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AN OXYGEN-BRIDGED [15]ANNULENONE AND ITS CONVERSION TO DIATROPIC [15]ANNULENIUM IONS

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THE higher [4n+3]annulenones[1], higher members of tropone (n = 1), have been studied recently[2a-g]. We have previously reported the preparation and the magnetic properties of oxygen bridged annulenones in which inner hydrogens were replaced by furan oxygens.

We now report the synthesis of a novel diatropic oxygen-bridged [15]annulenone **4** and its conversion to the diatropic [15]annulenium ions (**6a** - **c**).

Wittig reaction of 2,2'-(difuryl ketone)-5,5'-dicarbaldehyde **1**[4] and 1,4-(tetramethylenebistriphenylphosphonium)bromide **2**[5] in DMF with methanolic LiOMe at 90° gave a mixture of products from which 2,5:12,15-diepoxy-6,7:10,11-cis,cis-8,9-dihydro[15]annulenone **3** was obtained in ca. 15% yield by chromatography over silica gel [orange yellow prisms, m.p. 148 - 150°, mass spectrum m/e 240 (M^+); λ_{max}^{MeOH} 205 (18,300), 236.5 (28,400), 260 (16,100), 324 (13,200), and 410 nm (ε 5,740); ν_{max}^{KBr} 1618 cm^{-1}; nmr (90 MHz, $CDCl_3$) τ 2.73 and 3.78 (4H, ABq, $J_{3,4}=J_{13,14}=3.5$ Hz, H-3, H-14, H-4, H-13), 3.89 (2H, d, $J_{6,7}=J_{10,11}=11.8$ Hz, H-6, H-11), 4.05 - 4.37 (2H, m, H-7, H-10), 6.88 - 7.17 (4H, m, H-8, H-9); irradiation at the frequency of H-7, H-10 collapsed the signal due to H-8, H-9 into a broadend singlet, and irradiation at the frequency of H-8, H-9 collapsed the signal due to H-7, H-10 into a doublet $J_{6,7}= J_{10,11}=11.8$ Hz thus confirming the di-cis-stereochemistry.

Bromination of compound **3** was achieved with N-bromosuccinimide in CCl_4 in presence of benzoyl peroxide in a sealed tube for 15 min. at 145° (bath). The monobromo-compound[6] was obtained in ca. 90% yield as an unstable yellow oil which was immediately treated with

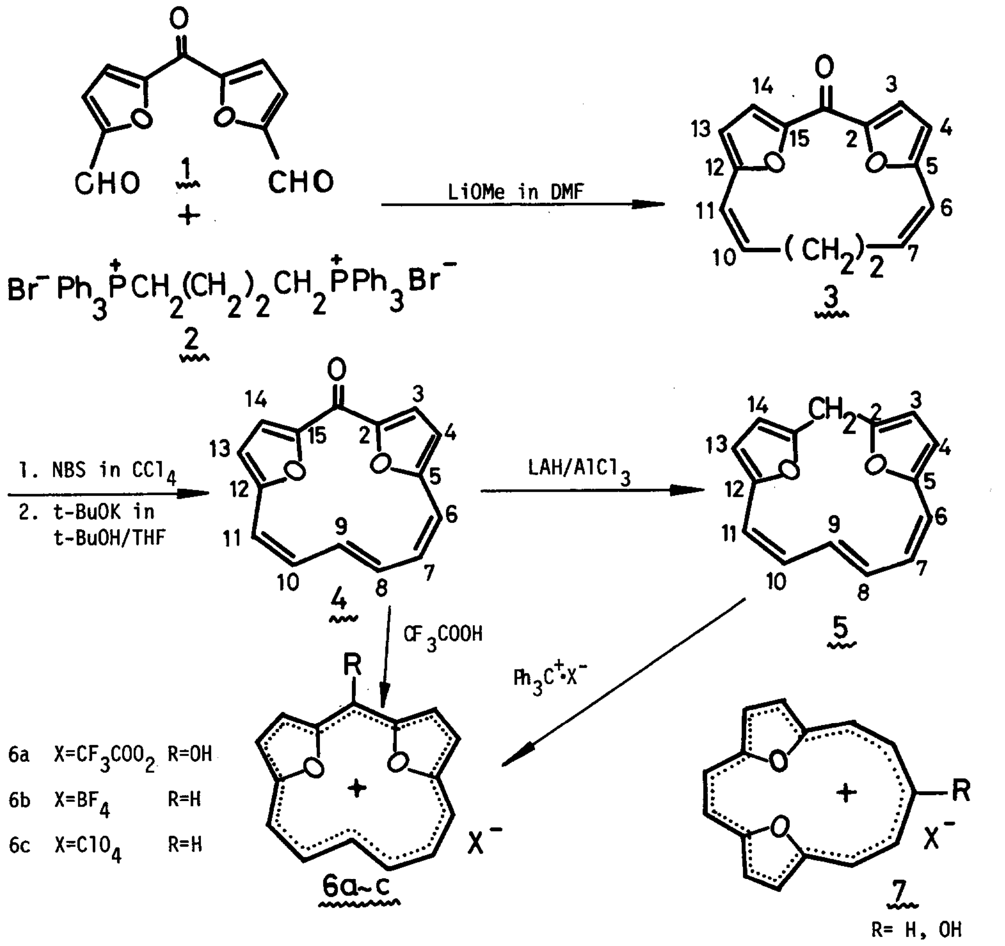

Table 1. $\Delta\tau$ vs. E/S for 4 with $Eu(fod)_3$*

Protons	$\frac{[4]}{[Eu(fod)_3]}$ X $\Delta\tau$
H-3, 14	10.1
H-4, 13	2.7
H-8, 9	2.8
H-6, 7 and H-10, 11	1.9

