Reaction of Dienes 2 and Dichlorocarbene. To a mixture of the diene **2a** (212 mg, 1.0 mmol) and benzyltriethylammonium chloride (5 mg) in CHCl₃ (2 mL) was added dropwise a 50% NaOH solution (1 mL) at 0 °C. The viscous mixture was sonicated for 1 h while the temperature was kept at 0-5 °C. The mixture was diluted with water (5 mL) and extracted 3 times with CHCl₃. The combined organic phase was dried, concentrated, and separated by chromatography to give 118 mg (40%) of cyclopropanes **21a** and 169 mg (45%) of bicyclopropane **22**. A similar reaction of diene **2b** afforded a 70% yield of cyclopropanes **21b**.

Intramolecular Cyclization of Dienes 4 and 5. A sample of 4a (238 mg, 1.0 mmol) in xylene (7 mL) was refluxed for 16 h. After volatiles were removed, separation of the residue on a SiO₂ column (0.1% EA) resulted in 70 mg (33%) of 3,4-di-hydro-3,4,9-trimethylcarbazoles 23, 36 mg (17%) of 3,4,9-trimethylcarbazole (25), and 44 mg (28%) of 2-cyano-1-methylindole (27). Similarly, compound 5a underwent cyclization in refluxing xylene to give 18% of 3,4-dihydro-4,9-dimethyl-3-phenylcarbazole (24), 35% of 4,9-dimethyl-3-phenylcarbazole (26), and 28% of 2-cyano-1-methylindole (27).

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Registry No. 1a, 101383-72-6; 1b, 101383-73-7; 2a, 117872-99-8; 2b, 117873-00-4; 3a, 117873-01-5; 3b, 117873-02-6; 4a, 117873-18-4; 4b, 117873-22-0; 5a, 117873-19-5; 5b, 117873-21-9; 7, 117873-03-7; 8, 101383-74-8; 9, 117873-04-8; 10, 117873-05-9; 11, 101383-75-9; 12, 101383-76-0; 13, 117873-06-0; 14, 101383-77-1; 15, 117873-07-1; 16, 117873-08-2; 17, 117873-09-3; 18, 117873-10-6; 19, 117873-11-7; 20, 117873-12-8; cis-21a, 117873-13-9; trans-21a, 117956-68-0; cis-21b, 117956-69-1; trans-21b, 117956-70-4; 22, 117873-14-0; 23, 117873-15-1; 24, 117873-16-2; 25, 89455-51-6; 26, 117873-17-3; 27 60680-97-9; CH₃CH=CH-o-C₆H₄-N(Me)CH₂CN, 117873-20-8; PhCH=CHCHO, 104-55-2; α -(N-methylanilino)acetonitrile, 36602-08-1; crotonaldehyde, 4170-30-3; 2,4-hexadienal, 80466-34-8; N-methylaniline, 100-61-8; maleic anhydride, 108-31-6; Nphenylmaleimide, 941-69-5; benzoquinone, 106-51-4; naphthoquinone, 130-15-4; dimethyl acetylenedicarboxylate, 762-42-5; tetracyanoethylene, 670-54-2; chlorosulfonyl isocyanate, 1189-71-5; benzenethiol, 108-98-5.

Supplementary Material Available: Full spectroscopic data for compounds 1–27 and X-ray data of compound 18 including the ORTEP drawing, atomic coordinates, bond lengths, and bond angles (14 pages). Ordering information is given on any current masthead page.

Notes

Dihydroazepines from Ring-Closure Reaction of α -Allylamino Dienenitriles

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The α -amino acrylonitriles have been extensively used as acceptors in Michael reactions¹ and as the dienophiles in Diels-Alder reactions.² The electron-withdrawing effect of the cyano group accounts for the feasibility of these reactions. On the other hand, we have found that α -amino dienenitriles undergo cycloadditions with electron-deficient alkenes.³ Although the reaction mechanism is not fully understood, the electron-donating property of the amino group seems to be the controlling factor. In continuation of this study, we tested the intramolecular reactions of α -allylamino dienenitriles (4-8). However, formation of bicyclic azetidines from intramolecular [4 + 2] cycloadditions may be disfavored owing to the severe ring strains. In this paper we describe an alternative thermal pathway of compounds 4-8 to yield 4,5-dihydroazepines (9-13).

