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The Synthesis of Alkenes from Carbonyl Compounds and Carbanions α to Silicon. Stereoselective Synthesis of 1-Trimethylsilylbuta-1,3-dienes[1]

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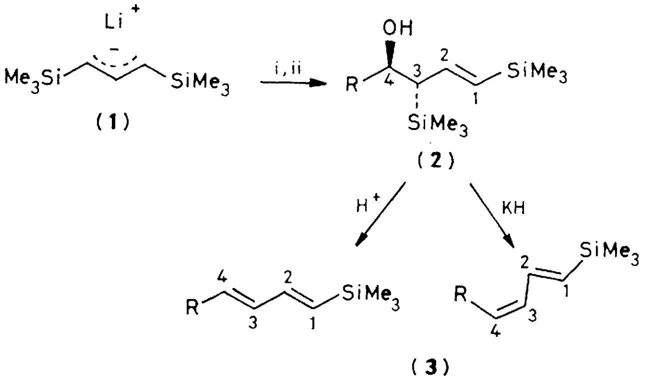
Reactions of aldehydes with the 1,3-bis(trimethylsilyl)propenyl anion in the presence of magnesium bromide or trimethyl borate give stereoselectively the alcohols (**2**) which can be transformed stereospecifically to either (1*E*, 3*E*)- or (1*E*, 3*Z*)-1-trimethylsilylbuta-1,3-dienes.

The presence of the butadiene structure in a number of insect pheromones and the recent interest in the chemistry of leukotrienes suggest that new synthetic methods leading to the stereoselective synthesis of butadienes may be desirable. Previously, we and others have shown[2–4] that the regioselectivity in the reactions of the 1-trimethylsilylallyl carbanion with carbonyl compounds is dependent on the nature of the counter-ion. We also noted that when a magnesium ion was used, the reaction was not only regioselective, but also stereoselective. The reaction was limited to the synthesis of terminal 1,3-dienes, however.

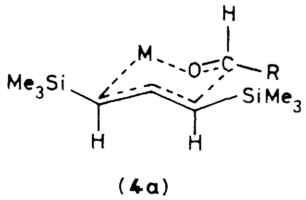
Recently, the reactions of 1,3-bis(trimethylsilyl)propenyllithium (**1**) with carbonyl compounds were reported,[5] which gave dienes directly, but in poor yields, and the synthetic potential of (**1**) was considered to be limited.[5] Independently, we have confirmed these results, and the stereoselectivity of the reaction was poor (Table 1).

However, when we added anhydrous magnesium bromide to (**1**) prior to its reaction with carbonyl compounds, good yields ($>80\%$) of the alcohols (**2**) could be isolated. The reaction shows good stereoselectivity; in the case of benzaldehyde, the major stereoisomer of (**2**) had the (*E*), (3*RS*,4*SR*)-stereochemistry. Since it is now well established that elimination from β-silanols can be made to proceed stereospecifically in either an *anti*- or a *syn*-manner,[6] the present method provides a stereoselective route for the synthesis of either the (1*E*,3*E*)- or the (1*E*,3*Z*)-dienes (**3**) (Table 1). With aliphatic aldehydes, while the stereoselectivity for the formation of the C(3)–C(4) single bond in (**2**) remained high, the stereochemical integrity of the C(1)–C(2) double bond was diminished. If a cyclic transition state is invoked for the reaction, the stereochemistry at C(1)–C(2) of (**2**) is governed by the relative proportions of (**4a**) and (**4b**) ($M = Mg^{+}$). It seems that although (**4a**) is preferred, some (**4b**) is nevertheless formed, leading to a *Z*-configuration for the C(1)–C(2) double bond.

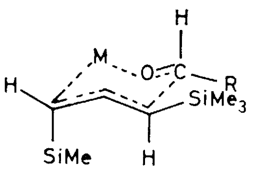


When trimethyl borate was used in place of magnesium bromide, the stereoselectivity of the reaction was further improved for aliphatic aldehydes.[4] The product (**2b**), for example, was $>99\%$ the (3*SR*,4*RS*)-compound and the C(1)–C(2) double bond was 92% *E*, 7% *Z*. It appears that with a covalent carbon–boron bond, the transition state (**4a**) ($M = B^{III}$) with the trimethylsilyl group equatorial is greatly preferred over (**4b**).

