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Dehydroannulenes. III. Synthesis and Properties of 1,5,10,14-Tetra-*tert*-butyl-6,8,15,17-tetrakisdehydro[18]annulene

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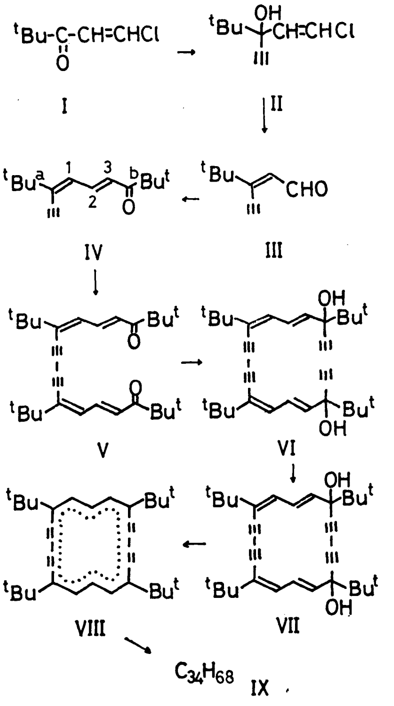
In order to find out substituent groups which provide stability and solubility to tetrakisdehydro[18]annulene system without appreciable electronic interaction with the annulene ring, the synthesis of 1,5,10,14-tetra-*tert*-butyl-6,8,15,17-tetrakisdehydro[18]annulene (VIII) has been catrried out starting from 3-*tert*-butyl-2-penten-4-ynal (III). It was found that the tetra-*tert*-butyl derivative (VIII) is strongly diatropic, and more stable and much more soluble than tetramethyl-, dimethyl-, diphenyl-, and tetraphenyl-analogues. The electronic spectrum of tetra-*tert*-butyl derivative (VIII) was found to be closely related with that of tetramethyltetrakisdehydro[18]annulene indicating a minor electronic perturbation of *tert*-butyl groups on the annulene ring.

As reported in previous papers,[1,2] replacement of methyl groups in 1,5,10,14-tetramethyl-6,8,15,17-tetrakisdehydro[18]annulene with two or four phenyl groups enhances the stability of phenyl substituted annulenes accompanying with marked decrease of their solubility in NMR solvents. Bathochromic shift of electronic spectra of the phenyl substituted annulenes as compared with that of tetramethyl analogue indicates that phenyl group exerts prominent electronic perturbation on the dehydroannulene nucleus. Consequently, it was desired to find out substituent group which provides stability and solubility without appreciable electronic interaction with annulene system. The present paper is concerned with the synthesis and properties of tetra-*tert*-butyltetrakisdehydro[18]annulene (VIII).

tert-Butyl β-chlorovinyl ketone (I), prepared from pinacolone *via* *tert*-butyl β-hydroxyvinyl ketone by the reported method,[3] was ethynylated with lithium acetylide in liquid ammonia. Ethynyl alcohol (II), thus obtained, was converted into 3-*tert*-butyl-2-penten-4-ynal by acid treatment. The aldehyde was found to be pure *cis*-isomer (III) with respect to the formyl and the ethynyl groups on the basis of NMR spectroscopy. The aldol condensation of pinacolone with III yielded dieneyne ketone (IV) as pale yellow crystals. Oxidative coupling of IV by cupric acetate in pyridine[4] gave diketone (V) in a high yield. The reaction of lithium acetylide–ethylenediamine complex[5] in tetrahydrofuran with the diketone (V) gave bis-ethynyl alcohol (VI) in 91.5% yield. Oxidative coupling of VI performed under high dilution conditions by cupric acetate in pyridine–methanol–ether yielded 18-membered cyclic glycol (VII) in an almost quantitative yield. Treatment of a suspension of the cyclic glycol (VII) in benzene with a solution of stannous chloride dihydrate in concentrated hydrochloric acid followed by chromatography on alumina yielded tetra-*tert*-butyltetrakisdehydro[18]annulene (VIII) as deep brown crystals. VIII gave reddish purple solution in organic solvents. Catalytic reduction of VIII in ethyl acetate over platinum catalyst yielded crystalline hydrocarbon (IX) corresponding to tetra-*tert*-butylcyclooctadecane. VIII forms 1:1 CT complex with 2,4,7-trinitrofluorenone, which seems to dissociate into components in a tetrahydrofuran solution, because the electronic spectrum was found to be a superposition of the components, and no CT band could be observed.



