

Heteroatom-bridged [17]Annulenones

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Summary Syntheses of [17]annulenone derivatives are reported, one of which has an appreciable paramagnetic ring current.

ANNULENONES which contain a $(4n + 3)$ membered ring are expected to be aromatic and to support a diamagnetic ring current whilst those with a $(4n + 1)$ membered ring are expected to be non-aromatic and to support a paramagnetic ring current. Although a number of large ring dehydroannulenes which confirm this prediction have been synthesised by Sondheimer and his co-workers¹ attempts to prepare the derived annulenones have not yet been successful.² We now report the synthesis of a [17]annulenone trioxide which supports a paramagnetic ring current.†

Reaction of 5-bromofuran-2-carbaldehyde³ with ethylene glycol gave the acetal (1) (82%), b.p. 122–124° at 10 mm Hg. Conversion of the acetal (1) into the lithio-derivative and treatment with ethyl *NN*-dimethylcarbamate⁴ gave, after removal of the protecting groups, the dialdehyde (2) (52%) as prisms, m.p. 189–191°, τ (all CDCl₃; all 60 MHz) 0.08 (s, 2H, CHO), and 2.26 and 2.61 (AB q, 4H, *J* 3.5 Hz, furan H). Perkin-type condensation of the dialdehyde (2)

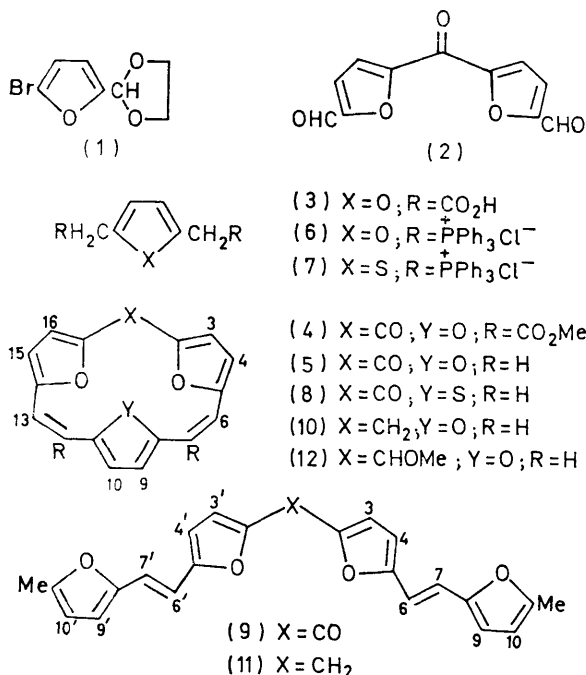
208°. On hydrolysis and decarboxylation ester (4) gave the annulenone (5) (4.4%). A better synthesis of macrocycle (5) was by Wittig reaction of the dialdehyde (2) with the bis (phosphonium chloride) (6)⁶ which proceeded in 8.0% yield. Compound (5) formed deep violet prisms, m.p. 233–236°, τ 3.28, 4.32 (ABq, 4H, *J* 3.5 Hz, 3-, 16-, 4-, 15-H), 4.32 (s, 2H, 9-, 10-H), and 5.03 (s, 4H, 6-, 7-, 12-, 13-H); ν_{\max} (all KBr) 1601 (C=O) cm⁻¹; λ_{\max} (all ether) 255, 267sh, 307sh, 314 nm with tailing into the visible (ϵ 25,000, 16,600, 47,000, 52,000, and 54,000 respectively).

Similarly a Wittig reaction between the dialdehyde (2) and the thiophen (7) gave the annulenone (8) (8.4%) as lustrous red-brown plates, m.p. 148–150°; τ 2.90, 3.88 (ABq, *J* 3.5 Hz 3-, 16-, 4-, 15-H), 3.25 (s, 2H, 9-, 10-H), and 3.67, 4.15 (ABq, 4H, *J* 12 Hz, 6-, 13-, 7-, 12-H); ν_{\max} 1600 (C=O) cm⁻¹; λ_{\max} 297 sh and 308 nm (19,800 and 22,700 respectively).

