

**Supersilylsilanes  $R^*SiX_3$ ; Cyclosilanes  $R^*X_2Si-SiX_2R^*$ ,  
Silylene  $R^*XSi$ , Cyclosilane  $(R^*XSi)_n$ , Disilene  $R^*XSi=SiXR^*$ ,  
Tetrasupersilyl-tetrahedro-tetrasilane [1]**

Supersilylsilanes  $R^*SiX_3$ ; Conversion into Disilanes  $R^*X_2Si-SiX_2R^*$ ,  
Silylenes  $R^*XSi$ , Cyclosilanes  $(R^*XSi)_n$ , Disilenes  $R^*XSi=SiXR^*$ ,  
Tetrasupersilyl-tetrahedro-tetrasilane [1]

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Silicon, Disilanes, Silylenes

*Supersilylmonohalosilanes*  $R^*RSiHCl$  ( $R^* = \text{Supersilyl} = \text{Si}t\text{Bu}_3$ ) react with Na in  $C_6H_6$  at  $65^\circ C$  or with  $NaC_{10}H_8$  in THF at  $-78^\circ C$  with formation of disupersilyldisilanes  $R^*RHSi-SiHRR^*$  in quantitative ( $R = H, Me$ ) or moderate yields ( $R = Ph$ ). In the latter case,  $R^*PhSiH_2$  is obtained additionally at  $65^\circ C$  (exclusively with Na in THF at  $65^\circ C$ ). Obviously, the supersilylsilanides  $NaSiHRR^*$  are generated as intermediates which react with educts  $R^*RSiHCl$  with NaCl elimination and formation of  $R^*RHSi-SiHRR^*$  ( $R = H, Me$ ) or  $R^*RSiH_2$  and  $R^*RSi$  ( $R = Ph$ ). The silylene intermediate  $R^*PhSi$  inserts into the SiH-bonds of the educt  $R^*PhSiHCl$  and of the product  $R^*PhSiH_2$  with formation of the disupersilyldisilanes  $R^*PhSiH-SiClPhR^*$  and  $R^*PhSiH-SiHPhR^*$  which are reduced by Na at  $65^\circ C$  to  $R^*PhSiH_2$  (and by  $NaC_{10}H_8$  at low temperatures to give  $R^*PhSiH-SiHPhR^*$ ). The addition of  $NaR^*$  to  $R^*RSiHCl$  in THF at low temperatures leads with NaCl elimination to  $R^*_2RSiH$  ( $R = H, Me$ ) or to  $R^*RHSi-SiHRR^*$  ( $R = Me$ ) besides  $R^*Cl$ , or to  $R^*RHSi-SiClRR^*$  ( $R = Ph$ ) besides  $R^*H$  and  $NaR$ , whereas the addition of  $R^*PhSiHCl$  to  $NaR^*$  in THF at low temperatures results in the formation of  $NaSiPhR^*_2$  besides  $R^*H$  and  $NaCl$ . In the latter cases ( $R = Ph$ ),  $NaR^*$  react with  $R^*PhSiHCl$  to release the silylene  $R^*PhSi$ , the transitory existence of which could be proven by trapping it with  $Et_3SiH$  (formation of  $R^*Ph(Et_3Si)-SiH$ ). Subsequently,  $R^*PhSi$  inserts into the SiH bond of  $R^*PhSiHCl$  (addition of  $NaR^*$  to  $R^*PhSiHCl$ ) or into the NaSi bond of  $NaR^*$  (addition of  $R^*PhSiHCl$  to  $NaR^*$ ). – *Supersilyldihalosilanes*  $R^*SiHCl_2$  are converted by Mg in  $C_6H_6$  at  $65^\circ C$  into cyclosilanes  $(R^*SiH)_n$  ( $n = 3, 4$ ) and  $R^*PhSiBrCl$  by Na at low temperatures – via the silylene  $R^*PhSi$  – into the disilene  $R^*PhSi=SiPhR^*$ , which is reduced by excess Na to an anion radical. – *Supersilyltrihalosilanes*  $R^*SiBr_2Cl$ ,  $R^*SiBr_3$  and  $R^*SiI_3$  react with Na,  $NaC_{10}H_8$  or  $NaR^*$  in THF with formation of tetrasupersilyl-tetrahedro-tetrasilane  $(R^*Si)_4$  in quantitative yields, whereas the reactions of  $R^*SiCl_3$  with  $LiC_{10}H_8$  in THF at  $45^\circ C$  lead to  $(R^*Si)_4$  only in moderate yields. Obviously, the tetrahedrane is formed from  $R^*SiHal_3$  via  $R^*SiHal_2Na$  and  $R^*HalSi=SiHalR^*$  as reaction intermediates. The results lead to the following conclusions: (i) Silylenes play a rôle in dehalogenation of “sterically overloaded” supersilylhalosilanes  $R^*R_{3-n}SiHal_n$ . – (ii) A straight-forward procedure for a high-yield synthesis of  $(R^*Si)_4$  from easily available educts consists in supersilanidation of  $SiH_2Cl_2$  with  $NaR^*$ , bromination of the formed supersilylsilane  $R^*SiH_2Cl$  with  $Br_2$  and dehalogenation of the bromination product  $R^*SiBr_2Cl$  with Na.