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SYNTHESIS OF 1,5,10,14-TETRAPHENYL-6,8,15,17-TETRADEHYDRO[18]ANNULENE

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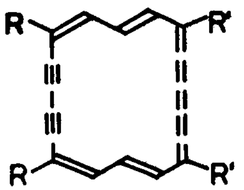
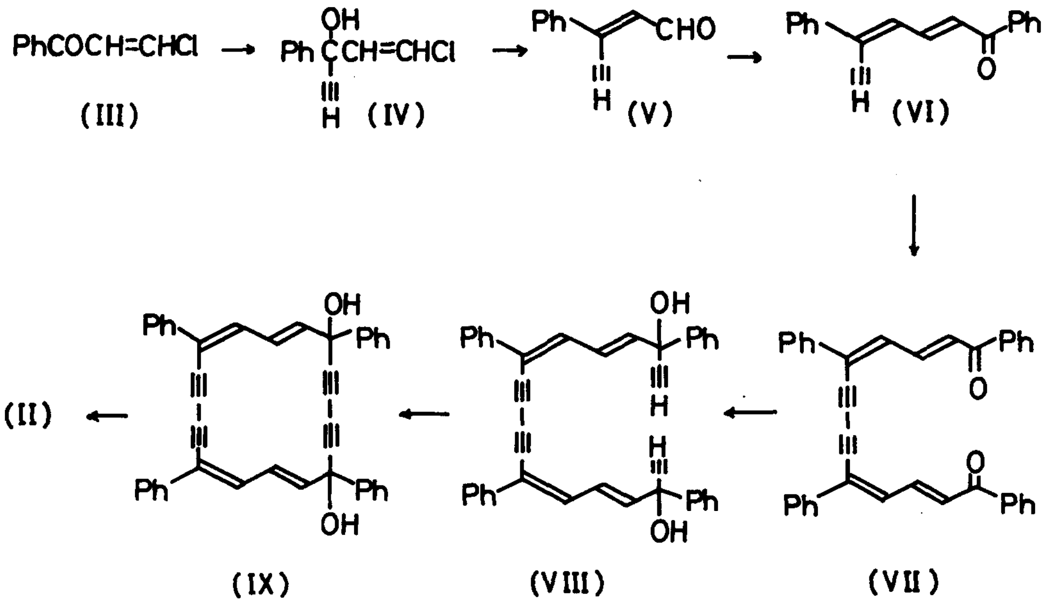
In a previous paper, we have reported the synthesis and the aromatic properties of 1,5,10,14-tetramethyl-6,8,15,17-tetradehydro[18]annulene (I) (1). Now, we wish to report the synthesis of 1,5,10,14-tetraphenyl-6,8,15,17-tetradehydro[18]annulene (II).



R=R'=Me (I)

R=R'=Ph (II)

The ethynylation of chlorovinyl phenyl ketone (III) (2) by means of ethynylmagnesium bromide in tetrahydrofuran or lithium acetylide in liquid ammonia afforded the ethynylcarbinol (IV) [Yield: 65-90%. Bp 118-119°C/3.5 mmHg. Found: C, 68.52; H, 4.78; Cl, 17.73%. Calcd. for $C_{11}H_9OCl$: C, 68.58; H, 4.71; Cl, 18.40%]. Treatment of the ethynylcarbinol (IV) with 2N sulfuric acid containing tetrahydrofuran resulted in the formation of the unstable en-yne aldehyde (V) [Yield: 61%. Pale yellow plates. Mp ca. 65°C. 2,4-Dinitrophenylhydrazone: orange needles, mp 177-178°C. Found: C, 60.71; H, 3.59; N, 16.70%. Calcd. for $C_{17}H_{12}O_4N_4$: C, 60.71; H, 3.60; N, 16.66%]. It was revealed on the basis of NMR spectroscopy that the en-yne aldehyde (V) holds cis-configuration with respect to the ethynyl and the formyl groups. The en-yne aldehyde (V) was condensed with acetophenone to yield the dien-yne ketone (VI) [Yield: 91%. Yellow crystals. Mp 82.8-83.4°C. Found: C, 88.01; H, 5.44%. Calcd. for $C_{18}H_{14}O$:



