38.91, 39.42, 56.31, 59.24, 65.32, 74.23, 83.34, 85.79, 93.86, 94.87, 109.49, 129.68, 134.08, 142.04, 172.23, 234.13; MS, m/e 456 (M^+), 372 ($M^+ - 3CO$). **46a**: IR ($CHCl_3$) 1970, 1890, 1730 cm^{-1}; ^1H NMR 0.98 (3 H, d, J = 7), 1.18 (3 H, d, J = 7), 2.03 (3 H, s), 2.07–2.17 (1 H, m), 2.20–2.30 (1 H, m), 2.30–2.42 (1 H, m), 3.08–3.18 (2 H, m), 3.38 (3 H, s), 3.36–3.42 (1 H, m), 3.70 (3 H, s), 3.98 (2 H, ABX, J_{AX} = 3, J_{BX} = 7, J_{AB} = 12), 4.80 (1 H, t, J = 7), 4.93 (1 H, d, J = 7), 5.25–5.45 (2 H, m), 5.45–5.56 (2 H, m); ^{13}C NMR δ 17.00, 19.36, 21.54, 31.64, 39.24, 41.50, 56.32, 59.09, 65.28, 74.10, 83.50, 85.70, 94.24, 108.09, 128.57, 134.70, 142.26, 171.56, 231.13; MS, m/e 456, 372. **46b**: IR ($CHCl_3$) 1970, 1890, 1730 cm^{-1}; ^1H NMR δ 0.98 (3 H, d, J = 7), 1.23 (3 H, d, J = 7), 2.07 (3 H, s), 2.10–2.30 (2 H, m), 2.35–2.42 (1 H, m), 3.05–3.15 (1 H, m), 3.18–3.25 (1 H, m), 3.40 (3 H, s), 3.70 (3 H, s), 4.00 (2 H, ABX, J_{AX} = 4, J_{BX} = 8, J_{AB} = 12), 4.84 (1 H, t, J = 7), 4.95 (1 H, d, J = 7), 5.28–5.42 (2 H, m), 5.45–5.55 (2 H, m); ^{13}C NMR δ 16.87, 19.36, 21.57, 31.43, 39.10, 41.64, 56.31, 59.38, 65.49, 74.02, 83.26, 85.74, 94.09, 94.24, 108.21, 128.73, 134.17, 142.30, 172.00, 234.16; MS, m/e 456, 372.

Preparation of 47. A yellow solution of the complex **39b** (680 mg, 1.43 mmol) in ether (70 mL) was exposed to sunlight until the yellow color turned to colorless. A precipitate was filtered off to give decomplexation product (400 mg). A mixture of above compound (400 mg) and 5% Pd/C in ethyl acetate (40 mL) was stirred at room temperature under 1 atm of hydrogen to give 400 mg of hydrogenated product: ^1H NMR δ 0.86 (3 H, d, J = 7), 1.16 (3 H, d, J = 7), 1.20–2.02 (7 H, m), 3.19 (1 H, d, J = 7), 3.05–3.20 (1 H, m), 3.66 (6 H, s), 3.76 (3 H, s), 6.70–7.24 (4 H, m). A mixture of hydrogenated product (400 mg, 1.19 mmol) and potassium acetate (240 mg, 2.45 mmol) in dry DMSO (15 mL) was heated at 135 °C for 2.5 h. The mixture was quenched with water and extracted with ether, and usual workup gave compound **47** (280 mg, 82%): IR ($CHCl_3$) 1730, 1600, 1590 cm^{-1}; ^1H NMR δ 0.86 (3 H, d, J = 7), 1.16 (3 H, d, J = 7), 1.20–2.31 (9 H, m), 3.15–3.22 (1 H, m), 3.60 (3 H, s), 3.77 (3 H, s), 6.85–7.20 (4 H, m); ^{13}C NMR δ 19.68, 21.00, 24.92, 30.24, 31.67, 36.79, 37.13, 41.68, 51.24, 55.34, 110.47, 120.57, 126.45, 126.70, 135.91, 156.98, 178.77; MS, m/e 278, 135.

