amount of catalyst used indicate that this palladium species is unstable and decomposes readily in the absence coordinating ligands.

In summary, stereospecific reduction of (*E*)- and (*Z*)-γ-monosubstituted allylic chlorides has been accomplished via low-temperature hydride capture of the corresponding π-allylpalladium complexes. In addition, cross-coupling of a (*Z*)-γ-monosubstituted allylic chloride with an organometallic reagent has been achieved without loss of double bond geometry. Key to these processes is the use of reactive, coordinatively unsaturated palladium species which promote C–H and C–C bond forming reactions prior to isomerization of the allylic double bond. Although the latter process furnishes predominantly "head to head" coupled products, formation of regioisomers remains a problem. Further refinement of this coupling methodology is currently underway.

Experimental Section

General. THF was freshly distilled under N_2 from K containing benzophenone as an indicator. Manipulations involving air- and moisture-sensitive reagents were carried out using standard Schlenk techniques. Purification of dienes was achieved by preparative thin-layer chromatography using SiO_2 impregnated with $AgNO_3$ (20%) as the stationary phase and hexanes (100%) as the eluant. Gas chromatographic analyses were carried out on a Hewlett-Packard Model 5890A chromatograph equipped with a flame-ionization detector and a DB-1 capillary column (15 m × 0.25 mm i.d., film thickness: 0.25 μm). Mass spectral analyses were performed on a Hewlett-Packard Model 5985B GC/MS/DS using electron impact (70 eV). Gas-phase IR spectra were obtained using a Bruker GC/FT/IR Model IFS85. ^1H and ^{13}C NMR spectra were obtained on a Bruker Model WM400 NMR spectrometer.

Preparation of Octene Isomers. Authentic samples of 1-octene,[15a] 2(*E*)-octene,[19] and 2(*Z*)-octene[15a] were prepared by standard literature procedures.

Preparation of Allylic Substrates.[20] 1-Chloro-2(*E*)-octene and 1-chloro-2(*Z*)-octene were prepared[21] from the corresponding alcohols[22,23] which were obtained by stereospecific reduction of 2-octyn-1-ol.[24] 1-Acetoxy-2(*E*)-octene and 1-acetoxy-2(*Z*)-octene were obtained by acetylation of the corresponding alcohols with acetic anhydride/pyridine.

Hydride Reduction of Allylic Chlorides in the Presence of Pd(0). To a stirred solution of $Pd(PPh_3)_2$, **8a** (0.1 g, 0.14 mmol) in THF (20 mL), cooled to the desired temperature in a specially designed reaction flask[14] was added, via cannula, *E* or *Z* isomers of 1-chloro-2-octene (0.02 g, in 2 mL of THF, 0.14 mmol). After 10 min 5 equiv of DIBAH were added to the addition tube and allowed to equilibrate with the temperature of the surrounding reaction mixture for 15 min. These reagents were then delivered to the main reaction chamber by carefully pressurizing the addition tube with N_2. Reactions were monitored by gas chromatographic analysis of aliquots removed at 10-min intervals. Octene peaks (GC trace) were identified by GC/MS and by coinjection of authentic samples. Yields were calculated using *n*-decane as an internal standard.

Coupling Reactions Using Di-μ-chloro-di(π-crotyl)dipalladium (8b).[12] A solution of **8b** (0.56 g, 0.14 mmol) in THF (20 mL) was stirred at room temperature under an atmosphere of N_2 until it had completely dissolved (ca. 5 min). The solution was then cooled to −78 °C, and **3a** (0.14 mmol in 1 mL of THF) was added via cannula, followed by vinylzirconene **9b** (1.5 equiv). Solutions were warmed overnight to room temperature. Equilibration of π-allylpalladium complexes with maleic anhydride was achieved by adding this ligand (dissolved in THF) by syringe, to cooled solutions (−78 °C) of **8b**. After stirring at −78 °C for 30 min **9b** was added, and the reaction mixture warmed to room temperature overnight.

