

3,15,18,30-TETRA-t-BUTYL-1,16-DIDEHYDRO[30]ANNULENE.

A DIATROPIC 30π ELECTRON SYSTEM

Masahiko Iyoda and Masazumi Nakagawa

Department of Chemistry, Faculty of Science, Osaka University

Toyonaka, Osaka 560, Japan

(Received in Japan 13 September 1973; received in UK for publication 10 October 1973)

A series of didehydro[$4n+2$]annulenes ($n=3, 4, 5$ and 6) containing an acetylene and a butatriene linkages in the cyclic system has been shown to have high conformational stability and to sustain a fairly large diamagnetic ring current (1-4). In view of this fact, the higher member of this series of didehydroannulene can be regarded as an adequate model compound to test the validity limit of Hückel's rule for aromaticity.

In the present paper we describe the synthesis and diatropic property of 3,15,18,30-tetra-t-butyl-1,16-didehydro[30]annulene (VII).

Dimethyl acetal (II) derived from t-butyl-enyne aldehyde (I) (5) was converted into Grignard derivative and treated with trimethylchlorosilane. The product was hydrolyzed with aqueous acetic acid to give trimethylsilyl aldehyde (III, pale yellow liquid, b.p. $93-94^{\circ}\text{C}/6$ mmHg, 92.9%). To a mixture of III, acetic acid, ethanol and piperidine was added gradually a solution of freshly distilled crotonaldehyde (2.5 eq.) in ethanol. The reaction product was chromatographed on silica gel and eluted with n-hexane-benzene (1:1). Desired pentaenynaldehyde (IV_b , M^+ 312) was obtained in 25% yield together with trienynaldehyde (IV_a , 11%) (3) and heptaenynaldehyde (IV_c , 3.4%, M^+ 364). Aldol condensation of IV_b with pinacolone yielded ethynylhexaene ketone (V, 38%, M^+ 322) as unstable orange crystals. Elemental analyses indicate that V is gradually oxidized by atmospheric oxygen. A solution of V in tetrahydrofuran was added over a period of 10 hrs. to a suspension of finely powdered potassium hydroxide in liquid ammonia at -34°C , and the mixture was stirred for further

members of tetra-t-butyldidehydroannulenes of this series. The other stereoisomer (VI_b) also gave VII under analogous reaction conditions. No satisfactory elemental analyses could be obtained owing to the unstable nature of VII. Full hydrogenation of VII in ethyl acetate-acetic acid over platinum oxide catalyst at -15~-20°C (6 hrs.) and then at room temperature (2 hrs.) yielded colorless crystals [57%, m.p. 77-87°C, Mass (m/e) 644 (M⁺), 587 (M-57), 57 (t-Bu, base peak). Calcd. for C₄₆H₉₂: 645.24]. The electronic spectrum of VII shown in Table 1 was obtained using a solution prepared by dissolving fresh VII which was derived from VI_b (1.4 mg). The ε-values were estimated assuming quantitative conversion of VI_b into VII without decomposition or formation of by-product.

Table 1. Electronic Spectrum of Tetra-t-butyldidehydro[30]annulene (VII) in Tetrahydrofuran at -78°C. λ_{max} (ε) nm

275.5 (18000), 324* (43000), 338 (56000), 352 (54000), 401* (78000),
451 (190000), 572 (11000), 607 (11000), 660* (8300)

An asterisk indicates shoulder. Tailing up to 1120 nm was observed.

In contrast to the absorption curves with distinct vibrational fine structure of the lower members of this series of dehydroannulenes, broad and structureless feature of the absorption curves of VII seems to reflect an increasing flexibility of dehydroannulene skeleton along with an increase in ring size.