As illustrated in Fig. 1, 60 MHz NMR spectrum

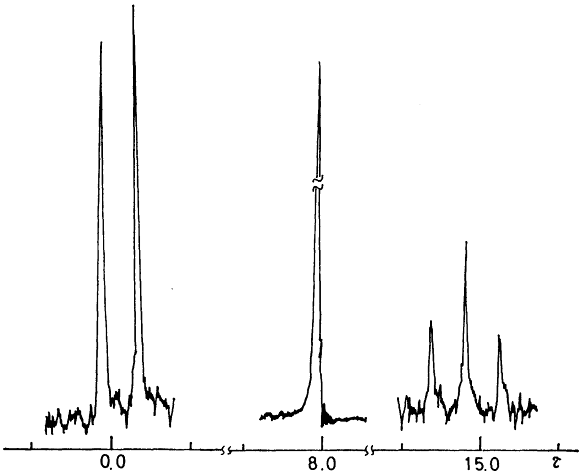


Fig. 1. 60 MHz NMR spectrum of VIII in $CDCl_3$. The signals of inner and outer protons are amplified.

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clearly indicates that the annulene (VIII) is strongly diatropic exhibiting the inner proton signal at a extremely high field (t, $J=13$ Hz, τ 14.89 ($CDCl_3$)) and the outer proton signal at a fairly low field (d, $J=13$ Hz, τ 0.04, ($CDCl_3$)).[6] An appreciable down-field shift of the signal of *tert*-butyl protons (s, τ 7.98 ($CDCl_3$)) can be reasonably ascribed to the deshielding effect of diamagnetic ring current in the 18π-electron system.

Tetra-*tert*-butyltetrakisdehydro[18]annulene (VIII) was found to be more stable and much more soluble than the tetramethyl-,[1] dimethyldiphenyl-[2b,c] and tetraphenyl analogues.[2a,c] The electronic spectrum of VIII shown in Fig. 2 was found to be closely related with that of tetramethyltetrakisdehydro[18]annulene[1] except for a minor bathochromic shift in tetra-*tert*-butyl derivative, thus indicating that the electronic interaction of *tert*-butyl group upon the tetrakisdehydro[18]annulene nucleus is nearly the same as that of methyl group.

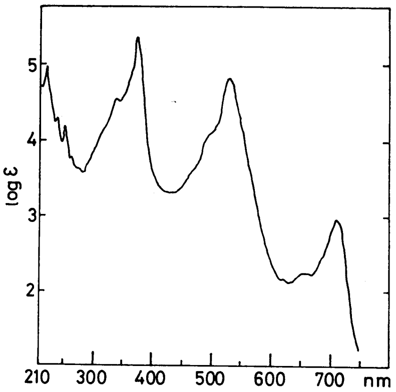

Fig. 2. Electronic spectrum of VIII in THF.

The properties found in tetra-*tert*-butyltetradehydro-[18]annulene (VIII) indicate that the requisite of the substituent, *i.e.*, increase of stability and solubility without enhancement of electronic perturbation, is essentially fulfilled by *tert*-butyl group.

Experimental

All melting and boiling points are not corrected. The IR spectra were measured on a Hitachi EPI-2 or EPI-G3 spectrometer, and the strong, medium and weak bands were indicated by S, M, and W, respectively. The UV spectra, obtained on a Hitachi EPS-3T spectrophotometer, were recorded in nm and the ε-values were given in parentheses. Shoulder was denoted by sh. The mass spectra were measured on a Hitachi RM-50 spectrometer. The NMR spectra were obtained on a Varian A-60 spectrometer. The chemical shifts are given in τ-values with respect to TMS as an internal standard, and the coupling constants are recorded in Hz.

tert-*Butyl β-Chlorovinyl Ketone (I).* The β-chlorovinyl ketone (I) was obtained from *tert*-butyl β-hydroxyvinyl ketone by the reported method[3] in 86% yield as pale yellow liquid, bp 61.5—73 °C/2793 Pa, n_D^{20} 1.4578 (lit, value, bp 65—70 °C/3990 Pa, n_D^{20} 1.4598),[3] NMR (neat): 8.86 (s, 9H, *tert*-butyl-H), 2.62—3.32 (dd, $J=13$, 2H, olefinic H).