6(*E*),8(*E*)-Heptadecadiene (10): FT/IR (vapor) 3171 (w), 2934 (s), 2864 (m), 1462 (w), 1352 (w), 984 (w), cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.05–5.95 (2 H, m), 5.63–5.50 (2 H, m), 2.05 (4 H, q, *J* = 7 Hz), 1.42–1.18 (18 H, 2 br s), 0.88 (6 H, t, *J* = 7 Hz); ^{13}C NMR, alkene-C, δ 132.46, 30.48; methyl and methylene-C, δ 32.53, 31.77, 31.69, 29.63, 29.40, 29.36, 29.11, 28.82, 22.57, 22.52, 13.94; MS *m/e* (%, rel int) 236 (33), 165 (3), 152 (4), 151 (5), 138 (14), 137 (8), 124 (25), 123 (17), 110 (46), 109 (42), 96 (54), 95 (69), 83 (19), 82 (68), 81 (85), 79 (44), 69 (19), 68 (25), 67 (100), 55 (17), 54 (12), 43 (13), 41 (18). Anal. Calcd for $C_{17}H_{32}$: C, 86.44; H, 13.56. Found: C, 86.55; H, 13.41.

3-Pentyl-1,4(*E*)-dodecadiene (11): FT/IR (vapor) 3084 (w), 2966 (m), 2934 (s), 2866 (m), 1637 (w), 1556 (w), 1464 (w), 1352 (w), 968 (w), 914 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.64 (1 H, ddd, *J* = 17, 10, 7.5 Hz), 5.33 (1 H, dt, *J* = 15.5, 6 Hz), 5.20 (1 H, ddt, *J* = 15.5, 7.5, 1.5 Hz), 4.92 (1 H, ddt, *J* = 17, 2, 1 Hz), 4.87 (1 H, ddt, *J* = 10, 2, 1.5 Hz), 2.54 (1 H, br quintet, *J* = 7 Hz), 1.96 (2 H, q, *J* = 7 Hz), 1.32–1.12 (18 H, m), 0.81 (6 H, t, *J* = 7 Hz); ^{13}C NMR, alkene-C, δ 142.64, 132.98, 130.48, 113.20; methyl and methlene-C, δ 46.68, 34.86, 32.54, 29.09, 29.04, 27.05, 26.73, 22.56, 22.52, 22.47, 13.92; MS *m/e* (%, rel int) 236 (3), 207 (8), 165 (16), 138 (7), 137 (29), 124 (13), 123 (27), 110 (27), 109 (61), 96 (24), 95 (88), 83 (18), 82 (27), 81 (89), 79 (39), 69 (23), 68 (37), 67 (100), 55 (21), 43 (18), 41 (23). Anal. Calcd for $C_{17}H_{32}$: C, 86.44; H, 13.56. Found: C, 86.41; H, 13.56.

6(*Z*),9(*E*)-Heptadecadiene (12): FT/IR (vapor) 3018 (w), 2966 (m), 2934 (s), 2866 (m), 1460 (w), 1385 (w), 1350 (w), 966 (w), 714 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.47–5.31 (4 H, m), 2.72 (2 H, t, *J* = 6 Hz), 2.01 (4 H, q, *J* = 7 Hz), 1.39–1.16 (16 H, bm), 0.87 (6 H, t, *J* = 7 Hz); ^{13}C NMR, alkene-C, δ 130.94, 130.56, 128.42, 127.86; methyl and methylene-C, δ 32.49, 31.80, 31.50, 30.76, 30.39, 29.64, 29.51, 29.28, 29.10, 27.04, 22.47, 22.26, 13.92; MS *m/e* (%, rel int) 236 (15), 152 (4), 151 (3), 138 (10), 137 (7), 124 (21), 123 (14), 110 (40), 109 (34), 96 (57), 95 (67), 83 (21), 81 (95), 79 (39), 69 (28), 18 (37), 67 (100), 55 (34), 54 (26), 43 (17), 41 (34). Anal. Calcd for $C_{17}H_{32}$: C, 86.44; H, 13.56. Found: C, 86.32; H, 13.41.

Supplementary Material Available: Tables of hydride reduction, hydride capture, and product ratios, apparatus figure, and in situ generation of coordinatively unsaturated palladium from **8b** (figure) (6 pages). Ordering information is given on any current masthead page.

