

A solution of trienyne ketone (II) (2) in tetrahydrofuran was slowly added to a stirred suspension of finely powdered potassium hydroxide in liquid ammonia. The reaction mixture was worked up to give III as colorless crystals (66%). The cyclic glycol (III) was found to be a 1:1 mixture of diastereomers and could be separated on chromatography on silica gel [III_a: mp 230.5-231.5°C, M⁺ 488. III_b: mp 170.0-171.0°C, M⁺ 488. Calcd. for C₃₄H₄₈O₂ = 488.7]. A mixture of III_a and III_b was dissolved in ether saturated with hydrogen chloride. Finely powdered stannous chloride dihydrate was added to the solution under stirring in nitrogen atmosphere at -60°C. Chromatographic purification of the product on alumina gave tetra-*t*-butyldidehydro[18]annulene [IV, dark reddish violet crystals, mp ca. 260°C (dec.), M⁺ 454. Found: C, 89.72; H, 10.18%. Calcd. for C₃₄H₄₈: C, 89.80; H, 10.20%. Mol. wt., 454.6] in a yield of 93%. IV forms 1:1 π-complex with 2,4,7-trinitrofluorenone [deep violet needles, mp ca. 260°C (dec.). Found: C, 73.37; H, 6.63; N, 5.43%. Calcd. for C₃₄H₄₈·C₁₃H₅N₃O₇: C, 73.32; H, 6.68; N, 5.46%]. Full hydrogenation of IV in ethyl acetate-acetic acid (1:1) over platinum catalyst followed by chromatography on alumina afforded tetra-*t*-butylcyclooctadecane [mp 151.0-154.0°C, M⁺ 476. Found: C, 85.62; H, 14.13%. Calcd. for C₃₄H₅₈: C, 85.63; H, 14.37%. Mol. wt., 476.8].

Condensation of acetophenone with dienyne aldehyde (I) (2) gave trienyne ketone [V, yellow crystals, 76%, mp 59.5-60.0°C. Found: C, 86.26; H, 7.56%. Calcd. for C₁₉H₂₀O: C, 86.32; H, 7.63%]. The Favorskii reaction of V according to the reaction conditions used in the preparation of III gave cyclic glycol (VI) as yellow solid. The crude glycol (VI) was used without further purification in the dehydroxylative aromatization reaction. Treatment of VI in ether with stannous chloride dihydrate in the presence of hydrogen chloride at -60°C afforded di-*t*-butyl-diphenyldidehydro[18]annulene [VII, 33% based on V, deep violet crystals, mp 235°C (dec.), M⁺ 494. Found: C, 92.16; H, 7.67%. Calcd. for C₃₈H₃₈: C, 92.26; H, 7.74%. Mol. wt., 494.7]. VII gave 1:1 π-complex with 2,4,7-trinitrofluorenone [deep violet needles, mp 250°C (dec.). Found: C, 75.06; H, 5.23; N, 5.49%. Calcd. for C₃₈H₃₈·C₁₃H₅N₃O₇: C, 75.63; H, 5.35; N, 5.19%].

Both of the didehydro[18]annulenes (IV and VII) were found to be fairly stable compounds. IV and VII gave orange red and violet solutions, respectively.

The electronic spectral data of IV and VII are summarized in Table 1. The absorption curves of IV and VII consist of three main bands and closely related with those of tetrasubstituted didehydro[14]- and tetrahydro[18]annulenes (1, 3).

Table 1. Electronic spectra of IV and VII in tetrahydrofuran. λ_{\max} in nm (ϵ)

	217(11,300), 255*(5,810), 267.5(8,360), 342*(44,400), 356(94,400),
IV	372(447,000), 464*(4,790), 499(10,600), 530(19,100), 607(100), 647*(89), 669(116), 681(116), 720*(138), 751(316)
	240*(12,900), 249.5(14,000), 267*(12,000), 281.5(16,200), 367*(51,800),
VII	389*(171,000), 401(330,000), 534*(17,900), 575(48,000), 673*(150), 701(231), 785(980)

* indicates shoulder.

