Reaction of Dienes 2 and Dichlorocarbene. To a mixture of the diene **2a** (212 mg, 1.0 mmol) and benzyltriethylammonium chloride (5 mg) in $CHCl_3$ (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 $CHCl_3$. 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 SiO_2 column (0.1% EA) resulted in 70 mg (33%) of 3,4-dihydro-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**).

Acknowledgment. We are grateful to Professor Shie-Ming Peng (Department of Chemistry, National Taiwan University) for the X-ray measurement and to the National Science Council (ROC) for financial support.

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; $CH_3CH{=}CH$-*o*-C_6H_4-$N(Me)CH_2CN$, 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; *N*-phenylmaleimide, 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

Jim-Min Fang,* Chau-Chen Yang, and Yu-Wen Wang

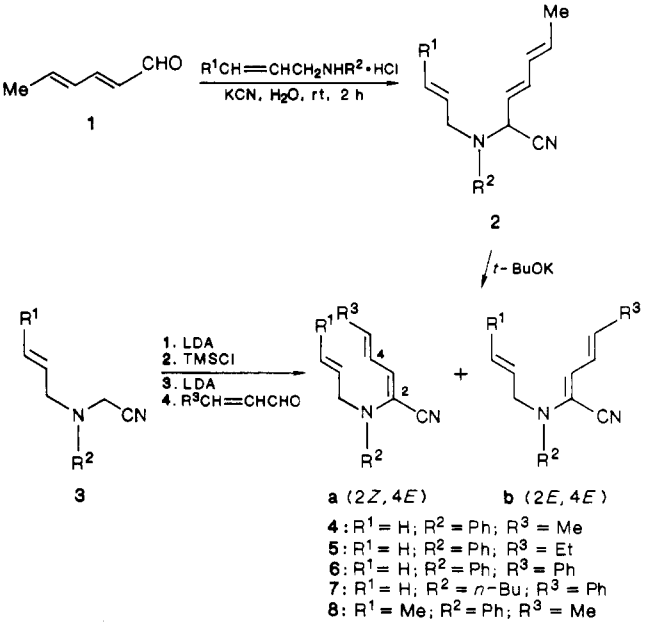
Department of Chemistry, National Taiwan University, Taipei, 10764, Taiwan, Republic of China

Received June 29, 1988

The α-amino acrylonitriles have been extensively used as acceptors in Michael reactions[1] 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** (R^3 = Et) upon

Scheme I



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 2*E*,4*E* and 2*Z*,4*E* isomers, which were separated by chromatography and their structures unambiguously determined.[3,6] In general, the 2*Z* isomer was

(1) (a) Ahlbrecht, H.; Pfaff, K. *Synthesis* **1978**, 897. (b) Ahlbrecht, H.; Pfaff, K. *Ibid.* **1980**, 413. (c) Ahlbrecht, H.; von Daacke, A. *Ibid.* **1984**, 610. (d) Ahlbrecht, H.; Pfaff, K. *Ibid.* **1985**, 421.

(2) (a) Stella, L.; Boucher, J. L. *Tetrahedron Lett.* **1982**, *23*, 953. (b) Stella, L.; Boucher, J. L. *Tetrahedron* **1985**, *41*, 875.

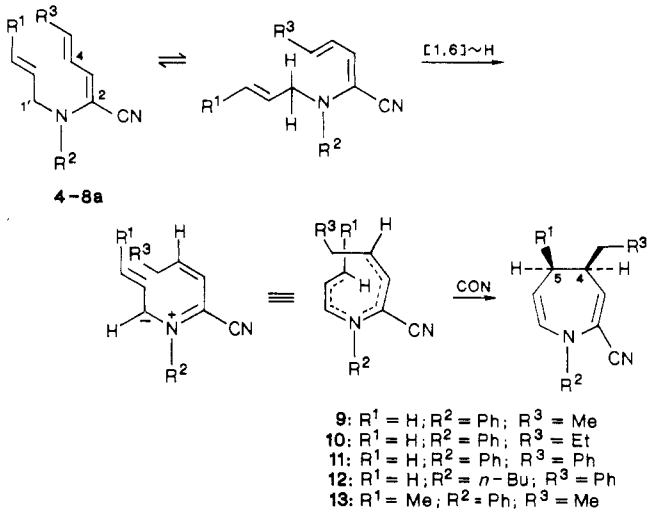
(3) Fang, J. M.; Yang, C. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1356.

