J = 8.4, 1.3 Hz, H-8), 7.96 (1 H, dd, J = 8.7, 1.2 Hz, H-5), 8.42 (1 H, s, H-3), 9.17 (1 H, s, H-1); ^{13}C NMR δ 29.1 (CH_2), 106.5 (C-3′), 110.2 (C-4′), 122.9 (C-5), 126.8 (C-7), 127.1 (C-4), 128.0 (C-8), 128.2 (C-9), 130.2 (C-6), 134.4 (C-10), 141.2 (C-5′), 143.2 (C-3), 151.9 (C-1), 153.0 (C-2′). Anal. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30. Found: C, 80.18; H, 5.28.

4-(3′,4′-Dimethoxybenzyl)isoquinoline (6c). The reaction of 4.3 mmol of **3** with 4.5 mmol of 3,4-dimethoxybenzaldehyde gave 1.19 g of crude **6c**. Column chromatography (neutral alumina, 7:3 hexane/ether) afforded 0.71 g of material, which was recrystallized from cyclohexane to give 0.68 g (58%, two crops) of pure **6c**: colorless needles, mp 83.5–84.0 °C; ^{1}H NMR δ 3.78 (3 H, s, OCH_3), 3.83 (3 H, s, OCH_3), 4.33 (2 H, s, CH_2), 6.71 (1 H, dd, J = 8.0, 2.0 Hz, H-5′), 6.73 (1 H, d, J = 2.0 Hz, H-2′), 6.75 (1 H, d, J = 8.0 Hz, H-6′), 7.57 (1 H, ddd, J = 8.0, 6.9, 1.2 Hz, H-7), 7.65 (1 H, ddd, J = 8.4, 6.9, 1.5 Hz, H-6), 7.93 (1 H, dd, J = 8.4, 1.2 Hz, H-5), 7.98 (1 H, dd, J = 8.0, 1.5 Hz, H-8), 8.40 (1 H, s, H-3), 9.18 (1 H, s, H-1); ^{13}C NMR δ 35.8 (CH_2), 55.7 (OCH_3), 111.2 (C-5′), 111.7 (C-2′), 120.4 (C-6′), 123.2 (C-5), 126.7 (C-7), 128.0 (C-8), 128.4 (C-9), 129.6 (C-4), 130.1 (C-6), 132.0 (C-1′), 134.6 (C-10), 143.3 (C-3), 147.4 (C-3′ or C-4′), 148.9 (C-3′ or C-4′), 151.9 (C-1). Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13. Found: C, 77.28; H, 6.19.

4-(4′-Quinolylmethyl)isoquinoline (6d). The reaction of 1.2 mmol of **3** with 1.3 mmol of 4-quinolinecarboxaldehyde gave 0.28 g of crude semisolid, which was recrystallized from THF to give 0.21 g (65%, two crops) of pure **6d**: mp 181.0–182.0 °C; ^{1}H NMR δ 4.78 (2 H, s, CH_2), 6.78 (1 H, d, J = 4.5 Hz, H-3′), 7.57–7.64 (3 H, m, H-7, H-6′, H-7′), 7.72–7.77 (2 H, m, H-6, H-5′), 8.01–8.05 (1 H, m, H-8′), 8.15 (1 H, dd, J = 8.5, 1.3 Hz, H-5), 8.18 (1 H, dd, J = 8.6, 1.3 Hz, H-8), 8.33 (1 H, s, H-3), 8.68 (1 H, d, J = 4.5 Hz, H-2′), 9.24 (1 H, s, H-1); ^{13}C NMR δ 32.0 (CH_2), 120.9 (C-3′), 122.7 (C-5′), 122.9 (C-5), 129.1 (C-6), 130.2 (C-8), 134.5 (C-10), 143.8 (C-3), 144.9 (C-4′), 147.9 (C-9′), 150.0 (C-2′), 152.2 (C-1), and signals at δ 126.6, 127.0, 127.1 (2 C), 128.2, and 130.5 that could not be assigned. Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.42; H, 5.22. Found: C, 84.16; H, 5.34.

