Communications to the Editor

[Chem. Pharm. Bull. 25(3) 511—514 (1977)]

UDC 547.521.04 : 547.727.04

Syntheses of Alkyl Substituted Bis-oxido-bridged[15]annulenones

Methyl substituted bis-oxido-bridged [15]annulenones III and VIII, $n=3$ members of $[4n+3]$annulenone, were prepared starting from 2,15-dimethoxycarbonyl-[15]annulenone I. Annulenones III and VIII have no appreciable amount of a diamagnetic ring current due to the nonplanar conformations. On the contrary, VI and XI sustain a strong diamagnetic ring current as a consequence of the delocalized14π electron system, whose planarity is enforced by ring formation. On protonation, annulenone III and VIII were converted into stable annulenium ions IIIa and VIIIa, respectively.

Keywords——alkyl substituted [15]annulenones; diamagnetic ring current of [15]-annulenones; reduction of [15]annulenones with metal hydride; addition of Grignard reagent to [15] annulenone; dehydrogenations of dihydro[15]annulenones; NMR spectra of oxygen-bridged [15]annulenium ions; 14π aromatic ions and their UV spectra

Several dehydro-[1] and oxygen-bridged [15]annulenones,[2] $n=3$ members of $[4n+3]$-annulenone, have been synthesized and investigated in terms of diamagnetic ring current. If planar, [15]annulenones should sustain a diamagnetic ring current, because they contain 14π electrons. Few studies have been done on the chemical properties of higher annulenones.[3] We now report the reactions of 2,15-dimethoxycarbonyl bis-oxido-[15]annulenone I[2a] with metal hydrides and MeMgI. These reactions proceed by 1,4-addition mechanism to give dihydro [15]annulenones (II, IV, and X). New substituted annulenones (III, VIII, and XI) can be prepared, when the above reactions are coupled with the subsequent dehydrogenation.

Reaction of five equivalent moles of mixed hydride ($LiAlH_4$: $AlCl_3=1:4$) with I in ether at 0° gave II (53%), pale yellow needles, mp 118—120°, Mass Spectrum *m/e*: 268($C_{17}H_{16}O_3$,, M^+); IR ν_{max}^{KBr} cm^{-1}: 1690 (ν C=O). Dehydrogenation of II with DDQ in benzene at 25° gave III. (35%), yellow prisms mp 157°, Mass Spectrum *m/e*: 266 ($C_{17}H_{14}O_3$, M^+); IR ν_{max}^{KBr} cm^{-1}: 1640 (ν C=O); UV λ_{max}^{MeOH} nm (ε): 222 (14730), 264 (17500), 293 (17900), 300 sh (17200), 320 (15900), and 420 (6220); NMR, see Table I.

In parallel with the formation of II, I reacted with one equivalent mole of MeMgI in ether/THF at 25°, giving dihydroannulenone IV (90%), pale yellow needles, mp 118—120°, Mass Spectrum *m/e*: 370 ($C_{20}H_{18}O_7$; M^+), IR ν_{max}^{KBr} cm^{-1}: 1750, 1710 (ν C=O, ester). The similar dehydrogenation afforded V, reddish orange prisms, mp 178—179°, which on concentrated H_2SO_4 treatment at 25° yielded the corresponding anhydride VI, red prisms (CH_3CN), decomp 260° (without melting) in an almost quantitative yield; IR ν_{max}^{KBr} cm^{-1}: 1760, 1750, 1720 (ν C=O anhydride), 1660 (ν C=O, ketone); UV λ_{max}^{MeOH} nm (ε): 264 (30000), 356 (42900), 490 sh (7900) and 514 (8900); NMR (in DMSO-d_6), see Table II. The conversion is best monitored by a distinct colour change due to [15]annulenium ions Va (blue) and VIa (purple) in solution. Compound VI was hydrolysed by 3% aq. KOH solution to give VII, dark red prisms, mp 185°, which was decarboxylated with copper chromite in quinoline at 170° for 5 minutes. Annulenone VIII was obtained as red prisms, mp 179°, mass spectrum *m/e*: 252 ($C_{16}H_{12}O_3$, M^+); IR ν_{max}^{KBr} cm^{-1}: 1645

---

[1] *a*) G.P. Cotterrell, G.H. Mitchell, F. Sondheimer, and G.M. Pilling, *J. Am. Chem. Soc.*, **93**, 259 (1971); *b*) P.D. Howes, E. LeGoff, and F. Sondheimer, *Tetrahedron Letters*, **1972**, 3695; *c*) P.D. Howes and F. Sondheimer, *J. Am. Chem. Soc.*, **94**, 8261 (1972).

