42, 10), 270 (100), 234 (m*). Anal. Calcd for $C_{19}H_{14}O_7$: C, 64.4; H, 4.0. Found: C, 64.2; H, 4.0.

The above compound **17** (16 mg, 0.04 mmol) was treated with 2 mL of 3% aqueous sodium hydroxide, and the mixture was stirred at room temperature for 45 min. The mixture was acidified with 3% hydrochloric acid; the resulting red precipitate was collected and, after recrystallization from chloroform–hexane (2:3), afforded 11 mg (96%) of digitopurpone (**16**), mp 210 °C, identical with a sample of the compound prepared above.

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Registry No. **1**, 496-64-0; **4**, 475-38-7; **5**, 14569-45-0; **6**, 2961-04-8; **6** triacetate, 75314-06-6; **7**, 4988-51-6; **7** tetraacetate, 6047-49-0; **8**, 87712-25-2; **8** acetate, 75314-06-6; **9a**, 78226-68-3; **9b**, 87712-26-3; **10**, 87712-27-4; **11**, 87712-28-5; **12b**, 14554-10-0; **13b**, 13720-75-7; **14b**, 87712-29-6; **15**, 476-56-2; **16**, 34425-57-5; **17**, 87728-26-5.

Regioselective Synthesis of Trimethylsilyl-Substituted α-Allenic Alcohols via Propargylic Organoboranes

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The chemistry of propargylic anions of 1-(trimethylsilyl)-1-alkynes has received considerable attention in recent years.[1] Various organometallic reagents (M = Li, Mg, Al, Si, Ti, Cu, Zn, Sn) have been used to control the regio- and stereoselectivity of the condensation reactions with aldehydes and ketones. We now report that the propargylic organoborane intermediates[2] derived from the corresponding lithium reagents react with aldehydes and certain ketones with high regioselectivity to form the corresponding trimethylsilyl-substituted α-allenic alcohols.

A general reaction sequence is outlined in Scheme I. Metalation of 1-(trimethylsilyl)propyne with *tert*-butyllithium by the procedure described previously (THF, 0 °C, 1 h)[1a] afforded the lithium reagent **1**. Treatment of **1** with 1 equiv of *B*-methoxy-9-borabicyclo[3.3.1]nonane (0 °C, 35 min) followed by the addition of $^4/_3$ equiv of $BF_3{\cdot}OEt_2$ (0 °C, 15 min)[3] provided the corresponding propargylic organoborane **3**. To the reaction mixture were then added aldehydes or ketones (room temperature, 1.5 h), which on oxidative workup gave the corresponding trimethylsilyl-substituted α-allenic alcohols **5** in excellent isolated yields (Table I). None of the corresponding β-acetylenic alcohols were detected.[4] The reactions of aldehydes and ketones with **3** to form α-allenic alcohols were assumed to proceed through a six-center electronic transfer with propargylic–allenic rearrangement as proposed previously.[2f] The reactions with **4** under similar conditions at room temperature were much less regioselective. For example, the reaction of hexanal with **4** gave a 35:65 mixture of α-allenic alcohol and β-acetylenic alcohol, whereas a 50:50 mixture was observed for acetone. However, the regioselectivity of the reaction was found to be dramatically affected by the reaction temperature. Thus, when the reaction with **4** was carried out at −78 °C and slowly warmed to room temperature, α-allenic alcohols were predominantly obtained as the products with all the aldehydes used and certain ketones (Table I).[4]

It is interesting to note from Table I that **3** and **4** exhibited some unusual characteristics. Both aldehydes and ketones reacted with **3** to form the corresponding α-allenic alcohols. This is in sharp contrast with the fact that the condensations of ketones with the propargylic titanium reagent derived from 1-(trimethylsilyl)propyne were unsuccessful.[1a] It was also indicated that the propargylic organoboranes derived from lithium chloropropagylide and trialkylboranes reacted with ketones to give mixtures of α-allenic and β-acetylenic alcohols.[2a,5] The high regioselectivity for the formation of α-allenic alcohols from **4** at low temperature is also markedly different from that of the titanium reagent derived from 1-(trimethylsilyl)-1-

