**Recovery of $Ter_2$*BOMe (23-25) from EA-B$Ter_2$* Adducts (18 and 19) and 8-HQ-B$Ter_2$* Adducts (20-22).** The following procedure is representative.

To a solution of 8-HQ-B(4-$^d$Ic$r_2$) adduct 21 (2.15 g, 5 mmol) in a mixture of $Et_2O$ (10 mL) and methanol (2 mL) was added anhydrous HCl in $Et_2O$ (5.0 mL, 1.0 M, 5 mmol) at 0 °C and the reaction stirred for 0.5 h. There was an instantaneous precipitation of the 8-HQ·HCl salt. $^{11}$B NMR analysis of the reaction mixture revealed a complete disappearance of the peak at δ 15 ppm, corresponding to the 8-HQ-B(4-$^d$Ic$r_2$) adduct 21, and the appearance of a new peak at δ 53 ppm, corresponding to 4-$^d$Ic$r_2$BOMe (24). The volatiles were then pumped off under vacuum (10 mm), and the resulting mixture was extracted with pentane (2 × 15 mL). The clear pentane extract was decanted into another flask and concentrated to obtain 4-$^d$Ic$r_2$BOMe (24) as a colorless liquid: yield 1.48 g (94%).

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# Chiral Synthesis via Organoboranes. 36. Exceptionally Enantioselective Allylborations of Representative Heterocyclic Aldehydes at −100 °C under Salt-Free Conditions

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Chiral terpenyl-based allylborane reagents ($Ter_2$*$BCH_2CH{=}CH_2$, 1-3) undergo facile condensation with representative heterocyclic aldehydes (HetCHO) at −100 °C (in the absence of $Mg^{2+}$ salts) and afford the corresponding homoallylic alcohols (HetCH*(OH)$CH_2CH{=}CH_2$, 12-19) in enantiomeric purities approaching 100% ee. A new workup procedure involving 8-hydroxyquinoline (8-HQ) has been utilized for the convenient isolation of the product alcohols.

Heterocyclic natural products are exceptionally valuable both as targets for total synthesis as well as for biomedical and pharmaceutical research, owing to their unique structural features and remarkably diverse medicinal value. Recently, a number of heterocyclic natural products which exhibit extremely useful biological activities have been isolated from marine and other natural sources.[1,2] A characteristic feature in the structures of these natural products is the presence of various α-heterocyclic carbinol moieties (Chart I).

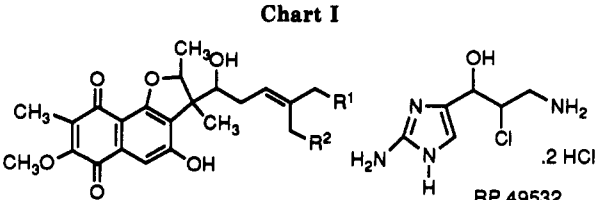
A highly stereoselective synthesis of such heterocyclic natural products requires remarkably enantioselective (≥99% ee) synthetic methods for the construction of heterocyclic carbinol moieties. To our knowledge, such truly general and perfectly enantioselective (≥99% ee) methods have not been reported in the literature for the synthesis of various heterocyclic carbinols.

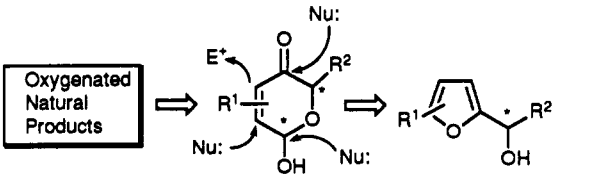
Further, it is well-known that enantiomerically pure 2-furanylcarbinols can be transformed into hydropyranone intermediates which are valuable for the asymmetric synthesis of innumerable oxygenated natural products (Scheme I).[3,4]