[2] *a*) H. Ogawa, N. Shimojo, H. Kato, and H. Saikachi, *Tetrahedron*, **30**, 1033 (1974); *b*) H. Ogawa, H. Kato, N. Ibii, T.M. Cresp, and M.V. Sargent, *Tetradedron Letters*, **1974**, 3889.

[3] Chemical properties of higher members of $[4n+3]$annulenone have been investigated in bridged [11]-annulenones ($n=2$ members) by E. Vogel and his group. For a recent review on annulenones, see M.V. Sargent and T.M. Cresp, *Topics in Current Chem.*, **57**, 111—143, Springer Verlag, Berlin, Heidelberg, New York, 1975.

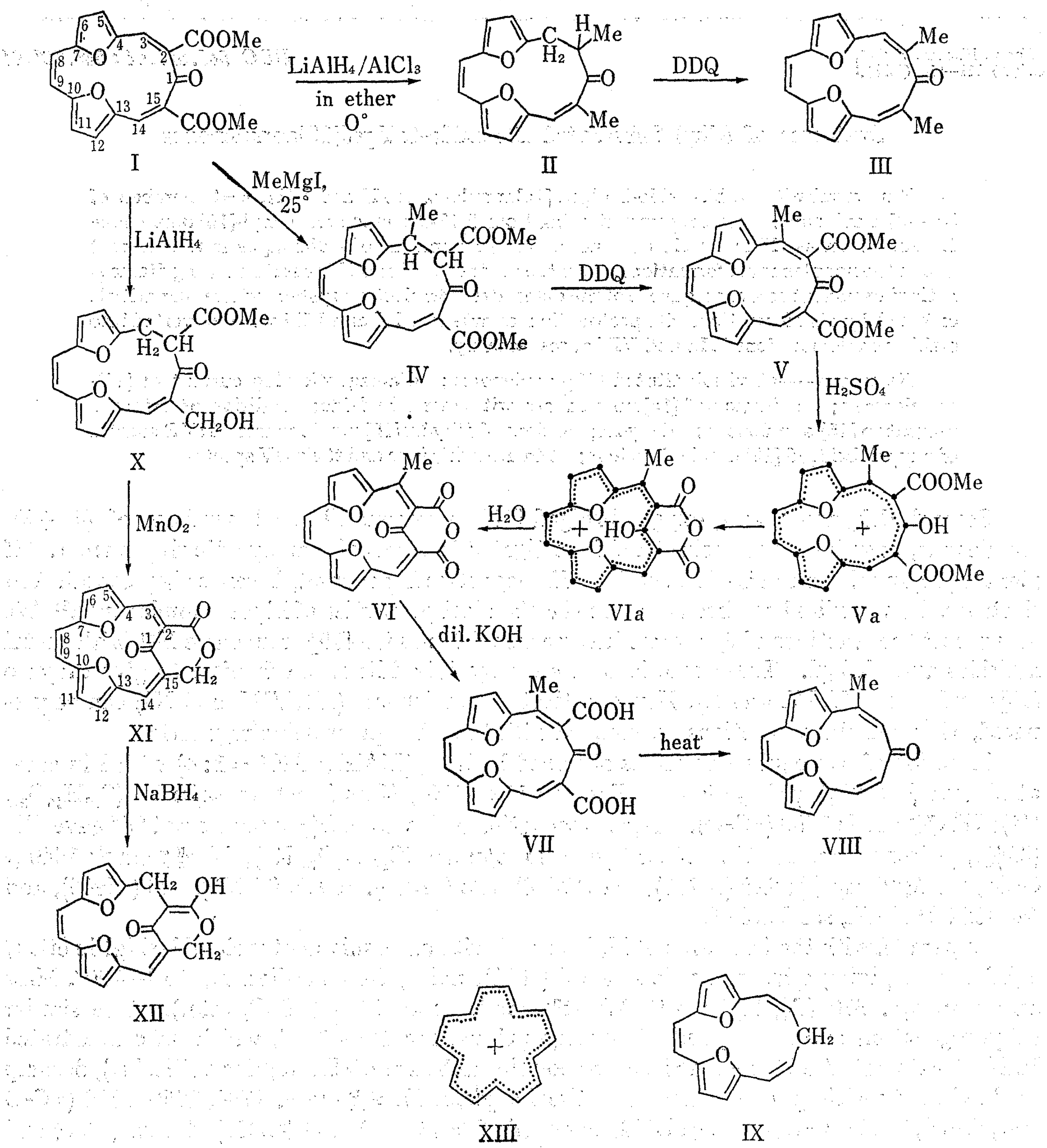

Chart 1

(ν C=O); UV $\lambda_{\max}^{\text{MeOH}}$ nm (ε): 260 (11800), 322 (38800), 408 (6600) and 440—460 (5000); NMR, see Table I.

