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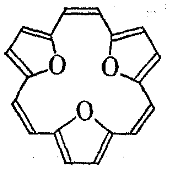
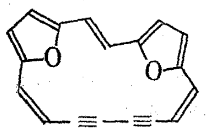
# Synthesis of 2,5:14,17-Diepoxy-8,10-bisdehydro[17]annulenone

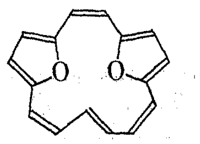
The synthesis of 2,5: 14,17-diepoxy-8,10-bisdehydro[17]annulenone (III) is described The paratropicity of III is discussed in terms of 1,4: 13,16-diepoxycycloheptadeca-1,3,5,11,13,15-hexa-ene-7,9-di-yne (VII), as a model system.

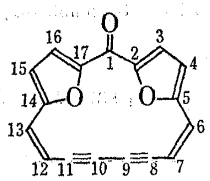
**Keywords**——Wittig reaction between dialdehyde and bisphosphorane; bisoxido-bridged [17]annulenone; paratropicity of [$4n+1$]annulenone; ring current effect in annulenes influenced by contour of the loop; reduction of annulenone by metal hydride; UV spectrum of [17]annulenones; perturbation of furan ring in $4n\pi$ systems; Eglinton coupling

Planar cyclic conjugated systems such as Ia,[1] Ib,[2] and II[3] have been prepared so far. In these compounds each furan ring supplies not only one *s-cis*-diene unit, but also eliminates repulsions which occur inevitably between inner hydrogens of medium annulenes. The diatropicity[4] of furan ring (as an oxo[5]annulene) incorporated in annulene systems is reinforced, if the resulting bridged annulene contains $4n+2\pi$ electrons. Thus, Ia and Ib are strongly diatropic ($18\pi$). Conversely, the diatropicity of furan ring is diminished, if the system contains $4n$ $\pi$ electrons. In fact, furan rings lose diatropic character in bisoxido-bridged [16]annulene (II) as a consequence of the circulation of $\pi$ electrons ($16\pi$). In higher annulenones, however, the expected diatropicity and paratropicity are much less than annulenes of similar ring size.[5] Therefore, incorporation of furan rings may destroy the expected paratropicity of the resulting bridged [$4n+1$]annulenone, because diatropicity of furan rings counteracts the expected character of the annulenone. Inspection of a molecular model suggests that bridged bisdehydro[17]annulenone (III) should be planar. If III is paratropic, the $^1$H-nuclear magnetic


Ia
($18\pi$)


Ib
($18\pi$)


II
($16\pi$)



III
($16\pi$)

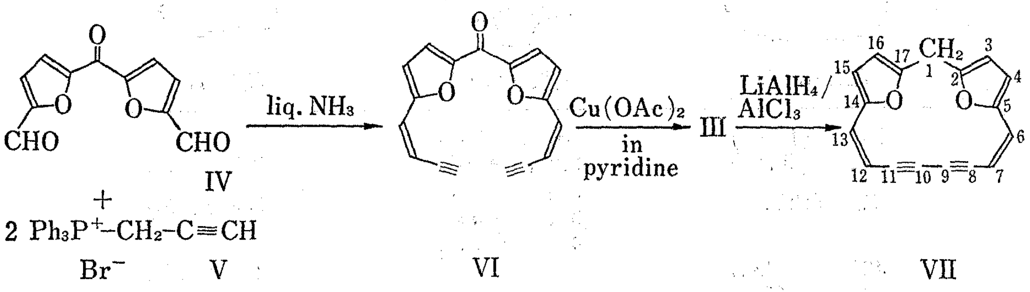


Chart 1

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1) G.M. Badger, J.A. Elix, and G.E. Lewis, *Austral. J. Chem.*, **19**, 1221 (1966).

2) H. Ogawa and H. Kato, *Tetrahedron Letters*, **1977**, in press.

3) H. Ogawa, M. Kubo, and I. Tabushi, *Tetrahedron Letters*, **1973**, 361.

4) For terminology and for reading references to the developement of these concepts, see F. Sondheimer, *Accounts Chem. Res.*, **5**, 81 (1972).

5) For a review of higher annulenones, see M.V. Sargent and T.M. Cresp, *Topics in Current Chem.*, **57**, 111—143, Springer Verlag, Berlin, Heidelberg, New York, 1975.

resonance (NMR) spectrum should show resonances at considerably high field as a result of an induced paramagnetic ring current, as was already observed in trisdehydro[17]annulenones,[6] *e.g.*, IX Table II).

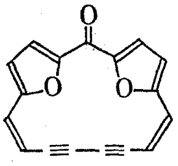
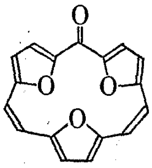
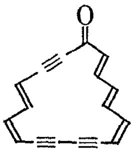
Wittig reaction of bis(5-formyl-2-furyl) ketone (IV)[7] with 2 molar equivalents of propargyl triphenylphosphonium bromide (V)[8] in acetonitrile in the presence of liq. $NH_3$ at −60° gave a mixture of products, from which di-*cis* isomer (VI) was isolated in 25% yield by column chromatography ($SiO_2$, benzene); a very unstable oil,[9] IR $\nu_{\max}^{CHCl_3}$ cm$^{-1}$: 3295, 3250 ($\nu$ C≡CH), 2075 ($\nu$ C≡C), 1610 ($\nu$ C=O) and 820 (*cis* CH=CH); UV $\lambda_{\max}^{CHCl_3}$ nm (rel. int.) 279 (0.53), 309 (0.51) and 388 (1.00). Oxidative coupling of VI with copper(II) acetate under a high dilution condition in pyridine at 50° gave 2,5:14,17-diepoxy-8,10-bisdehydro[17]annulenone III (1.5—2.0%), dark red prisms, decomp. 180° (without melting); Mass Spectrum *m/e*: 260 ($M^+$, $C_{17}H_8O_3$), 232 ($M^+$—CO); IR $\nu_{\max}^{KBr}$ cm$^{-1}$: 2200 ($\nu$ C≡C), 1590 ($\nu$ C=O), 1473 and 842 ($\delta$ CH=CH, *cis*); NMR and UV spectra, see Table I and II, respectively. $LiAlH_4/AlCl_3$ reduction of III at 0° gave homoannulene VII (90%), yellow prisms, mp 133—135°; Mass Spectrum *m/e*: 246 ($M^+$, $C_{17}H_{10}O_2$); IR $\nu_{\max}^{KBr}$ cm$^{-1}$: 2170 ($\nu$ C≡C); UV $\lambda_{\max}^{MeOH}$ nm ($\varepsilon$): 219 (18100), 294 (27300), 426 (4380) and 448 (3380); NMR spectrum, see Table I.

