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RESEARCH ARTICLE

ONE-STEP SYNTHETIC OFP-TERT-BUTYLCALIX[4]ARENE DERIVATIVE VIA DIRECT BENZOYLATION: MECHANISM REACTION STUDIES

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Abstract

The aim of research the synthesis of 5,11,17,23-tetra(t-butyl)-25-monohydroxy-26,27,28-tribenzoyloxycalix[4]arene (TBMTCA) material were by one-step synthesized by benzoylation reaction of 5,11,17,23-tetra(t-butyl)-25,26,27,28-tetrahydroxycalix[4]arene (TBCA) and benzoyl chloride is (1: 3,7) mol and the refluxing 3 hours at room temperature and predicted mechanism reaction models. The product reaction of synthesis was carried out by means of FTIR and 1H-NMR spectroscopy. The results material of5,11,17,23-tetra(t-butyl)-25-monohydroxy-26,27,28-tribenzoyloxycalix[4]arene (TBMTCA)synthesized was light yellow crystalline having melting point 306-3090C in 90,2 % yields

Introduction:-

Calixarenes are cavities containing metacyclophane which are recently utilized as a versatile host molecule. One of the most important aspects of host-guest chemistry is molecular recognition [10, 11, 13]. Gutsche and his coworkers discovered the selective esterification of p-tert-butylcalix[4]arene. They reported that one monoester, two diesters, and triesters under carefully controlled reaction conditions could be prepared selectively [6,10,13]. The base-induced condensation of p-tert-butylphenol and formaldehyde is shown to yield tb-calix[4]arene or calixarenes [7,8]. Calixarenes are phenolic metacyclophanes with right cone-like structures, which possess an upper rim defined by the para positions of the aromatic rings and a lower rim defined by oxygen atoms. The conformation of calixarenes allows the formation of complexes with cation, anion, and neutral molecules [1].Calixarenes are Unix because the calixarene is a cavity containing a macrocyclic compound.

Experimental

Apparatus

IR spectra were recorded with a Shimadzu FTIR-PRESTIGE 21. A spectrometer as KBr pellets. Melting points were obtained with an electrothermal Digital Point Apparatus, and ^{1}H-NMR spectrum was obtained in the designated solvent ($CDCl_3$) on AGILENT Varian NMR 400 MHz proton Nuclear Magnetic Resonance Spectrometer.

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Procedure:-

5,11,17,23-Tetra-tert.butyl-25,26,27,28-tetrahydroxycalix[4]arene (TBCA)

Structure identification were performed using FTIR and H-NMR. The compounds of p-tert.butylcalix[4]arene was preparedaccordingto the procedure reported previously [6,7]. Recrystalisazed from chloroform and methanol, yields rendement 46,07% yield of a white crystal, melting point 342-345^{0}C, IR spectra were determined on SHIMADZU PRESTIGE 21 spectrometer, FTIR (KBr/ cm^{-1}), VOH 3232,70 cm^{-1}, VC=C 3055,24 cm^{-1} and 1604,77 cm^{-1}, VCH2 1458,18 cm^{-1}, VCH3 1365,6 cm^{-1}. H-NMR spectra were determined on AGILENT Varian NMR 400 MHz Proton Nuclear Magnetic Resonance Spectrometry, ^{1}H-NMR (400 MHz, $CDCl_3$). **δ** 4,3848: 4,3805 and **δ** 3,4124; **δ** 3,4816 (two pairs of d, 8H, $ArCH_2Ar$, J=13 Hz and J=14 Hz), **δ** 7,1757 (s,7H,ArH), **δ** 7,0483 (s,1H,ArH), **δ** 10,3367(s,4H,OH), **δ** 1,2523(s,36H,$C(CH_3)_3$), **δ** 1,5555(s, 2H, my be is H_2O protons) shown at Figure 2

5,11,17,23-Tetra-tert.butyl-25-monohydroxy-26,27,28-tribenzoyloxycalix[4]arene (TBMTCA)

