1650, 1160, 1150 cm^{-1}; ^{1}H NMR 2.80 (1 H, br, H-C$_2$), 4.10 (2 H, q, J = 7 Hz, OCH_2CH$_3$), 5.62 (1 H, d, J = 16 Hz, CH=CHCOOR), 6.88 (1 H, dd, J = 16, 8 Hz, CH=CHCOOR); mass spectrum, m/e 456 (M$^+$, base), 441, 411, 303, 302, 301. Anal. Calcd for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48. Found: C, 81.63; H, 11.45.

Compound **9**, after careful crystallization from methanol, had the following: mp 64–66 °C; $[\alpha]_D$ +11.1° (c 0.53); IR ν_{max} 1720 (C=O), 1380 cm^{-1}; ^{1}H NMR 2.80 (1 H, br, H-C$_2$), 9.58 (1 H, br with splitting, CHO); mass spectrum, m/e 386 (M$^+$, base), 372, 371, 233, 232, 231. Anal. Calcd for $C_{27}H_{46}O$: C, 83.87; H, 11.99. Found: C, 83.90; H, 12.01.

Reaction of Epoxide 3. Using the general procedure with an epoxide/ylide 1:2 molar ratio, the reaction time was 22 h; products **10** and **11** were isolated by using a mixture of hexane and ether (8:2) as eluent. **10** and **11** were obtained with yields of 22% and 22%, respectively; no starting material was recovered and other products were not identified.

Product **10** is a colorless viscous oil (bp 180 °C (0.7 mmHg)): $[\alpha]_D$ +26.0° (c 0.50); IR ν_{max} 1735, 1720 (C=O α,β-unsaturated ester), 1650, 1240, 1040, 1020 cm^{-1}; ^{1}H NMR 2.80 (1 H, br, H-C$_2$), 4.10 (2 H, t, J = 6 Hz, OCH_2CH$_2$CH$_2$CH$_3$), 4.60 (1 H, three unresolved signals, CHOCOCH$_3$), 5.70 (1 H, d with splitting, J = 15 Hz, CH=CHCOOR), 6.93 (1 H, dd, J = 15, 8 Hz, CH=CHCOOR); mass spectrum, m/e 430 (M$^+$), 415, 401, 375, 374, 370, 357, 355, 315, 314, 242, 149 (base). Anal. Calcd for $C_{27}H_{42}O_4$: C, 75.31; H, 9.83. Found: C, 75.40; H, 9.85.

Product **11** is a colorless viscous oil (bp 165 °C (0.7 mmHg)): $[\alpha]_D$ +26.5° (c 0.45); IR ν_{max} 1735, 1720 (C=O α,β-unsaturated ester), 1650, 1240, 1150, 1040 cm^{-1}; ^{1}H NMR 2.83 (1 H, br, H-C$_2$), 4.18 (2 H, q, J = 7 Hz, OCH_2CH$_3$), 4.60 (1 H, three unresolved signals, CHOCOCH$_3$), 5.73 (1 H, d, J = 15 Hz, CH=CHCOOR), 6.93 (1 H, dd, J = 15, 8 Hz, CH=CHCOOR); mass spectrum, m/e 402 (M$^+$), 204, 202, 200, 198, 149 (base). Anal. Calcd for $C_{25}H_{38}O_4$: C, 74.59; H, 9.52. Found: C, 74.70; H, 9.45.

Reaction of Epoxide 5. Using the general procedure with an epoxide/ylide 1:2 molar ratio, the reaction time was 50 h; products **12** and **13** were isolated by using a mixture of benzene–ether (95:5) as eluent (yields 36% and 12%, respectively). Some starting material (34%) was recovered.

