Dehydroannulenes. XI. Synthesis and Properties of 3,11,14,22-Tetra-*t*-butyl-1,12-bisdehydro[22]annulene

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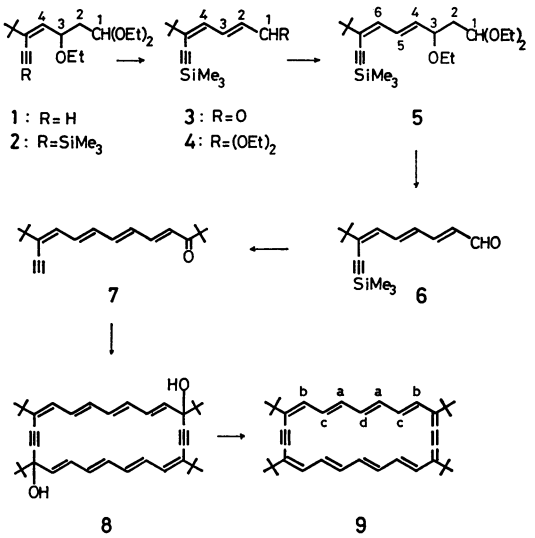
7-*t*-Butyl-9-trimethylsilyl-2,4,6-nonatrien-8-ynal prepared from 5-*t*-butyl-7-trimethylsilyl-2,4-heptadien-6-ynal diethyl acetal was converted into 8-*t*-butyl-1,3,5,7-decatetraen-7-ynyl *t*-butyl ketone. Treatment of the tetraenyne ketone with potassium hydroxide in liquid ammonia gave 22-membered cyclic glycol in a high yield. Reductive dehydroxylation of the cyclic glycol by tin(II) chloride and hydrogen chloride yielded tetra-*t*-butylbisdehydro[22]annulene in good yield. The [22]annulene was found to be strongly diatropic and conformationally stable.

The stable nature, strong diatropicity and high conformational stability observed in 3,9,12,18-tetrasubstituted 1,10-bisdehydro[18]annulenes[1] provide a stimulus to further efforts to synthesize higher analogues of this series of bisdehydro[4n+2]annulenes.

In this paper we wish to report the synthesis and properties of 3,11,14,22-tetra-*t*-butyl-1,12-bisdehydro-[22]annulene (**9**).

Synthesis. The synthesis of the bisdehydro[22]-annulene (**9**) has been achieved by the reaction sequence shown in Scheme. Because the diethyl acetal of 5-*t*-butyl-2,4-heptadien-6-ynal[2] was found to be rather unstable, 5-*t*-butyl-3-ethoxy-4-hepten-6-ynal diethyl acetal (**1**)[1] was converted into the trimethylsilyl derivative (**2**) in 92% yield on successive treatment with ethylmagnesium bromide and trimethylchlorosilane. Treatment of **2** with an aqueous acetic acid containing sodium acetate afforded trimethylsilyl derivative of 5-*t*-butyl-2,4-heptadien-6-ynal (**3**) in a yield of 89%, which was converted into the diethyl acetal (**4**) in the usual method. The reaction of ethyl vinyl ether with **4** in benzene in the presence of boron trifluoride etherate[2,3] gave ethoxy acetal (**5**) in 86% yield. Trimethylsilyltrienyne aldehyde (**6**) was obtained on treatment of **5** with an aqueous acetic acid containing sodium acetate. The trienyne aldehyde (**6**) was found to be fairly stable and could be isolated on rapid distillation *in vacuo* in a yield of 87%.



Scheme.

The aldol condensation of pinacolone with the trienyne aldehyde (**6**) under alkaline conditions resulted in tetraenyne ketone (**7**) in 60% yield accompanying the cleavage of trimethylsilyl group.

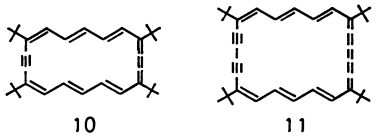
A diluted solution of the tetraenyne ketone (**7**) in tetrahydrofuran was added slowly to a stirred suspension of finely powdered potassium hydroxide in liquid ammonia. The 22-membered cyclic glycol (**8**) was obtained as a mixture of diastereomers which could be separated into the high melting isomer (**8a**, 31%) and the low melting isomer (**8b**, 58%) upon chromatography on alumina. The diastereomers (**8a**, and **8b**) gave identical electronic and NMR spectra, but slight difference was observed between their IR spectra measured by KBr-disk method.