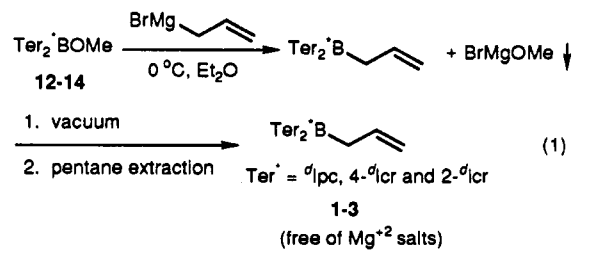
Similarly, the thiophenyl-, pyridyl-, and other heterocyclic carbinols of high optical purity are also useful for the stereoselective synthesis of many other important heterocyclic compounds.[5] Consequently, with a view to support such synthetic applications, we undertook a systematic examination of the asymmetric allylboration of representative heterocyclic aldehydes 4-11 with the diterpenylallylboranes 1-3 at −100 °C, in the absence of $Mg^{2+}$ salts (Scheme II).[6]

## Results and Discussion

*B*-Allyldiisopinocampheylborane ($^d$Ipc$_2$BAll, 1), *B*-allylbis(4-isocaranyl)borane (4-$^d$Ic$r_2$BAll, 2), and *B*-allylbis(2-isocaranyl)borane (2-$^d$Ic$r_2$BAll, 3) were prepared in chemically pure form starting from the corresponding methoxyditerpenylboranes ($Ter_2$*BOMe), according to the previously reported procedures (eq 1):[6]

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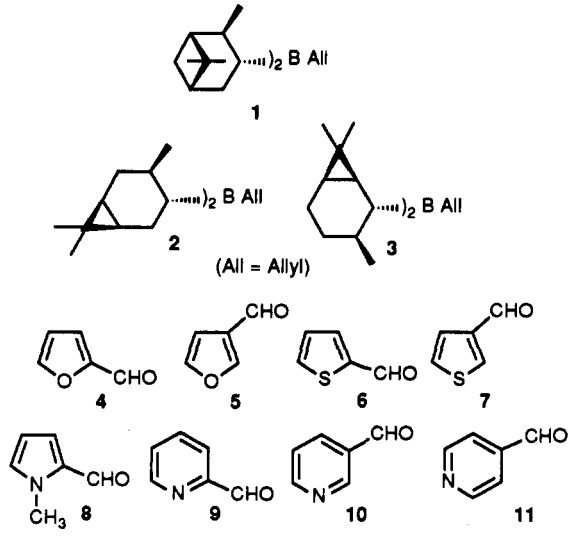
0022-3263/92/1957-6614$03.00/0 

**Table I. Asymmetric Allylboration of Representative Heterocyclic Aldehydes with 1-3 at −100 °C**

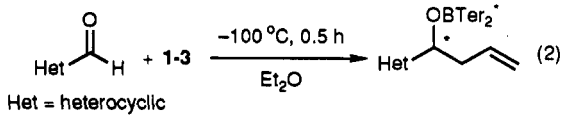
| entry | aldehyde | product | % ee[a] (% yield)[b] $^dIpc_2BAll$ (1) | 4-$^dICr_2BAll$ (2) | 2-$^dICr_2BAll$ (3) |
|---|---|---|---|---|---|
| 1 | 4 | 1-(2-furyl)-3-buten-1-ol (12) | ≥99 (91, *S*) | | |
| 2 | 5 | 1-(3-furyl)-3-buten-1-ol (13) | ≥91 (80, *S*) | | ≥99 (88, *R*) |
| 3 | 6 | 1-(2-thiophene-yl)-3-buten-1-ol (14) | 80 (90, *S*) | | |
| 4 | 7 | 1-(3-thiophene-yl)-3-buten-1-ol (15) | 75 (82, *S*) | | ≥99 (83, *R*) |
| 5 | 8 | 1-(1-methyl-2-pyrrolyl)-3-buten-1-ol (16) | ≥99 (78, *S*) | | |
| 6 | 9 | 1-(2-pyridyl)-3-buten-1-ol (17) | ≥99 (85, *S*) | | |
| 7 | 10 | 1-(3-pyridyl)-3-buten-1-ol (18) | ≥96 (84, *S*) | | |
| 8 | 11 | 1-(4-pyridyl)-3-buten-1-ol (19) | | ≥99 (78, *S*) | |

[a] Determined by capillary GC analysis of the corresponding Mosher ester derivatives of various heterocyclic alcohols. [b] Isolated yields of pure, distilled samples.

