Dehydroannulenes. V. Synthesis and Properties of 1,6,12,17-Tetra-*t*-butyl-2,4,13,15-tetrakisdehydro[22]annulene

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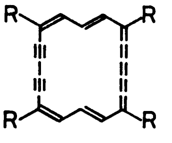
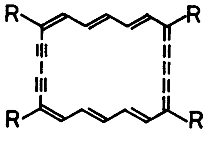
(Received April 23, 1976)

The synthesis of 1,6,12,17-tetra-*t*-butyl-2,4-13,15-tetrakisdehydro[22]annulene has been performed. The tetrakisdehydro[22]annulene was found to be strongly diatropic having high conformational stability.

In view of strong diatropicity and high conformational stability of tetrasubstituted tetrakisdehydro[18]-annulene (I)[1-4] synthesis of higher analogue of I, tetrakisdehydro[22]annulene (II), seemed to be of considerable interest for the purpose gaining further insight into the aromaticity of macrocyclic $[4n+2]\pi$-electron system. The present paper is concerned with the synthesis and properties of tetra-*t*-butyltetrakisdehydro[22]annulene (XII=II, R=*t*-Bu).[5]

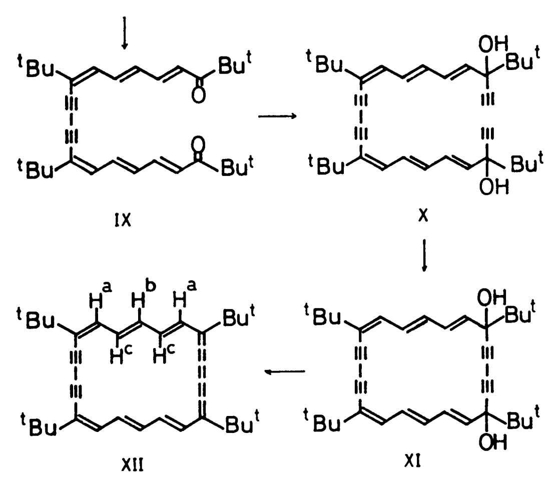


I



II

3-*t*-Butyl-2-penten-4-ynal (IV) obtained from III[3] was converted into diethyl acetal (V) in the usual way. Condensation of ethyl vinyl ether[6] with V in benzene in the presence of boron trifluoride etherate yielded ethoxy acetal (VI) in a high yield. Unstable 5-*t*-butyl-2,4-heptadien-6-ynal (VII) obtained on treatment of VI with hydrogen chloride in aqueous dioxane was condensed with pinacolone to give trienyne ketone (VIII). Oxidative coupling of the trienyne ketone (VIII) with copper(II) acetate monohydrate in pyridine–methanol[7] yielded hexaendiyne diketone (IX). Bis-ethynylation of the diketone (IX) could be achieved by lithium acetylide–ethylenediamine complex[8] in tetrahydrofuran saturated with acetylene. Bis-ethynyl alcohol (X) obtained in a high yield was oxidatively coupled with copper(II) acetate in pyridine–methanol under high dilution conditions using ether as an entraining solvent to give cyclic glycol (XI). The fact that the 22-membered cyclic glycol (XI) could be obtained in 77.5% yield seems to be attributable to the molecular geometry of X favorable for intramolecular oxidative coupling.



Finely powdered tin(II) chloride dehydrate was added at −60 °C under nitrogen atmosphere to a stirred solution of the cyclic glycol (XI) in ether saturated with hydrogen chloride. Resulting deep blue violet reaction mixture was worked up rapidly at a low temperature. Chromatography of the product on alumina at −20 °C followed by elution with dichloromethane–pentane gave tetra-*t*-butyltetrakisdehydro[22]-annulene (XII) as unstable dark violet crystals in a yield of 85%. The crystals of XII changed quickly to colorless solid at *ca.* 100 °C on attempted melting point determination. Full hydrogenation of XII over platinum catalyst gave tetra-*t*-butylcyclodocosane.