Preparation of Tosylate 48. To a mixture of $LiAlH_4$ (55 mg, 1.45 mmol) in ether (15 mL) was added a solution of **47** (200 mg, 0.74 mmol) at 0 °C. The mixture was stirred for 1.5 h, and usual workup afforded 175 mg of alcohol. The above alcohol was reacted with tosyl chloride (200 mg, 1.1 mmol) in pyridine (4 mL) to give **48** (200 mg, 73%): ^1H NMR δ 0.73 (3 H, d, J = 7), 1.15 (3 H, d, J = 7), 1.10–1.70 (9 H, m), 2.40 (3 H, s), 2.95–3.20 (1 H, m), 3.73 (3 H, s), 4.00 (2 H, t, J = 7), 6.70–7.18 (4 H, m), 7.26 (2 H, d, J = 7), 7.72 (2 H, d, J = 7).

Preparation of 49. To a mixture of CuI (470 mg, 2.47 mmol) in ether (10 mL) was added 3.54 mL of i-BuLi (1.4 M in ether, 4.95 mmol) at −40 °C over 10 min under nitrogen. After being stirred for 10 min, a solution of 48 (200 mg, 0.50 mmol) in ether (10 mL) was added to the above mixture at −20 °C, and the reaction mixture was stirred for 3 h and then quenched with aqueous NH_4Cl. The mixture was extracted with ether, and usual workup afforded 135 mg (94%) of **49**: ^1H NMR δ 0.84 (9 H, d, J = 7), 0.95–1.70 (14 H, m), 3.00–3.25 (1 H, m), 3.76 (3 H, s), 6.70–7.20 (4 H, m).

Preparation of Methyl 2(R*),6(R*),10-Trimethylundecanoate (50). To a mixture of **49** (135 mg, 0.47 mmol) and sodium metaperiodate (2.0 g, 9.35 mmol) in water (15 mL), carbon tetrachloride (3 mL), and acetonitrile (3 mL) was added 15 mg of ruthenium trichloride hydrate, and the mixture was stirred vigorously for 16 h at room temperature and diluted with water. The mixture was extracted with CH_2Cl_2, and evaporated in vacuo. The residue was dissolved in ether and treated with diazomethane. Usual workup gave 67 mg (60%) of **50**: IR ($CHCl_3$) 1725, 1380, 1360 cm^{-1}; ^1H NMR δ 0.82 (3 H, d, J = 7), 0.85 (6 H, d, J = 7), 1.14 (3 H, d, J = 7), 1.00–1.70 (14 H, m), 2.42 (1 H, m), 3.72 (3 H, s); ^{13}C NMR δ 17.13, 19.63, 22.63, 22.72, 24.72, 24.78, 28.01, 32.65, 34.18, 36.91, 37.29, 39.37, 39.54, 51.41, 177.42; MS, m/e 242, 211, 157, 152.

Nucleophilic Addition to 51 To Give 52. To a solution of 2-methyl-1,3-dithian (150 mg, 1.12 mmol) in THF (4 mL) was added 0.70 mL of n-BuLi (1.6 M in hexane, 1.12 mmol) at −35 °C under nitrogen, and the mixture was stirred for 30 min and then cooled to −78 °C. To the above mixture was added 2 mL of HMPA and then a solution of complex **51** (150 mg, 0.38 mmol) in THF (4 mL), and the reaction mixture was stirred at 0 °C for 4 h. The mixture was cooled to −78 °C, and 0.29 mL of trifluoroacetic acid (3.7 mmol) was added to the above reaction mixture. After being stirred for 1 h at −78 °C , the mixture was poured into 10 mL of aqueous ammonia and further stirred for 1 h. The mixture was extracted with ether, and the extract was evaporated in vacuo. The residue was treated with dilute HCl, and usual workup afforded 15 mg of **52**: IR ($CHCl_3$) 1670 cm^{-1}; ^1H NMR δ 0.96 (3 H, d, J = 7), 0.99 (3 H, d, J = 7), 1.01 (3 H, d, J = 7), 1.60 (3 H, s), 1.80–3.20 (15 H, m), 3.31 (3 H, s), 5.30 (2 H, m), 6.65 (1 H, m); MS, exact mass calcd for $C_{21}H_{34}O_2S_2$ 382.1953, found 382.1976.

