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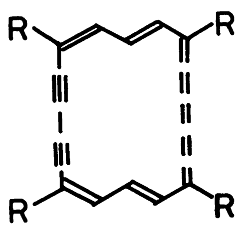
1,14-DIMETHYL-5,10-DIPHENYL- AND 1,5,10,14-TETRA-*tert*-BUTYL-6,8,15,17-TETRADEHYDRO[18]ANNULENES

Tsutomu KATAKAMI, Sachiyo TOMITA, Kunisuke FUKUI, and Masazumi NAKAGAWA
Department of Chemistry, Faculty of Science, Osaka University
Toyonaka, Osaka 560

1,14-Dimethyl-5,10-diphenyl- and 1,5,10,14-tetra-*tert*-butyl-6,8,15,17-tetradehydro[18]annulenes have been synthesized, and their aromatic nature was demonstrated by the NMR spectra. The tetra-*tert*-butyltetradehydro[18]annulene was found to be more stable and soluble than the other tetrasubstituted analogues.

In the previous papers we have reported the syntheses of tetramethyl- (I)1) and tetraphenyltetradehydro[18]annulenes (II).2) Now we wish to report the syntheses of 1,14-dimethyl-5,10-diphenyl- and 1,5,10,14-tetra-*tert*-butyl-6,8,15,17-tetradehydro[18]annulenes.

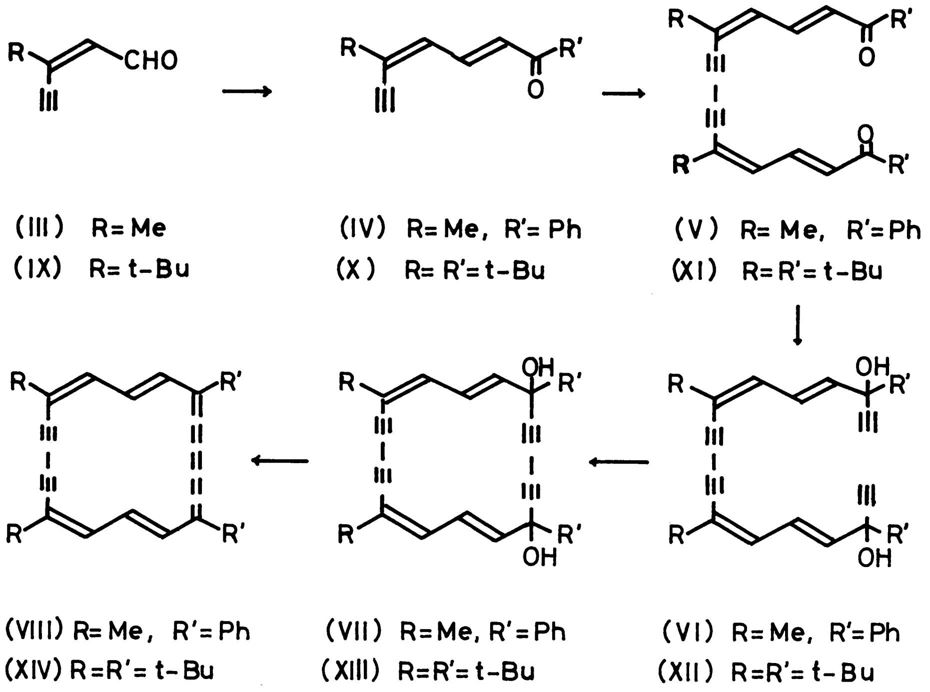


I : R=Me

II : R=Ph

The dienyne ketone (IV) was obtained by the condensation of acetophenone with the *cis*-enyne aldehyde (III)1) according to the reported method3) with modification. The Eglinton's oxidative coupling4) of the dienyne ketone (IV) gave crystalline diketone (V) as scarcely soluble yellow needles. The reaction of lithium acetylide-ethylenediamine complex5) in benzene with the diketone (V) afforded diethynyl glycol (VI) in 67% yield. Oxidative coupling of the glycol (VI) by means of cupric acetate in pyridine-methanol was performed under a high dilution condition using ether as an entraining solvent. Cyclic glycol (VII) was obtained as a viscous yellow liquid after chromatographic purification on alumina. A suspension of the cyclic glycol (VII) in pentane-benzene (2:1) was mixed with a solution of stannous chloride in concentrated hydrochloric acid. A benzene solution of the reaction product was chromatographed on alumina to give purple black crystals in an almost quantitative yield. The crystals were recrystallized from petroleum ether-benzene to yield pure VIII as purple black needles. The crystals showed no melting point, but turned to colorless at ca. 94°C. The full hydrogenation of VIII in ethyl acetate over platinum catalyst resulted in a colorless liquid which gave a molecular ion peak (M^+) at 432 in the mass spectrum (Calcd for $C_{32}H_{48}$ = 432.7).

