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High Yield Synthesis of Cyclic Phosphites, Phosphates, Sulphites and Sulphates of Catechol and Glycol Mediated by Hypervalent Silicon Centres

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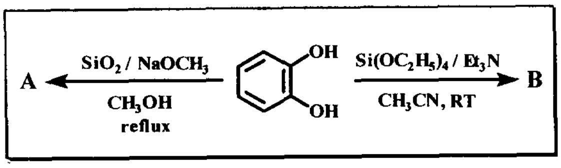
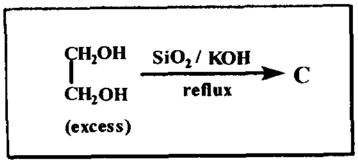
Abstract: Room temperature reactions of both tris(catecholato)silicate, $M_2[Si(o\text{-}C_6H_4O_2)_3]$ {M=Na, Et_3NH} and glycolato silicate, $K_2[Si_2(O_2C_2H_4)_5]$ with PCl_3, $POCl_3$, $SOCl_2$ and SO_2Cl_2 proceed exothermally and afford easy isolation of the corresponding cyclic derivatives of catechol/glycol **(1-8)** in high yield, exemplifying the merit of hypervalent silicon centres in synthesis. $(Et_3NH)_2[Si(o\text{-}C_6H_4O_2)_3]$ afford near quantitative conversions. © 1997 Elsevier Science Ltd.

Recent studies have clearly demonstrated multifaceted[1] interest associated with penta-and hexa-coordinated silicon species(hypervalent compounds). Examples such as catecholato and glycolato silicates have received particular attention due to their ready synthesis[2] starting from cheap and easily available silicon sources viz. silica/silica gel and scope for conversion to useful materials[3]. Besides, sodium and potassium salts of tris(catecholato) silicate have been the subject of several interesting reactions involving a variety of organometallic reagents which have led to the synthesis of silanes and organosilanes[4].

We report in this paper the results of our study on the reactions of three hypervalent silicon species namely $Na_2[Si(o\text{-}C_6H_4O_2)_3]$ **(A)**, $(Et_3NH)_2[Si(o\text{-}C_6H_4O_2)_3]$ **(B)** and $K_2[Si_2(O_2C_2H_4)_5]$ **(C)** with chlorides and oxychlorides of phosphorus and sulphur which interestingly have led to the convenient isolation of organophosphorus and sulphur compounds containing catechol / glycol moiety in high yields.

Reported procedures were slightly modified by taking precisely the stoichiometric amounts of the reagents[2,5] in the present synthesis of $Na_2[Si(o\text{-}C_6H_4O_2)_3]$ **(A)**, $(Et_3NH)_2[Si(o\text{-}C_6H_4O_2)_3]$ **(B)** and $K_2[Si_2(O_2C_2H_4)_5]$ **(C)**. Compound **(B)** was obtained in quantitative yield by a room temperature reaction in acetonitrile of $Si(OC_2H_5)_4$, Et_3N and catechol.





Reaction of **A**, **B** and **C** with the phosphorus and sulphur reagents have been performed as per the general procedure described below.

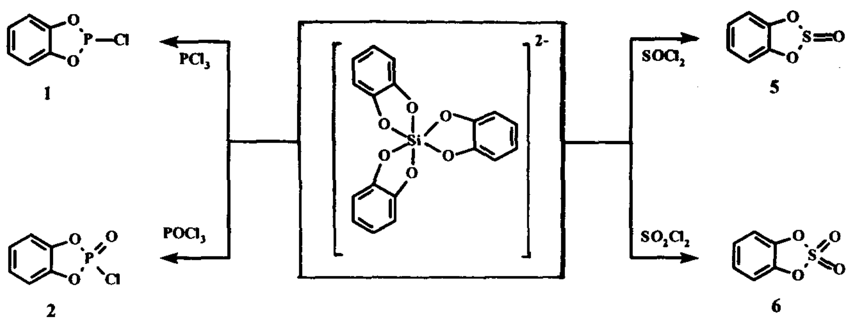
General Procedure: All the reactions were carried out by taking a five fold excess of the phosphorus or sulphur reagent in a side-arm flask and reacting it with the catecholato or glycolato silicate, added at room temperature in small amounts in 15 minutes. After 3 hours of stirring, the contents were filtered and insoluble residue (MCl & SiO_2) was washed with hexane (20 mL). The filtrate along with the hexane washings was pumped off to remove solvent and excess reagent and obtained the cyclic product. The results of all the reactions are given in Table 1.