As illustrated in Fig. 1, XII showed closely related electronic spectrum to that of tetra-*t*-butyltetrakisdehydro[18]annulane (I, R=*t*-Bu)[3] except for considerable bathochromic shift in XII. The NMR spectrum of XII is shown in Fig. 2. The fact that the outer protons (H^a and H^b) resonate at unusually low field and the inner protons (H^c) exhibit signals at fairly high field clearly demonstrates the induction of diamagnetic ring current indicating the aromatic nature of the tetrakisdehydro[22]annulene (XII). The fact that the NMR spectra of XII obtained at 30 °C and −40 °C exhibit no essential change (Table 1) indicates the conformational stability of the 22-membered ring with delocalized π-electron system containing formal diacetylene and hexapentaene units. The coalescence temperature of XII could not be determined owing rather rapid decomposition of XII at temperature higher than 30 °C.

The difference in chemical shifts between the signal of inner protons (τ_i) and the lowest field signal of outer protons (τ_o) can be regarded as an approximate measure of ring current. The τ_i—τ_o-value ($\Delta\tau$) for tetra-*t*-butyltetrakisdehydro[18]annulene (I, R=*t*-Bu) has

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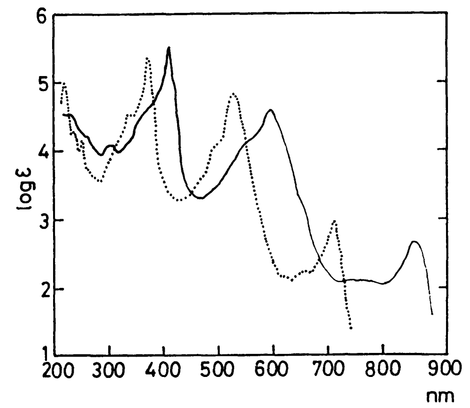


Fig. 1. Electronic spectra in THF of tetra-*t*-butyltetrakisdehydro[18]annulene (I, R=*t*-Bu) (······) and tetra-*t*-butyltetrakisdehydro[22]annulene (XII) (——).

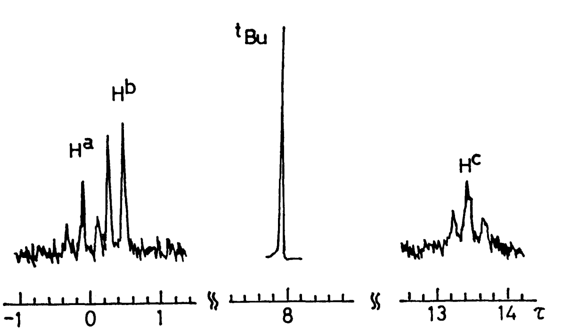
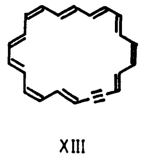


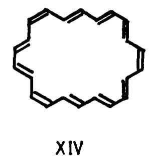
Fig. 2. NMR spectrum of tetra-*t*-butyltetrakisdehydro-[22]annulene (XII).
60 MHz, in $CDCl_3$, at 30 °C.

Table 1. NMR Parameters of tetra-*t*-butyltetrakisdehydro[22]annulene (XII), 60 MHz, $CDCl_3$

Temperature	H_b	H^a	*t*-Bu	H^c
−40 °C	−0.43 t *J*=13	0.09 d *J*=13	7.88 s	13.71 t *J*=13
+30 °C	−0.16 t *J*=13	0.33 d *J*=13	7.93 s	13.44 t *J*=13

been found to be $\Delta\tau=14.83$,[3] whereas an appreciable decrease in the value, $\Delta\tau=13.44-(-0.16)=13.60$, was observed for tetra-*t*-butyltetrakisdehydro[22]annulene (XII). The $\Delta\tau$-values for I and XII can be compared reasonably well, since these compounds have similar geometries and planarities. Therefore, the marked decrease in the $\Delta\tau$-value for XII as compared with that for I(R=*t*-Bu) can be regarded as an evidence for theoretically predicted decrease of resonance energy[9] or ring-current intensity[10] along with increase of ring size.


XIII


XIV

It has been reported that monodehydro[22]annulene (XIII) exhibits signals of outer protons at τ1.55—3.75 and these of inner protons at τ6.55—9.30.[11] The NMR spectrum of [22]annulene (XIV) has been found to be temperature dependent indicating conformational mobility of the molecule (coalescence temperature, *ca.* 20 °C). At −90 °C, XIV showed outer proton signals at τ 0.35—0.7 and 0.9—1.5, and inner proton signals at τ 10.4—11.2.[12] A much higher diatropicity and conformational stability of XII as compared with XIII and XIV indicate that symmetrical 'acetylene-cumulene'-dehydroannulenes containing equalized acetylenic and cumulenic linkages in the cyclic system are one of the most adequate structure for the study of aromaticity of macrocyclic system.