Two methods were utilized to prepare α -allylamino dienenitriles as depicted in Scheme I. Condensation of the commercially available 2,4-hexadienal, allylamine, and potassium cyanide afforded 2-amino 3,5-dienenitrile 2, which isomerized to 2,4-dienenitriles 5 (R³ = Et) upon



treatment with t-BuOK.⁴ Syntheses of various α -allylamino dienenitriles were also achieved by condensation of appropriate α -allylamino acetonitriles **3** with α,β -unsaturated aldehydes according to the Peterson procedure.⁵ The diene prepared from either method comprised nearly equal amounts of 2E,4E and 2Z,4E isomers, which were separated by chromatography and their structures unambiguously determined.^{3,6} In general, the 2Z isomer was

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the more polar component on SiO_2 . The 3-H resonance of the 2Z isomer occurred at a lower field due to the deshielding effect of cyano group.⁷

The 2Z,4E isomer of α -allylamino dienenitriles 4-8a readily underwent cyclization in refluxing xylene. After 16-24 h, the reaction gave exclusively 4,5-dihydroazepines 9-13 in ~90% isolated yields. The structures of dihydroazepines 9-13 were determined from their spectral data. The IR absorption at ~2200 cm⁻¹ was attributed to the cyano group. The C-3 proton appeared at a lower field than the C-6 proton ($\Delta \delta > 0.5$), indicating the deshielding effect of cyano group. In contrast, the 2E,4E isomers (4-8b, HPLC pure) were inert in refluxing xylene. No change of 4-8b was observed even at an 160 °C for a prolonged period (36 h). A reaction mechanism was proposed as shown in Scheme II to account for this result.

A [1, 6] hydrogen shift is considered the primary step in the sequence.⁸ Only the allylic proton (NCH_2) in the proximity of C_5 would be feasible for migration. While $C_{1'}$ and C_5 in 2E,4E isomers were too remote to effect any reaction, the hydrogen shift could take place via the 3,4-cis conformation in the 2Z, 4E isomers. The electron-donating property of amino group was presumed to facilitate the process of hydrogen shift. By investigating a model, the resulting eight-electron intermediate would be in the helical conformation, which is suitable for cyclization to the observed dihydroazepines but unfavorable to form five-membered ring compounds. In agreement with the proposed mechanism, transformation of 8a to dihydroazepine 13 with the 4,5-cis configuration followed the stereospecific process of conrotatory electrocyclization.⁹ The 4- and 5-H in 13 exhibited a small coupling constant of 2.4 Hz corresponding to a 65° dihedral angle in a Dreiding model.¹⁰

So far, only a few dihydroazepines have been reported.^{10b,11} Dihydroazepins can be used as analogues of dihydropyridines in pharmaceutical studies, or as precursors of azepines for theoretical studies related to aromaticity. Since dihydroazepines 9-13 contain both the electrophilic functional groups of enamines¹² and the nucleophilic groups of alkenenitriles,^{4,13} they should be accessible to various derivatives for further studies.

Experimental Section

General information concerning instrumentation and material was described previously.¹⁴ Precaution should be taken in experiments involving the use of cyanides. Although it may not cause any hazard in small-scale preparation, performance of these experiments in a well-ventilated hood is highly recommended. Compounds 6, 7, and 8 were prepared in yields of 87%, 83%, and 83%, respectively, by a procedure similar to that for compound 4.

