Dehydroannulenes. X. Synthesis and Properties of 3,9,12,18-Tetrasubstituted-1,10-bisdehydro[18]annulenes

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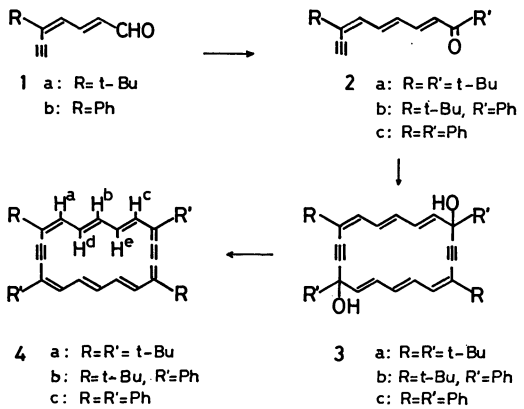
The cyclic dimerization of 1,7-disubstituted-1-oxo-2,4,6-nonatrien-8-ynes on treatment with a suspension of potassium hydroxide in liquid ammonia to give tetrasubstituted 18-membered cyclic glycols has been achieved. The cyclic glycols could be converted into 3,9,12,18-tetrasubstituted 1,10-bisdehydro[18]annulenes which were found to be conformationally stable and strongly diatropic.

As reported in previous papers,[1] 1,5-disubstituted 1-oxo-2,4-heptadien-6-ynes gave 14-membered cyclic glycols on treatment with a suspension of potassium hydroxide in liquid ammonia, and the cyclic glycols could be converted into 3,7,10,14-tetra-substituted 1,8-bisdehydro[14]annulenes by reductive dehydroxylation. The finding seemed to open a new route leading to higher members of bisdehydro[4n+2]annulenes provided that the cyclic dimerization can be realized for higher ethynylpolyene ketones.

In this paper we wish to report the cyclic dimerization of ethynyltriene ketones (**2**) to give 18-membered cyclic glycols (**3**) and their transformation into tetrasubstituted bisdehydro[18]-annulenes (**4**).[1]

Synthesis. The ethynyltriene ketones (**2a**[3,4] and **2c**[5]) were prepared by the reported methods. The trienyne ketone (**2b**) was obtained by the aldol condensation of acetophenone with 3-*t*-butyl-2,4-heptadien-6-ynal (**1a**).[3,4] A solution of ethynyltriene ketone (**2**) in tetrahydrofuran was added to a stirred suspension of finely powdered potassium hydroxide in liquid ammonia at *ca.* −35 °C. The cyclic glycol (**3a**) was obtained as a 1:1 mixture of diastereomers and could be separated into a high melting and a low melting isomers on chromatography on silica gel. Because the 18-membered cyclic glycols (**3b** and **3c**) were found to be difficult to purify, slightly crude materials were subjected to the following reductive dehydroxylation.



Scheme.

Finely powdered tin(II) chloride dihydrate was added to a stirred solution of **3a** in ether saturated with hydrogen chloride at −60 °C under nitrogen atmosphere. Resulting deeply colored solution was worked up and the product was chromatographed on alumina to give 3,9,12,18-tetra-*t*-butyl-1,10-bisdehydro[18]annulene (**4a**) as reddish violet crystals in 93% yield. Catalytic hydrogenation of **4a** over platinum catalyst yielded tetra-*t*-butyl-cyclooctadecane.

3,12-Di-*t*-butyl-9,18-diphenyl-1,10-bisdehydro[18]-annulene (**4b**) was obtained by a similar procedure as deep violet crystals.

Taking the poor solubility of **3c** and presumably of **4c** into account, a dilute solution of **3c** in dichloromethane was mixed with a solution of tin(II) chloride dihydrate in concentrated hydrochloric acid at −15 °C. 3,9,12,18-Tetraphenyl-1,10-bisdehydro[18]annulene (**4c**) was obtained as deep violet crystals in 59% yield. Full hydrogenation of **4c** over platinum catalyst yielded tetraphenylcyclooctadecane.

