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THE MECHANISM OF NUCLEOPHILIC SUBSTITUTION AT SILICON: SOLVENT INFLUENCE ON THE RATES OF ORGANOMETALLIC–ORGANOSILANE COUPLING REACTIONS

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Summary

Kinetic studies of coupling reactions of Grignard reagents with organosilane derivatives (Si—F, Si—OMe) in ether, tetrahydrofuran and dimethoxyethane show that the rate increases in the order Et_2O < THF < DME. The retention of configuration at silicon in these reactions cannot be explained by the S_Ni—*Si* mechanism involving electrophilic assistance at silicon.

In a preliminary communication [1] we discussed the rate differences in nucleophilic substitution reactions of functionally substituted silicon compounds (F, Cl, OMe, H). The results showed that for reactions occurring with configurational retention the rates were of the same order with only a slight dependence on the nature of the leaving group Si—X. We explained this by the slow formation of a pentacoordinated silicon compound, followed by rapid cleavage of the Si—X bond. We prefer this mechanism to that of S_Ni—*Si* [2] in which the reaction driving force is electrophilic assistance to the Si—X bond cleavage.

S_Ni–Si

A number of our stereochemical results [3] confirm our view that electrophilic assistance for the Si—X bond breaking is not an important factor in the substitution reaction mechanism for carbon nucleophiles. This is illustrated by a few examples as follows from the reactions studied [3]:

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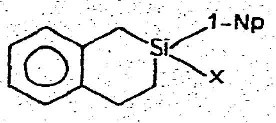
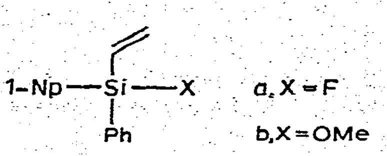
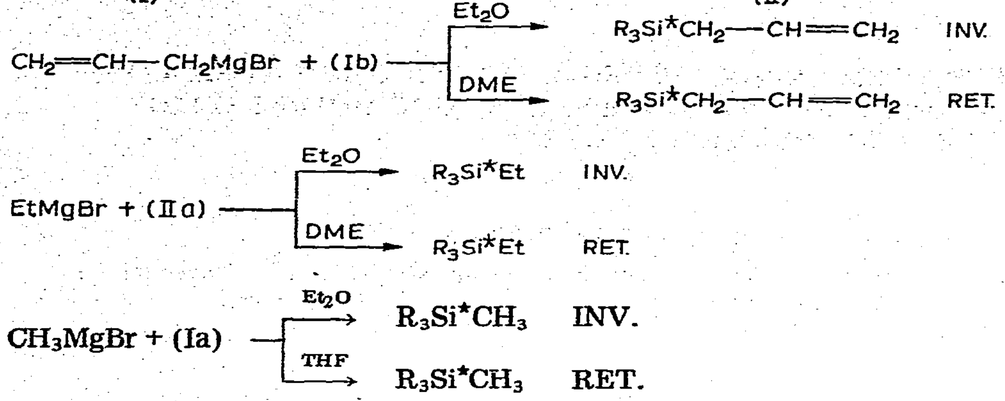


(I)



(II)



(THF: tetrahydrofuran; DME: 1,2-dimethoxyethane).

These results show a change towards retention stereochemistry with increasing solvent basicity. In the S_N *i—Si* mechanism a more basic solvent, giving greater solvation, should lower the ability of the magnesium atom to give electrophilic assistance. Thus such a solvent should not favour retention of configuration at silicon. The S_N *i—Si* mechanism, involving electrophilic assistance as the driving force, does not satisfactorily explain substitution by carbon nucleophiles.

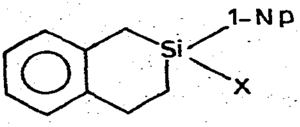
We emphasise the restriction to carbon nucleophiles (RMgX, RLi). In fact for reactions of $LiAlH_4$ with a menthoxygermane [4] and reduction of silicon derivatives by $(i\text{-}Bu)_2AlH$ [5], one observes a tendency towards configurational inversion with increasing solvating power of the solvent. The results show the complexity of a general mechanism for nucleophilic substitution at silicon: according to the nature of the attacking atom (C or H) in the nucleophilic reactant, an increase in the solvating power of the solvent can favour either retention or inversion of configuration.