Experimental

All melting and boiling points are not corrected. The IR spectra were measured with a Hitachi EPI-2 or EPI-G3 spectrometer, and 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 with a Hitachi RM-50 spectrometer. The NMR spectra obtained on a Varian A-60 spectrometer were given in τ-values with respect to TMS as an internal standard, and the coupling constants (*J*) are recorded in Hz. Silica gel (Merck, Kiesel Gel 60) or alumina (Merck, Act. II-III) was used for column chromatography, unless otherwise stated.

3-t-Butyl-2-penten-4-ynal Diethyl Acetal (V). To a mixture of slightly crude IV (63.70 g, bp 47—50 °C/400 Pa) obtained from III (88.0 g)[3] and ethyl orthoformate (160 ml) was added a solution of *p*-toluenesulfonic acid monohydrate (6.00 g, 0.968 mmol). The mixture was stirred at 30 °C for 24 h under nitrogen atmosphere, and then chilled on an ice-bath. The cooled reaction mixture was poured onto ice-water containing sodium hydrogencarbonate. The organic layer was separated and the aqueous layer was extracted with ether (100 ml×2). The combined organic layer was washed successively with sodium hydrogencarbonate and sodium chloride solutions, dried (K_2CO_3), concentrated *in vacuo*, and distilled, yielding V: 84.11 g, 78.5% based on III; bp 78–79 °C/400 Pa; MS: *m/e* 210 (M^+); IR (CCl_4): 3320 m (C≡CH), 2085 w (C≡C), 1628 w (C=C), 1200–1000 s (C–O–C) cm^{-1}; NMR (CCl_4): 4.24 (d, 1, *J*=7.5, olefinic), 4.78 (d, 1, *J*=7.5, acetal), 6.48 (m, 4, $-CH_2-$), 6.89 (s, 1, C≡CH), 8.83 (t, 6, *J*=7.0. CH_3), 8.83 (s, 9, *t*-Bu). Elemental analyses gave unstisfactory results presumably owing to extremely facile hydrolysis of V.

5-t-Butyl-3-ethoxy-4-hepten-6-ynal Diethyl Acetal (VI). A solution of boron trifluoride etherate (20 mg) in benzene (1 ml) was added to a solution of V (7.40 g, 0.0352 mol) in the same solvent (20 ml) at 40 °C, and then a solution of ethyl vinyl ether (2.79 g, 0.0387 mol) in the same solvent (5 ml) was slowly added. After the mixture had been kept at the same temperature for further 2 h. Finely powdered potassium carbonate was added to the cooled reaction mixture resulting in a yellow solution. The inorganic material was removed by filtration and washed with ether. The combined organic layer and washings were concentrated under reduced pressure, and distilled *in vacuo*, giving VI: 8.98 g, 90.4%; bp 110—111 °C/400 Pa; MS: *m/e* 282 (M^+); IR (CCl_4): 3320 m (C≡CH), 2070 w (C≡C), 1620 w (C=C), 1150—1050 s (C–O–C) cm^{-1}; NMR (CCl_4): 4.36 (d, 1, *J*=9.0, H^4), 5.42 (m, 1, H^1), 5.64 (m, 1, H^3), 6.56 (m, 6, O–CH_2–), 6.83 (s, 1, C≡CH), 8.30 (m, 2, H^2), 8.85

(t, 9, J=7.0, $\mathrm{CH_3}$).

Found: C, 71.89; H, 10.61%. Calcd for $\mathrm{C_{17}H_{30}O_3}$: C, 72.30; H, 10.71%.

Although VI gave rather unsatisfactory elemental analysis, it was used without further purification in the following reaction.