Solution of 1,5 g (2,32 mmol) of t-butylcalix[4]arene derivative (1) in 50 mL $CHCl_3$ dry, 2 mL of pyridine and then, 1,4 mL (10,33 mmol) of benzoyl chloride is (1:5)mol in 20 mL chloroform was added slowly. The mixture refluxing was stirred at room temperature for 24 h. After removed the solvents by evaporation, the residue was triturated with methanol. After filtration, the crude product was recrystallized from $CHCl_3$ to give 1,80 g (90,2%) yellow crystalline. mp = 306-309^{0}C, IR spectra were determined on SHIMADZU PRESTIGE 21 spectrometer, FTIR (KBr/ cm^{-1}), VOH 3448,72 cm^{-1}, VC=C 2924,09 cm^{-1} and 1627,92 cm^{-1}, VCH_2 1473,62 cm^{-1} , VCH_3 1365,6 cm^{-1}, VCH_3 1365,6 cm^{-1}, VC=O 1720,5 cm^{-1}, H-NMR spectra were determined on AGILENT Varian NMR 400 MHz Proton Nuclear Magnetic Resonance Spectrometry, ^{1}H-NMR (400 MHz, $CDCl_3$). **δ** 3,5152 and **δ** 3,4836 and **δ** 4,3929; 4,3756 (two pairs of d, 8H, $ArCH_2Ar$, J=13 Hz), **δ** 7,1779 (s,8H,ArH), **δ** 8,12 (d,3H,Ar-C), **δ** 8,06 (d,1H,Ar-C), **δ** 7,624 (t,2H,Ar-C), **δ** 7,492 (m,3H,Ar-C), **δ** 7,334 (t,2H,Ar-C), **δ** 7,049 (m,4H,Ar-C), **δ** 10,3370 (s,1H,OH), **δ** 1,2534 (s,36H,$C(CH_3)_3$).Shown at Fig. 2

Result And Discussion:-

The synthesis of TBCA [3,4,5] via fragmentation siclooctamer to form p-tb-calix[4]arene was carried out using previously reported methods [7]. The synthesis was performed using p-t-Butyl-phenol, formaldehyde, and NaOH as the catalyst, and the synthesis of TBMTCA/ derivative 2[5] was carried out using procedure modification previously [3,4,5,9,12]. Fragmentation siclooctamer to form p-t-butylcalix[4]arene and Spectra FTIR p-tb-Calix[4]arene. at Figure 1 bellow

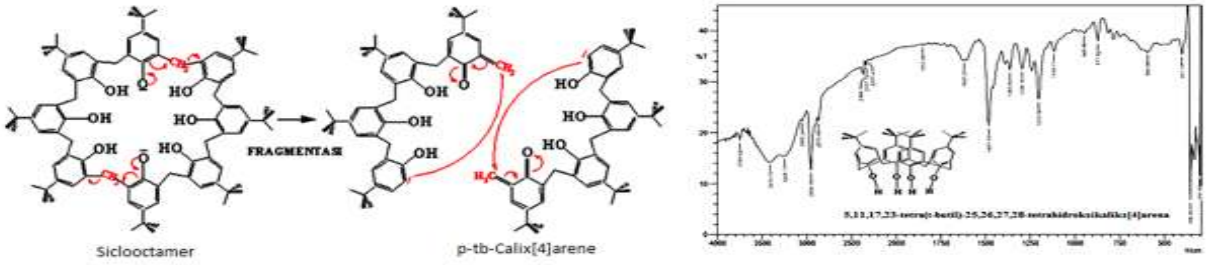

Figure 1: Fragmentation siclooctamer to form p-tb-butylcalix[4]arene and spectra FTIR of p-tb-butylcalix[4]arene