Small diamagnetic shifts are observed, when the proton resonances of III and VIII were compared with those of the bis-oxido-bridged homoannulene IX,[4] a cyclic model chosen for comparison, in which no ring current can exist (see Table I). Thus, annulenones III and VIII sustain no appreciable amount of a diamagnetic ring current, suggesting these molecules adopt less planar conformations. In the NMR spectrum of the anhydride VI, however, all of the protons resonate at considerably lower field than those of III and VIII (see Table II). For comparison, compound XII is considered as a more suitable model. This compound could be prepared by the following reaction sequence.

---

4) H. Ogawa and M. Kubo, *Tetrahedron*, **29**, 809 (1973).

TABLE I. Chemical Shifts (τ) for Protons of III, VIII and IX (in $CDCl_3$, J=Hz)

Protons	III	VIII	IX	Δ(III−IX)	Δ(VIII−IX)
H-2	—	3.14 s	4.03 dt J=11.5, 5.8	—	−0.89
H-3, 14	3.18 s	3.04 d, H_{14} J=12.5	3.50 d, J=11.5	−0.32	−0.46
Furan	3.11 s	2.75 d 2.84 d 2.85 d J=3.5 2.89 d	3.35 d 3.46 d J=3.5	−0.24∼−0.35	−0.60∼−0.51 −0.61∼−0.57
H-8, 9	3.35 s	3.06 s	3.60 s	−0.25	−0.54
H-15	—	2.86 d J=12.5			
Methyl	7.43 s	7.46 s			

TABLE II. Chemical Shifts (τ) for Protons of VI, XI and XII (in d_6-DMSO, J=Hz)

Protons	VI	XI	XII	Δ(VI−XII)	Δ(XI−XII)
Furan	1.52 d 1.73 d 2.07 d J=3.5 2.14 d	1.72, 1H, J=3.5 2.10∼2.12, 3H, J=3.5	3.26 d 3.37 d 3.47 d J=3.5∼4.0 3.76 d	−1.74 −1.64 −1.40 −1.62	−1.54 −1.26 −1.36 −1.65
H-3	—	2.28 s	—	—	—
H-8, 9	2.38 s	2.36 s 2.38 s	3.87 3.88	−1.49 −1.50	−1.51 −1.50
H-14	1.44 s	1.50 s	3.19 br. s	−1.75	−1.69
Methylene	—	AB system centered at 4.07 and 4.33 J=14	AB system centered at 5.06 and 5.27, J=11; AB system centred at 6.04 and 6.16, J=15: −1.00, br. s		
OH	—	—			
Methyl	7.90 s	—	—		

Compound I on reduction with $LiAlH_4$ in THF at 20—25° for a short period gave X (92%), pale yellow prisms, mp 97—99°, which was oxidized with MnO_2 to give XI (60%), deep red prisms, mp 260°; IR ν_{max}^{KBr} cm^{-1}: 1710 (ν C=O, lactone), 1640 (ν C=O, ketone). The $NaBH_4$ reduction of XI in EtOH at room temperature gave XII (61%), mp 190°, orange red prisms; IR ν_{max}^{KBr} cm^{-1}: 3450 (ν OH), 1650 (ν C=O) and 1630; NMR, see Table II.

Passing from the model XII to the annulenones VI and XI causes shifts to lower field. From these data, VI and XI are strongly diatropic, as a consequence of the delocalized 14π systems. The anhydride and lactone substitutions suggest to hold the molecules in rigid and planar conformations. Carbocyclic nonbridged [15]annulenium ion XIII, whose preparation has not yet been realized, is expected to have a minimum strain, when the overcrowded inner hydrogens are replaced by oxygen bridges, as in present case.

Treatment of III and VIII with trifluoroacetic acid led to the corresponding [15]annulenium ions IIIa and VIIIa, NMR, see Fig. 1. These ions can be kept in conc. H_2SO_4 without decomposition, showing $\lambda_{max}^{H_2SO_4}$ nm (ε): 280 (10140), 345 (77100), 367 (55100), and 505 (10500) in IIIa, and $\lambda_{max}^{H_2SO_4}$ nm (ε): 272 (10600), 343 (76600), 362 (77400), 490 infl. (11500), 498 (13900), 510 (10400) and 550 (1640) in VIIIa, respectively.