The stereoisomers of (**3**) can be readily separated by chromatography. With the borate method, we have routinely isolated stereochemically pure (1*E*,3*E*)- or (1*E*,3*Z*)-isomers (Table 2) by



(**4a**)



(**4b**)

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Table 1. Synthesis of buta-1,3-dienes (**3**) from reactions of (**1**) and aldehydes RCHO.

Additive	R	% Yield of (**2**)	Conditions[b] for (**2**) → (**3**)	% Yield of (**3**)	Distribution of stereoisomers of (**3**)[c] (%) 1*E*, 3*E*	1*E*, 3*Z*	1*Z*, 3*E*	1*Z*, 3*Z*
None[d]	Pr^n	—[a]	—[a]	34	60	40	—	—
	$n\text{-}C_8H_{17}$	—	—	27	73	24	3	—
	Ph	—	—	77	77	20	3	—
$MgBr_2$[e]	Pr^n	74	H^+	94	68	3	29	—
			KH	94	2	63	—	35
	$n\text{-}C_8H_{17}$	80	H^+	92	72	2	26	—
			KH	91	1	67	—	32
	Ph	80	H^+	92	90	6	4	—
			KH	94	9	87	—	4
$B(OMe)_3$[f]	Pr^n	52	H^+	94	92	<1	7	—
			KH	94	<1	90	—	9
	$n\text{-}C_8H_{17}$	50	H^+	95	92	<1	7	—
			KH	93	<1	90	—	0
	Ph	50	H^+	91	84	2	15	—
			KH	90	6	81	—	13

[a] The dienes (**3**) were formed directly. [b] H^+: sulphuric acid–tetrahydrofuran (THF); KH: THF as solvent. [c] Determined by g.l.c. using a 10 ft 6% OV-101 column (o.d. 1/8 in) with a HP 5730A Gas Chromatograph, column temp. 100—250 °C. [d] Compound (**1**) was generated from 1,3-bis(trimethylsilyl)propene at −76 °C with s-butyl-lithium in tetramethylethylenediamine–THF or t-butyl-lithium in hexamethylphosphoric triamide–THF. [e] Anhydrous magnesium bromide (2 mol. equiv.) was added to a solution of (**1**) at −76 °C for 1 h, and the aldehyde was then added. [f] To a solution of trimethyl borate (1 mol. equiv.) in THF was added a solution of (**1**) at −76 °C. The mixture was stirred for 30 min and quenched with aqueous ammonium chloride–methylene dichloride. The methylene dichloride solution was dried and evaporated, and the residue was dissolved in ether. The aldehyde was added and the mixture was stirred at room temperature for 2 days. Work-up was by the usual procedures.

Table 2. Selected 200 MHz ^1H n.m.r. data (vinylic and methine protons only) for (**2**) and (**3**) in $CDCl_3$.[a]

Compound		δ Values 1-H	2-H	3-H	4-H	*J*/Hz $J_{1,2}$	$J_{2,3}$	$J_{3,4}$
(**2a**)		5.54(d)	6.00(dd)	1.75(dd)	3.82(m)	18.7	9.8	6.4
(**3a**)	(1*E*, 3*E*)	5.70(d)	6.47(dd)	6.04(dd)	5.72(dt)	18.5	9.8	15.3
	(1*Z*, 3*E*)	5.49(d)	6.77(dd)	6.26(dd)	5.73(dt)	14.2	10.7	15.2
	(1*E*, 3*Z*)	5.82(d)	6.81(dd)	6.00(t)	5.44(dt)	18.3	10.6	10.6
	(1*Z*, 3*Z*)	5.62(d)	7.10(dd)	6.21(t)	5.54(dt)	14.3	10.6	10.6

[a] Data for (**2b,c**) and (**3b,c**) are comparable with data for (**2a**) and (**3a**).

preparative g.l.c. or t.l.c.[‡] We are now studying the replacement of the trimethylsilyl group with various electrophiles, a reaction generally found to be highly stereospecific with either retention or inversion in vinylsilanes.[7]

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[‡] Preparative g.l.c.: 10% OV-101, 6ft × 1/4 in column; oven temperature 120—240 °C. T.l.c.: silica gel with hexane as eluant.

References

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