Use of α-Anilino Dienenitriles as Nucleophiles in Cycloadditions

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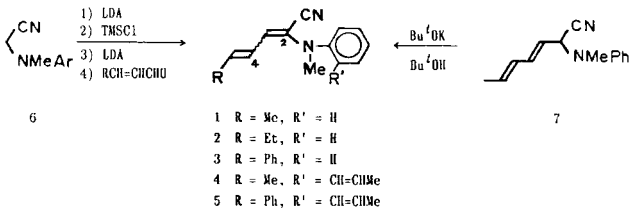
The α-anilino dienenitriles **1–5** were prepared. The dienes **1–3** reacted with dichlorocarbene and electrophiles containing electron-deficient double bonds such as maleic anhydride, benzoquinone, dimethyl acetylenedicarboxylate, tetracyanoethylene, and chlorosulfonyl isocyanate. The diarylmethylamines **8–10**, generated by cycloaddition of α-anilino dienenitriles and maleic anhydride, were successfully transformed into acridones **15–17**. Intramolecular cyclization of trienes **4** and **5** yielded the carbazoles and dihydro derivatives, accompanied by formation of 2-cyano-1-methylindole.

Introduction

Extensive study of α-amino nitriles has demonstrated their uses as precursors of α-amino acids[1] and as equivalents of acyl nucleophiles (C=O Umpolung).[2] The electron-withdrawing cyano group usually dominates over the electron-donating amino group in most of reactions. For example, the inductive effect of the cyano group causes the α-proton in α-(*N*,*N*-diethylamino)acetonitrile to become acidic enough for metalation with LDA.[3] The α-

Scheme I



6

1 R = Me, R' = H
2 R = Et, R' = H
3 R = Ph, R' = H
4 R = Me, R' = CH=CHMe
5 R = Ph, R' = CH=CHMe

7

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0022-3263/89/1954-0477$01.50/0

Table I. Some Pertinent Data of Dienes 1–5, Diarylamines 8–14, Acridones 15–17, Cyclobutane 18, Dienoates 19–20, Cyclopropanes 21 and 22, and Carbazoles 25 and 26

compd	yield (%)	mp (°C)	color	M^+: m/z (rel intens)	ν_{max} (cm^{-1})	chemical shift (δ)
1	84		yellow	198 (64)	**1a**, 2200; **1b**, 2220	**1a/1b**: 6.26/6.62 (H-3), 6.49/6.29 (H-4), 5.85/6.17 (H-5)
2	92		yellow	212 (8)	**2a**, 2222; **2b**, 2220	**2a/2b**: 6.26/6.62 (H-3), 6.45/6.26 (H-4), 5.91/6.15 (H-5)
3	85	**3a**, 99–101; **3b**, 84–86	yellow	260 (100)	**3a**, 2210; **3b**, 2210	**3a/3b**: 6.30/6.74 (H-3), 6.61 (H-5)[a]
4	82		yellow	238 (48)	**4a**, 2225; **4b**, 2220	**4a/4b**: 5.72/6.04 (H-3), 6.46/5.85 (H-4), 5.67/5.80 (H-5)
5a	84	130–132	yellow	300 (32	2200	5.88 (H-3), 6.51 (H-5)
8	80	129–130	yellow	267 (10)	1830, 1760	2.63 ($ArCH_3$), 3.47 (NCH_3)
9	90	87–89	yellow	281 (100)	1825, 1755	3.47 (NCH_3)
10	85	150–151	yellow	329 (100)	1770, 1740	3.54 (NCH_3)
11	75	141–143	yellow	342 (100)	1770, 1720	2.68 ($ArCH_3$), 3.40 (NCH_3)
12	67	126–128	blue	277 (61)	1660, 1620	2.71 ($ArCH_3$), 3.23 (NCH_3)
13	88	73–74	purple	341 (14)	1665	3.30 (NCH_3)
14	62		yellow	313 (100)	1730	2.05 ($ArCH_3$), 3.21 (NCH_3), 3.87, 3.90 (CO_2CH_3)
15	55	183–184	green	295 (100)	1720	3.80 (NCH_3), 8.43 (H-8)
16	62	159–161	green	309 (100	1725	3.80 (NCH_3), 8.42 (H-8)
17	32	205–207	green	357 (100)	1710	3.88 (NCH_3), 8.45 (H-8)
18	97	128–130	maroon	340 (6)	2200, 1640	3.89 (H-1′, dd, J = 10, 10), 4.96 (H-3), 108.5 (C-3)
19	78	138–139	yellow	338 (1)	2223, 1663	6.08 (H-4), 7.68 (H-3), 111.2 (C-4), 190.3 (C=O)
20	66	94–96	yellow	270 (37)	2229, 1680	3.32 (NMe), 3.75 (OMe), 6.08 (H-4), 7.53 (H-3), 112.5 (C-4), 168.1 (C=O)
21a[b]	40			294 (10)[c]	2215	trans/cis: 2.23/2.70 (H-1′), 3.15/3.12 (NCH_3)
21b[b]	70			294 (10)[c]	2215	trans/cis: 2.05/2.44 (H-1′), 3.18/3.19 (NCH_3)
22	45			376 (20)[c]	2230	3.16 (NCH_3)
25	*d*	94–96		209 (100)	1600	2.42 (Me), 2.77 (Me), 3.75 (NMe), 8.22 (H-5)
26	*d*	120–122		271 (100)	1600	2.78 ($ArCH_3$), 3.85 (NCH_3), 8.25 (H-5)