2-(N-Allylanilino)-2,4-hexadienenitrile (4). Anilinoacetonitrile was prepared in a 62% yield by condensation of formaldehyde, aniline, and potassium cyanide in the presence of sodium bisulfite.¹⁵ To a solution of anilinoacetonitrile (1.98 g, 15 mmol) in pyridine (3 mL) and CH₂Cl₂ (5 mL) was added dropwise 1.29 mL (15 mmol) of allyl bromide. The mixture was vigorously stirred for 2 h, poured into ice-water, and extracted with ethyl acetate (EtOAc). The combined extracts were washed with dilute HCl, dried over anhydrous Na_2SO_4 , and concentrated in vacuo to give 2.10 g (81%) of compound 3 after purification on a SiO_2 column. A solution of lithium diisopropylamide (LDA) was prepared from n-BuLi (5.62 mL, 9 mmol, 1.6 M in hexane) and diisopropylamine (1.32 mL, 9.5 mmol) in THF (6 mL). A solution of compound 3 (1.55 g, 9 mmol) in THF (10 mL) was added dropwise at 0 °C. After the solution was stirred for 20 min, freshly distilled chlorotrimethylsilane (1.15 mL, 9 mmol) was added dropwise. After 30 min, a LDA solution (9 mmol in 6 mL of THF) was added. After being stirred for 45 min, the mixture was cooled to -78 °C, and freshly distilled crotonaldehyde (0.83 mL, 10 mmol) was added dropwise. The mixture was gradually warmed to room temperature and stirred for 12 h. The mixture was quenched by addition of saturated NH₄Cl solution and extracted with EtOAc. The combined extracts were dried (Na₂SO₄), concentrated, and subjected to flash chromatography to give 1.61 g of compounds 4a and 4b (1:1) in an 80% total yield. 4a (2Z, 4E): yellow oil; HPLC (1% EtOAc in hexane) $t_{\rm R}$ 6.9 min; IR (neat) 3080, 2210, 1630, 1600, 1500, 900 cm⁻¹; MS, m/z (rel intensity) 224 [M⁺] (6) 168 (70), 77 (100), 51 (50); ¹H NMR (CDCl₃, 90 MHz) δ 1.76 (3 H, d, J = 6 Hz), 4.07 (2 H, d, J = 6 Hz), 5.20 (1 H, d, J = 10 Hz), 5.26 (1 H, d, J = 18 Hz), 5.75 (1 H, m), 6.10 (2 H, m, H-4, H-5)6.33 (1 H, d, J = 10 Hz, H-3), 6.78 (3 H, m), 7.15 (2 H, m). Anal. Calcd for C₁₅H₁₆N₂: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.58; H, 7.21; N, 12.24. 4b (2E,4E): yellow oil; HPLC $t_{\rm R}$ 5.3 min; IR (neat) 3080, 2200, 1630, 1600, 1500, 900 cm⁻¹; MS, m/z (rel intensity) 224 [M⁺] (5), 168 (85), 77 (100), 51 (60); ¹H NMR (CDCl₃) δ 1.88 (3 H, d, J = 6 Hz), 4.18 (2 H, d, J = 5 Hz), 5.19 (1 H, d, J = 12 Hz), 5.24 (1 H, d, J = 18 Hz), 5.70 (2 H, m), 6.21 (1 H, d, J = 11 Hz, H-3), 6.45 (1 H, dd, J = 15, 10 Hz, H-4), 6.97 (3 H, d, J = 8 Hz), 7.23 (2 H, t, J = 8 Hz). Anal. Calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 81.15; H, 7.21; N, 12.48.

2-(N-Allylanilino)-2,4-heptadienenitrile (5). Allylaniline (1.06 g, 8 mmol) was added at 0 °C to a mixture of 2,4-hexadienal (0.77 g, 8 mmol) and 1.34 mL of 6 N HCl. The mixture was stirred for 40 min, KCN (0.7 g, 10 mmol) was added, and the solution was stirred for additional 2 h until the yellow organic phase separated from the aqueous phase. The aqueous phase was extracted with EtOAc. The combined organic phase was dried (Na₂SO₄), concentrated, and purified by chromatography to give 1.64 g of compound 2. A solution of the solution of the different (13 mL) was treated with a solution of the mixture was diluted with water and extracted with EtOAc. The combined extracts were dried (Na₂SO₄), concentrated, and subjected to chromatography to give 1.62 g of compounds **5a** and **5b** (1:1) in an 85% overall