Finely powdered tin(II) chloride dihydrate was added at −60 °C to a stirred suspension of the diastereomeric mixture of cyclic glycol (**8**) in ether containing hydrogen chloride under nitrogen atmosphere. The reaction mixture was worked up in the usual way and purified by chromatography on alumina to give 3,11,14,22-tetra-*t*-butyl-1,12-bisdehydro[22]annulene (**9**) in a yield of 94%.

Full hydrogenation of **9** in ethyl acetate and acetic acid over platinum catalyst at −15——20 °C afforded crystalline tetra-*t*-butylcyclodocosane as a mixture of stereoisomers. Recrystallization of the mixture resulted in a crude separation of stereoisomers. The bisdehydro[22]annulene (**9**) gave 1 : 1 CT complex with 2,4,7-trinitrofluorenone.

Properties. The tetra-*t*-butylbisdehydro[22]annulene (**9**) was found to be rather stable compound and could be kept without decomposition in a dark place at room temperature for a long period.

The electronic spectrum of **9** showed representative aromatic characteristic exhibiting three distinct main absorption bands. As illustrated in Fig. 1, the spectrum of **9** shows close similarity with those of 3,9,12,18-tetra-*t*-butyl-1,10-bisdehydro[18]annulene (**10**)[1] and 1,6,12,17-tetra-*t*-butyl-2,4,13,15-tetrakisdehydro[22]annulene (**11**).[2]



The ^{1}H NMR spectrum and the parameters are shown in Fig. 2 and Table, respectively. The minor

Table. ^{1}H NMR parameters of **9** in $CDCl_3$

	Temp/°C	H^a	H^b	*t*-Bu	H^c	H^d
60 MHz	30	0.79, t J=13 Hz	1.24, d J=13 Hz	8.18, s	10.82, m	
	70	0.81, t J=13 Hz	1.26, d J=13 Hz	8.21, s	10.68, m	
100 MHz	35	0.84, t J=13 Hz	1.28, d J=13 Hz	8.20, s	10.87, t J=13 Hz	10.83, t J=13 Hz
	0	0.80, t J=13 Hz	1.25, d J=13 Hz	8.19, s	10.99, t J=13 Hz	10.94, t J=13 Hz
	−30	0.74, t J=13 Hz	1.20, d J=13 Hz	8.18, s	11.10, t J=13 Hz	11.04, t J=13 Hz
	−50	0.69, t J=13 Hz	1.17, d J=13 Hz	8.17, s	11.18, t J=13 Hz	11.11, t J=13 Hz

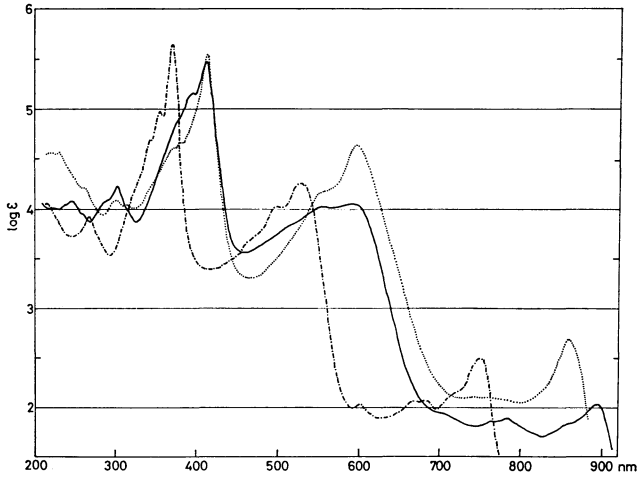


Fig. 1. Electronic spectra of **9** (——), **10** (—·—·) and **11** (·····) in THF.

