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TRANSESTERIFICATION OF CYCLIC ESTERS

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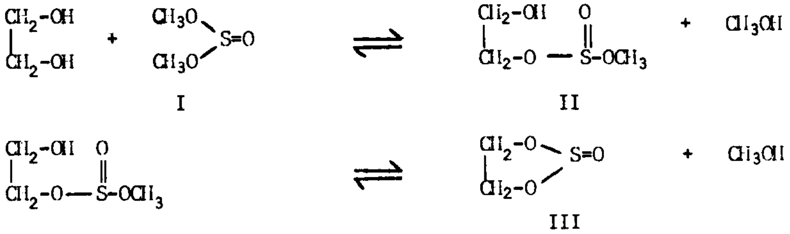
Transesterification has been used to prepare various cyclic esters from dialkyl esters and diols (1,2,3). The reaction has been presumed to take place in two steps, for example,



Reaction occurs on heating to about 100° and since the equilibria lie fairly centrally, one component, typically methanol, is removed to force the reaction to completion. The equilibration is both acid and base catalysed.

Davis (4), studying the ethylene sulphite-methanol equilibrium by gas chromatography, was unable to find any evidence for the existence of intermediate II.

While studying the reactions of alkoxides on sulphites (5) we obtained clear evidence, from nmr spectroscopy, for this compound and for the analogous carbonate ester $HO.CH_2CH_2O.CO.OCH_3$.

The sulphite and methanol, or the diol and dimethyl sulphite, could be reacted thermally (3 hr. at 120°) or by adding either dry HCl gas or an approximately 10^{-2}M solution of NaOH in MeOH. Catalysed equilibration, particularly with base which reacts slowly with sulphites, has the disadvantage that hydroxyl proton exchange rates decrease after several minutes and this broadens coupled resonances. We believe that this is caused by intensive drying by the reaction products such as sodium methyl sulphite.

Figure 1 shows the spectrum of the ethylene sulphite-methanol system at 60 Mc/sec. Figure 2 shows the spectrum of the intermediate (II) in detail at 100 Mc/sec. It consists of a methyl resonance at τ = 6.32 ppm (from TMS) superimposed on an $AA'B_2$ pattern from the methylene protons. The complex multiplet from the A protons (5.96 ppm) is assigned to the $-CH_2.O.SO.-$ group from