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yield. 5a (2Z,4E): yellow oil; HPLC (1% EtOAc) t_R 7.3 min (1% EA); IR (neat) 3040, 2210, 1640, 1600, 1500, 981 cm⁻¹; MS, m/z(rel intensity) 238 [M⁺] (35), 209 (24), 195 (100), 181 (18), 168 (32), 77 (65); ¹H NMR (CDCl₃) δ 0.96 (3 H, t, J = 7.4 Hz), 2.13 (2 H, q, J = 7.4 Hz), 4.11 (2 H, dd, J = 5.4, 1.5 Hz), 5.27 (2 H, 1.5 Hz)), 5.27 (2 H, 1.5 Hz), 5.27 (2 H, 1.5 Hz)), 5.27 (2 H, 1.5 Hz))m), 5.91 (1 H, m), 6.14 (2 H, m), 6.61 (1 H, d, J = 9.8 Hz, H-3), 6.84 (3 H, m), 7.25 (2 H, m); ¹³C NMR (CDCl₃, 75 MHz) δ 12.7 (q), 26.2 (t), 54.2 (t), 114.6 (s), 115.5 (d, 2 C), 117.6 (s), 117.8 (t), 120.1 (d), 123.1 (d), 129.2 (d, 2 C), 133.0 (d), 140.1 (d), 145.8 (d), 146.2 (s). 5b (2E,4E): yellow oil; HPLC $t_{\rm R}$ 6.2 min; IR (neat) 3037, 2220, 1639, 1572, 966 cm⁻¹; MS, m/z (rel intensity) 238 [M⁺] (44), 209 (20), 195 (100), 181 (15), 168 (35), 77 (77); ¹H NMR (CDCl₃) δ 1.04 (3 H, t, J = 7.5 Hz), 2.19 (2 H, q, J = 7.5 Hz), 4.20 (2 H, dd, J = 5.5, 1.5 Hz), 5.22 (2 H, m), 5.88 (2 H, m), 6.34 (1 H, d, J = 11.2 Hz), 6.46 (1 H, m), 6.99 (3 H, m), 7.28 (2 H, m); ¹³C NMR (CDCl₃) § 13.2 (q), 26.1 (t), 54.7 (t), 114.9 (s), 117.5 (t), 117.8 (s), 120.1 (d, 2 C), 122.7 (d), 124.7 (d), 129.2 (d, 2 C), 129.9 (d), 133.1 (d), 140.9 (d), 145.3 (s). Anal. of 5b. Calcd for C₁₆H₁₈N₂: C, 80.64; H, 7.61; N, 11.75. Found: C, 80.74; H, 7.58; N, 11.78.

2-(N-Allylanilino)-5-phenyl-2,4-pentadienenitrile (6). 6a (2Z,4E): yellow oil; HPLC (1% EtOAc) $t_{\rm R}$ 7.4 min; IR (neat) 3060, 2210, 1635, 1600, 1500, 900 cm⁻¹; MS, m/z (rel intensity) 286 [M⁺] (24), 246 (20), 146 (100), 77 (80); ¹H NMR (CDCl₃) δ 4.20 (2 H, d, J = 5 Hz), 5.28 (1 H, d, J = 10 Hz), 5.31 (1 H, d, J = 17 Hz), 5.90 (1 H, m), 6.65 (1 H, d, J = 10 Hz, H-3), 6.90 (7 H, m), 7.25 (5 H, m). 6b (2E,4E): yellow crystals; mp 49–50 °C; $t_{\rm R}$ 6.1 mir, IR (KBr) 3060, 2200, 1635, 1600, 1500, 900 cm⁻¹; MS, m/z (rel intensity) 286 [M⁺] (20), 246 (18), 146 (100), 77 (88); ¹H NMR (CDCl₃) δ 4.17 (2 H, d, J = 5 Hz), 5.18 (1 H, d, J = 11 Hz), 5.21 (1 H, d, J = 17 Hz), 5.75 (1 H, m), 6.23 (1 H, d, J = 10 Hz, H-3), 6.44 (1 H, d, J = 15 Hz, H-5), 7.20 (11 H, m). Anal. of 6b. Calcd for C₂₀H₁₈N₂: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.63; H, 6.35; N, 9.81.

