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# 3,7,12,16-TETRA-t-BUTYL-1,8,10-TRIDEHYDRO[16]ANNULENE.
# A STRONGLY PARATROPIC 16π-ELECTRON SYSTEM

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It was considered to be of considerable interest to prepare dehydro[4n]-annulenes containing formal acetylenic and cumulenic linkages in the cyclic system in view of high conformational stability and strong diatropicity of the [4n+2]-counterparts (1). The present paper is concerned with the synthesis and paratropicity of tridehydro[16]annulene containing a butatriene and a butadiyne (or an acetylene and a hexapentaene) units in the ring system.

Hydroxy acetal (III) obtained by the reaction of lithio derivative of pentynal diethyl acetal (I) (2) with diene ketone (II) (3) was treated without purification with an aqueous acetic acid to give hydroxyaldehyde (IV, colorless prisms, mp 80.5-82.0°C, 57% based on I or II) (4). The aldol condensation of the hydroxyaldehyde (IV) with pinacolone afforded hydroxy ketone (V, colorless crystals, mp 62.0-63.0°C, 76%). Treatment of the ketone (V) with lithium acetylide-ethylenediamine complex in tetrahydrofuran yielded diethynyl glycol (VI, colorless crystals, mp 110.5-111.0°C, nearly quantitative yield). Oxidative coupling of the diethynyl glycol (VI) by cupric acetate in pyridine under a high dilution condition resulted in the formation of 16-membered cyclic glycol (VII). The cyclic glycol (VII) could be separated into diastereomers ($VII_a$, colorless crystals, mp 217.5-219.0°C (dec.), 21% and $VII_b$, colorless crystals, mp 187.0-188.0°C, 14%) on chromatography on silica gel. The cyclic glycol ($VII_a$ or $VII_b$) was treated with powdered stannous chloride dihydrate in ether saturated with

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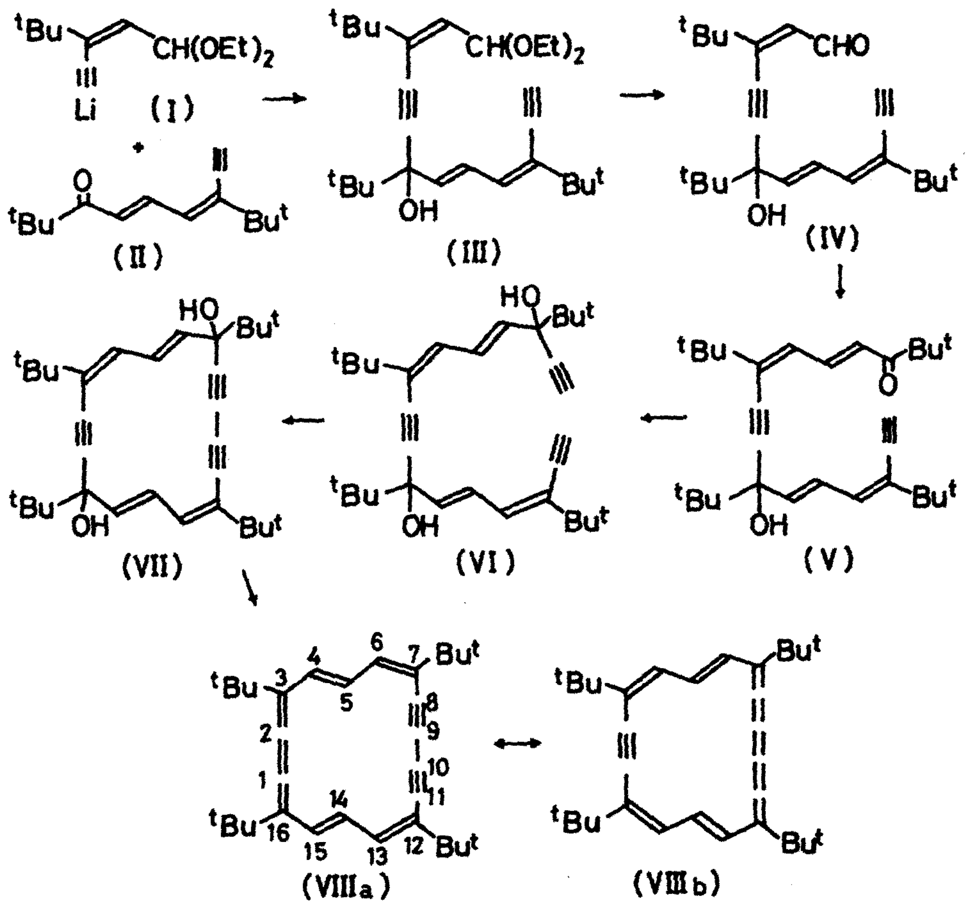

hydrogen chloride. After the reaction mixture had been worked up by the usual way, the product was chromatographed on alumina (Merck, Act. II-III) to give 3,7,12,16-tetra-*t*-butyl-1,8,10-tridehydro[16]annulene (VIII, deep blue leaflets, mp 155.5-157.0°C (dec.), Found: C, 89.99; H, 10.13%. Calcd. for $C_{32}H_{42}$: C, 90.08; H, 9.92%, 84% based on $VII_a$, 88% based on $VII_b$). The tridehydro[16]-annulene (VIII) was found to be fairly stable in crystalline state. But gradual change of electronic spectrum indicates slow decomposition of VIII in solution. The electronic spectrum illustrated in Fig. 1 was found to be rather similar to those of [16]annulene, di- and tridehydro[16]annulenes (5). The 100 MHz n.m.r. spectrum of VIII in deuteriochloroform is shown in Fig. 2. The inner protons in the tridehydroannulene (VIII) exhibit signals at extremely low field ($\tau$ -7.10, d.d, J=11.0, 15.5 Hz, 2H) and the outer protons resonate at fairly high field ($\tau$

