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Jörg Gloede; Burkhard Costisella; Karsten Gloe

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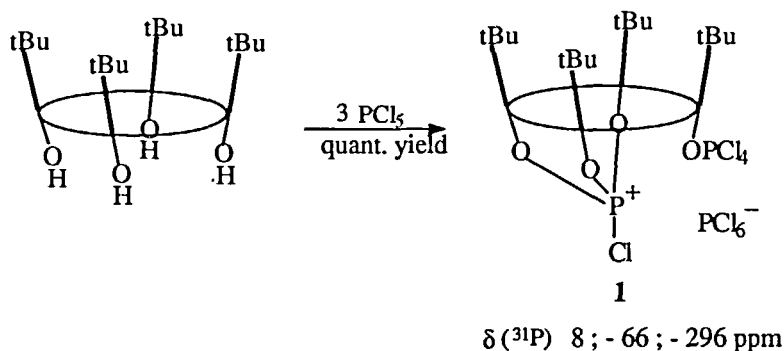
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P-BRIDGED CALIXARENE PHOSPHATE AND THIOPHOSPHATE - SYNTHESIS AND PROPERTIES

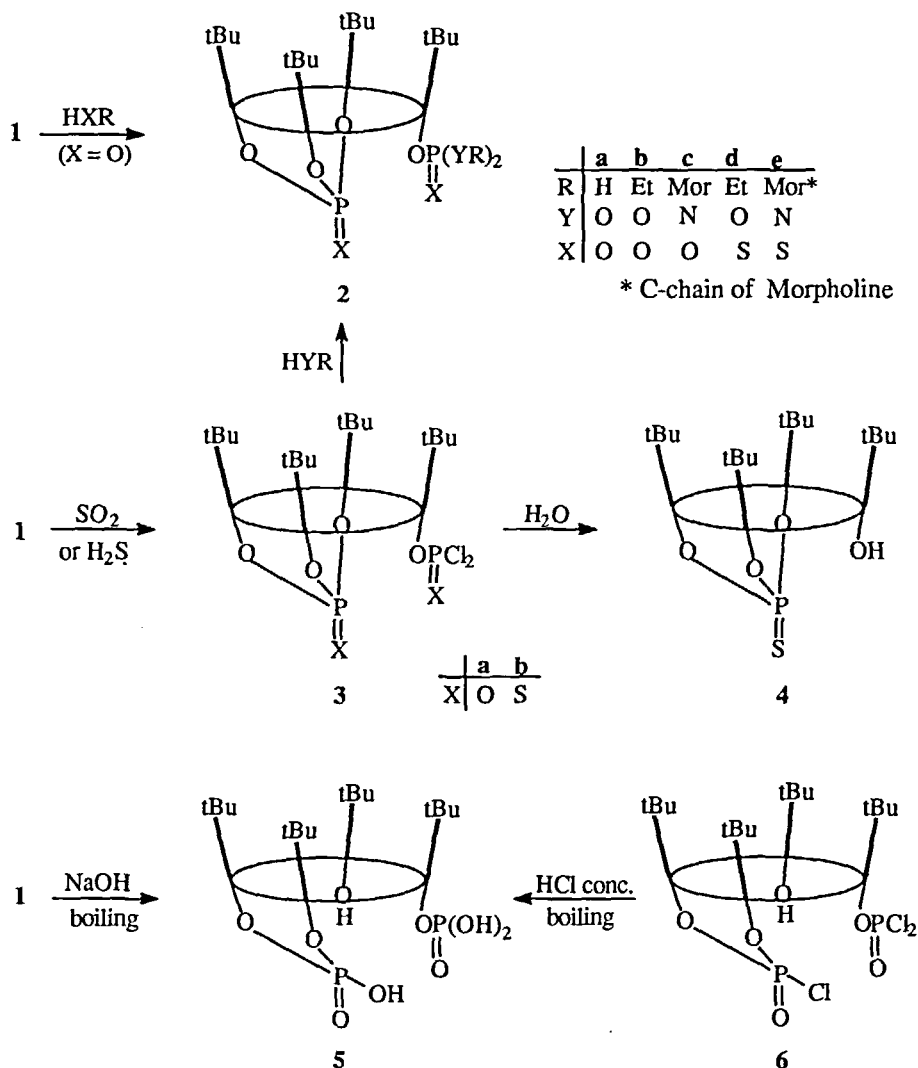
JÖRG GLOEDE, BURKHARD COSTISELLA and KARSTEN GLOE
 Institut für Angewandte Chemie Berlin-Adlershof e.V., Rudower Chaussee 5,
 12489 Berlin, and Institut für Anorganische Chemie, Technische Universität,
 Mommsenstr.13, 01062 Dresden, Germany

Abstract The P-bridged calix[4]arene derivative **1**, formed from tert.butylcalix[4]-arene and phosphorus pentachloride, reacts with water, ethanol, sulfur dioxide, morpholine, hydrogen sulphide and mercaptan to give the new 1,2,3-bridged tert.-butyl-calix[4]-arene diphosphate **2a-c** and **3a**, dithiophosphate **2d**, **2e** and **3b** and mono-thiophosphate **4**. The alkaline hydrolysis of **1** proceeds to the 1,2-bridged calixarene diphosphate **5**, which also is formed by acidic hydrolysis of **6**, obtained from tert.-butylcalix[4]arene and phosphorus oxychloride. The compound **7**, formed from tert.-butylcalix[6]arene and phosphorus pentachloride, reacts with water, ethanol and hydrogen sulphide to give the P-bridged tert.butylcalix[6]arene diphosphate **8a** and dithiophosphate **8b**.

