3040, 1710, 1646, 1612, 895 cm^{-1}; NMR (CCl_4) 6.33 (dd, J = 17, 11 Hz, 1 H), 5.43 (t, J = 7 Hz, 1 H), 5.03 (d, J = 17 Hz, 1 H), 4.93 (d, J = 11 Hz, 1 H), 3.73 (q, J = 6 Hz, 1 H), 3.13 (s, 1 H), 2.43 (d, J = 6 Hz, 2 H), 2.55–1.25 (m, 7 H), 1.73 (s, 3 H), 0.90 (d, J = 8 Hz, 6 H) ppm.

***cis*-Octalone 2.** A solution of ketol **7** (1.120 g, 5 mmol) and *p*-TsOH (86 mg, 0.5 mmol) in benzene (12.5 mL) was heated to 42 °C. After 1 h the solution was diluted with Et_2O (30 mL), washed with aqueous $NaHCO_3$, and dried. Purification on silica gel afforded 865 mg (84% yield) of *cis*-octalone **2**: IR (neat) 3035, 1709, 1630 cm^{-1}; ^1H NMR (CCl_4) 5.34 (br s, 1 H), 2.34 (dd, 1 H, J = 5.3, 9.8 Hz), 2.1–2.5 (m, 3 H), 1.88–2.08 (m, 4 H), 1.54–1.88 (m, 4 H), 1.66 (s, 3 H), 1.48 (m, 1 H), 0.91 (d, 3 H, J = 7 Hz), 0.81 (d, 3 H, J = 7 Hz) ppm; ^{13}C NMR ($CDCl_3$) 214 (s), 135.5 (s), 121.6 (d), 54.5 (d), 44.2 (d), 39.8 (t), 36.5 (d), 28.5 (d), 27.3 (t), 26.1 (t), 24.3 (t), 21.8 (q), 21.2 (q), 15.5 (q) ppm; mass spectrum, m/e 206 (M^+), 191, 163, 149, 124, 55, 43, 41. Anal. Calcd for $C_{14}H_{22}O$: C, 168.15; H, 22.18. Found: C, 168.23; H, 22.29.

α-Methylene Ketone 1. A mixture of paraformaldehyde (180 mg, 6 mmol) and *N*-methylanilinium trifluoroacetate (284 mg, 4 mmol) in 3 mL of THF was refluxed for 20 min. *cis*-Octalone **2** (206 mg, 1 mmol) was added and the resulting solution was refluxed 3 h more. After cooling, the reaction mixture was diluted with Et_2O (20 mL) and hydrolyzed with 20 mL of half-saturated $NaHCO_3$ solution. The crude product was extracted with Et_2O and dried. Purification on a silica gel column afforded 140 mg of α-methylene ketone **1** (64% yield) along with 61 mg of recovered octalone **2**: IR (neat) 3090, 3040, 1693, 1620, 932 cm^{-1}; area $\nu_{C=O}$/area $\nu_{C=C}$ = 2.6;[14] NMR ($CDCl_3$) 5.59 (m, 1 H, methylenic), 5.36 (m, 1 H, vinylic), 5.0 (m, 1 H, methylenic), 2.6–2.2 (br m, 3 H), 1.90 (br m, 5 H), 1.66 (s, 3 H), 1.25 (br m, 2 H), 1.85 (br d, J = 6 Hz, 6 H) ppm.

Natural chiloscyphone (**1**): IR (neat) 1670, 1629, 935 cm^{-1}; area $\nu_{C=O}$/area $\nu_{C=C}$ = 6; NMR ($CDCl_3$) 5.96 (s, 1 H methylenic), 5.75 (d, J = 1.2, 1 H, methylenic), 5.42 (m, 1 H, vinylic), 3.59 (q, J = 6.9, 2.0 Hz, 1 H, methine), 2.53 (m, 2 H), 2.0 (m, 3H), 1.83 (d, J = 1.2 Hz, 3 H), 1.67 (m, 1 H), 1.37 (m, 3 H), 0.96 (s, 3 H), 0.85 (d, J = 5.5, 3 H).

Acknowledgment. We are indebted to Professor A. Matsuo for kindly providing us with the IR and NMR spectra of natural chiloscyphone. We thank Dr. M. G. Bock (Merck Sharp and Dohme Research Laboratories) for helpful discussions.

Registry No. 1, 78183-88-7; 2, 78109-27-0; **2a**, 78109-28-1; **4**, 37865-96-6; (*E*)-**5**, 78109-29-2; (*E*)-**6**, 78109-30-5; (*E*)-**6** ethylene glycol, 78109-31-6; (*E*)-**7**, 78109-32-7; isoprene oxide, 1838-94-4; (*E*)-6-(2-methyl-1,3-dioxol-2-yl)-2-methyl-2-hexenal, 78109-33-8; isobutyraldehyde, 78-84-2.