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Reductive Decyanization of α-Amino Nitriles by Borane

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α-Amino nitriles 1 are useful intermediates for the preparation of α-amino acids (via the Strecker synthesis),[1] aldehydes, ketones,[2] enamines,[3] β-diamines,[4] and other functionalized organic compounds.[5] The synthesis of

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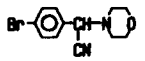
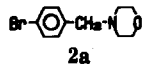
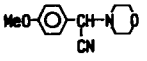
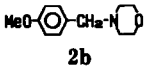
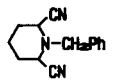
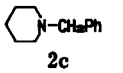
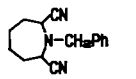
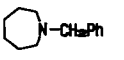
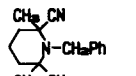
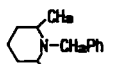
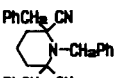
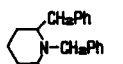
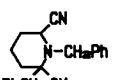
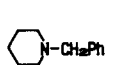
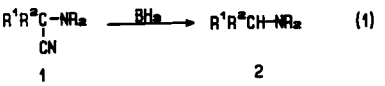
Table I. Reductive Decyanization of α-Amino Nitriles[a]

amino nitrile	BH_3 (mol)	time h	amines	yield %
 1a	2.0	19	 2a	97
 1b	2.0	40	 2b	94
 1c	3.0	3	 2c	71
 1d	3.0	2.5	 2d	74
 1e[b]	3.0	3	 2e	89[c]
 1f[b]	3.2	19	 2f	91[d]
 1g[e] (R_f = 0.28)[f]	4.1	4	 2g	91[g]
1h[e] (R_f = 0.53)[f]	4.0	4	2g	91[h]

[a] Performed in THF at room temperature. [b] Trans isomers. [c] Trans:cis = 80:20. [d] Trans:cis = 78:22. [e] Compounds 1g and 1h are diastereomers. [f] Silica gel, elution with benzene/ethyl acetate (10:1)). [g] Erythro:threo = 11.89. [h] Erythro:threo = 35:65.

amines from α-amino nitriles is also possible because the cyano group can be reductively removed. For example, sodium metal was effective for such a reduction, although the reaction conditions were drastic.[6] It was also reported that α-amino nitriles underwent reductive decyanization by treatment with sodium borohydride in methanol to afford the corresponding amines.[7] However, not all α-amino nitriles undergo reductive decyanization under these conditions. For example, both cyano groups of α,α′-dicyano amines were not removed.[8] Although a modified procedure that used *i*-PrOH as the solvent was effective,[8] a large excess of $NaBH_4$ and forcing conditions were required. We report here that borane effects the reductive decyanization of 1 under mild conditions to give amines 2 in excellent yield (eq 1).

The experimental procedure is quite simple. Borane–THF complex (THF solution, 2–3 mol equiv) was added

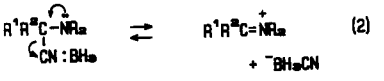


(1)

to a THF solution of 1 at room temperature. The solution was stirred for 2–40 h at room temperature. The reaction was then quenched with a small amount of water, and 1,4-diazabicyclo[2.2.2]octane (DABCO) (3–6 mol equiv) was added to decompose the borane complex of the product. After workup and purification, the amine 2 was obtained in good yield. Representative results are shown in Table I.

The effectiveness of this reaction was well demonstrated by the ready decyanization of α,α′-dicyano amines. The smooth reduction of 1c (rt, 3 h) to 2c (74%) contrasted sharply with the poor results of control experiments that employed known procedures.[6,7] Thus, attempted reduction with $NaBH_4$/MeOH[6] gave no 2c, whereas reduction with $NaBH_4$/*i*-PrOH[7] gave 2c in only 47% yield under forcing conditions (reflux, 21 h).

The reaction may involve an iminium intermediate. For example, the reduction of *cis*-2,6-dimethyl-2,6-dicyanopiperidine afforded a 4:1 mixture of *trans*- and *cis*-2,6-dimethylpiperidine.[9] The generation of an iminium ion 3 can be explained in terms of a "push–pull" mechanism (eq 2). Subsequent attack by the borate ion supplies



(2)

hydride to the iminium carbon. Because the product amine 2 is irreversibly complexed with borane, the use of 2–3 mol of BH_3–THF complex is required. It is interesting to note that the amino group of 1 is *not* irreversibly complexed with BH_3 because of the decreased electron density on nitrogen brought about by the inductive effect of the adjacent CN group.[10]

Experimental Section

Materials. Borane–THF complex (1.0 M THF solution) was purchased from Aldrich Chemical Co. and its concentration was determined by titration.[11] α-Amino nitriles 1a,[2] 1b,[2] 1c,[7] and 1d were prepared by the Strecker reaction of the corresponding aldehyde or ketone. The other amino nitriles (1e,[7] 1f, and 1g) were prepared by alkylation of, or aldehyde addition to, 1c.