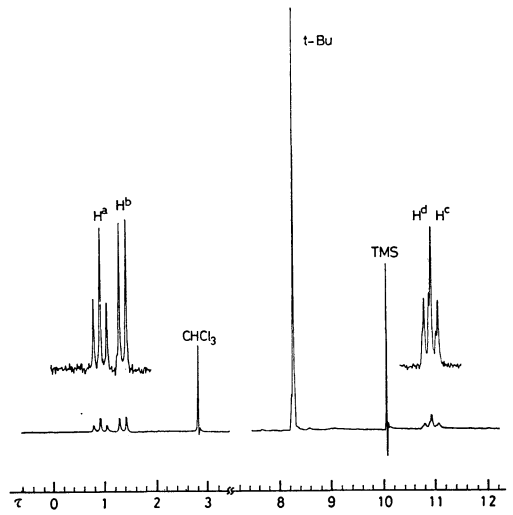


Fig. 2. 100 MHz ^{1}H NMR spectrum of **9** in $CDCl_3$ at 35 °C.

difference between the spectra measured at various temperatures indicates the conformational stability of **9**. An attempted measurement at 80 °C in deuteriobromoform resulted in a rapid decomposition of **9**. The ^{1}H NMR spectrum reveals that the bisdehydro[22]annulene (**9**) is strongly diatropic being stronger than that of monodehydro[22]annulene.[4] It has been reported that the parent [22]annulene[5] gave high-field multiplet at τ 10.4—11.2 (inner protons) and low-field multiplets at τ 0.35—0.7 and 0.9—1.5 (outer protons) at −90 °C being almost the same with the parameters of **9** obtained at 36 °C. However, obvious high-field and low-field shifts of outer and inner proton signals of **9** were observed as compared with those of the lower analogues, *i.e.*, 3,7,10,14-tetra-*t*-butyl-1,8-bisdehydro[14]annulene[6] and 3,9,12,18-tetra-*t*-butyl-1,10-bisdehydro[18]annulene (**10**).[1] The X-ray structure analysis of **9** revealed that the polyene parts in **9** have slight bond-alternation, and also one of the sp-sp linkages in **9** has more acetylenic and the other has more cumulenic character in contrast to the highly symmetrical structure of tetra-*t*-butylbisdehydro[18]annulene (**10**).[8] It has been predicted theoretically that the resonance energies per π-electron of [4n+2]annulenes should decrease and the bond-alternation should increase along with the increase of ring size.[9] Also the decrease of ring current in larger ring has been concluded theoretically.[9b,d,10] Consequently, the results obtained on bisdehydro[18]- and [22]annulenes (**10** and **9**) provide experimental supports to justify the theoretical prediction.

Experimental

All melting points were determined on a Mettler FP-2 apparatus and uncorrected. IR spectra were measured on a Hitachi EPI-2 or EPI-G3 spectrophotometer and only significant maxima are recorded. The intensities are denoted by the following abbreviation: strong=s, medium=m and weak=w. Electronic spectra were obtained on a Hitachi EPS-3T spectrophotometer and the shoulder was indicated by an asterisk. The NMR spectra were measured on a Varian A-60 or a XL-100 spectrometer using TMS as an internal standard and recorded in τ-unit. The mass spectra were obtained on a Hitachi RM-50 spectrometer operated at 70 eV of ionization potential. The TLC was performed on Kiesel Gel GF_{254} (Merck) plates. Silica gel (Merck, Kiesel Gel 60) or alumina (Merck, act. II-III) were used in the column chromatography, unless otherwise stated. Evaporation of the solvent was performed under reduced pressure.

5-t-Butyl-2,4-heptadien-6-ynal Diethyl Acetal. A solution of *p*-toluenesulfonic acid monohydrate (300 mg, 1.58 mmol) in ethanol (1 ml) was added to a solution of 5-*t*-butyl-2,4-heptadien-6-ynal[2] (2.88 g, 0.0178 mol) in triethyl ortho-

formate (7.70 g, 0.0520 mol). After being stirred overnight, the reaction mixture was worked up in the usual way. The residue obtained on evaporation of the solvent was distilled through a short column to furnish the diethyl acetal, a yellow liquid, bp 105 °C/267 Pa, 2.60 g, 62%; NMR(CCl_4): 3.27 (1H, dd, J=10.0, 15.5 Hz, H^{β}), 3.79 (1H, d, J=10 Hz, H^{γ}), 4.47 (1H, dd, J=5.0, 15.5 Hz, H^{α}), 5.09 (1H, d, J=5.0 Hz, acetal-H), 6.46 (4H, q, J=7.0 Hz, $-CH_2-$), 6.52 (6H, q, J=7.0 Hz, CH_3), 8.85 (9H, s, *t*-Bu).