2-(Allyl-n-butylamino)-5-phenyl-2,4-pentadienenitrile (7). **7a** (2Z,4E): yellow oil; HPLC (1% EtOAc) $t_{\rm R}$ 7.2 min; IR (neat) 3080, 2200, 1619, 1564, 975 cm⁻¹; MS, m/z (rel intensity) 266 [M⁺] (100), 225 (29), 223 (58), 212 (45), 181 (34), 175 (98), 169 (34), 115 (51), 91 (98); ¹H NMR (CDCl₃) δ 0.92 (3 H, t, J = 7.2 Hz), 1.34 (2 H, m), 1.49 (2 H, m), 2.85 (2 H, t, J = 7.2 Hz), 3.50 (2 H, d, d)J = 5.3 Hz), 5.18 (1 H, dd, J = 10.2, 1.5 Hz), 5.26 (1 H, dd, J =18.2, 1.5 Hz), 5.83 (1 H, m), 6.46 (1 H, d, J = 11.0 Hz, H-3), 6.72(1 H, d, J = 15.2 Hz), 7.26 (1 H, dd, J = 15.2, 11.0 Hz), 7.31 (3)H, m), 7.45 (2 H, m); ¹³C NMR (CDCl₃) δ 13.7 (q), 20.1 (t), 30.1 (t), 53.1 (t), 58.1 (t), 116.2 (s), 117.9 (t), 121.7 (s), 122.0 (d), 126.9 (d, 2 C), 128.6 (d, 2 C), 134.0 (d), 135.2 (d), 135.3 (d), 136.2 (d), 136.9 (s). 7b (2E,4E): yellow oil; HPLC t_R 6.1 min; IR (neat) 3058 2217, 1638, 1608, 988, 929 cm⁻¹; MS, m/z (rel intensity) 266 [M⁺] (100), 225 (27), 223 (60), 212 (45), 181 (34), 174 (8), 169 (35), 116 (45) 91 (60); ¹H NMR (CDCl₃) δ 0.97 (3 H, t, J = 7.2 Hz), 1.34 (2 H, m), 1.54 (2 H, m), 3.22 (2 H, t, J = 7.3 Hz), 3.79 (2 H, d,J = 5.3 Hz), 5.21 (2 H, m), 5.74 (1 H, m), 5.85 (1 H, d, J = 11.0Hz, H-3), 6.50 (1 H, d, J = 15.3 Hz), 7.13 (1 H, dd, J = 15.3, 11.0 Hz), 7.22 (3 H, m), 7.42 (2 H, m); ¹³C NMR (CDCl₃) δ 13.6 (q), 19.8 (t), 29.5 (t), 50.7 (t), 52.9 (t), 114.5 (d), 117.1 (s), 117.3 (t), 122.3 (s), 125.2 (d), 125.7 (d, 2 C), 126.9 (d), 128.4 (d, 2C), 129.6 (d), 132.5 (d), 137.3 (s). Anal. of 7b. Calcd for C₁₈H₂₂N₂: C, 81.16; H, 8.32; N, 10.52. Found: C, 82.12; H, 7.98; N, 10.54.

2-(N-Crotylanilino)-2,4-hexadienenitrile (8). 8a (2Z,4E): yellow oil; HPLC (2% EtOAc) t_R 6.4 min; IR (neat) 3040, 2210, 1600, 1500, 960 cm⁻¹; MS, m/z (rel intensity) 238 [M⁺] (74), 223 (17), 209 (9), 183 (100), 168 (23), 157 (89), 156 (83), 77 (52), 55 (55); ¹H NMR (CDCl₃) δ 1.70 (3 H, dd, J = 6.4, 1.5 Hz), 1.80 (3 H, dd, J = 7.2, 1.4 Hz), 4.02 (2 H, dd, J = 7.3, 1.4 Hz), 5.56 (1 H, m), 5.72 (1 H, m), 6.14 (1 H, m), 6.25 (1 H, m), 6.62 (1 H, d, J = 11.2 Hz, H-3), 6.64 (3 H, m), 7.25 (2 H, m); ¹³C NMR (CDCl₃) δ 17.6 (q), 18.9 (q), 53.3 (t), 114.4 (s), 115.2 (d, 2 C), 117.6 (s), 119.8 (d), 125.4 (d), 125.6 (d), 129.2 (d, 2 C), 129.4 (d), 139.4 (d), 140.8 (d), 145.9 (s). 8b (2E, 4E): yellow oil; HPLC t_R 4.8 min; IR (neat) 3040, 2210, 1600, 1500, 960 cm⁻¹; MS, m/z (rel intensity) 238 [M⁺] (94), 223 (15), 209 (7), 183 (100), 169 (22), 168 (24), 157 (95), 156 (73), 77 (57), 55 (70); ¹H NMR (CDCl₃, 300 MHz) δ 1.66 (3 H, dd, J = 6.4, 1.5 Hz), 1.85 (3 H, dd, J = 7.2, 1.5 Hz), 4.12 (2 H, dd, J = 7.2, 1.5 Hz), 5.50 (1 H, m), 5.63 (1 H, m), 5.85 (1 H, m, H-5), 6.31 (1 H, d, J = 11.1 Hz, H-3), 6.48 (1 H, dd, J = 11.1, 1.5 Hz, H-4), 7.01 (3 H, m), 7.28 (2 H, m); $^{13}\mathrm{C}$ NMR (CDCl₃) δ 17.7 (q), 18.6 (q), 54.0 (t), 115.1 (s, CN), 117.7 (s), 120.6 (d, 2 C), 122.6 (d), 125.7 (d), 127.1 (d), 128.9 (d), 129.2 (d, 2 C), 129.5 (d), 133.6 (d), 145.4 (s). Anal. of **8b**. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.51; H, 7.65; N, 11.68.