It is of interest that XII was converted gradually to XI, when the solution of XII was left in the air.

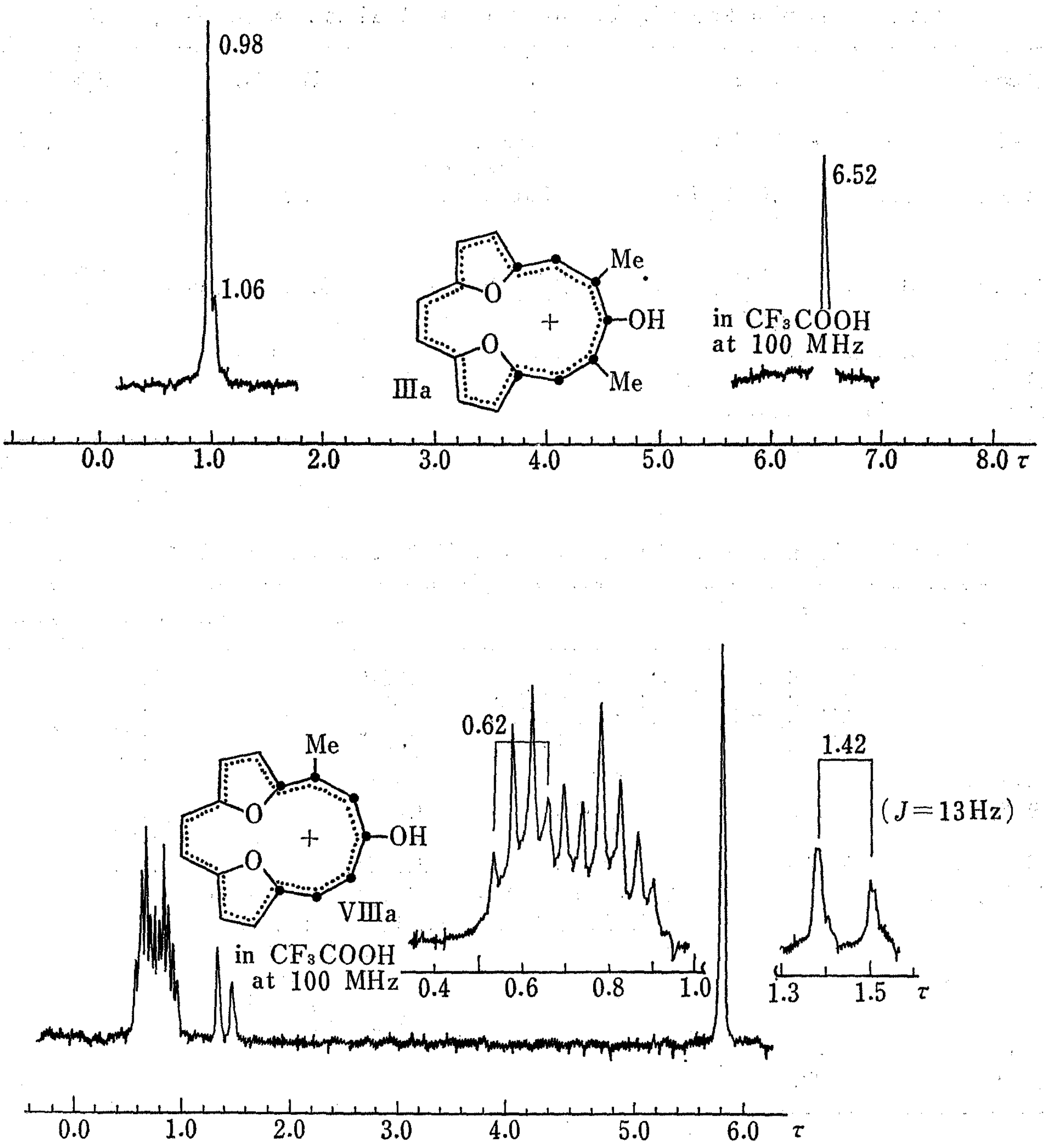

Fig. 1. The NMR Spectra of Bis-oxido-bridged [15]annulenium Ions IIIa and VIIIa

Faculty of Pharmaceutical Sciences
Kyushu University
Maedashi, Fukuoka

Institute of General Chemistry,
Kurume Technical College
Komorino, Kurume

Haru Ogawa
Hidefumi Kato

Yōichi Taniguchi

Received October 18, 1976