*5-t-Butyl-3-ethoxy-7-trimethylsilyl-4-hepten-6-ynal Diethyl Acetal (**2**).* To a stirred solution of ethylmagnesium bromide (prepared from magnesium, 1.91 g, 0.0786 mol, ethyl bromide, 10.30 g, 0.0945 mol and THF, 30 ml) was added dropwise at 10—20 °C under nitrogen atmosphere a solution of the ethoxy acetal[2] (**1**, 14.80 g, 0.0524 mol) in the same solvent (30 ml) under ice-cooling. The mixture was stirred at 20 °C for further 30 min and then chilled on an ice-bath. Trimethylchlorosilane (10.26 g, 0.0945 mol) was added to the mixture at 0 °C. After being stirred for 1 h at the same temperature, ammonium chloride solution was added to the reaction mixture. The aqueous layer was extracted with ether (50 ml×3) and the extracts were combined with the organic layer. The combined organic layer was washed successively with water and brine, and dried ($MgSO_4$). The residue obtained on evaporation of the solvent was distilled *in vacuo* to give **2**, pale yellow liquid, bp 122—130 °C/333 Pa, 17.02 g, 91.6%; mass (*m/e*): 354 (M^+); IR(neat): 2125 m (–C≡C–), 1616 vw (C=C), 1250 s ($Si-CH_3$), 875 s, 842 vs, 758 m (Si–C) cm^{-1}; NMR(CCl_4): 4.45 (1H, d, J=8.5 Hz, H^4), 5.43 (1H, t, J=6.0 Hz, H^2), 5.67 (1H, m, H^3), 6.56 (6H, m, $O-CH_2-$), 8.32 (2H, t, J=6.0 Hz, H^2), 8.84 (9H, t, J=7.0 Hz, $-CH_3$), 8.88 (9H, s, *t*-Bu), 9.80 (9H, s, $-SiMe_3$).

Found: C, 67.48; H, 10.58%. Calcd for $C_{20}H_{38}O_3Si$: C, 67.75; H, 10.80%.

*5-t-Butyl-7-trimethylsilyl-2,4-heptadien-6-ynal (**3**).* A mixture of **2** (6.74 g, 0.0190 mol), sodium acetate (6.50 g, 0.0792 mol), acetic acid (56 ml) and water (4 ml) was stirred at 80 °C for 6 h under nitrogen atmosphere, and then allowed to stand overnight at room temperature. The reaction mixture was poured onto saturated sodium carbonate solution and extracted with ether (50 ml×2). The extracts were washed successively with saturated sodium carbonate and sodium chloride solutions, and dried ($MgSO_4$). The product obtained on evaporation of the solvent was distilled using a short-path appratus to give **3**, a yellow liquid, bp 105—108 °C/333 Pa, 3.98 g, 89.3%; mass (*m/e*): 234 (M^+); IR(neat): 2810 w (CHO), 2120 m, (–C≡C–), 1687 vs (CHO), 1613 vs (C=C), 1244 s, 1221 m ($Si-CH_3$), 878 vs, 843 vs, 759 s (Si–C) cm^{-1}; NMR(CCl_4): 0.42 (1H, d, J=8.0 Hz, H^1), 2.49 (1H, dd, J=11.5, 15.5 Hz, H^3), 3.50 (1H, d, J=11.5 Hz, H^4), 3.88 (1H, dd, J=8.0 Hz, 11.5 Hz, H^2), 8.78 (9H, s, *t*-Bu), 9.70 (9H, s, $Si-Me_3$).

The trimethylsilyl aldehyde (**3**) was more stable than 5-*t*-butyl-2,4-heptadien-6-ynal, but gradually decomposed on standing in air under diffused light at room temperature. Less satisfactory elemental analysis was obtained owing to the unstable nature.

*2,4-Dinitrophenylhydrazone of **3**.* A solution of 2,4-dinitrophenylhydrazine (95 mg, 0.48 mmol) in phosphoric acid (1 ml) and ethanol (1 ml) was added to a solution of **3** (56 mg, 0.24 mmol) in ethanol (15 ml). After the mixture had been allowed to stand at room temperature for 30 min, red precipitate deposited was collected by filtration and washed with ethanol to give the hydrazone, 62 mg, 63%, which was recrystallized from ethyl acetate to give red crystals, mp 201—202 °C (dec).

