

## Alkylations of Resorcarenes and Calix[4]pyrroles in Phase Transfer Catalytic Systems

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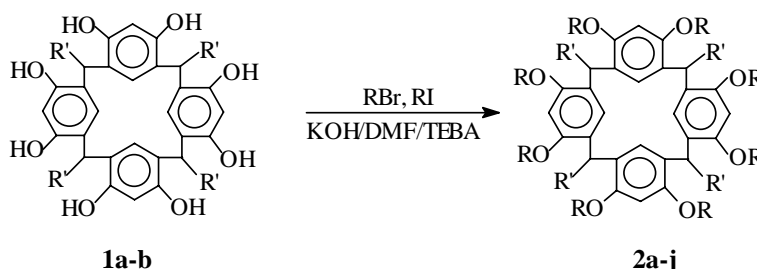
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**Abstract:** Resorcarenes **1a-b** ( $R' = \text{Ph}, p\text{-MeOC}_6\text{H}_4$ ) were fully alkylated with alkyl iodides or bromides in TEBA/KOH/DMF solid-liquid PTC process with 63-82% yields, whereas the three calix[4]pyrroles **3a-b** ( $2R = 2\text{Me}, (\text{CH}_2)_4, (\text{CH}_2)_5$ ) were alkylated with alkyl iodides in TBAB/50%NaOH/ $\text{CH}_2\text{Cl}_2$  liquid-liquid PTC system with lower yields (10-38%).

**Keywords:** Resorcarenes, calix[4]pyrrole, alkylation, phase transfer catalysis.

Calix[n]arenes are cyclic oligomers made up of phenols and formaldehyde. This versatile class of compounds has been extensively studied in the last decade mainly in order to obtain new complexing agents by appropriate functionalization of the parent molecule<sup>1</sup>. Resorcarenes<sup>2</sup> and calix[4]pyrroles<sup>3</sup> are two subgroup members of the family of calixarenes and also attracted increasing interests. As part of a programme aimed at the synthesis of new easy-to-make calixarene molecules, we decided to investigate the alkylation of some calixarenes in Phase Transfer Catalysis (PTC) conditions<sup>4</sup>. Here we wish to report the preliminary results of alkylation reaction of resorcarenes and calix[4]pyrroles.

Resorcarenes have been used as starting material for the synthesis of cavitands<sup>5</sup> in which the dialkylation reaction especially with  $\text{CH}_2\text{BrCl}$  was thoroughly investigated and recently one paper reported the benzylation of **1** ( $R' = \text{Me}$ )<sup>6</sup>. We initially wish to carry out

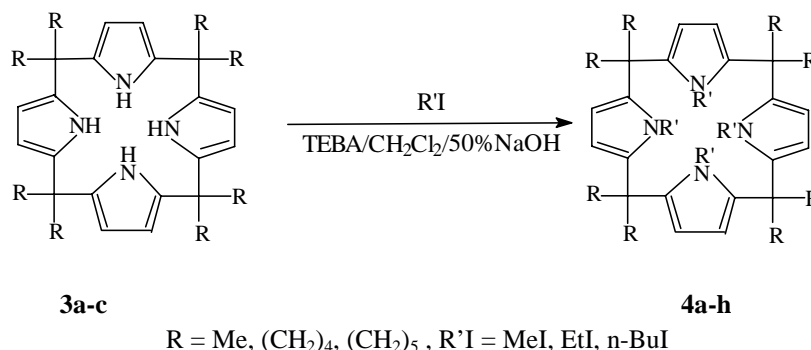


$R' = \text{Ph}, p\text{-MeOC}_6\text{H}_4$ ,

$\text{RX} = \text{MeI}, \text{EtBr}, \text{BuBr}, \text{EtI}, \text{BuI}, \text{BrCH}_2\text{Ph}, \text{BrCH}_2\text{COPh}, \text{BrCH}_2\text{CO}_2\text{Et}$

the alkylation of resorcarenes in liquid-liquid phase transfer catalysis (PTC) system such as TEBA/50% NaOH/toluene. But the resorcarenes reacted immediately with sodium

hydroxide to form the sodium phenolate which precipitated from the reaction mixture as a thick mass and could not effectively be transferred into the organic phase. By using the solid potassium hydroxide in stronger polar solvents N, N-dimethylformamide in the presence of triethylbenzylammonium chloride (TEBA) as the catalyst, the resorcarens **1a-b** reacted smoothly with the excess of alkyl bromide or iodide (molar ratio is 1:16) to gave the expected fully alkylated products in 72 hours with high yields (63-82%). By using the bromoacetophenone and ethyl bromoacetate, the functional carbonyl and carboxyl groups were introduced to the resorcarene ring.



Prompted by the successful alkylation of resorcarenes, we carried out the alkylation of the calix[4]pyrroles **3a-c** ( $R = \text{Me}, (\text{CH}_2)_4, (\text{CH}_2)_5$ ), which were prepared by the condensation of the pyrrole with acetone, cyclopentanone and cyclohexanone. Under the liquid-liquid PTC conditions (TEBA/50%NaOH/ $\text{CH}_2\text{Cl}_2$ ), calix[4]pyrroles **3a-c** reacted with excess ratio (1:16) of methyl, ethyl and n-butyl iodide at room temperature to give the N-alkylation products **4a-h** in lower yields (10-38%). This result is very similar to the that of the alkylation with the system of NaH/18-crown-6-ether/THF<sup>6</sup>. The disadvantage of this method is that some partial alkylation products (mono-, di- and trialkylation) were also formed in the process and is very difficult to be separated. The other alkylating agents such as ethyl bromide, n-butyl bromide and benzyl bromide did not give the expected N-alkylation products. Further study on the functional derivatives of calixarens is ongoing.

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