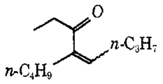
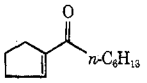
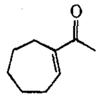
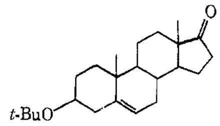
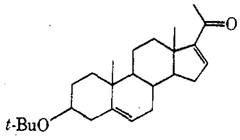
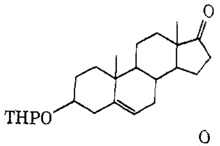
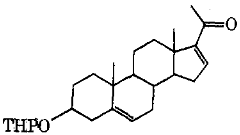
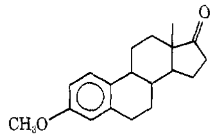
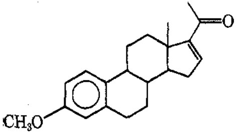
Table I. Synthesis of α,β-Unsaturated Ketones 9

Starting material 4	R_3 in phosphonate 5	Isolated yields, %		Product
		6	9	
$CH_3(CH_2)_5CHO$	n-C_6H_{13}	73	62	(E)- and (Z)-8-tetradecen-7-one
$(n\text{-}C_4H_9)_2C{=}O$	CH_2CH_3	81	44	
Cyclopentanone	n-C_6H_{13}	94	57	
Cyclohexanone	H	74	0	1-Cyclohexene-1-carboxaldehyde
	i-C_3H_7	88	45	1-Isobutyryl-1-cyclohexene
Cycloheptanone	CH_3	89	57	
	CH_2CH_3	90	70	
	i-C_3H_7	35	55	
	n-C_6H_{13}	96	72	
Cyclooctanone	CH_3	82	74	(E)-1-Acetyl-1-cyclooctene
Cyclododecanone	CH_3	92	81	1:1 (E)- and (Z)-1-acetyl-1-cyclododecene
	CH_3	74	74	
	CH_3	77	72	
	CH_3	62	78	

and 25 ml of brine, and dried over anhydrous magnesium sulfate. The product was chromatographed on Merck silica gel F254 in 1:1 ether–hexane to afford 301 mg (76%) of the tetrahydropyranyl ether of 3β-hydroxypregna-5,16-dien-20-one having melting point and spectral data in accord with literature values.[10]

Acknowledgment. We would like to thank the National Institutes of Health (GM-22978-01 and HD-6-2855) for their generous financial support. We also wish to thank G. D. Searle and Co. for a generous gift of steroid intermediates.

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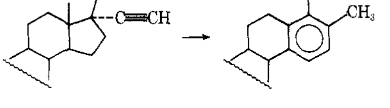

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(5) For an alternative approach to **3** using 1,3-dithianes as the acyl carbanion equivalent, see D. Seebach, M. Kolb, and B.-T. Gröbel, *Tetrahedron Lett.*, 3171 (1974).

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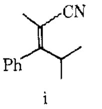
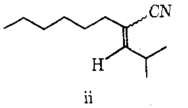
(7) Unlike the oxidative decyanation of secondary nitriles (ref 4), HMPA was required for the successful oxidation decyanation of α,β-unsaturated nitriles.

(8) For example, i and ii afford the corresponding α,β-unsaturated ketones in 0 and 6% yield, respectively.



i



ii

(9) All compounds had ir, NMR, and mass spectral data in accord with assigned structures.

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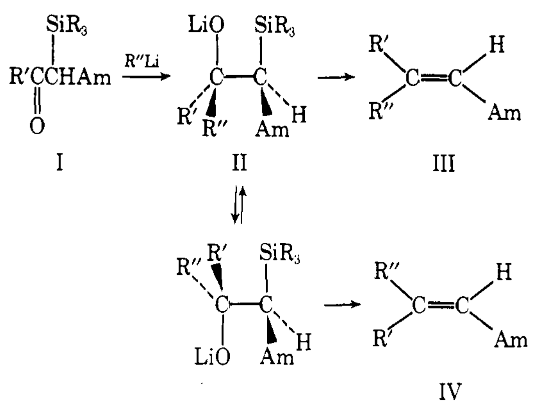
Reaction of β-Ketosilanes with Alkyllithium. A Stereoselective Synthesis of Trisubstituted Ethylenes

Summary: Reaction of β-ketosilanes with alkyllithium reagents afforded predominantly one diastereoisomer of possible two β-hydroxysilanes, which gave trisubstituted ethylenes stereoselectively by acidic or basic workup.