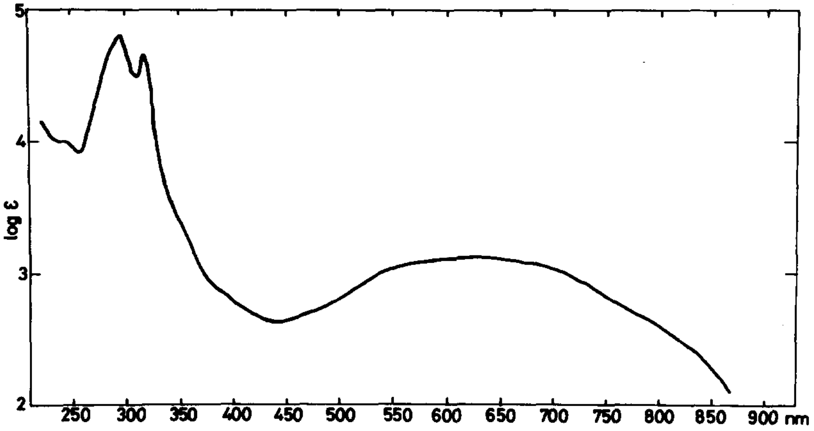

Fig. 1. Electronic spectrum of VIII in cyclohexane.

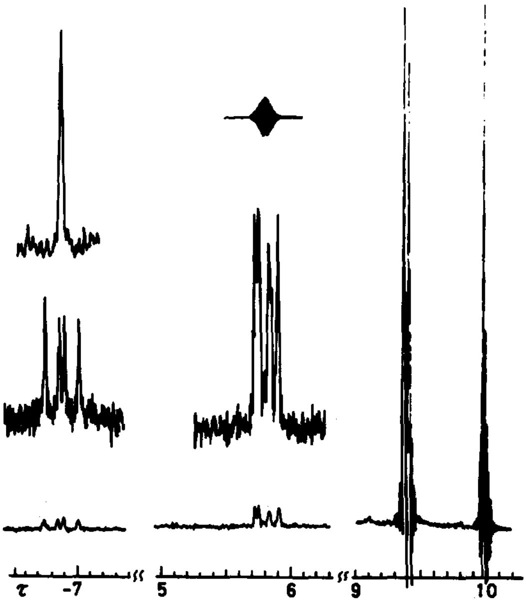

Fig. 2. 100 MHz n.m.r. spectrum of VIII in $CDCl_3$ at 36°C.

5.81, d, J=11.0 Hz, 2H and τ 5.85, d, J=15.5 Hz, 2H). Also, an appreciable high field shift of signals of t-butyl protons was observed (τ 9.39, s and τ 9.43, s, 36H). Strong paratropicity of the tridehydro[16]annulene (VIII) is clearly demonstrated by these n.m.r. spectral patterns. As summarized in Table, the n.m.r. spectra of VIII showed no essential temperature dependency, thus indicating high conformational stability of the tridehydroannulene ring.

The strong paratropicity of VIII seems to be attributable to the planar structure due to conformational stability and to a decrease of bond-alternation by the contribution of resonance structures ($VIII_a$ and $VIII_b$) which are presumably in nearly the same energy state, because 1,3,9-tridehydro[16]annulene consisting of the same number of $sp^2$- and sp-hybridized carbon atoms has been reported to show conformational mobility and to have less paratropicity than VIII (6).

Table. 100 MHz n.m.r. spectra of VIII ($\tau$-values in $CDBr_3$)

| | 36°C | 70°C | 100°C |
|---|---|---|---|
| inner-H | -7.17, d.d<br>(J=11, 15 Hz) | -7.08, d.d<br>(J=11, 15 Hz) | -6.95, d.d<br>(J=11, 15 Hz) |
| outer-H | 5.89, d<br>(J=11 Hz) | 5.86, d<br>(J=11 Hz) | 5.85, d<br>(J=11 Hz) |
| | 5.95, d<br>(J=15 Hz) | 5.87, d<br>(J=15 Hz) | 5.82, d<br>(J=15 Hz) |
| *t*=Bu | 9.43, s<br>9.46, s | 9.43, s<br>9.45, s | 9.42, s<br>9.44, s |

## References and Note

1) For review, see, " Topics in Nonbenzenoid Aromatic Chemistry, Vol. 1 ", Hirokawa Publishing Co., Tokyo (1974), p. 191.

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4) All new crystalline compounds described in this paper gave satisfactory elemental analyses and their IR, n.m.r. and mass spectral data were consistent with the assigned structures.

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