In order to verify our hypothesis we have studied the rate as a function of the solvent in Grignard coupling reactions with Si—X (X = F, OMe). We chose reactions which occur with retention of configuration at silicon, in view of our postulate that the reaction rate should increase with an increasing solvating ability of the solvent. In contrast, with electrophilic assistance as the driving force (S_N *i—Si*), we should observe a decrease or just a slight increase in rate with increasing solvent basicity. We therefore studied the rates of reaction of the silicon derivatives (I) and (II) with a number of Grignard reagents. The reactions occur with predominant retention of configuration in the solvents diethyl ether, tetrahydrofuran and dimethoxyethane (Et_2O, THF, DME). The experimental results are given in Table 1.

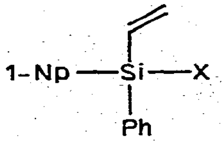
The Grignard reagent was used in large (20-fold) excess in order to keep its concentration effectively constant during the reaction. Our study of competitive reactions [1] showed that in the case of configurational retention the

TABLE 1

STEREOCHEMISTRY AND RATES OF REACTION OF ORGANOSILANE DERIVATIVES WITH GRIGNARD REAGENTS IN VARIOUS SOLVENTS



(Ia), X = F
(Ib), X = OMe



(IIa), X = F
(IIb), X = OMe

Reactant (0.02 mol/l)	Organometallic[a] (0.4 mol/l)	Stereochemistry[b]		Absolute rate[c]	k_{THF}/k_{Et_2O}	k_{DME}/k_{THF}	k_{DME}/k_{Et_2O}
(Ia)	n-PrMgBr	Et_2O	RET.	6×10^{-4}	75	24	1800
		THF	RET.[b]	4.5×10^{-2}			
		DME	RET.[b]	1.1			
(Ia)	n-BuMgBr	Et_2O	RET.	6×10^{-4}			≈1300
		DME	RET.[b]	≈ 0.8			
(Ia)	i-BuMgBr	Et_2O	RET.[b]	2.8×10^{-4}	39	14	500
		THF	RET.[b]	1.1×10^{-2}			
		DME	RET.[b]	0.15			
(Ib)	n-PrMgBr	Et_2O	RET.	4.7×10^{-4}	10	120	1200
		THF	RET.[b]	4.9×10^{-3}			
		DME	RET.[b]	0.6			
(Ib)	n-BuMgBr	Et_2O	RET.	2.7×10^{-4}	13	108	1400
		THF	RET.[b]	3.5×10^{-3}			
		DME	RET.[b]	0.38			
(Ib)	i-BuMgBr	Et_2O	RET.[b]	1.7×10^{-5}	3	40	120
		THF	RET.[b]	5.3×10^{-5}			
		DME	RET.[b]	2×10^{-3}			
(IIb)	n-PrMgBr	Et_2O		1×10^{-5}	8	20	170
		THF	RET.	8.3×10^{-5}			
		DME	RET.	1.7×10^{-3}			
(IIa)	n-PrMgBr	Et_2O	INV.	1.7×10^{-4}	36	2.8	100
		THF	RET.				
		DME	RET.	1.7×10^{-2}			
(IIa)	n-BuMgBr	Et_2O	INV.	$\approx 5 \times 10^{-5}$			200-300
		DME	RET.	$\approx 1 \times 10^{-2}$			
(IIa)	BenzMgCl	Et_2O	INV.	5.4×10^{-4}	215	≥50	$\geq 10^4$
		THF	INV.	0.11			
		DME	INV.	≥ 5			

[a] Pr, propyl; Bu, butyl; Benz, benzyl. [b] Stereochemistry deduced from known stereochemistries.
[c] All results given in $\min^{-1}$ $(\text{mole/l})^{-n}$ using log 10.

substitution reaction is first order in the silicon derivative.