2-Cyano-4-ethyl-1-phenyl-4,5-dihydro-1H-azepine (9). Triene 4a (224 mg, 1 mmol) was dissolved in 5 mL of xylene and the solution was refluxed for 16 h under an atmosphere of N_2 . Complete consumption of **4a** was revealed by the TLC analysis. The solvent was removed in vacuo, and the residue was purifed on a SiO₂ column by elution with 2% EtOAc in hexane to give a pale yellow oil of dihydroazepine 9 (202 mg, 90%). Compounds 10-13 were obtained similarly from the thermal reactions of 5-8a in yields of 92%, 90%, 87%, and 88%, respectively. 9: IR (neat) 3034, 2960, 2200, 1645, 1600, 1495, 750 cm⁻¹; MS, m/z (rel intensity) 224 [M⁺] (31), 195 (81), 168 (25), 77 (100); ¹H NMR $(CDCl_3) \delta 1.04 (3 H, t, J = 7.2 Hz), 1.59 (2 H, dq, J = 7.2, 7.3 Hz),$ 2.24 (1 H, m), 2.37 (1 H, m), 2.72 (1 H, m), 4.81 (1 H, ddd, J = 10.2, 10.1, 3.2 Hz, H-6), 5.97 (1 H, d, J = 6.4 Hz, H-3), 6.32 (1 H, d, J = 10.1 Hz, H-7), 7.23 (3 H, m), 7.41 (2 H, t, J = 8.0 Hz); ¹³C NMR (CDCl₃) δ 11.7 (q), 28.2 (t), 32.3 (t, C-5), 41.5 (d, C-4), 105.9 (d, C-6), 116.1 (s, CN), 118.3 (s, C-2), 122.9 (d, 2 C), 125.5 (d), 129.2 (d, 2 C), 130.2 (d, C-3), 135.4 (d, C-7), 144.3 (s). Anal. Calcd for C₁₅H₁₆N₂: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.16; H, 7.20; N, 12.48.

2-Cyano-1-phenyl-4-propyl-4,5-dihydro-1*H***-azepine** (10): yellow oil; IR (neat) 3040, 2960, 2200, 1645, 1600, 750 cm⁻¹; MS, m/z (rel intensity) 238 [M⁺] (76), 209 (24), 195 (100), 181 (11), 168 (27), 130 (10), 104 (16), 92 (16), 77 (40); ¹H NMR (CDCl₃) δ 0.93 (3 H, t, J = 6.2 Hz), 1.44 (4 H, m), 2.19 (1 H, m), 2.30 (1 H, m), 2.74 (1 H, m), 4.75 (1 H, m), 5.91 (1 H, d, J = 6.2 Hz), 6.25 (1 H, d, J = 11.1 Hz), 7.17 (3 H, m), 7.35 (2 H, m); ¹³C NMR (CDCl₃) δ 13.9 (q), 20.4 (t), 32.6 (t), 37.4 (t), 39.6 (d), 105.9 (d), 116.0 (s), 118.3 (s), 122.8 (d, 2 C), 125.4 (d), 129.2 (d, 2 C), 130.1 (d), 135.6 (d), 144.3 (s). Anal. Calcd for C₁₆H₁₈N₂: C, 80.64; H, 7.61; N, 11.75. Found: C, 80.60; H, 7.63; N, 11.72.