*1-Chloro-3-*tert*-butyl-1-penten-4-yn-3-ol (II).* To a solution of lithium acetylide (from lithium 2.45 g, 0.35 mol) in liquid ammonia (450 ml) was added slowly a solution of the β-chlorovinyl ketone (I, 25.30 g, 0.172 mol) in ether (100 ml). The ammonia was allowed to evaporate under continuous stirring. The residue was mixed with ether (300 ml) and chilled to −30 °C, and then saturated aqueous ammonium chloride solution (150 ml) was slowly added to the mixture. The organic layer was separated and the aqueous layer was extracted with ether. The combined ethereal solution was dried (magnesium sulfate), and the solvent was removed under reduced pressure. The residue on distillation under reduced pressure gave forerun, colorless liquid, bp 50—55 °C/266 Pa, 5.24 g, 17%, and then gave II, colorless liquid, bp 55—59 °C/266 Pa, 20.17 g, 67%, IR (neat): 3600—3360 (OH), 3320 (−C≡CH), 1055 (C–O), 1620 (C=C) cm^{-1}, NMR (CCl_4): 8.98 (s, 9H, *tert*-butyl-H), 7.36 (s, 1H, ethynyl-H), 6.87 (s, 1H, -OH), 3.38—4.08 (dd, $J=13$, 2H, olefinic-H).

Found: C, 62.29; H, 7.59; Cl, 20.37%. Calcd for $C_9H_{13}OCl$: C, 62.61; H, 7.59; Cl, 20.53%.

The forerun was found to be fairly pure and could be used without purification for the subsequent reaction.

*3-*tert*-Butyl-2-penten-4-ynal (III).* A mixture of the β-chlorovinyl alcohol (III, 10.7 g, 0.062 mol), 2M sulfuric acid (300 ml) and tetrahydrofuran (10 ml) was stirred at 40 °C under nitrogen atmosphere for 46 hr under shielding from light. The reaction mixture was saturated with ammonium sulfate, and the aqueous layer was extracted with ether. The extracts were combined with the organic layer and worked up in the usual way. The residue obtained on evaporating the solvent under reduced pressure was dissolved in carbon tetrachloride and chromatographed on alumina (Brockmann, Act. II—III, 50 g). The carbon tetrachloride eluates were concentrated under reduced pressure, and the residue was distilled *in vacuo*. The pentynal (III) was obtained as an unstable pale yellow liquid, bp 60—62 °C/665 Pa, 5.32 g, 63%, IR (neat): 3270 (−C≡CH), 2750 (−CHO), 1680 (C=O) cm^{-1}, NMR (CCl_4): 8.77 (s, 9H, *tert*-butyl-H), 6.05 (s, ethynyl-H), 3.73 (d, $J=8$, 1H, olefinic-H), −0.20 (d, $J=8$, 1H, -CHO).

The aldehyde (III) containing a small amount of II was used in the following reaction, because it was difficult to remove a minor quantity of II in III by distillation and chromatography. Found: C, 78.02; H, 8.82%. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88%.

*1,5-Di-*tert*-butyl-2,4-pentadien-5-yn-1-one (IV).* An ice-cooled solution of sodium hydroxide (0.622 g, 15.2 mmol) in 99% ethanol (4 ml) and water (4 ml) was added in a portion to a stirred solution of the pentynal (III, 0.833 g, 6.12 mmol) and pinacolone (0.632 g, 6.32 mmol) in 99% ethanol (33 ml) under cooling on an ice-bath. After 24 hr, the reaction was quenched on addition of 1M sulfuric acid (10 ml). The mixture was extracted with ether. The extracts, after being washed and dried, were concentrated under reduced pressure to yield reddish brown liquid. The liquid dissolved in petroleum ether was passed through a column of silica gel (Merck, 10 g). The crystals obtained on concentrating the filtrate were collected and washed with a small amount of cold petroleum ether to give pure IV, pale yellow cubes, mp 52.9—54.9 °C, 0.377 g, IR (neat): 3330 (−C≡CH), 1660 (C=O), 1595 (C=C), 975 (*trans* C=C) cm,$^{-1}$ NMR (CCl_4): 8.87 (s, 9H, *tert*-butyl^a–H), 8.82 (s, 9H, *tert*-butyl^b–H), 6.45 (s, 1H, ethynyl-H), 3.56 (d, $J=11$, olefinic-H^1), 3.43 (d, $J=14$, olefinic-H^2). Found: C, 82.52; H, 10.02%. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16%.