4-Methylisoquinoline (6e) and Bis(4′-isoquinolyl)methane (8). Enamine **3** (5.0 mmol) in THF was prepared as described earlier. Paraldehyde was heated in a side-arm test tube equipped with a gas-delivery system, and gaseous formaldehyde was allowed to bubble through the stirred solution of **3** for 10 min at room temperature. After 4 h, the standard oxidation, workup, and column chromatography (neutral alumina, 7:3 hexane/ether) procedures afforded 0.27 g of a mixture containing **6e** (57%) and **1** (43%). The ^{13}C NMR spectrum of a pure sample of **6e**, obtained by repeated column chromatography of the mixture, was in excellent agreement with that reported by Smith:[16] δ15.8 (CH_3), 123.1 (C-5), 126.9 (C-7), 127.3 (C-4), 128.1 (C-8), 128.2 (C-9), 130.2 (C-6), 135.3 (C-10), 142.7 (C-3), 151.0 (C-1).

Further elution of the column with pure ether afforded 0.10 g of material, which was recrystallized from cyclohexane to give 0.07 g of pure **8**: yellow needles, mp 176.0–177.0 °C; ^{1}H NMR δ 4.76 (2 H, s, CH_2), 7.62 (2 H, ddd, J = 8.0, 6.9, 1.2 Hz, H-7), 7.69 (2 H, ddd, J = 8.3, 6.9, 1.5 Hz, H-6), 7.97 (2 H, br dd, J = 8.3, 1.2 Hz, H-5), 8.01 (2 H, br dd, J = 8.0, 1.5 Hz, H-8), 8.18 (2 H, s, H-3), 9.19 (2 H, s, H-1); ^{13}C NMR δ 30.4 (CH_2), 122.6 (C-5), 126.9 (C-7), 128.0 (C-4 or C-9), 128.1 (C-4 or C-9), 128.2 (C-8), 130.5 (C-6), 134.5 (C-10), 143.3 (C-3), 151.8 (C-1). Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.42; H, 5.22; N, 10.36. Found: C, 84.60; H, 5.23; N, 10.29.

Acknowledgment. This research was supported by a grant from the Texas Christian University Research Fund (Grant 5-23957). The Varian XL-300 NMR spectrometer was purchased with a generous gift from Dr. Malcolm K. Brachman. The hospitality of the Department of Chemistry of The University of Texas at Austin and especially Professor John C. Gilbert during the preparation of the manuscript is gratefully acknowledged.

Registry No. 1, 119-65-3; **3**, 114273-47-1; **6a**, 10166-05-9; **6b**, 114273-40-4; **6c**, 114273-41-5; **6d**, 114273-42-6; **6e**, 1196-39-0; **6f**, 114273-43-7; **6q**, 80998-95-4; **7**, 114273-44-8; **8**, 114273-45-9, 112370-05-5; EtCHO, 123-38-6; $PhCH_2CHO$, 122-78-1; benzaldehyde, 100-52-7; furfural, 98-01-1; 3,4-dimethoxybenzaldehyde, 120-14-9; 4-quinolinecarboxaldehyde, 4363-93-3; 1-ethyl-4-(2′-furylmethyl)isoquinoline, 114273-46-0.

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A Mild Synthesis of 1,3-Diynes

Andrew S. Kende* and Cynthia A. Smith

Department of Chemistry, University of Rochester, Rochester, New York 14627

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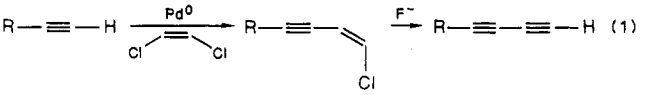
A substantial number of conjugated polyacetylenes, often having antibacterial or antifungal activity, have been isolated from Basidiomycetes fungi and from higher plants of the Compositae family.[1] Despite their frequent occurrence, few methods are available for the synthesis of terminal conjugated polyacetylenes, especially those possessing base-sensitive functionality.[2] The most widely used method is a modification of the Cadiot–Chodkiewicz reaction in which an alkynylcopper is coupled with a 1-bromoacetylene of the type BrC≡CR, where R is $SiMe_3$ or C(OH)R′R″. The resulting diyne can then be deprotected with alkali to liberate the terminal acetylene.[3] However, the yields of this sequence are moderate and byproducts are frequently isolated, although improved yields have been reported employing preformed copper(I) acetylides.[4]

We now report a mild two-step synthesis of 1,3-diynes from terminal acetylenes which is compatible with a wide range of functional groups, including base-sensitive ones. The first step of this synthesis involves a palladium(0)-catalyzed coupling of a terminal alkyne with *cis*-1,2-dichloroethylene to yield a cis chloro enyne.[5] We find that treatment of the chloro enyne with tetra-*n*-butylammonium fluoride then provides the 1,3-diyne in good overall yield (Table I). Our sequence is summarized in eq 1.