Scheme I

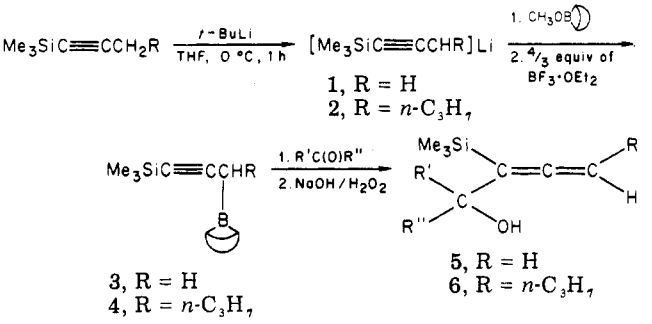

Table I. Reactions of Representative Aldehydes and Ketones with 3 and 4

R	R′	R″	isolated yield of 5 or 6,[a-c] %
H	n-C_5H_{11}	H	82
	i-C_3H_7	H	82
	t-C_4H_9	H	85
	C_6H_5	H	88
	(E)-CH_3CH=CH	H	79
	CH_3	CH_3	86
	C_2H_5	C_2H_5	91
	-$(CH_2)_5$-		91
	CH_3	C_6H_5	93
n-C_3H_7	n-C_5H_{11}	H	78 (88:12)
	i-C_3H_7	H	74 (88:12)
	C_6H_5	H	72 (87:13)
	CH_3	CH_3	71 (91:9)
	C_2H_5	C_2H_5	75 (83:17)
	-$(CH_2)_5$-		76 (91:9)
	CH_3	C_6H_5	88 (54:46)

[a] Isolated pure materials by vacuum distillation of 10-mmol reactions. [b] Combined yields of α-allenic alcohols and β-acetylanic alcohols in **6**. [c] The numbers in parentheses are ratios of α-allenic alcohols:β-acetylenic alcohols determined by GLC.

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(4) The isolated products were analyzed by GLC and fully characterized by IR and ^1H and ^{13}C NMR spectroscopy.

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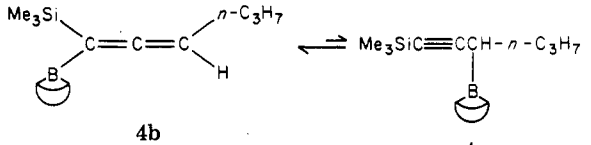
0022-3263/83/1948-5376$01.50/0

butyne in which an exclusive formation of β-acetylenic alcohols was observed.[1a]

The IR spectrum of **3** in the reaction mixture showed a very strong acetylenic absorption at 2150 cm^{-1},[6] and only a weak allenic absorption at 1940 cm^{-1},[6] indicating that it existed predominantly as a propargylic species. On the other hand, **4** exhibited only a weak acetylenic absorption at 2160 cm^{-1} and a very strong allenic absorption at 1920 cm^{-1}, suggesting that it existed mainly as an allenic species.[7] The intermediates **3** and **4** were also isolated and characterized. Subsequent to the addition of $BF_3{\cdot}OEt_2$, the reaction solvent and the byproduct methyl borate were removed under reduced pressure. Pentane was introduced and the solid $LiBF_4$ byproduct was allowed to settle.[3] The supernatant liquid was decanted into a 100-mL flask, and pentane was evaporated under a water aspirator vacuum and further evaporated under a high vacuum (5×10^{-3} torr). In the case of **3**, a white solid was obtained. The ^1H and ^{13}C NMR spectra (in $CDCl_3$, room temperature) showed that **3** formed a 1:1 complex with THF. In the case of **4**, a liquid was obtained. It was further distilled under vacuum (120 °C (0.8 torr)). The ^1H NMR spectrum (in $CDCl_3$, room temperature) showed a very broad peak around δ 4.8, typical chemical shift for allenic protons, suggesting the existence of a rapid exchange between the allenic structure **4b** and the acetylenic structure **4a**.[2a] The