Found: C, 57.81; H, 6.39; N, 13.27%. Calcd for $C_{20}H_{26}N_2O_4Si$: C, 57.95; H, 6.32; N, 13.52%.

*5-t-Butyl-7-trimethylsilyl-2,4-heptadien-6-ynal Diethyl Acetal (**4**).* To a mixture of **3** (3.98 g, 0.017 mol) and triethyl orthoformate (30 ml) was added a solution of *p*-toluenesulfonic acid monohydrate (400 mg, 2.10 mmol) in ethanol (4 ml). After being stirred for 20 h at room temperature, the reaction mixture chilled in an ice-bath was poured onto an ice-cooled sodium carbonate solution, and extracted with ether (30 ml×3). The extracts were washed successively with saturated sodium carbonate and sodium chloride solutions, and dried (K_2CO_3). The residue obtained on evaporation of the solvent was distilled under reduced pressure to yield **4**, a pale yellow liquid, bp 118—120 °C/333 Pa, 4.92 g, 94%; mass (*m/e*): 308 (M^+), 263 (M^+-45); IR (neat): 2125 m (–C≡C–), 1644 vw (C=C), 1248 s, 1227 w ($Si-CH_3$), 881 vs, 842 vs, 760 m (Si–C) cm^{-1}; NMR(CCl_4): 3.20 (1H, dd, J=11.0, 15.5 Hz, H^3), 3.77 (1H, d, J=11.0 Hz, H^4), 4.37 (1H, dd, J=5.0, 15.5 Hz, H^2), 5.07 (1H, d, J=5.0 Hz, H^1), 6.49 (4H, m, $-CH_2-$), 8.83 (6H, t, J=7.0 Hz, $-CH_3$), 8.85 (9H, s, *t*-Bu), 9.76 (9H, s, $Si-Me_3$).

Found: C, 70.50; H, 10.30%. Calcd for $C_{18}H_{32}O_2Si$: C, 70.08; H, 10.46%.

*7-t-Butyl-3-ethoxy-9-trimethylsilyl-4,6-nonadien-8-ynal Diethyl Acetal (**5**).* A mixture of borontrifluoride etherate (20 mg) in benzene (1 ml) was added at 35 °C to a solution of **4** (4.92 g, 0.0159 mol) in the same solvent (20 ml), and a solution of ethyl vinyl ether (1.40 g, 0.0194 mol) in the same solvent (5 ml) was slowly added at the same temperature. After the mixture had been kept at the same temperature for 20 min, finely powdered potassium carbonate (1.0 g) was added. The inorganic material was removed by filtration and washed with ether. The residue obtained on evaporation of the filtrate and washings was distilled *in vacuo* to give **5**, a pale yellow liquid, bp 120—124 °C/1.2 Pa, 5.20 g, 86%; mass (*m/e*): 380 (M^+), 334 (M^+-46); IR(neat): 2120 m (–C≡C–), 1640 vw (C=C), 1248 s ($Si-CH_3$), 880 vs, 842 vs, 758 m (Si–C) cm^{-1}; NMR(CCl_4): 3.39 (1H, dd, J=10.5, 14.5 Hz, H^5), 3.81 (1H, d, J=10.5 Hz, H^6), 4.42 (1H, dd, J=7.0, 14.5 Hz, H^4), 5.44 (1H, t, J=5.5 Hz, H^1), 6.04—6.88 (7H, m, $O-CH_2-$, O–CH–), 8.29 (2H, m, H^2), 8.85 (18H, t, J=7.0 Hz, $-CH_3$), 8.86 (9H, s, *t*-Bu), 9.78 (9H, s, $Si-Me_3$).

Found: C, 69.14; H, 10.38%. Calcd for $C_{22}H_{40}O_3Si$: C, 69.42; H, 10.59%.