Synthesis of Dicyano Amines. 1-Benzyl-2,7-dicyanoperhydroazepine (1d). This compound was prepared in 57% yield.[7] The diastereomeric ratio *R**,*S**:*R**,*R** = 2:1. *R**,*R** isomer: oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.72–2.07 (m, 8 H, $-(CH_2)_4-$), 3.76 (d, *J* = 13.5 Hz, 1 H, $PhCH_aH_b$), 3.92 (t, *J* = 4.7 Hz, 2 H, $-CHCN$), 4.22 (d, *J* = 13.5 Hz, 1 H, $PhCH_aH_b$), 7.32–7.37 (m, 5 H, Ar*H*); IR (neat) 2220 (CN) cm^{-1}; MS *m*/*z* (rel intensity) 239 (M^+; 5), 148 (42), 91 (100). *R**,*S** isomer: mp 75–76 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.76–1.92 (m, 4 H), 1.97–2.12 (m, 4 H), 3.96 (dd, *J* = 5.3, 7.2 Hz, 2 H), 3.99 (s, 2 H), 7.26–7.40 (m, 5 H); IR (KBr) 2210 (CN) cm^{-1}; MS *m*/*z* (rel intensity) 239 (M^+; 14), 148 (53), 91 (100). Anal. Calcd for $C_{15}H_{17}N_3$: C, 75.28; H, 7.16; N, 17.56. Found: C, 75.33; H, 7.18; N, 17.55.

1,2,6-Tribenzyl-2,6-dicyanopiperidine (1f). This compound was prepared in 69% yield:[7] colorless crystals; mp 217 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.50–1.73 (m, 6 H, $-(CH_2)_3-$); 2.64 (d, *J* = 13.2 Hz, 2 H, $PhCH_aH_b$), 3.26 (d, *J* = 13.2 Hz, 2 H, $PhCH_aH_b$), 4.58 (s, 2 H, $PhCH_2N$), 7.26–7.46 (m, 15 H, Ar*H*); IR (KBr) 2310

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(CN) cm^{-1}. Anal. Calcd for $C_{28}H_{27}N_3 \cdot 0.2H_2O$: C, 82.20; H, 6.75; N, 10.27. Found: C, 82.00; H, 6.74; N, 10.24.

1-Benzyl-2,6-dicyano-2-(α-hydroxybenzyl)piperidine (1g and 1h). A 5:2 THF/hexane solution (14 mL) of lithium diisopropylamide (6 mmol) was added drop by drop to a THF (20 mL) solution of 1-benzyl-2,6-dicyanopiperidine (1.13 g, 5.0 mmol) at −78 °C over 15 min. Benzaldehyde (0.68 g, 6.30 mmol) was then added, and stirring was continued for 1 h at −78 °C. Workup and purification by column chromatography on silica gel (benzene/ethyl acetate (10:1)) gave 1.36 g (80%) of a 7:3 mixture of two stereoisomers, **1g** (the more polar) and **1h** (the less polar), as a colorless oil. The isomers were separated by preparative TLC on silica gel (benzene/ethyl acetate (10:1)).

1g: R_f = 0.28 (benzene/ethyl acetate (10:1)); colorless crystals; mp 148–149 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.37–1.58 (m, 2 H, $-CH_2CH_2CH_2-$), 1.63–2.00 (m, 4 H, $-CH_2CH_2CH_2-$), 2.68 (d, J = 3.6 Hz, 1 H, O*H*), 3.82 (dd, J = 2.6, 7.1 Hz, 1 H, C*H*CN), 3.87 (d, J = 14.2 Hz, 1 H, $PhCH_aH_b$), 5.04 (d, J = 14.2 Hz, 1 H, $PhCH_aH_b$), 5.10 (d, J = 3.6 Hz, 1 H, C*H*OH), 7.26–7.45 (m, 8 H, Ar*H*), 7.45–7.52 (m, 2 H, Ar*H*); IR (KBr) 3450, 2225, 1488, 1446, 1052, 746, 700 cm^{-1}. Anal. Calcd for $C_{21}H_{21}N_3O$: C, 76.10; H, 6.38; N, 12.67. Found: C, 76.10; H, 6.44; N, 12.63.