Palladium(0)-catalyzed coupling of terminal acetylenes with *trans*-1,2-dichloroethylene, in our hands, also proceeds in good yields, but attempted conversion of the resulting trans chloro enynes to diynes with tetra-*n*-butylammonium fluoride gave only traces of diynes even under vigorous conditions. This is consistent with the finding that the syn elimination of HCl from trans chloro enynes requires a stronger base.[6]

Our method is experimentally simple and can be extended to the synthesis of 1,3,5-triynes by repetition of the procedure. In the course of this investigation an interesting

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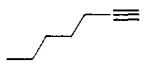
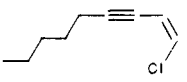
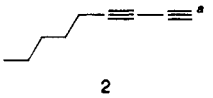
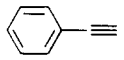
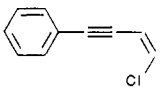
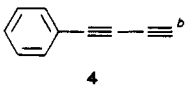
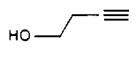
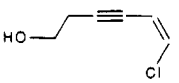
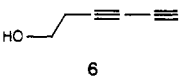
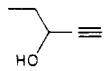
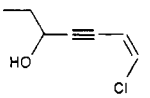
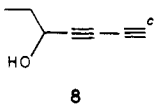
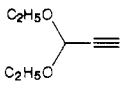
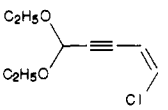
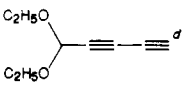
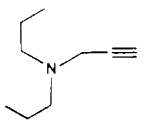
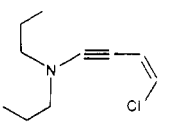
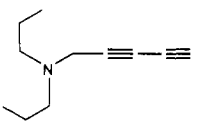
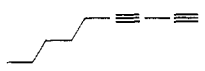
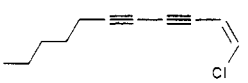
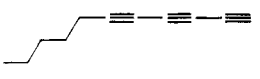
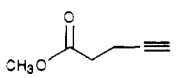
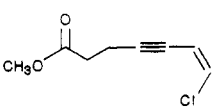
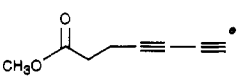
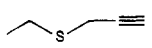
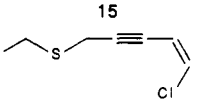
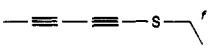
0022-3263/88/1953-2655$01.50/0

Table I

acetylene	chloro enyne	diyne	overall yield, %
	 1	 2	67
	 3	 4	68
	 5	 6	73
	 7	 8	73
	 9	 10	70
	 11	 12	61
	 13	 14	42
	 15	 16	52
	 17	 18	75

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exception was noted during the fluoride dehydrochlorination of the enyne **17** (Table I). The sole isolated product was the known diyne **18**. It is likely that this product arises from a fluoride-catalyzed prototropic isomerization sequence facilitated by the enhanced acidity of the propargylic protons in the primary coupling product **17**.

Experimental Section

Proton NMR spectra were recorded on a Nicolet QE-300 spectrophotometer and chemical shifts are reported in parts per million downfield from tetramethylsilane. The infrared spectra were recorded on a Perkin-Elmer 1310 spectrophotometer and were calibrated against the 1601 cm^{-1} peak of polystyrene. Mass spectra were obtained by electron impact on a VG-7035 mass spectrometer. ultraviolet spectra were measured on a Perkin-Elmer 200 spectrophotometer in methanol.

All reactions were run in flame-dried flasks under an atmosphere of argon. Tetrahydrofuran and benzene were distilled from sodium and benzophenone prior to use. Unless otherwise mentioned, the chemicals were used as received from commercial sources. All the diynes were prepared by the same general procedure unless otherwise noted. Products were purified by liquid chromatography on silica gel or Florisil and by Kugelrohr distillation.