4b **4a**

existence of such a mobile equilibration between **4a** and **4b** could be used to account for the effect of temperature on the regioselectivity of the reaction as proposed earlier for a similar phenomenon.[2a] However, the present results indicate that **4a** is thermodynamically less stable but kinetically more reactive than **4b** toward aldehydes and certain ketones. At lower temperatures, the rate of equilibration becomes faster than the subsequent reaction with aldehydes and certain ketones and thus **4a** becomes the major reacting species. This change of reactivity in comparison with the earlier case[2a] may be attributed to the presence of the trimethylsilyl group as well as the change in the position of the alkyl substituent. The isolated intermediates **3** and **4** gave the same products when treated with aldehydes and ketones as those obtained by in situ preparation of the intermediates.

This one-pot procedure offers a simple and efficient method for the preparation of a variety of α-allenic alcohols. The effects on the regio- and stereoselectivity by using other ligands on both boron and silicon atoms are under further investigation. The extension of this work to other carbon electrophiles is in process.

Experimental Section

All operations were carried out under dry nitrogen atmosphere, with oven-dried glassware, syringes, and needles. GLC analyses were performed on a Varian 1440 gas chromatograph with a 5 ft × 0.125 in. column packed with 3% SE-30 on 100/120 Supelcoport. Peak integrations were carried out on a Hewlett-Packard 3390A integrator. The ^1H and ^{13}C NMR spectra were recorded on Varian EM-360 and Varian CFT-20 NMR spectrometers, respectively ($CDCl_3$, Me_4Si). The IR spectra were taken on Beckman IR 8 spectrometer.

Materials. THF was distilled from $LiAlH_4$, $BF_3{\cdot}OEt_2$ and Me_3SiCl from CaH_2. Aldehydes and ketones were also distilled under nitrogen prior to use. *B*-Methoxy-9-borabicyclo[3.3.1]nonane was prepared as described previously.[8] *tert*-Butyllithium in pentane was obtained from Alfa. 1-(Trimethylsilyl)propyne was purchased from Petrarch. 1-(Trimethylsilyl)-1-hexyne was prepared as described previously.[9]

Condensation of Hexanal with 3. The following reaction procedure is representative for the reactions of aldehydes and ketones with **3**. To a 100-mL reaction flask equipped with a magnetic stirring bar were successively added with syringes 1.48 mL of 1-(trimethylsilyl)propyne (1.12 g, 10 mmol) and 10 mL of THF. The reaction flask was cooled to 0 °C and charged with 5.93 mL of *tert*-butyllithium (1.69 M in pentane, 10 mmol). After 1 h, 1.64 mL of *B*-methoxy-9-borabicyclo[3.3.1]nonane (1.52 g, 10 mmol) was added. After an additional 35 min of stirring, 1.64 mL of $BF_3{\cdot}OEt_2$ (1.89 g, 13.33 mmol) was introduced. The reaction mixture was kept at 0 °C for 15 min and then warmed to room temperature to form **3**. Hexanal (1.20 mL, 1.00 g, 10 mmol) was then added. After 1.5 h, 4 mL of 3 N NaOH and 3.5 mL of 30% H_2O_2 were added to oxidize the organoborane byproduct. The organic layer was separated and washed with water to remove *cis*-1,5-cyclooctanediol. The solvent was evaporated and the residue distilled to give 1.73 g (82% yield) of a colorless liquid, 3-(trimethylsilyl)-1,2-nonadien-4-ol: bp 43 °C (5×10^{-3} torr); IR (neat) 3450 (OH), 2950, 1935 (C=C=C), 1250, 835 cm^{-1}; ^1H NMR (60 MHz) δ 4.55 (d, 2 H, J = 2 Hz), 4.25 (br, 1 H), 2.15 (br, 1 H, OH) 1.1–1.6 (br, 8 H), 0.90 (t, 3 H), 0.13 (s, 9 H); ^{13}C NMR (20 MHz) δ 207.6, 100.8, 71.3, 70.9, 38.0, 31.9, 25.5, 22.7, 14.1, –0.7. GLC analysis showed that the product is essentially pure (>99%).