Compound **12** is a colorless viscous oil (bp 165 °C (0.9 mmHg)): $[\alpha]_D$ −27.9° (c 0.44); IR ν_{max} 1720 (C=O α,β-unsaturated ester), 1650, 1170, 1155, 1110, 1060 cm^{-1}; ^{1}H NMR 2.78 (1 H, br, H-C$_2$), 3.75 (4 H, singlet, OCH$_2$CH$_2$O), 4.04 (2 H, t, J = 7 Hz, OCH_2CH$_2$CH$_2$CH$_3$), 5.64 (1 H, d, J = 16 Hz, CH=CHCOOR), 6.87 (1 H, dd, J = 16, 8 Hz, CH=CHCOOR); mass spectrum, m/e 430 (M$^+$, base), 415, 402, 386, 369, 368, 358, 357, 316, 315, 252. Anal. Calcd for $C_{27}H_{42}O_4$: C 75.31; H, 9.83. found: C, 75.37; H, 9.85.

Product **13** after crystallization from methanol had the following: mp 92–96 °C; $[\alpha]_D$ −32.0° (c 0.44); IR ν_{max} 1720 (C=O α,β-unsaturated ester), 1650, 1205, 1170, 1155, 1105, 1035 cm^{-1}; ^{1}H NMR 2.80 (1 H, br, H-C$_2$), 3.84 (4 H, s, OCH$_2$CH$_2$O), 4.12 (2 H, q, J = 7 Hz, OCH_2CH$_3$), 5.72 (1 H, d, J = 16 Hz, CH=CHCOOR), 6.97 (1 H, dd, J = 16, 7 Hz, CH=CHCOOR) (in CDCl$_3$); mass spectrum, m/e 402 (M$^+$, base), 388, 387, 358, 357, 342, 341, 340, 330, 329, 325, 317, 315, 314. Anal. Calcd for $C_{25}H_{38}O_4$: C, 74.59; H, 9.52. Found: C, 74.61; H, 9.43.

Reaction of Epoxide 6. Using the general procedure with an epoxide/ylide 1:2 molar ratio, the reaction time was 26 h; products **14** and **15** were isolated by using a mixture of benzene–ether (8:2) as eluent (yields 30% and 6%, respectively). Some starting material (6%) was recovered; other products were not identified.

Compound **14** is a colorless viscous oil (bp 130 °C (0.7 mmHg)): $[\alpha]_D$ −16.5° (c 0.92); IR ν_{max} 3620, 1720 (C=O α,β-unsaturated ester), 1650, 1150 cm^{-1}; ^{1}H NMR 2.75 (1 H, br, H-C$_2$), 4.13 (2 H, t, J = 6 Hz, OCH_2CH$_2$CH$_2$CH$_3$), 5.75 (1 H, d with splitting, J = 15 Hz, CH=CHCOOR), 7.03 (1 H, dd, J = 15, 8 Hz, CH=CHCOOR); mass spectrum, m/e 402 (M$^+$), 384, 374, 370, 369, 297, 295, 280, 149 (base). Anal. Calcd for $C_{26}H_{42}O_3$: C, 77.56; H, 10.52. Found: C, 77.59; H, 10.49.

Compound **15** is a colorless viscous oil (bp 120 °C (0.7 mmHg)): $[\alpha]_D$ −14.0° (c 0.27); IR ν_{max} 3620, 1720 (C=O α,β-unsaturated ester), 1650, 1150 cm^{-1}; ^{1}H NMR 2.75 (1 H, br, H-C$_2$), 4.20 (2 H, q, J = 7 OCH_2CH$_2$), 5.75 (1 H, d with splitting, J = 15 Hz, CH=CHCOOR), 7.05 (1 H, dd, J = 15, 8 Hz, CH=CHCOOR); mass spectrum, m/e 374 (M$^+$), 358, 356, 342, 341, 317, 316, 304, 301, 300, 286, 279, 148 (base). Anal. Calcd for $C_{24}H_{38}O_3$; C, 76.96; H, 10.23. Found: C, 76.91; H, 10.25.