Sir: Recent progress in organic synthesis via silicon compounds has disclosed novel procedures for the synthesis of 1,2-disubstituted ethylenes with rigorous stereochemistry.[1–7] We describe herein a novel procedure for the stereoselective synthesis of trisubstituted ethylenes via reaction of β-ketosilanes with alkyllithium reagents followed by syn-elimination under basic conditions or by anti-elimination on acid treatment.[8,9]

Treatment of 5-trimethylsilyl-4-decanone (Ia)[10] with methyllithium at −78 °C afforded a reaction mixture containing IIa[11] whose corresponding alcohol was obtained in 80% yield by hydrolytic workup. Treatment of the reaction mixture with potassium *tert*-butoxide afforded (E)-4-methyl-4-decene (IIIa)[12] in 74% overall yield (stereoselectivity 91%). When the reaction mixture was treated with glacial acetic acid saturated with sodium acetate (−15 °C for 30 min and room temperature overnight), the Z isomer (IVa) was obtained in 69% overall yield (stereoselectivity 88%).[14] Similar reaction of 5-triethylsilyl-4-decanone (Ic) with methyllithium gave IIIa in 76% yield (stereoselectivity 91%) by treatment with potassium *tert*-butoxide and IVa in 57% overall yield (stereoselectivity 90%) by treatment with glacial acetic acid saturated with sodium acetate.[15]



a, R = Me; R' = *n*-Pr; R'' = Me
b, R = Me; R' = Me; R'' = *n*-Pr
c, R = Et; R' = *n*-Pr; R'' = Me

Further information about the stereoselectivity of this olefin synthesis was obtained from the reaction of 3-trimethylsilyl-2-octanone (Ib) with propyllithium. Treatment of the reaction mixture with potassium *tert*-butoxide gave IVa in 25% yield (stereoselectivity 96%) via IIb.[16]

When methylmagnesium bromide, in place of methyllithium, was treated with β-ketosilane Ia, IVa was obtained in 22% (stereoselectivity 77%) after acidic workup (glacial acid saturated with sodium acetate). Reaction of Ia with phenyllithium gave 4-phenyl-4-decene (52% overall yield, 39/61 E/Z) after treatment of the reaction mixture with concentrated sulfuric acid.[17]

These data show that β-hydroxysilanes are produced from β-ketosilanes and alkyllithium reagents in high stereoselectivity. The potassium salt of the alcohol produces a trisubstituted ethylene by syn-elimination of trimethylsilyl and hydroxy groups whereas treatment with acid in the presence of nucleophile induces anti-elimination of these two groups.[1-3,6]

Preparation of 4-methyl-4(E)-decene (IIIa) and the Z isomer (IVa) are representative. A stirred solution of 5-trimethylsilyl-4-decanone (Ia, 0.23 g, 1 mmol) in 5 ml of THF was treated with methyllithium (3 mmol, 3.5 ml of 0.85 M ethereal solution) at −78 °C and the reaction mixture was stirred at room temperature overnight. Addition of 1.0 g (9 mmol) of potassium *tert*-butoxide and refluxing of the reaction mixture for 1 h gave IIIa (74% overall yield, 91/9 E/Z): NMR (CCl_4) δ 0.6–1.04 (6 H, m), 1.04–1.5 (8 H, m), 1.55 (3 H, br s), 1.70–2.20 (4 H, m), 5.05 (1 H, br t, J = 7 Hz). When the reaction mixture from Ia and methyllithium (−78 °C for 15 min, then room temperature for 1 h) was treated with 10 ml of glacial acetic acid saturated with sodium acetate under stirring at −15 °C for 30 min and at room temperature overnight, workup gave IVa (69%, 12/88 E/Z): NMR (CCl_4) δ 0.88 (6 H, t, J = 6 Hz), 1.03–1.57 (8 H, m), 1.63 (3 H, br s), 1.70–2.17 (4 H, m), 5.00 (1 H, t, J = 7 Hz); MS m/e (rel intensity, %), 154 (M^+, 11), 111 (13), 97 (22), 84 (16), 69 (52), 55 (100).