The silica gel column was further eluted with ether or benzene. Concentration of the eluates under reduced pressure yielded reddish orange liquid (0.796 g), which showed identical IR and NMR spectra with those of crystalline IV, and could be used without further purification for the subsequent reaction.

*1,5,10,14-Tetra-*tert*-butyl-2,4,10,12-tetradecatetraene-6,8-diyne-1,14-dione (V).* To a stirred solution of cupric acetate monohydrate (6.314 g, 31.8 mmol) in pyridine (19.5 ml) and methanol (19.5 ml) was added a solution of IV (1.388 g, 6.36 mmol) in methanol (15.7 ml). After being stirred overnight at room temperature, the reaction mixture was poured into ice-cooled 1M sulfuric acid (150 ml). The mixture containing yellow crystals was extracted with ether. The extracts, after washing and drying, were concentrated under reduced pressure. Yellow crystals thus obtained were dissolved in benzene, and the solution was passed through a column of alumina (Brockmann, Act. II—III, 10 g). Crystals obtained from the yellow cubes, mp 202.8—205.0 °C (dec.), 1.198 g, IR (KBr-disk): 1675 (C=O), 1592 (C=C), 1000—990 (doublet, filtrate were recrystallized from benzene to give diketone (V), *trans* C=C) cm^{-1}. Found: C, 82.66; H, 9.63%. Calcd for $C_{30}H_{42}O_2$: C, 82.90; H, 9.74%.

*3,7,12,16-Tetra-*tert*-butyl-4,6,12,14-octadecatetraene-1,8,10,17-tetrayne-3,16-diol (VI).* To an ice-cooled and stirred suspension of lithium acetylide–ethylenediamine complex[5] (1.288 g) in tetrahydrofuran (90 ml) was added a solution of the diketone (III, 0.410 g, 0.95 mmol) in the same solvent (55 ml). After the cooling bath was removed, the mixture was stirred for further 2 hr at room temperature. Saturated aqueous ammonium chloride solution (100 ml) was added to the reaction mixture under ice-cooling. The aqueous layer was extracted with ether, and the extracts were combined with the organic layer. The combined organic layer was washed 3 times with saturated sodium chloride solution and dried, and evaporated under reduced pressure to give light brown solid. The solid dissolved in ethyl acetate was passed through a short column of alumina (Brockmann, Act. II—III, 3 g). Evaporation of the filtrate under reduced pressure gave faintly orange fine crystals, 0.420 g, 91.5%, which were recrystallized from cyclohexane to give pure VI, colorless crystals, mp 185.8—187.9 °C (dec.), IR (KBr–disk): 3560—3400 (doublet, OH), 3300—3260 (doublet, –C≡CH), 980—965 (doublet, *trans* C=C) cm^{-1}. Found: C, 83.90; H, 9.53%. Calcd for $C_{34}H_{46}O_2$: C, 83.65; H, 9.79%.

*3,7,12,16-Tetra-*tert*-butyl-4,6,12,14-cyclooctadecatetraene-1,8,10,-17-tetrayne-3,16-diol (VII).* A solution of VI (0.359 g) in pyridine (25 ml) and ether (25 ml) was added over 5 hr-period to a vigorously stirred and refluxing solution of cupric acetate monohydrate (1.16 g) in pyridine (45 ml) and ether (45 ml) using a high dilution apparatus. After the mixture had been stirred for further 2 hr at the same temperature, stirring was continued for 1 hr at room temperature. The ice-cooled reaction mixture, after *ca.* 1/3 volume of the solvents had been removed under reduced pressure, was poured into ice-cooled 2M hydrochloric acid (450 ml). The organic layer was separated, and the aqueous layer was extracted with ether. The extracts combined with the organic layer were worked up in the usual way. Brown solid obtained on evaporating the solvent was dissolved in ethyl acetate, and the solution was passed through a short column of alumina (Brockmann, Act. II—III, 3 g). Slightly crude VI, faintly brown fine crystals, 0.347 g, 96.0%, obtained on evaporating the filtrate, were recrystallized twice from ethanol to give analytical specimen, colorless crystals, mp 239.8—240.3 °C (dec.). The crystals contained 1 mol of ethanol as a solvent of crystallization, which could be removed upon heating to 70 °C *in vacuo* for 48 hr.