Efficient Synthesis of a New Nucleophilic Acetaldehyde Equivalent: (*Z*)-2-(Trimethylsiloxy)vinyllithium

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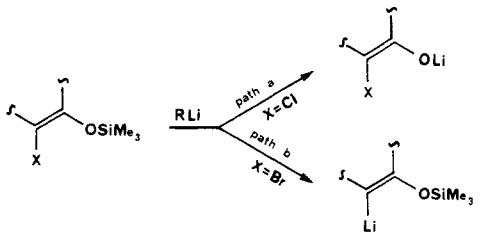
It is well-known that the trialkylsilyl enol ethers are readily cleaved by organometallic reagents.[1] Particularly, this is the case of the β-chloro(trimethylsilyl) enol ethers which are transformed into β-chloro enolates by reaction with methyllithium[2] (Scheme I, path a). We report our finding that with β-bromo(trimethylsilyl) enol ethers and *tert*-butyllithium, the selectivity of this reaction is reversed; i.e., the halogen–metal exchange reaction is faster than the oxygen–silicon cleavage (path b). Thus 2-halo(trimethylsilyl) enol ethers may be converted either to 2-halo enolates or vinyllithium reagents, depending on the halogen and reaction conditions.

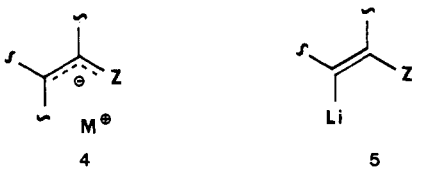
Scheme I



(*Z*)-[(Trimethylsiloxy)vinyl]lithium (**1**) is a relatively stable nucleophilic acetaldehyde equivalent (over 20 h in diethyl ether at −70 °C).

This compound is conveniently prepared (path b) by reaction of *tert*-butyllithium in diethyl ether at −70 °C with (*Z*)-2-bromo-1-(trimethylsiloxy)ethylene.[3] At low temperature, the anion **1** reacts with carbonyl compounds to produce the alcohols **2** (Scheme II), which are easily hydrolyzed into unsaturated carbonyl compounds **3** (see Table I).

In addition to ambident anions **4** (Z = NR,[4,5] $NNMe_2$,[6] O[7]), available since the pioneering work of Stork and Dowd,[4] the vinylic anions **5** (Z = OR,[8] OLi,[9] NR_2[8b,10]) constitute a new class of nucleophilic aldehyde and ketone equivalents of considerable synthetic value.



4 5

Several characteristic advantages of the new reagent **1** should be mentioned: the ease of its preparation, the availability of its precursor (*Z*)-2-bromo(trimethylsiloxy)ethylene (95% *Z*),[3] and the well-known ease of hydrolysis of the generated labile trimethylsiloxy derivatives.

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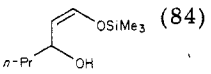
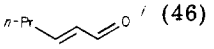
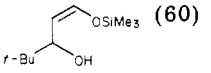
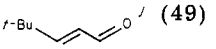
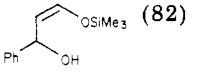
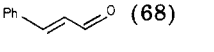
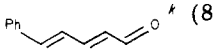
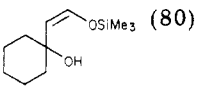
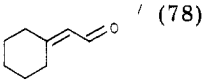
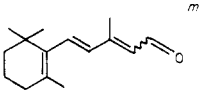
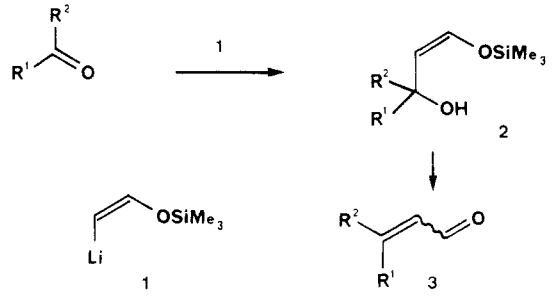
Table I. Reaction of (*Z*)-2-(Trimethylsiloxy)vinyllithium with Aldehydes and Ketones

electrophile	conditions[a]	adduct 2[b,c] (yield, %)[d]	hydrolysis product 3[e,f] (yield, %)[g]
butanal		 (84)	 [i] (46)
2,3-dimethylpropanal		 (60)	 [j] (49)
benzaldehyde		 (82)	 (68)
cinnamaldehyde	30 min, −75 °C		 [k] (86)
cyclohexanone	16 h, −75 °C	 (80)	 [l] (78)
β-ionone	2 h, −50 °C		 [m] (44)[h]

[a] Contact time after addition of the electrophile. [b] Hydrolysis with 5% aqueous Na_2CO_3 solution. [c] Characterized by spectral data. [d] Yields of crude products based upon starting electrophiles. [e] Hydrolysis with hydrochloric acid in THF solution. [f] All products exhibited satisfactory NMR, IR, and mass spectral data. [g] Nonoptimized yields of distilled products, based upon starting electrophiles (intermediate adducts **2** were not isolated). [h] Purified by distillation and chromatography on silica gel. [i] See ref 12. [j] See ref 8d. [k] See ref 11. [l] See ref 8b,c and 13. [m] See ref 5a,b and 14.

