

DINAPHTHO[2,1-f:2',1'-m]-3,10-DI-t-BUTYL-1,8-DIDEHYDRO[14]ANNULENE.

A DIATROPIC ANNELATED ANNULENE

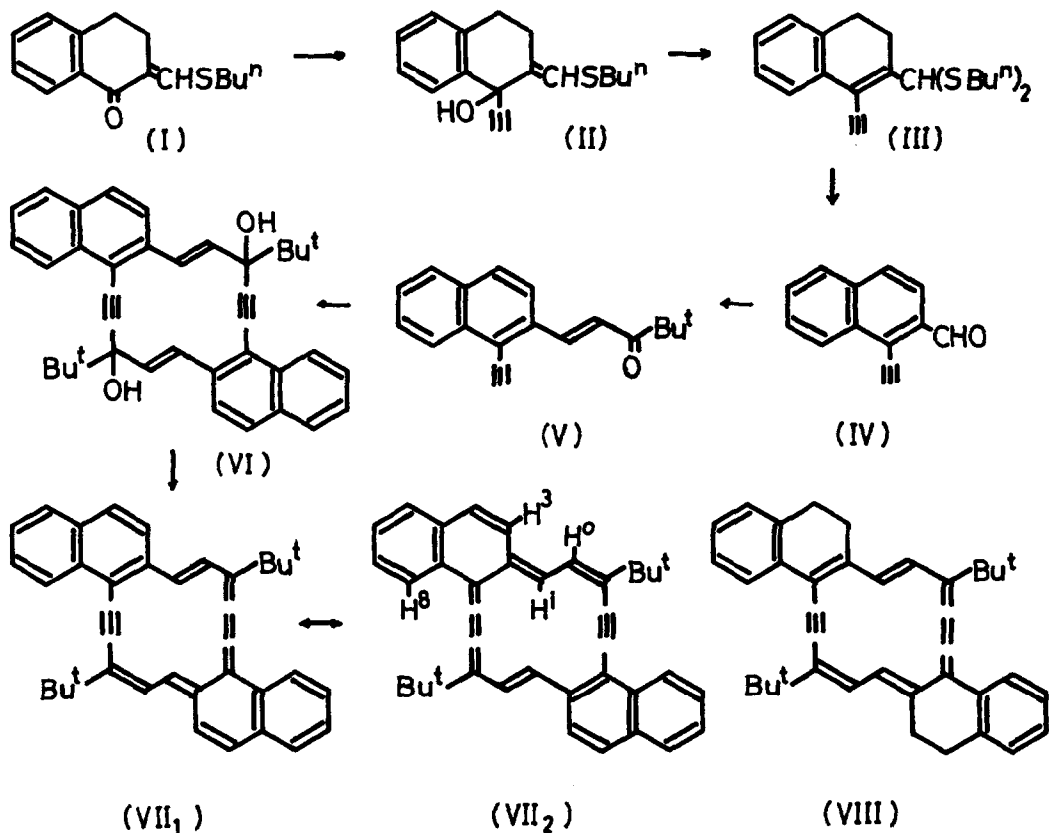
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The properties of $[4n+2]$ annulenes annelated with benzenoid nuclei are of considerable interest with regard to the participation of benzenoid π -electrons to the macrocyclic systems (1). 1,8-Didehydro[14]annulenes (2) seem to be an appropriate system for the examination of the effect of fused benzenoid nuclei, because the didehydroannulenes have been found to be highly stable and strongly diatropic.

In this paper we wish to report the synthesis and properties of dinaphtho-di-t-butyl-didehydro[14]annulene (VII).

The resonance energies of naphthalene and 1,2-dihydronaphthalene have been estimated to be 61 Kcal/mole and 40 Kcal/mole, respectively (3). Therefore, destruction of one benzene system in naphthalene nucleus to form 1,2-naphthoquinone type structure may require much less energy as compared with the energy of transformation of benzene into o-quinoid structure. Taking this into consideration, we have carried out the synthesis of didehydro[14]annulene annelated with two naphthalene nuclei. Enolthioether (I, yellow liquid, b.p. 167-172°C/ 9×10^{-3} mmHg) prepared by the reaction of n-butylmercaptan with 2-hydroxymethyl-enetetralone was ethynylated with lithium acetylide-ethylene diamine complex (4) to give ethynyl alcohol (II). II was treated without purification with n-butylmercaptan in the presence of p-toluenesulfonic acid to afford ethynylthioacetal (III, indistillable yellow liquid, 97% based on I). Dehydrogenation of crude III with DDQ followed by hydrolysis by means of an aqueous acetonitrile containing methyl iodide (5) yielded 1-ethynyl-2-naphthaldehyde (IV, yellow



plates, m.p. 139.4–140.3°C, 37% based on III). IV was converted into *t*-butyl ketone (V, pale yellow leaflets, m.p. 114.7–115.3°C, 39.2%) by the condensation with pinacolone. A solution of V in tetrahydrofuran was added to a stirred suspension of potassium hydroxide in liquid ammonia. The reaction mixture was worked up by the usual way to give cyclic glycol (VI, colorless crystals, m.p. 279.0–279.5°C (dec.), Mass (m/e) 524 (M^+), 90%).

