

Preliminary communication

SILAFUNCTIONAL COMPOUNDS IN ORGANIC SYNTHESIS

XXVI*. SILYL GROUPS SYNTHETICALLY EQUIVALENT TO THE HYDROXY GROUP

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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 alkoxy-silyl groups.

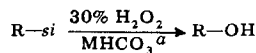
Alcohol synthesis via oxidative cleavage of the carbon—silicon bond, especially the “unactivated” alkyl—silicon bond [2], must enhance the synthetic utility of organosilicon compounds. We have recently developed the oxidation of organo-alkoxysilanes and organofluorosilanes by MCPBA or H_2O_2 [3–6]. Quite 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.

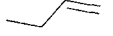
Brief comments will be made on the individual case. For $R-SiMe_2H$, $R-SiMe_2F$, $R-SiMe_2(NEt_2)$, and $R-SiMe_2(OR')$, the following general procedure can be employed. To a solution of a silicon compound in MeOH and THF (4 ml each

*For part XXV, see ref. 1.

TABLE 1



si =

—SiMe ₂ H (100%)	—SiMe ₂ F (92%)	—SiMe ₂ Cl (93%)	—SiMeCl ₂ (77%)	—SiCl ₃ (68%)
—SiMe ₂ (NEt ₂) (83%)	—SiMe ₂ (OR') [5] (94%) ^b	—SiMe(OR') ₂ [5] (96%) ^b	—Si(OR') ₃ (91%) ^b	
—SiMe ₂ OSiMe ₂ R ^c (72%)	—SiMe ₂ () ^c (100%)	—SiMe ₂ 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 KHCO₃ (1 equiv.) and 30% H₂O₂ (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 NaHSO₃ 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 KHCO₃ in THF prior to the addition of H₂O₂.

The allyl—silicon bond should be cleaved at first to the fluorosilyl derivative. Thus, the allylsilane is treated with KHF₂ (2 equiv.) and CF₃COOH (3 equiv.) in dry CHCl₃ at room temperature [9]. After evaporation of the volatile materials, the resulting fluorosilane is subjected to H₂O₂-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 (CF₃CO)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 CF₃COOH (5 equiv./50°C/1.5 h [10], followed by evaporation of the volatile materials) and a mixture of KHF₂ (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 BF₃/2CH₃COOH or HBF₄ for the protodesilylation of phenylsilanes [7].

Applications of the present procedures will be reported elsewhere.

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