In conclusion, the present method provides a mild and rapid method for the DNA synthesis during the whole synthetic procedure in the phosphothio ester approach using the phenylthio group.

Registry No. **1a**, 94189-75-0; **1b**, 4836-13-9; **1c**, 6711-37-1; **1d**, 86979-56-8; **2a**, 106502-50-5; **2b**, 106469-69-6; **2c**, 106469-70-9; **2d**, 106469-71-0; **3a**, 106469-72-1; **3b**, 106502-51-6; **3c**, 106502-52-7; **3d**, 106502-53-8; **4a**, 106502-55-0; **4b**, 106502-57-2; **4c**, 106502-59-4; **4d**, 106502-61-8; **5a**, 94189-78-3; **5b**, 106469-73-2; **5c**, 106469-74-3; **5d**, 87007-25-8; **6**, 94189-81-8; **7**, 106521-95-3; IDTrOH, 106502-46-9; IDTr-BBF, 106502-49-2; fully protected d-(CpGpGpCpApTpT), 106587-87-5; d(CpGpGpCpApTpT), 106469-75-4.

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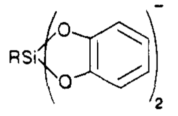
Reduction of Carbonyl Compounds with Pentacoordinate Hydridosilicates[1]

Summary: Bis(diolato)hydridosilicates, derived from trichlorosilane and catechol or 2,2′-dihydroxybiphenyl in THF, can reduce aldehydes and ketones without any catalyst in very high yield. Chemo- and stereoselectivity as well as the structure and reactivity relationship in the reduction is demonstrated.

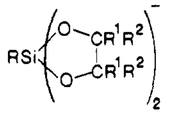
Sir: Hydrosilanes such as alkoxyhydrosilanes[2] and phenyldimethylhydrosilane[3] are capable of reducing carbonyl compounds by nucleophilic catalysis with fluoride ions. Pentacoordinate hydridosilicates $[R_3SiHF]^-$ are postulated frequently as reactive species, although there is no structural proof of the intermediate. Perrozzi and Martin[4] have reported the formation of a pentacoordinate hydridosilicate by the reaction of trichlorosilane ($HSiCl_3$) with the dilithio derivative of hexafluorocumyl alcohol as a hygroscopic high-melting solid which was not analytically pure.

Reduction of carbonyl compounds with pentacoordinate hydridosilicates seemed interesting from both a mechanistic and practical point of view. We report herein a new entry of such species which appeared very useful and interesting.

Among numerous pentacoordinate silicon compounds,[5] Frye was the first to prepare bis(*o*-arenediolato)organosilicate (**1**) and other 1,2-diolato derivatives.[6]



1

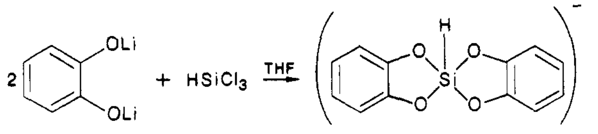


2

R = alkyl or Aryl

Later, Holmes et al. studied detailed structures of a variety of bis(1,2-diolato)silicates,[7] but these works have not extended to the corresponding hydridosilicates. We thought that bis(1,2-diolato)hydridosilicates could be prepared similarly and might behave as a typical pentacoordinate hydridosilicate.

Dilithium catecholate (**3**), prepared by the reaction of catechol and butyllithium in THF, was used to prepare bis(1,2-benzenediolato)hydridosilicate (**4**). Trichlorosilane and **3** were mixed first at −78 °C to give a heterogeneous viscous slurry which was warmed gradually to a slightly turbid solution at about 0 °C. It became a clear solution when it was dissolved in a large excess of THF.



3 4

The solution was unstable at room temperature and all attempts to isolate **4** failed to result in the formation of bis(1,2-phenyldioxy)silane. However, it turns out that **4**

$$R^1COR^2 \xrightarrow[2.\ H_2O]{1.\ 4} R^1R^2CHOH$$

in the solution reduces aldehydes and ketones without any catalyst.

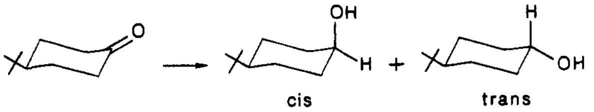
Besides catechol (**5**), 2,2′-dihydroxybiphenyl (**6**) also provides a ligand which produces an effective reducing agent. However, aliphatic diols such as 1,2-ethanediol and pinacol produce reducing agents which are less effective and monoalcohols were totally uneffective to reduce ketones under the conditions.

