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The Synthesis of Dibenzo-Annelated Annulenes Using Reductive Coupling. Bisdehydrodibenzo[14]-, -[16]-, -[18]-, -[20]-, and -[22]annulene

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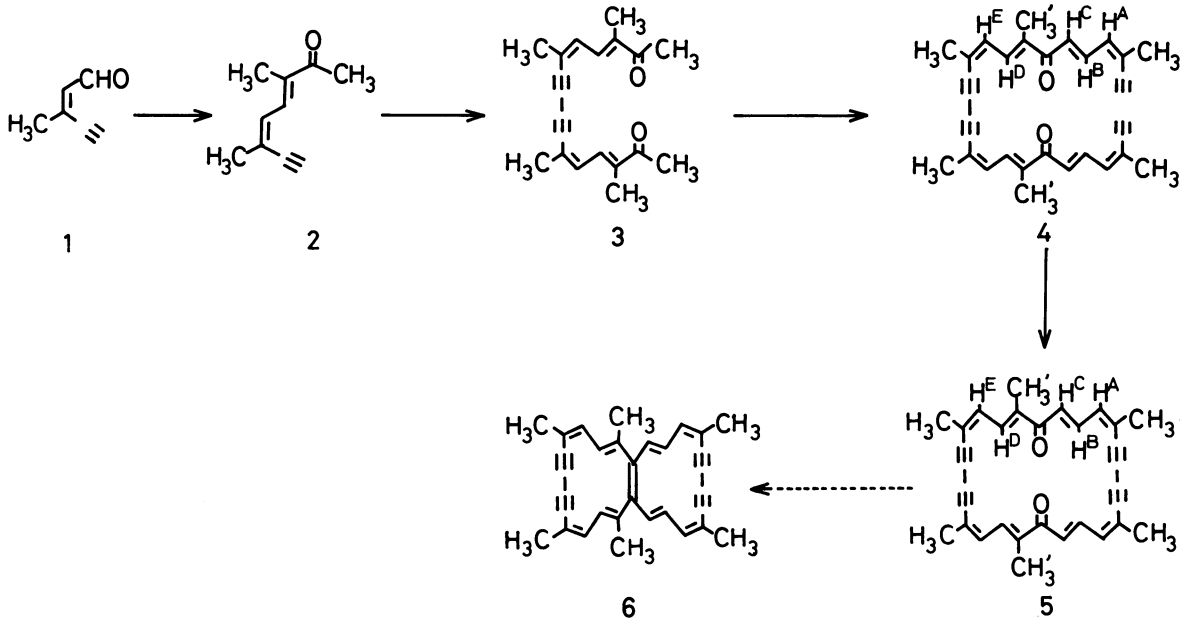
Bisdehydrodibenzo[14]-, -[16]-, -[18]-, -[20]-, and -[22]annulene were synthesized by intramolecular reductive couplings using a low-valent titanium reagent. These bisdehydrodibenzo-annulenes proved to be atropic from an examination of the ^{1}H NMR spectra.

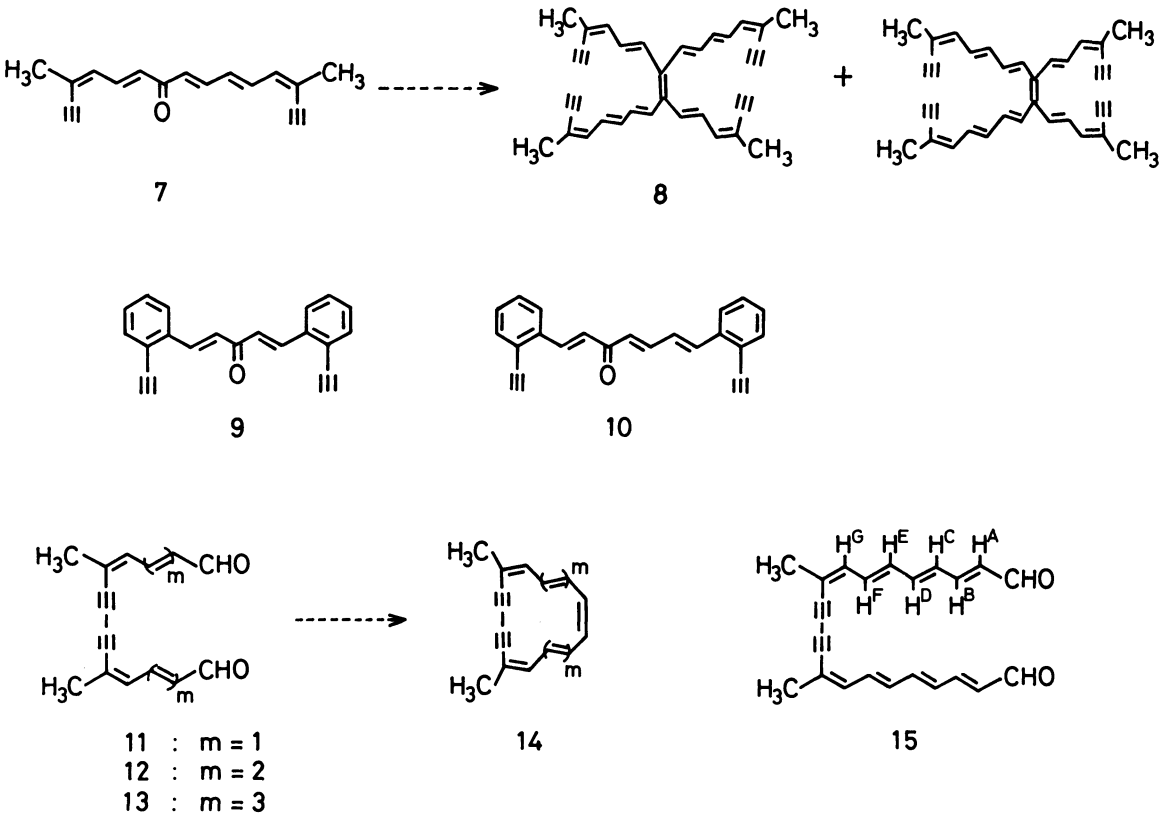
The reductive coupling of carbonyl compounds with a low-valent titanium reagent, developed by McMurry[1] and modified by several workers,[2] provides a new synthetic tool for formation of carbon–carbon double bond, which enabled chemists synthesis of a vast variety of crowded[3] or twisted[4] olefines inaccessible by usual method. In 1977, McMurry and Kees showed the potential of the method in medium- and large-ring carbocyclic synthesis by preparing cycloalkenes.[5] This intrigued us for preparation of annulenes and dehydroannulenes which usually requires lengthy reaction steps. When we commenced the present study, there had been no reports of annulene synthesis by low-valent titanium reagent, although, recently, two reports of preparation of doubly bridged [16]-[6a] and [24]annulene[6b] have appeared. In this paper, we describe attempts to prepare annulenoannulene and annulenes, and a successful synthesis of dibenzo-annelated bisdehydro-[14]-, -[16]-, -[18]-, -[20]-, and -[22]annulenes, using reductive couplings of carbonyl compounds.

