

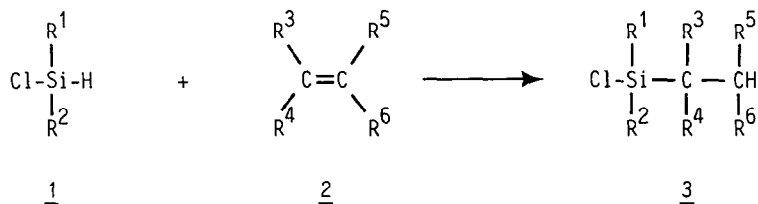
HYDROSILYLATION OF TETRASUBSTITUTED OLEFINS

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Summary: Tetrasubstituted olefins are hydrosilylated under very mild conditions with dimethyl- or butylmethylchlorosilane and aluminium chloride as catalyst. Application of this procedure to 2,3-dimethyl-2-butene yields thexyldimethylsilyl chloride, a new silicon based protective group reagent.

The widespread use of hindered triorganosilyl groups such as tert-butyldimethylsilyl ¹, tert-butyldiphenylsilyl ² or triisopropylsilyl ³ derivatives for the purpose of masking hydroxyl functions stems from the stability of the silyl ethers towards a multitude of functional group transformations together with the possibility of their specific and mild removal by either fluoride ion or aqueous acid ⁴. However, the preparation of the corresponding silylating agents - silyl chlorides or silyl triflates - either requires the use of hazardous tert-butyllithium ^{1,2} or is a twostep process ^{3,5}.

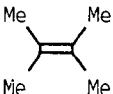
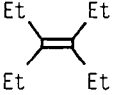
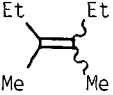
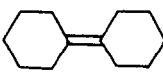
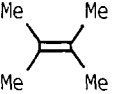
In this and the accompanying letter we report on an easy and innocuous preparation of a silylating agent and its usefulness for the protection of various functional groups. In order to obtain the hydrolytic stability desired for silyl ethers ⁶ the dimethylsilyl group has to carry a third alkyl substituent which is attached to the silicon by a quarternary C-atom. Reaction of chlorosilanes 1 with tetrasubstituted olefins 2 to the corresponding chlorosilanes 3 was therefore investigated.



Hydrosilylation of olefins is known to proceed under a great variety of reaction conditions. The process is initiated not only thermally ^{7a,b} but also with catalysts such as radical initiators ^{7a,b}, bases ^{7a,b}, Lewis acids (e.g. BCl₃, B(OH)₃, AlCl₃) ^{7a,c} or

transition metals (eg. Ni, Pd, Pt, Co, Rh, Ir) ^{7a,b}. The hydrosilylation of tetrasubstituted olefins with dialkylchlorosilanes has not been described previously ⁸. However, we found that tetrasubstituted olefins react with dialkylchlorosilanes in the presence of a catalytic amount of aluminium chloride, as shown in Table 1.