Tert.butylcalix[4]arene¹ reacts with 3 moles phosphorus pentachloride to give the compound **1**.² This P-bridged calixarene derivative has three different P atoms ($\sigma^4\lambda^5$, $\sigma^5\lambda^5$ and $\sigma^6\lambda^5$ phosphorus). **1** is a good starting material for the synthesis of calixarene phosphates and thiophosphates.³



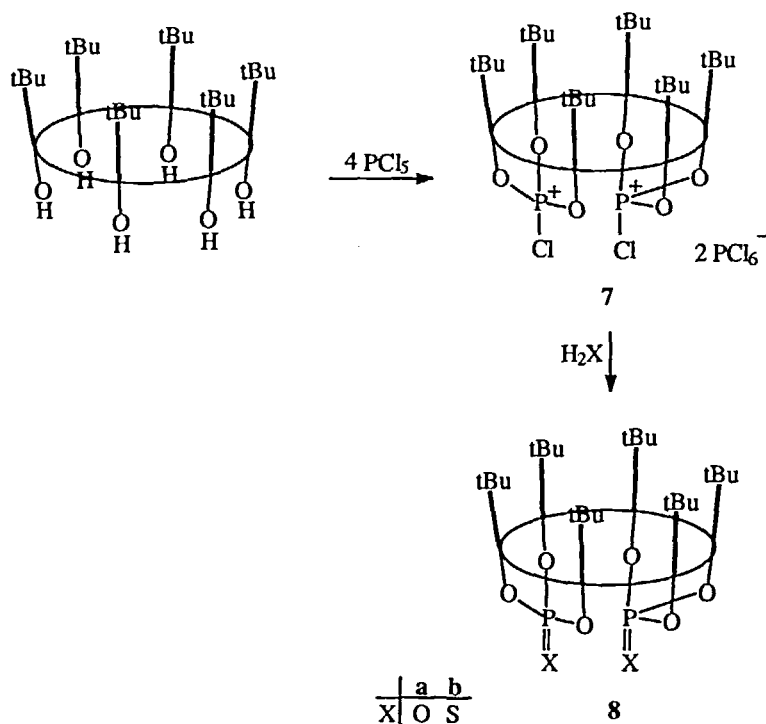
The hydrolysis and the alcoholysis of **1** give the calixarene derivatives **2a** (δ -3,5, -22,3 ppm) and **2b** (δ -6,5, -22,5 ppm). These compounds have a cyclic and an acyclic phosphate group on the lower rim of the calixarene skeleton.



The reaction of **1** with sulfur dioxide proceeds to the dichloride **3a** (δ -2,5, -22,3 ppm), which reacts with water, alcohols and amines to produce the P-bridged calixarene diphosphate **2a**, **2b** and **2c** (δ 7,7, -22,0 ppm) in good yields. The reaction with hydrogen sulphide gives the corresponding dithio-dichloride **3b** (δ 46,9, 53,0 ppm). Its hydrolysis

proceeds under the splitting of the acyclic P-O bond to the monothiophosphate **4** (δ 46,0 ppm). The reaction of **1** with ethyl mercaptan gives **4** (δ 46,9 ppm), as well. The alcoholysis and the aminolysis of **3b** proceeds to the expected dithiophosphate **2d** (δ 46,6, 61,9 ppm) and **2e** (δ 46,1, 67,4 ppm). The X-ray structure investigations shown that the calixarene diphosphates **2b** and **2d** exist in the partial cone conformation in the crystalline state. All 1,2,3-bridged calixarene derivatives (**2**, **3** and **4**) are stable compounds (m.p. 250-350°C) and they shown interesting results by NMR investigations (phosphorus, carbon, oxygen and proton NMR and addition of shift reagent).^{4,5}

The splitting of the P-bridge of **1** is successful when boiled with 1*n* sodium hydroxide solution. The calixarene derivative **5** (δ -3,8, -8,8 ppm) was formed, which has a 1,2-bridge. The acidic hydrolysis of the trichloride **6** (δ 4,1, 1,4 ppm), formed from tert.butylcalix[4]arene and phosphorus oxychloride,⁶ also proceeds to **5**.



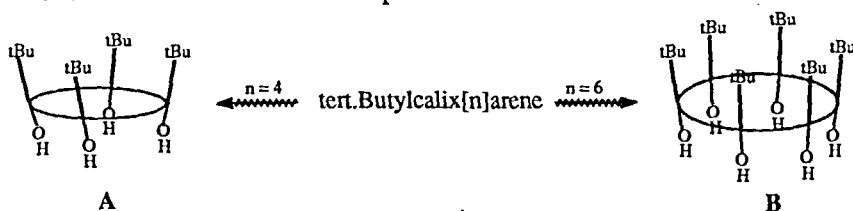
Tert.butylcalix[6]arene reacts with 4 moles phosphorus pentachloride to yield the calixarene derivative **7** (δ 12,7, 10,3, -296 ppm). It is a bis-chlorophosphonium salt with two P-bridges. The hydrolysis of **7** gives the calix[6]arene diphosphate **8a** (δ -22

ppm, m.p. 514°C), which was described by Grynszpan, Aleksuk and Biali,⁷ and the thiolysis with hydrogen sulphide gives the corresponding dithiophosphate **8b** (δ 46 ppm, m.p. 512°C).

The calixarene diphosphates were tested as selective receptors for lanthanides.

REFERENCES AND NOTES

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