4-Benzyl-2-cyano-1-phenyl-4,5-dihydro-1*H***-azepine** (11): yellow oil; IR (neat) 3028, 2917, 2225, 1655, 1590, 760 cm⁻¹; MS, m/z (rel intensity) 286 [M⁺] (6), 195 (100), 146 (33), 77 (92); ¹H NMR (CDCl₃) δ 2.20 (2 H, m), 2.80 (3 H, m), 4.60 (1 H, m), 5.73 (1 H, d, J = 6 Hz), 6.16 (1 H, d, J = 10 Hz), 7.20 (10 H, m); ¹³C NMR (CDCl₃) δ 32.3 (t), 41.3 (t), 41.6 (d), 105.7 (d), 116.1 (s), 118.6 (s), 123.6 (d, 2 C), 126.1 (d), 126.4 (d), 128.5 (d, 2 C), 129.0 (d, 2 C), 129.3 (d, 2 C), 130.7 (d), 133.3 (d), 139.3 (s), 144.5 (s). Anal. Calcd for C₂₀H₁₈N₂: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.85; H, 6.35; N, 9.78.

4-Benzyl-1-*n***-butyl-2-cyano-4,5-dihydro-1***H***-azepine (12): yellow oil; IR (neat) 3050, 2221, 1654, 1604, 745 cm⁻¹; MS, m/z (rel intensity) 266 [M⁺] (11), 175 (100), 119 (62), 92 (25); ¹H NMR (CDCl₃) \delta 0.92 (3 H, t, J = 7.2 Hz), 1.33 (2 H, m), 1.59 (2 H, m), 2.00 (1 H, m), 2.28 (1 H, m), 2.62 (1 H, m), 2.76 (2 H, m), 3.36 (2 H, m), 4.60 (1 H, m), 5.10 (1 H, d, J = 5.6 Hz), 5.71 (1 H, d, J = 9.7 Hz), 7.16 (3 H, m), 7.28 (2 H, m); ¹³C NMR (CDCl₃) \delta 13.7 (q), 19.6 (t), 32.7 (t, 2 C), 42.2 (t), 42.3 (d), 55.2 (t), 105.0 (d), 116.7 (s), 116.9 (s), 126.3 (d), 127.3 (d), 128.3 (d), 128.5 (d), 128.9 (d), 129.1 (d), 132.6 (d), 139.7 (s). Anal. Calcd for C₁₈H₂₂N₂: C, 81.16; H, 8.32; N, 10.52. Found: C, 81.20; H, 8.34; N, 10.49.**

2-Cyano-4-ethyl-5-methyl-1-phenyl-4,5-dihydro-1*H*-azepine (13): yellow oil; IR (neat) 3042, 2225, 1647, 1620, 1590, 959, 915, 763 cm⁻¹; MS, m/z (rel intensity) 238 [M⁺] (82), 223 (51), 209 (100), 181 (21), 104 (24), 77 (68); ¹H NMR (CDCl₃) δ 0.97 (3 H, t, J = 7.5 Hz), 1.02 (3 H, d, J = 6.9 Hz), 1.45 (2 H, m), 2.58 (1 H, m, H-5), 2.66 (1 H, m, H-4), 4.78 (1 H, dd, J = 10.1, 6.4 Hz, H-6), 5.85 (1 H, d, J = 6.7 Hz, H-3), 6.25 (1 H, d, J = 10.1 Hz, H-7), 7.21 (3 H, m), 7.36 (2 H, m); on irradiation of δ 1.02, the signal of H-5 at δ 2.58 became a double of doublet ($J_{5.6} = 6.4$ Hz, $J_{4.5} = 2.4$ Hz); ¹³C NMR (CDCl₃) δ 12.5 (q), 19.3 (q), 25.4 (t), 36.6 (d), 45.7 (d), 112.4 (d), 115.7 (s), 118.1 (s), 123.1 (d, 2 C), 125.6 (d), 128.9 (d), 129.2 (d, 2 C), 133.7 (d), 144.3 (s). Anal. Calcd for C₁₆H₁₈N₂: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.60; H, 7.63; N, 11.72.