*5-*t*-Butyl-2,4-heptadien-6-ynal (VII).* A mixture of VI (10.00 g, 0.0354 mol), dioxane (60 ml) and 3M hydrochloric acid (50 ml) was vigorously stirred under nitrogen atmosphere at 50 °C for 3 h, and then at 40 °C for 18 h. The reaction mixture was chilled and the organic layer was separated. The aqueous layer was extracted with ether. The combined organic layer was washed successively with saturated sodium hydrogen carbonate and sodium chloride solutions, dried ($\mathrm{Na_2SO_4}$), concentrated under reduced pressure, and rapidly distilled *in vacuo* under nitrogen atmosphere using short neck distilling flask to give VII: yellow liquid; 4.06 g, 70.7%; bp 60—70 °C/200 Pa; IR ($\mathrm{CCl_4}$): 3300 m (C≡CH), 2810 w, 2730 w (CHO), 1687 s (C=O), 1616 s (C=C), 977 s (*trans* CH=CH) $\mathrm{cm^{-1}}$; NMR ($\mathrm{CCl_4}$): 0.56 (d, 1, J=7.5, CHO), 2.47 (dd, 1, J=11, 15, $\mathrm{H^3}$), 3.46 (d, 1, J=11, $\mathrm{H^4}$), 3.87 (dd, 1, J=7.5, 11, $\mathrm{H^2}$), 8.81 (s, 9, *t*-Bu).

VII was found to be unstable changing to a red viscous liquid on standing at room-temperature for 1 h, but could be kept for several days at −20 °C under nitrogen atmosphere, and was best stored as an ether solution at 0 °C. VII gave no satisfactory elemental analyses.

Since the aldehyde (VII) decomposed partly during distillation, the reaction product was passed through a short column of alumina, and the slightly crude VII obtained on concentrating the filtrate was used without purification for further reaction.

2,4-Dinitrophenylhydrazone of VII. The crude hydrazone was obtained from VII (88 mg, 0.54 mmol), ethanol (7.4 ml), phosphoric acid (0.6 ml) and 2,4-dinitrophenylhydrazine (100 mg, 0.50 mmol), and was purified by chromatography on silica gel. Elution with petroleum ether–benzene yielded pure 2,4-dinitrophenylhydrazone: red crystals; 160 mg, 93%; mp 194.0-194.9 °C (from petroleum ether–benzene).

Found: C, 59.39; H, 5.35; N, 16.59%. Calcd for $\mathrm{C_{17}H_{18}N_4O_4}$: C, 59.64; H, 5.30; N, 16.37%.

*9-*t*-Butyl-2,2-dimethyl-4,6,8-undecatrien-10-yn-3-one (VIII).* VI (12.2 g, 0.0433 mol) was converted into VII according to the above procedure, and the crude product dissolved in carbon tetrachloride was passed through a short column of alumina. Elution with the same solvent yielded slightly crude VII (4.91 g, light brown liquid). A solution of sodium hydroxide (2.00 g, 50.0 mmol) in ethanol (5 ml) and water (5 ml) was added under nitrogen atmosphere to a solution of the crude VII (4.91 g) and pinacolone (5.00 g, 50.0 mmol) in ethanol (60 ml) maintained at 0 °C. After being kept at 22 °C for 36 h, the reaction mixture was poured onto ice-cooled 3 M hydrochloric acid (50 ml), and extracted with ether (20 ml×3). The extract was washed successively with water and saturated sodium chloride solution, dried ($\mathrm{Na_2SO_4}$), and concentrated under reduced pressure. The residue was chromatographed on alumina to give VIII: pale yellow crystals (from methanol); 3.20 g, The mother liquor of crystallization was chromatographed on silica gel, yielding further crop of VIII: 2.08 g (total yield, 5.28 g, 50.0%). An analytical specimen of VIII was obtained on further recrystallization from pentane: mp 92.5—93.5 °C; IR ($\mathrm{CCl_4}$): 3300 m (C≡CH), 1678 s (C=O), 1591 s (C=C), 999 s (*trans* CH=CH) $\mathrm{cm^{-1}}$; NMR ($\mathrm{CCl_4}$): 2.40—3.85 (m, 5, olefinic), 6.69 (s, 1, C≡CH), 8.83 (s, 9, *t*-Bu), 8.88 (s, 9, *t*-Bu); UV (99% EtOH): $\lambda_{\max}$ 230 sh (5520), 239 (6670), 336 (37900) nm.

Found: C, 83.80; H, 9.97%. Calcd for $\mathrm{C_{17}H_{24}O}$: C, 83.55; H, 9.90%.