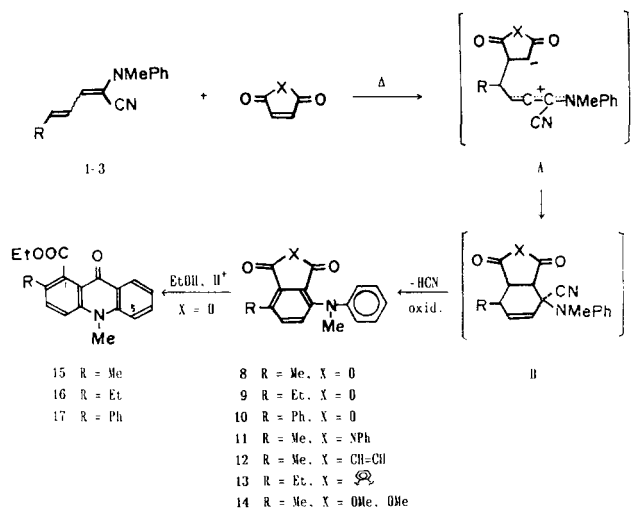
[a] The H-5 signal of **3b** was in the region mixing with resonances of aromatic protons. [b] Both compounds comprised two diastereomers (~10:1), which were inseparable by chromatography. [c] The mass was counted on ^{35}Cl. [d] Variable yields were obtained, depending on degrees of oxidation of their dihydrocarbazoles **23** and **24**.

amino alkenenitriles can function as the acceptors in Michael reactions[4] and as dienophiles in Diels–Alder reactions.[5] On the other hand, our preliminary study has revealed a different reactivity of α-amino dienenitriles, whose reactions appear to be controlled by the electron-donating amino group.[6] We report here the preparation, reactions, and application of a series of α-anilino dienenitriles (**1–5**).

Results and Discussion

Preparation of α-Anilino Dienenitriles. Dienes **1–5** were synthesized by two preparative methods (Scheme I), via the Peterson reactions of α-anilinoacetonitriles **6** with α,β-unsaturated aldehydes[7] and via isomerization of 3,5-dienenitrile **7**, which was readily obtained from the Strecker reaction of commercially available 2,4-hexadienal.[8] A precursor, *N*-methyl-*o*-propenylaniline, for synthesis of dienes **4** and **5**, was prepared from the aza-Claisen rearrangement of *N*,*N*-allylmethylaniline, followed by in situ double-bond migration (EtOH, H_2SO_4, 160 °C, 6 h).[9] The Peterson reaction was usually performed at −78 °C to give nearly equal amounts of the (2*E*,4*E*)- and (2*Z*,4*E*)-dienenitriles. However, the reaction at −100 °C resulted in a single product of 2*E* configuration,[10] e.g., **5a**. The structures of dienes **1–5** were determined from their spectra. Some pertinent physical and spectroscopic data are listed in Table I. In general, the 2*Z* isomer was the more polar component on SiO_2. The resonances of C-3 and H-3 in the 2*Z* isomer usually appeared at lower fields owing to the effect of the cyano group.[11]