Properties. The bisdehydro[18]annulenes (**4a, b, c**) were found to be fairly stable being much stable than the corresponding tetrakisdehydro[18]annulenes.[6] 2,4,7-Trinitrofluorenone gave 1 : 1 CT complexes with **4a** and **4b**. However, CT complex with a definite composition could not be obtained with **4c**.

The electronic spectra of **4a, b, c** consist of three main absorption maxima characteristic of aromatic [4n+2]annulenes and showed close similarity to each other except for bathochromic shift along with the increase of phenyl substitution.[7] The numerical data of the electronic spectra are recorded in Table 1.

The ^{1}H NMR spectra of **4a, b, c** revealed that they sustain strong diamagnetic ring current exhibiting the inner proton signals at high field and those of outer protons at low field. The ^{1}H NMR parameters are summarized in Table 2. Replacement of *t*-butyl group by phenyl caused low field shift of inner and outer proton signals in **4b** and **4c**, which can be attributed, at least partly, to the deshielding effect of the diamagnetic ring current induced in phenyl groups. On the other hand, low field shift of *o*-proton signal of phenyl group as compared with that of *m,p*-protons indicate that the ring current in annulene ring exerts deshielding effect on the phenyl protons, and the *o*-protons suffer pronounced shift owing to their proximate position to the annulene nucleus. As recorded in Table 3, the ^{1}H NMR spectra of **4a** were found to be temperature independent being essentially unchanged up to 110 °C. This fact indicates the conformational stability of the tetrasubstituted 1,10-bisdehydro[18]annulene system. An attempted measurement of the NMR spectrum at 150 °C in deuteriobromo-

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Table 1. Electronic spectra of **4a, b, c** in THF (λ_{max} in nm (ε))

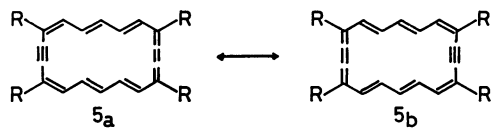
4a	217(11300), 255*(5810), 267.5(8360), 342*(44400), 356(94400), 372(447000), 464*(4790), 499(10600), 539(19100), 607(100), 646*(89), 669(116), 681(116), 720*(138), 751(316)
4b	240*(12900), 249.5(14000), 267*(12000), 281.5(16200), 367*(51800), 389*(171000), 401(330000), 534*(17900), 574(48000), 673*(150), 701(231), 785(980)
4c	261(25000), 293(26300), 411(106300), 431(506800), 572(20600), 615(48600), 735(270), 826(1560)

Table 2. ^{1}H NMR spectra of **4a** in deuteriobromoform

Temp (°C)	$H^{a,c}$	H^{b}	$H^{d,e}$	*t*-Bu
36	0.68, d J=13 Hz	0.18, t J=13 Hz	13.64, t J=13 Hz	8.09, s
70	0.78, d J=13 Hz	0.30, t J=13 Hz	13.46, t J=13 Hz	8.10, s
110	0.81, d J=13 Hz	0.44, t J=13 Hz	13.28, t J=13 Hz	8.10, s

form resulted in a rapid decomposition of **4a**. Because the planar structure of **4a** has been revealed by the X-ray structure analysis,[8] the minor high field and low field shifts of outer and inner proton signals at higher temperature should be a reflection of increasing deviation of the annulene perimeter from the mean molecular plane owing to the increase of thermal vibration at higher temperature.

It has been generally recognized that dehydroannulenes have higher conformational stability than the corresponding annulenes. The conformational stability of dehydroannulene, which is rendered by the rigid and straight nature of acetylenic bond, is favorable for the study of aromaticity of annulene system. But, on the other hand, the diatropicity of dehydroannulene is suppressed by the perturbation of acetylenic linkage. On the contrary, dehydroannulenes containing an acetylenic and a cumulenic bonds ('acetylene-cumulene'-dehydroannulenes), such as 1,8-bisdehydro[14]annulene[9] and its tetrasubstituted derivatives[1] and **4a,b,c**, showed strong diatropicity and high conformational stability being the most adequate tool for the study of aromaticity of macrocyclic system. Because the acetylenic and cumulenic bonds in 1,8-bisdehydro[14]annulene[10] and in **4a**[8] have been proved to be identical by the X-ray structure analyses being a hybrid of acetylene and butatriene, the strong diatropicity in 'acetylene-cumulene'-dehydroannulene can be attributed to the presence of equivalent valence-bond structures such as **5a**↔**5b**.