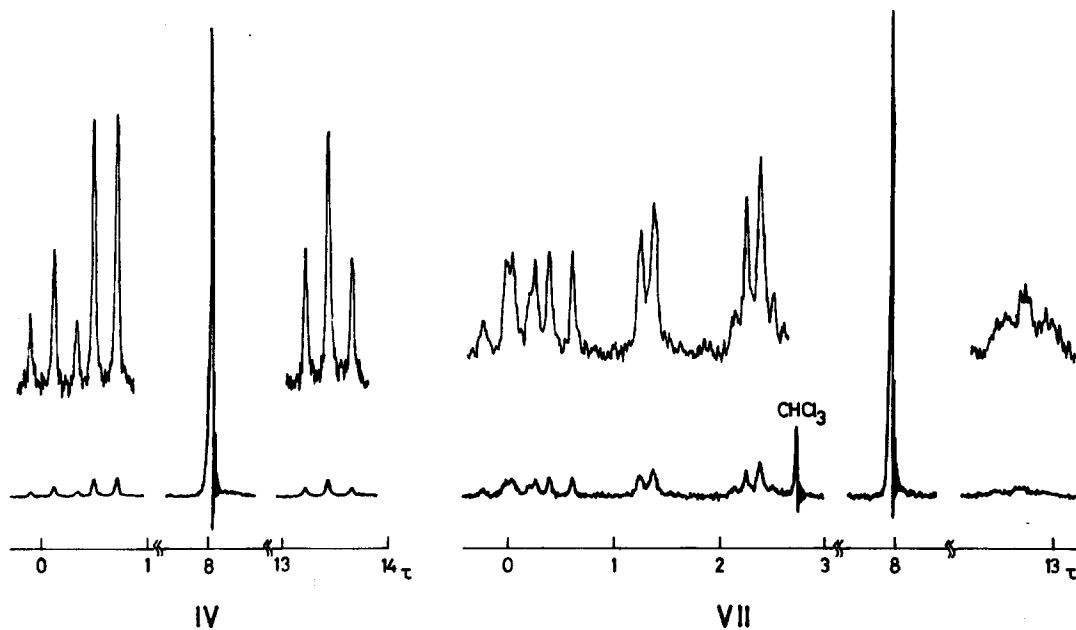


Fig. 1. NMR spectra of IV and VII in CDCl_3 (60 MHz)

As is illustrated in Fig.1, both of the didehydro[18]annulenes (IV and VII) exhibit "aromatic" NMR spectra indicating the presence of a strong diamagnetic

induced ring-current [IV: outer protons, H^a, τ 0.13, t, J=13 Hz; H^b, 0.62, d, J=13 Hz; protons of t-butyl, 8.03, s; inner protons, H^c, 13.42, t, J=13 Hz. VII: outer protons, H^a and H^b, -0.21~0.62, m, (6H); o-protons of phenyl, 1.33, m, (4H); m,p-protons of phenyl, 2.33, m, (6H); protons of t-butyl, 7.98, s, (18 H); inner protons, H^c, 13.28, m, (4H)].

As recorded in Table 2, the NMR spectrum of IV is not temperature-dependent, being essentially unchanged up to 110°C. This fact indicates the high conformational stability of 1,10-didehydro[18]annulene system. An attempted measurement of the NMR spectrum at 150°C in CDBr₃ resulted in a rapid decomposition of IV.

Table 2. NMR spectrum of IV in CDBr₃ (60 MHz)

	H ^a	H ^b	<u>t</u> -Bu	H ^c
36°C	0.18, t J=13 Hz	0.68, d J=13 Hz	8.09, s	13.64, t J=13 Hz
70°C	0.30, t J=13 Hz	0.78, d J=13 Hz	8.10, s	13.46, t J=13 Hz
110°C	0.44, t J=13 Hz	0.81, d J=13 Hz	8.10, s	13.28, t J=13 Hz

Acknowledgement. We gratefully acknowledge the award of Toray Science and Technology Grants from Toray Science Foundation.

References

1. K. Fukui, T. Nomoto, S. Nakatsuji, and M. Nakagawa, the preceding paper.
2. M. Iyoda, H. Miyazaki, and M. Nakagawa, Chem. Commun., in the press.
3. T. Katakami, S. Tomita, K. Fukui, and M. Nakagawa, Chemistry Letters, 1972, 225.