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SYNTHESIS OF BENZANNELATED TRISDEHYDRO[10.10.2][14]ANNULENO[14]ANNULENES

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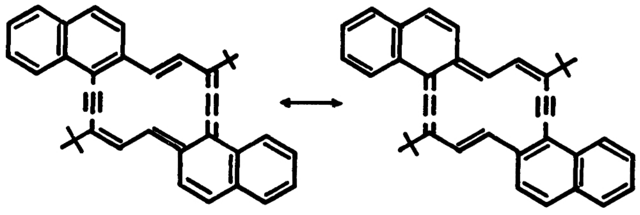
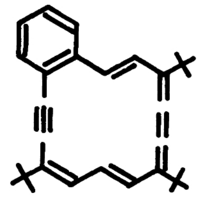
Our recent studies seem to indicate that annulenoannulenes consisting of two same size nuclei should be fused systems of two diatropic moieties. In order to obtain further information on the nature of annulenoannulene, the synthesis of dibenzo- and benzotrisdehydro[14]annuleno[14]annulenes has been performed.

Annelation of one or more benzenoid rings for annulene rings usually causes progressive reduction of tropicities of the cyclic systems.1∿6) However, it has been found that the dinaphtho-di-*t*-butylbisdehydro[14]annulene (I) sustains a strong diamagnetic ring current comparable to non-annelated analogues,7) and the important role of equivalent Kekulé structures ($I_a \leftrightarrow I_b$) in π-electron delocalization in annelated annulene ring has been pointed out by the present authors (M.N. and M.I.).8) Similar results have been obtained recently on dibenzo derivatives of dihydropyrene9) and hexahydrocoronene series.10)

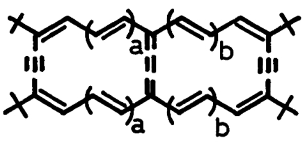
Our recent studies on diatropic annulenoannulenes (II)11∿17) seem to suggest that the bicyclic annulenes (II) should be regarded as fused systems consisting of two diatropic moieties, but not as peripheral conjugated systems perturbed by the central acetylenic bridge.



Ia Ib



III



II : a=b=1, II : a=1, b=2

II : a=b=2, II : a=1, b=3

If the dibenzotrisdehydro[14]annuleno[14]annulene (XVI) is a peripheral 22π-electron system being a resonance hybrid of two equivalent Kekulé structures containing *o*-quinonoid system, a marked increase of diatropicity should be observed as compared with the monobenzo analogue (XXII) just as the case of I, but if the