1h: R_f = 0.53 (benzene/ethyl acetate (10:1)); colorless crystals; mp 210–212 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.37–1.47 (m, 1 H), 1.60–1.72 (m, 1 H), 1.72–1.88 (m, 3 H), 1.95–2.05 (m, 1 H) (the preceding 6 H: $-(CH_2)_3-$), 3.46 (s, 1 H), 3.92 (d, J = 13.5 Hz, 1 H, $PhCH_aH_b$), 3.95 (m, 1 H), 4.54 (d, J = 13.5 Hz, 1 H, $PhCH_aH_b$), 5.36 (s, 1 H, C*H*OH), 7.36–7.46 (m, 8 H, Ar*H*), 7.56–7.60 (m, 2 H, Ar*H*); IR (KBr) 3500, 2220, 1446, 1057, 756, 700 cm^{-1}. Anal. Calcd for $C_{21}H_{21}N_3O$: C, 76.10; H, 6.38; N, 12.67. Found: C, 76.36; H, 6.46; N, 12.42.

Decyanization of (4-Bromophenyl)-1-morpholinoacetonitrile (1a) by Borane. Typical Procedure. Borane–THF complex (1.1 M THF solution, 2.0 mL, 2.2 mmol) was added to a THF (5 mL) solution of **1a** (281 mg, 1.0 mmol) at room temperature. The solution was stirred for 40 h at that temperature. Water (1.0 mL) and 1,4-diazabicyclo[2.2.2]octane (680 mg, 6.0 mmol) were then added, and the mixture was stirred for 14 h at room temperature. The mixture was diluted with dichloromethane (10 mL), dried ($MgSO_4$), and then concentrated under reduced pressure. The oily residue was purified by column chromatography on silica gel (EtOAc/benzene (1:1)) to give 1-[(4-bromophenyl)methyl]morpholine (**2a**; 249 mg, 97%) as colorless crystals: mp 82–83 °C (lit.[12] mp 83–84 °C).

1,2,6-Tribenzylpiperidine (2f). Decyanization of **1f** gave a 78:22 mixture of *R*,R** and *R*,S** isomers: colorless oil; ^1H NMR (500 MHz, $CDCl_3$; *R*,R** isomer) δ 1.2–1.5 (m, 3 H), 1.5–1.7 (m, 3 H) (the preceding 6 H, $-(CH_2)_3-$), 2.61 (dd, J = 8.8, 13.2 Hz, 2 H, $PhCH_aH_b$), 2.96 (dd, J = 5.8, 13.2 Hz, 2 H, $PhCH_aH_b$), 3.05–3.15 (m, 2 H, −NC*H*−), 3.87 (d, J = 14.3 Hz, 1 H, $PhCH_aH_bN$), 3.90 (d, J = 14.3 Hz, 1 H, $PhCH_aH_bN$), 6.9–7.3 (m, 13 H, Ar*H*), 7.31 (t, J = 7.7 Hz, 1 H, Ar*H*), 7.47 (d, J = 7.4 Hz, 2 H, Ar*H*); ^1H NMR (500 MHz, $CDCl_3$; *R*,S** isomer) δ 2.42 (dd, J = 10.5, 13.2 Hz, 2 H, $PhCH_aH_b$), 2.85–2.9 (m, 2 H, −NC*H*−), 3.01 (dd, J = 3.3, 13.2 Hz, 2 H, $PhCH_aH_b$), 4.02 (s, 2 H, $PhCH_2N$); IR (KBr) 3050, 2860, 2930, 1495, 1450, 1030, 740, 730, 700 cm^{-1}. Anal. Calcd for $C_{26}H_{29}N \cdot 0.4H_2O$: C, 86.09; H, 8.28; N, 3.86. Found: C, 86.14; H, 8.05; N, 3.85.