FIG. 1

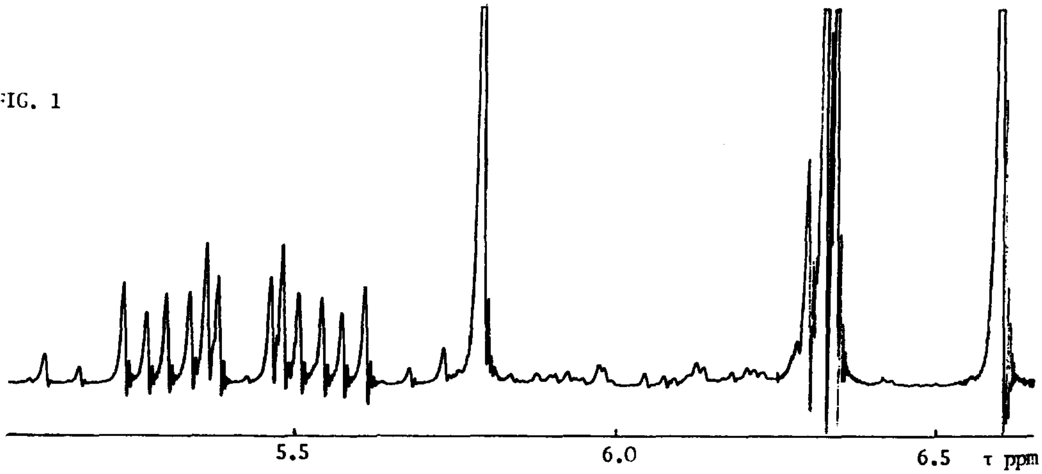


FIG. 2

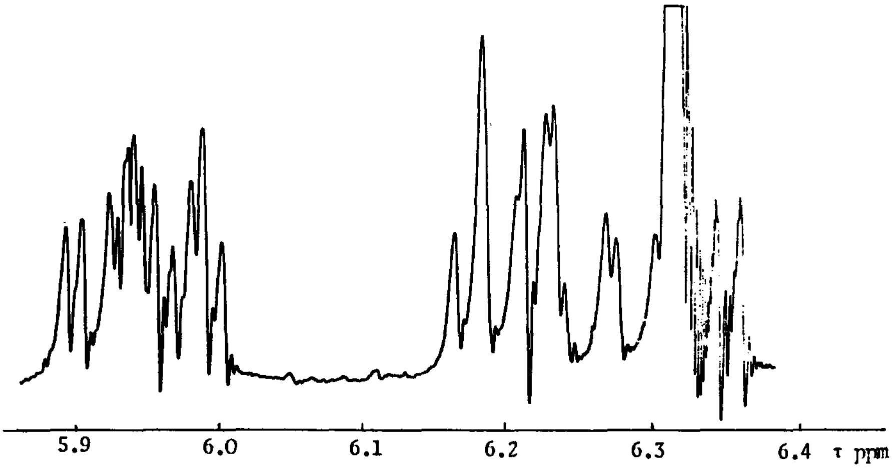
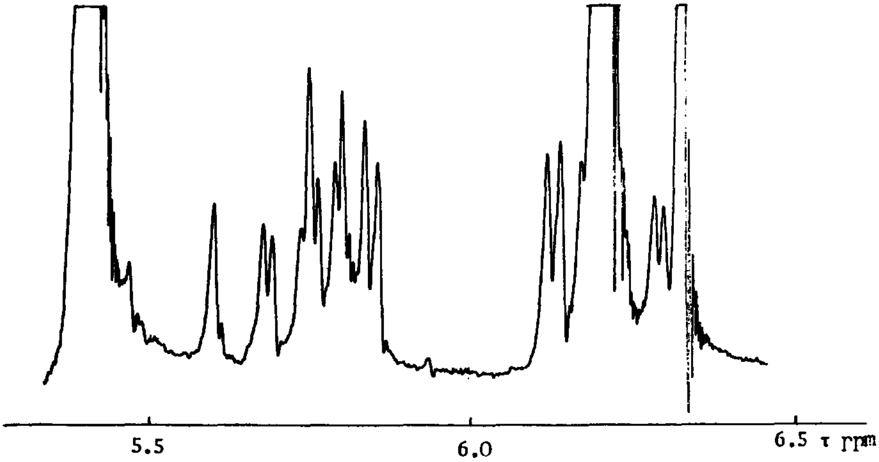


FIG. 3



chemical shift (ethylene sulphite (III) has a complex AA'BB' spectrum centered at 5.43 ppm; ethandiol has methylene protons at 6.34 ppm; dimethyl sulphite (I) has methyl protons at 6.33 ppm), and from the greater complexity arising from proton magnetic non-equivalence caused by the anisotropy of the S=O bond. The other multiplet centered at 6.21 ppm is assigned from shift, and from broadening when hydroxyl proton exchange rates become slow.

The spectrum (Fig. 3) of the intermediate in the ethylene carbonate-methanol equilibrium shows the methyl resonance at 6.34 ppm adjacent to a symmetrical A_2B_2 pattern at 5.80 ppm and 6.20 ppm. The dimethyl carbonate resonance is superimposed at 6.23 ppm.

A study was also made of systems of trimethylene, tetramethylethylene and meso-2,3-dimethylethylene sulphites and methanol. No evidence was found for the formation of a trans-esterification intermediate in these cases. However, this could reflect the experimental difficulties of detecting small concentrations of intermediates where spectra are much more complex. The rate of alkoxy exchange with five-membered cyclic sulphites was reduced by methyl substituents.

No intermediate could be detected in the ethylene phenylboronate-methanol system.

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