Scheme II



[4 + 2] Cycloadditions. Either the 2*E* or 2*Z* isomer of α-anilino dienenitrile **1** underwent cyclization smoothly with maleic anhydride in refluxing toluene to give an 80% yield of diarylamine **8**. High yields of diarylamines **9** and **10** were similarly prepared from dienes **2** and **3**. Cycloadditions with *N*-phenylmaleimide, benzoquinone, naphthoquinone, and dimethyl acetylenedicarboxylate also lead to the desired products (**11–14**). The reaction was presumed to proceed via the dipolar mechanism as depicted in Scheme II. The electron-donating property of amino group may facilitate the formation of the zwitterionic in-

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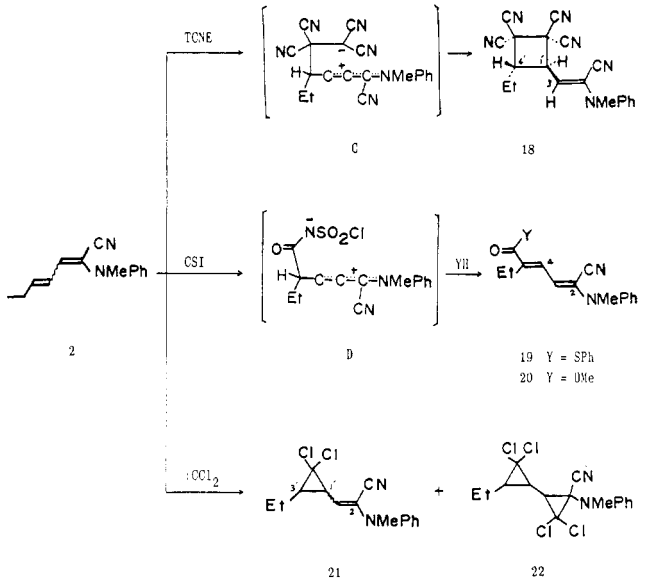
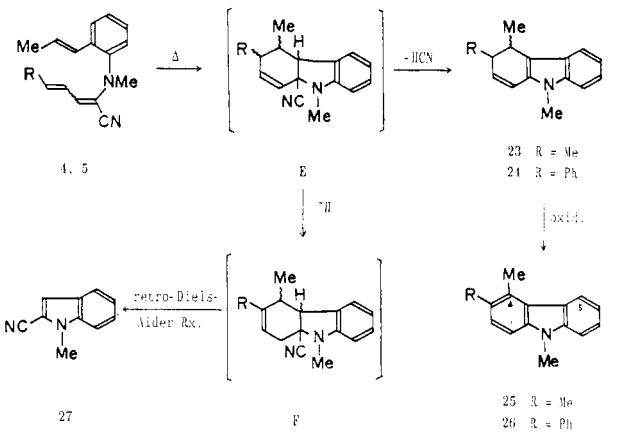
Scheme III



Scheme IV



termediate (A).[12] Elimination of HCN from the ring intermediate B would occur at the elevated reaction temperature,[13] and subsequent oxidative aromatization would afford the observed products. The [4 + 2] cycloaddition did not occur in the presence of $ZnBr_2$ (1 equiv). The α-amino dienenitriles decomposed on treatment with $AlCl_3$.[14] Thus, the Lewis acid might coordinate with the amino or cyano group to lower the nucleophilicity of dienes **1–5** instead of playing a role in enhancement of the electrophilicity of dienophiles. Attempts to isolate the intermediates B at lower reaction temperature were in vain. An application to the synthesis of acridones **15–17** was exploited by using the acid-catalyzed cyclization of diarylamines **8–10**.[15] Since different substituents could be easily introduced to the aromatic ring and the diene moieties of α-anilino dienenitriles, various biologically important acridones would be accessible by this procedure.[16]