General Procedure for the Formation of the Chloro Enyne. Preparation of 11. To a stirred solution of 3-(dipropylamino)-1-propyne (1.0 g, 7.18 mmol) in 75 mL of dry benzene under argon was added anhydrous *n*-butylamine (3.55 mL, 35.9 mmol) followed by *cis*-1,2-dichloroethylene (1.09 mL, 14.4 mmol). To this solution was added copper(I) iodide (0.205 g, 1.08 mmol) followed by tetrakis(triphenylphosphine)palladium(0) (0.415 g, 0.359 mmol). The mixture was stirred for 16 h. The organic phase was washed with 2 × 25 mL of brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the residue was purified by liquid chromatography over Florisil (hexane elution) to yield 0.96 g (67%) of a pale yellow oil: ^1H NMR ($CDCl_3$) δ 6.35 (1 H, d, J = 7.4 Hz), 5.88 (1 H, dd, J = 1.6, 7.4 Hz), 3.60 (2 H, d, J = 1.6 Hz), 2.46 (4 H, t), 1.50 (4 H, m), 0.90 (6 H, t); IR (thin film) 3080, 2970, 2220, 1590, 1460, 1320, 1080, 720 cm^{-1}; MS (70 eV), m/e (relative intensity) 199 (M^+, 3.72), 172 (26.60), 170 (100.0), 101 (27.9), 99 (81.84), 73 (13.02), 43 (33.48), 41 (26.0), 32 (46.5).

General Procedure for the Formation of the Diyne. Preparation of 12. To a stirred solution of **11** (0.5 g, 2.50 mmol) in 50 mL of dry THF under argon was added 1.0 M tetra-*n*-butylammonium fluoride in THF (6.26 mL, 6.26 mmol). The mixture was stirred for 20 h. The organic phase was washed with 20 mL of saturated ammonium chloride solution and 2 × 10 mL of brine and then dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the residue purified by chromatography on Florisil (hexane elution) to yield 0.37 g (90.3%) of a clear oil: ^{1}H NMR ($CDCl_3$) δ 3.48 (2 H, s), 2.45 (4 H, t), 2.02 (1 H, s), 1.48 (4 H, m), 0.91 (6 H, t); IR (thin film) 3300, 2980, 2240, 1590, 1460, 1320, 1080, 720 cm^{-1}; MS (70 eV), *m/e* (relative intensity) 163 (M^+, 7), 134 (75), 111 (14), 109 (10), 99 (32), 85 (21), 69 (37), 63 (33), 57 (71), 43 (100), 39 (18).

(*Z*)-1-Chloro-1-nonen-3-yne (1): purified by Kugelrohr distillation, 85% yield; ^{1}H NMR ($CDCl_3$) δ 6.29 (1 H, d, J = 5.3 Hz), 5.86 (1 H, dd, J = 1.8, 5.3 Hz), 3.39 (2 H, dt, J = 1.8, 6.8 Hz), 1.61–1.30 (6 H, m), 0.91 (3 H, t); IR (thin film) 3080, 2960, 2210, 1460, 1330, 720 cm^{-1}; MS (70 eV), *m/e* 156 (M^+), 143, 119, 105, 91, 69, 55, 41.

1,3-Nonadiyne (2): purified by Kugelrohr distillation, 79% yield; ^{1}H NMR ($CDCl_3$) δ 2.27 (2 H, t), 1.97 (1 H, s), 1.58–1.34 (6 H, m), 0.91 (3 H, t); IR (thin film) 3300, 2940, 2220, 1460, 1240, 720 cm^{-1}; MS (70 eV), *m/e* 121 ($M^+ + 1$), 120 (M^+), 105, 91, 79, 77, 65, 56.

(*Z*)-1-Chloro-4-phenyl-1-buten-3-yne (3): purified by Kugelrohr distillation, 75% yield; ^{1}H NMR ($CDCl_3$) δ 7.53–7.35 (5 H, m), 6.46 (1 H, d, J = 7.4 Hz), 6.11 (1 H, d, J = 7.4 Hz); IR (thin film) 3080, 3020, 2200, 1600, 1460, 1440, 1340, 760 cm^{-1}; MS (70 eV), *m/e* 129, 96, 94, 39, 27.

4-Phenyl-1,3-butadiyne (4): purified by Kugelrohr distillation, 87% yield; ^{1}H NMR ($CDCl_3$) δ 7.53–7.28 (5 H, m), 2.49 (1 H, s); IR (thin film) 3300, 3060, 2200, 1590, 1485, 1440, 1220, 750, 690 cm^{-1}; MS (70 eV), *m/e* 126 (M^+), 125, 98, 74, 63, 49, 32.

