Tetra-t-butyltetradehydro[22]annulene

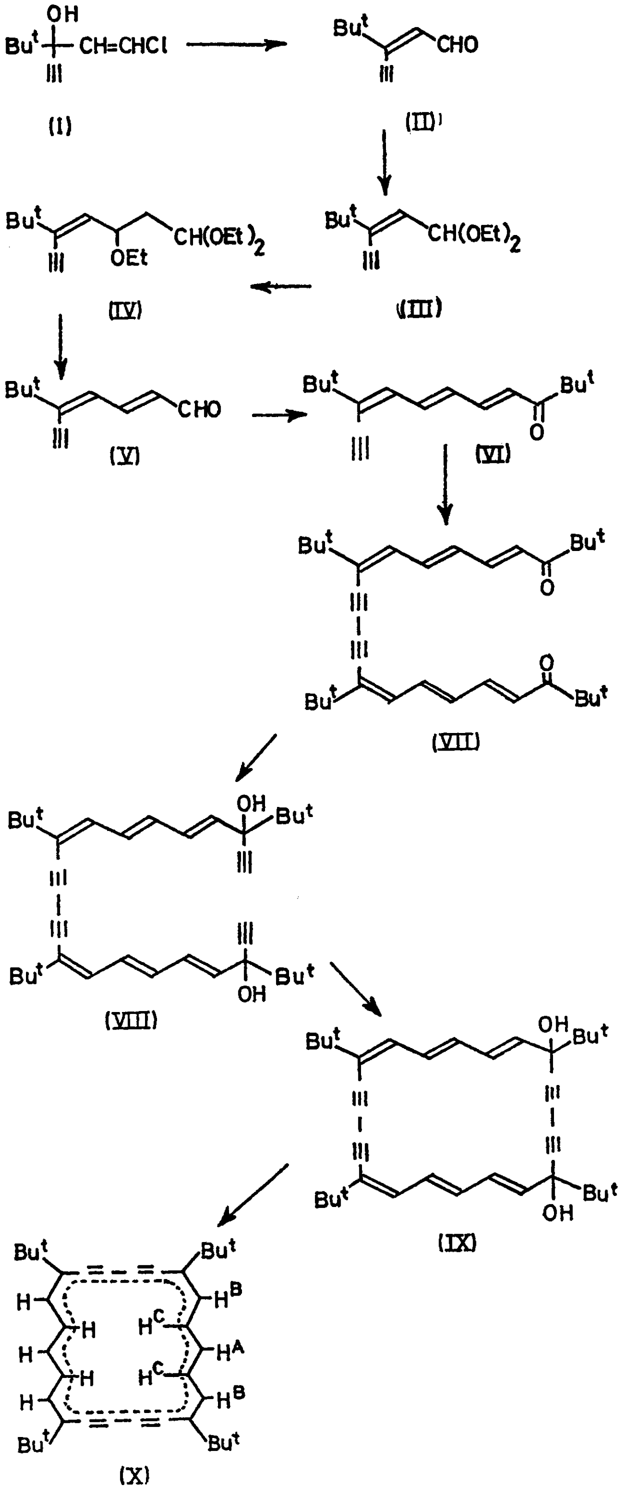
By MASAHIKO IYODA, HIDEAKI MIYAZAKI, and MASAZUMI NAKAGAWA*
(*Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan*)

Summary 1,6,12,17-Tetra-t-butyl-2,4,13,15-tetradehydro-[22]annulene has been synthesized and shown to be aromatic and to have fairly high conformational stability by n.m.r. spectroscopy.

