

3,13,16,26-TETRA-t-BUTYL-1,14-DIDEHYDRO[26]ANNULENE

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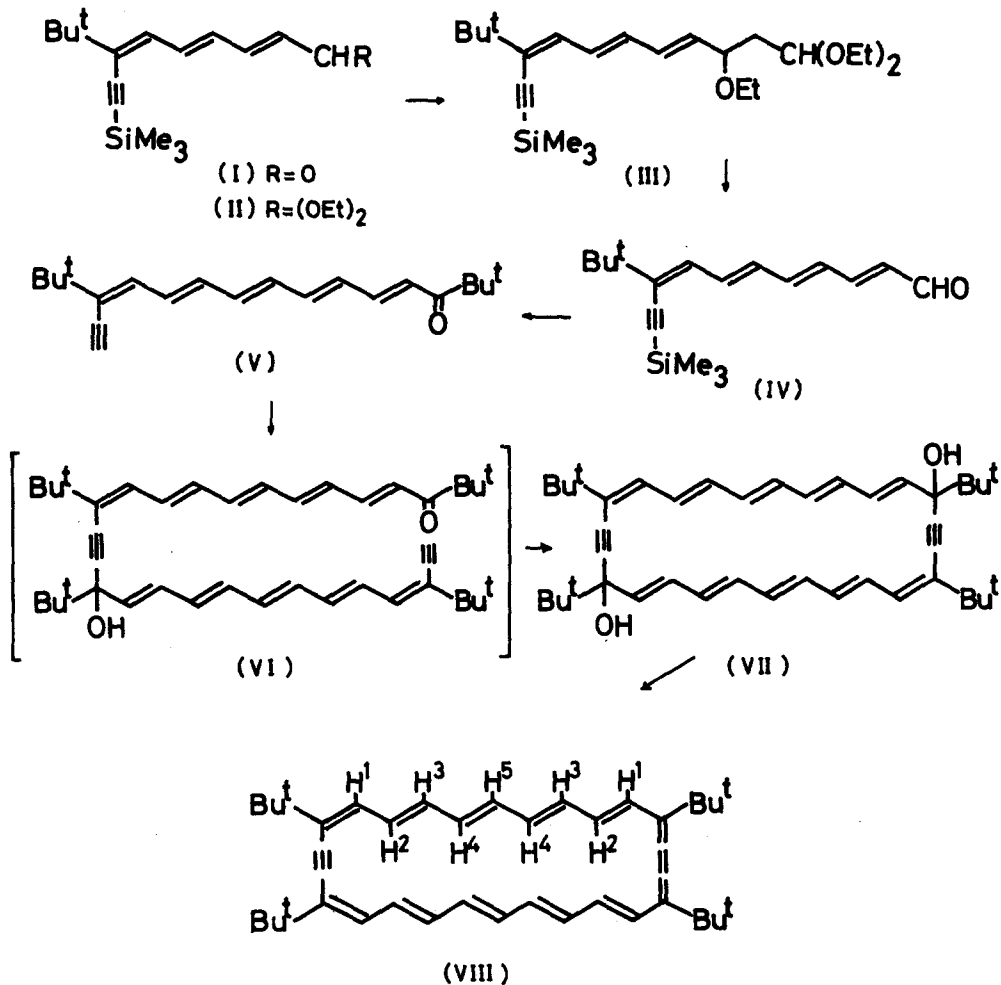
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In the previous papers, we reported the syntheses of tetrasubstituted didehydro[14]-, didehydro[18]- and didehydro[22]annulenes by dehydroxylation aromatization of cyclic polyendiyne glycols prepared by the cyclic dimerization of polyenyne ketone under conditions of the Favorskii reaction (1,2,3).

In view of the fairly strong diamagnetic ring current still observed in tetra-t-butyldidehydro[22]annulene (3), the synthesis of tetra-t-butyldidehydro[26]annulene (VIII) which has an analogous molecular framework seemed to be of considerable interest.

Trimethylsilyltriene aldehyde (I), a key intermediate in the synthesis of tetra-t-butyldidehydro[22]annulene, was converted into diethyl acetal (II) by the usual method. The diethyl acetal (II) obtained as a viscous yellow liquid [b.p. 126-128°C/0.013 mmHg] was treated with ethyl vinyl ether in the presence of borontrifluoride-etherate (4) in benzene to obtain ethoxy triene acetal (III) as a viscous yellow liquid. Treatment of the acetal (III) with an aqueous acetic acid containing sodium acetate afforded trimethylsilyltetraene aldehyde (IV) as a viscous orange yellow liquid. Condensation of pinacolone with IV under an alkaline condition yielded pentaene ketone (V) as orange crystals [m.p. 92-94°C, a 41% overall yield based on II]. A dilute solution of the ketone (V) in tetrahydrofuran was added over a period of 12 hours to a stirred suspension of finely powdered potassium hydroxide in liquid ammonia at the boiling point of

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ammonia and stirring was continued for further 8 hours at the same temperature. Crude 26-membered cyclic glycol (VII) obtained as yellow crystals was chromatographed on alumina, resulting in a separation of diastereomers, VII_a [pale yellow crystals, m.p. 277°C (decom.), 33%] and VII_b [lemon yellow crystals, m.p. 236.0-236.5°C, 60%]. The mass spectra of VII_a and VII_b exhibited molecular ion peak (M⁺) at 592 being consistent with the molecular weight of the cyclic glycol (VII) [Calcd. for C₄₂H₅₈O₂ = 592.9]. It was found that a slow addition of a dilute solution of pentaenynone (V) is essential to obtain the cyclic glycol (VII) in a high yield (93%). In view of this fact, it seems likely that the cyclic

dimerization of V under the condition of the Favorskii reaction proceeds through two steps with the intervention of initially formed keto-alcohol (VI).