Reduction of Aldehyde 9. Aldehyde **9** (50 mg) in ether (ca. 3 mL) was treated with AlLiH$_4$ (ca. 5 mg) and allowed to stand at gentle reflux for 30 min. The excess hydride was decomposed with H$_2$O. From the reaction mixture, worked up in the usual way, 2β-(hydroxymethyl)-A-norcholestane (**17**) was isolated by chromatography on silica gel, using a 7:3 benzene–ether mixture as eluent.

Compound **17**, after several crystallizations from methanol, had the following: mp 144–146 °C; $[\alpha]_D$ +28.0° (c 0.14); IR ν_{max} 3630 (OH), 1040, 1020 cm^{-1}; ^{1}H NMR 3.35 (2 H, unresolved d, CH$_2$OH); mass spectrum, m/e 388 (M$^+$), 373, 248, 234, 233 (base).

Registry No. **1**, 17343-82-7; **2**, 2789-50-6; **3**, 53755-30-9; **4**, 1753-61-3; **5**, 10429-04-6; **6**, 968-54-7; **7**, 96096-33-2; **7** (acid), 96096-34-3; **8**, 96096-35-4; **9**, 96150-04-8; **10**, 96096-36-5; **11**, 96096-37-6; **12**, 96096-38-7; **13**, 96096-39-8; **14**, 96096-40-1; **15**, 96096-41-2; *cis*-**16**, 96096-42-3; *trans*-**16**, 96096-43-4; **17**, 7044-12-4; tributyl(carbethoxymethyl)phosphonium bromide, 1834-01-1; 2β,3-epoxy-5α-androstan-17β-ol, 6958-01-6; 5α-cholest-2-ene, 570-73-0.

Synthesis of Trimethylsilyl-Substituted α-Allenic and β-Acetylenic Amines from Imines and Propargylic and Allenic Organoboranes

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The inhibitory action of certain α-allenic and β-acetylenic amines on mitochondrial monoamine oxidase (MAO), a flavin-linked enzyme which is responsible for the oxidative inactivation of the transmitter amines, has been the subject of intense interest in recent years.[1] This is due to the correlation between the inactivation of MAO and the relief of depression which has been exploited clinically. Several synthetic methods have been developed to prepare these amines.[1-3] One approach involved the use of imines to react with allenic and propargylic organometallic reagents.[3] The reactions produced β-acetylenic amines or mixtures of β-acetylenic amines and the corresponding α-allenic amines depending on the structure of imines and the nature of the organometallic reagents. We recently reported that the condensation reactions of aldehydes and ketones with propargylic organoborane intermediates derived from 1-(trimethylsilyl)-1-alkynes produced trimethylsilyl-substituted α-allenic alcohols with high regioselectivity and excellent isolated yields.[4] Our continuing interest in the chemistry of propargylic and allenic organoboranes has led us to explore their reactions with