Table 1: Hydrosilylation of Tetrasubstituted Olefins ^a

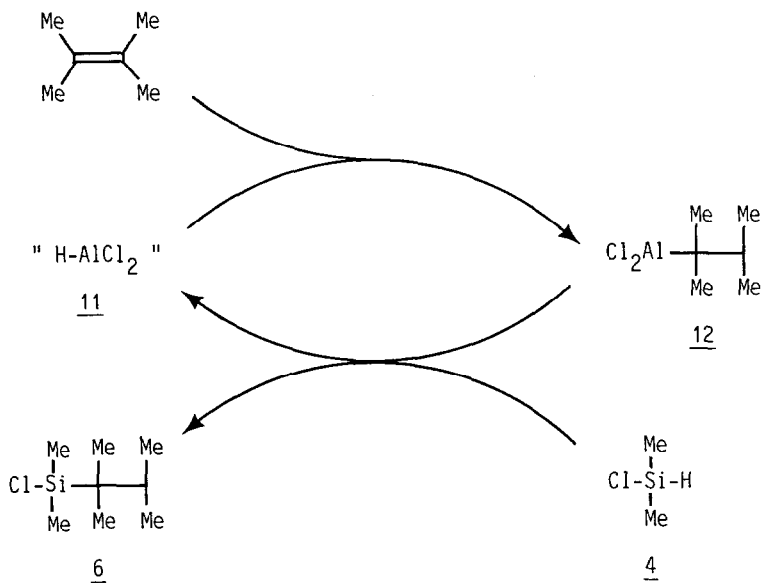
Silanes	Olefins ⁹	Products (% yield ^b)
$\begin{array}{c} \text{Me} \\ \\ \text{Cl-Si-H} \\ \\ \text{Me} \\ \underline{4} \end{array}$		$\begin{array}{c} \text{Me} \quad \text{Me} \quad \text{Me} \\ \quad \quad \\ \text{Cl-Si} - \text{C} - \text{C} \\ \quad \quad \\ \text{Me} \quad \text{Me} \quad \text{Me} \\ \underline{6} \end{array} \quad (93 \%)$
$\underline{4}$		$\begin{array}{c} \text{Me} \quad \text{Et} \quad \text{Et} \\ \quad \quad \\ \text{Cl-Si} - \text{C} - \text{C} \\ \quad \quad \\ \text{Me} \quad \text{Et} \quad \text{Et} \\ \underline{7} \end{array} \quad (80 \%)$
$\underline{4}$		$\begin{array}{c} \text{Me} \quad \text{Et} \quad \text{Et} \\ \quad \quad \\ \text{Cl-Si} - \text{C} - \text{C} \\ \quad \quad \\ \text{Me} \quad \text{Me} \quad \text{Me} \\ \underline{8} \end{array} \quad (50 \%)$
$\underline{4}$		$\begin{array}{c} \text{Me} \quad \text{C}_6\text{H}_{11} \quad \text{C}_6\text{H}_{11} \\ \quad \quad \\ \text{Cl-Si} - \text{C} - \text{C} \\ \quad \quad \\ \text{Me} \quad \text{C}_6\text{H}_{11} \quad \text{C}_6\text{H}_{11} \\ \underline{9} \end{array} \quad (67 \%)$
$\begin{array}{c} \text{Bu} \\ \\ \text{Cl-Si-H} \\ \\ \text{Me} \\ \underline{5} \end{array}$		$\begin{array}{c} \text{Bu} \quad \text{Me} \quad \text{Me} \\ \quad \quad \\ \text{Cl-Si} - \text{C} - \text{C} \\ \quad \quad \\ \text{Me} \quad \text{Me} \quad \text{Me} \\ \underline{10} \end{array} \quad (80 \%)$

^a Reaction conditions: no solvent; 5% to 10% AlCl_3 ; 25°C.

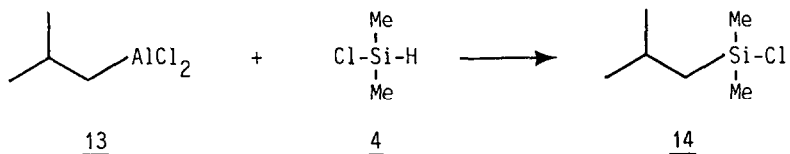
^b Yields of isolated products purified by distillation. IR, 250 MHz-NMR and MS spectra were fully consistent with the assigned structures.

The preparation of tetryldimethylsilyl chloride (6)¹⁰ demonstrates the simplicity of the hydrosilylation reaction: To a mixture of dimethylchlorosilane (10 ml, 92 mmol) and aluminium chloride (680 mg, 5 mmol) was added at 25°C 2,3-dimethyl-2-butene (11 ml, 91 mmol). After stirring for 4 hrs at ambient temperature the reaction mixture was filtered and distilled: 15,2 g (93%) 6¹¹.

We propose a mechanism that runs via the two catalytic intermediates 11¹² and 12.



The second step of the catalytic cycle, the alkyltransfer from aluminium to silicon, is supported by our observation that isobutyldichloroalane (13) reacts with 4 to produce isobutyldimethylchlorosilane (14) in 50% yield.



Further studies to corroborate the mechanism are in progress. The application of tetryldimethylsilyl chloride (TDS-Cl) for the protection of functional groups and the stability of the corresponding silyl derivatives are described in the accompanying paper¹³.

References and Notes

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10. The hexyl group = 2,3-dimethyl-2-butyl, using the nomenclature of Brown, H.C. "Boranes in Organic Chemistry", Cornell University Press, 1972.
11. Colourless liquid, bp. 55-56°C/10 Torr; $^1\text{H-NMR}$ (250 MHz, CDCl_3): 0,44 (s, 6H, Me_2Si); 0,94 (d, J = 6Hz, 6H, Me_2CH); 0,96 (s, 6H, Me_2C); 1,74³(m, 1H, HC) ppm.
12. Based on known AlCl_3 catalysed redistribution and disproportionation reactions of alkylchlorosilanes (ref. 14) it is assumed that " HAlCl_2 " is formed by the reaction of HSiClMe_2 with AlCl_3 .
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