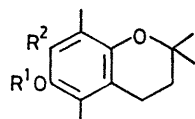


Oxygen Analogue of the Würster Salts; the Cation Radical from 2,3,4,7,8,9-Hexahydro-2,2,5,7,7,10-hexamethylbenzo[1,2-*b*:4,5-*b'*]dipyran

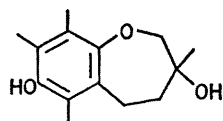
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Summary 2,3,4,7,8,9-Hexahydro-2,2,5,7,7,10-hexamethylbenzo[1,2-*b*:4,5-*b'*]dipyran (5) is sensitive to acids, which partly convert it into a cation radical (6) that can be isolated as the crystalline hexachloroantimonate by treating the dipyran with antimony(v) chloride.

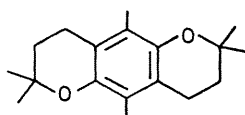
WHEN reporting that the ^1H n.m.r. spectra of compounds such as (1) in the tocopherol series are sensitive to acids we suggested¹ that electronic contributions not only from both oxygen atoms but also from the benzylic methylene group were essential. Such contributions require the oxygen functions to lie in the plane of the benzene ring and one benzylic CH bond to lie perpendicular to it. We have confirmed these requirements. The methyl ether (2) is not sensitive (the methoxy group is rotated out-of-plane by two *ortho* substituents²) whereas the lower homologue (3) is as sensitive as the phenol (1). The phenol (4), in which the seven-membered ring forces both the ring oxygen function and the benzylic methylene group out of the correct alignments, is also insensitive. In contrast, the dipyran (5) is particularly sensitive because both the methylene groups can contribute.



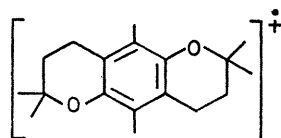
- (1) $\text{R}^1 = \text{H}; \text{R}^2 = \text{Me}$
(2) $\text{R}^1 = \text{R}^2 = \text{Me}$
(3) $\text{R}^1 = \text{Me}; \text{R}^2 = \text{H}$



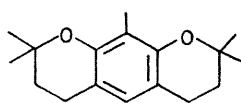
(4)



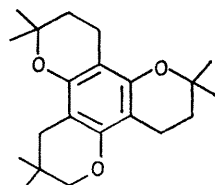
(5)



(6)



(7)



(8)

The dipyran³ (5) is the most sensitive compound we have yet found, and even chloroacetic acid, though not acetic acid, induces some broadening of the n.m.r. resonances. The cation radical (6) considered to be responsible for the effect has been obtained as the dark green, crystalline salt $[\text{C}_{18}\text{H}_{26}\text{O}_2]^+\cdot[\text{SbCl}_6]^-$ by treating the dipyran in tetrachloromethane with antimony(v) chloride. This salt gives the correct elementary analyses and, in the mass spectrometer, the expected ion m/e 274. The n.m.r.

spectrum in CD_3CN or CDCl_3 shows, as expected, only the signal emanating from the geminal methyl groups. Mild reduction regenerates the dipyran almost quantitatively.

The salt has λ_{max} 476 (sh 454) nm (ϵ 2.8×10^3) obeying Beer's Law at concentrations near 10^{-2}M and not affected by added dipyran. The same absorption is found in solutions of the dipyran in acid media, and the e.s.r. spectra are also closely parallel, thus supporting the view that the cation radical (6) is indeed present in acidic media and is responsible for the n.m.r. effect. The visible absorption of a $1.8 \times 10^{-2}\text{M}$ solution of the dipyran in dichloromethane, *ca.* 0.4 M in trifluoroacetic acid, indicates that the cation radical concentration produced is *ca.* $4 \times 10^{-5}\text{M}$ (this slowly increases with time).

The e.s.r. spectrum of the dipyran in acidified dichloromethane is complex and temperature variable. At 40 °C a low-frequency modulated 15-line spectrum is observed having splittings of 0.14 mT; at 10 °C a characteristic line-width alternation pattern appears; and at temperatures below -60 °C the spectrum becomes very complex and comprises nine groups of lines separated from one another by 0.24 mT. From these observations we conclude that above 10 °C a rapid chemical equilibrium is present, that between 10 and -60 °C intramolecular conversion is taking place, and that below -60 °C a 'frozen' conformer is being detected. The salt in dichloromethane gives at ordinary temperatures essentially the same e.s.r. spectrum, the signal intensity being consistent with a salt that is entirely a radical. Again the spectrum is temperature dependent, and between -30 and -110 °C the spectrum consists of nine lines having splittings of 0.26 mT; however,