**Scheme II**



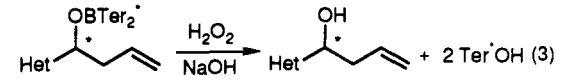

A solution of the heterocyclic aldehyde (4–11) in $Et_2O$ was cooled to −78 °C and added to $Ter_2$*BAll (1–3, free from $Mg^{+2}$ salts) in $Et_2O$ at −100 °C. Heterocyclic aldehydes undergo rapid (≤0.5 h) and essentially quantitative allylborations under these reaction conditions (eq 2):



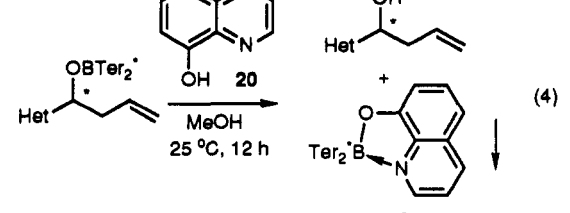

Het = heterocyclic

4-11

At this stage, however, we encountered an unusual problem. The isolation of chiral heterocyclic alcohols could not be achieved by the usual oxidative workup in a convenient manner, as many of the product alcohols boil in the range of the terpenol byproducts (eq 3):[7]




Consequently, we adopted a new workup procedure involving the chelating agent 8-hydroxyquinoline (8-HQ, **20**). As required by this procedure, solvent was pumped off from the reaction mixture at the conclusion of allylboration, using aspirator vacuum (14 mm). The terpenylborinate intermediate was dissolved in methanol and treated with a methanolic solution of **20**. The 8-HQ–$BTer_2$* adducts **21–23** separated out of the solution in all cases as fluorescent yellow solids,[8] making isolation of the chiral heterocyclic alcohols extremely simple (eq 4):




21-23

In this manner, the asymmetric allylborations of representative heterocyclic aldehydes were conducted with $Ter_2$*BAll reagents 1–3 at −100 °C, under salt-free conditions. These results are summarized in Table I.

The asymmetric allylborations of 2-furaldehyde (**4**), 3-furaldehyde (**5**), 1-methyl-2-pyrrolecarboxaldehyde (**8**), 2-pyridinecarboxaldehyde (**9**), and 3-pyridinecarbox-

(1) (a) Wu, Y.-C.; Chang, F.-R.; Duh, C.-Y.; Wang, S.-K. *Heterocycles* **1992**, *34*, 667. (b) Myint, S. H.; Cortes, A.; Laurens, A.; Hocquemiller, R.; Leboeuf, M.; Cav'e, A.; Cotte, J.; Que'ro, A.-M. *Phytochemistry* **1991**, *30*, 3335. (c) Jossang, A.; Dubaele, B.; Cav'e, A.; Bartoli, M.-H.; Be'riel, H. *J. Nat. Prod.* **1991**, *54*, 967. (d) Cortes, D.; Myint, S. H.; Hocquemiller, R. *Tetrahedron* **1991**, *47*, 8195. (e) Scholz, G.; Tochtermann, W. *Tetrahedron Lett.* **1991**, *32*, 5535. (f) Wakabayashi, N.; Spencer, S. L.; Waters, R. M.; Lusby, W. R. *J. Nat. Prod.* **1991**, *54*, 1419. (g) Rieser, M. J.; Kozolowski, J. F.; Wood, K. V.; McLaughlin, J. L. *Tetrahedron Lett.* **1991**, *32*, 1137. (h) Fang, X.-P.; Rupprecht, J. K.; Alkofahi, A.; Hui, Y.-H.; Liu, Y.-M; Smith, D. L.; Wood, K. V.; McLaughlin, J. L. *Heterocycles* **1991**, *32*, 11. (i) Myint, S. H.; Laurens, A.; Hocquemiller, R.; Cav'e, A.; Davoust, D.; Cortes, D. *Heterocycles* **1990**, *31*, 861. (j) Fukuzawa, A.; Aye, M.; Nakamura, M.; Tamura, M.; Murai, A. *Tetrahedron Lett.* **1990**, *31*, 4895. (k) Hisham, A.; Pieters, L. A. C.; Claeys, M.; Esmans, E.; Dommisse, R.; Vlietinck, A. J. *Ibid.* **1990**, *32*, 4649 and references cited therein. (l) Ojika, M.; Yoshida, Y.; Nakayama, Y.; Yamada, K. *Ibid.* **1990**, *32*, 4907. This listing is not exhaustive.