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Scheme I

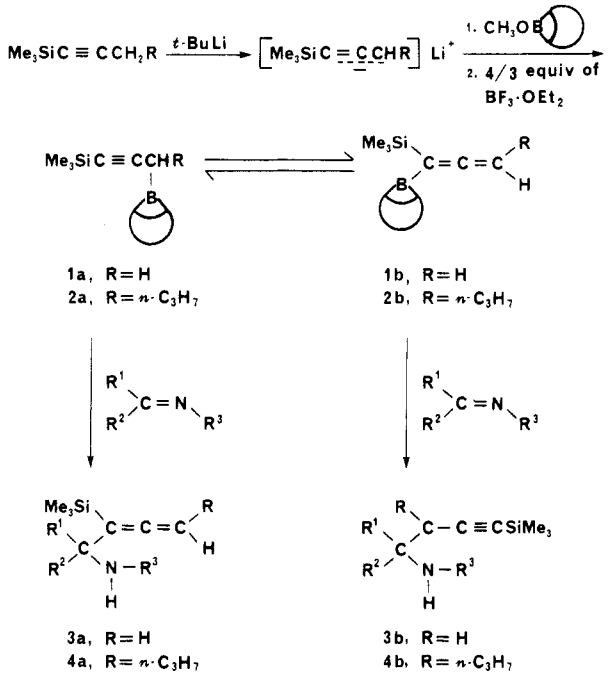

Table I. Reactions of Representative Imines with 1 and 2

entry	R	R^1	R^2	R^3	isolated yield,[a,b] %
1	H	H	C_6H_5	n-C_3H_7	75 (>99:1)
2		H	C_6H_5	c-C_6H_{11}	68 (>99:1)
3		H	C_6H_5	C_6H_5	62[c] (>99:1)
4		H	(E)-CH_3CH=CH	c-C_6H_{11}	56 (>99:1)
5		—$(CH_2)_5$—		C_6H_5	62 (>99:1)
6		—$(CH_2)_5$—		n-C_6H_{13}	44 (27:73)[d]
7	n-C_3H_7	H	C_6H_5	n-C_3H_7	83 (>99:1)
8		H	C_6H_5	c-C_6H_{11}	67 (80:20)
9		H	C_6H_5	C_6H_5	61 (<1:99)
10		H	(E)-CH_3CH=CH	c-C_6H_{11}	65 (48:52)[d]
11		H	i-C_3H_7	c-C_6H_{11}	86 (<1:99)
12		—$(CH_2)_5$—		C_6H_5	66 (<1:99)
13		—$(CH_2)_5$—		n-C_6H_{13}	59 (<1:99)

[a] Combined yields of **3a** + **3b** or **4a** + **4b**. The products were identified by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. [b] The numbers in parentheses are ratios of **3a**:**3b** or **4a**:**4b** determined by IR and ^{13}C NMR spectroscopy unless otherwise indicated. [c] Isolated as the hydrochloride adduct. [d] The ratio was determined by GLC.

imines. We now report that these condensation reactions produced trimethylsilyl-substituted α-allenic or β-acetylenic amines with high regioselectivity in several representative cases.

The reactions were carried out by adding imines[5] to organoborane **1** or **2** derived from 1-(trimethylsilyl)-1-alkyne as described previously (Scheme I).[4] After oxidative workup, the condensation adducts **3** or **4** were isolated (Table I). Our earlier studies indicated that propargylic borane **1a** or **2a** was in rapid equilibration with its corresponding allenic isomer **1b** or **2b**.[4] Presumably, the reactions with the propargylic species **1a** or **2a** through a six-center electronic transfer produced the allenic adducts, whereas the corresponding allenic species **1b** or **2b** produced the acetylenic adducts.

The results in Table I indicated that the allenic vs. acetylenic distribution could be dramatically influenced by the change of the structure of imines as well as the organoborane reagents. The reactions with **1** seem to favor the formation of the allenic adducts. The α-allenic amines were produced exclusively except in the case of entry 6 where β-acetylenic amine was formed predominantly. This is in general agreement with our earlier observation for the reactions of several representative aldehydes and ketones with **1** which produced α-allenic alcohols exclusively.[4] However, it is interesting to note from Table I that when imine derived from benzaldehyde and n-propylamine (entry 1) was changed to cyclohexanone and n-hexylamine (entry 6), a dramatic change of the regioselectivity was observed. An equally dramatic change was also observed when the amine counterpart of the imine derived from cyclohexanone and aniline was changed to n-hexylamine (entry 5 vs. entry 6). Presumably in the case of entry 6, the rearrangement of **1a** to the thermodynamically less stable **1b** followed by the reaction of imine with **1b** became the predominant reaction pathway.

The allenic vs. acetylenic distributions for the reactions with **2** were even more dramatically affected by the structures of imines. It is worth noting that imines derived from benzaldehyde and aliphatic amines (entries 7 and 8) produced the α-allenic amines when treated with **2**. Substituting the aliphatic amine with aniline resulted in an almost complete reversal of selectivity with β-acetylenic amine being formed exclusively (entry 9). Replacing benzaldehyde with isobutyraldehyde (entry 8 vs. entry 11) also produced a dramatic change of regioselectivity. Finally, imine derived from cyclohexanone and n-hexylamine produced only β-acetylenic amine (entry 13), in sharp contrast with the result in entry 7 where imine derived from benzaldehyde and n-propylamine was utilized.