Experimental

All melting points were measured on a Mettler FP-2 apparatus and uncorrected. The IR spectra were obtained on a Hitachi EPI-2 or EPI-G3 spectrophotometer and only the significant absorptions were recorded (s=strong, m=medium and w=weak). The NMR spectra obtained on a Varian A-60 or XL-100 spectrometer were recorded in τ-values with respect to TMS used as an internal standard. The mass spectra were obtained on a Hitachi RM-50 spectrometer (ionization potential=70 eV). TLC was performed on Kieselgel GF_{254}(Merck) plates. The adsorbents used in column chromatography were silica gel (Merck, Kieselgel 60) or alumina (Merck, act. II—III), unless stated otherwise. Evaporation of solvent was performed under reduced pressure.

1,4,10,13-Tetra-t-butyl-4,6,8,13,15,17-cyclooctadecahexaene-2,11-diyne-1,10-diol (3a). To a stirred suspension of finely powdered potassium hydroxide (900 mg, 1.60 mmol) in liquid ammonia (180 ml) was added at −34 °C a solution of **2a** (320 mg, 1.13 mmol) in THF (30 ml) over a period of 5 h. After being stirred for further 3 h at the same temperature, ammonium chloride (1.80 g, 33.6 mmol) was added and the ammonia was allowed to evaporate. Water and ether (20 ml) were added to the residue. The aqueous layer was washed successively with water and brine, and dried ($MgSO_4$). Evaporation of the solvent yielded pale yellow crystals, which were washed with hexane to give a mixture of diastereomers of **3a**, colorless crystals, 212 mg, 66.3%. The mixture was chromatographed on silica gel. Elution with benzene gave the high melting isomer of **3a**, colorless crystals, mp 230.5—231.5 °C; mass (*m/e*): 488 (M^+), 470 (M^+-18), 431 (M^+-57), 57 (*t*-Bu, base peak); IR(KBr-disk): 3560 m (OH), 2180 vw (−C≡C−), 1563 w (C=C), 985 vs (*trans* −CH=CH−) cm^{-1}; NMR($CDCl_3$): 2.75—4.20 (10H, m, olefinic), 8.2 (2H, br s, OH), 8.80 (18H, s, *t*-Bu), 8.92 (18H, s, *t*-Bu); UV: $\lambda_{max}^{99\%EtOH}$ (ε): 230 (21100), 280.5 (86900), 291 (113000), 327.5 (13800) nm.

Found: C, 83.53; H, 9.93%. Calcd for $C_{34}H_{48}O_2$: C, 83.55; H, 9.90%.

Elution with benzene-ether (19:1) gave the low melting isomer of **3a**, colorless crystals, mp 170.0—171.0 °C; mass (*m/e*): 488 (M^+), 470 (M^+-18), 431 (M^+-57), 57 (*t*-Bu, base peak); IR(KBr-disk): 3480 m, 3340 m (OH), 2180 vw (−C≡C−), 1563 w (C=C), 985 vs (*trans* −CH=CH−) cm^{-1}; NMR($CDCl_3$): 2.75—4.20 (10H, m, olefinic), 8.01 (2H, s, OH), 8.80 (18H, s, *t*-Bu), 8.92 (18H, s, *t*-Bu); UV: $\lambda_{max}^{99\%EtOH}$ (ε) 230 (18200), 280.5 (76300), 291 (98400), 327.5 (12300) nm.

Found: C, 83.72; H, 10.76%. Calcd for $C_{34}H_{48}O_2$: C, 83.55; H, 9.90%.