After standing for 2 h at room temperature, the hydridosilicate (**7**) derived from **6** and trichlorosilane gave cyclohexanol in 96% yield by the reaction with cyclohexanone, while **4** gave the product in 60% yield under the same conditions.

Yields of primary and secondary alcohols are generally excellent, but esters such as methyl benzoate were not reduced. Results are listed in Table I.

Both **4** and **7** predominantly afforded 2-cyclohexenol as the 1,2-reduction product from 2-cyclohexenone. Chemoselectivity in the reduction was also demonstrated by the competitive reduction of a mixture of pentanal and cyclohexanone. The ratios of primary and secondary alcohols were 75/25 for **4** at 0 °C and 79/21 for **7** at room temperature. These are fairly larger than the corresponding value (63/37) from a mixture of butanal and methyl ethyl ketone reduced by $LiAlH_4$ at 25 °C[8] but smaller than those from a mixture of hexanal and cyclohexanone with $LiAlH(O\text{-}t\text{-}Bu)_3$ at 0 °C (87/13)[9] and $LiAlH(OCEt_3)_3$ at 0 °C (94/6).[9]

Stereoselectivity in the reduction of 4-*tert*-butylcyclohexanone was examined with **4** and **7**. Cis and trans alcohols were obtained in ratios of 44/56 and 67/33 with **4** and **7**, respectively.



It is known that the ratio of the cis alcohol to the trans increases when the steric bulkiness of reducing reagents increases. Thus a simple reducing reagent, $LiAlH_4$, gave

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[1] Chemistry of Organosilicon Compounds. 227.

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[7] (a) Holmes, R. R.; Day, R. O.; Harland, J. J.; Sau, A. C.; Holmes, J. M. *Organometallics* **1984**, *3*, 341. (b) Holmes, R. R.; Day, R. O.; Harland, J. J.; Holmes, J. M. *Ibid.* **1984**, 3, 347.

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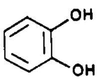
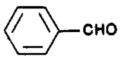
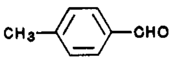
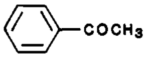
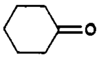
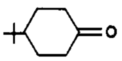
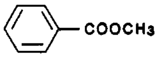
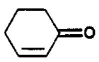
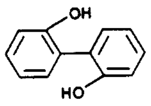
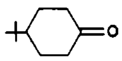
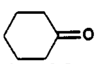
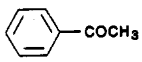
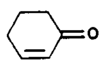
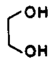
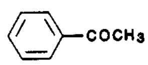
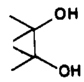
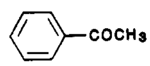
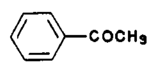
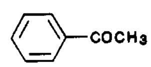
Table I. Reduction of Carbonyl Compounds with Bis(diolato)hydridosilicate

alcohol	carbonyl compd	conditions	% yield[a]
 5		0 °C, 2 h	96
5		0 °C, 2 h	96
5		0 °C, 2 h	98
5		0 °C, 2 h	95
5		0 °C, 2 h	92[b]
5		rt,[g] 12 h	0
5		0 °C, 2 h	85[c]
 6		rt, 5 h	92[d]
6		rt, 5 h	100
6	CH_3CO-n-C_5H_{11}	rt, 5 h	90
6	$(CH_3)_3CCHO$	rt, 5 h	92[e]
6	$(CH_3)_2CHCOCH(CH_3)_2$	rt, 30 h	50[e]
6		rt, 5 h	97
6		rt, 5 h	91[f]
		rt, 12 h	50[e]
		rt, 12 h	50[e]
EtOH		reflux, 24 h	0
PhOH		reflux, 40 h	0

[a] Isolated by TLC or distillation. [b] Cis/trans = 44/56 as determined by GLC. See text. [c] 2-Cyclohexenol was the sole product. [d] Cis/trans = 67/33 as determined by GLC. [e] Determined by GLC. [f] 2-Cyclohexenol/cyclohexanone = 97/3. [g] rt = room temperature.

the alcohol with a cis/trans ratio of 10/90,[10] whereas stereically bulky reducing reagents such as LiAlH(i-Bu)$_2$-t-Bu,[11] NaBH(OCHMe$_2$)$_3$,[10] and LiBH(sec-Bu)$_3$[12] gave the product in ratios of 49/51, 20–25/75–80, and 96.5/3.5, respectively. Judging from these data, 4 and 7 are the reducing reagents of fairly large steric bulkiness.