Results and Discussion

Firstly, we attempted an intramolecular reductive coupling of the cyclic diketone **5**, prepared as illustrated in Scheme 1, to obtain a tetrakisdehydro-[14]annuleno[14]annulene **6**, but this attempt was unsuccessful. Then, since we had it in mind that the [4*n*]annuleno[4*n*]annulenes have not yet been known[7] and one of the desired products should be the precursor **8** of tetrakisdehydro[16]annuleno[16]annulene, we tried an intramolecular reductive coupling of the acyclic ketone **7**,[8] but some attempts did not meet with success. Thus, since the couplings using **5** and **7** gave polymeric products, we used the dibenzo-fused acyclic ketones **9**[9] and **10**[10] which are more stable than the methylated ketones **5** and **7**. However, these attempts were also unsuccessful, which led us to use more reactive aldehydes than ketones. Then we attempted intramolecular couplings of the dialde-



Scheme 1.



hydes **11**—**13**[11] to obtain the corresponding bisdehydroannulenes **14**; but the products of these reactions always gave only polymeric materials. Thus, since we learnd that these fully conjugated dialdehydes **11**—**13** or the products from them are insufferable against the reaction conditions employing $TiCl_3$ and $LiAlH_4$ in 1,2-dimethoxyethane, we tried to use the benzo-fused dialdehydes **20**, **22**—**26**. These dialdehydes were prepared by oxidative couplings of *o*-ethynylbenzaldehyde **16**[12] and/or its homologated aldehydes **17**—**19**.[13,14] The symmetrical dialdehydes **20**, **22**, **24**, and **26** were prepared from the corresponding monoaldehydes **16**—**18**, and **19**, respectively, in high yields, but the unsymmetrical dialdehydes **23** and **25** were obtained in moderate yields, since the symmetrical dialdehydes also formed. Rather surprisingly, we could not obtain the dialdehyde **21** by the oxidative coupling between **16** and **17** or by Wittig condensation with the dialdehyde **20** and 1.3 molar equivalent of [(1,3-dioxolan-2-yl)methyl]triphenylphosphonium bromide according to the procedure employed for the homologation of the aldehyde **16**.[13,14]

The intramolecular reductive couplings of these aldehydes **20**, **22**—**26** were carried out in the presence of $TiCl_3$ and $LiAlH_4$ in refluxing 1,2-dimethoxyethane under argon atmosphere, giving rise to the dibenzo-annelated bisdehydro[14]- **28**, -[16]- **29**, -[18]- **30**, -[20]- **31**, and -[22]annulene **32** in low yields. The didenzo[10]annulene **27** did not form from the dialdehyde **20**, presumably due to a severe steric strain expected for the structure.

The ^1H NMR chemical shifts of the dibenzoannulenes **28**—**32** thus obtained are listed in Table 1. The assignments of the resonances to the indiviual protons were made on the basis of multiplicities and coupling constants and the assumption that protons in a similar environment resonate at similar field, and were further clarified by the use of decoupling experiments where necessary. As we see from the Table 1, an examination of the chemical shifts suggests that these benzo-annelated annulenes **28**—**32** are atropic, since the high- or low-field shifts due to the olefinic inner or outer protons are not observed.

In conclusion, the results from this study indicate that the effectiveness of the reductive coupling in annulene synthesis greatly depends on the stability of the used conjugated carbonyl compounds and the products derived from them.

