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LETTERS**Phosphorylation of *p*-tert-Butylthiocalix[4]arene:
Reaction with Phosphorus Trichloride.**Igor S. Antipin,^{a*} Ivan I. Stoikov,^a Aidar T. Gubaidullin,^b Igor A. Litvinov,^b Dirk Weber,^c
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Abstract: The synthesis of the first phosphorylated derivatives of *p*-tert-butylthiocalix[4]arene was achieved by reaction with phosphorus trichloride. The product containing two cyclic P(III) atoms is not hydrolytically stable. The *flattened 1,2-alternate* conformation of a P(IV) derivative was established by ¹H, ¹³C, ³¹P NMR experiments and X-ray analysis. © 1999 Elsevier Science Ltd. All rights reserved.

In recent years supramolecular chemistry has been drawn to the calix[n]arenes due to their ability to act as pre-organizing complexing agents, carriers and potential biomimics as well as being able to undergo multiple functionalization.^{1,2} The insertion of phosphorus containing moieties into calix[n]arenes allows extension of the possibilities for engineering of supramolecular systems.^{3,4} We are currently studying the phosphorylation of thiocalix[4]arene **1**, which was recently synthesized in a satisfactory yield by the condensation of *tert*-butylphenol and sulfur under basic conditions at elevated temperatures.⁵ Of course, the presence of the four sulfur atoms could bring new features into the chemical behavior of calixarenes.

In the present paper the first synthesis and structural analysis of phosphorylated thiocalix[4]arenes in the solution and crystalline state are reported. Phosphorus trichloride was chosen as the phosphorylation reagent because the P-Cl compounds are very useful starting materials for further transformations.

The phosphorylation of **1** by PCl₃ with the commonly used procedure (toluene, NEt₃ (excess), room temperature) yields a single product which shows an intense (100%) peak in the MALDI spectrum at *m/z* 848.⁶ In the ³¹P NMR spectrum of the reaction mixture one resonance at δ 170.2 is observed. This value is in the range for three-coordinate phosphorus. The comparison with the ³¹P chemical shifts of model compounds **3a** (δ 168.4) and **3b** (δ 170.4)⁷ suggest the formation of cyclic chlorophosphite **2** (Scheme 1). However, during attempts at isolation, **2** decomposed to give free *p*-tert-butylthiocalix[4]arene, as well as other unidentified products. So the product obtained is less hydrolytically stable than corresponding cyclic chlorophosphite of *p*-tert-butylcalix[4]arene.⁸ The influence of a sulfur atom in the dioxathiophosphocin ring system may be responsible for such behavior (due to P-S interactions).

Using a slightly modified literature procedure⁹ we reacted **1** with the excess of PCl₃ in *p*-bromotoluene without base at elevated temperatures.¹⁰ After dilution of the reaction mixture with hexane, a colorless, crystalline precipitate was formed after 12 h (Scheme 1). These crystals were found to be a complex of