.95%) of a white crystals: m.p 205-207 °C; FTIR ($\text{KBr}/\text{cm}^{-1}$) ν_{OH} 3410.15, $\nu_{\text{C=C}}$ 1651.07, ν 987.55 and 925.83 (specific for vinyl group); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 8.0027 (-OH, 4H), 7.2595-6.6631 (H Ar, 12H), 6.2756-6.2414 (-CH allyl, 2H), 5.8124-5.4139 (=CH₂ Vinyl, 4 H), 4.5596-

4.3114 (-CH₂- bridge, 8H), and 3.4021–3.37464 (-CH₂- allyl, 4H).

Synthesis of 5,17-diallyl-25,26,27,28-tetrahydroxy calix[4]arene

25-27-diallyloxy-26,28-dihydroxycalix[4]arene (1.5 g) was dissolved in 20 mL N,N-diethylanilin and refluxed for 3 h. The mixture was cooled and poured in 20 mL ice water. Concentrated HCl (25 mL) was then added and the obtained solid was filtered. The solid was recrystallized using dichloromethane-methanol afforded 1.18 g (78.67%) of a light yellow crystals : m.p 214-216 °C; FTIR (KBr/cm⁻¹) ν_{OH} 3179.97, $\nu_{C=C}$ 1635.64 and 1604.77, ν 995.27 (specific for vinyl group); ¹HNMR (500 MHz, CDCl₃) δ : 10.2260 (-OH, 4H), 7.0787-6.7584 (H aromatic, 10 H), 5.8931-5.8588 (-CH allyl, 2 H), 5.0790-5.0949 (-CH₂- allyl, 4 H), 4.2760-3.4998 (-CH₂- bridge, 8 H), and 3.2016-3.1882 (=CH₂ vinyl, 4 H).

Polymerization reaction

5,17-diallyl-25,26,27,28-tetrahydroxycalix[4]arene (0.15 g) was dissolved in 15 mL chloroform in a 100 mL three neck round bottom flask equipped with condenser and a nitrogen flow pipe. Concentrated Sulfuric acid (0.4 mL) was then added (it was done 4 times every 30 min for polymerization process each 0.1 mL). Polymerization was performed for 5 h (the reaction was monitored using TLC). The polymerization was terminated by adding 0.5 mL methanol. Chloroform layer was washed using water until neutral, dried over Na₂SO₄ anhydrous, evaporated the solvent and dried in an exicator. The product was brown solid afforded 60%: m.p 338-340 °C; FTIR (KBr/cm⁻¹) ν_{OH} 3178.69, $\nu_{C=C}$ 1604.77. The disappearances of vinyl (-CH=CH₂) group at 995.27 cm⁻¹ as well as absorption at 1635.64 cm⁻¹.

Relative molecular weight of poly-5,17-diallyl-25,26,27,28-tetrahydroxy-calix[4]arene

Molecular weight determination of poly-5,7-diallyl-25,26,27,28-tetrahydroxy-calix[4]arene was done by udelahde viscometry methods based on time flow measuring in chloroform as the solvent. Various concentration had been made in 0.075; 0.150; 0.300; dan 0.600 g/L.

RESULT AND DISCUSSION

The synthesis of *p-t*-butilcaliks[4]arene was carried out using a previously reported method [15]. The synthesis was performed using *p-t*-butylphenol, formaldehyde and NaOH as the catalyst. The scheme of the reaction depicted in Fig. 3.