1-Benzyl-2-(α-hydroxybenzyl)piperidine (2g). Similarly, **1g** afforded a 91% yield of an 89:11 mixture of (*R*,S**)- and (*R*,R**)-**2g**.[13] **1h** gave 91% yield of a 65:35 mixture of (*R*,S**)- and (*R*,R**)-**2g**: a colorless oil; ^1H NMR (270 MHz, $CDCl_3$; *R*,S** isomer) δ 1.15–1.75 (m, 7 H, $-(CH_2)_3-$ and O*H*), 2.6–2.75 (m, 2 H, $-NCH_2CH_2-$), 2.9–3.05 (m, 1 H, −NC*H*−), 3.86 (d, J = 13.2 Hz, 1 H, $PhCH_aH_b$), 3.97 (d, J = 13.2 Hz, 1 H, $PhCH_aH_b$), 4.80 (d, J = 9.9 Hz, 1 H, C*H*OH), 7.2–7.3 (m, 6 H, Ar*H*), 7.3–7.4 (m, 4 H, Ar*H*); ^1H NMR (270 MHz, $CDCl_3$; *R*,R** isomer) δ 0.9–1.1 (m, 2 H), 2.0–2.15 (m, 1 H), 2.4–2.5 (m, 1 H) (the preceding 4 H, $-(CH_2)_3-$), 3.28 (d, J = 13.4 Hz, 1 H, $PhCH_aH_b$), 4.42 (d, J = 13.4 Hz, 1 H, $PhCH_aH_b$), 5.35 (d, J = 3.2 Hz, 1 H, C*H*OH); ^{13}C NMR ($CDCl_3$; *R*,S** isomer) δ 23.74, 23.84, 25.51, 53.20, 58.11, 65.69, 70.25, 125.71, 126.73, 127.11, 128.04, 128.40, 128.98, 138.57, 141.35; ^{13}C NMR ($CDCl_3$; *R*,R** isomer) δ 18.91, 18.98, 20.94, 45.15, 56.61, 64.17, 70.44, 127.24, 127.31, 127.56, 127.74, 128.20, 128.87, 139.10, 142.63; IR (neat) 3360, 2940, 1450, 1048, 700 cm^{-1} (for the 65:35 mixture). Anal. Calcd for $C_{19}H_{23}NO \cdot 0.1H_2O$: C, 80.58; H, 8.26; N, 4.95. Found: C, 80.62; H, 8.19; N, 4.96.

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A Tabtoxinine-Related Metabolite from *Pseudomonas Syringae* pv. *tabaci*[1]

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Many pathogenic bacteria excrete metabolites that are toxic to their hosts and play an important role in the virulence mechanisms underlying the corresponding diseases.[2] An understanding of the biosynthesis of these compounds and the self-protection mechanisms evolved by the producing bacteria may aid in the development of new and better forms of treatment of bacterial infections. The biosynthetic pathways are typically revealed through studies on a set of mutants deficient in toxin production/excretion where, ideally, each mutant is altered at only a single genetic locus. The best way of obtaining such mutants, is through gene disruption by transposon mutagenesis, with transposons (Tn# (# stands for n = 1, 2, 3, ...)) being DNA sequences that can insert themselves somewhat randomly into other DNA sequences, but once resident in a cell generally prevent further entry of identical transposons.[3] These transposons carry one or more antibiotic resistance genes, which allow for the selection of mutated bacteria on antibiotic-containing media, and the genes interrupted by a given transposon can be identified via hybridization with a radioactive probe. However, identification of the *functions* of the affected genes requires the identification/structural elucidation of metabolites that accumulate due to the biosynthetic blocks that were introduced. The tools of organic chemistry and molecular biology thus become very much complementary. We are using such a combined approach to unravel the virulence mechanisms of *Pseudomonas syringae* pv. *tabaci*, the cause of wildfire disease in tobacco, and report here on the structural elucidation of N^6-acetyl-5-hydroxy-5-(hydroxymethyl)lysine, **1**, from a Tn*5*-generated Tox^- mutant. **1** is chemically closely related to tabtoxinine,[4] **2**, which itself is obtained from tabtoxinine β-lactam,[4] **3**, by acid hydrolysis. **3** has been identified as the actual wildfire toxin;[5] however, *P. syringae* pv. *tabaci* excretes it as a nontoxic dipeptide with serine or threonine, the so-called tabtoxin,[6,7] from which **3** is liberated in planta by peptidases.[8,9] As judged by our chromatographic assays, 20 Tox^+ isolates of *P. syringae* pv. *tabaci* from diverse tobacco growing areas around the world produce **1** as a minor component (at 5% of the amount of **3**) whereas nine naturally occurring Tox^- strains do not. **1** therefore is

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