Experimental

All melting-points are uncorrected. IR spectra were measured on Hitachi 260-50 spectrophotometer as KBr disks; only significant maxima are reported. Electronic spectra were taken on Hitachi 220A spectrophotometer and recorded in nm. ε-Values are given in parentheses, shoulders being denoted by sh. Mass spectra were measured with JEOL JMS-D 200 spectrometer at 75 eV using a direct inlet system. ^1H NMR spectra were taken on JEOL FX-90Q (90 MHz) or Varian XL-200 (200 MHz) or

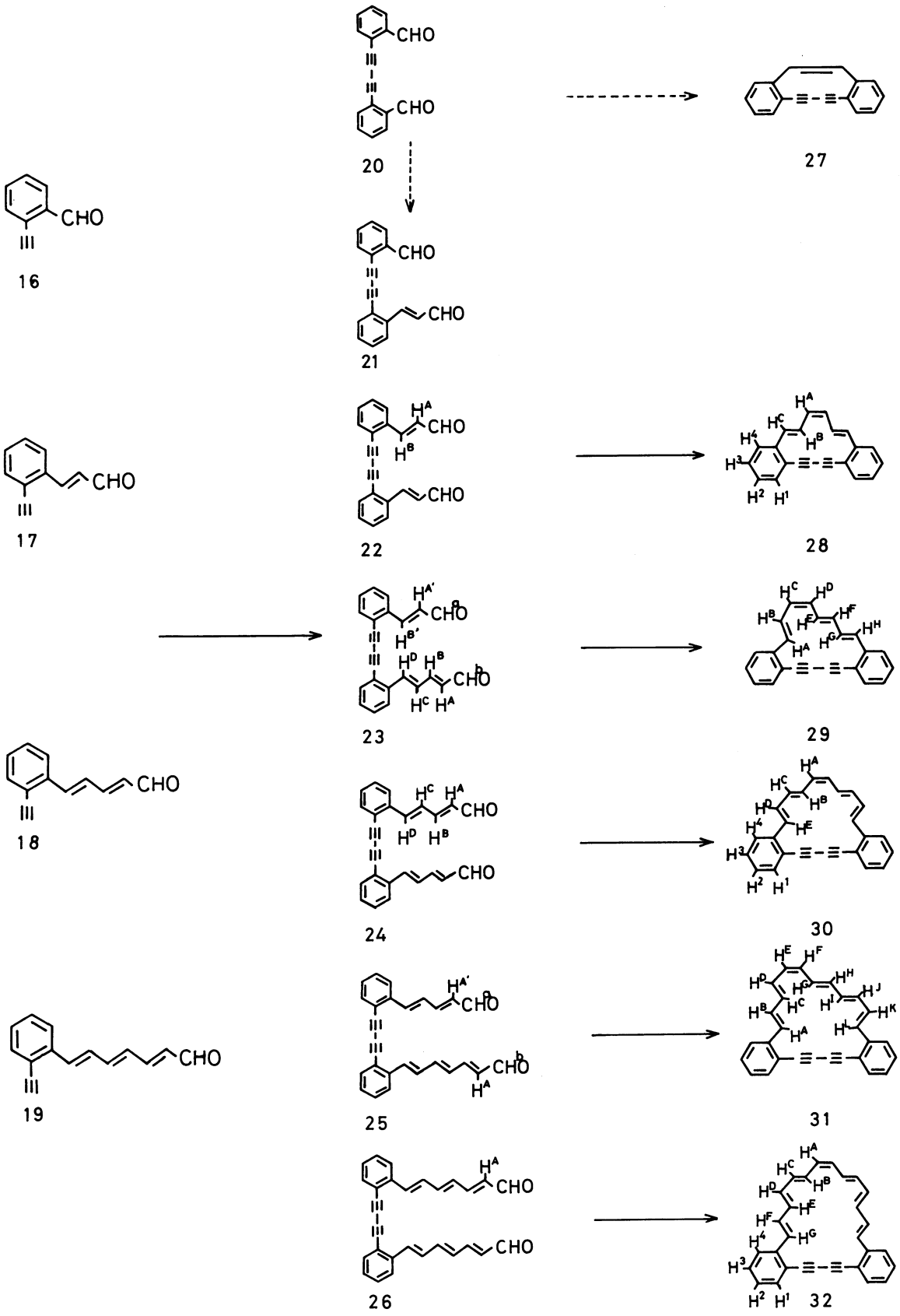

CHO
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Table 1. ^{1}H NMR Chemical Shifts of Dibenzo-Annelated Annulenes **28**—**32** (in $CDCl_3$), Determined at 21 °C (τ Value; Internal Standard, Me_4Si)

Compd	H^A	H^B	H^C	H^D	H^E	H^F	H^G	H^H	H^I	H^J	H^K	H^L	Benzenoid H
[14]-**28**[a]	3.00—3.13	3.20—3.37	2.83										2.14—2.66
[16]-**29**[a]	1.63	(2.42—3.10)	4.18	3.99	1.08	3.96	1.11	(2.42—3.10)					(2.42—3.10)
[18]-**30**[b]	(3.26—3.34)	3.73	(3.26—3.34)	2.76	3.68								(2.01—2.62)
[20]-**31**[b]	1.75	(3.22—3.50)	2.28	(3.69—4.02)	4.30	(3.69—4.02)		(3.22—3.50)	1.54	(3.22—3.50)	(3.69—4.02)	1.52	2.61—2.98
[22]-**32**[a]	(3.30—3.54)	3.80	(3.30	———	3.52)	2.60	3.70						2.02—2.68

a) At 200 MHz. b) At 270 MHz.