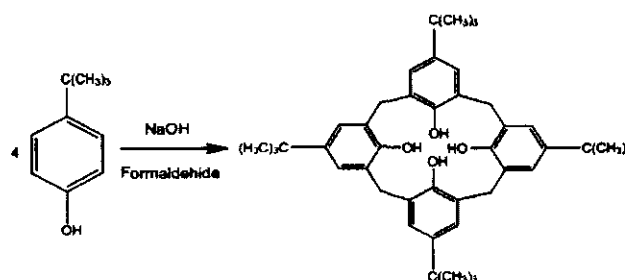


Fig 3. Reaction scheme of *p-t*-butylcalix[4]arene synthesis

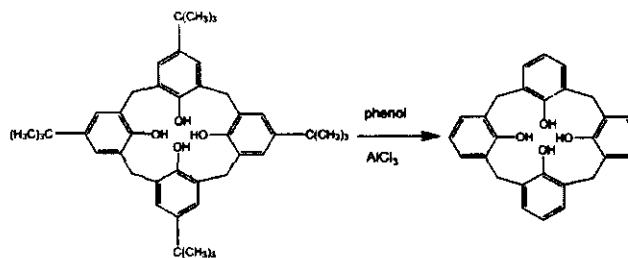


Fig 4. Debutylation of *p-t*-butylcalix[4]arene

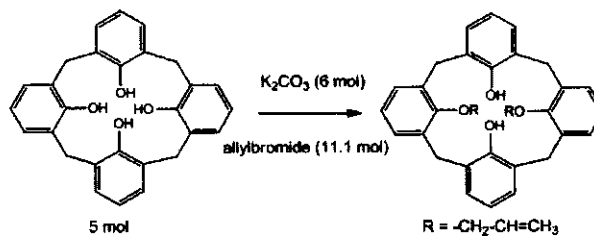


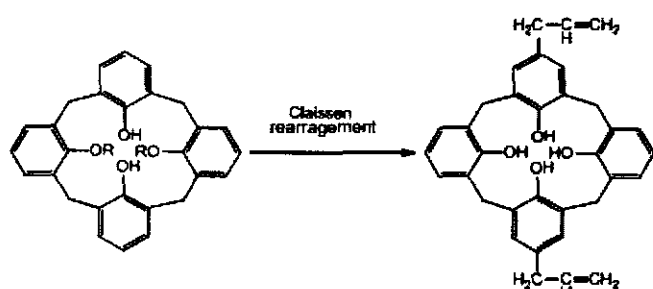
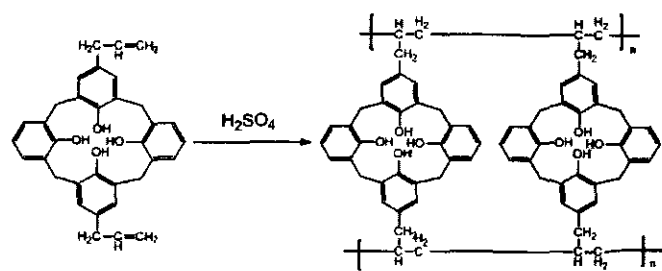
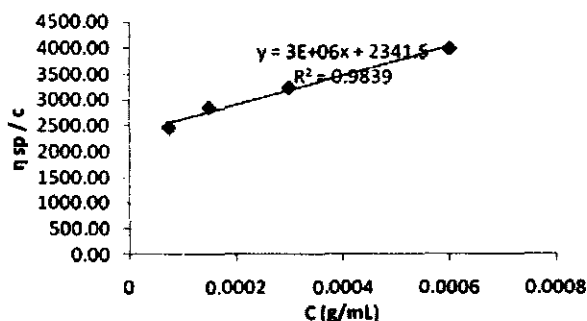
Fig 5. Allyloxy of 25,26,27,28-tetrahydroxycalix[4]arene

Debutylation is a Friedel-Craft alkylation (retro Friedel-Craft alkylation). Dealkylation of 4 tertier butyl groups of *p-t*-butylcalix[4]arene to 25,26,27,28-tetrahydroxycalix[4]arene is taken place in this reaction. The scheme of the reaction is depicted in Fig. 4. The disappearance of absorption at 1361.7 cm⁻¹ (for methyl group) at tertier butyl group indicated that the debutylation was taken place.

Gutsche and his co-workers reported that the calixarene allyl ethers were able to transform to the corresponding *p*-allylcalixarenes by the heat-induced Claisen rearrangement [8]. It is assumed that the partially *p*-allyl substituted calix[4]arenes could also be prepared from the corresponding partially allyloxyated calix[4]arenes in the same rearrangement. The two diallyl ethers were prepared according to the general procedures reported by Reinhoudt and his co-workers for the calix[4]arene's 1,2-dialkyl ethers and 1,3-dialkyl ethers [14,16]. Calix[4]arene 1,3-diallyl ether **2** was prepared by refluxing calix[4]arene with allyl bromide in CH₃CN in the presence of K₂CO₃. The reaction scheme is illustrated in Fig. 5.