*7-t-Butyl-9-trimethylsilyl-2,4,6-nonatrien-8-ynal (**5**).* A mixture of **5** (2.00 g, 5.26 mmol), sodium acetate (2.00 g, 24.4 mmol), acetic acid (18 ml) and water (2 ml) was stirred for 6 h at 60 °C, and then allowed to cool to room temperature. The reaction mixture was poured onto saturated sodium carbonate solution and extracted with ether (20 ml×3). The extracts were washed successively with saturated sodium carbonate and sodium chloride solutions, and dried ($MgSO_4$). The residue obtained on concentration of the extracts was distilled *in vacuo* using a short-path apparatus to give **6**, a viscous yellow liquid, bp 111—114 °C/2.7 Pa, 1.19 g, 86.9%; mass (*m/e*): 260 (M^+); IR(neat): 2810 w, 2725 w (CHO), 2120 m (–C≡C–), 1683 vs (C=O), 1612 s, 1597 s (C=C), 1247 s ($Si-CH_3$), 1007 m, 987 m (*trans* –CH=CH–), 880 vs, 843 vs, 759 m (Si–C) cm^{-1}; NMR (CCl_4): 0.43 (1H, d, J=4.0 Hz, CHO), 2.56—4.13 (5H, m, olefinic), 8.81 (9H, s, *t*-Bu), 9.72 (9H, s, $Si-Me_3$).

*2,4-Dinitrophenylhydrazone of **6**.* To a solution of **6** (134 mg, 0.515 mmol) in ethanol (8 ml) was added a solution of 2,4-dinitrophenylhydrazine (119 mg, 0.601 mmol) in phosphoric acid (1 ml) and ethanol (1 ml). After the mixture was allowed to stand for 30 min at room temperature, reddish

brown precipitate formed was filtered and washed with ethanol to give the hydrazone, 164 mg, 72.3%, which was dissolved in benzene and passed through a short column of silica gel. The crystals obtained from the filtrate were recrystallized from hexane–benzene (1:1) to yield pure 2,4-dinitrophenylhydrazone of **6**, reddish brown crystals, mp 208—211 °C.

Found: C, 60.09; H, 6.38; N, 12.69%. Calcd for $C_{22}H_{28}N_4O_4Si$: C, 59.98; H, 6.41; N, 12.72%.

8-t-Butyl-1,3,5,7-decatetraen-9-ynyl t-Butyl Ketone (8). A solution of sodium hydroxide (209 mg, 5.22 mmol) in 50% aqueous ethanol (2 ml) was added to a solution of **6** (1.00 g, 3.84 mmol) and pinacolone (522 mg, 5.21 mmol) in ethanol (10 ml) at 0 °C under nitrogen atmosphere. After being kept at room temperature for 24 h, the mixture was acidified with 3 M hydrochloric acid (10 ml) and extracted with ether (20 ml×3). The extracts were washed successively with sodium hydrogencarbonate solution and brine, and dried ($MgSO_4$). The residue obtained on concentration of the extracts was chromatographed on alumina. Elution with hexane–benzene (9:1) afforded crystals, which were washed with methanol to give **7**, 618 mg, 59.5%. Recrystallization of the crystals from methanol gave analytical specimen of **7**, yellow crystals, mp 133.5—134.0 °C; mass (*m/e*): 270 (M^+); IR (CCl_4): 3325 m (–C≡CH), 2060 vw (–C≡C–), 1684 s (C=O), 1607 s (C=C), 1574 vs (C=C), 1070 vs, 1003 vs (*trans* –CH=CH–) cm^{-1}; NMR(CCl_4): 2.52—3.92 (7H, m, olefinic), 6.63 (1H, s, –C≡CH), 8.82 (9H, s, *t*-Bu), 8.86 (9H, s, *t*-Bu); UV: $\lambda_{max}^{99\%EtOH}$ (ε) 261 (5870), 359* (52000), 369 (53000) nm.

Found: C, 84.74; H, 9.75%. Calcd for $C_{19}H_{26}O$: C, 84.39; H, 9.69%.