3,9,12,18-Tetra-t-butyl-1,10-bisdehydro[18]annulene (4a). To a solution of the diastereomeric mixture of **3a** (105 mg, 0.215 mmol) in ether saturated with hydrogen chloride (10 ml) was added at −60 °C under nitrogen atmosphere finely powdered tin(II) chloride dihydrate (400 mg, 1.77 mmol). The mixture was vigorously stirred at the same temperature for 10 min. The reaction mixture was poured onto ice-cooled sodium hydrogencarbonate solution. The mixture was extracted with ether and the ethereal solution was dried (K_2CO_3). Evaporation of the solution furnished dark red crystals, which were chromatographed on alumina (Woelm, act. I) and eluted with hexane–dichloromethane (19:1) to afford pure **4a**, dark reddish violet crystals, 91 mg, 93%. The crystals obtained on rechromatography on alumina were

Table 3. ^{1}H NMR parameters of **4a, b, c** at 36 °C[a)]

	H^a, H^c	H^b	H^d, H^e	*t*-Bu	*o*-H of Ph	*m,p*-H of Ph
4a, 60 MHz $CDCl_3$	0.62, d, 4H J=13 Hz	0.13, t, 2H J=13 Hz	13.42, t, 4H J=13 Hz	8.03, s, 36H		
4b, 60 MHz $CDCl_3$	−0.21—0.62, m, 6H		13.28, m, 4H	7.98, s, 18H	1.33, m, 4H	2.33, m, 6H
4c, 100 MHz-FT, THF-d_8	−0.04, d J=13 Hz	−0.20, t J=13 Hz	12.70, t J=13 Hz		1.24, d	2.07—2.80, m

a) For NMR charts of **4a** and **4c**, see Ref. 2.

washed successively with ether and hexane to give analytical specimen of **2a**, mp 260 °C (dec); mass (*m/e*): 454 (M^+), 397 (M^+-57), 57 (*t*-Bu, base peak); IR(KBr-disk): 3030 w, 2950 s, 2000 vw (–C≡C–↔–C=C=), 1041 m, 987 vs, 878 w cm^{-1}.

Found: C, 89.72; H, 10.18%. Calcd for $C_{34}H_{46}$: C, 89.80; H, 10.20%.

*CT Complex of **4a** with 2,4,7-Trinitrofluorenone.* A solution of **4a** (31.5 mg, 0.0694 mmol) in benzene–methanol (1:1, 40 ml) was mixed with a solution of the trinitrofluorenone (43.5 mg, 0.138 mmol) in benzene–methanol (2 : 1, 9 ml) at 40—50 °C. The solution was kept at 0 °C to deposite the CT complex, deep violet needles, mp *ca.* 260 °C, 41 mg, 77%.

Found: C, 73.37; H, 6.63; N, 5.43%. Calcd for $C_{34}H_{46}\cdot C_{13}H_5N_3O_7$: C, 73.32; H, 6.68; N, 5.46%.

The CT complex was found to be more stable and less soluble in organic solvents than **4a**. The electronic spectrum of the complex showed no CT band being a superposition of the spectra of components.

*Catalytic Hydrogenation of **4a**.* A solution of **4a** (42 mg, 0.0924 mmol) in ethyl acetate (25 ml) was added to platinum catalyst (from 150 mg of platinum(IV) oxide) in acetic acid (25 ml). The mixture was vigorously stirred at room temperature under hydrogen atmosphere for 2.5 h and the catalyst was removed by filtration and washed with ether (50 ml). The combined organic layer was washed successively with water, sodium hydrogencarbonate solution and brine, and dried ($MgSO_4$). Evaporation of the solvent gave a crystalline solid, which was chromatographed on alumina (Woelm, act. I) and eluted with hexane to yield 1,4,10,13-tetra-*t*-butyl-cyclooctadecane, 40 mg, 91%. An analytical specimen was prepared by recrystallization from ethyl acetate–methanol, colorless crystals, mp 151—154 °C; mass (*m/e*): 476 (M^+), 419 (M^+-57), 57 (*t*-Bu, base peak); IR(CCl_4): 2940 s, 2860 m, 1475 m, 1393 m, 1365 m cm^{-1}; NMR(CCl_4): 8.63 (32H, br s, $-CH_2-$, –CH=), 9.11 (36H, s, *t*-Bu).