Table I. Chemical Shifts for Protons of III and VII (in $\tau$, $J$ in Hz)

| Protons[a] | a<br>III in<br>$CDCl_3$ | | b<br>III in<br>$CF_3COOH$ | | c<br>VII in<br>$CDCl_3$ | | Difference, $\tau$<br>$\Delta$ (a—c) | <br>$\Delta$ (b—c) |
|---|---|---|---|---|---|---|---|---|
| H-3, 16 | 2.90 d | $J$ = 4.0 | 2.86 d | $J$ = 4.0 | 3.96 s | | −1.06 | −1.10 |
| H-4, 15 | 3.92 d | | 4.10 d | | 3.96 s | | −0.04 | +0.14 |
| H-6, 14 | 3.95 d | $J$ = 11.4 | 4.28 d | $J$ = 11.0 | 3.69 d | $J$ = 11.0 | +0.26 | +0.59 |
| H-7, 12 | 5.04 d | | 5.30 d | | 4.82 d | | +0.22 | +0.48 |
| $CH_2$ | — | | — | | 5.95 s | | — | — |

[a] For convenience, the numbering of the homoannulene VII has been coincided with that of annulenone III.

Table II. Absorption Maxima of Oxygen-bridged and Trisdehydro[17]Annulenones

|  III |  VIII[7] |  IX[6] |
|---|---|---|
| $\lambda_{\max}^{CCl_4}$ nm ($\varepsilon$) | $\lambda_{\max}^{Et_2O}$ nm ($\varepsilon$) | $\lambda_{\max}^{Et_2O}$ ($\varepsilon$) |
| 261 (46700) | 266sh (16800) | |
| 291 (66700) | 295sh (68000) | 293 (61000) |
| 309 (106600) | 304 (81000)<br>308 (82000) | 304 (74000) |
| | 403 (1100) | |
| 463 (480) | | 463 (1000) |
| 480 (500) | | |
| 515sh (430) | 520sh (780) | *ca.* 500 (830) |
| 558sh (240) | 560 (940) | *ca.* 540 (360) |
| 613 (40) | 610 (660) | |

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[6] J. Griffiths and F. Sondheimer, *J. Am. Chem. Soc.*, **91**, 7518 (1969).
[7] T.M. Cresp and M.V. Sargent, *J. Chem. Soc. Perkin. I*, **1973**, 2961.
[8] K. Eiter and H. Oediger, *Ann.*, **682**, 62 (1965).
[9] Efforts to take a clean NMR spectrum failed, since a rapid polymerization ocurred on concentration.

As shown in Table I, all the protons of III were found to have nearly the same chemical shifts as those of homoannulene VII. Thus, annulenone III proved to sustain no paramagnetic ring current. Furthermore, the NMR spectrum of III in $CF_3COOH$ shows no remarkable change of the chemical shifts, suggesting the corresponding [17]annulenium ion is not formed on protonation. On contact with conc. $H_2SO_4$ III causes a rapid decomposition. These observations make a marked contrast with our experiences which could be obtained from bis-oxido-bridged [15]annulenones.10)

As expected, paratropicity is destroyed in III by the perturbation of furan rings, and III should be characterized only as a cyclic polyenone. On the other hand, the ultraviolet (UV) spectrum of III is closely resemble to those of planar nonbridged trisdehydro[17]annulenone (IX) and bridged 2,5:8,11:14,17-tri-epoxy-[17] annulenone (VIII), which are both paratropic, see Table II. Therefore, it is of interest that annulenone III is only differed from its magnetic susceptibility from those of paratropic 16$\pi$ homologues, keeping the electronic properties nearly the same with those of IX and VIII. The lack of paratropicity of III is partly due to the contracted conjugation loop.11)

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10) *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, *Tetrahedron Letters*, **1974**, 3889; *c*) H. Ogawa, H. Kato, and Taniguchi, *Chem. Pharm. Bull.* (Tokyo), **25**, 653 (1977).

11) Experimental evidence that the contour of the loop of annulene is one of the factors to determine the magnitude of the ring current has been obtained by Boekelheide, *et al.* [see R.B. DuVernet, T. Otsubo, J.A. Lawson, and V. Boekelheide, *J. Am. Chem. Soc.*, **97**, 1629 (1975)]. From our recent results this effect is also valid in the case of Ib. The diamagnetic ring current in Ib is, to some extent, decreased as compared with that of Ia. The "frozen" $^1$H-NMR spectrum of Ib (at $-53°$) shows the signals of the outer protons at $\tau$ 1.32—2.10, and the inner proton at $\tau$ 9.64, whist that of Ia indicates outer protons at $\tau$ 1.32 and 1.34, see references 1 and 2.