As a model for these systems we have synthesised the linear ketone (9); τ 2.41, 3.46 (ABq, 4H, *J* 3.5 Hz, 3-, 3'-, 4, 4'-H), 2.85, 3.22 (ABq, 4H, *J* 15 Hz, 6-, 6'-, 7-, 7'-H), 3.58, 3.89 (ABq, 4H, *J* 3.5 Hz, 9-, 9'-, 10-, 10'-H), and 6.72 br (s, 6H, Me) (see structural formula for assignment of signals); the usual long-range coupling found in sylvan derivatives was also apparent. On the basis of this model, protons 3 and 16 in macrocycle (5) are shifted upfield by 0.87 p.p.m., and protons 4 and 15 by 0.86 p.p.m. On treatment of compound (5) with excess of LiAlH₄/AlCl₃ in ether under reflux smooth conversion (95%) into the 'homoannulene' (10) occurred; τ 3.72 (s, 2H, 9-, 10-H), 3.89, 4.02 (ABq, 4H, *J* 3.5 Hz, 4-, 15-, 3-, 16-H), 4.20 (s, 4H, 6-, 7-, 12-, 13-H), and 6.00 (s, 2H, CH₂). Similar reduction of linear ketone (9) gave the alkane (11) (94%); τ 3.28 (s, 4H, olefinic H), 3.72–4.02 (m, 8H, furan H), 5.97 (s, 2H, CH₂), and 7.67 (s, 6H, Me). The chemical shifts of the protons in this molecule are in the same range as the similar protons in the cyclic alkane (10). Hence peripheral cyclic conjugation in this 'homoannulene' does not occur. On comparison of macrocycle (5) with compound (10) the olefinic protons of (5) are shifted upfield by 0.83 p.p.m. and protons 9 and 10 by 0.60 p.p.m. We regard these comparisons as strong evidence that compound (5) sustains an appreciable paramagnetic ring current.

Reduction of macrocycle (5) with NaBH₄ and methylation gave the methyl ether (12); τ 3.89, 4.18 (ABq, 4H, 3-, 16-, 4-, 15-H), 3.98 (s, 2H, 9-, 10-H), 4.55 (s, 4H, 6-, 7-, 12-, 13-H), 5.33 (s, 1H, methine H), and 6.56 (s, 3H, OMe). Comparison of the chemical shifts of the protons in 'homoannulene' (12) with those of compound (10) indicates that (12) supports a small paramagnetic ring current. Since compound (10) has no paramagnetic ring current the unusual behaviour of (12) cannot be due to 'homoantiaromaticity'⁷

with the furan (3)⁵ gave, after esterification and chromatography, the ester (4) (2.1%) as orange prisms, m.p. 206–



† Very recently the preparation of [15]annulenone-4,7:10,13-dioxide-2,15-dicarboxylic anhydride has been reported (see H. Ogawa, N. Shimojo, and M. Yoshida, *Tetrahedron Letters*, 1971, 2013). This molecule, presumably held in a planar conformation by the anhydride substituent, supports a diamagnetic ring current. It will be of interest to determine whether the parent annulenone dioxide is aromatic or not. A bridged [11]annulenone has also been reported; however, this system does not support a diamagnetic ring current (see W. Grimme, J. Riesdorff, W. Jüneman, and E. Vogel, *J. Amer. Chem. Soc.* 1970, **92**, 6335).

and is presumably due to a degree of polarity in the carbon–methyl ether derived from a tridehydro[17] annulenone.² oxygen bond. This effect has also been observed in the

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¹ G. M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.*, 1968, **90**, 5610; G. W. Brown and F. Sondheimer, *ibid.*, 1969, **91**, 760; J. Griffiths and F. Sondheimer, *ibid.*, 1969, **91**, 7518; G. P. Cotterell, G. H. Mitchell, F. Sondheimer, and G. M. Pilling, *ibid.*, 1971, **93**, 259.

² F. Sondheimer, *Pure and Applied Chem.*, in the press. We thank Professor Sondheimer for a pre-print of this review and for discussions.

³ Z. N. Nazarova, *Zhur. obshchei Khim.*, 1954, **24**, 575.

⁴ U. Michael and A. Hörnfeldt, *Tetrahedron Letters*, 1970, 5219.

⁵ K. Y. Novitskii, K. Y. Yurev, and V. N. Zhingareva, *Zhur. obshchei Khim.*, 1962, **32**, 3303.

⁶ H. Saikachi, H. Ogawa, Y. Minami, and K. Sato, *Chem. and Pharm. Bull. (Japan)*, 1970, **18**, 465. In agreement with these authors we found 1,6-elimination of triphenylphosphine to be a major side reaction.

⁷ S. Winstein, Chem. Soc. Special Publ. No. 21, Chemical Society, London, 1967.