(2) (a) Otsuka, M.; Nishio, T.; Oshitari, T.; Owa, T.; Sugiura, Y.; Maeda, K.; Ohno, M.; Kobayashi, S. *Heterocycles* **1992**, *33*, 27. (b) Barrett, A. G. M.; Lebold, S. A. *J. Org. Chem.* **1991**, *56*, 4875. (c) Funayama, S.; Ishibashi, M.; Komiyama, K.; Omura, S. *Ibid.* **1990**, *55*, 1132. (d) Kogen, H.; Kadokawa, H.; Kurabayshi, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1240. (e) Paquette, L. A., Sweeney, T. J. *J. Org. Chem.* **1990**, *55*, 1703. (f) Commercon, A.; Possinet, G. *Tetrahedron* Lett. **1990**, *31*, 3871 and references cited therein.

(3) (a) Martin, S. F.; Guinn, D. E. *J. Org. Chem.* **1987**, *52*, 5588 and references cited therein. (b) Maier, M. E.; Schoffling, B. *Tetrahedron Lett.* **1991**, *32*, 53. (c) Paterson, I.; Lister, A.; Ryan, G. R. *Ibid.* **1991**, *32*, 1749. (d) Tanis, S. P., McMills, M. C.; Scahill, T. A.; Kloosterman, D. A. *Ibid.* **1990**, *31*, 1977. (e) Honda, T.; Kobayashi, Y.; Tsubuki, M. *Ibid.* **1990**, *30*, 4891.

(4) (4) Achmatowicz, O. In *Organic Synthesis Today* and *Tomorrow*; Trost, B. M., Hutchinson, C. R., Eds.; Pergamon Press: Oxford, 1981; pp 307–318. (b) Zamojski, A.; Grynkiewicz, G. In *Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1984; pp 141–235. (c) Coppola, G. M.; Schuster, H. F. *Asymmetric Synthesis*; Wiley: New York, 1987; p 25.

(5) (a) Deeter, J.; Frazier, J.; Staten, G.; Staszak, M.; Wiegel, L. *Tetrahedron Lett.* **1990**, *31*, 7101. (b) Farr, R. A.; Peet, N. P.; Kang, M. S. *Ibid.* **1990**, *31*, 7109. (c) Soai, K.; Hori, H.; Niwa, S. *Heterocycles* **1989**, *29*, 2065 and references cited therein.

(6) Racherla, U. S.; Brown, H. C. *J. Org. Chem.* **1991**, 56, 401.

(7) In our preliminary study on the allylboration of heterocyclic aldehydes with *B*-allyl-9-BBN at −100 °C, oxidation workup was successful as cyclooctanediol was water soluble and did not interfere with product isolation. See the preceeding paper in this issue for useful discussion.

(8) The isolated yields of the 8-hydroxyquinoline adducts were generally excellent (80–85%).

aldehyde (10) with *B*-allyldiisopinocampheylborane ($^d$Ipc$_2$BAll, 1) afford the corresponding heterocyclic homoallylic alcohols in extremely high enantiomeric purities (91–≥99% ee, entries 1, 2, and 5–7). On the contrary, the allylation of 2-thiophenecarboxaldehyde (6) and 3-thiophenecarboxaldehyde (7) with $^d$Ipc$_2$BAll (1) is not equally enantioselective (75–80% ee, entries 3 and 4). At present, we do not have a satisfactory explanation for this behavior. In the past, we reported that *B*-allylbis(4-isocaranyl)borane (4-$^d$Icr$_2$BAll, 2) and *B*-allylbis(2-isocaranyl)borane (2-$^d$Icr$_2$BAll, 3) are more enantioselective than $^d$Ipc$_2$BAll (1) for the asymmetric allylboration of aldehydes.[9] Indeed, 4-$^d$Icr$_2$BAll (2) achieves the allylboration of 3-pyridinecarboxaldehyde (11) in ≥99% ee (entry 8). The enantioselectivities in allylborations of 3-furaldehyde (5) and 3-thiophenecarboxaldehyde (7) could also be improved from 91 to ≥99% ee and 75 to ≥99% ee, respectively, utilizing 2-$^d$Icr$_2$BAll (3, entries 2 and 4).