Found: C, 85.62; H, 14.13%. Calcd for $C_{34}H_{68}$: C, 85.63; H, 14.37%.

*6-t-Butyl-1,3,5-octatrien-7-ynyl Phenyl Ketone (**2b**).* To a solution of sodium hydroxide (0.88 g, 0.022 mol) in aqueous ethanol (1:1, 6 ml) was added at 0 °C a solution of **1a** (3.56 g, 0.0219 mol) and acetophenone (2.64 g, 0.0220 mol) in ethanol (30 ml) under nitrogen atmosphere. The mixture was kept at the same temperature for 3 h and then acidified with 1 M sulfuric acid (20 ml). The mixture was extracted with ether (50 ml×3). The combined extract was washed successively with water, saturated sodium hydrogencarbonate solution and brine, and dried ($MgSO_4$). The residue obtained on evaporating the solvent was chromatographed on silica gel and eluted successively with hexane, benzene and ether–benzene to give **2b**, 4.41 g, 76%. Recrystallization of the material from petroleum ether (bp 40—60 °C) afforded an analytical specimen of **2b**, yellow crystals, mp 59.5—60.0 °C; mass (*m/e*): 264 (M^+); IR($CHCl_3$): 3320 m (C≡CH), 2060 vw (–C≡C–), 1658 s (C=O), 1590 s, 1550 s (C=C), 1016 s, 1002 s (*trans* –CH=CH–) cm^{-1}; NMR($CDCl_3$): 1.98—3.72 (10H, m, olefinic and aromatic), 6.50 (1H, s, C≡CH), 8.81 (9H, s, *t*-Bu); UV: $\lambda_{max}^{99\%\,EtOH}$ (ε) 225* (8710), 267.5 (10300), 359 (39100) nm.

Found: C, 86.27; H, 7.56%. Calcd for $C_{38}H_{38}$: C, 86.32; H, 7.63%.

*3,12-Di-t-butyl-9,18-diphenyl-1,10-bisdehydro[18]annulene (**4b**).* A solution of **2b** (350 mg, 1.32 mmol) in THF (50 ml) was added over 8 h-period to a stirred suspension of powdered potassium hydroxide (1.00 g, 17.8 mmol) in liquid ammonia (200 ml) at −34 °C. After being stirred for further 2 h at the same temperature, ammonium chloride (2.00 g, 37.4 mmol) was added and the ammonia was allowed to evaporate. The residue was mixed water and ether (20 ml). The aqueous layer was extracted with ether (15 ml×2). The combined organic layer was washed successively with water and brine, and dried ($MgSO_4$). Evaporation of the solvent yielded crude **3b**, light brown solid, *ca.* 350 mg. As the formation of **3b** was confirmed by spectroscopy and TLC analysis and the purification of **3b** was found to be difficult, the crude **3b** was used in the following reaction.

To a solution of the crude **3b** (*ca.* 350 mg) in ether (10 ml) was added at −60 °C ether saturated with hydrogen chloride (10 ml) and finely powdered tin(II) chloride dihydrate (1.00 g, 4.43 mmol). The mixture was vigorously stirred for 10 min at the same temperature and then poured onto an ice-cooled solution of sodium hydrogencarbonate. Ether was added to the mixture and the organic layer was separated, and dried (K_2CO_3). Evaporation of the solvent yielded violet crystals, which were chromatographed on alumina (Woelm, act. I) and eluted with hexane–benzene (4:1—1:1) to give pure **4b**, deep violet crystals, 108 mg, 33% based on **2b**. An analytical specimen was obtained on recrystallizing the crystals from benzene–methanol, mp 235 °C (dec); mass (*m/e*): 494 (M^+), 57 (*t*-Bu, base peak); IR(KBr-disk): 3025 w, 2950 m, 2010 vw (–C≡C–↔–C=C=), 1595 m (C=C), 983 s (*trans* –CH=CH–), 766 s (phenyl) cm^{-1}.

