

8,11-Imino-2,5:14,17-diepoxy[17]annulenone

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Summary The synthesis of an antiaromatic [17]annulenone containing a pyrrolic unit is described; the NH resonance occurs at extremely low field in its ^1H n.m.r. spectrum

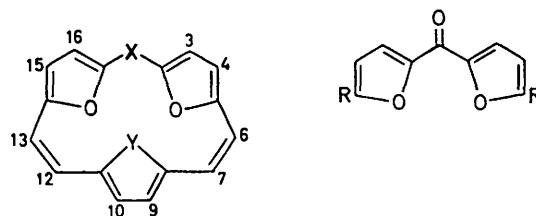
treatment with $\text{LiAlH}_4\text{-AlCl}_3$ in ether the ketone was reduced to the alkane (**11**) (71%) which formed yellow prisms, m.p. $126\text{--}128^\circ$ (from light petroleum).§ A comparison of the n.m.r. spectrum of the annulenone (**10**) with that of the alkane (**11**) shows that the olefinic "outer protons" (6-, 7-, 12-, 13-H) are shifted upfield by an average of 0.90 p.p.m., the 9,10-protons by 0.76 p.p.m., and that the inner NH proton is shifted downfield by 5.9 p.p.m. [$\tau - 8.3$

In an earlier communication¹ we described the synthesis of the heteroatom bridged [17]annulenone (**1**), a paratropic $4n\pi$ electron system. This molecule contains only "outer" protons which, as expected for an antiaromatic system, resonate at unusually high field. In antiaromatic compounds it is the "inner" protons which experience the greatest effect of the paramagnetic ring current since they are shifted to lower field more than the "outer" protons are shifted to higher field.² It would therefore be of interest to prepare a [17]annulenone similar to (**1**) which contained inner proton(s). We have investigated the synthesis of a pyrrolic analogue of (**1**) in which the NH proton is inside the ring.

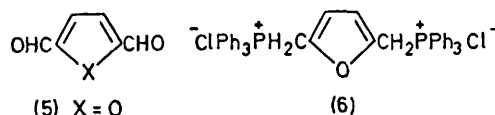
Chloromethylation of difuryl ketone (**2**)³ with chlorodimethyl ether and tin(IV) chloride in dichloromethane at $0\text{--}25^\circ$ gave the bis(chloromethyl) compound (**3**)† (ca. 50%), as orange prisms, m.p. $119\text{--}120^\circ$.‡ (**3**) was converted into the phosphonium salt (**4**) (94%) by treatment with triphenylphosphine in *NN*-dimethylformamide (DMF) at 100° . Wittig reaction of (**4**) with furan-2,5-dicarbaldehyde (**5**)⁴ constitutes a more convenient synthesis of the annulenone (**1**) (9.65%) than that previously reported,¹ since, in contrast to (**6**), the salt (**4**) does not eliminate triphenylphosphine on treatment with base.

Pyrrole-2,5-dicarbaldehyde (**7**) was required for Wittig reaction with (**4**). Vilsmeier-Haack formylation of pyrrole with an excess of POCl_3 in DMF at 130° gave pyrrole-2-carbaldehyde (38%), pyrrole-2,4-dicarbaldehyde,⁵ (9%), and (**7**) in only 0.3% yield, m.p. $121\text{--}122^\circ$.‡ In contrast, Vilsmeier-Haack formylation⁶ of ethyl pyrrole-2-thiolcarboxylate⁵ gave the 4-formyl isomer (**8**)⁵ (22%), and the 5-formyl isomer (**9**) (59%). Desulphurisation⁷ of the latter with deactivated W-2 Raney nickel in boiling acetone (2 h) gave (**7**) in 36% yield.

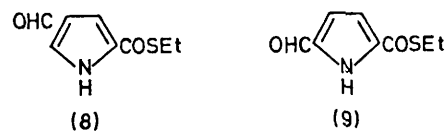
Wittig reaction between (**7**) and (**4**) yielded the pyrrolic macrocycle (**10**) (13.8%) as purple needles, (from dichloromethane-light petroleum), m.p. $299\text{--}300^\circ$ (decomp.).§ On



- (1) X = CO, Y = O
 (10) X = CO, Y = NH
 (11) X = CH₂, Y = NH
 (2) R = H
 (3) R = CH₂Cl
 (4) R = CH₂⁺PPh₃Cl⁻



- (5) X = O
 (7) X = NH
 (12) X = NMe



in (**10**), -2.4 in (**11**)], thus demonstrating the existence of a paramagnetic ring current. By contrast to this 16π electron antiaromatic system, in the aromatic 18π electron porphyrin systems the resonances due to the inner NH protons occur in the region $\tau 12\text{--}14$.⁸ There is a difference of 22 p.p.m. between the NH resonances in the two systems.

† All new compounds gave satisfactory elemental analyses or high resolution mass spectra.

‡ 60 MHz n.m.r. spectrum in agreement with the structure assigned.

§ Structure assignment in agreement with u.v. and 90 MHz n.m.r. spectra.

This provides compelling evidence for the antiaromaticity of (10).

N-Methylation of the dialdehyde (7) was achieved in 90% yield using MeI-K₂CO₃-DMF at room temperature and gave

(12) as feathery needles, m.p. 95–96°. On Wittig reaction with (4) none of the *N*-methylated analogue of (10) could be isolated.

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¹ T. M. Cresp and M. V. Sargent, *Chem. Comm.*, 1971, 1457.

² See K. G. Untch and D. C. Wysocki, *J. Amer. Chem. Soc.*, 1967, **89**, 6386 and references therein.

³ U. Michael and A. Hörnfeldt, *Tetrahedron Letters*, 1970, 5219.

⁴ G. Drechsler and G. Kopperschlaeger, East G.P., 26,542 (*Chem. Abs.*, 1964, **61**, 4315).

⁵ C. E. Loader and H. J. Anderson, *Tetrahedron*, 1969, **25**, 3879.

⁶ After our work was completed this reaction was reported by other workers, see P. Fournari, M. Farnier, and C. Fournier, *Bull. Soc. chim. France*, 1972, 283.

⁷ See E. Bullock, T.-S. Chen, and C. E. Loader, *Canad. J. Chem.*, 1966, **44**, 1007.

⁸ K. M. Smith, *Quart. Rev.*, 1971, **25**, 31.