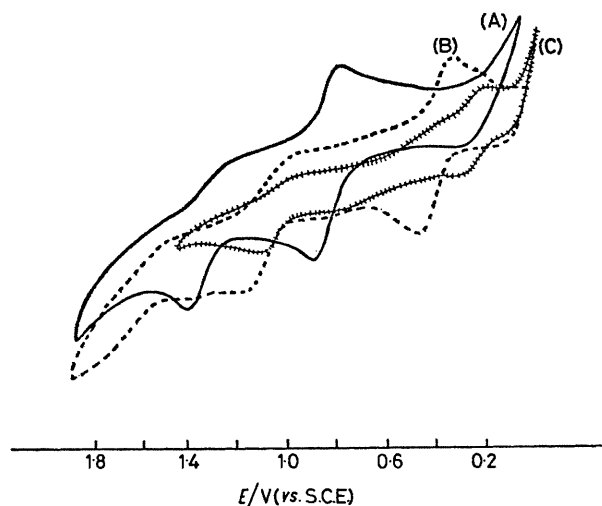


FIGURE. Cyclic voltammograms for the oxidation at 22 °C of a 2 mM solution of the dipyran (5) in (i) dichloromethane (A), (ii) dichloromethane-trifluoroacetic acid (9:1 v/v) (B), and (iii) trifluoroacetic acid (C). The supporting electrolyte was tetrabutylammonium fluoroborate and the sweep rate 86 mV s⁻¹.

the temperature region now shows no increase in fine structure, probably because of interactions with the anti-mony nuclei (^{121}Sb , $I = 5/2$; ^{123}Sb , $I = 7/2$).

Attempts to correlate the ease of removal of one electron with structural features by means of cyclic voltammetry are hampered by the sensitivity to acids of the voltammograms of the chromanol (**1**) and the dipyrans (**5**). The former has already been studied by Svanholm, Bechgaard, and Parker,⁴ who found it necessary to use an acidic medium to prevent loss of the phenolic proton. In these circumstances the first electron was removed at 0.80 V, presumably generating a cation radical related to (**6**), and a second at 1.34 V corresponding to the formation of the dication. In dichloromethane without acid, the dipyrans (**5**) shows two separate oxidation peaks, at 0.85 and 1.37 V (Figure), a seemingly very satisfactory correspondence, but the addition of acid now causes major changes including peak shifts of more than 500 mV, and we find that the chromanol (**1**) is similarly affected but that 1,4-dimethoxybenzene is not. Such shifts are much larger than those known to be produced merely by variations in solvents, and we attribute them specifically to the presence of acid although we are not yet able to interpret them.

Fortunately, the charge transfer bands in π -complexes with tetracyanoethylene⁵ (Table) confirm that electron availability is promoted by fusion with a dihydropyran

TABLE. Charge-transfer bands of complexes of tetracyanoethylene with alkoxybenzenes and related chromans^a

Compound	$\lambda_{\text{max}}/\text{nm}$	Bathochromic shift/nm
1,3-Dimethoxybenzene ⁵	548	
Dipyrans (7)	615	67
1,3,5-Trimethoxybenzene ⁵	552	
Tripyrans (8)	670	118
1,4-Dimethoxybenzene ⁵	616	
Benzoxepin (4)	590	-26
Benzopyran (1)	716	100
Dipyrans (5)	780	164

^a For solutions in dichloromethane 1.5×10^{-3} M in both components.

ring, and show that the effect is *ca.* three times larger (shifts of *ca.* 90 nm per fusion) for a quinol nucleus than for a resorcinol nucleus (shifts of *ca.* 35 nm per fusion). Indeed, the shifts for the dipyrans (**5**) are comparable with those for aromatic amines and its cation radical salt can be regarded as the first oxygen analogue of the Würster salts⁶ discovered in 1879.

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¹ I. Al-Khayat, F. M. Dean, D. A. Matkin, B. Parvizi, M. L. Robinson, and C. Thebtaranonth, *J.C.S. Chem. Comm.*, 1978, 265.

² G. Baddeley, N. H. P. Smith, and P. A. Vickars, *J. Chem. Soc.*, 1956, 2455; A. Zweig, J. E. Lehnsen, and M. A. Murray, *J. Amer. Chem. Soc.*, 1963, **85**, 3933.

³ V. L. Frampton, W. A. Skinner, P. Cambour, and P. S. Bailey, *J. Amer. Chem. Soc.*, 1960, **82**, 4632.

⁴ U. Svanholm, K. Bechgaard, and V. D. Parker, *J. Amer. Chem. Soc.*, 1974, **96**, 2409.

⁵ E. M. Voigt and C. Reid, *J. Amer. Chem. Soc.*, 1964, **86**, 3930; A. Zweig, *J. Phys. Chem.*, 1963, **67**, 506.

⁶ C. Würster and R. Sendtner, *Ber.*, 1879, **12**, 1803, 2071; L. Michaelis, *Chem. Rev.*, 1935, **16**, 243.