

SYNTHESES OF DIBENZO[*c*; *j*]-7,14-DI-*t*-BUTYL-1,8-BISDEHYDRO[14]ANNULENE AND
 BENZO[*c*]-NAPHTHO[1,2-*j*]-7,14-DI-*t*-BUTYL-1,8-BISDEHYDRO[14]ANNULENE

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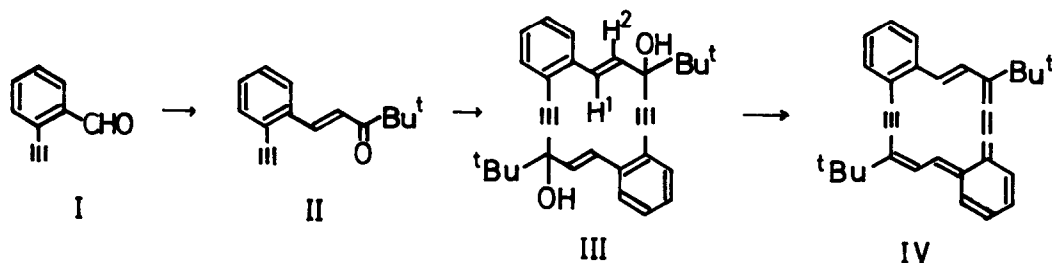
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Suppression of diatropicity of 1,8-bisdehydro[14]annulene by annelation with a benzene (1) was found to be larger than the case of fusion with a naphthalene nucleus (2). In view of the fact that annelation of 1,8-bisdehydro[14]annulene with two naphthalene nuclei at the positions which make possible to write equivalent valence-bond structures including fused benzenoid rings enhanced markedly the diatropicity of the annulene at the expense of stability of the molecule (3), synthesis of dibenzobisdehydro[14]annulene (IV) seemed to be of interest in comparison of the diatropicity with the dinaphtho analogue.

The aldol condensation of 2-ethynylbenzaldehyde (I) (4) with pinacolone (KOH-EtOH-H₂O) yielded *o*-ethynylbenzalpinacolone (II), yellow crystals, mp 102.1-102.6°C, 46.6%. A solution of II in tetrahydrofuran was slowly added to a stirred suspension of powdered potassium hydroxide in liquid ammonia at -30~-40°C. The product was chromatographed on silica gel (Merck) and eluted with ether-benzene (1:5). Fourteen membered cyclic glycol (III) was obtained as colorless crystals, mp 265.3-267.7°C, 67%, M⁺ 424, NMR (CDCl₃): τ 2.18 (d, J=16 Hz, 2H, H¹), 2.68 (m, 8H, phenyl-H), 3.55 (d, J=16, 2H, H²), 8.00 (broad s, 2H, OH), 8.83 (s, 18H, *t*-Bu). Treatment of III in ether with stannous chloride dihydrate in the same solvent saturated with hydrogen chloride under nitrogen atmosphere gave a deep blue solution, which rapidly changed into pale yellow solution even at -78°C. However, a diluted solution could be kept for a while, and the elec-



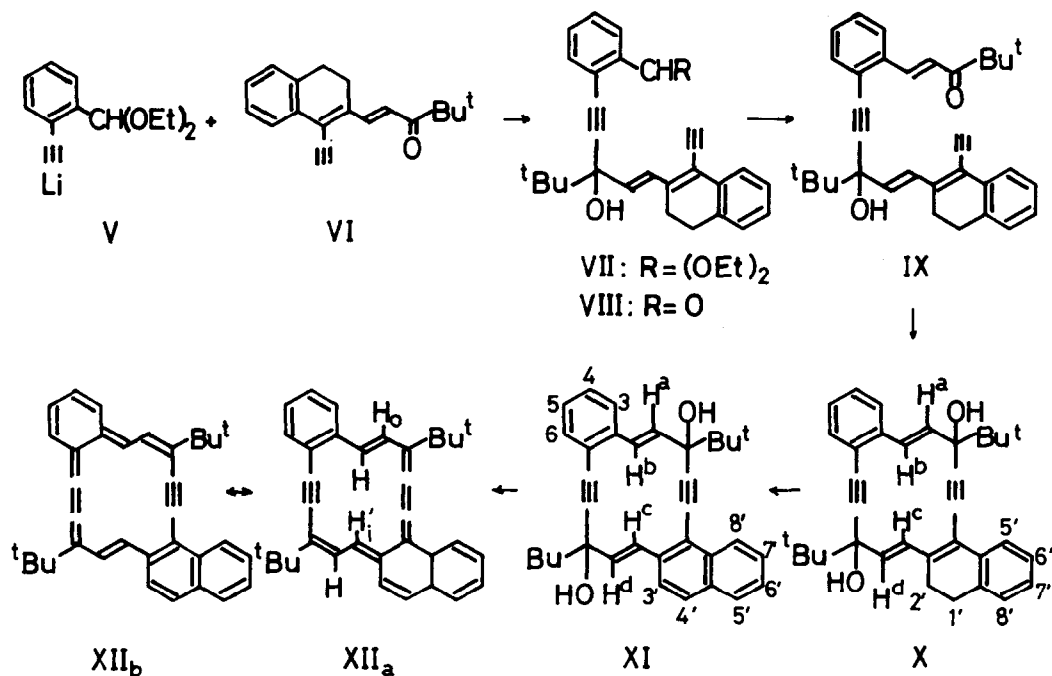
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tronic spectrum could be measured at -78°C . A diluted solution of accurately weighed III in tetrahydrofuran was mixed at -78°C with a solution of stannous chloride dihydrate in the same solvent saturated with hydrogen chloride. After being kept at -50°C for 5 min., the solution was subjected directly to measurement of electronic spectrum. The ϵ -values were estimated assuming quantitative conversion of III into IV. As illustrated in Fig. 1, close similarity of the absorption curve with that of dinaphtho-di-*t*-butylbisdehydro[14]annulene (3) showed formation of dibenzo-di-*t*-butylbisdehydro[14]annulene (IV). However, all attempts to measure the NMR spectrum of IV could not be realized owing to rapid decomposition in rather concentrated solution suitable for NMR spectroscopy.

