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# A SPIROCYCLIC CHROMAN FROM A SPIROEPOXYCYCLOHEXADIENONE

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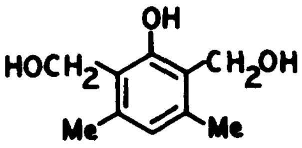
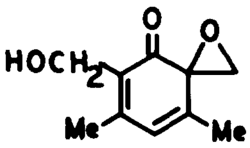
Summary: Reaction between the hydroxymethylspiroepoxycyclohexadienone (2) and chlorotrimethylsilane gave the spirocyclic chroman (3) whose crystal structure has been determined. The chroman presumably arose by dimerisation of an intermediate *o*-quinone methide (5). The stereochemistry of the chroman (3) in solution is also considered.

In the course of investigating the reactions of spiroepoxycyclohexadienones with nucleophiles[1], we carried out a reaction between the hydroxymethyl derivative (2) and chlorotrimethylsilane as a means of initiating possible ring-expansion, ring-opening and/or rearrangement processes. We wish to report the results of this investigation.

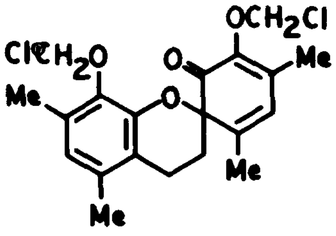
The hydroxymethylspiroepoxycyclohexadienone (2)[2] was prepared in 73% yield by the sodium periodate (methanol)[3] oxidation of 2,6-bis(hydroxymethyl)-3,5-dimethylphenol (1) which in turn was prepared by hydroxymethylation[4] of 3,5-dimethylphenol. The spiro compound (2) showed no propensity to undergo a Diels-Alder dimerisation to produce a tricyclic dimer[5] and we conclude that the presence of the methyl and hydroxymethyl substituents on the cyclohexadienone ring provide sufficient steric bulk to prevent this reaction.



(1)



(2)



(3)

On reaction with chlorotrimethylsilane in dichloromethane at 25° for 35 min, the spiroepoxy compound (2) gave rise to a yellow crystalline compound m.p. 110-112°C in yields consistently between 40-50% and subsequently, this compound was shown to be the spirocyclic chroman (3). The compound m.p. 110-112°C was shown to have a molecular weight of 396.0895 ($M^{+\cdot}$) and a corresponding molecular formula of $C_{20}H_{22}Cl_2O_4$ (elemental analysis) which suggested a dimeric structure of some description obtained from compound (2). An infrared spectrum (1675 and 1650 $cm^{-1}$) suggested the presence of a dienone chromophore which was corroborated by the u.v. absorption spectrum ($\lambda_{max}$ 332, log $\varepsilon$ 3.47)[6]. The proton decoupled $^{13}C$ n.m.r. spectrum ($CDCl_3$) showed only 17 resonance peaks due to apparent overlap of some of the absorption lines. Although four different methyl groups ($\delta$ 16.7-28.2) could be distinguished indicating a compound with no obvious elements of internal symmetry, the remainder of the spectrum could not be easily rationalized. Similarly, the $^1H$ n.m.r. spectrum could not be satisfactorily interpreted and for these reasons we determined a crystal structure of the compound m.p. 110-112°C.

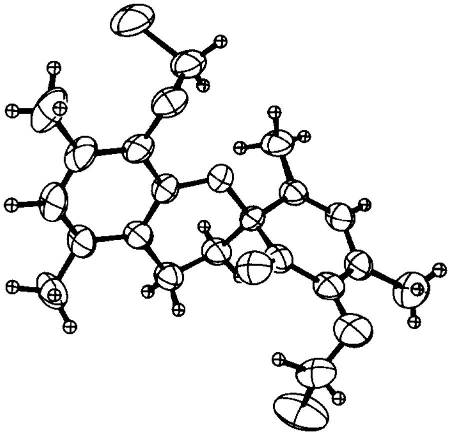
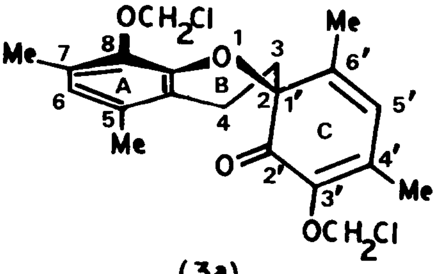


