A Convenient Synthesis of Annulene Polyoxides from Sucrose

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1,6-EPOXY[10]ANNULENE (I)[1,2], *syn*-1,6:8,13-diepoxy[14]annulene (II)[2,3] and 1,4:7,10:13,16-triepoxy[18]annulene (III)[4] all exhibit peripheral π-electron delocalisation and aromaticity. As these compounds contain $(4n + 2)$ peripheral π-electrons ($n = 2,3,4$) it appears probable that Hückel's rule is valid for such bridged annulenes. Further evidence could be provided by a comparison of the above compounds with some analogous bridged $4n$ π-systems.

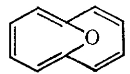
A convenient synthesis of triepoxy[18]annulene (III), two isomers of 1,4:7,10:13,16:19,22-tetraepoxy[24]annulene (IV)†‡ and two isomers of 1,4:7,10:13,16:19,22:25,28-pentaepoxy[24]annulene (V)†‡ is now described.

In 1944 Haworth and Jones[5] showed that 5-chloromethyl-2-furfural (VI) could readily be obtained by treating sucrose with hydrogen chloride. The reaction of this chloromethyl compound (VI) with triphenylphosphine in benzene solution gave the phosphonium salt (VII), m.p. 228—230°. The slow addition of lithium ethoxide to a solution of this salt (VII) in dimethylformamide, accomplished a self-Wittig reaction, presumably *via* the ylid (VIII). The complex mixture of products from this reaction was separated by column chromatography on alumina.

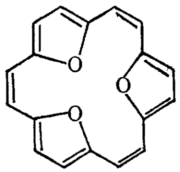
The trioxide (III) (0·07% yield) was isolated as red plates, identical in all respects with an authentic sample.[4]

The isomer of tetraepoxy[24]annulene with higher R_F (IVa) (0·7%) crystallised from ether–light petroleum as violet-black prisms, m.p. 216—217°. The u.v. spectrum (ether) showed λ_{max} 256 (ϵ 12,100), 328sh (49,500), 343 (104,000), and 360 mμ (146,000). The second isomer of tetraepoxy[24]annulene (IVb) (0·8%) crystallised from chloroform as violet prisms, m.p. 269—270°, and the u.v. spectrum (chloroform) exhibited λ_{max} 260 (ϵ 14,400), 335sh (52,200), 349 (108,000), 362 (156,000), and 370sh mμ (130,000). Both of the isomeric tetraepoxy[24]annulene showed two distinct regions of absorption in the n.m.r. spectrum. The major absorption occurs at considerably higher field (τ 4·1—5·2) than for acyclic vinylfurans,[6] while the minor absorption occurs at very low field [τ 1·30—1·40; 3H in (IVa); 4H in (IVb)]. However, these spectra do not define the configuration of (IVa) and (IVb) unambiguously, so the n.m.r. spectra cannot be interpreted at this stage. It seems possible that the minor, low-field bands may be due to internal protons.[10]

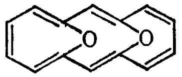
Two isomers of pentaepoxy[30]annulene (V) were also isolated. The isomer with higher R_F (Va) (0·4% yield) crystallised from ether as deep-red to black prisms, m.p. 218—220°, and showed λ_{max} (ether) at 234 (ϵ 34,500), 299 (17,500), 319 (20,000), 410 (73,900) and a shoulder at 480 mμ (6,600) in the u.v. spectrum. The second isomer (Vb) (0·15%) crystallised from ether as deep-red needles, m.p. 192—194°. The u.v. spectrum (ether) showed maxima at 298 (22,700), 313



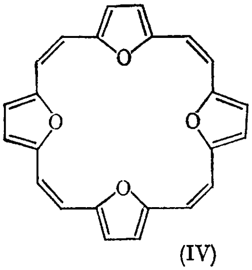
(I)



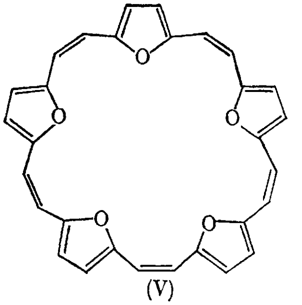
(III)



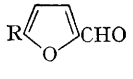
(II)



(IV)



(V)



(VI) $R{=}CH_2Cl$

(VII) $R{=}CH_2\overset{+}{P}Ph_3Cl^-$

(VIII) $R{\cdot}CH{\cdot}PPh_3$

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† The formulae for both tetraepoxy[24]annulene (IV) and pentaepoxy[30]annulene (V) are presented as the all-*cis* isomers, for although both compounds could be isolated in two geometrically isomeric forms, their configuration has not yet been determined. The individual isomers are designated (IVa), (IVb) and (Va), (Vb) respectively, according to the relative R_F values on alumina eluted with 5% ether–light petroleum.

‡ Satisfactory high-resolution mass spectra were obtained for these compounds.

(23,000), 412 (83,700) and shoulders at 400 (76,500), 465 (8,100), and 500 mμ (6,800). The n.m.r. spectra of the isomeric pentaepoxy[30]annulene (Va, Vb) showed chemical shifts akin to those of acyclic vinylfurans[6] (τ 3·3—4·0) and the band positions show little variation (±0·2 τ) over the temperature range investigated (+40° to −40°). This relatively high-field absorption is in marked contrast to that observed for the aromatic $4n + 2$ peripheral π-system, triepoxy[18]annulene (τ 1·32, 1·34),[4] but parallels that of the related annulenes, namely pentadehydro- and tridehydro-[30]annulene,[7] where excessive ring size invalidates Hückel's rule.[8]

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