Scheme II



Experimental Section

The following experiments illustrate typical procedures.

5-Phenyl-2,4-pentadienal. *tert*-Butyllithium (4 mmol, 2.2 mL, 1.8 M in *n*-pentane) was added dropwise to a solution of (*Z*)-2-bromo-1-(trimethylsiloxy)ethylene (0.43 g, 2.2 mmol) in 15 mL of diethyl ether at −70 °C under dry nitrogen. Following 90 min of stirring at −70 °C (in order to destroy the generated *t*-BuBr), cinnamaldehyde (0.28 g, 2.1 mmol) in 1 mL of diethyl ether was added over a 5-min period. After 30 min at −75 °C, the reaction mixture was allowed to warm to 0–5 °C (20 min). Then, a solution of 2 mL of 1.5 N hydrochloric acid in 10 mL of tetrahydrofuran was added. After an additional 30 min, the reaction mixture was extracted with diethyl ether and distilled [bp 115–120 °C (0.1 mmHg)] to yield 0.29 g (86%) of 5-phenyl-2,4-pentadienal: IR (liquid) 1675, 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.25 (dd, *J* = 8, 14.7 Hz, 1), 6.9–7.5 (m, 8), 9.55 (d, *J* = 8 Hz, 1) (see the literature[11] for comparison).

(*Z*)-1-(Trimethylsiloxy)-1-hexen-3-ol. Butanal (1.02 g, 2.1 mmol) in 1 mL of diethyl ether was added to (*Z*)-[2-(trimethylsilyloxy)vinyl]lithium prepared as above. After warming to 0 °C, the reaction mixture was quenched with Na_2CO_3 solution (5%). After the workup, 0.33 g (84% yield) of crude 1-(trimethylsiloxy)-1-hexen-3-ol was obtained: IR (liquid) 3400 (br), 1658 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.20 (d, *J* = 4.7 Hz, 1), 5.35 (m, 1), 4.56 (m, 1), 3.2 (br s, 1, OH exchange with D_2O), 1.90–0.80 (m, 7), 0.20 (s, 9).

(*Z*)-1-(Trimethylsiloxy)-4,4-dimethyl-1-penten-3-ol: IR (liquid) 3450 (br), 1660 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.27 (d, *J* = 6 Hz, 1), 4.60 (dd, *J* = 6, 7.3 Hz, 1), 4.22 (d, *J* = 7.3 Hz, 1), 3.1 (br, s, 1, OH exchange with D_2O), 0.90 (s, 9), 0.20 (s, 9).

(*Z*)-3-(Trimethylsiloxy)-1-phenyl-2-propen-1-ol: IR (liquid) 3490 (br), 1655 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4–7.35 (m, 5), 6.29 (d, *J* = 6 Hz, 1), 5.73 (d, *J* = 8 Hz, 1), 4.85 (dd, *J* = 6, 8 Hz, 1), 2.75 (br, s, 1, OH exchange with D_2O), 0.20 (s, 9).

1-[(*Z*)-2-(Trimethylsiloxy)vinyl]cyclohexanol: IR (liquid) 3420 (br), 1655 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.05 (d, *J* = 6.7 Hz, 1), 4.53 (d, *J* = 6.7 Hz, 1), 3.7 (br, s, 1, OH exchange with D_2O), 1.5–1.0 (m, 10), 0.15 (s, 9).

Registry No. 1, 78108-48-2; 2 (R¹ = Pr; R² = H), 78108-49-3; 2 (R¹ = *t*-Bu; R² = H), 78108-50-6; 2 (R¹ = Ph; R² = H), 78108-51-7; 2 (R¹ = R² = cyclohexyl), 78108-52-8; 3 (R¹ = Pr; R² = H), 505-57-7; 3 (R¹ = *t*-Bu; R² = H), 926-37-4; 3 (R¹ = C=CHPh; R² = H), 13466-40-5; 3 (R¹ = R² = cyclohexyl), 1713-63-9; 3 (R¹ = CH=CH(2,6,6-trimethyl-1-cyclohexen-1-yl); R² = CH_3), 1209-68-3; butanal, 123-72-8; 2,2-dimethylpropanal, 630-19-3; benzaldehyde, 100-52-7; cinnamaldehyde, 104-55-2; cyclohexanone, 108-94-1; β-ionone, 14901-07-6.

Oxazoline Chemistry. Preparation of Isoquinolines and 2,2′-Bisoxazolines

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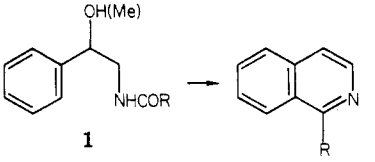
The Pictet–Gams synthesis[1] of fully aromatic isoquinolines (eq 1) via 2-hydroxy(or methoxy)phenethyl-



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