(*Z*)-1-Chloro-6-hydroxy-1-hexen-3-yne (5): purified by Kugelrohr distillation, 99% yield; ^{1}H NMR ($CDCl_3$) δ 6.35 (1 H, d, J = 7.4 Hz), 5.88 (1 H, dd, J = 1.8, 7.4 Hz), 3.79 (2 H, d, J = 6.0 Hz), 2.67 (2 H, dt, J = 1.8, 6.0 Hz), 2.11 (1 H, bs); IR (thin film) 3600–3100, 3100, 2980, 2200, 1600, 1340, 1050, 850, 720 cm^{-1}; MS (70 eV), *m/e* 108 ($M^+ - 18$), 97, 92, 63, 61, 38, 31, 27.

3,5-Hexadiyn-1-ol (6): purified by chromatography on SiO_2 (75% hexane/25% ethyl acetate), 73% yield; ^{1}H NMR ($CDCl_3$) δ 6.19 (1 H, d), 5.89 (1 H, d), 3.77 (2 H, t), 2.55 (2 H, t), 2.05 (1 H, s), 2.01 (1 H, s); IR (thin film) 3600–3100, 3300, 2960, 2210, 1590, 1050, 740 cm^{-1}.

(*Z*)-1-Chloro-5-hydroxy-1-hepten-3-yne (7): purified by chromatography on SiO_2 (75% hexane/25% ethyl acetate), 95% yield; ^{1}H NMR ($CDCl_3$) δ 6.40 (1 H, d), 5.91 (1 H, d), 4.53 (1 H, q), 2.07 (1 H, d), 1.80 (2 H, quin), 1.06 (3 H, t); IR (thin film) 3600–3100, 3080, 3000, 1600, 1340, 1140, 1040, 730 cm^{-1}; MS (70 eV), *m/e* 144 (M^+), 126, 111, 104, 88, 75, 49, 39.

5-Hydroxy-1,3-heptadiyne (8): purified by chromatography on Florisil (hexane elution), 77% yield; ^{1}H NMR ($CDCl_3$) δ 4.36 (1 H, t), 2.60 (1 H, bs), 2.20 (1 H, s), 1.75 (2 H, quin), 1.02 (3 H, t); IR (thin film) 3600–3100, 3300, 2980, 1450, 1380, 1250, 960 cm^{-1}; MS (70 eV), *m/e* 108 (M^+), 107, 91, 79, 55, 43, 32.

(*Z*)-1-Chloro-5,5-diethoxy-1-penten-3-yne (9): purified by chromatography on SiO_2 (hexane elution), 88% yield; ^{1}H NMR ($CDCl_3$) δ 6.46 (1 H, d), 5.94 (1 H, d), 5.40 (1 H, s), 3.80 (2 H, q), 3.64 (2 H, q), 1.26 (6 H, t); MS (70 eV), *m/e* 187 ($M^+ - 1$), 159, 143, 115, 87, 51, 39; IR (thin film) 3080, 2990, 2200, 1590, 1320, 1130, 1050, 720 cm^{-1}.

5,5-Diethoxy-1,3-pentadiyne (10): purified by chromatography on Florisil (70% hexane/30% ethyl acetate), 79% yield; ^{1}H NMR ($CDCl_3$) δ 5.30 (1 H, s), 3.75 (2 H, q), 3.61 (2 H, q), 2.23 (1 H, s), 1.25 (6 H, t); IR (thin film) 3300, 2990, 2220, 1440, 1220, 1140, 1040, 1010, 900 cm^{-1}; MS (70 eV), *m/e* 123 ($M^+ - 29$), 107, 79, 62, 51, 39.

(*Z*)-1-Chloro-1-undecene-3,5-diyne (13): purified by chromatography on Florisil (hexane elution), 67% yield; ^{1}H NMR ($CDCl_3$) δ 6.33 (1 H, d), 5.88 (1 H, d), 2.50 (2 H, t), 1.75–1.2 (6 H, m), 0.90 (3 H, t); IR (thin film) 3080, 2970, 2200, 1590, 1450, 720 cm^{-1}.