Condensation of Hexanal with 4. A similar procedure was used except that 2.03 mL of 1-(trimethylsilyl)-1-hexyne (1.54 g, 10 mmol) was used and the reaction flask was first cooled to –78 °C before hexanal was added. The reaction mixture was kept at –78 °C for 1 h and then slowly warmed to room temperature over 30 min. After the usual workup, 1.98 g (78% yield) of 7-(trimethylsilyl)-7,8-dodecadien-6-ol was obtained as a colorless liquid. GLC analyses both before and after the distillation showed the presence of 12% of the corresponding β-acetylenic alcohol. The product had the following: bp 66 °C (1×10^{-2} torr); IR (neat) 3450 (OH), 2950, 1940 (C=C=C), 1245, 835 cm^{-1}; ^1H NMR (60 MHz) δ 5.20 (dt, 1 H, J = 2,8 Hz), 4.23 (m, 1 H), 1.9 (m, 3 H), 1.1–1.7 (br, 10 H), 0.9 (m, 6 H), 0.13 (S, 9 H); ^{13}C NMR (20 MHz) δ 204.1, 102.6, 89.0, 70.8, 38.1, 31.9, 30.6, 25.4, 22.9, 22.7, 14.0, 13.8, –0.7. The presence of a minor amount of β-acetylenic alcohol was also detected by IR (2170 cm^{-1}, C≡C) and ^{13}C NMR.

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Registry No. **5** (R′ = n-C_5H_{11}; R″ = H), 87655-75-2; **5** (R′ = i-C_3H_7; R″ = H), 87655-76-3; **5** (R′ = C_6H_5; R″ = H), 78808-49-8; **5** (R′ = (*E*)-CH_3CH=CH; R″ = H), 87655-77-4; **5** (R′ = R″ = CH_3), 79015-65-9; **5** (R′ = R″ = C_2H_5), 87655-78-5; **5** (R′ = R″ = $(CH_2)_5$), 79015-67-1; **5** (R′ = CH_3; R″ = C_6H_5), 87655-79-6; **6** (R′ = n-C_5H_{11}; R″ = H) (α-allenic), 87655-80-9; **6** (R′ = n-C_5H_{11}; R″ = H) (β-acetylenic), 87655-81-0; **6** (R′ = i-C_3H_7; R″ = H) (α-allenic), 87655-82-1; **6** (R′ = i-C_3H_7; R″ = H) (β-acetylenic), 87655-83-2; **6** (R′ = C_6H_5; R″ = H) (α-allenic), 87655-84-3; **6** (R′ = C_6H_5; R″ = H) (β-acetylenic), 87655-85-4; **6** (R′ = R″ = CH_3) (α-allenic), 87655-86-5; **6** (R′ = R″ = CH_3) (β-acetylenic), 87655-87-6; **6** (R′ = R″ = C_2H_5) (α-allenic), 87655-88-7; **6** (R′ = R″ = C_2H_5) (β-acetylenic), 87655-89-8; **6** (R′ = R″ = $(CH_2)_5$) (α-allenic), 87655-90-1; **6** = R′ = R″ = $(CH_2)_5$) (β-acetylenic), 87655-91-2; **6** (R′ = CH_3; R″ = C_6H_5) (α-allenic), 87681-09-2; **6** (R′ = CH_3; R″ = C_6H_5) (β-acetylenic), 87655-92-3; $Me_3SiC{\equiv}CCH_3$, 6224-91-5; $Me_3SiC{\equiv}C(CH_2)_3CH_3$, 3844-94-8; n-$C_5H_{11}C(O)H$, 66-25-1; i-$C_3H_7C(O)H$, 78-84-2; $C_6H_5C(O)H$, 100-52-7; (*E*)-CH_3CH=$CHC(O)H$, 123-73-9; $CH_3C(O)CH_3$, 67-64-1; $C_2H_5C(O)C_2H_5$, 96-22-0; $CH_3C(O)C_6H_5$, 98-86-2; cyclohexanone, 108-94-1.

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