It must be mentioned that the 8-HQ–BTer$_2$ adducts (21–23) are air-stable and nonhygroscopic. Consequently, the filtration of these adducts is conveniently carried out in open air, and the products are isolated by simple distillation in 80–90% isolated yields.[10]

**Absolute Stereochemical Assignments**: The experimentally observed stereoselectivities of $^d$Ipc$_2$BAll (1), 4-$^d$Icr$_2$BAll (2), and 2-$^d$Icr$_2$BAll (3) in the asymmetric allylation of heterocyclic aldehydes are in complete agreement with the predicted stereochemical preferences of these reagents based on our earlier results (Table I).[9] For example, our previous results predict that allylboration of 2-furaldehyde (4) with $^d$Ipc$_2$BAll (1) would provide (*S*)-1-(2-furyl)-3-buten-1-ol. Indeed, the actual experiment provided the expected (*S*)-(+)-1-(2-furyl)-3-buten-1-ol (12) in ≥99% ee. The homoallylic alcohol, (+)-12, was assigned the *S*-absolute configuration by a comparison of its sign of optical rotation with its known enantiomer, (*R*)-(−)-1-(2-furyl)-3-buten-1-ol, (−)-12.[12b] Sato and co-workers proved the absolute configuration of (−)-12 by correlation with the reported (*R*)-α-hydroxypentanoic acid[15] by the following sequence: (1) $H_2$, Pd/C; (2) $Ac_2O$, Pyr; (3) $NaIO_4$, $RuCl_3 \cdot 3H_2O$ (cat.), $CCl_4$–$CH_3CN$–$H_2O$ (2:2:3); (3) $K_2CO_3$, MeOH–$H_2O$ (4:1).[12b] The absolute configurations of the rest of the alcohols 13–19 resulting from the allylboration of 5–11 with $^d$Ipc$_2$BAll (1) have been assigned based on analogy. In our earlier work, we established that $^d$Ipc$_2$BAll (1) and 4-$^d$Icr$_2$BAll (2) exhibit identical stereochemical preference in allylboration and afford homoallylic alcohols of the same absolute configuration, while 2-$^d$Icr$_2$BAll (3) shows opposite stereochemical preference and provides homoallylic alcohols of the opposite absolute configuration.[9] Therefore, the absolute configurations of 13, 15, and 19, resulting from 4-$^d$Icr$_2$BAll (2) and 2-$^d$Icr$_2$BAll (3), were assigned in this manner.

## Experimental Section

All equipment was dried in an oven at 150 °C for several hours prior to use and assembled hot under a stream of nitrogen. All manipulations involving air-sensitive materials were carefully performed under a nitrogen atmosphere according to the procedures described elsewhere.[11] All $^{11}$B NMR spectra were recorded at 96 MHz on a Gemini-300 BB NMR instrument. All $^1$H and $^{13}$C NMR spectra were recorded at 200 and 50 MHz (Gemini-200 BB spectrometer), respectively. Optical rotation measurements were performed on a Rudolph Autopol III automatic polarimeter. THF was freshly distilled over sodium benzophenone ketyl prior to use. Anhydrous $Et_2O$ was purchased from Mallinckrodt and was used in all experiments without further purification. Borane–methyl sulfide (BMS) and allylmagnesium bromide were purchased from the Aldrich Chemical Co.

**Preparation of Allylborane Reagents 1–3 Free of $Mg^{2+}$ Salts.** The following procedure described for *B*-allyldiisopinocampheylborane ($^d$Ipc$_2$BAll, 1) is representative.[6]

Allylmagnesium bromide in ether (49 mL, 1.0 M, 49 mmol) was added dropwise to a well-stirred solution of *B*-methoxydiisopinocampheylborane (15.8 g, 50 mmol) in ether (50 mL) at 0 °C. Following addition, stirring was continued for 1 h at 25 °C and ether was pumped off under aspirator vacuum (15 mm, 2 h). The residue was carefully extracted with pentane (2 × 100 mL) under nitrogen while the reaction mixture was stirred. Next, stirring was discontinued to permit the $Mg^{2+}$ salts to settle, and the clear supernatant pentane extract was transferred into another flask with a double-ended needle through a Kramer filter.[11] Evaporation of pentane (15 mm, 2 h) afforded the pure *B*-allyldiisopinocampheylborane ($^d$Ipc$_2$BAll, 1, free of $Mg^{2+}$ salts) in essentially quantitative yield.

