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THE SYNTHESIS OF ALKENES FROM CARBONYL COMPOUNDS AND CARBANIONS α TO SILICON. VIII: REGIOSELECTIVITY IN THE REACTIONS OF 1-TRIMETHYLSILYLALLYL CARBANION AND THE SYNTHESIS OF 1,3-DIENES[1].

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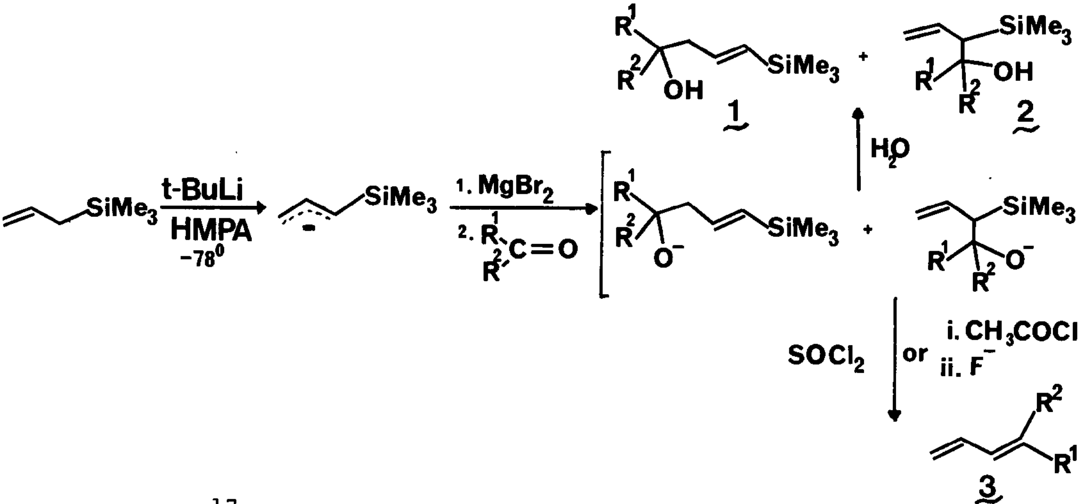
Olefination of aldehydes and ketones with α-silyl carbanions has been developed into a reaction of considerable scope[2-4]. Stereochemical control of the reaction can now be achieved with some degree of certainty[5-8]. Various functionalized carbanions[9,10] could be employed and the reaction is thus quite useful for the synthesis of substituted olefins[1,4]. One problem which has not been resolved is the control of regioselectivity in the reactions of α-silylallyl carbanions with aldehydes and ketones. It has been found by several groups[11-14] that α-silylallyl carbanions reacted with carbonyl compounds to give exclusively the γ-products. The regioselectivity did not appear to be affected by the substituents on silicon, the counter ion, the solvent, nor for that matter, the carbonyl compounds. This precluded the conversion of carbonyl compounds into 1,3-dienes by the subsequent β-elimination of R_3SiO^-.

We have now found reaction conditions which permit 1-trimethylsilylallyl carbanion to react with aldehydes and ketones giving regioselectively the α-products (**2**). Thus, to a stirred solution of allyltrimethylsilane (2mmol) in 10 ml tetrahydrofuran at -78°, a solution of t-butyllithium (2.1 mmol, 1.8M in n-pentane) (or n-butyllithium) was added dropwise. This was followed by the addition of 0.5 ml hexamethylphosphoramide (or TMEDA) and the reaction mixture was stirred at -78° for 2 hrs. To the mixture, a solution of freshly prepared magnesium bromide (4 mmol, in 30 ml either and 10 ml benzene)[15] was added at -78°. At that point, decolorization occurred and a cloudy mixture was formed. After 3/4 hr, a solution of the carbonyl compound (2 mmol) in 2 ml tetrahydrofuran was added and the mixture was stirred for another hr. The reaction mixture was allowed to warm up to room temperature and worked up to give the products. Under these conditions, the products obtained were usually a mixture of α- and γ- isomers with the α-isomer predominating (Table 1).

The role of magnesium bromide is critical in moderating the regioselectivity of the reaction. Other metal halides, e.g. zinc chloride[16] or



cadmium iodide[17], were found not to be effective. The change in regioselectivity does not appear to be due to the formation of the α-silylallyl magnesium bromide, because the Grignard reagent, generated independently from the bromo-precursor, reacted with acetophenone to give only the γ-product (1a)[12,13]. The explanation we favour at the moment is that magnesium bromide complexes with the carbonyl compound thus rendering it a more reactive electrophile. It is well known that in the reactions of ambident anions, the regioselectivity depends on the reactivity of the electrophile[18,19]. In support of this explanation, we have found that the same regioselectivity was obtained if magnesium bromide was pre-mixed with the carbonyl compound and the mixture was added dropwise to a solution of 1-trimethylsilylallyl lithium.