1,4,12,15-Tetra-t-butyl-4,6,8,10,15,17,19,21-cyclodocosaoctaene-2,13-diyne-1,12-diol (8). A solution of the tetraenyne ketone (**7**, 160 mg, 0.592 mmol) in THF (60 ml) was added very slowly through a Hershberg dropping funnel over a period of 8 hr to a stirred suspension of finely powdered potassium hydroxide (2.00 g, 35.7 mmol) in liquid ammonia (150 ml) at −34 °C. After being stirred for further 6 h at the same temperature, ammonium chloride (4.00 g, 0.0748 mol) was added to the reaction mixture, and the ammonia was allowed to evaporate. The residue was treated with 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 ($MgSO_4$). The yellow crystals obtained on evaporation of the solvent were chromatographed on alumina (40 g). Elution with ether–benzene (1:49—1:19) afforded high melting isomer (**8a**), colorless crystals, 56 mg, 31%, which were washed thoroughly with ethyl acetate to give pure specimen, mp 252 °C (dec); mass (*m/e*): 540 (M^+), 483 (M^+—57), 57 (*t*-Bu^+, base peak); IR(KBr-disk): 3570 m (–OH), 2190 vw (–C≡C–), 1638 vw, 1607 w (C=C), 1001 vs, 977 vs, 960 s (*trans* –CH=CH–) cm^{-1}; NMR($CDCl_3$): 2.8—4.2 (14H, m, olefinic), 8.35 (2H, s, –OH, disappeared on addition of D_2O), 8.79 (18H, s, *t*-Bu), 8.90 (18H, s, *t*-Bu); UV: $\lambda_{max}^{99\%EtOH}$ (ε) 248.5 (22600), 292* (50600), 307 (120000), 320 (137000), 341* (34800), 359 (27800) nm.

Found: C, 84.15; H, 9.61%. Calcd for $C_{38}O_{52}O_2$: C, 84.39; H, 9.69%.

Further elution with ether–benzene (1:3) gave low melting isomer (**8b**), colorless crystals, 105 mg, 58%, which were washed with ethyl acetate to give pure material, mp 220—221 °C; mass (*m/e*): 540 (M^+), 483 (M^+—57, base peak), 57 (*t*-Bu^+); IR(KBr-disk): 3530 m, 3465 m (–OH), 2180 vw (–C≡C–), 1634 w, 1590 vw (C=O), 993 vs (*trans* –CH=CH–) cm^{-1}; NMR($CDCl_3$): 2.8—4.2 (14H, m, olefinic), 8.31 (2H, s, –OH, disappeared on addition of D_2O), 8.80 (18H, s, *t*-Bu), 8.90 (18H, s, *t*-Bu); UV: $\lambda_{max}^{99\%EtOH}$ (ε) 248.5 (22200), 292* (45400), 307 (109000), 320 (160000), 341* (34200), 359 (26100) nm.

Found: C, 84.56; H, 9.84%. Calcd for $C_{38}H_{52}O_2$: C, 84.39; H, 9.69%.

3,11,14,22-Tetra-t-butyl-1,12-bisdehydro[22]annulene (9). To a suspension of **8** (a mixture of diastereomers, 136 mg, 0.251 mmol) in ether (10 ml) was added ether saturated with hydrogen chloride (10 ml) at −60 °C under nitrogen atmosphere. Finely powdered tin(II) chloride dihydrate (600 mg, 2.66 mmol) was added to the mixture at the same temperature. After being stirred vigorously for 15 min at −60 °C, the reaction mixture was poured onto ice-cooled sodium carbonate solution, and extracted with dichloromethane. The extract, after being washed with brine, and dried (K_2CO_3), was chromatographed on alumina (Woelm, act. I). Elution with carbon tetrachloride–dichloromethane (19:1) afforded pure **9**, 120 mg, 94.2%. An analytical specimen was prepared on recrystallization from benzene–methanol, dark violet crystals, mp *ca.* 230 °C (dec); mass (*m/e*): 506 (M^+), 449 (M^+—57), 57 (*t*-Bu^+, base peak); IR(KBr-disk): 3020 w, 2950 s, 992 vs, 881 w; UV: λ_{max}^{THF} (ε) 221.5 (10400), 248 (11900), 261* (8810), 277* (9200), 290 (12100), 302.5 (17100), 316.5* (9610), 377* (7720), 395 (147000), 412.5 (300000), 512* (6640), 556 (10400), 591 (11300), 712* (83), 757* (72), 782 (77), 853* (66), 895 (106) nm.

Found: C, 90.38; H, 9.92%. Calcd for $C_{38}H_{50}$: C, 90.05; H, 9.95%.