**Representative Procedure for the Allylboration of Representative Heterocyclic Aldehydes with the Reagents 1–3 at −100 °C Using 8-HQ Workup.** The allylboration of 2-furaldehyde (4) with *B*-allyldiisopinocampheylborane (1) at −100 °C, in the absence of $Mg^{2+}$ salts, is representative. Anhydrous ether (100 mL) was added to neat $^d$Ipc$_2$BAll (1), and the resulting solution was cooled to −100 °C. A solution of 2-furaldehyde (4.8 g, 50 mmol) in ether (50 mL), maintained at −78 °C, was slowly added along the side of the flask to the solution of $^d$Ipc$_2$BAll (1) at −100 °C. The reaction mixture was stirred for 1 h at the temperature, and methanol (1 mL) was added to quench the reaction. Next, the volatile components were pumped off from the reaction mixture at 0 °C, and methanol (50 mL) was added. This was followed by the addition of a solution of 8-hydroxyquinoline (7.98 g, 55 mmol) in methanol (50 mL). The solution was stirred overnight at 25 °C to obtain a crystalline, fluorescent yellow solid of 8-HQ–B$^d$Ipc$_2$ which was readily filtered off in open air. Concentration of the methanolic solution, followed by distillation, afforded the desired (*S*)-(−)-1-(2-furyl)-3-buten-1-ol (12, bp 80 °C (3 mm)) in excellent yield (6.27 g, 91%).[12b] Capillary GC analysis of its Mosher ester on an SPB-5 column (30 meters) established the enantiomeric purity of the alcohol to be ≥99% ee: $[\alpha]^{23}_D$ = −38.6° (*c* 2.04, $CHCl_3$);[12] $^1$H NMR ($CDCl_3$, 200 MHz) δ 2.56 (t, 2 H, *J* = 7.2 Hz), 3.01 (d, 1 H, *J* = 4.9 Hz), 4.66 (q, 1 H, *J* = 5.7 Hz), 4.95–5.34 (m, 2 H), 5.63–5.90 (m, 1 H), 6.10–6.50 (m, 2 H), 7.33 (d, 1 H, *J* = 2.0 Hz); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 40.07, 67.05, 106.34, 110.37, 118.41, 134.22, 142.19, 156.59; MS (70 eV, 250 °C) *m/z* 138 ($M^+$, 1.09), 121 (M − OH, 14.41), 97 (M − $C_3H_5$, 100), 69 (12.70); IR (neat) 3366 (s), 1638 (m) $cm^{-1}$.

(*R*)-1-(3-Furyl)-3-buten-1-ol (13): 88% yield; bp 58 °C (1 mm); $[\alpha]^{23}_D$ = +10.8° (*c* 1.54, EtOH); ≥99% ee by capillary GC analysis; $^1$H NMR ($CDCl_3$, 200 MHz) δ 2.27–2.62 (m, 3 H), 4.58–4.83 (m, 1 H), 5.01–5.30 (m, 2 H), 5.65–6.00 (m, 1 H), 6.39 (m, 1 H), 7.38 (m, 2 H); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 42.52, 66.28, 108.90, 118.77, 128.86, 134.57, 139.47, 143.69; MS (70 eV, 250 °C) *m/z* 138 ($M^+$, 9.68), 121 (M − OH, 100), 97 (M − $C_3H_5$, 86.40), 69 (63.52); IR (neat) 3373 (s), 1638 (m), 1591 (w), 1500 (m) $cm^{-1}$. Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.29. Found: C, 69.23; H, 7.45.