Table 1. Results of Reactions of (A) (B) and (C) with PCl_3, $POCl_3$, $SOCl_2$, and SO_2Cl_2

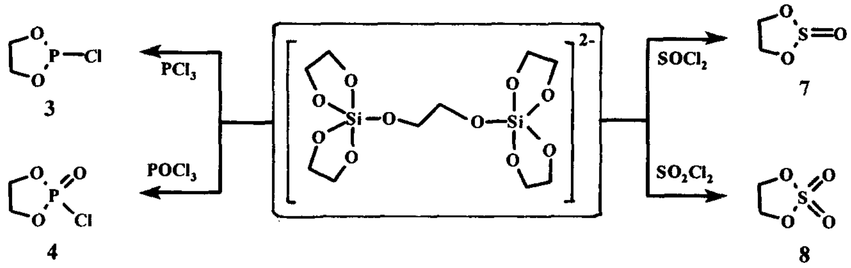
Reagent	Silicon Compound	Compounds isolated	Yield (%)
PCl_3	**A**	**1**	**80**
	B	**1**	**95**
	C	**3**	**80**
$POCl_3$	**A**	**2**	**75**
	B	**2**	**85**
	C	**4**	**60**
$SOCl_2$	**A**	**5**	**75**
	B	**5**	**90**
	C	**7**	**75**
SO_2Cl_2	**A**	**6**	**75**
	B	**6**	**90**
	C	**8**	**70**

i) All the reactions have been performed using 2g of the silicon substrate.
ii) In all the cases, reactants were stirred at room temperature for 3 hours.
iii) Compounds (**1-8**) were characterized on the basis of their physical, spectroscopic (IR, NMR & Mass) and analytical data in some cases which agreed well with the reported data.

Scheme 1 and 2 show various organophosphorus and sulphur compounds synthesized in this study by employing hypervalent silicon compounds. A number of recent reports have highlighted the importance of compounds **1-8** for a variety of purposes viz. polymer precursors and additives[6], surfactants[7], antiviral reagents[8], hydroxy alkylating agents[9], biological model compounds[10] as well as reagents in organic synthesis[11].



Scheme 1



Scheme 2

The merits of the present route for the synthesis of **1-8** are i) faster reaction ii) easier workup procedure and iii) high yield of products (60-95%). The use of (Et$_3$NH)$_2$[Si(o-C$_6$H$_4$O$_2$)$_3$] **(B)** which is synthetically more useful enable the isolation of compounds **1**, **2**, **5** and **6** in near quantitative yield. Reactions performed under neat conditions are found to proceed faster compared to those in presence of solvents (hexane or benzene). The preparation of **1-8** by normal condensation procedure involving catechol and glycol have some difficulties[12].

It may be mentioned that in all the previous study of reactions of **A**, **B** and **C**[4], catechol and glycol moieties were not found to be a part of products isolated which is in contrast to the results obtained in this study. Presumably, the known enhanced reactivity[1] of hypervalent silicon species **A**, **B** and **C** and chlorinating nature of the reagents considered have dictated the course of these reactions.

In conclusion, (C$_6$H$_4$O$_2$)PCl, (C$_2$H$_4$O$_2$)PCl (and their oxides) as well as sulphite and sulphate of catechol and glycol which are highly useful compounds can be made conveniently and in high yield via hypervalent silicon species possessing catechol and glycol moieties.

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