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(9) 1,1-Disubstituted ethylenes were prepared by analogous procedures: (a) P. F. Hudrlik and D. Peterson, *Tetrahedron Lett.*, 1785 (1972); (b) R. A. Ruden and B. L. Gaffney, *Synth. Commun.*, **5**, 15 (1975).
(10) Prepared from trimethylvinylsilane, butyllithium, and butyraldehyde analogously to the reported procedure (ref 2) for the preparation of β-ketosilanes. This ketosilane was also prepared from trimethylvinylsilane, butyllithium, and butyryl chloride in 45% overall yield: bp 110–120 °C (23 mm).
(11) Compound IIa was not isolated. Stereochemistry of IIa as well as its corresponding alcohol could not be determined but estimated from the stereochemistry of olefins prepared by syn- and anti-elimination.
(12) The structure of IIIa and IVa are based on the NMR. The chemical shift of 7-methyl signal in 3-propyl-7-methyl-2(Z),6(E)-decadien-1-ol is recorded to be at δ 1.57 ppm, whereas that of the 6(Z) isomer is recorded to be at 1.66 (ref 13). The observed chemical shift of vinylic methyl of IIIa appeared at δ 1.55 ppm and that of the Z isomer (IVa) at 1.63.
(13) (a) S. B. Bowlus and J. A. Katzenellenbogen, *J. Org. Chem.*, **38**, 2733 (1973); *Tetrahedron Lett.*, 1277 (1973); (b) M. P. Cooke, Jr., *Tetrahedron Lett.*, 1281 (1973).
(14) This mixture did not contain other isomers. We could not detect (Z)- and (E)-4-methyl-3-decene from the product mixture.
(15) Further attempts for preparation of olefins: treatment with thioglycolic acid, 61% yield, 46/54 E/Z; $BF_3 \cdot OEt_2$, 82, 37/63. Treatment of the reaction mixture with ammonium chloride gave β-hydroxysilane (IIa', Li = H) which gave IVa: treatment with AcOH saturated with ACONa, 46% yield, 10:90 E/Z; AcOH–KF, 72, 12/88; H_2SO_4–KF, 84, 18/82; H_2SO_4, 69, 24/76.
(16) Propyllithium may abstract proton from methyl ketone in Ib. This side reaction may lower the overall yield of IVa.
(17) Treatment of the reaction mixture with potassium *tert*-butoxide or glacial acetic acid saturated with sodium acetate did not give any olefin. Sulfuric acid produces a benzyl-type cation which gives 4-phenyl-4-decene by the elimination of trimethylsilyl group.

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Stereoselective Synthesis of Vinylsilanes from Alkynylsilanes by Reductive Alkylation via Hydroboration and Carbodemetalation

Summary: Hydroboration of 1-trimethylsilyl-1-alkyne with dicyclohexylborane gave 1-trimethylsilylvinylborane regio- and stereoselectively whose successive treatment with methyllithium, cuprous iodide, and alkyl halides afforded 1,2-dialkylvinylsilane with strict geometry.

Sir: Organosilicon compounds have attracted much attention as versatile reagents for organic synthesis,[1] for example, vinylsilanes have been shown to be useful precursor for ketones, vinyl halides, and olefins of predictable stereochemistry.[2,3] We wish to describe here a novel stereoselective and generally applicable procedure for the reductive 1,2-dialkylvinylsilanes with fixed configuration, which is based on regioselective hydroboration of 1-alkynylsilane to vinylborane and the following stereoselective transmetalation and carbodemetalation.[4]

Hydroboration of 1-trimethylsilyl-1-octyne (I, R = n-C_6H_{13}) with excess dicyclohexylborane gave vinylborane II (R = n-C_6H_{13}) regioselectively.[5,6] Excess borane was quenched with 1-butene and the resulting mixture was treated with