88.34; H, 5.44%]. The cupric acetate-pyridine oxidation (3) of the ketone (VI) gave the diketone (VII) [Yield: 89%. Orange crystals. Mp 159.7-160.2°C. Found: C, 88.55; H, 5.00%. Calcd. for $C_{38}H_{26}O_2$: C, 88.69; 5.09%]. The introduction of ethynyl groups to the carbonyl carbons of VII was achieved by lithium acetylide-ethylene diamine complex (4) in tetrahydrofuran. The diethynyl compound (VIII) was obtained as a viscous yellow liquid after a chromatographic purification on alumina. This substance was subjected to the Eglinton's oxidative coupling under a high dilution condition employing ether as an entraining agent (5). Since all attempts to get the cyclic glycol (IX) in crystalline state were failed, a benzene solution of the crude glycol (IX), which was obtained by percolation of the coupling product in benzene through a short column of alumina, was mixed with a solution of stannous chloride in concentrated hydrochloric acid. The black violet crystals deposited were recrystallized from benzene to give pure tetraphenyltetradehydro[18]annulene (II) [Yield: 30% based on the diketone (VII). The crystals showed no melting point, but underwent color change at ca. 190°C. Found: C, 94.83; H, 4.98%. Calcd. for $C_{42}H_{26}$: C, 95.06; H, 4.94 %. UV (in tetrahydrofuran) λ_{max} (ε): 245 (23,300), 261 (24,800), 302 (27,000), 351 (26,300), 372 (38,000), 428 (273,000), 615 (108,000), 772 (4,110) nm].

The aromatic nature of the 18 membered ring of II was established by the NMR spectrum of II. As is summarized in Table 1, the induction of diamagnetic ring current by external magnetic field is manifested by the facts that the outer proton resonance occurs at extremely low field, and the inner protons exhibit a triplet at considerably high field. The multiplet at τ 1.3 can be assigned to the signal of o-protons of the phenyl groups which are affected the deshielding effect both of the ring current of the benzene ring and the annulene system. At first sight, the down-field shift of the signals of the annulene ring protons as compared with those of the tetramethyl derivative (I) [Outer-H, τ 0.34, and inner-H, τ 15.24 in THF-d_8] seems to be attributable to the anisotropic effect of benzene rings. However, estimation of the effect on the assumption of coplanar conformation of the phenyl groups with the annulene ring using Johnson-Bovey's diagramm (7) revealed that the magnitude of down-field shift should be _ca_. 0.6 ppm for the outer protons, and _ca_. 0.3 ppm for the inner protons. Therefore, the marked down-field shift of the signal of inner protons can not be explained in terms of an anisotropic effect of the substituent groups. It is evident that further NMR data of tetradehydro[18]annulenes bearing various type of substituents are required to give a conclusive account for the interesting NMR spectral behavior. Studies along this line are now in progress.

Table 1. The NMR spectrum of II in THF-d_8 (6)

τ -Value	Multiplicity	J in Hz	Assignment
-0.31	doublet	13	outer protons
1.3	multiplet		_o_-protons of phenyl groups
2.4	multiplet		_m_,_p_-protons of phenyl groups
13.19	triplet	13	inner protons

The tetraphenyltetradehydro[18]annulene (II), thus prepared, was found to be more stable than the tetramethyltetradehydro[18]annulene (I) (1). A solution of the tetraphenyl derivative (II) in benzene or in tetrahydrofuran could be kept at room temperature without decomposition for several weeks.

The tetraphenyltetradehydro[18]annulene (II) forms 1:1 π-complex with 2,4,7-trinitrofluorenone [Found: C, 77.26; H, 3.89; N, 4.83%. Calcd. for $C_{42}H_{26} \cdot C_{13}H_5O_7N_3$: C, 78.09; H, 3.69; N, 4.99%]. The deep blue-violet complex decomposed at ca. 240°C.

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6. The NMR measurement was performed on a JNM-60HL-spectrometer operated at 60 MHz by external lock-field sweep method. The proton signals of the solvent (THF-d_8) were used as internal standards. The authors are grateful to Dr. K. Hatada and Mr. H. Okuda of the Faculty of Scientific Engineering, Osaka University for the mesurement.
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