(*S*)-1-(2-Thiophene-yl-3-buten-1-ol (14): 90% yield; bp 94 °C (3 mm) (lit.[13] bp 89–91 °C (1 mm)); $[\alpha]^{23}_D$ = −5.2° (*c* 1.10, EtOH); 80% ee by capillary GC analysis; $^1$H NMR ($CDCl_3$, 200 MHz) δ 2.53 (t, 2 H, *J* = 6.8 Hz), 3.19 (d, 1 H, *J* = 4 Hz), 4.78–5.31 (m, 3 H), 5.60–5.95 (m, 1 H), 6.82–7.35 (m, 3 H); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 43.67, 69.48, 118.60, 124.74, 126.85, 134.32, 148.33; MS (70 eV, 250 °C) *m/z* 154 ($M^+$, 0.47), 135 (M − $H_2O$, 48.4), 113 (M − $C_3H_5$, 100), 91 (18.5), 85 (53.7); IR (neat) 3373 (s), 1638 (m) $cm^{-1}$.

(*R*)-1-(3-Thiophene-yl)-3-buten-1-ol (15): 83% yield; bp 91 °C (1 mm) (lit.[13] bp 90–91 °C (1 mm)); $[\alpha]^{23}_D$ +14.4° (*c* 1.61, EtOH); ≥99% ee by capillary GC analysis; $^1$H NMR ($CDCl_3$, 200

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(10) This is a significant advantage over the ethanolamine workup.

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(12) (a) Shur, A. M.; Matyushinskii, B. V. *Uchenye Zapiski Kishinev. Univ.* **1953**, *7*, 97; *Chem. Abstr.* **1955**, *49*, 11618. (b) Kusakabe, M.; Kitano, Y.; Kobayashi, Y.; Sato, F. *J. Org. Chem.* **1989**, *54*, 2085.

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MHz) δ 2.42–2.61 (m, 3 H), 4.75 (m, 1 H), 5.01–5.20 (m, 2 H), 5.65–5.92 (m, 1 H), 7.00–7.42 (m, 3 H); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 43.00, 69.72, 118.61, 121.05, 126.00, 126.30, 134.63, 145.78; MS (70 eV, 250 °C) $m/z$ 154 ($M^+$, 0.88), 137 (M – OH, 11.19), 113 (M – $C_3H_5$, 83.72), 85 (100), 45 (22.44); IR (neat) 3359 (s), 1635 (m) $cm^{-1}$.

**(*S*)-1-(1-Methyl-2-pyrrolyl)-3-buten-1-ol (16)**: 78% yield; bp 82–84 °C (0.7 mm); $[\alpha]^{23}D$ = –12.1° (*c* 1.25, EtOH); ≥99% ee by capillary GC analysis; $^1$H NMR ($CDCl_3$, 200 MHz) δ 2.30 (m, 1 H), 2.56–2.70 (m, 2 H), 6.56 (m, 1 H); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 33.97, 40.67, 65.85, 106.43, 106.77, 118.07, 123.33, 134.44, 135.29; MS (70 eV, 250 °C) $m/z$ 151 ($M^+$, 4.77), 110 (M – $C_3H_5$, 100), 82 (M – $C_3H_5$ – $H_2O$, 64.28), 67 (22.53); IR (neat) 3386 (s), $cm^{-1}$. Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.74; H, 8.90; N, 9.19.

**(*S*)-1-(2-Pyridyl)-3-buten-1-ol (17)**: 85% yield; bp 72 °C (0.4 mm) (lit.[14] bp 80 °C (0.1 mm)); $[\alpha]^{23}_D$ = –32.5° (*c* 3.5, EtOH); ≥99% ee by capillary GC analysis; $^1$H NMR ($CDCl_3$, 200 MHz) δ 2.35–2.86 (m, 2 H), 4.60–5.46 (m, 4 H), 5.67–6.05 (m, 1 H), 6.48 (m, 1 H), 7.01–7.90 (m, 3 H); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 42.83, 72.93, 118.04, 120.83, 122.60, 134.71, 137.08, 148.83, 162.86; MS (70 eV, 250 °C) $m/z$ 150 (M + H, 4.62), 130 (M – H – $H_2O$, 9.84), 108 (M – $C_3H_5$, 100), 78 (55.43), 53 (16.77); IR (neat) 3306 (s), 1635 (m), 1591 (s), 1568 (m) $cm^{-1}$.