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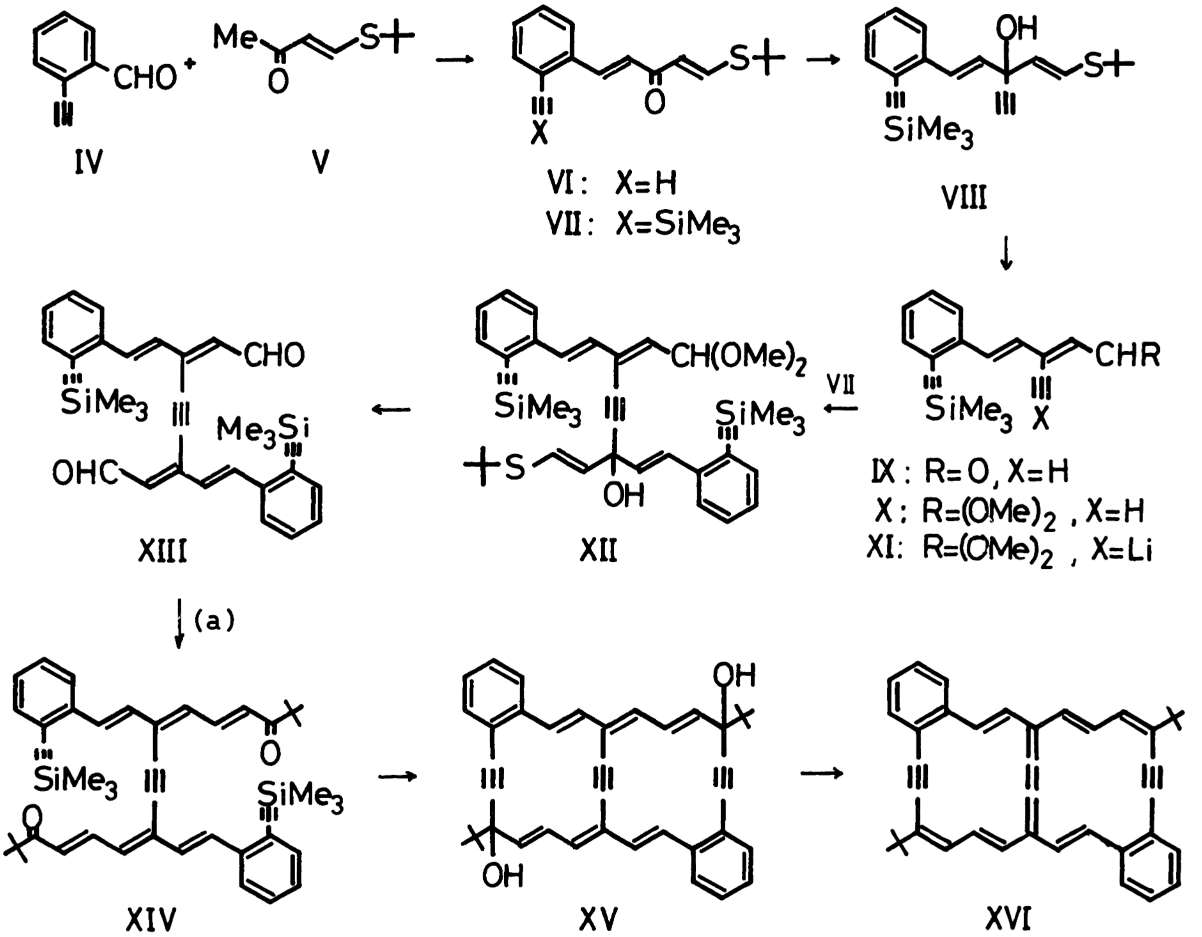
dibenzo derivative (XVI) is a condensed system consisting of two 14π-electron systems, the ^{1}H NMR spectrum should be similar to that of benzo-tri-*t*-Butyl-bisdehydro[14]annulene (III)18) or the monobenzo annelated annulenoannulene (XXII).

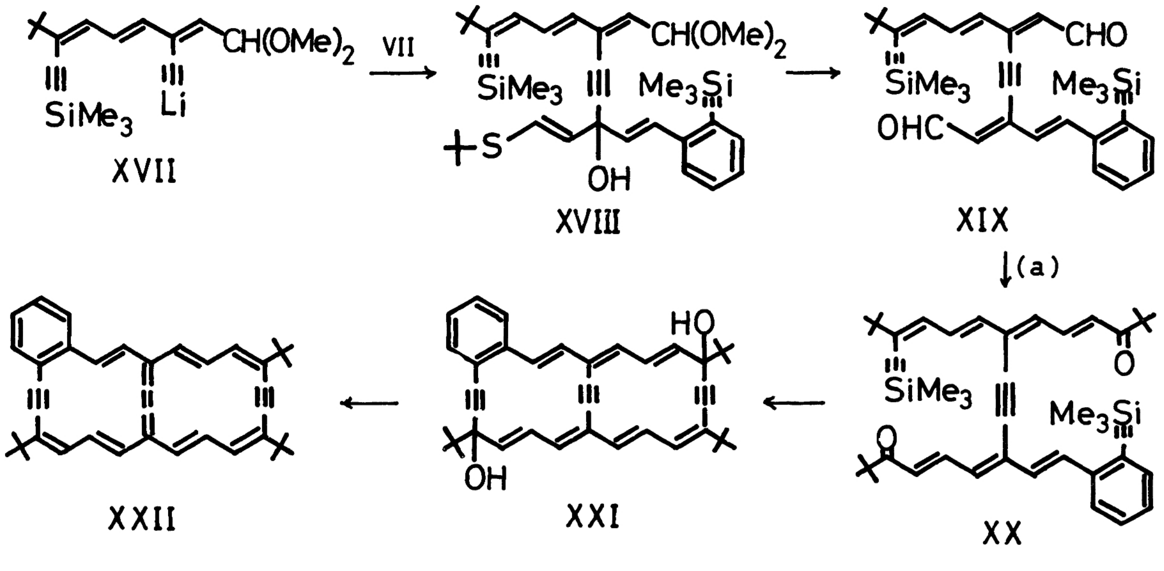
This communication is concerned with the synthesis of dibenzo- and benzo-trisdehydro[14]annuleno[14]annulenes (XVI and XXII), and their properties will be discussed in the subsequent paper.

