

Nano CaCO₃ : An Unique Condensation Agent for the Preparation of Monosubstituted Calix[4]arene by Ring-opening Reaction

Shu Ling GONG*, Wei WANG, Peng Fei FANG, Yuan Yin CHEN

College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072

Abstract: Nano CaCO₃ was used as a condensation agent in the ring-opening reaction of *p-tert*-butylcalix[4]arene with epichlorohydrin to afford 5,11,17,23-tetra-*tert*-butyl-26,27,28-trihydroxy-25-(1'-chloro-2'-hydroxy-3'-propyl)calix[4]arene regioselectively in 52% yield. The yield was less than 2% by using normal CaCO₃ instead of nano one under the same conditions.

Keywords: Nano CaCO₃, epoxide, calix[4]arene, monofunctionalization.

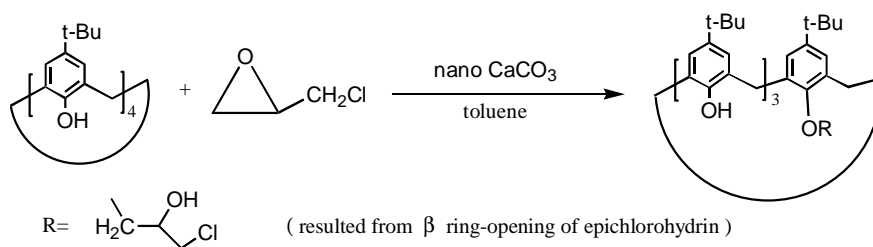
Calixarenes have been used as building blocks for the synthesis of a large number of host molecules because they are readily accessible for chemical modification on both lower and upper rims by attachment of a wide range of potential ligating groups¹. Epoxide is one of the most versatile intermediates in organic synthesis, and a large variety of reagents can open its oxirane ring², although little is known about the ring-opening reaction of epoxides by calixarenes³. On the other hand, it is well known that nano CaCO₃ as a high grade filling and a white pigment, is widely used in the rubber, plastic, papermaking, coating, ink and pharmaceutical industry⁴. As nano CaCO₃ can not dissolve in water or organic solvents, it has never been used as a base or condensation agent in any chemical reaction. However, we have found that nano CaCO₃ can be used as a condensation agent in a few special cases, for example, when one of the reactants is calix[4]arene, epichlorohydrin reacted with it selectively to afford monosubstituted product in good yield (**Scheme 1**). Here is the experimental result.

To a suspension of nano CaCO₃ (0.200 g, 2 mmol, supplied by Inter Mongolia Mengxi High-tech Materials Co. Ltd., average particle size was 20 nm) in toluene (50 mL), *p-tert*-butylcalix[4]arene (0.740 g, 1 mmol) and epichlorohydrin (7-8 mmol) were added. The reaction mixture was stirred for five days at 100°C. After centrifugation and evaporation of the solvent, the residue was extracted with CH₂Cl₂. The extract was passed through a silica column to afford a white product, 5, 11, 17, 23-tetra-*tert*-butyl-26, 27,28-trihydroxy-25-(1'-chloro-2'-hydroxy-3'-propyl)calix[4]arene⁵, a β cleavage product of epichlorohydrin, in 52% yield. The β cleavage was proved by the appearance of a CHO resonance at 70.5 ppm, a ArOCH₂ signal at 78.1 ppm and a CH₂Cl signal at 43.9 ppm in its ¹³C DEPT NMR. Using normal CaCO₃ instead of nano CaCO₃, the

*E-mail: gongsl@chem.whu.edu.cn

yield was less than 2% under the same conditions. No reaction could be observed in the absence of CaCO_3 . Other oxiranes gave similar results. For example, allyl glycidyl ether, the β cleavage product was obtained in 70% yield.

Scheme 1.



In conclusion, the nano CaCO_3 can be used as a unique condensation agent in the reaction of *p-tert-butylcalix[4]arene* with epoxides to afford monosubstituted *p-tert-butylcalix[4]arene* derivatives.

Acknowledgments

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References and Notes

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5. 11,17,23-Tetra-*tert*-butyl-26,27,28-trihydroxy-25-(1'-chloro-2'-hydroxy-3'-propyl)calix-[4]-arene. mp: 116°C -118°C; $^1\text{H NMR}$ (300MHz, CDCl_3) 1.19 (s, 9H, *t*-Bu), 1.21 (s, 18H, *t*-Bu), 1.23 (s, 9H, *t*-Bu), 3.47 (d, 2H, 13.5Hz, ArCH_2Ar), 3.48 (d, 2H, 13.2Hz, ArCH_2Ar), 3.83 (dd, 1H, 11.4Hz, 7.5Hz, ClCH_2 -), 3.90 (dd, 1H, 11.4Hz, 5.1Hz, ClCH_2 -), 4.25 (dd, 1H, 13.8Hz, 1.5Hz, Ar-O-CH_2 -), 4.26 (dd, 1H, 13.8Hz, 1.5Hz, Ar-O-CH_2 -), 4.33 (d, 2H, 13.5Hz, ArCH_2Ar), 4.37 (d, 2H, 13.2Hz, ArCH_2Ar), 4.39 (m, 1H, $-\text{CH}(-\text{OH})$), 4.35 (overlapped, 1H, $-\text{OH}$), 7.01, 7.07, 7.08 (d each, 2H each, 2.1Hz each, *H*-Ar), 7.11 (s, 2H, *H*-Ar), 9.61, 9.71, 10.28 (s each, 1H each, $-\text{OH}$); MS (FAB) m/z 741 $[\text{M}+\text{H}]^+$.

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