Our earlier studies showed that the regioselectivity of the reaction between **2** and aldehyde or ketone can be dramatically affected by the reaction temperature.[4] However, this was not observed with imine. This is simply due to the fact that imines are much less reactive toward **2** than aldehydes and certain ketones. No appreciable amount of the condensation product was observed when the reaction was carried out at −78 °C and then quenched immediately after the reaction mixture was warmed to room temperature. This indicates that the rate of equilibration between **2a** and **2b** is much faster than the rates of the condensation reactions with imines. The regioselectivity is simply determined by the difference of the energy barriers of the two subsequent condensation reaction pathways.

The ready availability of imines with diverse structures[5] coupled with the high regioselectivity of the reactions with **1** and **2** offers a simple method for the preparation of a variety of trimethylsilyl-substituted α-allenic and β-acetylenic amines. The trimethylsilyl-substituted allenic structure has been found to be very useful in many interesting chemical transformations.[6] We are currently exploring the effects on the regio- and stereoselectivity by using other ligands on both silicon and boron atoms of **1** and **2**. The transformations of these trimethylsilyl-substituted α-allenic and β-acetylenic amines to other chemical structures are in progress.

Experimental Section

General procedures described in Chapter 9 of ref 7 for the manipulation of organoborane and other organometallic reagents were employed. All glassware, syringes, and needles were dried in an oven at 140 °C for several hours and cooled in a stream of

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dry nitrogen before use. GLC analysis were carried out on a Varian 3700 gas chromatograph equipped with a 10-m fused-silica capillary column coated with OV-101 liquid phase. Peak integrations were performed on a Hewlett-Packard 3390A integrator. ^1H and ^{13}C NMR spectra were recorded on Varian EM-360 (60 MHz in ^1H) and Varian CFT-20 (20 MHz in ^{13}C) NMR spectrometers, respectively. IR spectra were taken on a Beckman IR-8 spectrometer. Mass spectra were obtained on a Finnigan 4021 instrument. Elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, TN.

Materials. The preparation of *B*-methoxy-9-borabicyclo-[3.3.1]nonane and purification of BF_3·OEt_2 were described elsewhere.[7] *tert*-Butyllithium in pentane was obtained from Alfa. 1-(Trimethylsilyl)propyne was purchased from Petrarch. 1-(Trimethylsilyl)-1-hexyne was prepared as described earlier.[8] Imines were prepared by reacting various primary amines with aldehydes and ketones[5] and stored under nitrogen after distillation. Basic alumina of grade II–III was obtained from Merck.

Condensation of Imine with 1. The following procedure for the reaction between 1 and imine derived from benzaldehyde and *n*-propylamine (entry 1) is representative. The organoborane 1 (10 mmol) was prepared as described previously.[4] To the reaction flask was then added via syringe 1.60 mL (1.47 g, 10 mmol) of imine derived from benzaldehyde and *n*-propylamine at room temperature. After stirring for 50 h, 4 mL of 3 N NaOH and 3.5 mL of 30% H_2O_2 were introduced dropwise at 0 °C. The organic layer was then separated and extracted with 4 N HCl (3 × 25 mL). The combined extracts were neutralized with aqueous sodium bicarbonate solution. The neutralized solution was then extracted with ether. The combined extracts were dried over anhydrous sodium sulfate. After removing of solvent at reduced pressure, the red oily residue was column chromatographed on basic alumina using petroleum ether and petroleum ether–ether (95:5) as eluents. Distillation on a short-path distilling head afforded 1.944 g (75% yield) of 4-phenyl-4-(*n*-propylamino)-3-(trimethylsilyl)-1,2-butadiene as a pale yellow liquid: bp 96 °C (5×10^{-3} torr); IR (neat) 3350 (w), 1930 (s, C=C=C), 1450 (m), 1245 (s), 830 (s), 750 (m), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4 (s, 5 H), 4.75 (d, 2 H, J = 3 Hz), 4.65 (t, 1 H, J = 3 Hz), 2.45 (t, 2 H), 2.05 (br, 1 H), 1.55 (m, 2 H), 0.9 (t, 3 H), −0.05 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 207.8, 143.4, 128.1, 127.8, 127.1, 99.8, 71.7, 62.2, 49.7, 23.2, 11.9, −1.2. Anal. Calcd for $C_{16}H_{25}NSi$: C, 74.06; H, 9.71; N, 5.40. Found: C, 74.08; H, 9.48; N, 5.38.