The mechanism synthetic routes of 5,11,17,23-tetra(t-butyl)-25-monohydroxy-26,27,28-tribenzoyloxycalix[4]arenes (TBMTCA) are shown in Scheme 1. Compound TBCA[3,4,5] and TBMTCA was synthesized according to published [3,6,7,9,12].The synthesis of 5,11,17,23-tetra(t-butyl)-25-monohydroxy-26,27,28-tribenzoyloxycalix[4]arenes (TBMTCA) by reaction p-tert-butylcalix[4]arene with benzoyl chloride and pyridine as a catalyst and the synthesis of the 5,11,17,23-tetra(t-butyl)-25,26,27,28-tetrahydroxycalix[4]arene [7,8]. The structures of 5,11,17,23-tetra(t-butyl)-25-monohydroxy-26,27,28-tribenzoyloxycalix[4]arenes (4,13) were confirmed by FTIR spectra and ^{1}H-NMR spectra. It was shown in **Figures**1 and **Figure** 2.

The structure of 5,11,17,23-tetra(t-butyl)-25-monohydroxy-26,27,28-tribenzoyloxy calix[4]arenes (TBMTCA) were characterized by ^{1}H-NMR spectra compound of TBCA and TBMTCA respectively were assigned to appropriate protons in **Figures 2**