For all the Grignard reagents used, whether there is retention or inversion, or a transition from one to the other, a rate increase is observed on passing from Et_2O to THF to DME. In the case of derivatives (Ia) and (Ib), which react with retention, the speed increases as a function of the solvating power of the solvent. The reaction of compound (IIa) with n-C_3H_7MgBr shows a stereochemistry change between Et_2O (INV) and THF (RET), however, the rate of substitution also decreases in the order: DME > THF > Et_2O. The same order is found for the reaction with configurational inversion of (IIa) with $PhCH_2MgCl$ in the three solvents used.

Increasing the solvent basicity leads to a higher rate increase for the change between THF and Et_2O for Si—F; for SiOMe the larger increase is from DME to THF. It must be concluded that the leaving group polarisability influences the reaction rate.

In conclusion the large rate increase for nucleophilic substitution at silicon with the increasing solvating power of the medium confirms our previous results [1]. Thus electrophilic assistance is not the substitution reaction driving force for carbon nucleophiles. The mechanism involves a slow nucleophilic attack leading to formation of a pentacoordinated silicon intermediate.

Experimental

The reactions were carried out in a three-necked flask fitted with stirrer, condenser and septum cap, under a positive pressure of nitrogen (dried by passage though a Grignard solution). The temperature was kept at 25° in a thermostat bath.

GLC apparatus

GIRDEL 75 FHI equipped with a capillary column (20 m × 0.5 mm) packed with OV 17 silicones. Column temperature 190-230°, nitrogen flow rate $\simeq$ 4 ml/mm.

GLC measurements

The sampling technique was by peak height measurement using an internal standard for the reference height. This reference height was the same for any one kinetic run, as determined by interpolation of the values from two different injections for each measurement. The method has the advantage of only considering the concentration to be a linear function of the peak height between the two measured values. For each reaction two standard points were used to plot relationship $|C| = f(h)$ where C is the product concentration and h its peak height.

Solvents

THF and DME were distilled from $LiAlH_4$ under nitrogen and stored for short periods, in the dark, under nitrogen.

Reactants

Derivatives of 1-naphthyl-2-sila-2-tetrahydro-1,2,3,4-naphthalene were prepared as previously described [6], as were derivatives of 1-naphthylphenylvinylsilane [7].

Grignard reagents were prepared under nitrogen by the normal method.

Typical reaction

(Ia) + n-propylmagnesium bromide/Et_2O (25°). [n-Propylmagnesium bromide] 0.4 mole·l^{-1}; [Si—F] 0.02 mole·l^{-1}; total volume 50 ml. 2×10^{-2} mole n-propylmagnesium bromide, i.e. 10.5 ml 1.9 M + 19.5 ml Et_2O; 1×10^{-3} mole Si—F, i.e. 292 mg (292.20 mg) + 20 ml Et_2O.

TABLE 2. GLC DATA

Time (min)	h_E (cm)	h_F (cm)	h_F^S (cm)	[F] ($\times 10^3$)	$\frac{[F_0]}{[F]}$	$\log_{10} \frac{[F_0]}{[F]}$	k min^{-1} (mole/l)$^{-n}$
2	13.6	15.55	13.4	18.4			
	11.4	12.6					
30	13.25	14.2	12.8	17.6	1.045	0.01912	6.8×10^{-4}
	11.05	11.8					
90	12.85	12.4	11.6	16.1	1.143	0.05805	6.6×10^{-4}
	10.8	10.35					
180	13.25	11.2	10.0	14.0	1.314	0.11860	6.7×10^{-4}
	11.55	9.6					
360	13.4	8.35	7.45	10.75	1.712	0.23350	6.5×10^{-4}
	11.3	7.05					
E_1	12.65	15.8	14.9	20.3		Average	6.6×10^{-4}
	10.65	13.0					
E_2	13.3	7.5	6.7	9.3		Standard height	
	11.35	6.3				12 cm	

Sampling: 1 ml in [20 ml 0.2 *N* HCl + 3 ml Et_2O] + 1 ml Ph_3SiAll (2 g/l; standard); one extraction with 2 ml Et_2O. The ether phase was dried over Na_2SO_4 and injected into the GLC (Oven 230°; Inj. 280°). Standard points: E_1 29.63 mg/5 ml; E_2 14.36 mg/5ml. E_1 and E_2: same treatment as the samples. See Table 2 for data.

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