

## Spectroscopic Evidence for the Existence of a Stable Acidic Ortho-ester

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WHEN *cis*-3,4-dihydroxytetrahydrofuran (anhydroerythritol) was treated with an excess of trifluoroacetic anhydride for a limited time, a crystalline compound m.p. 118—120° (from acetone) was isolated. Analyses corresponded to a molecular formula  $C_6H_7F_3O_4$ , *i.e.*, a monotrifluoroacetate of the original diol. However, since a trifluoroacetate carbonyl stretching band was absent from the

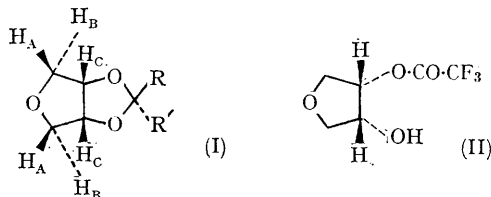
solid-state i.r. spectrum, we assign to it one of the cyclic ortho-ester structures (I).

The proton n.m.r. spectrum<sup>1</sup> of a freshly prepared solution in trideuteroacetonitrile showed a pattern which is characteristic of such a cyclic structure: a multiplet centred at  $\tau$  5.03 being due to the bridgehead protons  $H_C$ ; a multiplet which (neglecting the coupling to the bridgehead protons)

approximated to an AB quartet due to the non-equivalent protons of the methylene groups:  $H_A \tau$  6.56;  $H_B \tau$  5.92;  $J_{AB}$  11.8 c./sec. On standing, a second similar set of peaks appeared in the spectrum corresponding to the second isomer:  $H_C \tau$  4.87;  $H_A \tau$  6.53;  $H_B \tau$  6.01;  $J_{AB}$  11.8 c./sec. Equilibrium was reached after about 90 min., when the conversion into the second isomer was approximately 25% complete. We assign to the more stable initial compound and its isomer the structures (I;  $R = CF_3$ ,  $R' = OH$ ) and (I;  $R = OH$ ,  $R' = CF_3$ ) respectively. This assignment is consistent with the greater downfield shift of the bridgehead protons in the second isomer where the  $H_C$ -C and C- $CF_3$  bonds are in a *trans*-parallel arrangement, wherein the electron-attracting  $CF_3$  group exerts a maximum effect on the protons  $H_C$ .

The fluorine n.m.r. spectrum<sup>1</sup> of the equilibrium mixture shows peaks at  $\phi^* + 85.29$ ,  $84.43$ , and  $74.80$  of relative intensity 9.5 : 3.4 : 1. The first two peaks are due to the  $CF_3$  fluorines in the major (I;  $R = CF_3$ ,  $R' = OH$ ) and minor (I;  $R = OH$ ,  $R' = CF_3$ ) cyclic components respectively, while the chemical shift of the third peak shows<sup>2</sup> that it is due to a small amount of an open-chain normal trifluoroacetate. It appears therefore that in solution an equilibrium between the two cyclic structures (I) and the open-chain trifluoroacetate (II) is set up. I.r. spectra of a chloroform

solution confirmed the presence of a small amount of the compound (II):  $\lambda_{max}$  1780  $cm^{-1}$



Trialkyl ortho-esters are well known,<sup>3</sup> but we believe that the compound (I;  $R = CF_3$ ,  $R' = OH$ ) is the first case of a dialkyl ortho-ester (acidic ortho-ester<sup>3</sup>) being isolated. The demonstration of the existence of the equilibrium between the cyclic (I) and open-chain (II) structures provides confirmation of the long-held view that such acidic ortho-esters are intermediates in the migration of acyl groups in vicinal hydroxy-esters.<sup>4</sup> The unusual stability of the ortho-ester in the present case is due to the presence of the electron-withdrawing  $CF_3$  group, and is paralleled by the stability towards hydrolysis of ketals derived from 1,1,1-trifluoroacetone.<sup>5</sup>

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<sup>1</sup> N.m.r. spectra were determined at 40.004 and 37.644 Mc./sec. for protons and fluorine respectively. The assignments in the proton spectra are based on comparisons with extensive series of spectra of cyclic and open-chain esters of anhydroerythritol: spectra of the two types are easily distinguished. Chemical shifts in fluorine spectra are referenced to internal trichlorofluoromethane and are expressed as  $\phi^*$ -values (p.p.m.) (G.V.D. Tiers and G. Filipovich, *J. Phys. Chem.*, 1959, **63**, 761).

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