Reactions with TCNE, CSI, and Dichlorocarbene. The diene **2a** (2*E*,4*E* isomer) reacted rapidly with tetracyanoethylene (TCNE) at 28 °C to give a single product (**18**). The reaction of diene **2b** (2*Z*,4*E* isomer) and TCNE also resulted in the same product, although it required 16 h for completion. The structure of cyclobutane **18** was established by the single crystal diffraction method (supplementary material). In the ^1H NMR spectrum, a vinyl proton (H-3) appeared at a relatively high field of δ 4.96, which indicated the 2*E* configuration.[4b] The protons on the cyclobutane ring exhibited a large coupling constant of 10 Hz for the trans configuration.[17] Since the concerted $[2\pi_S + 2\pi_S]$ cycloaddition is thermally forbidden,[18] the stepwise mechanism (Scheme III) is suggested by the stereochemical outcome,[19] i.e., both **2a** and **2b** giving the thermodynamically stable cyclobutane **18**. When MeOH was used as a polar solvent, the reaction also afforded cyclobutane **18**. However, no products were obtained that would represent interception of the zwitterionic intermediates by MeOH.[20] The reaction of dienes **2a,b** and chlorosulfonyl isocyanate (CSI) did not result in any cycloaddition product. The reaction gave exclusively thioester **19** and methyl ester **20** on subsequent treatment with benzenethiol and methanol, respectively. These compounds were presumably produced by elaboration of the zwitterion D. The structural assignments were supported by spectroscopic evidence. Compounds **19** and **20** exhibited IR absorptions at 1663 and 1680 cm^{-1}, respectively, for the conjugated carbonyl groups. The ^{13}C signals at δ 190 and 168 were attributable to the resonances of COSPh and CO_2Me. The 2*E*,4*E* configurations were inferred by occurrence of C-3 protons at a relatively high field of δ 6.08 and C-4 protons at the lower fields (δ 7.68/7.53).[21] Although CSI is known to react with most of dienes to give β-lactams,[22] the present reaction of 1-anilino-1-cyano dienes represents the first report of formation of esters from CSI. The reaction of dienes **2** and dichlorocarbene, generated in situ from $CHCl_3$ and NaOH, was carried out at 0 °C with ultrasonication in the presence of a phase-transfer agent.[23] While the reaction of **2b** gave a 70% yield of cyclopropane **21b**, the reaction of **2a** produced 40% of **21a** and 45% of bicyclopropane **22**. Cyclopropanes **21a,b** comprised mainly the trans isomers (~90%), which were inferred from their C-1′ protons appearing at higher fields with the smaller $J_{1',3'}$ coupling constants.[17b] The stereochemistry in bicyclopropane **22** was not determined.

Intramolecular Cyclizations. Either the triene **4a** or **4b** was transformed into a mixture of dihydrocarbazoles **23**, carbazole **25**, and indole **27** in refluxing xylene. Similar intramolecular cyclization of the triene **5a** afforded the dihydrocarbazole **24**, carbazole **26**, and indole **27**. Compound **27**, mp 69–70.5 °C, was readily identified as 2-cyano-1-methylindole (lit.[24] mp 68–69 °C). The loss of

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cyano group in compounds **23–26** was indicated by the lack of IR absorptions at ~2200 cm^{-1}. The dihydrocarbazoles **23** and **24** were prone to oxidation in the air to give, respectively, the crystalline carbazoles **25** and **26**, which displayed characteristic resonances of H-5 at δ ~8.2. The intramolecular [4 + 2] cyclizations presumably gave the intermediate E (Scheme IV). Subsequent loss of HCN would produce the dihydrocarbazoles,[13] and isomerization of E (catalyzed by HCN?) followed by the retro-Diels–Alder reaction would afford indole **27**.[25]

Conclusion

We have provided two convenient and general methods for preparation of α-anilino dienenitriles, which appear to be stable. These dienes function as nucleophiles in cycloadditions with electron-deficient double bonds and in the insertion reaction with dichlorocarbene. This paper also demonstrates the feasibility of intramolecular cycloadditions of appropriate α-anilino dienenitriles (**4** and **5**). The reactions possibly proceed via the dipolar mechanism as indicated by the stereochemical outcome of products. The diarylamines obtained from cycloadditions of α-anilino dienenitriles with maleic anhydride are used for subsequent conversion to biologically important acridones. From the point of view in organic synthesis, an α-amino dienenitrile can be considered as an equivalent of dienamine equipped with a potential leaving group (HCN).[26] The reaction with chlorosulfonyl isocyanate can be visualized as the homologation of an α-amino dienenitrile with a carboxylic group at the δ-position.