Combusion of the cyclic glycol (VI) was found to be difficult, and satisfactory elemental analysis could be obtained on a sample admixed with sucrose. Found: C, 84.74; H, 9.39%. Calcd for $C_{34}H_{44}O_2$: C, 84.25; H, 9.15%.

*1,5,10,14-Tetra-*tert*-butyl-6,8,15,17-tetrakisdehydro[18]annulene (VIII).* A solution of stannous chloride dihydrate (0.6 g) in concentrated hydrochloric acid (4 ml) was added in a portion to a vigorously stirred suspension of the cyclic glycol (VII, 0.149 g, 0.308 mmol) in benzene (15 ml) under nitrogen atmosphere. After 30 min, cold water was added to the deep reddish purple reaction mixture. The organic layer was washed with water (3 times), saturated sodium hydrogencarbonate–sodium chloride solution and water, and dried over sodium sulfate in a refrigerator for 3 hr. Residue obtained on concentrating the organic layer under reduced pressure was dissolved in cyclohexane, and passed through a column of alumina (Merck, Act. I, 5 g) and eluted with the same solvent. The filtrate and eluates were combined, and concentrated under reduced pressure. Deep brown fine crystals deposited were collected and washed twice with a small amount of cold petroleum ether to give pure tetra-*tert*-butyltetrakisdehydro-[18]annulene (VIII), mp *ca.* 180 °C (dec.), 0.127 g, 90%, UV: $\lambda_{\mathrm{max}}^{\mathrm{THF}}$ 219.5 (97600), 237.8 (19400), 250 (16300), 261 (5740), 275 (4240), 337 (35500), 374 (231000), 407.5 sh (12800), 524.5 (68700), 621 (151), 656 (186), 707 (932), IR (KBr–disk): 2950 (S), 2900 (M), 2870 (S), 1525 (W), 1480 (M), 1460 (S), 1395 (W), 1365 (M), 1285 (M), 1235 (S), 1195 (S), 1065 (M), 1025 (S), 1010 (S), 965 (M), 885(S), 858(S) cm^{-1}, NMR (THF-d_8): 7.98 (s, *tert*-butyl-H), 14.92 (t, $J=13$, inner-H), 0.02 (d, $J=13$, outer-H). Found: C, 90.56; H, 9.44%. Calcd for $C_{34}H_{42}$: C, 90.61; H, 9.39%.

VIII was found to be fairly stable even in crystalline state. Crystals of VIII which were placed in a refrigerator (−20 °C) for 3 days still held 70% purity indicating higher stability of VIII than the tetramethyl analogue.[1]

*1,5,10,14-Tetra-*tert*-butylcyclooctadecane (IX).* VIII (207.3 mg, 0.4277 mmol) in ethyl acetate (90 ml) was hydrogenated over pre-reduced platinum oxide catalyst ($PtO_2 \cdot 2H_2O$, 536.2 mg). After 1.5 hr, 139 ml (27 °C) of hydrogen was absorbed (theoretical volume, 136.9 ml). Yellowish solid obtained was dissolved in petroleum ether, and the solution was passed through a short column of alumina (Merck, Act. I, 2 g). Residue obtained on evaporating the filtrate was recrystallized from ethyl acetate to give tetra-*tert*-butylcyclooctadecane (IX), colorless crystals, mp 189—190 °C. Found: C, 86.08; H, 13.74%, M$^+$ 476. Calcd for $C_{34}H_{68}$: C, 85.63; H, 14.37%, Mol. wt., 476.9.

CT Complex of VIII with Trinitrofluorenone. A mixture of VIII (30.46 mg, 0.0676 mmol), 2,4,7-trinitrofluorenone (41.05 mg, 0.130 mmol), benzene (3 ml) and methanol (3 ml) was refluxed for a short period, and allowed to stand overnight in a refrigerator. Reddish purple crystals deposited were collected and washed successively with petroleum ether and benzene to give pure complex, reddish purple crystals, which showed no melting point, but underwent color change at *ca.* 215 °C. Found: C, 73.60; H, 6.09; N, 5.46%. Calcd for $C_{34}H_{42} \cdot C_{13}H_5O_7N_3$: C, 73.70; H, 6.19; N, 5.49%.

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6) The chemical shifts of the outer protons given in the preliminary report (Ref. 2b) (−0.02 in THF-d_8 and −0.04 in $CDCl_3$) were erroneous.