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

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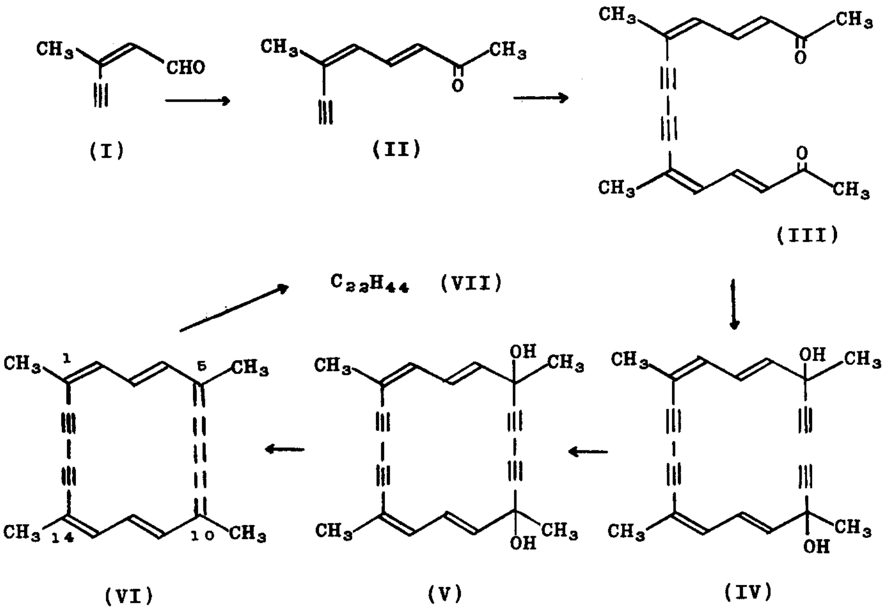
The experimental verification of Hückel's prediction on aromaticity has been achieved recently on numerous instances, especially on annulenes and dehydroannulenes by F. Sondheimer (1).

We wish to report the synthesis of a new eighteen membered aromatic system, 1,5,10,14-tetramethyl-6,8,15,17-tetradehydro-[18]annulene (VI), which contains a diacetylene and a hexapentaene units in the cycle.

The reaction of ethynylmagnesium bromide (2) with methyl chlorovinyl ketone gave the corresponding ethynyl carbinol in a good yield (81%). The anionotropic rearrangement of the ethynyl carbinol according to the method of Heilbron (3) afforded the en-yne aldehyde (I). The cis-trans ratio of I was estimated to be



ca. 95:5 on the basis of n.m.r. spectroscopy, and I was used without separation to the subsequent reaction. The condensation of acetone with the en-yne aldehyde (I) was performed according to the procedure of Heilbron (3) with a modification to yield the dien-yne ketone (II). The oxidative coupling of II with cupric acetate in pyridine (4) afforded 6,11-dimethylhexadeca-3,5,11,13-tetraen-7,9-diyn-2,15-dione [III, m.p. 94-95°C, pale yellow plates. Found: C, 81.27; H, 6.83. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%] in a quantitative yield. The bis-ethynylation reaction of the dimethyl ketone (III) employing usual ethynylation reagents, such as sodium or lithium acetylide in liquid ammonia and ethynylmagnesium bromide in tetrahydrofuran, gave fruitless results. After several experimentations, it was found that monolithium acetylide-ethylene diamine complex (5) is most appropriate. The chromatographic purification of the reaction product gave the bis-ethynyl carbinol (IV) as a yellow viscous oil in a yield of 63%. All attempts to crystallize IV were failed, but the IR. [3370 (-OH), 3300 (-C≡CH), 2190, 2050 (-C≡C-) and 970 cm^{-1} (trans-ethylene)] and n.m.r. spectra in carbon tetrachloride [8.46 s (6H) methyl, 8.05 s (6H) methyl, 7.46 s (2H) ethynyl, 6.90 broad (2H) alcohol, 4.20 d (J=15 cps) (2H) olefin, 3.70 dd (J=11 and 2) (2H) olefin, 3.07 τ dd (J=15 and 11) (2H) olefin][a,b] were found to be consistent with the structure of IV. The oxidative coupling of the bis-ethynyl carbinol (IV) in pyridine-methanol under a high dilution condition employing diethyl ether as an entraining solvent resulted predominantly in the intra-molecular cyclization. The chromatography of the coupling product on alumina yielded two kinds of crystals in a yield of 69.3%, i.e., V_a [m.p. 228-230°C (decom.), Found: C, 83.17; 6.22. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37%. Mol. wt., Found: 325 (vapor-phase osmometry). Calcd. for $C_{22}H_{20}O_2$: 316. IR. 3360 (singlet) (-OH), 2190, 2150 (-C≡C-), 968 cm^{-1} (trans-ethylene). UV. (ethanol) λ_{max} 245* (28,600), 254 (49,400), 263.5 (61,400), 292 (5,120), 308* (6,570), 327 (11,600), 344 (18,800), 368 mμ (ε

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a) T.M.S. was used as an internal standard. The s, d and dd are the abbreviation of singlet, doublet and double doublet, respectively.

b) The addition of D_2O caused the disappearance of the signal at 6.90 τ and the appearance of a new signal due to H_2O at 5.27 τ .

c) The asterisks on the figures indicate the shoulders.

