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Dedicated to V. F. Mironov on His 60th Anniversary

Chemoselective Acylation of Monosubstituted Thiacalix[4]arene with Di-*tert*-butyl Dicarbonate

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Abstract—Mono-, di-, and tetrasubstituted derivatives of *p-tert*-butylthiacalix[4]arene containing *tert*-butylcarbamate, *tert*-butylcarbonate, and *tert*-butyl fragments have been prepared for the first time. Depending on the reaction conditions (reagents ratio, temperature, and the presence of a base), the interaction of the monoamine derivative of *p-tert*-butylthiacalix[4]arene with di-*tert*-butyl dicarbonate can lead to the formation of mono-, di-, and tetrasubstituted products.

Keywords: thiacalix[4]arene, amino derivative, Boc-anhydride, alkylation, acylation

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Molecular frameworks like cyclodextrins [1], crown ethers [2], pillararenes [3, 4], and calixarenes [5] are the most important objects of supramolecular chemistry. Thiacalix[4]arene derivatives have attracted special attention as synthetic receptors for various anions, cations, and neutral molecules [6–14]. The possibility of preparation of mono-, di-, tri-, and tetrasubstituted [13, 15–19] derivatives of *p-tert*-butylthiacalix[4]arene as well as the existence of different stereoisomers make the thiacalix[4]arene scaffold a convenient building block for the creation of a variety of supramolecular systems. Partially substituted derivatives of *p-tert*-butylthiacalix[4]arene are advantageous for the preparation of polyfunctional derivatives owing to the possibility of coexistence of different functional groups in their structure [15]. Amino group is a convenient functional site for the modification of macrocycles and macromolecules due to the possibility of its acylation in aqueous as well as organic media. Many new synthetic receptors sensitive to anions, cations, and neutral molecules have been prepared based on amino derivatives of *p-tert*-butylthiacalix[4]arene. We have earlier elaborated a chemoselective method for the preparation of monophthalimide derivative of *p-tert*-butylthiacalix[4]arene **2** (Scheme 1) [20].

Many derivatives of *p-tert*-butylthiacalix[4]arene have been prepared basing on macrocycle **2** [20–22]. A drawback of phthalimide group is its instability in the presence of bases and nucleophilic agents. At the same time, *tert*-butyloxycarbonyl (Boc) fragments are stable in the presence of nucleophiles and bases yet can be easily removed under conditions of acid catalysis. Therefore, the use of Boc fragment as the protective group can extend the synthetic capability of differently substituted derivatives of *p-tert*-butylthiacalix[4]arene. This study aimed to investigate the interaction of di-*tert*-butyl dicarbonate with monoamino derivative of *p-tert*-butylthiacalix[4]arene in view of the preparation of Boc-protected derivatives.

It is well known that the interaction of di-*tert*-butyl dicarbonate (Boc_2O) with amines occurs under mild conditions with high yield in organic as well as aqueous-organic media. The only side products of the reactions are easily removable *tert*-butanol and carbon dioxide. For example, macrocycle **4** was obtained in high yield using equimolar amounts of thiacalixarene **3** and di-*tert*-butyl dicarbonate. The reaction was performed in CH_2Cl_2 during 1 h at room temperature. Besides the major reaction product (macrocycle **4**), traces of an atypical product of *p-tert*-butylthiacalix[4]-arene acylation **5** were found in the reaction mixture (Scheme 1). When the reaction temperature was increased to 40°C and 10% excess of Boc_2O was used, the yield of the 1,3-disubstituted product **5** was 5%,