Because it was anticipated that replacement one of two benzene rings with a naphthalene nucleus may afford stability, we have carried out the synthesis of benzo-naphtho-di-*t*-butylbisdehydro[14]annulene (XII).

Crude hydroxy acetal (VII, light brown liquid) obtained by the reaction of lithio derivative (V) of 2-ethynylbenzaldehyde diethyl acetal (4) with ketone (VI) (5) was hydrolyzed with aqueous tartaric acid to give hydroxyaldehyde (VIII) as an amorphous yellow solid, mp $44-46^{\circ}\text{C}$, 53%, M^+ 362 (6). Product of the condensation of VIII with pinacolone (9 eq.) (KOH-EtOH-H₂O, under N₂, $15-18^{\circ}\text{C}$, 40 hrs.) was chromatographed on silica gel (Merck). Elution with ether-benzene (1:19) gave IX, pale yellow amorphous solid, mp $49-50^{\circ}\text{C}$, 62%, M^+ 476 (6).

Crystals obtained on treatment of IX in tetrahydrofuran with a suspension of potassium hydroxide in liquid ammonia at the boiling point were chromato-



graphed on alumina (Merck, Act. II-III). Elution with benzene-ether (9:1~8:2) gave a diastereomer of 14-membered cyclic glycol (X_a), colorless crystals, mp 199.5-201.5°C, 4%, M^+ 476, NMR ($CDCl_3$): τ 2.02 (d, $J=15.8$ Hz, 1H, H^b), 2.13 (d, $J=16.0$, 1H, H^c), 2.20-2.90 (m, 8H, H^a-H^e , $H^{a'}-H^{e'}$), 3.51 (d, $J=15.8$, 1H, H^a), 3.78 (d, $J=16.0$, 1H, H^d), 7.19 (m, 1H, $H^{1'}$), 7.37 (m, 1H, $H^{2'}$), 7.72 (s, 1H, OH), 8.79 (s, 9H, t -Bu), 8.85 (s, 9H, t -Bu). Further elution with ether and ether-ethyl acetate (1:1) yielded another diastereomer (X_b), colorless crystals, mp 203.0-204.0°C, 64%, M^+ 476, NMR ($CDCl_3$): τ 2.05 (d, $J=16.0$ Hz, 1H, H^b), 2.13 (d, $J=16.0$, 1H, H^c), 2.02-2.90 (m, 8H, H^a-H^e , $H^{a'}-H^{e'}$), 3.51 (d, $J=16.0$, 1H, H^a), 3.80 (d, $J=16.0$, H^d), 7.13 (m, 1H, $H^{1'}$), 7.41 (m, 1H, $H^{2'}$), 7.76 (s, 1H, OH), 7.82 (s, 1H, OH), 8.81 (s, 9H, t -Bu), 8.85 (s, 9H, t -Bu).

A solution of X_b and DDQ (2 eq.) in benzene was stirred at 60°C for 1 hr., and the solution was passed through a column of alumina (Merck, Act. II-III). Elution with ether and ether-ethyl acetate (1:1) gave XI, colorless crystals, mp ca. 212°C (dec.), 61%, M^+ 474, NMR ($CDCl_3$): τ 1.57 (m, 1H, $H^{a'}$), 1.90 (d, $J=16.0$ Hz, 1H, H^b), 1.86 (d, $J=16.0$, 1H, H^c), 2.05-2.75 (m, 9H, H^a-H^e , $H^{a'}-H^{e'}$), 3.40 (d, $J=16.0$, 1H, H^a), 3.48 (d, $J=16.0$, 1H, H^d), 7.63 (s, 1H, OH), 7.72 (s, 1H, OH), 8.74 (s, 9H, t -Bu), 8.80 (s, 9H, t -Bu).