20,100)]$^{c)}$ and V_b [m.p. 220-223°C (decom.), Found: C, 83.61; H, 6.38. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.23%. Mol. wt., Found: 312 (vapor-phase osmometry). Calcd. for $C_{22}H_{20}O_2$: 316. IR. 3330, 3270 (doublet) (-OH), 2190, 2150 (-C≡C-), 972 cm^{-1} (trans-ethylene). UV. (ethanol) λ_{max} 246* (27,700) 254 (49,500), 263 (63,500), 292 (3,300), 307* (5,110), 326 (10,500), 344 (17,600), 369 mμ (ε 19,300)]$^{c)}$. As indicated above, the analytical and the spectroscopic data of both of the crystals, V_a and V_b, were found to be almost identical, however, the determination of the mixed melting point showed an appreciable depression. These facts seem to indicate that the crystals, V_a and V_b, are the meso- and the dl-isomers of the eighteen membered cyclic glycol (V).

A suspension of V (V_a or V_b, or a mixture of both of them) in n-pentane-benzene (2:1) was mixed with a solution of stannous chloride dihydrate in concentrated hydrochloric acid and stirred under an atmosphere of nitrogen (6). Further amount of benzene was added to the stirred mixture in small portions. A benzene solution of the reaction product was chromatographed on alumina yielding purple black crystalline powder in a yield of 56% together with the recovered glycol (V). A solution of the crystalline powder in benzene-petroleum ether (1:1) was kept in a refrigerator (-14°C) resulting in black purple cubes with metallic lustre [Found: C, 93.56; H, 6.40. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43%. The crystals had no melting point, but underwent color change to yellowish brown at ca. 180°C. IR. (KBr-disk) 2940, 2910, 2840, 1535, 1495, 1485, 1365, 1350, 1277, 1265, 1150, 1020, 953, 880, 860 cm^{-1}. UV. (tetrahydrofuran) λ_{max} 217.5 (78,000), 237 (15,200), 248.5 (14,700), 259* (5,150), 266* (4,120), 272* (3,670), 290* (4,810), 306* (10,400), 334.5 (35,100), 371 (228,000), 440* (2,160), 452 (3,230), 490 (11,400), 520.5 (74,200), 582* (185), 596 (124), 622 (121), 639* (129), 652 (164), 682 (318), 705 (614), 720 mμ (ε 37)]$^{c)}$. The full hydrogenation of the purple black crystals in acetic acid over pre-reduced platinum catalyst (hydrogen absorption: obs., 12.75. calcd. for VI, 13 moles) followed by chromatography on alumina gave a colorless oil which could be recrystallized from ethyl acetate-methanol at a low temperature. The hydrogenation product was the tetramethylcyclooctadecane (VII), since the elemental analysis and the molecular weight determined by a massspectrometry [Found: C, 85.60; H, 14.02. Mol. wt. (M/e), 308] and the n.m.r. spectrum [9.15 (CH_3), 8.73 (CH_2), 8.2 τ (CH)] were found to be consistent with the structure of VII ($C_{22}H_{44}$: Mol. wt., 308).

The tetramethyl-tetradehydro-[18]annulene (VI) thus prepared, containing 18 out-of-plane π-electrons, should be aromatic, since Hückel's rule is obeyed (n=4), and also the molecule might presumably be planar having only two "inner" protons in remote positions. In accord with the expectation, the n.m.r. spectrum of the tetradehydro-[18]annulene (VI) provides the evidence for π-electron delocalization[d]. The n.m.r. spectrum of VI in perdeutero-tetrahydrofuran exhibited three groups of signals, but some difficulties were encountered in detecting the high field signals owing to the poor solubility of VI in deuterated solvents. However, the high field portion of spectrum was scanned 10 times and treated by means of C.A.T. technique[e] clearly revealing the presence of signals at an extremely high field (The signals are shown in the right upper part of Fig. 1). The singlet at 7.42 τ is assigned to the protons of methyl groups, the doublet at 0.34 τ (J=16 cps) is due to the four equivalent outer protons, and the triplet