JEOL GX-270 (270 MHz) spectrometer, and refer to solutions in $CDCl_3$, in τ-values with TMS as an internal standard. The coupling constants (J) are given in Hz. Alumina (II-III) or silica-gel (Merck) was used for column chromatography. Progress of most reactions was followed by TLC using Merck precoated silica-gel. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled from sodium benzophenone under nitrogen atmosphere before use. The organic extracts were dried over anhyd sodium sulfate or magnesium sulfate prior to solvent removal.

3,6-Dimethyl-3,5-octadien-7-yn-2-one (2). This compound was prepared from 3-methyl-2-penten-4-ynal (**1**)[15] and 2-butanone as reported.[16]

3,6,11,14-Tetramethyl-3,5,11,13-hexadecatetraene-7,9-diyne-2,5-dione (3). A soln of the ketone **2** (4.40 g, 30 mmol) in methanol (42 ml) was added dropwise to a stirred soln of copper(II) acetate monohydrate (12.2 g) in pyridine (142 ml) and methanol (142 ml) during 45 min at room temp. After stirring for a further 3.5 h at the same temp, the reaction mixture was poured into water and extracted with benzene. The extracts were washed with 7% hydrochloric acid until it turned acidic, and then with aq sodium hydrogencarbonate, and dried. The residual red liquid, after solvent removal, was chromatographed on alumina (4.0×6.0 cm). The fractions eluted with benzene gave the diketone **3** (3.51 g, 80%). Recrystallization from methanol afforded yellow needles: Mp 111—113 °C (lit, [16] mp 110—112 °C).

3,8,11,16,19,24-Hexamethyl-3,5,8,10,16,18,21,23-hexaicosaoctaene-1,12,14,25-tetrayne-7,20-dione (4). A soln of the aldehyde **1** (2.60 g, 27.6 mmol) in dry benzene (8 ml) was added dropwise during 10 min to an ice-cooled, stirred soln of the diketone **3** (2.00 g 6.80 mmol) in dry benzene (40 ml) containing ethanolic sodium ethoxide (11 ml), prepared from sodium (750 mg) and abs ethanol (50 ml). After stirring for a further 4.5 h under an ice-bath, the reaction was quenched by addition of acetic acid. Then the mixture was poured onto water and extracted with benzene. The extracts were washed with aq sodium hydrogencarbonate soln and brine, and dried. The residual dark red liquid, after solvent removal, was chromatographed on alumina (4.0×12.0 cm). The fractions eluted with hexane–ether (1:1) gave the diketone **4** (2.21 g, 72.8%). Recrystallization from hexane–benzene afforded yellow needles : Mp 114 °C (decomp); MS m/z 446 (M^+, 3%) and 78 (100); mol wt 446.5; IR 3300, 3240 (-C≡CH), 2200, 2100 (-C≡C-), 1640 (C=O), 1595 (C=C), and 995 cm^{-1} (trans C=C); UV_{max} (THF) 246 sh (24200), 258 sh (26700), 284 (27000), 302 sh (27300) 353 (35400), 385 (34500), 420 nm sh (19800); ^{1}H NMR (90 MHz) τ=2.25 (dd, 15, 12, 2H, H^B), 2.50 (d, 12, 2H, H^D), 3.15 (d, 15, 2H, H^C), 3.18 (d, 12, 2H, H^A or H^E), 3.53 (d, 12, 2H, H^A or H^E), 6.57 (s, 2H, -C≡CH), 7.90 (s, 6H, CH_3'), and 8.03 (s, 12H, CH_3).

Found: C, 85.13; H, 6.80%. Calcd for $C_{32}H_{30}O_2$:C, 86.06; H, 6.77%. Attempts to improve the elemental analysis failed.

2,5,10,13,18,23-Hexamethyl-2,4,10,12,15,17,23,25-cyclohexaicosaoctaene-6,8,19,21-tetrayne-1,14-dione (5). A soln of the acyclic diketone **4** (6.00 g, 13.4 mmol) in ether (80 ml), methanol (80 ml), and pyridine (200 ml) was added dropwise during 11 h to a stirred, refluxing mixture of anhyd copper(II) acetate (20 g) in ether (1200 ml), methanol (400 ml), and pyridine (1400 ml) at 50 °C, using high-dilution apparatus. After being refluxed for a further 1 h,

the mixture was allowed to stand overnight at room temp. Then the mixture was concentrated to ca. 400 ml under reduced pressure below 35 °C, and the concentrate was worked up as for the isolation of **3**. The residual dark red liquid, after solvent removal, was chromatographed on alumina (4.0×10.0 cm). The fractions eluted with ether–benzene (1:1) gave the cyclic diketone **5** (1.50 g, 25%). Recrystallization from chloroform–ethanol afforded yellow needles: Mp 120 °C (decomp); MS *m/z* 444 (M^+, 25%) and 178 (100); mol wt 444.5; IR 2180 (-C≡C-), 1635, 1610, 1590, 1570, (C=O, C=C), 985, and 970 cm^{-1} (trans C=C); UV_{max} (THF) 253 (29500), 291 (31900), 329 sh (43900), 350 (47900), and 403 nm sh (15800); ^1H NMR (200 MHz) τ=2.45 (d, 11, 2H, H^D), 2.47 (dd, 16, 11, 2H, H^B), 3.20 (d, 11, 2H, H^A or H^E), 3.43 (d, 11, 2H, H^A or H^E), 3.54 (d, 16, 2H, H^C), 7.94 (s, 6H, CH_3'), and 7.97 (s, 12H, CH_3).

Found: C, 86.23; H, 6.31%. Calcd for $C_{32}H_{28}O_2$:C, 86.45; H, 6.35%.

