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REGIOSELECTION IN THE HYDROFORMYLATION OF t-BUTYLDIPHENYLSILYLALKENES: A NEW APPROACH TO ALDOL SYNTHESIS

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Summary

Hydroformylation of (Z)-alkenes bearing a t-butyldiphenylsilyl group (TBDPS) yields, almost exclusively, β-silylaldehydes and the methodology has been used to establish a new aldol synthesis.

Recently, we established that a sterically demanding silyl substituent efficiently directs the Ni(O)-catalysed hydrocyanation of alkynes.[1] In this letter, we show that similar control is possible in the Rh(O)-catalysed hydroformylation of alkenes. A series of t-butyldiphenylsilylalkenes was hydroformylated and the results are summarised in the Table.

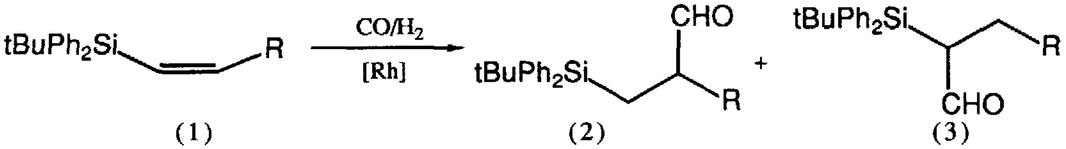
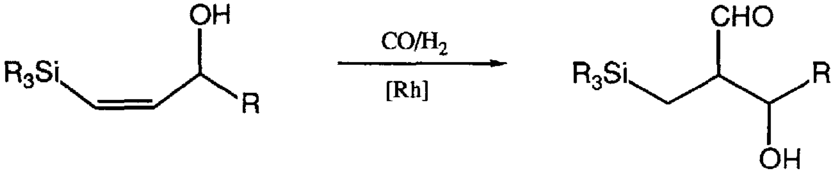


Table: Hydroformylation of t-butyldiphenylsilylalkenes (1)[a]

Entry	Alkene(1;R=)	Time(h)	Temp(°C)	(2):(3)	%Yield
1	1a Bu	94	80	96:4	80
2	1b CH_2OMe	6	50	97:3	73[c]
3	1b CH_2OMe	20	50	97:3	83[b]
4	1c CH_2OSiMe_3	20	70	>98:2	70
5	1d CH(OMe)Me	20	80	>98:2	17
6	1e CH(OH)Me	20	80	>98:2	35
7	1e CH(OH)Me	66	80	>98:2	83
8	1f Ch(OH)Pr	90	80	>98:2	51

a Reactions carried out in benzene using $RhH(CO)(PPh_3)_3$,Ph_3P, CO/H_2(1:1)(400psi), catalyst: ligand: substrate ratio 1:50:300. b 60 equiv of Et_3N added. c See text for discussion of by-products.

In all cases the t-butyldiphenylsilyl group provided excellent regiocontrol, with most reactions providing β-silylaldehydes in high yields. The branched ether, 1d, (entry No. 5) reacted very sluggishly, suggesting that this system is prevented from binding to the metal by steric hindrance. However, the corresponding alcohol, 1e, (entry Nos. 6 and 7) gave high yields of the aldol product with longer reaction times.



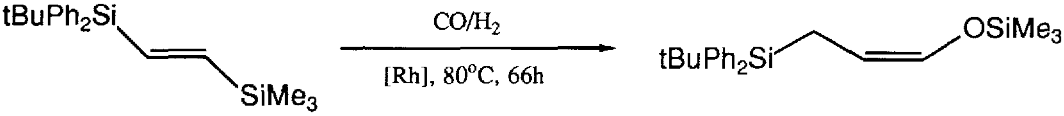
(1e) (2e)

The homologous alcohol, 1f, gave only a moderate yield (entry No. 8) due to a competing retro-aldol reaction of the product.

Unfortunately, no diastereoselection was observed where a chiral substituent was present (entries 5 to 8) but reactions of alkenes bearing other substituents are under investigation. Rearrangement of the starting alkene was a problem only in the case of 1b, which produced, along with recovered starting material, aldehyde 2b (73%) and (Z)-t-$BuPh_2SiCH_2CH=CHOMe$ (12%) (entry No. 2). This rearrangement could be suppressed by the inclusion of triethylamine in the reaction cleanly providing β-silylaldehyde 2b in 83% yield (entry No. 3).

In contrast to the nickel(O) catalysed hydrocyanation of alkynes[1], other, less bulky, silyl substituents e.g. Me_3Si, Ph_3Si and $^tBuMe_2Si$, gave unsatisfactory regiocontrol. Exceptions were for reactions of styrene derivatives. Thus reactions of (Z)- or (E)-β-trimethylsilylstyrene gave exclusively the branched aldehyde in good yields (>80%). These reactions appear to be mainly under electronic control as hydroformylation of styrene itself under these conditions also gave predominantly the branched aldehyde (yield >90%) with ca 90% of branched aldehyde.[2]

In cases where carbonylation occurred at the carbon atom α- to silicon the α-silylaldehyde was converted, in situ, to the corresponding silylenol ether. Thus, hydroformylation of (E)-1-(t-butyldiphenylsilyl)-2-trimethylsilylethene (4) gave the (Z)-silylenol ether (5) in 60% yield. Such rearrangements are known to occur at higher temperatures.[3] This last reaction also illustrates the unique regioselection conferred on the hydroformylation of a 1,2-bis-silylalkene by steric effects.



(4) (5)

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