Dimethyldiphenyltetradehydro[18]annulene (VIII) forms 1:1 π-complex with



(III) R=Me
(IX) R=t-Bu

(IV) R=Me, R'=Ph
(X) R=R'=t-Bu

(V) R=Me, R'=Ph
(XI) R=R'=t-Bu

(VI) R=Me, R'=Ph
(XII) R=R'=t-Bu

(VII) R=Me, R'=Ph
(XIII) R=R'=t-Bu

(VIII) R=Me, R'=Ph
(XIV) R=R'=t-Bu

2,4,7-trinitrofluorenone [mp 178-180°C (dec.)].

The NMR spectrum (Fig. 1) indicates that the tetradehydro[18]annulene (VIII) sustains a strong diamagnetic induced ring-current. Triplet at τ 14.20 (J=14 Hz) can be assigned unequivocally to the inner protons, and doublets at τ 0.12 (J=14 Hz) and 0.54 (J=14 Hz) can be assigned to outer protons adjacent to the phenyl and the methyl groups, respectively. A lower-field multiplet in the aromatic region (τ 1.36) can be pertinently assigned to the o-protons of the phenyl groups, which suffer the deshielding effect of the annulene system, and higher-field multiplet around τ 2.5 to the m,p-protons of the phenyl groups. The signals of methyl protons appeared at τ 6.56 as a sharp singlet.

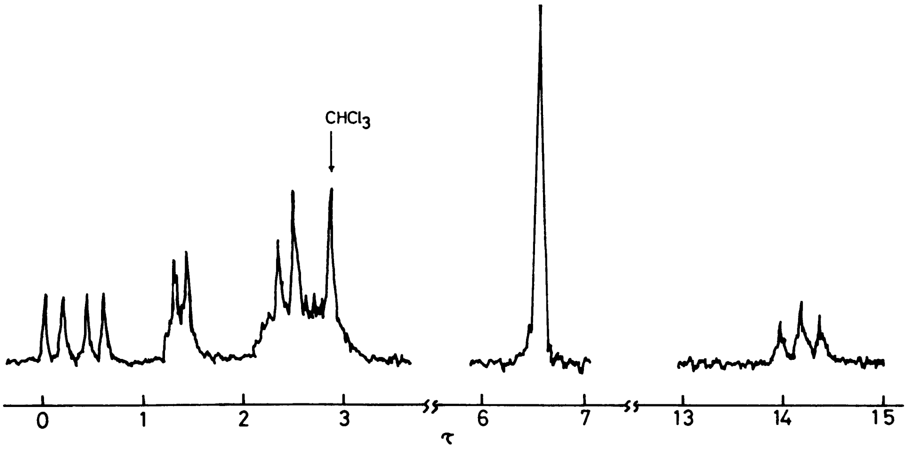


Fig. 1. NMR spectrum of VIII in $CDCl_3$ at 60 MHz

The absorption curves of the tetradehydro[18]annulenes I, II, and VIII) are recorded in Fig. 2. The regular bathochromic shift and the intensification of the longest-wavelength band according to the increase in the number of phenyl groups clearly indicate the effect of perturbation of the phenyl groups.