An Intramolecular Reductive Coupling of The Cyclic Diketone 5. The reaction was carried out under the same conditions as those described below for the dialdehyde **23**; however no monomeric product was obtained.

3,13-Dimethyl-3,5,8,10,12-pentadecapentaene-1,14-diyn-7-one (7). This compound was prepared as reported.[8]

1,5-Bis(*o*-ethynylphenyl)-1,4-dien-3-one (9) and 1,7-Bis(*o*-ethynylphenyl)-1,4,6-heptatrien-3-one (10). These compounds were prepared as reported.[9,10]

Intermolecular Reductive Couplings of The Ketones 9 and 10. These reactions were also carried out under the same conditions as those employed for the dialdehyde **22** (vide infra); however no dimeric product was obtained.

5,10-Dimethyl-2,4,10,12-tetradecatetraene-6,8-diynedial (11) and 7,12-Dimethyl-2,4,6,12,14,16-octadecahexaene-8,10-diynedial (12). The dialdehydes **11** and **12** were prepared as reported.[11]

9,14-Dimethyl-2,4,6,8,14,16,18,20-docosaoctaene-10,12-diynedial 15 (13: *m*=3). A soln of 9-methyl-2,4,6,8-undecatetraene-10-ynal[11] (2.47 g, 14.3 mmol) in pyridine (39 ml) and methanol (39 ml) was added dropwise during 40 min to a stirred soln of copper(II) acetate monohydrate (19.2 g) in pyridine (155 ml) and methanol (155 ml) at 16 °C. After stirring overnight at room temp, the reaction mixture was worked up as in the preparation of **3**. The residual red liquid, after solvent removal, was chromatoraphed on alumina (4.0×9 cm). The fractions eluted with ether gave the dialdehyde **15** (960 mg, 39.1%). Recrystallization from hexane–benzene afforded red cubes: Mp 164—166 °C; MS *m/z* 342 (M^+, 28%) and 81 (100); mol wt 342.4; IR 2170 (-C≡C-), 1675 (-CHO), 1610, 1590, 1570 (C=C), 1010, and 990 cm^{-1} (trans C=C); UV_{max} (THF) 254 sh (16300), 264 (18200), 290 sh (18900), 302 sh (22600), 315 sh (27100), 347 sh (50000), 364 (60200), 408 (52900), and 457 nm sh (30300); ^1H NMR (90 MHz) τ=0.42 (d, 8, 2H, CHO), 2.84 (dd, 15, 10.5, 2H, H^F), 2.94—3.78 (m, 6H, H^B, H^C, H^D), 3.35 (dd, 16, 10, 2H, H^E), 3.52 (d, 10, 2H, H^G), 3.83 (dd, 15, 8, 2H, H^A), and 7.97 (S, 6H, CH_3).

Found: C, 84.42; H, 6.53%. Calcd for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47%.

Intramolecular Reductive Couplings of The Dialdehydes 11—13. These reactions were carried out under the similar conditions as described for the dialdehyde **22** (vide infra); however no monomeric product was obtained.

2,3:8,9-Dibenzodeca-4,6-diyndial (20). A soln of the dialdehyde **16**[12] (2.00 g 15.4 mmol) in pyridine (31 ml) was added dropwise during 1.5 h to a stirred soln of copper(II) acetate monohydrate (31 g) in pyridine (91 ml) at 47—49 °C. After stirring for a further 2 h at the same temp, the reaction mixture was worked up as in the isolation of **3**. The residual red liquid, after solvent removal, was chromatographed on alumina (3.7×6.5 cm). The fractions eluted with hexane–ether (2:3) gave the dialdehyde **20** (1.03 g, 52%). Recrystallization from benzene afforded yellow needles: Mp 163—164 °C; MS *m/z* 258 (M^+, 100%); mol wt 258.2; IR 2270, 2200 (-C≡C-), and 1700 cm^{-1} (-CHO); UV_{max} (THF) 227 sh (57000), 235 (61900), 244 sh (57100), 261 sh (35100), 270 sh (27200), 286 sh (14100), 308 (17900), 334 (23200), and 355 nm (20000); ^1H NMR (90 MHz) τ=−0.60 (s, 2H, CHO), 1.90—2.10 (m, 2H, benzenoid H), and 2.17—2.57 (m, 6H, benzenoid H).

Found: C, 83.51; H, 3.70%. Calcd for $C_{18}H_{10}O_2$: C, 83.71; H, 3.90%.

4,5: 10,11-Dibenzo-2,12-tetradecadiene-6,8-diynedial (22). A soln of the aldehyde **17**[13] (2.00 g, 12.8 mmol) in pyridine (25 ml) was added dropwise during 1 h to a stirred soln of copper(II) acetate monohydrate (24.6 g) in pyridine (75 ml) at 52—56 °C. After stirring for a further 3 h at the same temp, the reaction mixture was worked up as in the preparation of **3**. The residual dark brown liquid, after solvent removal, was chromatographed on alumina (3.7×9 cm). The fractions eluted with hexane–ether (1:4) gave the dialdehyde **22** (1.49 g, 60%). Recrystallization from hexane–benzene afforded yellow needles: Mp 203—204 °C; MS *m/z* 310 (M^+, 17%) and 254 (100); mol wt 310.3; IR 2200 (-C≡C-), 1680 (-CHO), and 980 cm^{-1} (trans C=C) UV_{max} (THF) 224 sh (18700), 254 (32200), 277 (28500), 294 sh (24000), 330 sh (12600), and 367 nm sh (8360); ^1H NMR (90 MHz) τ=0.10 (d, 8, 2H, CHO), 1.98 (d, 16, 2H, H^B), 2.13—2.65 (m, 8H, benzenoid H), and 3.15 (dd, 16, 8, 2H, H^A).