(4) Fang, J. M.; Chang, H. T. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1945.

(5) Ager, D. J. *Synthesis* **1984**, 384.

0022-3263/89/1954-0481$01.50/0

Scheme II



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

The 2*Z*,4*E* 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 2*E*,4*E* 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 2*E*,4*E* isomers were too remote to effect any reaction, the hydrogen shift could take place via the 3,4-cis conformation in the 2*Z*,4*E* 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 enamines[12] 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 CH_2Cl_2 (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 NH_4Cl solution and extracted with EtOAc. The combined extracts were dried (Na_2SO_4), concentrated, and subjected to flash chromatography to give 1.61 g of compounds **4a** and **4b** (1:1) in an 80% total yield. **4a** (2*Z*,4*E*): yellow oil; HPLC (1% EtOAc in hexane) t_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 ($CDCl_3$, 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 $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.58; H, 7.21; N, 12.24. **4b** (2*E*,4*E*): yellow oil; HPLC t_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 ($CDCl_3$) 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 (Na_2SO_4), concentrated, and purified by chromatography to give 1.64 g of compound **2**. A solution of compound **2** (1.64 g) in THF (13 mL) was treated with a solution of *t*-BuOK (84 mg, 0.75 mmol) in *t*-BuOH (5 mL) at 0 °C for 2 h. The mixture was diluted with water and extracted with EtOAc. The combined extracts were dried (Na_2SO_4), concentrated, and subjected to chromatography to give 1.62 g of compounds **5a** and **5b** (1:1) in an 85% overall

(6) Stevenart-De Mesmaeker, N.; Merenyi, R.; Viehe, H. G. *Tetrahedron Lett.* **1987**, *28*, 2591.
(7) Costtisella, B.; Gross, H. *Tetrahedron* **1982**, *38*, 139.
(8) (a) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970; p 128. (b) Reinhoudt, D. N.; Visser, G. W.; Verboom, W.; Benders, P. H.; Pennings, L. M. *J. Am. Chem. Soc.* **1983**, *105*, 4775.
(9) Huisgen, R.; Dahmen, A.; Huber, H. *J. Am. Chem. Soc.* **1967**, *89*, 7130.
(10) (a) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870. (b) Claremon, D. A.; McClure, D. E.; Springer, J. P.; Baldwin, J. J. *J. Org. Chem.* **1984**, *49*, 3871.
(11) (a) Brignell, P. J.; Bullock, E.; Eisner, U.; Gregory, B.; Johnson, A. W.; Williams, H. *J. Chem. Soc.* **1963**, 4819. (b) Paquette, L. A. *Tetrahedron Lett.* **1963**, 2027. (c) Vogel, E. *Angew. Chem.* **1980**, *92*, 1053.
(12) Granik, V. G. *Russ. Chem. Rev.* **1984**, *53*, 383.
(13) Ahlbrecht, H.; von Daacke, A. *Synthesis* **1987**, 24.
(14) Fang, J. M.; Liao, L. F.; Hong, B. C. *J. Org. Chem.* **1986**, *51*, 2828.
(15) Boyer, J. H.; Kooi, J. *J. Am. Chem. Soc.* **1976**, *98*, 1099.