Found: C, 92.16; H, 7.67%. Calcd for $C_{38}H_{38}$: C, 92.26; H, 7.74%.

*CT Complex of **4b** with 2,4,7-Trinitrofluorenone.* A solution of **4b** (45.3 mg, 0.0916 mmol) in benzene–methanol (1:1, 40 ml) kept at 40 °C was mixed with a solution of the trinitro compound (57.7 mg, 0.183 mmol) in the same solvent (20 ml). The mixture was allowed to stand at 0 °C to deposite the CT complex, deep violet needles, mp *ca.* 250 °C (dec), 46.6 mg, 62.8%.

Found: C, 75.06; H, 5.23; N, 5.49%. Calcd for $C_{38}H_{38}\cdot C_{13}H_5N_3O_7$: C, 75.63; H, 5.35; N, 5.19%.

*3,9,12,18-Tetraphenyl-1,10-bisdehydro[18]annulene (**4c**).* A solution of **2c** (0.150 g, 0.77 mmol) in THF (40 ml) was added over 3 h-period at −34 °C to a stirred suspension of potassium hydroxide (3.00 g, 5.36 mmol) in liquid ammonia (200 ml). After the mixture had been stirred overnight at the same temperature, ammonium chloride (6.0 g, 0.113 mol)

was added. The residue obtained after being allowed the ammonia to evaporate was extracted with benzene (200 ml). The extract was washed with water, and dried ($MgSO_4$). Light solid (0.148 g) obtained on evaporating the solvent was dissolved in a small amount of benzene. Hexane was added to the benzene solution to precipitate **3c**, crystalline solid, 76 mg, 53%, which was found to be difficult to purify. A solution of tin(II) chloride dihydrate (0.30 g) in concentrated hydrochloric acid (5.0 ml) was added at −15 °C to a solution of the crude cyclic glycol (**3c**, 76 mg, 0.13 mmol) in dichloromethane (200 ml). After being stirred for 10 min at the same temperature, a solution of sodium carbonate was added to the mixture. The organic layer was washed with water, and dried ($MgSO_4$). The solution was passed through a short column of alumina (10 g). The residue obtained on concentrating the filtrate was triturated with benzene–hexane and the crystals deposited were washed with the same solvent to give **4c**, dark violet needles, mp 250 °C (dec), 41 mg, 59%. The tetraphenyl derivative (**4c**) was found to be sparingly soluble and stable compound. The crystals were recrystallized from THF and repeatedly chromatographed on alumina (Woelm, act. I) to give an analytical sample, mass (*m/e*): 534 (M^+); IR (KBr-disk): 2040 (–C≡C–↔–C=C=), 1595 (C=C), 980 (*trans* –CH=CH–), 761 (phenyl) cm^{-1}.

Found: C, 94.37; H, 5.61%. Calcd for $C_{42}H_{30}$: C, 94.34; H, 5.66%.

Catalytic Hydrogenation of ***4c***. Platinic oxide (100 mg) was added to a solution of **4c** (30 mg) in THF–ethyl acetate (1:1, 30 ml), and the mixture was vigorously stirred under hydrogen atmosphere for 3 h. The catalyst was removed by filtration and washed with benzene. The residue obtained on evaporation of the filtrate and washing was dissolved in hexane (5 ml) and passed through a thin layer of silica gel (0.2 g). Evaporation of the filtrate afforded colorless crystals, 27 mg, 90%, which were recrystallized twice from hexane–pentane to give 1,4,10,13-tetraphenylcyclooctadecane, mp 146—152 °C; mass (*m/e*): 556 (M^+); NMR(CD_2Cl_2): 2.83 (20H, s, aromatic), 7.35 (4H, m, –CH=), 8—9 (28H, m, $-CH_2-$).

Found: C, 90.80; H, 9.49%. Calcd for $C_{42}H_{52}$: C, 90.59; H, 9.41%.

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