*9,14-Di-*t*-butyl-2,2,21,21-tetramethyl-4,6,8,14,16,18-docosahexaen-10,12-diyn-3,20-dione (IX).* A solution of VIII (3.00 g, 0.0123 mol) in pyridine (15 ml) and methanol (15 ml) was added to a stirred mixture of copper(II) acetate monohydrate (15.00 g, 0.0752 mol), pyridine (50 ml) and methanol (50 ml) at 30 °C. The mixture, after being stirred for 15 h at 30—35 °C, was poured onto ice-cooled 2 M hydrochloric acid, and extracted with ether (100 ml×4). The extract was washed successively with diluted hydrochloric acid, saturated sodium hydrogencarbonate and saturated sodium chloride solutions, and dried ($\mathrm{MgSO_4}$). Crystalline residue obtained on concentrating the extract *in vacuo* was chromatographed on alumina and eluted with benzene to give IX: yellow crystals (washed with methanol); 2.49 g, 83.3%. An analytical sample was obtained on recrystallization from methanol: yellow crystals; mp 171.5—172.5 °C; MS: *m/e* 486 ($\mathrm{M^+}$), 429 (M−57); IR ($\mathrm{CCl_4}$): 1678 m (C=O), 1592 s (C=C), 999s (*trans* CH=CH) $\mathrm{cm^{-1}}$; NMR ($\mathrm{CDCl_3}$): 2.40—3.81 (m, 10, olefinic), 8.78 (s, 18, *t*-Bu), 8.84 (s, 18, *t*-Bu); UV (99% EtOH): $\lambda_{\max}$ 246.5 (23100), 288 sh (22300), 325 sh (39800), 343 (46200), 385 (41200), 425 sh (24300) nm.

Found: C, 83.73; H, 9.41%. Calcd for $\mathrm{C_{34}H_{46}O_2}$: C, 83.90; H, 9.53%.

*9,14-Di-*t*-butyl-2,2,21,21-tetramethyl-3,20-diethynyl-4,6,8,14,-16,18-docosahexaen-10,12-diyne-3,20-diol (X).* To a stirred mixture of lithium acetylide-ethylenediamine complex[8] (3.00 g, 0.0326 mol) in THF (60 ml) saturated with acetylene was added at 30 °C a solution of IX (1.60 g, 0.00329 mol) in THF (15 ml). After being stirred for further 2 h at 30 °C under bubbling of acetylene, the reaction mixture was chilled in an ice-salt-bath, and saturated ammonium chloride solution was added dropwise at a rate to maintain the internal temperature at −5—0 °C. Then water was added to the mixture, and the organic layer was separated. The aqueous layer was extracted with ether (30 ml×3), and the extract was combined with the organic layer. The combined organic layer was washed with diluted hydrochloric acid and saturated brine, successively, dried ($\mathrm{MgSO_4}$), and concentrated under reduced pressure. Chromatography of the residue on alumina followed by elution with benzene yielded an amorphous solid (1.71 g, 96.6%) which was washed thoroughly with pentane to give X: pale yellow crystalline powder; mp 148—150 °C; MS: *m/e* 538 ($\mathrm{M^+}$), 481 (M−57), 436 (M−57—18); IR ($\mathrm{CHCl_3}$): 3590 m (OH), 3317 m (C≡CH), 2193 w, 2106 w (C≡C), 1600 w (C=C), 995 s (*trans* CH=CH) $\mathrm{cm^{-1}}$; UV (99% EtOH): $\lambda_{\max}$ 223.5 (29500), 262.5 (27500), 280 sh (31900), 293 (4300), 305 (49100), 327 (39300), 347 (38300), 369 (31500), 397.5 (22600) nm.

Found: C, 84.38; H, 9.34%. Calcd for $\mathrm{C_{38}H_{50}O_2}$: C, 84.71; H, 9.35%.

