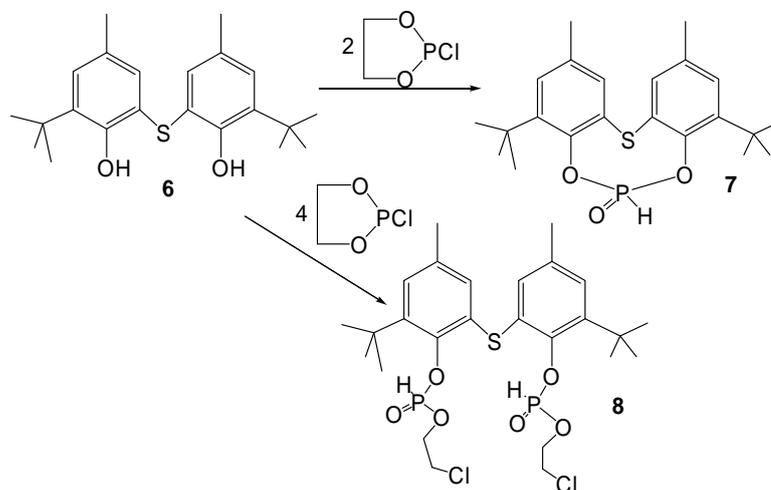


## Phosphorylation of *p*-*tert*-butyl(thia)calixarenes by ethylene chlorophosphite

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The reaction of bisphenol **6** containing sulfur bridged atoms with ethylene chlorophosphite with reagent ratio 1:2 was carried out. As a result, a cyclic phosphonoyl derivative **7** was obtained. However, using a 4-fold excess of phosphorylating reagent leads to the formation of glass-like compound **8**. In a  $^{31}\text{P}$  NMR spectrum of this compound, one signal at 1.6 ppm ( $^1J_{\text{PH}}=730.6$  Hz) is observed which is characteristic of acyclic phosphites. An  $^1\text{H}$  NMR spectroscopy and elemental analysis of this compound allowed us to determine the structure of product **8**. It is interesting to note that using the phosphorylating reagent ethylene chlorophosphite led to a significant increase in the yield of compound **7** in comparison with the known method [V. Kh. Kadyrova, P. A. Kirpichnikov, N. A. Mukmeneva, G. P. Gren and N. S. Kolyubakina, *Zh. Obshch. Khim.*, 1971, **41**, 1688 (in Russian)].



**Compound 7.** The mixture of 0.50 g (1.39 mmol) bis(1-hydroxy-4-methyl-6-*tert*-butylphenyl)sulfide and 0.25 ml (2.78 mmol) ethylene chlorophosphite in 10 ml *p*-bromotoluene in an argon atmosphere was heated with stirring for 6 h at 150 °C. Then the solvent was removed. A pure sample of **7** was obtained by recrystallization of the resulting solid from *n*-hexane. Yield of product **7** 0.50 g (84%), mp 181 °C. Found (%): C, 66.26; H, 7.96; P, 7.10. Calc. for  $\text{C}_{22}\text{H}_{29}\text{O}_3\text{PS}$  (%): C, 65.32; H, 7.23; P, 7.66.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.13 d (1H, P-H,

$^1J_{\text{PH}}=756.7$  Hz), 7.35 s (2H, Ar-H), 7.16 s (2H, Ar-H), 2.29 s (6H, Ar- $\text{CH}_3$ ), 1.39 s (18H, Ar-C( $\text{CH}_3$ ) $_3$ ).  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): -3.3 s ( $^1J_{\text{PH}}=756.7$  Hz).

*2,2'-Bis[hydro(2-chloroethoxy)phosphoryloxy]-3,3'-di(tert-butyl)-5,5'-dimethyl-1,1'-diphenylsulfide* **8**. The mixture of 0.50 g (1.39 mmol) bis(1-hydroxy-4-methyl-6-*tert*-butylphenyl)sulfide and 0.49 ml (5.56 mmol) ethylene chlorophosphite in 10 ml *p*-bromotoluene in an argon atmosphere was heated with stirring for 6 h at 150 °C. Then the solvent was removed. A pure sample of **8** was obtained by recrystallization of the resulting solid from *n*-hexane. Yield of product **8** 0.61 g (68%), mp 65 °C. Found (%): C, 50.55; H, 6.38; P, 9.74. Calc. for  $\text{C}_{26}\text{H}_{38}\text{Cl}_2\text{O}_6\text{P}_2\text{S}$  (%): C, 51.07; H, 6.26; P, 10.13.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.12 d (2H, P-H,  $^1J_{\text{PH}}=730.6$  Hz), 7.33 s (2H, Ar-H), 7.15 s (2H, Ar-H), 3.66-4.32 m (8H, P(O)- $\text{CH}_2$ - $\text{CH}_2$ -Cl), 2.25 s (6H, Ar- $\text{CH}_3$ ), 1.37 s (18H, Ar-C( $\text{CH}_3$ ) $_3$ ).  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 1.6 s ( $^1J_{\text{PH}}=730.6$  Hz).