The conversion of aldehydes and ketones into 1,3-dienes can therefore be achieved easily. The crude mixture of the alkoxides of 1 and 2 obtained as described, was quenched with thionyl chloride[1] before work-up. The 1,3-diene could be purified by distillation or TLC, in an overall isolated yield of ~50% (Table 2). Alternatively, the diene could be generated by quenching the alkoxides with acetyl chloride and the resultant acetates treated with tetraethylammonium fluoride in acetonitrile[20].

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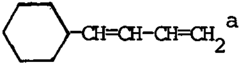
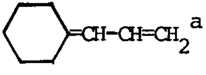
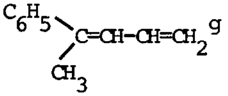
Table 1. Regioselectivity in the reaction of 1-trimethylsilylallyl carbanion with acetophenone and benzaldehyde.

Compound	Reaction Conditions	Relative Amount	
		γ	α
a. R^1=Ph, R^2=CH_3	n-Butyllithium	100%	
	n-BuLi/TMEDA/$ZnCl_2$	100%	
	n-BuLi/TMEDA/CdI_2	100%[a]	
	n-BuLi/TMEDA/$MgBr_2$	8%	92%[b]
	n-BuLi/$MgBr_2$	14%	86%[b]
	n-BuLi/TMEDA/$MgBr_2$ premixed with carbonyl compound.	43%	57%[b]
	t-BuLi/HMPA/$MgBr_2$	<5%	>95%[c]
	t-BuLi/HMPA/$MgBr_2$ premixed	~20%	~80%[c]
b. R^1=Ph, R^2=H	t-BuLi/HMPA	100%	
	t-BuLi/HMPA/$MgBr_2$ premixed	40%	60%[e]
	t-BuLi/HMPA/$MgBr_2$	40%	60%[d]

a. The yield of the γ-alcohol is poor. There is however no α-product.
b. 2 diastereomers were formed in a ratio of 2:1 according to nmr.
c. obtained as diene. d. one diastereomer was formed according to nmr.
e. some of the α-product was obtained as the diene.

Table 2. Diene Synthesis from carbonyl compounds and 1-trimethylsilylallyl carbanion

Product	Reaction Conditions	Isolated Yield (%)[b]	^{1}H NMR[c]; IR[d]; and M.S. data[e]
$CH_3(CH_2)_9CH=CH-CH=CH_2$[a]	A	54	0.9(t,3H), 1.4(16H), 2.1(2H), 4.8 to 5.4(m,2H), 5.8 to 6.5(m,3H); 2930, 2860, 1465, 1600; 194(12), 67(100).
	B	42	1.0 to 2.1(m,11H), 4.9 to 5.4(m,2H) 5.6 to 6.7(m,3H); 2930, 2860, 1600, 1450; 136(63), 67(100).
$C_6H_5-CH=CH-CH=CH_2$[a]	A	50	[f]4.9 to 5.4(m,2H), 6.1 to 6.7(m,3H), 7.0 to 7.4(M,5H); 1600, 1630, 945; 130(83), 129(100).
	A	49	[f]1.7(m,6H), 1.9 to 2.4(m,4H), 4.8 to 5.2(m,2H), 5.4 to 5.9(m,1H), 6.2 to 6.8(m,1H); 2900, 2830, 1610, 1440; 122(29), 79(100).
 $(C_6H_5)(CH_3)C=CH-CH=CH_2$[g]	A	43	2.1(br.s,3H), 4.8 to 5.5(m,2H), 6.0 to 6.9(m,2H), 7.1 to 7.4(m,5H); 1630, 1600, 1495, 1445; 144(22), 129(100).

Reaction conditions were described in text. Method A: The crude alkoxide mixture was quenched with thionyl chloride. Method B: The crude alkoxide mixture was quenched with acetyl chloride followed by tetraethylammonium fluoride.

a. Product purity was checked by GC-MS to be one isomer.
b. Isolated yield of products by distillation or preparative thin layer chromatography.
c. ^{1}H NMR are reported in δ ppm in CCl_4 solution.
d. IR spectra are reported in cm^{-1} as neat.
e. MS data are in m/e (% abundance).
f. Identical NMR and IR data as obtained by E.J. Corey and D.E. Cane, J. Org. Chem. 34, 3053 (1969).
g. Two isomers in ratio of about 1:1 was detected by GC/MS after purification by distillation. Before distillation the ratio was about 2:1.