2-Ethynylstyryl ketone (VI, yellow cryst., mp 99.9-101.4°C, mass(m/e): 270 (M$^+$))19) obtained by the aldol condensation of 2-ethynylbenzaldehyde (IV)20) with *t*-butylthiovinyl methyl ketone (V)12) was treated successively with lithium diethylamide and trimethylchlorosilane to give trimethylsilyl derivative (VII, yellow cryst., mp 96.6-97.4°C, 54.0%).21) The product (VIII) of reaction of VII with lithium acetylide in THF was treated without isolation with 1M sulfuric acid to yield the aldehyde (IX, yellow cryst., mp 64.1-65.2°C, 73.8%, mass(m/e): 278 (M$^+$)), which was converted into the lithio derivative (XI) of the dimethyl acetal (X) in the usual way. An acid treatment of the product (XII) of the reaction of XI with VII gave the dialdehyde (XIII, yellow cryst., mp 138.5-139.0°C, 38.5%, mass (m/e): 530 (M$^+$)). The carbanion (a) derived from diethyl 3,3-dimethyl-2-oxobutyl-phosphonate (t-BuCOCH$_2$P(O)(OEt)$_2$)22) was allowed to react with XIII to give the



diketone (XIV, yellow cryst., mp 140.5-141.3°C, 67.4%, mass(m/e): 694 (M$^+$)). A solution of XIV in THF was added at -35°C to a stirred suspension of potassium hydroxide in liquid ammonia. Chromatographic purification of the product on alumina gave pure bicyclic glycol (XV, pale yellow fine cryst., mp 270°C (dec.), 95.0%, mass(m/e): 550 (M$^+$)).23) A solution of XV in THF was mixed at -55°C with a solution of tin(II) chloride dihydrate in ether saturated with hydrogen chloride, and then dichloromethane was added to the mixture. The reaction mixture was worked up in the usual manner to give slightly crude XVI (74.8%) which was chromatographed on alumina to afford pure XVI (deep greenish violet cryst., mp > 280°C, mass(m/e): 516 (M$^+$)).

The synthesis of benzotrisdehydro[14]annuleno[14]annulene (XXII) could be achieved by an analogous reaction sequence. The lithio derivative (XVII) of dimethyl acetal12) was allowed to react with the trimethylsilyl ketone (VII) to yield the hydroxy acetal (XVIII) which was treated with an acid to give the dialdehyde (XIX, yellow cryst., mp 113.7-115.0°C (dec.), 44.0%, mass(m/e): 536 (M$^+$)). The dialdehyde (XIX) was found to be rather unstable. The reaction of carbanion of the ketophosphonate (a) with the dialdehyde (XIX) in DME afforded the diketone (XX, yellow cryst., mp 175.5-176.5°C (dec.), 58.3%, mass(m/e): 700 (M$^+$)).