* Very marked line broadening occurred at E/S = 0.153.

t-BuOK in t-BuOH/THF at room temperature. The annulenone **4** was purified by plc on silica gel and it formed orange-red needles; m.p. 212 - 215° (from cyclohexane) in *ca*. 9 - 16% yield; mass spectrum *m/e* 238 (M^+); λ_{max}^{MeOH} 231 (15,200), 304.5 (30,500), 320 (30,750), 325 (31,300), 347.5 (21,550), and 415 nm (ε 5,400); ν_{max}^{KBr} 1608, 1598 (C=O) cm^{-1}; nmr (90 MHz, $CDCl_3$) τ 1.95 and 2.82 (4H, ABq, $J_{3,4}=J_{13,14}=3.6$Hz, H-3, H-14, H-4, H-13), 2.92 (4H, m, H-6, H-7, H-10, H-11), and 3.92 (2H, m, H-8, H-9).

The n.m.r. spectrum of **4** determined in CD_2Cl_2/CS_2 was found to be temperature dependent. Only the high field multiplet markedly lost its fine structure on cooling: at -80° it was a very broad signal ($w_{h/2}$ 30 Hz) and at -90° it could no longer be discerned. Compound **4** is thus conformationally "mobile" due to the rapid interchange of H-8 and H-9 on the *trans*-double bond. The room temperature spectrum was altered on the addition of $Eu(fod)_3$. The result (see Table 1) shows that H-8 and H-9 are affected to a greater extent than H-6, H-7, H-10, and H-11.[7] This evidence supports the *trans*-stereochemistry of the 8,9-double bond since the average distance of H-8 and H-9 from the carbonyl group is smaller than for H-6, H-7, H-10 and H-11. The [15]annulenone **4** is diatropic since the furan protons H-3, H-14, H-4 and H-13 are at considerably lower field than the similar protons in the atropic system **3**. Assuming that the chemical shift of the outer proton on the *trans*-double bond (H-8) in the "nonmobile" spectrum of **4** is similar to that of H-6, H-7, H-10 and H-11 (*ca*. τ 2.9) then it is estimated that the chemical shift of the internal proton (H-9) should be *ca*. τ 4.9 in keeping with the diatropicity of **4**.

The diepoxyhomo[14]annulene **5** (*ca*. 80% yield) was prepared by treatment of **4** with LAH / $AlCl_3$ [m.p. 103 - 105°, yellow prisms, mass spectrum *m/e* 224 (M^+), λ_{max}^{MeOH} 245 sh (10,300), 275 sh (26,700), 279.5 (27,500), and 377.5 nm (ε 8,400); ν_{max}^{KBr} 939 cm^{-1} (trans); nmr (90 MHz, $CDCl_3$) τ 3.28 - 3.89 (6H, m, H-6, H-7, H-8, H-9, H-10 and H-11), 3.40 (2H, broad d, $J_{3,4}=J_{13,14}=3.5$ Hz, H-4 and H-13), 3.77 (2H, dt, $J_{CH_2,3}=J_{CH_2,14}=0.9$ Hz, $J_{3.4}=J_{13,14}$ = 3.5 Hz, H-3 and H-14), and 5.84 (2H, broad s, CH_2); irradiation at the frequency of the methylene protons collapsed H-3 and H-14 into a doublet, J=3.5 Hz, and irradiation at the frequency of H-4 and H-13 collapsed the CH_2 protons into a triplet, J= 0.9 Hz). The homoannulene **5** was converted to the corresponding crystalline [15]annulenium salts [**6b** (X = BF_4 , R = H) red-brown prisms (MeCN), decomp. 225° without melting; nmr (60 MHz, MeCN) complex multiplet τ 0.20 - 0.82; **6c**, (X = ClO_4 , R = H), fine red crystals, decomp. >300°, which was extremely insoluble in most solvents].

The annulenone **4** gave rise to a diatropic 1-hydroxy[15]annulenium ion on protonation. The n.m.r. spectrum of **4** in CF$_3$COOH exhibited all the protons at τ 0.00 - 1.00 due to the formation of **6a**. The room temperature spectra of **6a** and **6b** did not show high field resonances for the internal protons of these diatropic species, indicating that the coalescence temperatures of **6a** and **6b** may be higher than for **4** (*ca*. -90°) and the high field resonances are too broad at ambient temperature to be observed. The solution of **4** in CF$_3$COOH or conc. H$_2$SO$_4$ was stable indefinitely and the characteristic acid lability of the furan system was no longer observed since **4** could be almost quantitatively recovered when the solution was quenched with water.

The electronic spectrum of **4** in 70% HClO$_4$ showed maxima at 344 (84,500), 353 (94,500), 450 (5,960), 468 (5,940), 485 (7,950), and 515 nm (ε 8,700) which are similar to those obtained for the 4,7:10,13-diepoxy[15]annulenium ions **7**.[8] The ion **6b** (MeCN) had a similar spectrum with maxima at 340 (166,700), 445 (4,100), 470 (9,400), and 478 nm (ε 10,650).

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