Found: C, 85.06; H, 4.26%. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55%.

4,5: 10,11-Dibenzo-2,12,14-hexadecatriene-6,8-diynedial (23). A soln of the aldehyde **17** (2.10 g, 14 mmol) and the aldehyde **18** (2.50 g, 14 mmol) in pyridine (45 ml) and methanol (45 ml) was added dropwise during 1 h to a stirred soln of copper(II) acetate monohydrate (22 g) in pyridine (170 ml) and methanol (170 ml) at room temp, and stirring was continued for a further 16 h at the same temp. Then the mixture was worked up as in the isolation of **3**. The residue, after solvent removal, was chromatoraphed on alumina (4.5×13 cm). The early fractions eluted with hexane–ether (2:3) gave the dialdehyde **22** (0.54 g, 13%). The following fractions eluted with benzene–chloroform (4:1) gave the dialdehyde **23** (2.03 g, 43%). Recrystallization from hexane–benzene afforded yellow cubes: Mp 176—177 °C; MS *m/z* 336 (M^+, 14%) and 252 (100); mol wt 336.3; IR 2240 (-C≡C-), 1680 (-CHO), and 990 cm^1 (trans C=C); UV_{max} (THF) 235 sh (32000), 261 (40900), 271 (38300), 285 (45700), 301 (39400), 313 (40600), and 338 nm sh (32700); ^1H NMR (90 MHz) τ=0.19 (d, 7.5, 1H, H^b), 0.35 (d, 7, 1H, H^a), 2.04 (d, 16, 1H, $H^{B'}$), 2.26—2.93 (m, 11H, H^B, H^C, H^D, and benzenoid H), 3.20 (dd, 16, 7.5, 1H, $H^{A'}$), and 3.71 (dd, 14, 8, 1H, H^A).

Found: C, 85.41; H, 4.99%. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79%.

The later fractions eluted with chloroform gave the

dialdehyde **24** (vide infra) (1.08 g, 21%).

6,7:12,13-Dibenzo-2,4,14,16-octadecatetraene-8,10-diynedial (24). A soln of the aldehyde **18**[14] (363 mg, 2.0 mmol) in pyridine (4 ml) was added dropwise during 20 min to a stirred soln of copper(II) acetate monohydrate (3.8 g) in pyridine (11 ml) at 50 °C. After stirring for a further 3 h at the same temp, the reaction mixture was worked up as in the preparation of **3**. The residual yellow solid, after solvent removal, was chromatographed on alumina (3.7×9 cm). The fractions eluted with hexane–ether (3:7) gave the dialdehyde **24** (257 mg, 71%). Recrystallization from benzene afforded yellow needles: Mp 170—171 °C; MS *m/z* 362 (M^+, 10%) and 289 (100); mol wt 362.4; IR 2270, 2210 (-C≡C-), 1680 (-CHO), 1620 (C=C), and 985 cm^{-1} (trans C=C); UV_{max} (THF) 227 (24600), 269 (32800), 283 sh (30800), 300 (42400), 327 (42600), and 355 nm sh (30100); ^1H NMR (90 MHz) τ=0.28 (d, 8, 2H, CHO), 2.22—3.03 (m, 14H, H^B, H^C, H^D, and benzenoid H), and 3.65 (dd, 14, 8, 2H, H^A).

Found: C, 86.42; H, 5.29%. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01%.

6,7:12,13-Dibenzo-2,4,14,16,18-icosapentaene-8,10-diynedial (25). A soln of the aldehyde **18**[14] (2.10 g, 11.5 mmol) and the aldehyde **19**[14] (2.42 g, 11.6 mmol) in pyridine (50 ml) was added dropwise during 20 min to a stirred soln of copper(II) acetate monohydrate (46 g) in pyridine (140 ml) at 50 °C. After stirring for a further 1 h at the same temp, the mixture was poured into water, and extracted with chloroform. The combined extracts were washed with 7% hydrochloric acid until it turned acidic, water, aq sodium hydrogencarbonate soln, and brine, successively, and dried over anhyd calcium chloride. The residue, after solvent removal, was chromatographed on alumina (4.2×5.0 cm). The early fractions eluted with ether–benzene (4:1) gave the dialdehyde **24** (260 mg, 6.0%). The following fractions eluted with ether–benzene (1:1) gave the dialdehyde **25** (560 mg, 12%). Recrystallization from hexane–chloroform afforded yellow microcrystals: Mp 156—157 °C; MS *m/z* 388 (M^+, 10%) and 289 (100); mol wt 388.4; IR 2200 (-C≡C-), 1680 (-CHO), and 990 cm^1 (trans C=C); UV_{max} (THF) 225 (26300), 240 sh (22900), 272 (28000), 284 sh (30300), 300 sh (36400), 310 sh (43800), and 340 nm (45800); ^1H NMR (90 MHz) τ=0.34 (d, 8, 1H, H^a), 0.41 (d, 7.7, 1H, H^b), 2.21—3.50 (m, 16H, olefinic and benzenoid H), 3.71 (dd, 14, 8, 1H, $H^{A'}$), and 3.85 (dd, 15, 7.7, 1H, H^A).