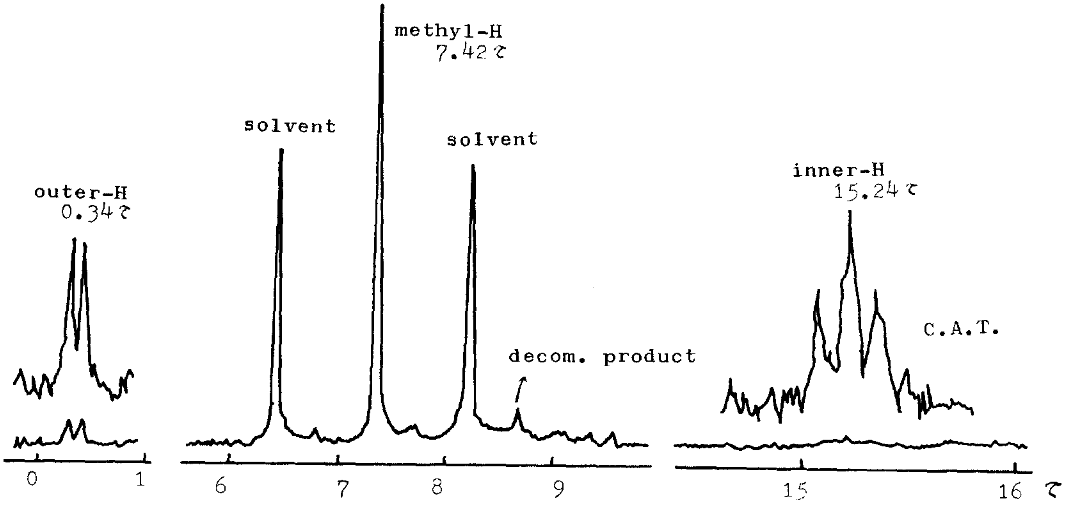

Fig. 1. The N.m.r. Spectrum of the Tetramethyl-tetradehydro-[18]annulene (VI) in THF-d_8 at 22.5°C.

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[d] The measurements were performed on a JNM-4H-100 spectrometer at 100 Mc/sec. The authors wish to thank Dr. K. Hatada and Mr. Y. Terawaki of the Faculty of Scientific Engineering, Osaka University for the measurements.

[e] A JNM-RA-I Spectral Accumulator (Japan Electron Optics Laboratory) was used.

at 15.24 τ (J=1.6 cps) to the two equivalent inner protons.

The n.m.r. spectrum of VI exhibits essentially no change in the region of -60 to +64°C indicating the rigidity of the molecule provided by the presence of the straight rods of diacetylene and hexapentaene units. The data are summarized in Table I. Both of the signals due to the outer protons and the methyl protons shift to more lower field with the decreasing temperature, on the other hand, the high field signals arising from the inner protons move to more higher field at lower temperature, but the magnitude of the shifts was found to be very much smaller than those of reported for [14]- and for [18]annulenes (1b, 7).

TABLE I

The N.m.r. Spectra of the Tetradehydro-[18]annulene (VI)

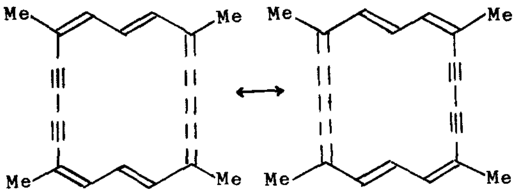
Temp. (°C)	outer protons doublet (center)	methyl protons singlet	inner protons triplet (center)
-60	0.10 τ	6.65 τ	15.66 τ
-40	0.15	6.81	15.56
-20	0.19	6.98	15.49
0	0.27	7.20	15.38
22.5	0.34	7.42	15.23 (15.24)$^{+}$
40	0.41	7.60	15.09
64^{++}	0.44	7.78	14.99

+ This value was obtained by a C.A.T. method in $CDCl_3$ (cf., Fig. 1).

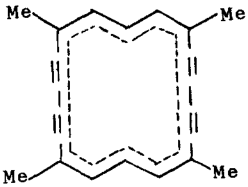
++ The measurement at higher than 64°C could not be realized owing to the decomposition of VI.

The n.m.r. spectrum not only indicates the delocalization of π-electrons in the rather rigid planar or near planar molecule, also suggests the equivalence of the outer protons. Therefore, the structure of the tetradehydro-[18]-annulene (VI) can be regarded as the resonance hybrid of the two Kekulé-structures (VI_a and VI_b) or may be represented more appropriately by the symmetrical formula, VIc.

The tetramethyl-tetradehydro-[18]annulene (VI) was found to be rather unstable compound. Exposure of the crystals of VI to air and a diffused day light at a room temperature caused a complete decomposition in a few hours, however, a solution of pure VI in benzene-petroleum ether could be kept without decompo-



(VI$_a$) (VI$_b$)



(VI$_c$)

sition for two weeks in a refrigerator.

It was found that VI forms a 1:1 π-complex with 2,4,7-trinitrofluorenone [purple black needles. The crystals had no melting point, but a color change to grey was observed at ca. 210°C. Found: C, 69.46; H, 3.86; N, 7.14. Calcd. for $C_{35}H_{23}O_7N_3$: C, 70.34; H, 3.88; N, 7.03%].

Further studies on the chemical properties of VI are now in progress.

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