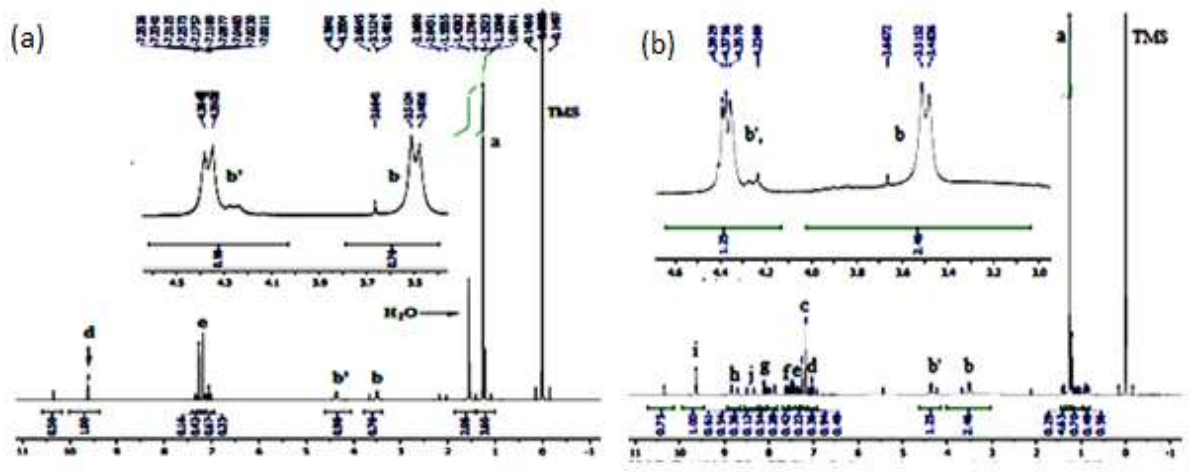

Figure 2, Spectrum ^{1}H-NMR(400 MHz, $CDCl_3$) of (a) TBCA and (b) TBMTCA

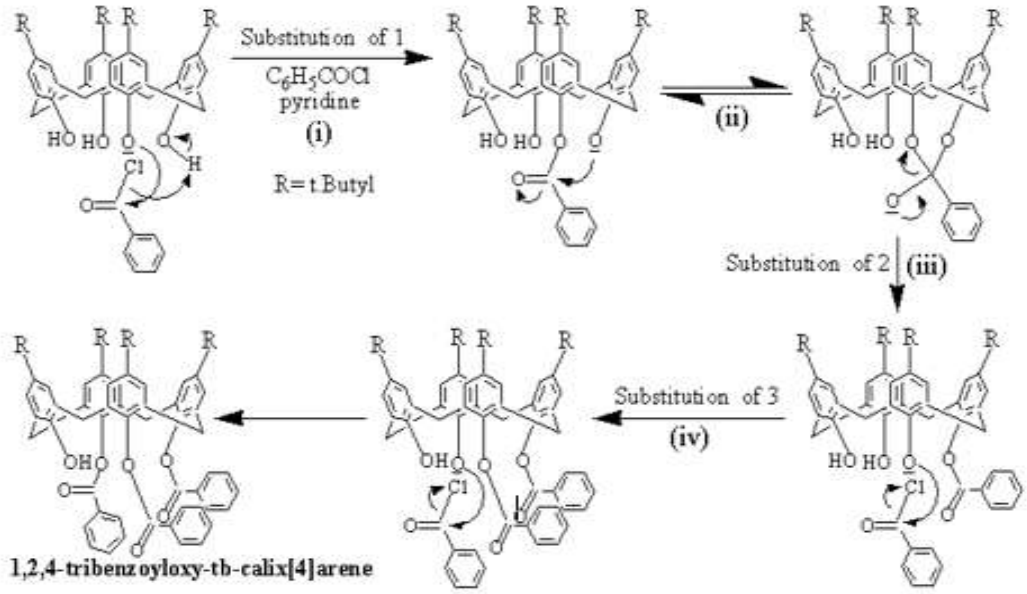

Figure 3. Propose Model Synthetic Routes Mechanism Reaction Pathways for 1,2,3- Trisubstitution

The routes mechanism in**Figure3**is a normal direct substitution approach. The phenolic hydroxyl groups of tb-calix[4]arenes were directly substitution with benzoyl chloride, the benzoylation reaction was finished by using pyridine in refluxing chloroform for 3 hours to give tribenzoyloxy-tb-calix[4]arene (TBMTCA) yields 90,0%. The structure of the product was characterized by^{1}H-NMR. The spectrum ^{1}H-NMR (400 MHz, $CDCl_3$) spectroscopy besides other character peaks of each group, ^{1}H-NMR spectrum of the compound target (TBMTCA) shows the typical chiral p-tert.butylcalix[4]arene (TBCA)[3,4,5] characteristics such as four pairs of doublets at 3,4- 4,4 ppm for the eight bridge methylene protons groups and the phenyl group signals usually have complicated peaks at about 6,9-8,2 ppm (groups of phenyl or Ar-C) and a singlet at 1,2534 ppm for the t-butyl groups according to the different deshielding zone of t-butyl groups. Zone peaks at 7,1779 ppm were observed for the aromatic hydrogen atoms. Inchemistry, regioselectivity is the preference of one direction ofchemical bondmaking or breaking of all other mechanism reaction models in possible directions. This is a mechanism reaction in which one positional isomer is favored over another, leading to its predominance in the mixture of the products. For the instance, the addition reaction substituted benzoyl proceeds regioselectively to the more substituted. This term is often used synonymously with regiospecific. [15]. The ^{1}H-NMR spectrum of shows in **Figure** 2indicates the high symmetry of the product. The produced 1,2,4-trisubstituted routes of mechanism reaction is i-iv as shown in **Figure** 3. This first route of mechanism reaction via substituted benzoylation producest-butyl-monobenzoyloxycalix[4]arenes. This second route of mechanism reaction via substituted benzoylation, suggests that the migration of benzoyl groups is much

slower than the second routeof benzoylation [6,10,13]. This routes the final mechanism reaction models via substituted benzoylation. This suggests that the migration of benzoyl groups is much slower than final benzoylation.

Conclusion:-

Compound of 5,11,17,23-tetra(t-butyl)-25-monohydroxy-26,27,28-tribenzoyloxycalix[4]arenes can be synthesized via thedirectmechanism reaction models form conversioncompound derivative 1 of 5,11,17,23-tetra(t-butyl)-25,26,27,28-tetrahydroxycalix[4]arene with benzoyl chloride via benzoylation reaction, comparative (1:3,7) mol, refluxing 3 hours and comparative (1:5) mol refluxing 24 hours, pyridine as a catalyst at room temperature via benzoylation reactions. Synthesized productseach was a solid light yellow crystalline, having m.p 306-309^{0}C and 304 – 310^{0}C respectively

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