Found: C, 86.48; H, 5.54%. Calcd for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19%.

The later fractions eluted with benzene–chloroform (1:1) gave the dialdehyde **26** (vide infra) (950 mg, 19%).

8,9:14,15-Dibenzo-2,4,6,16,18,20-docosahexaene-10,12-diynedial (26). A soln of the aldehyde **19**[14] (3.48 g, 16.7 mmol) in pyridine (33 ml) was added dropwise during 1.5 h to a stirred soln of copper(II) acetate monohydrate (32 g) in pyridine (98 ml) at 52—54 °C. After stirring for a further 1 h at the same temp, the reaction mixture was worked up as in the preparation of **3**. The residual red liquid, after solvent removal, was chromatographed on alumina (3.7×12 cm). The fractions eluted with benzene-chloroform (7:3) gave the dialdehyde **26** (1.97 g, 57%). Recrystallization from hexane–tetrahydrofuran afforded red cubes: Mp 186—188 °C; MS *m/z* 414 (M^+, 59%) and 396 (100); mol wt 414.4; IR 2200 (-C≡C-), 1670 (-CHO), 1620, 1600, 1580 (C=C), 1010, and 990 cm^{-1} (trans C=C); UV_{max} (THF) 241 (33700), 253 sh (23800), 283 (33000), 296 sh (35200), 321 (55400), 359 (66600), and 383 nm sh (59600); ^1H NMR (90 MHz) τ=0.41 (d, 9, 2H, CHO), 2.26—3.60 (m, 18H, olefinic and benzenoid H), and 3.79 (dd, 17, 9, 2H, H^A).

Found: C, 86.91; H, 5.55%. Calcd for $C_{30}H_{22}O_2$: C, 86.73; H, 5.35%.

Reductive Coupling of the dialdehyde **20** was carried out under the same conditions as those indicated for the dialdehyde **22**. But no monomeric compound was obtained.

3,5-Bisdehydro-1,2:7,8-dibenzo[14]annulene (28). $LiAlH_4$ (47 mg, 1.24 mmol) was added in one portion to titanium trichloride ($TiCl_3$) (327 mg, 2.12 mmol) in dry THF (20 ml) under argon. The resultant black mixture was heated under reflux for 15 min. To the mixture, a soln of the dialdehyde **22** (248 mg, 0.80 mmol) in dry THF (10 ml) was added dropwise during 10 h and then the mixture was stirred under reflux for a further 5 h. Then after addition of ethanol (5 ml), the mixture was filtered off to remove inorganic materials and the filtrate was concentrated under reduced pressure. The residue was chromatographed on alumina (10 g). The fractions eluted with hexane–benzene (1:1) gave the dibenzo[14]annulene **28** (60 mg, 27%). Recrystallization from hexane–benzene afforded yellow plates: Mp 193—195 °C; MS *m/z* 278 (M^+, 78%) and 276 (100); mol wt 278.3; IR 2150 (-C≡C-) and 950 cm^{-1} (trans C=C); UV_{max} (isooctane) 210 sh (64500), 236 sh (21000), 244 (23900), 289 (81000), 299 (82400), 307 (85300), 337 (20300), 372 (13700), and 414 nm sh (614); ^1H NMR (200 MHz) τ=2.14 (d, 8, 2H, H^4), 2.37—2.48 (m, 4H, H^1, H^2), 2.56—2.66 (m, 2H, H^3), 2.83 (d, 16, 2H, H^C), 3.00—3.13 (m, 2H, H^A), and 3.20—3.37 (m, 2H, H^B).

Found: C, 94.92; H, 4.92%. Calcd for $C_{22}H_{14}$:C, 95.14; H, 4.86%.

3,5-Bisdehydro-1,2:7,8-dibenzo[16]annulene (29). To a stirred, refluxed soln of $TiCl_3$ (0.61 g, 3.95 mmol) in 1,2-dimethoxyethane (DME) (40 ml) was added $LiAlH_4$ (90 mg, 2.38 mmol) in one portion under argon, and the mixture was refluxed for 30 min. To this mixture was added a soln of the dialdehyde **23** (0.50 g, 1.49 mmol) in DME (20 ml) during 8 h with stirring under reflux, and stirring was continued for a further 5 h under reflux. Then the reaction mixture was passed through Hyflo Super-Cel and washed with DME. The filtrate was concentrated, and the concentrate was extracted with benzene. The residue, after solvent removal, was chromatographed on silica-gel (20 g). The fractions eluted with hexane–benzene (4:1) gave the dibenzo[16]annulene **29** (90 mg, 20%). Recrystallization from hexane–benzene afforded red needles: Mp 159—161 °C; MS *m/z* 304 (M^+, 36%) and 306 (100); mol wt 304.3; IR 2200 (-C≡C-) and 960 cm^{-1} (trans C=C); UV_{max} (isooctane) 298 (77900), 308 sh (83900), 319 (93900), 390 (49700), 433 sh (24900), and 462 sh (16700); ^1H NMR (200 MHz) τ=1.08 (dd, 16, 10, 1H, H^E), 1.11 (dd, 16, 9, 1H, H^G), 1.69 (d, 16, 1H, H^A), 2.42—3.10 (m, 10H, H^B, H^H, and benzenoid H), 3.96 (dd, 15, 8, 1H, H^F), 3.99 (t, 10.5, 1H, H^D), and 4.18 (t, 10, 1H, H^C).