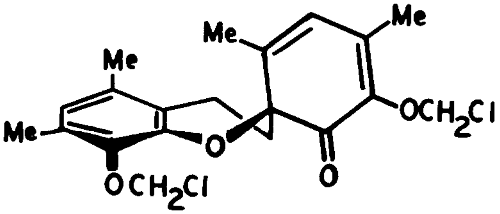
Figure 1

The compound $C_{20}H_{22}Cl_2O_4$ forms triclinic crystals belonging to the space group $P\bar{1}$, with $\underline{a}$ = 10.241(4), $\underline{b}$ = 9.067(2), $\underline{c}$ = 11.206(3) Å, $\alpha$ = 105.57(3), $\beta$ = 101.00(4), $\gamma$ = 91.09(3)° and $\underline{Z}$ = 2. The structure was solved by direct methods and refined with 2681 terms ($|F_o|>3\sigma|F_o|$) which had intensities measured on a Rigaku-AFC four-circle diffractometer with CuKα radiation. Anisotropic refinement of the non-hydrogen atoms by least-squares yielded a reliability index, $R = \Sigma\Delta F/\Sigma F_o$, of 0.071 with all hydrogens located. An ORTEP drawing of compound (3)[7] is shown in Figure 1. Ring B in compound (3) is in a half-chair form (3a) in which the dihedral angles for the bonds 1-2 and 3-4 with respect to the aromatic ring are 10.5 and 22.9° respectively. A CPK molecular model of the chroman (3) suggests that in solution, free rotation of both diastereotopic chloromethyl groups about the C-O bonds is not possible due to steric repulsion of the adjacent substituents. Also, limited conformational mobility in the half-chair ring B seems possible.

The $^1H$ n.m.r. could now be fully interpreted. The spectrum ($CDCl_3$, 25°) showed the $CH_3$ at C-6' at δ 1.98 (d, *J* 1.7 Hz) coupled to the vinylic proton (on C-5') at 5.84 (d, *J* 1.7 Hz); singlets at 2.02, 2.14 and 2.29 were assigned to the remaining methyls. The methylene protons in ring B at δ 2.10-2.80 (m) could not be completely resolved even at 270 MHz, however, part of the ABCD spin system could be seen at δ 2.72 (ddd, *J* 13, 4 and 2 Hz). The diastereotopic methylene protons of the chloromethoxy groups were observed as two AB pairs of doublets at δ 5.69 and 6.01 (2xd, *J* 5.9 Hz), and 5.85 and 5.93 (2xd, *J* 5.4 Hz). The remaining peak was observed at δ 6.60 (s, aromatic CH). The $^1H$ n.m.r. spectra of compound (3) determined in other solvents ($C_6D_6$, DMSO-$d_6$, acetone-$d_6$) showed solvent induced changes in the chemical shifts of some of the proton resonances (Δδ 0.25-0.65). This suggests that compound (3) may undergo conformational changes in solution which, presumably, results in a shift in the equilibrium position of the two possible half-chair conformers (3a) and (3b).

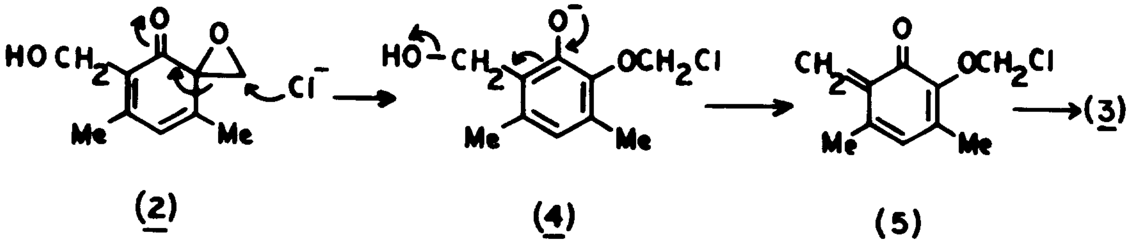


(3a)



(3b)

We consider that the product (3) was produced from the dimerisation[8-10] of an intermediate *o*-quinone methide (5) as shown in Scheme 1. We envisage the first step as a nucleophilic ring-opening of the epoxide ring by the chloride ion with cleavage of the carbon-carbon bond to form the phenoxide (4) which undergoes a 1,4-elimination to produce the quinone methide (5). Cycloaddition of two molecules of the reactive *o*-quinone methide (5) would then produce the spirocyclic chroman (3).



Scheme 1

The spirochroman (3) appears to undergo a number of facile reactions both under the influence of light and with nucleophiles and these reactions are being investigated at present.

## REFERENCES AND NOTES

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