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Carbon-13 NMR Spectra of Methyl-1,3-dioxolanes

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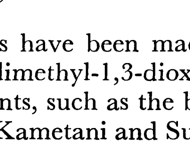
Synopsis. The ^{13}C NMR spectra of thirteen methyl substituted 1,3-dioxolanes were measured. The carbon chemical shifts of the methyl groups imply that the 1,3-transannular nonbonded interaction of the methyl groups is negligible, except in the cases of 2,2,4-trimethyl- and 2,2,4,5-tetramethyl-1,3-dioxolanes.

Various attempts have been made to determine the configurations of dimethyl-1,3-dioxolanes by means of the physical constants, such as the boiling point[1)] or the reflactive index.[2)] Kametani and Sumi have determined the steric configurations of some di- and trimethyl-1,3-dioxolanes by means of the ^{1}H NMR spectra.[3)] In this investigation the ^{13}C NMR spectra of methyl-substituted 1,3-dioxolanes were measured in order to probe the influence of stereochemistry on the carbon chemical shifts of these compounds.



Conformation of 1,3-dioxolane.

The carbon resonance for one of the methyl groups of *cis*-2,4-dimethyl-1,3-dioxolane (*cis*-**5**) that which appeared at δ 20.2 is assigned to the 2-methyl carbon, and at δ 18.9, to the 4-methyl one, on the basis of the chemical shifts of 2-methyl- (**2**) and 4-methyl-1,3-dioxolanes (**3**). The chemical shifts for the methyl groups of *trans*-**5** are similar to those of *cis*-**5**. The 1,3-transannular nonbonded interaction between 2- and 4-methyl groups of *cis*-**5** is practically negligible because of the high flexibility of the five-membered ring system.[4)] A similar observation was made in the ^{13}C NMR spectra of stereoisomeric 1,3-dimethylcyclopentanes.[4)] The carbon resonances for the methyl groups of *cis*-4,5-dimethyl-1,3-dioxolane (*cis*-**6**) moved upfield by 2.2 ppm compared to that of *trans*-**6**. Such upfield shifts may be due to the dihedral angle of the two vicinal methyl groups of *cis*-**6** being smaller than that of *trans*-**6**.[5)] In the case of 2,4,5-trimethyl-1,3-dioxolanes (**7**) the carbon resonances for the methyl groups appeared in two separate regions of the magnetic fields, at δ 20.7—21.3 and 14.3—17.4. Comparing the carbon chemical shifts for the methyl groups of **2**, **5**, and **6**, the signals in the former region are found to be of the 2-methyl, while those in the latter are of the 4- and 5-methyl carbons. Since the carbon chemical shifts for the 2-methyl groups of *trans*-2,2,4,5-tetramethyl-1,3-dioxolane (*trans*-**9**) are δ 27.4, the signal of 2,2,4-trimethyl-1,3-dioxolane (**8**) at δ 27.2 is assigned to the methyl group *cis*, and that at δ 25.9, to the one *trans*, to the 4-methyl group. Much as in the case of **8**, the methyl carbon resonance of the *cis*-**9** at δ 28.7 is ascribed to the one *cis* to the methyl group at the 4- and 5-positions. The chemical shifts for one of the 2-methyl groups of **8** and *cis*-**9** are the same as those for the methyl groups of 2,2-dimethyl-1,3-dioxolane (**4**), while the chemical shifts for the alternative methyl groups *cis* to the 4-methyl one moved downfield by 1.5—3.0 ppm. This indicates the presence of a 1,3-transannular nonbonded interaction between 2-, and 4- and/or 5-methyl groups in the compounds which have two methyl groups at the 2-position. Although the two 2-methyl groups of *trans*-**9** are indistinguishable

Table 1. ^{13}C Chemaical shifts of methyl-1,3-dioxolanes

1,3-Dioxolane	2-Me	4-Me	5-Me	C-2	C-4	C-5
Parent (**1**)				95.1	64.7	64.7
2-Methyl- (**2**)	19.8			101.7	65.0	65.0
4-Methyl- (**3**)		18.1		95.0	72.3	71.0
2,2-Dimethyl- (**4**)	25.7			108.5	64.5	64.5
cis-2,4-Dimethyl- (*cis*-**5**)	20.2	18.9		101.6	73.0	71.0
trans-2,4-Dimethyl- (*trans*-**5**)	20.2	18.5		100.7	71.8	72.0
cis-4,5-Dimethyl- (*cis*-**6**)		14.7	14.7	93.6	74.1	74.1
trans-4,5-Dimethyl- (*trans*-**6**)		16.9	16.9	94.0	78.8	78.8
r-2,*c*-4,*c*-5-Trimethyl- (*r*-2, *c*-4, *c*-5-**7**)	20.9	15.6	15.6	100.3	74.8	74.8
r-2,*c*-4,*t*-5-Trimethyl- (*r*-2, *c*-4, *t*-5-**7**)	20.7	17.4	17.2	100.2	80.0	78.2
r-2,*t*-4,*t*-5-Trimethyl- (*r*-2, *t*-4, *t*-5-**7**)	21.3	14.3	14.3	99.6	74.3	74.3
2,2,4-Trimethyl- (**8**)	27.2(*c*)[a)] 25.9(*t*)[b)]	18.6		108.7	72.0	70.9
cis-2,2,4,5-Tetramethyl- (*cis*-**9**)	28.7(*c*) 25.8(*t*)	15.6	15.6	107.2	74.0	74.0
trans-2,2,4,5-Tetramethyl- (*trans*-**9**)	27.4	16.9	16.9	107.4	78.3	78.3

a) *cis* to the 4-methyl group. b) *trans* to the 4-methyl group.

in ^{13}C NMR, the carbon resonance at δ 27.4 implies the presence of the 1,3-transannular nonbonded interaction.

Experimental

NMR Spectra. The ^{13}C FT-NMR spectra were obtained at 25.15 MHz with a JEOL JNM-MH-100 instrument equipped with a JNM-MFT-100 Fourier transform accessory. Samples were observed in 5-mm spinning tubes with $25\pm5\%$ solutions in $CDCl_3$ at 24 °C. All the chemical shifts are expressed in δ (ppm downfield from the internal TMS). Each observed chemical shift is estimated to be accurate to $\delta\pm0.1$.

1,3-Dioxolanes. The compounds employed in this study were prepared by the methods of Dauben *et al.*[6] and Carmack and Kelley:[7] **1**, bp 74—76 °C; **2**, bp 81—83 °C, **3**, bp 82—85 °C; **4**, bp 92—93 °C; **5**, bp 91 °C, separated by preparative GLC; **6**, bp 74—85 °C, separated by preparative GLC; **7**, bp 80—90 °C, separated by preparative GLC; **8**, bp 95—98 °C; **9**, bp 67—69 °C, separated by preparative GLC. All the compounds were checked by analytical GLC and by means of the IR and ^{1}H NMR spectra.

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