Next, the structure and reactivity relationship in the reduction was examined with substituted benzaldehydes. To 7 prepared first at −78 °C in THF was added a mixture of benzaldehyde (10 equiv) and a substituted benzaldehyde (10 equiv). After being kept at 26 °C for 5 h, the yields of both unsubstituted and substituted benzyl alcohols were analyzed by GC. The result is shown graphically in Figure 1. Excellent Hammett plots for the relative reactivities were obtained. Very recently, Yang and Tanner have suggested that the single electron transfer (SET)–hydrogen atom abstraction mechanism should be involved in the fluoride ion catalyzed reduction of carbonyl compounds with phenyldimethylsilane.[13] However, an excellent linear Hammett plot with a large positive ρ value (2.3, r = 0.99$_9$) indicates that the hydride transfer step should be involved in the rate-determining step at least in the present system. Further works are in progress.

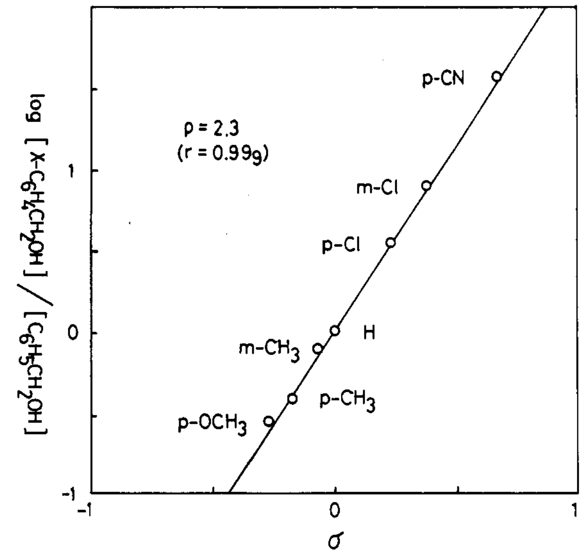


Figure 1. Hammett plots for the reduction of substituted benzaldehydes with bis(biphenyl-2,2′-diolato)hydridosilicate at 26 °C.

Registry No. 4, 106469-05-0; 5, 120-80-9; 6, 1806-29-7; 7, 106469-06-1; HO(CH$_2$)$_2$OH, 107-21-1; HOC(CH$_3$)$_2$C(CH$_3$)$_2$OH, 76-09-5; C$_6$H$_5$CHO, 100-52-7; 4-H$_3$CC$_6$H$_4$CHO, 104-87-0; C$_6$H$_5$COCH$_3$, 98-86-2; C$_6$H$_5$CO$_2$CH$_3$, 93-58-3; H$_3$CCOC$_5$H$_{11}$, 110-43-0; (CH$_3$)$_3$CCHO, 630-19-3; (CH$_3$)$_2$CHCOCH(CH$_3$)$_2$, 565-80-0; C$_6$H$_5$CH$_2$OH, 100-51-6; 4-H$_3$CC$_6$H$_4$CH$_2$OH, 589-18-4; C$_6$H$_5$CH(OH)CH$_3$, 98-85-1; (CH$_3$)$_3$CCH$_2$OH, 75-84-3; (CH$_3$)$_2$CHCH(OH)CH(CH$_3$)$_2$, 600-36-2; H$_3$CCH(OH)C$_5$H$_{11}$, 543-49-7; 4-butylcyclohexanone, 98-53-3; cyclohexanone, 108-94-1; 2-cyclohexen-1-one, 930-68-7; cyclohexanol, 108-93-0; *cis*-4-(1,1-dimethylethyl)cyclohexanol, 67590-15-2; *trans*-4-(1,1-dimethylethyl)cyclohexanol, 675901-13-0; 2-cyclohexen-1-ol, 822-67-3.

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On the Direct Formation of Episulfonium Ions from Alkenes. An Application to the Synthesis of Higher Order Carbocycles via Episulfonium Ion Initiated Polyene Cyclizations

Summary: The use of methyl benzenesulfenate–Lewis acid binary systems for effecting biomimetic polyene cyclizations initiated by episulfonium ions has been demonstrated. The efficiency of higher order annulation is related to the stereostructure of the polyene as well as the nature of the Lewis acid promoter.

Sir: Cationic polyene cyclizations have become widely utilized for the synthesis of naturally occurring ring systems.[1] There are, however, relatively few methods which