Experimental Section

Elemental analyses were carried out on a Perkin-Elmer 240c elemental analyzer. Infrared spectra were run on a Jasco IRA-1 spectrometer or a Perkin-Elmer 983G infrared spectrophotometer. The ^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a Varian EM-390 spectrometer, a JEOL JNM-FX100 spectrometer, or a Bruker AM-300 WB spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were recorded on a JEOL JMS-D300 spectrometer operating at an ionizing voltage of 70 eV. The X-ray diffraction data were collected on a CAD-4 diffractometer with all the experimental details (supplementary material). The analyses were carried out on a VAX 785 computer using NRCC SDP software.[27] Merck silica gel 60 F sheets were used for analytic thin-layer chromatography. Flash chromatography was performed as described by Still.[28] High-pressure liquid chromatography was carried out on a Waters Associate M45 liquid chromatograph, equipped with ultraviolet and refractive index detectors. The sample was analyzed and/or separated on a μ-Porasil column (0.78 cm × 25 cm) by elution with gradient of ethyl acetate (EA) and hexane. The flow rate of the indicated elution solvent is maintained at 5 mL/min, and the retention time of a compound is recorded accordingly.

Reactions requiring anhydrous conditions were performed under a nitrogen atmosphere, and the apparatuses were dried at 120 °C for at least 1 h before use. THF was distilled from sodium benzophenone ketyl under N_2. Dry diisopropylamine was distilled from CaH_2 under N_2. Other chemicals and solvents were commercially available reagent grade and were purified according to the standard procedure.[29] Commercial *n*-BuLi was standardized by the method of Kofron.[30] Ultrasonic reactions were carried out on a L & R T-14 ultrasonic apparatus.

Exemplary procedures are described as follows. All new compounds have compatible elemental analyses and spectral data (supplementary material).

Preparation of 2-(*N*-Methylanilino)-2,4-alkadienenitriles 1–5. Method A. Under an atmosphere of nitrogen, 24 mmol of LDA solution was prepared at 0 °C by addition of *n*-BuLi (15 mL, 24 mmol, 1.6 M in hexane) dropwise to a solution of diisopropylamine (3.5 mL, 25 mmol) in THF (12 mL). The LDA solution was cooled to −78 °C and a solution of α-(*N*-methylanilino)acetonitrile (2.9 g, 20 mmol) in THF (5 mL) was added dropwise. After the mixture was stirred for 20 min, the freshly distilled chlorotrimethylsilane (3.1 mL, 24 mmol) was added dropwise. After 30 min, a solution of LDA (24 mmol) in THF (12 mL) was added and the mixture was stirred for 45 min. After the addition of crotonaldehyde (2.0 mL, 24 mmol), the reaction mixture was warmed and stirred at room temperature for 10 h. Saturated NH_4Cl solution was added and the mixture was extracted with ethyl acetate. The combined organic phase was dried (Na_2SO_4), filtered, concentrated in vacuo, and chromatographed to give the desired dienenitriles (**1**, **3**, **4**, and **5**). **Method B.** To a mixture of 2,4-hexadienal (1.44 g, 15.0 mmol) and 2.6 mL of 6 N HCl was added dropwise 1.61 g of *N*-methylaniline (15.0 mmol) at 0 °C, followed by an aqueous KCN solution (1.05 g, 16.2 mmol, 5.0 mL). After stirring for 2 h, the upper layer of organic phase was separated and the bottom aqueous phase was extracted with ethyl acetate. The combined organic phase was washed with brine, dried, and purified by a short SiO_2 column to give 2.86 g of 2-(*N*-methylanilino)-3,5-heptadienenitrile (**7**). Compound **7** was treated with *t*-BuOK (1.30 g, 13.5 mmol) at 0 °C in a mixture of THF (10 mL) and *t*-BuOH (10 mL). After 1 h, the reaction was quenched by addition of water (20 mL), and the mixture was extracted with ethyl acetate. The combined organic phase was dried, concentrated, and chromatographed (1.5% EA) to afford 1.32 g (6.3 mmol) of **2a** and 1.31 g (6.2 mmol) of **2b**.

