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Note

Assignment of the location of the isopropylidene ring in 1-*C*-substituted-L-*threo*-glycerols by ^{13}C-n.m.r. spectroscopy*

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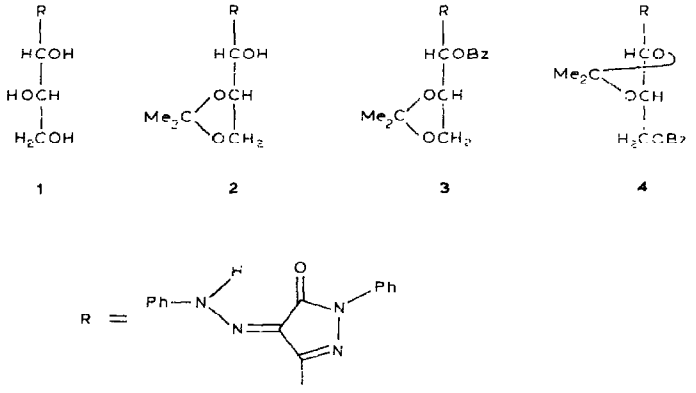
^{13}C-N.m.r. spectroscopy has been used for the assignment of the ring size of isopropylidene acetals[2,3] on the basis of the resonances of the acetal carbon atoms. In addition, the resonances of the carbons bearing a diol function are shifted by 5–10 p.p.m. upon isopropylidenation[4,5]. We now report on the ^{13}C-n.m.r. spectra of the products of isopropylidenation of 3-(L-*threo*-glycerol-1-yl)-1-phenyl-2-pyrazoline-4,5-dione 4-phenylhydrazone (**1**), under conditions of kinetic and thermodynamic control[6,7].



The assignments of the signals for primary and secondary carbons in the ^{13}C-n.m.r. spectrum of **1** were based on the characteristic chemical shifts as compared with those reported for polyols and their substituted analogues[8]. Thus, C-3 reson-

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ated at δ 62.36. The higher value (δ 73.47) for C-1 was due to the α-effect of the heterocyclic moiety. The signal for C-2 (δ 68.05) was shifted upfield markedly in comparison to that (δ 70.1–78.0) for polyols due to the β-effect of the heterocyclic ring. The signals for C-2 and C-3 of the 2,3-*O*-isopropylidene derivative **2** were at δ 66.27 and 75.90, respectively (downfield shifts of 3.91 and 7.85 p.p.m., respectively, reflecting the α-effect of the ketal ring), whereas a reverse shift (3.93 p.p.m.) was observed on the signal (δ 69.54) for C-1, reflecting the β-effect.

When **2** was benzoylated to give **3**, the signals for C-3 (δ 66.40) and C-2 (δ 75.91) were affected negligibly (downfield shifts of 0.13 and 0.01 p.p.m., respectively) and the signal (δ 70.5) for C-1 was shifted downfield by 0.96 p.p.m. as a consequence of the α-effect of the benzoyloxy group.

In the ^{13}C-n.m.r. spectrum of 3-(3-*O*-benzoyl-1,2-*O*-isopropylidene-L-*threo*-glycerol-1-yl)-1-phenyl-2-pyrazoline-4,5-dione 4-phenylhydrazone (**4**), the signal (δ 63.95) for C-3 was shifted downfield compared to that of **1**, due to its attachment to the benzoyloxy group. The signals for C-2 (δ 74.55) and C-1 (δ 76.94) had more pronounced downfield shifts compared to those of **1** due to the α-effect of the ketal ring. A correlation diagram is shown in Fig. 1.

Buchanan *et al.*[2,3] showed that the shifts of the signals of the acetal carbon atoms of dioxolane, dioxane, and dioxepane rings appear in the ranges 108.5–111.4, 97.1–101.1, and 100.8–102.3 p.p.m., respectively. The signals of the acetal carbons of **1–4** appeared within the range for dioxolane rings, and the higher values observed for **3** and **4** could be due to the deshielding effect of the benzoyl group. Thus, the signal of the acetal carbon in **2** appeared at δ 110.43, and at δ 111.72 after benzoylation. The signals of the methyl carbons lie within the range (δ 23.7–27.8) cited for

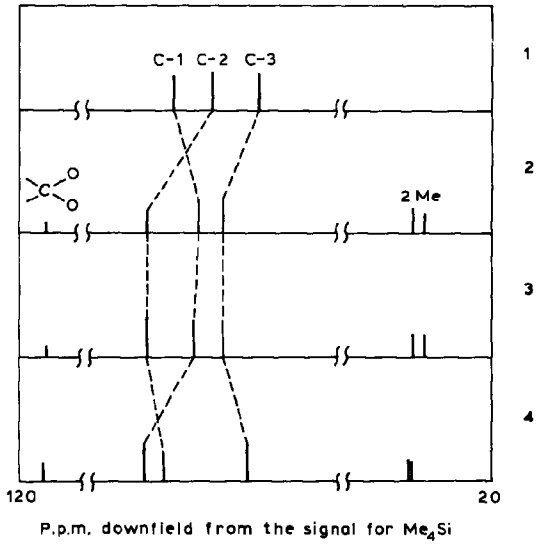

Fig. 1. Correlation diagram of ^{13}C-n.m.r. resonances of the glycerolyl part of **1–4**.

TABLE I

^{13}C-N.M.R. DATA (PROTON DECOUPLED, P.P.M.)

Resonance	1	2	3	4
Glycerolyl part				
C-1	73.47	69.54	70.50	74.55
C-2	68.05	75.90	75.91	76.94
C-3	62.36	66.27	66.40	63.95
$C\lessgtr^{O}_{O}$		110.43	111.72	111.50
CH_3		25.45	25.59	27.00
CH_3		26.76	26.65	27.18

dioxolane rings. The $\Delta\delta$ values for the methyl carbons for **1–4** agreed with the reported value for dioxolanes.

EXPERIMENTAL

^{13}C-n.m.r. spectra for solutions in $CDCl_3$ (**2–4**) and $(CD_3)_2SO$ (**1**) were recorded with a Varian XL-100 15 spectrometer (see Table I).

The compounds studied were prepared as indicated in refs. 6 and 9. 3-(L-*threo*-Glycerol-1-yl-1-phenyl-2-pyrazoline-4,5-dione 4-phenylhydrazone[9] (**1**), m.p. 113–115°. 3-(2,3-*O*-Isopropylidene-L-*threo*-glycerol-1-yl)-1-phenyl-2-pyrazoline-4,5-dione 4-phenylhydrazone[6] (**2**), m.p. 169–171°. 3-(1-*O*-Benzoyl-2,3-*O*-isopropylidene-L-*threo*-glycerol-1-yl)-1-phenyl-2-pyrazoline-4,5-dione 4-phenylhydrazone[6] (**3**), m.p. 158–159°. 3-(3-*O*-Benzoyl-1,2-*O*-isopropylidene-L-*threo*-glycerol-1-yl)-1-phenyl-2-pyrazoline-4,5-dione 4-phenylhydrazone[6] (**4**), m.p. 150–151°.

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