*1,6,12,17-Tetra-*t*-butyl-7,9,11,17,19,21-cyclodocosahexaen-2,4,13,15-tetrayn-1,6-diol (XI).* A solution of X (1.710 g) in ether (90 ml), pyridine (90 ml) and methanol (60 ml) was added over a period of 12 h to a stirred and refluxing solution (internal temperature, 50 °C) of copper(II) acetate monohydrate (18.0 g, 0.0902 mol) in ether (180 ml), pyridine (180 ml) and methanol (40 ml) using a high-dilution apparatus. After being refluxed for further 2 h, the reaction mixture was concentrated under reduced pressure to *ca.* 200 ml, and poured onto ice-cooled 2 M hydrochloric acid (600 ml). The mixture was extracted with ether (100 ml×4), and the extract was washed successively with 2 M hydrochloric acid, saturated sodium hydrogencarbonate solution and saturated brine, dried ($\mathrm{MgSO_4}$), and the solution was concentrated under reduced pressure, yielding a crystalline residue. Chromatography of the residue on alumina followed by elution with benzene gave XI (1.32 g, 77%), which was recrystallized from dichloromethane–pentane to yield pure XI: yellowish crystals, turned to dark brown soild at *ca.* 240 °C; MS: *m/e* 536 (M^+), 479 ($M-57$); IR (KBr-disk): 3340 m br. (OH), (988 s *trans* CH=CH) cm^{-1}; NMR ($CDCl_3$): 2.64—4.28 (m, 10, olefinic), 7.91 (br. s, 2, OH, disappeared on addition of D_2O), 8.81 (s, 18, *t*-Bu), 8.89 (s, 18, *t*-Bu); UV (99% EtOH): λ_{max} 279 sh (45400), 292 (83400), 302 (102000), 323.5 sh (12700), 360 sh (12500), 385 (17200), 409 (16200) nm.

Found: C, 84.92; H, 9.03%. Calcd for $C_{38}H_{48}O_2$: C, 85.02; H, 9.01%.

*1,6,12,17-Tetra-*t*-butyl-2,4,13,15-tetrakisdehydro[22]annulene (XII).* To a solution of XI (150 mg, 0.279 mmol) in ether saturated with hydrogen chloride (10 ml) was added under nitrogen atmosphere finely powdered tin(II) chloride dihydrate (450 mg, 1.99 mmol) at −60 °C. After being stirred for 30 min at the same temperature, resulting deep blue violet reaction mixture was mixed with ether (30 ml). The organic layer was washed successively with cold water and cold saturated sodium hydrogencarbonate solution, dried ($MgSO_4$), and concentrated under reduced pressure at a temperature below 0 °C. The dark violet residue was immediately chromatographed on alumina at −20 °C. Elution with dichloromethane–pentane (3 : 7) gave XII: 119 mg, 85%; dark violet crystals, turned to colorless solid at *ca.* 100 °C; IR (Nujol mull, measured at a low temperature): 988 (*trans* CH=CH) cm^{-1}; UV (THF): λ_{max} 222 (37000), 231 (37000), 263.5 (16000), 299 (13000), 311 (11000), 369 sh (41000), 382 (47000), 414 (35000), 552 sh (14000), 596 (46000), 732 (130), 768 (130), 858 (490) nm (*cf.*, Fig. 1); NMR: see, Table 1 and Fig. 2.

The crystals of XII decomposed rapidly on exposure to diffused daylight and air at room-temperature. Solutions of XII in pentane, ether or dichloromethane turned gradually to yellow on standing at 0 °C. TLC examination reveals that the product is a complex mixture. XII could be kept with slight decomposition at −78 °C in a diluted dichloromethane solution or crystalline state. XII gave poor elemental analysis and it would seem that the instability of XII is to blame.

Found: C, 89.92; H, 9.32%. Calcd for $C_{38}H_{46}$: C, 90.78; H, 9.22%.

Catalytic Hydrogenation of XII. A cold solution of XII (46 mg) in ethyl acetate (10 ml) was added at −20 °C to a mixture of acetic acid (20 ml) and ethyl acetate (10 ml) containing platinum catalyst (200 mg of platinum oxide was prereduced). The mixture was stirred under hydrogen atmosphere at −15—−20 °C for 3 h. After the mixture had been stirred overnight at room temperature, the catalyst was removed by filtration. The filtrate was mixed with ether and washed successively with water, saturated sodium hydrogencarbonate solution and saturated brine, dried ($MgSO_4$), and the solvent was removed under reduced pressure. Yellow oily residue, which crystallized on standing, was chromatographed on alumina, and eluted with pentane to give tetra-*t*-butylcyclodocosane: 42 mg, 86%; Colorless crystals (from ethyl acetate–methanol); mp 97—101 °C; MS: *m/e* 532 (M^+), 477 ($M-57$), 57 (base peak); IR (CCl_4): 2940 s, 2860 s, 1476 m, 1393 w, 1365 m cm^{-1}; NMR (CCl_4): 8.32 (m, CH_2, $-CH=$), 9.15 (s, CH_3).

Found: C, 85.81; H, 14.36%. Calcd for $C_{38}H_{76}$: C, 85.63; H, 14.37%.

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