Treatment of XX with potassium hydroxide in liquid ammonia gave XXI (high melting isomer, pale yellow fine cryst., mp *ca.* 245°C (dec.), mass(m/e): 538 (M$^+$-OH), 33.2%; low melting isomer, pale yellow fine cryst., mp *ca.* 240°C (dec.), mass(m/e): 538 (M$^+$-OH), 28.2%). Ether saturated with hydrogen chloride was added to a mixture of XXI (a mixture of the isomers), tin(II) chloride dihydrate and THF. After the mixture had been stirred at -60 ∿ -40°C for 30 min., the resulting deeply colored solution was worked up to give XXII (deep violet cryst., mp > 280°C, 86.1%, mass (m/e): 522 (M$^+$), 507 (M$^+$-Me), 465 (M$^+$-*t*-Bu)).

References and Notes

1) K. Endo, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 1970, 2557.

2) J. Ojima, Y. Yokoyama, and T. Yokoyama, *Chem. Lett.*, 1974, 1261; J. Ojima, K. Kimura, and T. Yokoyama, *ibid.*, 1975, 207; J. Ojima, Y. Yokoyama, and T. Yokoyama, *ibid.*, 1975, 487.

3) R. T. Weavers and F. Sondheimer, *Angew. Chem.*, 86, 167 (1974).

4) R. T. Weavers, R. R. Jones, and F. Sondheimer, *Tetrahedron Lett.*, 1975, 1043.

5) U. E. Meissner, A. Gensler, and H. A. Staab, *Angew. Chem.*, 88, 374 (1976); *idem*, *Tetrahedron Lett.*, 1977, 3.

6) M. Iyoda and M. Nakagawa, *Chem. Lett.*, 1975, 815.

7) M. Iyoda, M. Morigaki, and M. Nakagawa, *Tetrahedron Lett.*, 1974, 817.

8) M. Iyoda, M. Morigaki, and M. Nakagawa, *Tetrahedron Lett.*, 1974, 3677.

9) R. H. Mitchell, R. J. Carruthers, and L. Mazuch, *J. Am. Chem. Soc.*, 100, 1007 (1978).

10) T. Otsubo, R. Gray, and V. Boekelheide, *J. Am. Chem. Soc.*, 100, 2449 (1978).

11) T. Kashitani, M. Iyoda, S. Akiyama, and M. Nakagawa, *J. Am. Chem. Soc.*, 97, 4424 (1975).

12) S. Akiyama, M. Iyoda, and M. Nakagawa, *J. Am. Chem. Soc.*, 98, 6410 (1976).

13) M. Osuka, Y. Yoshikawa, S. Akiyama, and M. Nakagawa, *Tetrahedron Lett.*, 1977, 3719.

14) S. Nakatsuji, S. Akiyama, and M. Nakagawa, *Tetrahedron Lett.*, 1977, 3723.

15) S. Nakatsuji, S. Akiyama, and M. Nakagawa, *Tetrahedron Lett.*, 1978, 1483.

16) H. Nakanishi, S. Akiyama, and M. Nakagawa, *Chem. Lett.*, 1977, 1515.

17) Y. Kai, N. Yasuoka, N. Kasai, S. Akiyama, and M. Nakagawa, *Tetrahedron Lett.*, 1978, 1703.

18) A. Yasuhara, T. Satake, M. Iyoda, and M. Nakagawa, *Tetrahedron Lett.*, 1975, 895.

19) All the new compounds gave satisfactory elemental analyses, unless otherwise stated, and the NMR and IR spectra were found to be consistent with the assigned structures.

20) J. Ojima, T. Yokomachi, and T. Yokoyama, *Chem. Lett.*, 1972, 633.

21) A mixture of *cis* and *trans* isomers with respect to the carbonyl and *t*-butylthio groups.

22) G. Sturz, *Bull. Soc. Chim. France*, 1964, 2349.

23) The elemental analyses of XV gave unsatisfactory results, presumably owing to incomplete combustion.

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