**(*S*)-1-(3-Pyridyl)-3-buten-1-ol (18)**: 84% yield; bp 110 °C (0.8 mm) (lit.[14] bp 102 °C (0.1 mm)); $[\alpha]^{23}_D$ = –28.0° (*c* 1.03, EtOH); 96% ee by capillary GC analysis; $^1$H NMR ($CDCl_3$, 200 MHz) δ 2.42–2.66 (m, 2 H), 4.75 (m, 1 H), 4.95–5.30 (m, 3 H), 5.68–5.94 (m, 1 H), 7.20–7.35 (m, 1 H), 7.75 (m, 1 H), 8.30–8.52 (m, 2 H); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 43.79, 71.04, 118.54, 123.82, 134.40, 134.48, 140.72, 147.86, 148.43; MS (70 eV, 250 °C) $m/z$ 150 (M + H, 100), 132 (M + H – OH, 4.51), 108 (M – $C_3H_5$, 18.80); IR (neat) 3219 (s) 1635 (m), 1588 (m), 1575 (m) $cm^{-1}$.

**(*S*)-1-(4-Pyridyl)-3-buten-1-ol (19)**: 83% yield; bp 96 °C (0.8 mm) (lit.[14] bp 96 °C (0.1 mm)); $[\alpha]^{23}_D$ = –16.9° (*c* 1.62, EtOH); ≥99% ee by capillary GC analysis; $^1$H NMR ($CDCl_3$, 200 MHz) δ 2.50 (t, 2 H, *J* = 7.0 Hz), 4.76 (t, 1 H, *J* = 6.4 Hz), 5.01–5.20 (m, 3 H), 5.68–5.92 (m, 1 H), 7.31 (m, 2 H), 8.42 (m, 2 H); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 43.54, 71.87, 118.79, 121.53, 134.18, 149.52, 154.65; MS (70 eV, 250 °C) $m/z$ 150 (M + H, 0.76), 122 (M – $C_2H_4$, 17.34), 108 (M – $C_3H_6$, 100), 51 (45.49); IR (neat) 3199 (s), 1638 (m), 1598 (s), 1555 (m) $cm^{-1}$.

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**Supplementary Material Available:** $^{13}$C NMR spectra of 12–19 (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

# Formylsilanes. Chemoenzymatic and Chemical Syntheses of the 2,4-Dinitrophenylhydrazones of These Apparently Air- and Water-Stable Compounds

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Formylsilanes have long been reported to be notoriously unstable compounds. In fact, no formylsilane has been reported that was stable in air or in water nor are there any known hydrates, imines, or hydrazones of formylsilanes. We have found that monoamine oxidase catalyzes the oxidation of (aminomethyl)-*tert*-butyldimethylsilane in aqueous buffer at pH 9 to give, apparently, either formyl-*tert*-butyldimethylsilane or the corresponding hydrate, which is isolated as the 2,4-dinitrophenylhydrazone. The chemical synthesis of this same compound and the corresponding formyltrimethylsilane was carried out in low yields by a standard route to acylsilanes but in good yields by a new route involving conversion of (1,3-dioxolan-2-yl)tri-*n*-butylstannane to the corresponding silanes followed by acid hydrolysis. Although the formylsilane could not be isolated, it or its hydrate apparently is stable enough in water to survive incubation for several hours prior to the 2,4-dinitrophenylhydrazine trapping reaction.

## Introduction

Acylsilanes are well-studied compounds that are useful as intermediates in the preparation of silyl enol ethers,[1] in diastereoselective aldol condensations,[2] in the synthesis of β-hydroxysilanes,[3] and in the stereoselective synthesis of vinylsilanes.[4] The chemistry of formylsilanes, on the other hand, is virtually nonexistent because of the presumed difficulty in their preparation.[5] Until fairly recently the attempted synthesis of formyltrimethylsilane ($Me_3SiCHO$) had been the subject of decades of unsuccessful research.[5] However, evidence for the existence of $Me_3SiCHO$ at low temperatures was provided more recently by Ireland and Norbeck[6] and by Linderman and Suhr[7] who carried out a Swern oxidation of (trimethylsilyl)methanol at low temperature and isolated the products of nucleophilic attack on the presumed $Me_3SiCHO$ intermediate. Campion et al.[8] identified by NMR spectroscopy $Me_3SiCHO$ as the product of the low-temperature addition of 1 equiv of dry HCl to $Cp_2Zr(\eta^2\text{-}COSiMe_3)Cl$. The only report of a "stable" formylsilane has been for-

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