Journal of Organometallic Chemistry, 269 (1984) C37—C39
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SILAFUNCTIONAL COMPOUNDS IN ORGANIC SYNTHESIS

XXVI*. SILYL GROUPS SYNTHETICALLY EQUIVALENT TO THE HYDROXY GROUP

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(Received April 24th 1984)

Summary

Oxidative cleavage by H_2O_2 can be applied to alkyl-silicon compounds which contain hydro-, fluoro-, chloro-, amino-, siloxy-, allyl-, and phenyl-silyl groups as well as alkoxysilyl groups.

Alcohol synthesis via oxidative cleavage of the carbon—silicon bond, especially the "unactivated" alkyl—silicon bond [2], must enhance the synthetic utility of organosilicon compounds. We have recently developed the oxidation of organoalkoxysilanes and organofluorosilanes by MCPBA or H_2O_2 [3—6]. Quite recent publications [7,8] dealing with the applications of oxidative cleavage reactions prompted us to report our further development in this field.

We find that H_2O_2-oxidation can also be applied to alkyl-silicon compounds which contain hydro-, fluoro-, chloro-, amino-, siloxy-, allyl-, and phenyl-silyl groups. While the first four compounds can be subjected to the oxidation directly, in the last three compounds, the siloxane, allyl—silicon, and phenyl—silicon bonds must be cleaved by acids prior to the oxidation. Table 1 summarizes the silyl groups which are capable of being converted to a OH group, together with the previous results [5], upon treatment with 30% H_2O_2 under basic conditions in the presence of bicarbonate salts. The GLC yields given in parentheses were observed with n-octyl derivatives. Evidently, we are now in a position to be able to transform most of the common silafunctional groups into a OH group.

Brief comments will be made on the individual case. For R-$SiMe_2H$, R-$SiMe_2F$, R-$SiMe_2(NEt_2)$, and R-$SiMe_2(OR')$, the following general procedure can be employed. To a solution of a silicon compound in MeOH and THF (4 ml each

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*For part XXV, see ref. 1.

TABLE 1

$R\text{—}si \xrightarrow[\text{MHCO}_3{}^{a}]{30\%\ H_2O_2} R\text{—}OH$

si =

$\text{—SiMe}_2\text{H}$ (100%)	$\text{—SiMe}_2\text{F}$ (92%)	$\text{—SiMe}_2\text{Cl}$ (93%)	—SiMeCl_2 (77%)	—SiCl_3 (68%)
$\text{—SiMe}_2(\text{NEt}_2)$ (83%)	$\text{—SiMe}_2(\text{OR}')$ [5] (94%)[b]	$\text{—SiMe(OR}')_2$ [5] (96%)[b]	$\text{—Si(OR}')_3$ (91%)[b]	
$\text{—SiMe}_2\text{OSiMe}_2\text{R}$[c] (72%)	$\text{—SiMe}_2($  $)$[c] (100%)	$\text{—SiMe}_2\text{Ph}$[c] (70%)		

[a] M = Na or K. [b] OR′ = OEt. [c] A two-step procedure should be used (see text).

per 1 mmol) are added successively $KHCO_3$ (1 equiv.) and 30% H_2O_2 (6 equiv. per one Si—C bond) at room temperature. The mixture is refluxed with stirring for 6 h, resulting in the formation of white insoluble solids. To the mixture is slowly added a dilute $NaHSO_3$ solution at 0°C and then the mixture is extracted five times with ether, followed by the usual work-up.

For the chlorosilane series, excess amounts of bicarbonate salt must be used, taking into account the consumption by the neutralization of chlorosilanes. Further, it is recommended that organotrichlorosilanes are treated with methanol and $KHCO_3$ in THF prior to the addition of H_2O_2.

The allyl—silicon bond should be cleaved at first to the fluorosilyl derivative. Thus, the allylsilane is treated with KHF_2 (2 equiv.) and CF_3COOH (3 equiv.) in dry $CHCl_3$ at room temperature [9]. After evaporation of the volatile materials, the resulting fluorosilane is subjected to H_2O_2-oxidation in a single flask.

For the oxidation of siloxanes, essentially the same methods as those given for the allylsilane are employed, except for the necessity of additional $(CF_3CO)_2O$ (6 equiv.) as a dehydrating agent in the acid cleavage of the siloxane bond.

Protodesilylation of the phenylsilane by the same procedures as those given for the allylsilane gave unsatisfactory results. The phenyl—silicon bond should be transformed into the fluoro- or methoxy-silane in two steps via a labile trifluoroacetate by successive treatment with CF_3COOH (5 equiv./50°C/1.5 h [10], followed by evaporation of the volatile materials) and a mixture of KHF_2 (2 equiv.) and MeOH (3 equiv.). Subsequently, the oxidation is carried out in the usual manner. In connection with this procedure, it should be mentioned that Fleming has used $BF_3/2CH_3COOH$ or HBF_4 for the protodesilylation of phenylsilanes [7].

Applications of the present procedures will be reported elsewhere.

Acknowledgements. We thank Emeritus Professor Makoto Kumada for encouragement and Shinetsu Chemical Industrial Co., Ltd. for financial support of this work and for a gift of silicon compounds.

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