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ATTEMPTED SYNTHESIS OF DINAPHTHO-DI-t-BUTYLDIDEHYDRO[18]ANNULENE AND SYNTHESIS OF BIS(DIHYDRONAPHTHO)-ANALOGUE

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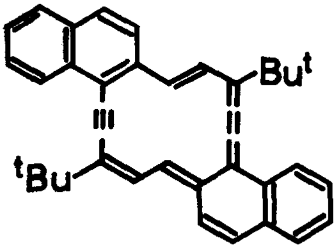
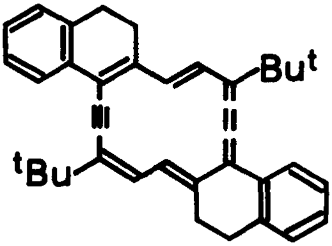
The finding that the diatropicity of dinaphtho[2,1-f:2',1'-m]-3,10-di-t-butyl-1,8-didehydro[14]annulene (I) (1) is comparable to that of non-annelated reference compound (II) (1) prompted us to prepare analogous 18π-electron system to get further information on the effect of annelation on the ring current of annulene system.



I



II

The preparation of bis(dihydronaphtho)-di-t-butyldidehydro[18]annulene (VIII) as a non-annelated reference compound was carried out by the reaction sequence outlined in Scheme 1.

Treatment of ethoxy acetal (III) (2) with aqueous dioxan-hydrochloric acid yielded aldehyde [V, pale yellow crystals, mp 110.0-111.8°C, m/e 208 (M^+), 48%] together with a small amount of IV [pale yellow liquid, 9%] which gave V on further treatment with hydrochloric acid in aqueous dioxan. The aldehyde (V) was

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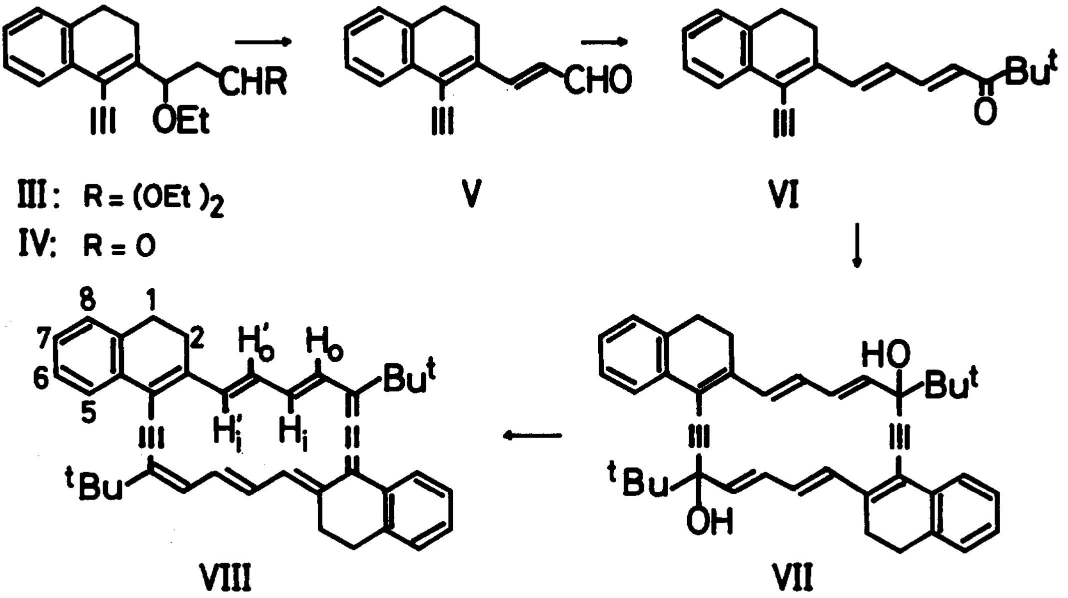
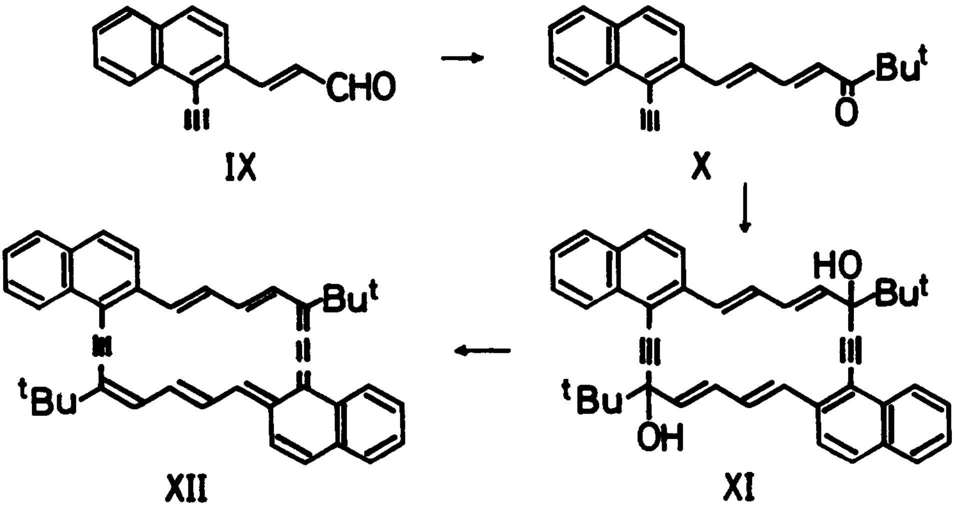
SCHEME 1.