Table 1. η_{sp}/C for Molecular Weight Determination

Conc (g/mL)	t (second)	η_{rel}	η_{sp}	η_{sp}/c
0	10.50			
0.000075	12.43	1.183809524	0.183809524	2450.79
0.00015	14.98	1.426666667	0.426666667	2844.44
0.0003	20.67	1.968571429	0.968571429	3228.57
0.0006	35.60	3.39047619	2.39047619	3984.13

**Fig 6.** Claisen rearrangement of 25,27-diallyloxy-26,28-dihydroxycalix[4]arene**Fig 7.** Polymerization of 5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene**Fig 8.** Graphic correlation of C versus η_{sp}/C of poly-5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene solution in chloroform

Claisen rearrangement of 25,27-diallyloxy-26,28-dihydroxycalix[4]arene was taken place using the presence of N,N-diethylaniline. The reaction was refluxed at 217 °C for 3 h. The solid product separated

after excess HCl addition to remove the remaining N,N-diethylaniline. The obtained solid was then recrystallized using chloroform-methanol and 5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene was obtained. The reaction scheme is illustrated in Fig. 6.

Based on FTIR and HNMR analyses, it can be concluded that Claisen rearrangement was taken place and 5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene was synthesized. HNMR spectra from the starting ethers, and the upfield shift of the allylic methylene hydrogen (from $\delta = 3.4$ to $\delta = 3.2$) indicated that allyl moieties had been transferred from the lower rim to the upper rim.

Polymerization of 5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene

Polymerization of 5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene using H_2SO_4 as the catalyst was carried out at room temperature (29 °C) under nitrogen atmosphere. The scheme of the reaction is depicted in Fig. 7.

The disappearances of vinyl ($-CH=CH_2$) group at 995.27 cm^{-1} as well as absorption at 1635.64 cm^{-1} showed that the polymerization was taken place.

Relative molecular weight of poly-5,7-diallyl-25,26,27,28-tetrahydroxy-calix[4]arene

Observation result for time flow in various concentration of poly-5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene and chloroform solvent were calculated from relatively viscosity (η_r), specific viscosity (η_{sp}) and relatively reductive viscosity (η_{sp}/C), as presented in Table 1.

Furthermore, based on Table 1, it can be obtained information about intrinsic viscosity from polymer solution which had been made using Huggins equation: $\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C$. Based on the equation, it

can be made a graphic $\frac{\eta_{sp}}{C}$ versus concentration (C).

By extrapolation to zero concentration, the intercept, intrinsic viscosity, $[\eta]$ of poly-5,7-diallyl-25,26,27,28-

tetrahydroxycalix[4]arene can be obtained as illustrated in Fig. 8.

The obtained intrinsic viscosity value is then added Mark-Houwink equation, $[\eta] = KM_v^a$. K and a is a constant which is depend on the polymer type and solvents. Based on Brandrup [17], K and a value for a certain polymer polypropylene polymer in chloroform at 30 °C are 2.18×10^{-2} mL/g and 0.725, respectively. By adding $[\eta]$, K, and a values to Mark-Houwink equation, it can be obtain that the relative molecular weight (M_r) and total repeated unit (n) of poly-5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene are 18,738 g/mol and 37, respectively.

CONCLUSION

Poly-5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene can be synthesized by the following steps: (1) cyclotetramerization to *p-t-b*-calix[4]arene, (2) Debutylation to 25,26,27,28-tetrahydroxycalix[4]arene, (3) allylation to 25,27-diallyloxy-26,28-dihydroxycalix[4]arene, (4) Claisen rearrangement to 5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene and (5) Polymerization. Poly-5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene synthesized product was a solid having m.p. 338-340 °C, and molecular weight 18,738 g/mol with repeated unit : 37.

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