yield. **5a** (2*Z*,4*E*): 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 ($CDCl_3$) 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, 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); ^{13}C NMR ($CDCl_3$, 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** (2*E*,4*E*): yellow oil; HPLC t_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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) δ 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 $C_{16}H_{18}N_2$: 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 (2*Z*,4*E*): yellow oil; HPLC (1% EtOAc) t_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 ($CDCl_3$) 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** (2*E*,4*E*): yellow crystals; mp 49–50 °C; t_R 6.1 min; 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 ($CDCl_3$) 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 $C_{20}H_{18}N_2$: 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 (2*Z*,4*E*): yellow oil; HPLC (1% EtOAc) t_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 ($CDCl_3$) 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, 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); ^{13}C NMR ($CDCl_3$) 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** (2*E*,4*E*): 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 ($CDCl_3$) 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 = 11.0 Hz, 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); ^{13}C NMR ($CDCl_3$) 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 $C_{18}H_{22}N_2$: 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 (2*Z*,4*E*): 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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** (2*E*,4*E*): 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 ($CDCl_3$, 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}C NMR ($CDCl_3$) 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-1*H*-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 SiO_2 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 ($CDCl_3$) δ 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); ^{13}C NMR ($CDCl_3$) 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 $C_{15}H_{16}N_2$: 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{16}H_{18}N_2$: 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{20}H_{18}N_2$: 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 ($CDCl_3$) δ 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); ^{13}C NMR ($CDCl_3$) δ 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 $C_{18}H_{22}N_2$: 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.60; H, 7.63; N, 11.72.

Acknowledgment. We thank the National Science Council (ROC) for financial support.

Registry No. **1**, 80466-34-8; **2**, 117679-33-1; **3** (R^1 = H, R^2 = Ph), 117679-34-2; **3** (R^1 = H, R^2 = Bu), 117679-50-2; **3** (R^1 = Me, 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.

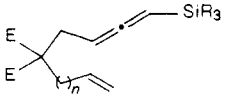
Synthesis of 4-(Dimethylphenylsilyl)buta-2,3-dien-1-ol and Its Use in Alkylation

Barry M. Trost* and James M. Tour

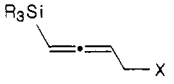
Department of Chemistry, Stanford University, Stanford, California 94305

Received July 15, 1988

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



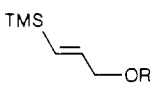
1
E = CO_2CH_3
R = alkyl or aryl



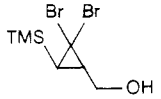
2
X = leaving group
R = alkyl or aryl

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 4. The dibromide 4 could, upon addition of excess *n*-

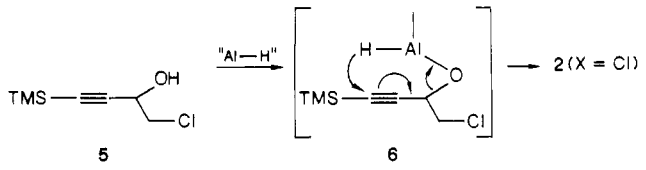


3a, R = H
b, R = TMS



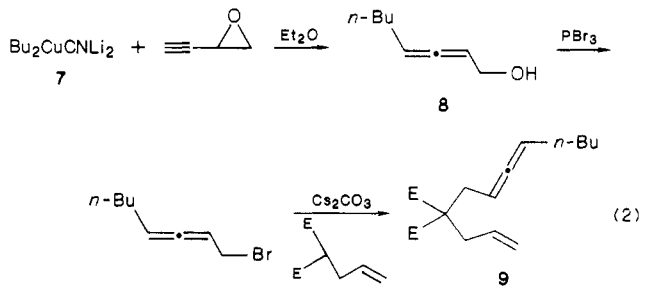
4

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 $PhHgCBr_3$[8] gave only trace amounts of the desired dibromide 4. Similarly, attempts to reduce the propargyl alcohol 5 with aluminum hydride reagents via six-membered transition state 6 were also unsuccessful (eq 1). We had observed that the higher order organo-



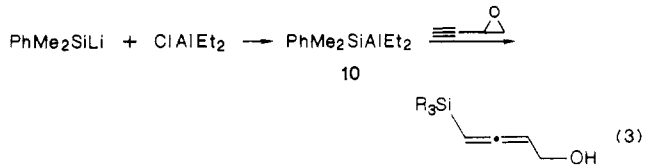
5 6 (1)

cuprate[9] 7 added cleanly to epoxybutyne to form the allenyl alcohol 8[10] in 58% yield.[11] Bromination of 8 with PBr_3 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 $(PhMe_2Si)_2CuCNLi_2$[12] to epoxybutyne afforded only traces of the desired product 2 (X = OH).