CT Complex of 9 with 2,4,7-Trinitrofluorenone. To a solution of **9** (25 mg, 0.049 mmol) in benzene–methanol (1:1, 40 ml) was added a solution of 2,4,7-trinitrofluorenone (31 mg, 0.098 mmol) in the same solvent (10 ml). The mixture was allowed to stand at 18 °C to deposite the CT complex, black violet crystals, mp *ca.* 260 °C (dec), 32 mg, 79%.

Found: C, 74.39; H, 6.67; N, 5.14%. Calcd for $C_{38}H_{50}\cdot C_{13}H_5N_3O_7$: C, 74.52; H, 6.74; N, 5.11%.

Catalytic Hydrogenation of 9. A mixture of **9** (32 mg, 0.063 mmol) and platinum(IV) oxide (100 mg) in acetic acid–ethyl acetate (1:1, 40 ml) was vigorously stirred under hydrogen at −15——20 °C overnight. The catalyst was removed by filtration and washed with ether (30 ml). The organic layer and washing were washed successively with water, saturated sodium carbonate and sodium chloride solutions, and dried ($MgSO_4$). Evaporation of the solvent gave a crystalline residue, which was chromatographed on alumina (Woelm, act. I) and eluted with hexane to give a mixture of stereoisomers of 1,4,12,15-tetra-*t*-butylcyclodocosane, 31 mg, 92%. Recrystallization of the crystals from ethyl acetate–methanol yielded colorless crystals, 15 mg, mp 104—112 °C; mass (*m/e*): 532 (M^+), 475 (M^+—57), 57 (*t*-Bu^+, base peak); IR(KBr-disk): 2930 vs, 2860 s, 1475 m, 1393 m, 1360 m cm^{-1}; NMR(CCl_4): 8.72 (40H, br s, $-CH_2-$, –CH–), 9.05 (36H, s, *t*-Bu).

Found: C, 85.35; H, 14.19%. Calcd for $C_{38}H_{76}$: C, 85.63; H, 14.37%.

The mother liquor of the recrystallization was concentrated, and the crystals deposited were recrystallized from ethyl acetate–methanol to give colorless crystals, 8 mg, mp 91—95 °C.

References

1) M. Iyoda and M. Nakagawa, *Tetrahedron Lett.*, **1972**, 3161; M. Iyoda, S. Akiyama, and M. Nakagawa, the preceding paper.

2) M. Iyoda, H. Miyazaki, and M. Nakagawa, *J. Chem.*

Soc., Chem. Commun., **1972**, 1003; M. Iyoda, H. Miyazaki, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, **49**, 2306 (1976).

3) M. Müller-Cunradi and K. Pieroth, U. S. Pat., 2165962 (1936); R. Rüegg, M. Montavon, G. Ryser, G. Saucy, U. Schwieter, and O. Isler, *Helv. Chim. Acta*, **42**, 854 (1959) and the preceding papers.

4) R. M. McQuilkin and F. Sondheimer, *J. Am. Chem. Soc.*, **92**, 6341 (1970).

5) R. M. McQuilkin, B. W. Metcalf, and F. Sondheimer, *Chem. Commun.*, **1971**, 338.

6) K. Fukui, T. Nomoto, S. Nakatsuji, and M. Nakagawa, *Tetrahedron Lett.*, **3157**; K. Fukui, T. Nomoto, S. Nakatsuji, S. Akiyama, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, **50**, 2758 (1977).

7) C. Kabuto, Y. Kitahara, M. Iyoda, and M. Nakagawa, *Tetrahedron Lett.*, **1976**, 2787.

8) C. Kabuto, Y. Kitahara, M. Iyoda, and M. Nakagawa, *Tetrahedron Lett.*, **1976**, 2791.

9) a) H. C. Longuet-Higgins and L. Salem, *Proc. R. Soc. London, Ser. A*, **251**, 172 (1954); b) H. C. Longuet-Higgins and L. Salem, *ibid.*, **257**, 445 (1960); c) C. A. Coulson and W. T. Dixon, *Tetrahedron*, **17**, 215 (1962); d) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965).

10) F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch.*, **22a**, 103 (1967); T. Nakajima and S. Kohda, *Bull. Chem. Soc. Jpn.*, **39**, 804 (1966); J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, **88**, 4811 (1966); H. P. Feyges, "Topics in Carbocyclic Chemistry," ed by D. Lloyd, Logos Press, London (1969), Vol. 1, p. 269.