Preparation of Diarylamines 8–14. A toluene solution (10 mL) of diene **1a** (396 mg, 2.0 mmol) and maleic anhydride (235 mg, 2.4 mmol) was refluxed for 16 h under a N_2 atmosphere. The volatiles were removed, and the residue was chromatographed on a SiO_2 column (10% EA) to give 427 mg (1.6 mmol, 80%) of diarylamine **8**. Except for **11** (in refluxing decalin, 16 h), other diarylamines **9**, **10**, **12**, **13**, and **14** were prepared similarly in refluxing xylene (12–30 h).

Preparation of Acridones 15–17. A solution of compound **8** (267 mg, 1.0 mmol) in EtOH (5 mL) was treated with concentrated H_2SO_4 (0.3 mL). The mixture was refluxed for 4 h, cooled, and poured into 20 mL of ice water. After being neutralized by addition of KOH solution, the mixture was extracted with ethyl acetate. The combined organic phase was dried (Na_2SO_4), concentrated, and separated on a SiO_2 column (40% EA) to give 162 mg (0.55 mmol) of acridone **15**. Acid-catalyzed cyclizations of **9** and **10** were similarly carried out to give acridones **16** and **17**, respectively.

Reaction of Dienes 2 and Tetracyanoethylene. A mixture of the diene **2a** (212 mg, 1.0 mmol) and tetracyanoethylene (154 mg, 1.2 mmol) in benzene (7 mL) was stirred for 1 h at room temperature. The solvent was removed, and the residue was triturated with $CHCl_3$ to give 330 mg (0.97 mmol) of cyclobutane **18** as maroon crystals.

Reaction of Dienes 2 and Chlorosulfonyl Isocyanate. To an ice-cold solution of the diene **2a** (212 mg, 1.0 mmol) in CH_2Cl_2 (7 mL) was added dropwise chlorosulfonyl isocyanate (142 mg, 1.0 mmol). The diene **2a** was entirely consumed in 5 min as revealed by the TLC analysis, while a similar reaction of **2b** took 30 min to completion. The dark reaction mixture was cooled to −78 °C and 121 mg (0.11 mL, 1.1 mmol) of benzenethiol was added. After 10 min, pyridine (97 μL, 1.2 mmol) was added. The mixture was washed with brine, dried, concentrated, and separated by chromatography to give 264 mg (78%) of thioester **19**. Methyl ester **20** was obtained in a 66% yield when methanol was used as the quenching agent instead of benzenethiol.

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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**).

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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; $CH_3CH{=}CH$-*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

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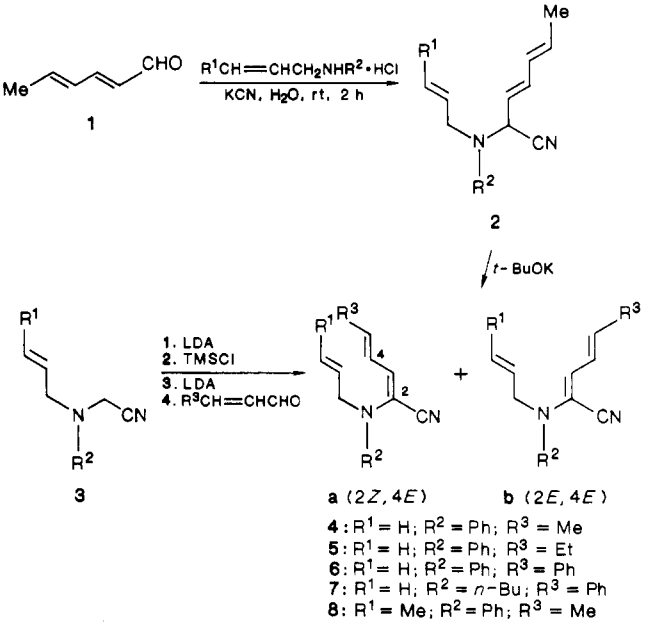
The α-amino acrylonitriles have been extensively used as acceptors in Michael reactions[1] and as the dienophiles in Diels–Alder reactions.[2] The electron-withdrawing effect of the cyano group accounts for the feasibility of these reactions. On the other hand, we have found that α-amino dienenitriles 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

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