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SYNTHESIS OF A [1,2-*c*]FURO[5,6-*c*]THIENOCYCLOÖCTATETRAENE AND A [1,2-*c*]THIENOCYCLOÖCTATETRAENE

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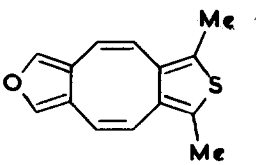
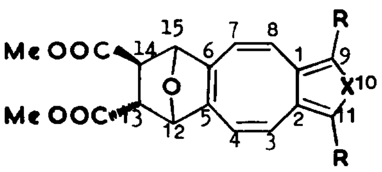
We wish to report the synthesis of 12,14-dimethyl[1,2-*c*]furo[5,6-*c*]thienocycloöctatetraene (I) and 9,11-dimethyl-5,6-[12,15-epoxy-13,14-bismethoxycarbonyl] cyclohexeno[1,2-*c*]thienocycloöctatetraene (II), substituted derivatives of the hitherto unknown heterocyclic systems containing a periphery of 16π and 12π-electrons, respectively.

Wittig reaction of 2,5-dimethylthiophene-3,4-dicarboxaldehyde (1) and furan-3,4-bis(methylenetriphenylphosphonium chloride) (2) with lithium methoxide in dimethylformamide at 90°, afforded the cyclic product (I) in 10% yield. After sublimation at 0.5 mm/70° compound (I) was obtained as colourless needles, m.p. 97°; mass spectrum, molecular ion at $^{m}/_{e}$ 228.0606 (calcd. for $C_{14}H_{12}OS$, 228.0608); λ_{max}^{EtOH} 210 (sh), 240 (sh) and 260 mμ with log ε 4.04, 4.32 and 4.41 respectively; n.m.r. (CCl_4, 60 M.c.p.s) τ 2.90 (s, 2 furan protons), 3.70 (s, 4 olefinic protons) and 7.81 (s, 6 methyl protons).

The Diels-Alder reaction of (I) with dimethyl fumarate in boiling benzene for 24 hr gave the adduct (II) in 30% yield. The adduct crystallised from ethanol in yellow prisms, m.p. 150°; mass spectrum, molecular ion at $^{m}/_{e}$ 372.1033 (calcd. for $C_{20}H_{20}O_5S$, 372.1031); λ_{max}^{EtOH} 210, 270 and 335 (broad) mμ with log ε 4.19, 4.27 and 3.40 respectively. The n.m.r. spectrum

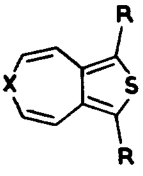


I.



II. X=S, R=Me

III. X=O, R=H



IV. X=O, R=Me

V. X=S, R=H

confirmed structure (II), showing two overlapping quartets (4H) centred at τ 3.70, 4.35 (J, 14 cps) and 3.80, 4.15 (J, 12 cps) due to the olefinic protons, a singlet superimposed on a doublet (total 2H) at 5.03 (J, 3 cps) due to protons 12, 15; singlets (3H each) at 6.23, 6.33 due to the methoxyl protons which are superimposed on a 1H methine proton signal, a doublet (1H) centred at 7.00 (J, 3 cps) due to the other methine proton, and a singlet at 7.85 (6H) due to the methyl protons.

The substituted [1,2-c]thienocycloöctatetraene (II) can superficially be considered to contain a 12 π-electron system, which is isoelectronic with the corresponding furan compound (III) (2), the thieno[3,4-d]oxepin (IV) (1) and the recently reported thieno[3,4-d]thiepin (V) (3).

Both of the adducts (II) and (III) and the thiepin (V) show marked ultraviolet absorption in the 300-400 mμ region, which must indicate some extended conjugation in these systems. However, the chemical shifts of the olefinic protons of (II) (4), and of the potential 16 π-system (I), provide little evidence for paramagnetic ring currents which might be expected if these heterocyles constituted delocalised π-systems (5). Furthermore the proton coupling constants across the olefinic bonds of (II) are in the range expected for vicinal couplings in cyclic, non-planar C_8-olefins (6). Hence it must be concluded that (I) and (II) are non-planar, non-aromatic systems, which exhibit only limited interation of the π-electrons.

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REFERENCES

1. K. Dimroth, G. Pohl and H. Follmann, Chem.Ber. 99, 634 (1966).
2. J.A. Elix, M.V. Sargent and F. Sondheimer, J.Amer.Chem.Soc. 89, 5080 (1967).
3. R.H. Schlessinger and G.S. Ponticello, J.Amer.Chem.Soc. 89, 7138 (1967). Tetrahedron Letters, 3017 (1968).
4. The olefinic protons of benzocycloöctatetraene exhibit τ 3.60 - 4.20; J.A. Elix, M.V. Sargent and F. Sondheimer, Chem.Commun. 509 (1966).
5. J.A. Pople and K.G. Untch, J.Amer.Chem.Soc. 88, 4811 (1966); H.C. Longuet-Higgins, Chem.Soc.Spec.Public. No. 21, 108 (1967).
6. F.A.L. Anet, J.Amer.Chem.Soc. 84, 671 (1962).