Found: C, 94.84; H, 5.17%. Calcd for $C_{24}H_{16}$:C, 94.70; H, 5.30%.

3,5-Bisdehydro-1,2:7,8-dibenzo[18]annulene (30). To the refluxing mixture of $LiAlH_4$ (47 mg, 1.24 mmol) and $TiCl_3$ (327 mg, 2.12 mmol) in dry DME (20 ml), prepared as described above, was added dropwise a soln of the dialdehyde **24** (290 mg, 0.80 mmol) in dry DME (10 ml)

during 6 h under argon and the mixture was stirred under reflux for a further 5 h. After work up as in the isolation of **29**, the residue was chromatographed on alumina (15 g). The fractions eluted with hexane–benzene (4:1) gave the dibenzo[18]annulene **30** (37 mg, 14%). Recrystallization from hexane–benzene afforded brown needles: Mp 261—263 °C; MS *m/z* 330 (M^+, 3%) and 302 (100); mol wt 330.4; IR 2200 (-C≡C-) and 960 cm^{-1} (trans C=C); UV_{max} (isooctane) 269 sh (22600), 284 sh (31400), 323 sh (70000), 342 (84300), 360 sh (33300), 417 (14800), 435 (14600), and 460 nm sh (8990); ^1H MNR (270 MHz) τ=2.01 (d, 8, 2H, H^4), 2.15 (d, 8, 2H, H^1), 2.48 (t, 8, 2H, H^3), 2.62 (t, 7.5, 2H, H^2), 2.76 (dd, 16.5, 6.5, 2H, H^D), 3.26—3.34 (m, 4H, H^A, H^C), 3.68 (d, 16.5, 2H, H^E), and 3.73 (dd, 16.5, 10, 2H, H^B).

Found: C, 94.42; H, 5.30%. Calcd for $C_{26}H_{18}$: C, 94.51; H, 5.49%.

3,5-Bisdehydro-1,2:7,8-dibenzo[20]annulene (31). To the black mixture of $TiCl_3$ (0.5 g, 3.3 mmol) and $LiAlH_4$ (75 mg, 2.0 mmol) in dry DME (40 ml), prepared as described above, a soln of the dialdehyde **25** (0.49 g, 1.26 mmol) in dry DME (20 ml) was added dropwise during 8 h and stirring was continued for a further 5 h under reflux. Then the mixture was worked up as in the isolation of **29**. The residue, after solvent removal, was chromatographed on silica-gel (20 g). The fractions eluted with hexane–benzene (2:1) gave the dibenzo[20]annulene **31** (40 mg, 8.7%). Recrystallization from hexane–dichloromethane afforded black cubes: Mp 300 °C (decomp); MS *m/z* 356 (M^+, 67%) and 339 (100); mol wt 356.4; IR 2200, 2150 (-C≡CH) and 990 cm^{-1} (trans C=C); UV_{max} (isooctane) 293 sh (46900), 320 sh (106000), 333 (121000), 413 sh (23300),435 (12600), 462 sh (19500), and 498 nm sh (14700); ^1H MNR (270 MHz) τ=1.52 (d, 16, 1H, H^L), 1.54 (dd, 16, 12, 1H, H^I), 1.75 (d, 16, 1H, H^A), 2.28 (dd, 16, 8, 1H, H^C), 2.61—2.98 (m, 8H, benzenoid H), 3.22—3.50 (m, 4H, H^B, H^J, H^G, H^H), 3.69—4.02 (m 3H, H^D, H^F, H^K), and 4.30 (dd, 12, 10, 1H, H^E).

Found: C, 94.24; H, 5.65%. Calcd for $C_{28}H_{20}$: C, 94.38; H, 5.66%.

3,5-Bisdehydro-1,2:7,8-dibenzo[22]annulene (32). To the refluxing mixture of $LiAlH_4$ (47 mg, 1.24 mmol) and $TiCl_3$ (327 mg, 2.12 mmol) in dry THF (20 ml), prepared as described above, was added dropwise a soln of the dialdehyde **26** (330 mg, 0.80 mmol) in dry THF (10 ml) during 10 h under argon and the mixture was stirred under reflux for a further 5 h. After work up as in the preparation of **28**, the residue, after solvent removal, was chromatographed on alumina (10 g). The fractions eluted with benzene gave the dibenzo[22]annulene **32** (12 mg, 4.0%). Recrystallization from hexane–benzene afforded brown needles: Mp ca. 300 °C (decomp); MS *m/z* 382 (M^+, 12%) and 57 (100); mol wt 382.4; IR 2200 (-C≡C-) and 980 cm^{-1} (trans C=C); UV_{max} (isooctane) 278 sh (28100), 297 (43200), 355 (113100), 420 sh (12600), 445 (15500), 464 (15100), and 501 nm sh (8200); ^1H NMR (200 MHz) τ=2.02 (d, 8, 2H, H^4), 2.18 (d. 8, 2H. H^1), 2.49 (t, 8, 2H, H^3), 2.60 (dd, 16, 11, 2H, H^F), 2.68 (t, 8, 2H, H^2), 3.30—3.54 (m, 8H, H^A, H^C, H^D, H^E), 3.70 (d, 16, 2H. H^G), and 3.80 (dd, 16, 10, 2H, H^B).

Found: C, 94.40; H, 5.69%. Calcd for $C_{30}H_{22}$: C, 94.20 H, 5.80%.

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