Tetrahedron Letters Vol. 21, pp 1791 - 1792
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0040-4039/80/0429-1791$02.00/0

# APPLICATION OF $^{13}$C N.M.R. IN A RE-EXAMINATION OF THE ISOPROPYLIDENATION OF D-RIBOSE DIETHYLDITHIOACETAL AND ERYTHRITOL

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Summary: The di-O-isopropylidene acetals resulting from the reaction of D-ribose diethyldithioacetal and erythritol with acidic acetone have been shown to contain 5- and 7- but not 6-membered rings.

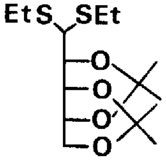
In a series of isopropylidene acetals of known structure the $^{13}$C chemical shifts of the acetal carbon[1,2] and the methyl groups[1] show a clear correlation with the acetal ring size. We have now examined the isopropylidenation of two polyols in which there is a possibility of forming isomeric acetals with varied ring sizes. Foster[3] reported that isopropylidenation of D-ribose diethyldithioacetal using acetone with $H_2SO_4$ and anhydrous $CuSO_4$ gave a di-O-isopropylidene compound, later assigned[4] the structure (1). Horton,[5] on the other hand, by an X-ray structure of a derived compound, provided evidence for the isomeric diacetal (2). Using anhydrous $CuSO_4$ as catalyst Szarek and Jones[6] detected (t.l.c.) two di-O-isopropylidene compounds and van Es[7] has recently described the isolation of (1) and (2) from such a reaction.

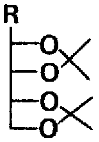
In our hands reaction under Foster's conditions[3] afforded two di-O-isopropylidene compounds, (2)$\{[\alpha]_D -93.6^\circ(CHCl_3)\}$ and (3)$\{[\alpha]_D -21.5^\circ(CHCl_3)\}$, each in 40% yield; the structures were deduced from the c.m.r. spectra (see Table). The spectrum of (2) showed the presence of two 5-membered 1,3-dioxolan rings.[1] (2) was converted [3] into the benzoate (4), m.p. 82-83°, $[\alpha]_D -32^\circ(CHCl_3)$ $\{$Lit.,[3] m.p. 79-80°, $[\alpha]_D -32^\circ\}$, whose c.m.r. spectrum (Table) again showed the presence of two 5-membered rings. In the c.m.r. spectrum of (3) two different ring-sizes were evident, automatically precluding (1) and (2) as structures and there was positive evidence for both a 5- and 7-membered ring. Under our conditions we had no evidence for the formation of (1), the other products being monoacetals.

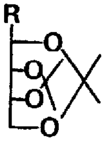
Acid catalysed reaction of acetone with erythritol gave the crystalline acetal(5)[8,9] (90%), while kinetic isopropylidenation using 2,2-dimethoxypropane afforded (5) (63%) and a syrupy isomer (6) (30%). The methyl signals for the 1,3-dioxepan ring in 3 and 6 are well separated, in contrast to the monocyclic dioxepan already described.[1] Treatment of

(6) with acidic acetone caused formation of (5) (90%). Stoddart[10] has reported the formation of 7 and 8 as minor products of methylenation of methyl D-ribonate and erythritol.

It is clear[1,2] that $^{13}$C spectroscopy is a valuable method of determining acetal ring sizes. Furthermore our results suggest that some previous assignments may be incorrect and that 7-membered isopropylidene acetals may be more common than previously supposed.


1


2 R=CH(SEt)$_2$
4 R=CH$_2$OBz
5 R=H


3 R=CH(SEt)$_2$
6 R=H

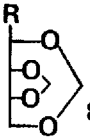

7 R=CO$_2$Me
8 R=H

Table. $^{13}$C Chemical Shifts (p.p.m. from Me$_4$Si, 20 MHz, CDCl$_3$) for Isopropylidene Acetals.

| Compound | Acetal Carbon | Methyl Carbons | Δδ Methyl Carbons | Ring size |
|---|---|---|---|---|
| 2 | 109.50<br>108.95 | not resolved | ⩽2.07 | 5,5 |
| 3 | 108.13 101.56 | 25.58 28.18<br>24.59 23.53 | 0.99 4.65 | 5,7 |
| 4 | 109.71<br>109.17 | 27.68<br>26.65<br>25.26<br>25.15 | 2.42<br>1.50 | 5,5 |
| 5 | 109.37 | 26.63<br>25.16 | 1.47 | 5,5 |
| 6 | 108.41 101.73 | 25.64 28.32<br>24.73 23.49 | 0.91 4.83 | 5,7 |

We thank Dr. Ian H. Sadler and his colleagues of Edinburgh University for the spectra.

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(Received in UK 28 February 1980)