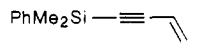
7 8 9 (2)

Conversely, we found that the silylalane 10,[13] easily generated from $PhMe_2SiLi$ and $ClAlEt_2$, added cleanly to epoxybutyne to form the desired allene 2 (X = OH) in 89% yield (eq 3). However, activation of the hydroxyl group



10 (3)

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



11

of 2 (X = OH) with CBr_4–Ph_3P[14] 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 palladium-catalyzed alkylation methodology.[15] Treatment of 2 (X

(1) Trost, B. M.; Tour, J. M. *J. Am. Chem. Soc.*, in press.
(2) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*, Wiley: New York, 1984. Rutledge, T. F. *Acetylenes and Allenes*, Reinhold: New York, 1969. Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes, and Cumulenes*; Elsevier: New York, 1981. Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604.
(3) Staudinger, H.; Ruzicka, L. *Helv. Chim. Acta* **1924**, *7*, 177. Clemer, W. D.; Solomans, I. A. *J. Am. Chem. Soc.* **1952**, *74*, 1870, 2245, 3838. Taylor, D. R. *Chem. Rev.* **1967**, *67*, 317. Bonnett, R.; Spark, A. A.; Tee, J. L.; Weedon, B. C. L. *Proc. Chem. Soc.* **1964**, 419. Sprecher, H. W.; Maier, R.; Barber, M.; Holman, R. T. *Biochemistry* **1965**, *4*, 1856. Suzuki, M.; Kurosawa, E. *Chem. Lett.* **1982**, 289. Warning, U.; Jakupovic, J.; Bohlmann, F.; Jones, S. P. *Ann.* **1987**, 467.
(4) Stork, G.; Jung, M. E.; Colvin, E.; Noel, Y. *J. Am. Chem. Soc.* **1974**, *96*, 3684.
(5) Maurin, R.; Bertrand, M. *Bull. Soc. Chim. Fr.* **1972**, 2349. Bertrand, M.; Maurin, M. *Bull. Soc. Chim. Fr.* **1967**, 2779. Bertrand, M.; Maurin, M.; Delépine, M. *C.R. Acad. Sci. Paris (C)* **1965**, *260*, 6122.
(6) Makosza, M.; Wawrzyniewicz, M. *Tetrahedron Lett.* **1969**, 4659.
(7) Skell, P. S.; Garner, A. Y. *J. Am. Chem. Soc.* **1956**, *78*, 5430.
(8) Seyferth, D.; Burlitch, J. M.; Minasz, R. J.; Mui, J. Y.-P.; Simmons, H. D., Jr.; Treiber, A. J. H.; Dowd, S. R. *J. Am. Chem. Soc.* **1965**, *87*, 4259.
(9) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005.
(10) Analogous 1-hydroxy-4-alkyl allenes have been prepared from epoxybutyne by using alkylboranes. See: Suzuki, A.; Miyaura, N.; Itoh, M. *Synthesis* **1973**, 305. 1-Hydroxy-4-alkynyl allenes have been prepared from epoxybutyne and organozinc reagents in the presence of Pd(0) catalysts. See: Kleijn, H.; Meijer, J.; Overbeek, G. C.; Vermeer, P. *Recueil* **1982**, *101*, 97.
(11) This reaction was unoptimized and the yield can undoubtedly be improved.
(12) Fleming, I.; Waterson, D. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1809.
(13) The silylalane has been added to activated vinylcyclopropanes and vinylaziradines. See: Fugami, K.; Oshima, K.; Utimato, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2509.
(14) Hooz, J.; Gilani, S. S. H. *Can. J. Chem.* **1968**, *46*, 86.

0022-3263/89/1954-0484$01.50/0