4-Phenyl-4-(phenylamino)-3-(trimethylsilyl)-1,2-butadiene Hydrochloride (entry 3). The reaction was carried out as in the earlier case except that the imine (1.81 g, 10 mmol) derived from benzaldehyde and aniline was first dissolved in 5 mL of THF and then transferred via cannula to the reaction flask containing 10 mmol of organoborane 1. The crude product was isolated as the hydrochloride of 4-phenyl-4-(phenylamino)-3-(trimethylsilyl)-1,2-butadiene and further recrystallized from acetone to afford 2.052 g (62%) of an analytically pure sample as pale yellow needles: mp 168–169 °C; IR (KBr) 3000–2500 (br), 1935 (s, C=C=C), 1400 (s), 1250 (s), 835 (s), 750 (m), 690 (s) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 7.72 (br, s, 10 H), 5.35 (d, 2 H, J = 2 Hz), 5.2 (t, 1 H, J = 2 Hz), 0.12 (s, 9 H); ^{13}C NMR (Me_2SO-d_6) δ 208.2, 142.6, 139.4, 128.9, 128.3, 128.2, 128.0, 121.4, 117.8, 97.0, 73.7, 59.8, −1.3; mass spectrum, m/e (relative intensity) 294 (M·HCl − Cl^-, 10), 201 (10), 182 (100), 150 (14), 128 (10), 104 (32), 77 (43), 73 (50). Anal. Calcd for $C_{19}H_{23}NSi$·HCl: C, 69.17; H, 7.33; N, 4.25. Found: C, 69.36; H, 7.41; N, 4.20.

Condensation of Imine with 2. The following procedure for the condensation between 2 and imine derived from benzaldehyde and *n*-propylamine (entry 7) is representative. The organoborane 2 (10 mmol) was prepared as described previously.[4] After cooling to −78 °C, the imine (1.60 mL, 1.47 g, 10 mmol) dissolved in 5 mL of THF was transferred by cannula into the reaction flask. The reaction mixture was kept at −78 °C for 1 h and then allowed to warm to room temperature and stirred overnight. After the usual workup as described earlier, the product was isolated by column chromatography on basic alumina using petroleum ether and petroleum ether–ether mixture (95:5) as eluents. A pale yellow liquid 2.514 g (83%) of 1-phenyl-1-(*n*-propylamino)-2-(trimethylsilyl)-2,3-heptadiene was obtained. The product had the following: IR (neat) 3350 (w), 1940 (s, C=C=C), 1450 (s), 1245 (s), 835 (s), 750 (m), 695 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35 (s, 5 H), 5.1 (dt, 1 H, J = 2, 7 Hz), 4.2 (d, 1 H, J = 2 Hz), 2.7–2.35 (m, 2 H), 2.35–1.85 (m, 2 H), 1.8 (s, 1 H), 1.8–1.2 (m, 4 H), 1.2–1.08 (m, 6 H), −0.05 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 204.9, 141.8, 128.5, 128.2, 127.5, 99.7, 89.3, 62.6, 49.4, 30.9, 23.3, 22.3, 14.0, 11.8, −1.0. Anal. Calcd for $C_{19}H_{31}NSi$: C, 75.68; H, 10.36; N, 4.64. Found: C, 75.13; H, 10.76; N, 4.64.