THEORETICAL calculations have predicted that the limit of aromaticity of $(4n + 2)\pi$-electron systems will lie between 22- and 26-membered rings,[1] and this was apparently confirmed experimentally by the fact that the diamagnetic ring current observed in monodehydro[22]annulene[2] and [22]annulene[3] could not be detected in tridehydro[26]-annulene.[4] However, recently it has been reported that monodehydro[26]annulene possess a diamagnetic ring-current.[5]

1,5,10,14-Tetra-substituted 6,8,15,17-tetradehydro[18]-annulenes show high conformational stability and possess a highly delocalized π-electron system,[6] and in view of this we have synthesized tetra-t-butyltetradehydro[22]annulene (X), which has an analagous rigid framework. t-Butyl substituted tetradehydro[22]annulene was studied in view of the higher stability and solubility of tetra-t-butyltetradehydro[18]annulene[6c] compared with non-t-butyl substituted tetradehydro[18]annulenes.

The carbinol (I) obtained from the reaction of chlorovinyl-t-butyl ketone[7] with lithium acetylide in liquid NH_3, was treated with 4N-H_2SO_4 sulphuric acid to yield the *cis*-enyne aldehyde (II). The crude aldehyde (II) was converted into the diethyl acetal (III) [79% based on (II)]



Condensation of ethyl vinyl ether[8] with (III) in the presence of BF_3 afforded the ether acetal (IV) (90%) which gave the dienyne aldehyde (V) (70%) on treatment with 3N-HCl in dioxan. The trienyne ketone (VI), pale yellow crystals, m.p. 92·5—93·5 °C, obtained by an aldol-type condensation of (V) with pinacolone was oxidatively coupled with $Cu(OAc)_2$ in pyridine–MeOH[9] to yield the diketone (VII), yellow crystals, m.p. 171·5—172·5 °C (83%). Reaction of diketone (VII) with lithium acetylide–ethylenediamine complex[10] in tetrahydrofuran gave the diethynyl glycol (VIII), m.p. 148—150 °C (97%). Oxidative coupling of (VIII) under high dilution conditions [$Cu(OAc)_2$–pyridine–MeOH] with ether as entraining solvent yielded the 22-membered cyclic glycol (IX), yellow crystals, m.p. *ca.* 240 °C (decomp.) (78%). Finely powdered $SnCl_2,2H_2O$ was added to a stirred solution of (IX) in ether saturated with HCl at −60 °C under nitrogen, resulting in a deep blue-violet solution. Chromatography on alumina at −20 °C gave tetra-t-butyltetradehydro[22]annulene (X) as dark violet crystals (85%). (X) was unstable and decomposed at *ca.* 100 °C to form colourless solid; λ_{max} (tetrahydrofuran) 222 (ϵ 37,000), 231 (37,000), 263·5 (16,000), 299 (13,000), 311 (11,000), 369sh (41,000), 382 (47,000), 414 (350,000), 552sh (14,000), 596 (46,000), 732 (130), 768 (130), and 858 nm (490). Because of its instability, (X) gave unsatisfactory elemental analyses. Hydrogenation of (X) in EtOAc–AcOH (1:1) over a platinum catalyst followed by chromatography on alumina afforded tetra-t-butylcyclodocosane (86%), m.p. 97—101 °C, M^+ 532. The n.m.r. spectrum of (X) is summarized in the Table. The fact that the outer protons (H^A and H^B) give signals at unusually low field and the inner protons (H^C) exhibit signals at fairly high field clearly demonstrates the existence of induced diamagnetic ring-current, indicating that (X) is aromatic. The n.m.r. spectra of (X) at 30 and −40 °C show no essential differences, reflecting the conformational stability of the 22-membered ring containing a diacetylene and a hexapentaene linkages. The coalescence temperature could not be determined owing to thermal decomposition.

TABLE

N.m.r. Spectra of (X) *in* $CDCl_3$ *at* 60 MHz (τ)

	H^A	H^B	Bu^t	H^C
−40 °C	−0·43 (t, *J* 13 Hz)	0·09 (d, *J* 13 Hz)	7·88 (s)	13·71 (t, *J* 13 Hz)
30 °C	−0·16 (t, *J* 13 Hz)	0·33 (d, *J* 13 Hz)	7·93 (s)	13·44 (t, *J* 13 Hz)

Crystalline compounds described in this paper gave, unless otherwise stated, satisfactory elemental analyses.

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