1,3,5-Undecatriyne (14): purified by chromatography on SiO_2 (hexane elution), 63% yield; ^{1}H NMR ($CDCl_3$) δ 2.39 (2 H, t), 1.99 (1 H, s), 1.71–1.20 (6 H, m), 0.91 (3 H, t); IR (thin film) 3300, 2980, 2210, 1590, 1460, 1380, 900, 730 cm^{-1}; UV (MeOH) 210, 222, 238, 273, 290, 311 nm.

(*Z*)-1-Carbomethoxy-6-chloro-5-hexen-3-yne (15): purified by chromatography on SiO_2 (80% hexane/20% ethyl acetate elution), 85% yield; ^{1}H NMR ($CDCl_3$) δ 6.32 (1 H, d), 5.83 (1 H, d), 3.71 (3 H, s), 2.72 (2 H, t), 2.60 (2 H, t); IR (thin film) 3080, 2970, 2210, 1700, 1590, 1460, 1370, 1200, 900, 730 cm^{-1}; MS (eV), *m/e* 172 (M^+), 141, 109, 99, 77, 51, 39.

4,6-Heptadiynoic acid methyl ester (16): purified by chromatography on SiO_2 (hexane elution), 64% yield; ^{1}H NMR ($CDCl_3$) δ 3.70 (3 H, s), 2.57 (4 H, s), 2.00 (1 H, s); IR (thin film) 3300, 3000, 2980, 2210, 1720, 1440, 1200, 1050, 620 cm^{-1}; MS (70 eV), *m/e* 136 (M^+), 121, 105, 77, 65, 51, 43.

(*Z*)-1-Chloro-5-(ethylthio)-1-penten-3-yne (17): purified by chromatography on SiO_2 (80% hexane/20% ethyl acetate), 97% yield; ^{1}H NMR ($CDCl_3$) δ 6.38 (1 H, d), 5.90 (1 H, dd, J = 2.0, 7.4 Hz), 3.48 (2 H, d, J = 2.0 Hz), 2.74 (2 H, q), 1.31 (3 H, t); IR (thin film) 3080, 2980, 2200, 1600, 1240, 850, 720 cm^{-1}; MS (70 eV), *m/e* 160 (M^+), 131, 99, 73, 63, 45, 27.

1-(Ethylthio)-1,3-pentadiyne (18): purified by chromatography on SiO_2 (80% hexane/20% ethyl acetate solution), 78% yield; ^{1}H NMR ($CDCl_3$) δ 2.78 (2 H, q), 1.99 (3 H, s), 1.41 (3 H, t); ^{13}C NMR ($CDCl_3$) 81 (s), 78 (s), 65 (s), 64 (s), 30 (t), 15 (q), 6 (q); IR (thin film) 2980, 2100, 1450, 1250, 960, 760 cm^{-1}; MS (70 eV), *m/e* 124 (M^+), 96, 69, 57, 43.

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Consequences of Twofold Bridging of the [10]Annulene System as in *cis*-10,11-Dihydrodicyclopenta[*cd*,*gh*]pentalene

Koichi Nakamura,[1] Corinne Vanucci,[2] and Leo A. Paquette*

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

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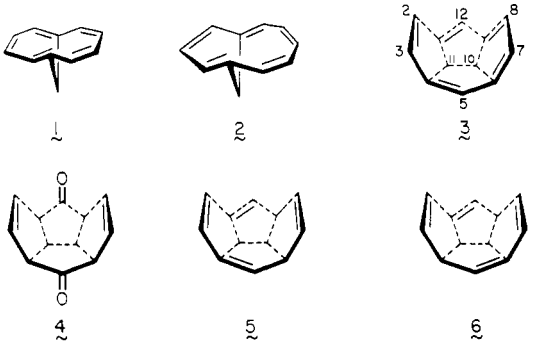
The concept of bridging a polyunsaturated macrocyclic hydrocarbon for the purpose of introducing conformational rigidity and maximizing $(4n + 2)\pi$ delocalization was first introduced by Vogel in 1964 for the [10]annulene core (see **1**).[3] In the intervening years, the concept has been extended to the 1,5-bridged isomer **2**,[4] but twofold bridging as in **3** has received only early theoretical attention.[5] As



1 2 3

4 5 6

(1) On sabbatical leave from the Tochigi Research Laboratories of the Kao Corporation, Japan, 1984–1985.

(2) Recipient of a "Bourse Lavoisier" postdoctoral fellowship awarded by the Ministère des Affaires Étrangères, Paris, France.

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