4-(Cyclohexylamino)-5-methyl-1-(trimethylsilyl)-3-propyl-1-hexyne (entry 11): colorless liquid, 2.642 g (86%); IR (neat) 2170 (s, C≡C), 1450 (s), 1380 (s), 1250 (s), 860 (s), 835 (s), 755 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.8–2.3 (br, 2 H), 2.3–1.2 (br, 17 H), 1.2–0.8 (m, 9 H), 0.15 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 109.4, 108.7, 86.9, 66.7, 61.8, 55.5, 55.1, 36.6, 36.1, 35.2, 34.4, 34.3, 33.8, 33.6, 33.5, 32.8, 32.0, 28.3, 27.4, 26.4, 25.8, 25.2, 25.1, 23.6, 22.8, 22.3, 21.2, 21.1, 20.1, 19.8, 19.0, 14.0, 0.4, 0.2. The ^{13}C NMR spectrum indicated the presence of both erythro and threo isomers. Anal. Calcd for $C_{19}H_{37}NSi$: C, 74.19; H, 12.13; N, 4.55. Found: C, 74.06; H, 12.09; N, 4.20.

1-(Trimethylsilyl)-3-[1-(phenylamino)cyclohexyl]-1-hexyne (entry 12): colorless liquid, 2.156 g (66%); IR (neat) 3450 (w), 2170 (s, C≡C), 1600 (s), 1495 (s), 1450 (m), 1320 (m), 1280 (m), 1250 (s), 1155 (m), 995 (m), 870 (s), 835 (s), 750 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–7.0 (m, 2 H), 6.95–6.6 (m, 3 H), 3.5 (s, 1 H), 2.8 (br, 1 H), 2.2–1.1 (br, 14 H), 0.9 (br, 3 H), 0.15 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 146.2, 128.8, 118.0, 116.9, 109.1, 87.5, 58.3, 41.1, 33.1, 32.4, 30.5, 26.0, 21.6, 21.3, 13.8, 0.2. Anal. Calcd for $C_{21}H_{33}NSi$: C, 77.00; H, 10.16; N, 4.28. Found: C, 76.88; H, 10.21; N, 4.14.

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A New Synthesis of 3-*n*-Butyl-4-bromo-5(*Z*)-(bromomethylidene)-2-(5*H*)-furanone, a Naturally Occurring Fimbrolide from *Delisia fimbriata* (Bonnemaisoniaceae)

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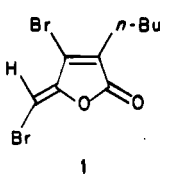
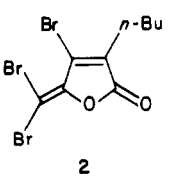
We have reported previously that lithium (*E*)-β-bromo-β-lithioacrylates react with electrophilic reagents such as carbonyl compounds[1] or acid anhydrides[2] to give the corresponding β-bromo- or β-bromo-γ-hydroxybutenolides after acidification. We now report the application of this methodology to a new synthesis of the dibromobutenolide 1 which is a member of a novel class



1



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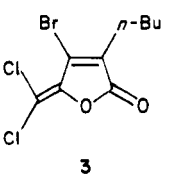

3

of halogenated antibiotics isolated from the red seaweed *Delisea fimbriata* (Bonnemaisonaceae).[3-5] An attempt was

(1) (a) Caine, D.; Samuels, W. D. *Tetrahedron Lett.* **1980**, 4057. (b) Caine, D.; Frobese, A. S.; Ukachukwu, V. C. *J. Org. Chem.* **1983**, *48*, 740.
(2) Caine, D.; Ukachukwu, V. C. *Tetrahedron Lett.* **1983**, *25*, 3959.

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