The 100 MHz NMR spectrum of VII in deuteriochloroform measured at -60°C using FT technique is presented in Fig. 1. The signals at τ 2.10-2.90 (center, τ 2.50, ca. 12H), τ 6.10-7.00 (center, τ 6.50, ca. 10H) and τ 8.56 could be assigned to outer protons, inner protons and protons of t-butyl groups, respectively. No essential change was observed in the NMR spectra measured at -40°C and -20°C. The fact that the inner protons exhibit signal at higher field than that of outer protons demonstrates the existence of a diamagnetic ring current. To our knowledge, this is the first instance of diatropic 30π electron system indicating the upper limit of aromaticity of [4n+2]annulene should lie above 30-membered ring.

Broadening of the signals of outer and inner protons of VII seems to be attributable to a decrease of rigidity of perimeter of the didehydro[30]annulene

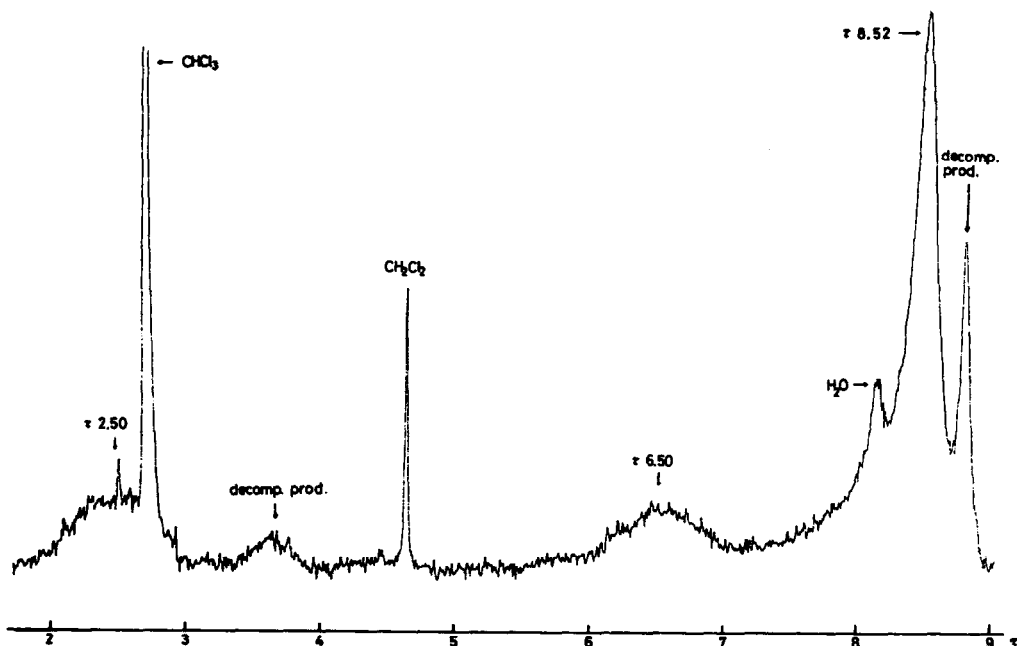


Fig. 1. 100 MHz FT-NMR spectrum of tetra-*t*-butylididehydro[30]annulene (VII)

as is reflected in the electronic spectrum. VII was found to be a scarcely soluble substance. A saturated solution decomposed fairly rapidly even at -40°C resulting in a black violet solid with less solubility. The rate of decomposition is decreased markedly on dilution of the solution suggesting an intermolecular mode of decomposition reaction. The NMR spectrum of decomposition product exhibits signals at $\tau 3.40\text{--}4.00$ (m) and $\tau 4.05\text{--}4.60$ (m). The electronic spectrum of decomposition product showed hypsochromic shift and hypochromism as compared with that of VII. The nature of decomposition product is not clear.

References

1. K. Fukui, T. Nomoto, S. Nakatsuji, and M. Nakagawa, Tetrahedron Letters, 1972, 3157.
2. M. Iyoda and M. Nakagawa, Tetrahedron Letters, 1972, 3161.
3. M. Iyoda and M. Nakagawa, Chem. Commun., 1972, 1003.
4. M. Iyoda and M. Nakagawa, Tetrahedron Letters, 1972, 4235.
5. T. Katakami, S. Tomita, K. Fukui, and M. Nakagawa, Chemistry Letters, 1972, 225.