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Registry No. 1, 80466-34-8; 2, 117679-33-1; 3 ($\mathbb{R}^1 = H, \mathbb{R}^2 = Ph$), 117679-34-2; 3 ($\mathbb{R}^1 = H, \mathbb{R}^2 = Bu$), 117679-50-2; 3 ($\mathbb{R}^1 = Me$, $\mathbb{R}^2 = Ph$), 117679-51-3; 49, 117679-35-3; 46, 117679-45-5; 5a, 117679-36-4; 5b, 117679-46-6; 6a, 117679-37-5; 6b, 117679-47-7;

7a, 117679-38-6; 7b, 117679-48-8; 8a, 117679-39-7; 8b, 117679-49-9; 9, 117679-40-0; 10, 117679-41-1; 11, 117679-42-2; 12, 117679-43-3; 13, 117679-44-4; PhCH=CHCHO, 104-55-2; anilinoacetonitrile, 3009-97-0; allyl bromide, 106-95-6; crotonaldehyde, 4170-30-3; allylaniline, 589-09-3.

Synthesis of 4-(Dimethylphenylsilyl)buta-2,3-dien-1-ol and Its Use in Alkylation

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During the course of our study directed toward the nickel-chromium-catalyzed cyclization of enallenes,¹ we became interested in using silvl-substituted enallenes such as 1. A logical synthesis of 1 involves the alkylation of



dimethyl malonate with the appropriate olefinic fragment and the allenylsilane 2. Although allenes are of widespread use as synthetic intermediates,² and there is a rapidly increasing number of isolated natural products containing an allene unit,³ there are no reported syntheses of a (1,3)disubstituted-allenyl)silane with a potential leaving group in the 4-position. The allenylsilane 2 could have many applications as a bifunctional electrophile.

Initially, we attempted to synthesize 2 (X = OH, OTMS)by the addition of dibromocarbene to the alcohol 3^4 to form The dibromide 4 could, upon addition of excess n-4.



butyllithium,⁵ form the desired allenylsilane 2 (X = OH). However, attempts to add dibromocarbene to 3a or 3b under phase-transfer conditions,⁶ homogeneous basic conditions,⁷ or with PhHgCBr₃⁸ gave only trace amounts of the desired dibromide 4. Similarly, attempts to reduce the propargyl alcohol 5 with aluminum hydride reagents

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cuprate⁹ 7 added cleanly to epoxybutyne to form the allenyl alcohol 8¹⁰ in 58% yield.¹¹ Bromination of 8 with PBr₃ in 53% yield and cesium carbonate promoted alkylation with dimethyl allylmalonate in 97% yield afforded the butylated enallene 9 (eq 2). Attempts to follow an analogous procedure with the addition of (PhMe₂Si)₂CuCNLi₂¹² to epoxybutyne afforded only traces of the desired product 2 (X = OH).



Conversely, we found that the silylalane 10,¹³ easily generated from PhMe₂SiLi and ClAlEt₂, added cleanly to epoxybutyne to form the desired allene 2 (X = OH) in 89%yield (eq 3). However, activation of the hydroxyl group



in 2 (X = OH) by conversion to the bromide using PBr_3 or to the tosylate using TsCl-pyridine or *n*-butyllithium and TsCl exclusively formed the enyne 11. Treatment

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of 2 (X = OH) with CBr_4 -Ph₃P¹⁴ afforded a mixture of 2 (X = Br) and 11 in a 2:1 ratio, respectively. Attempted alkylation of this mixture with dimethyl allylmalonate and cesium carbonate yielded only the elimination product 11 and recovered dimethyl allylmalonate.

Since activation of the alcohol moiety on the allene 2 (X = OH) caused the system to become extremely prone to elimination, we turned our attention to palladiumcatalyzed alkylation methodology.¹⁵ Treatment of 2 (X

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