converted into trieneyne ketone [VI, yellow rods, mp 123.0-124.0°C, m/e 290 (M^+), 77%] by the aldol condensation with pinacolone. A solution of VI in tetrahydrofuran was added to a suspension of potassium hydroxide in liquid ammonia to give a diastereomeric mixture of 18-membered cyclic glycol [VII, colorless crystals, mp _ca._ 265-270°C (dec.), 97%]. VII in tetrahydrofuran was mixed at -60°C with stannous chloride dihydrate and ether saturated with hydrogen chloride. The product obtained by working up the reaction mixture in the usual way was chromatographed on alumina and eluted with dichloromethane-_n_-hexane (1:3) to give bis-(dihydronaphtho)-di-_t_-butyldidehydro[18]annulene [VIII, dark blue violet needles, mp 280.5-281.1°C (dec.), m/e 546 (M^+), 71%, Anal. Found: C, 92.36; H, 7.74%, Calcd. for $C_{42}H_{42}$: C, 92.26; H, 7.74%, nmr ($CDCl_3$, 100 MHz) τ -0.02 (t, J=13.0 Hz, 2H, H_o'), 0.56 (d, J=13.0, 2H, H_o), 1.13 (d, J=7.0, 2H, H^5), 2.40~2.64 (m, 6H, H^6~ H^8), 5.76 (t, J=7.0, 4H, H^2), 6.60 (t, J=7.0, 4H, H^1), 7.98 (s, 18H, _t_-Bu), 12.93 (t, J=13.0, 2H, H_i), 12.99 (d, J=13.0, 2H, H_i')]. VIII was found to be stable and strongly diatropic compound. The electronic spectrum of VIII was shown in Fig. 1.

The route of attempted synthesis of dinaphtho-di-_t_-butyldidehydro[18]annulene (XII) was shown in Scheme 2.

SCHEME 2.



The condensation of aldehyde IX (2) in ethanol-dichloromethane (25:1) with pinacolone in the presence of aqueous potassium hydroxide yielded trieneyne ketone [X, yellow crystals, mp 137.1-139.0°C (dec.), m/e 288 (M^+), 46%]. The ketone (X) in tetrahydrofuran was added to a suspension of potassium hydroxide in liquid ammonia to give cyclic glycol [XI, colorless crystals, mp >300°C, 84%]. Chromatography of XI on alumina resulted in a crude separation into a soluble- and a less soluble-diastereomers in a ratio of 1:1. Dark green solution obtained by the reaction of the diastereomeric mixture of XI with stannous chloride dihydrate and tetrahydrofuran saturated with hydrogen chloride was found to be extremely unstable. However, the electronic spectrum at -78°C could be measured using a reaction mixture obtained by the reaction of highly diluted solution of XI in tetrahydrofuran with hydrogen chloride and stannous chloride dihydrate. The ε-values are estimated assuming quantitative conversion of XI into XII. As shown in Fig. 1, the close resembrance of absorption curve of the green reaction mixture with that of reference compound (VIII) indicates the formation of dinaphtho-di-*t*-butyldidehydro[18]annulene (XII). The highly unstable nature of XII is similar to that of 14-membered analogue (I) (1). The glycol (XI) dissolved in THF-d_8 was mixed at -50°C under atmosphere of nitrogen with stannous chloride

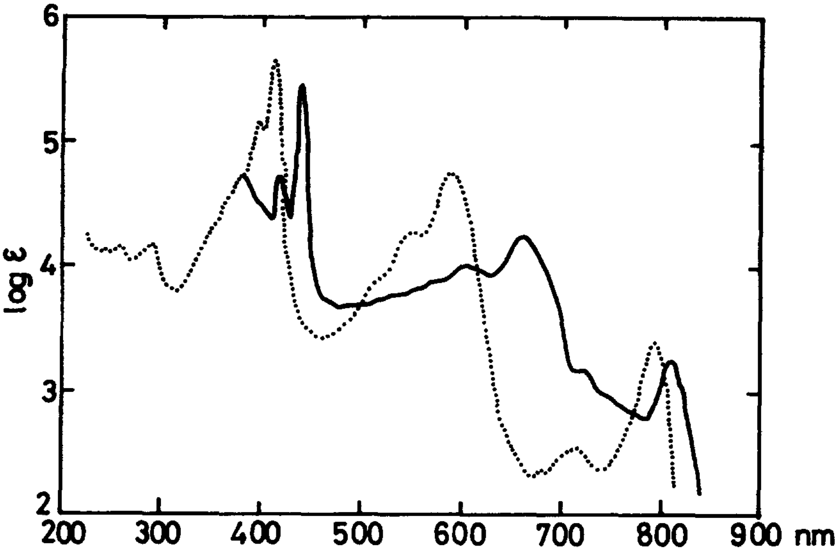


Fig. 1. The UV spectra of VIII (·········) and XII (———) in THF.

dihydrate and the same solvent saturated with deuterium chloride, and the resulting dark green solution was submitted to the measurement of nmr spectrum. All attempts to get clear spectrum were failed owing to the instability of XII in rather concentrated solution suited for nmr spectroscopy. However, signal of t-butyl protons could be observed as a singlet at τ 7.89 [100 MHz, THF-d_8 at -80°C]. Appearance of the signal at fairly low field seemed to indicate that the 18π-electron system in XII sustains a strong diamagnetic ring current presumably comparable to non-annelated analogue (VIII).

The strong diatropicity of I and presumably of XII comparable to non-annelated reference annulenes (II and VIII) is highly interesting, because it has been shown that fusion of benzenoid nucleus usually reduces the diatropicity of annulene ring (2,3,4). The strong diatropicity of I and XII seems to suggest that the equivalent Kekulé structures which can be written in I and XII play an important role in the delocalization of π-electrons in annelated annulene system.

References

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