A solution of XI in ether or tetrahydrofuran was treated with stannous chloride-hydrogen chloride under argon atmosphere at a low temperature resulting in a deep bluish purple solution. The deeply colored solution was found to be unstable and gradual decomposition was observed even at -40°C. Electronic spectrum could be obtained using a diluted solution prepared by a similar procedure used in the case of dibenzo analogue (IV). The absorption curve illustrated in Fig. 1, indicates clearly the formation of benzo-naphtho-di- t -butyl-

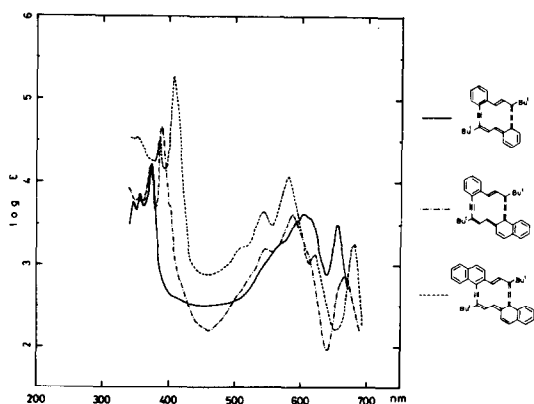


Fig. 1. Electronic spectra of annelated bisdehydro[14]annulenes in THF.

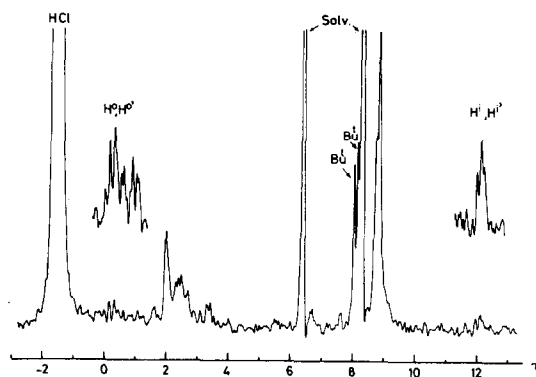


Fig. 2. 100 MHz NMR spectrum of XI in $THF-d_8$ at -51°C.

bisdehydro[14]annulene (XII) being closely related with that of dinaphtho-di-*t*-butylbisdehydro[14]annulene (3). A solution of stannous chloride dihydrate in THF- d_6 saturated with deuterium chloride was added at -78°C under argon atmosphere to a solution of XI in the same solvent placed in a NMR tube. After being shaken for 5 min. at -50°C , the solution was directly subjected to measurement of NMR spectrum at -51°C . As illustrated in Fig. 2, excessive signals were observed owing to a rather fast decomposition of XII in a concentrated solution. But the signals at τ 12.05, 8.11 and 8.01 could be assigned to the inner and two *t*-butyl protons, respectively. The signals at τ 0.15 and 0.50 could be ascribed to the outer protons. The assignment was confirmed by double resonance technique.

In view of the high conformational stability of 1,8-bisdehydro[14]annulene, the difference in chemical shifts between inner and outer protons ($\tau_i - \tau_o$) can be regarded as a measure of magnitude of ring current. The values for annelated bisdehydro[14]annulenes are summarized in Table. The value for benzonaphtho-di-*t*-butylbisdehydro[14]annulene (XII) was found to be smaller than that for analogous dinaphtho derivative (3). Two Kekulé type structures (XII_a and XII_b) are possible with respect to the annulene ring in XII. However, the struc-

Table. $\tau_i - \tau_o$ -Values for Annelated Bisdehydro[14]annulenes

	$\tau_i - \tau_o$	$\tau'_i - \tau'_o$
Monobenzo- (1)	8.16	7.62
Mononaphtho- (2)	11.02	10.70
Benzonaphtho-	11.90	11.55
Dinaphtho- (3)	13.67	—

tures are not equivalent containing 1,2-naphthoquinone structure in XII_a and *o*-benzoquinoid structure in XII_b. Consequently, enhancement of diatropicity by annelation with two benzenoid nuclei should be smaller in XII than the dinaphtho analogue. The mononaphtho derivative has a larger value than the monobenzo derivative indicating that annelation with a benzenoid system which requires larger energy in the transformation of benzenoid into *o*-quinoid structure suppresses more strongly the diatropicity of annulene ring. The observed value for XII seems to reflect combined effect of these two factors.

References and Note

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- 6) The IR, NMR and mass spectroscopic data are consistent with the assigned structure.