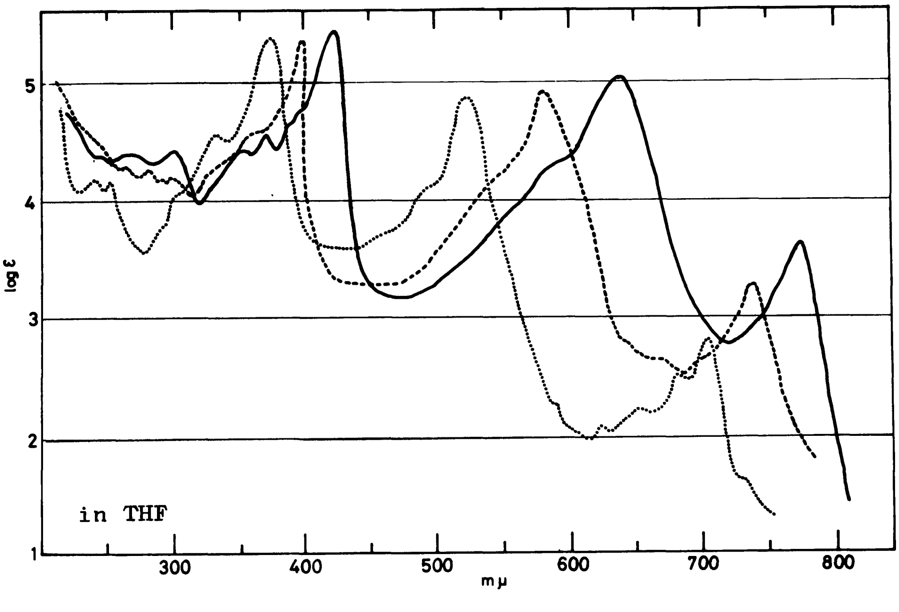


Fig. 2. Electronic spectra of the tetradehydro[18]annulenes.
·············· Me_4 (I); ------- Me_2Ph_2 (VIII); ——— Ph_4 (II)

It was observed that the stability of tetradehydro[18]annulenes increases with the increase of phenyl substitution (I < VIII < II) accompanying with the decrease in solubility in NMR solvents. Therefore, it was hoped to prepare stable and soluble tetradehydro[18]annulene bearing substituent groups which exert minor electronic effect on the dehydroannulene nucleus.

2-Chlorovinyl-tert-butyl-ethynylcarbinol obtained by the reaction of 2-chlorovinyl <u>tert</u>-butyl ketone[6] with lithium acetylide in liquid ammonia was treated with 4N sulfuric acid to yield cis-enyne aldehyde (IX). The condensation of the enyne aldehyde (IX) with pinacolone gave dienyne ketone (X) as pale yellow crystals [mp 52.9-54.9°C]. Diketone (XI) [yellow crystals, mp 202.8-205.0°C] prepared by the oxidative coupling of X according to the method of Eglinton[4] was ethynylated with lithiun acetylide-ethylenediamine complex[5] in tetrahydrofuran. Diethynyl glycol (XII) was obtained as colorless crystals [mp 185.5-187.9°C]. The oxidative coupling under a high dilution condition according to the procedure used in the preparation of VII yielded cyclic glycol (XIII) [colorless crystals, mp 239.8-240.3°C (dec.), 96%]. A solution of the cyclic glycol (XIII) in benzene was mixed with a solution of stannous chloride in concentrated hydrochloric acid. The product was chromatographed on alumina. Resulting dark brown crystals with metallic lustre (90%) were recrystallized from petroleum ether-benzene to give pure tetra-tert-butyltetradehydro[18]annulene (XIV) which decomposed at ca. 180°C. The dark brown crystals (XIV) gave beautiful reddish violet solutions in tetrahydrofuran and benzene. Hydrogenation of XIV in ethyl acetate over platinum catalyst gave tetra-tert-butylcyclooctadecane [mp 189.0-190.0°C, mass spectrum, M^+ 477. Calcd for $C_{34}H_{68}$ = 476.9].

As is summarized in Table 1, the NMR spectra indicate clearly the aromatic nature of the tetra-tert-butyltetradehydro[18]annulene (XIV).

Table 1. NMR Spectra of XIV (60 MHz)

	tert-Bu	Inner protons	Outer protons
THF-d_8	τ 7.98 s	14.92 t (J=13Hz)	-0.02 d (J=13Hz)
$CDCl_3$	7.98 s	14.89 t (J=13Hz)	-0.04 d (J=13Hz)

The electronic spectrum of XIV was found to be closely related with that of the tetramethyl analogue (I) except for a minor bathochromic shift [λ_{max} (tetrahydrofuran) 219.5 (ε 97,600), 238 (19,400), 250 (16,300), 261 (5,740), 275 (4,240), 337 (35,500), 374 (231,000), 407.5 sh (12,800), 524.5 (68,700), 621 (151), 656 (186), 707 nm (932). This fact indicates that the electronic effect of tert-butyl group on the tetradehydroannulene system is similar to that of methyl group.

XIV was found to be more stable and much more soluble than the other tetrasubstituted tetradehydro[18]annulenes (I, II and VIII). XIV forms 1:1 π-complex with 2,4,7-trinitrofluorenone [reddish purple crystals, mp 215°C (dec.)].

The crystalline compounds described in this paper gave satisfactory elemental analyses.

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