Ether saturated with hydrogen chloride was added to a suspension of VII_a in ether maintained at -75°C, and then finely powdered stannous chloride dihydrate was added at the same temperature to result in a deep green solution. The reaction product dissolved in dichloromethane was chromatographed on alumina at -15°C. Elution with dichloromethane-*n*-pentane yielded 3,13,16,26-tetra-*t*-butyl-1,14-didehydro[26]annulene (VIII) as black violet crystals in a yield of 89%. Similar treatment of VII_b afforded VIII in a 86% yield. The mass spectrum of VIII showed molecular ion peak (M^+) at 558 along with strong peaks at 501 ($M^+ - 57$) and 444 ($M^+ - 114$) being 57 ($\underline{t}\text{-Bu}^+$) as base peak [Calcd. for $C_{42}H_{54} = 558.9$]. The didehydro[26]annulene (VIII) was found to be rather unstable and decomposed on attempted melting point determination. Hydrogenation of VIII in ethyl acetate-acetic acid over platinum catalyst afforded tetra-*t*-butylcyclohexacosane, m.p. 111-113°C [91%, $M^+ 588$, Calcd. for $C_{42}H_{54} = 589.1$].

The electronic spectrum of VIII displayed a broad absorption curve [$\lambda_{\text{max}}^{\text{THF}}$ ($\epsilon \times 10^{-3}$) 223.5 (15), 268 sh (14), 280 (15), 285.5 (15), 316 (24), 330 (25), 427 (170), 442 sh (150), 584 (9.6), 840 sh (0.064), 930 (0.041), 975 (0.043) nm]

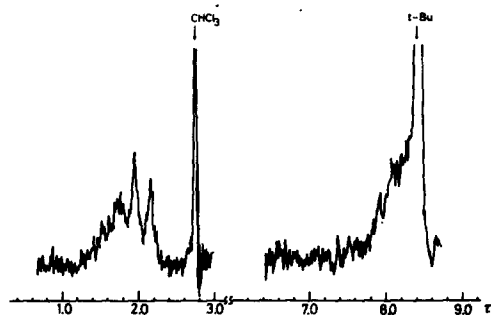


Fig. 1. The 60 MHz n.m.r. spectrum of tetra-*t*-butyl-didehydro[26]annulene (VIII) in $CDCl_3$

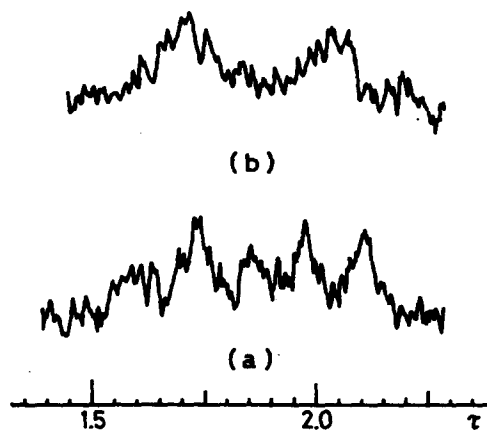


Fig. 2. The 100 MHz n.m.r. spectra of outer protons of didehydro[26]annulene (VIII) in $CDCl_3$. (a): normal spectrum. (b): irradiated at $\tau 8.20$.

in contrast with the rather sharp absorption curves of the lower members of dihydroannulenes (1,2,3).

In spite of theoretical prediction that the limit for aromaticity of cyclic conjugated $(4n+2)\pi$ electron systems will lie between 22- and 26-membered rings (5), monodehydro[26]annulene prepared recently by Metcalf and Sondheimer (6) has been proved to be diatropic. Consequently, the n.m.r. behavior of the didehydro[26]annulene (VIII) is of particular interest. As illustrated in Fig. 1, the n.m.r. spectrum of VIII exhibits signals of outer protons at τ 1.75 (poorly resolved double triplets, H^3 , H^5) and τ 2.05 (d, $J=13$ Hz, H^1). The signals of inner protons (H^2 , H^4) seemed to be submerged in the low-field tail of the signal of t-butyl protons (τ 8.39). The marked change in spectral pattern of outer protons on irradiation at τ 8.20-8.16 region as shown in Fig. 2 substantiated the presence of signals of inner protons in this region. The fact that the signals of outer protons were observed at fairly low-field indicates the presence of diamagnetic ring current in the didehydro[26]annulene (VIII) adding a further instance of aromatic 26π electron system.

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