Development of deep blue violet color was observed on addition of finely powdered stannous chloride dihydrate to a solution of VI in ether or tetrahydrofuran saturated with hydrogen chloride. It was found that the deep blue violet solution is fairly unstable, and rapid fading of the color was observed at room temperature. The solution was also sensitive to oxygen even at -78°C . However, in the absence of oxygen, the solution could be kept without appreciable color change at -78°C for a day. Although all attempts to isolate the reaction product

were unsuccessful, the formation of dinaphtho-di-*t*-butyl-didehydro[14]annulene (VII) could be confirmed on the basis of electronic and NMR spectroscopy. The reactions and spectroscopic measurements were performed under argon atmosphere using degassed solvent. Accurately weighed VI dissolved in tetrahydrofuran was mixed at -20°C with stannous chloride dihydrate and the same solvent saturated with hydrogen chloride. The resulting solution was directly subjected to the measurement of electronic spectrum at -78°C . The electronic spectrum was found to be closely related with that of bis(dihydronaphtho)-di-*t*-butyl-didehydro[14]-annulene (VIII)⁺, indicating the formation of VII (Fig. 1). The ϵ -values of VII were calculated assuming quantitative conversion of VI into VII. Deuterio-tetrahydrofuran and VI placed in a NMR tube were mixed at -78°C with a solution of stannous chloride dihydrate in the same solvent saturated with deuterium chloride. The mixture was shaken at -30°C for 5 minutes and used for the measurement of 100 MHz NMR spectra at -54°C (Fig. 2). The doublets at τ -0.22 ($J=15$ Hz, 2H) and τ 13.45 ($J=15$ Hz, 2H) could be assigned to outer protons (H^0) and inner protons (H^i), respectively. The assignment could be further confirmed by a double resonance technique, *i.e.*, the doublet at τ -0.22 changed to a sharp

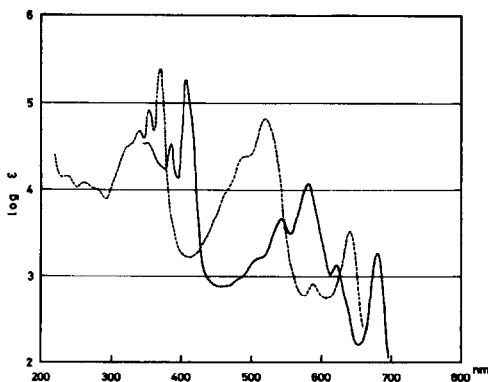


Fig. 1. UV Spectra of VII and VIII.

VII ——— ; VIII - - - - -

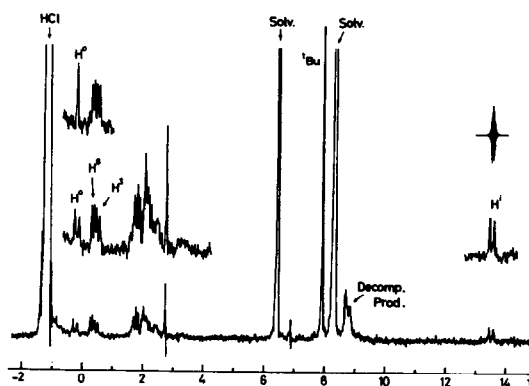


Fig. 2. NMR Spectra of VII.

The synthesis and properties of VIII will be reported elsewhere.

singlet on irradiation at τ 13.45. The doublets at τ 0.46 ($J=10$ Hz, 2H) and τ 0.29 ($J=8$ Hz, 2H) were assigned to H^3 , H^8 and the sharp singlet at τ 7.89 (18H) to *t*-butyl protons, respectively. The NMR spectrum clearly indicates the induction of a diamagnetic ring current in the annelated dehydroannulene ring ($VII_1 \leftrightarrow VII_2$). To our knowledge, this is the first example of diatropic non-bridged neutral annulene annelated with benzenoid nuclei.[†]

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[†] The 14π electron system in 3,4-benzo-1,6:8,18-propanediylidene[14]annulene has been reported to be diatropic (6).