ton NAW served as the phase for V, and polyethylene glycol adipate on Chemosorb served as the phase for IV. Nitrogen was used as the carrier gas when the flame-ionization detector was used; hydrogen was used in the case of the thermal-conductivity detector. The carrier-gas flow rate was 1.5-2.5 liters/h, and the analysis temperature was 60-160°.

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# ¹H and ¹³C NMR SPECTRA AND STRUCTURE OF 2-TRICHLOROMETHYL-4-METHYLENE-1,3-DIOXOLANES

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The ¹H and ¹³C NMR spectra of a number of 5-substituted 2-trichloromethyl-4-methylene-1,3-dioxolanes were studied. It was observed that the exocyclic double bond is in effective conjugation with the 3-O ring atom. The configuration of the substituents was established, and a conformational model of these heterocycles of the "envelope" type with the 1-O atom deviating from the plane in which the remaining ring atoms are situated is proposed. The applicability of the ¹³C NMR spectra for the determination of the configuration of the compounds is demonstrated.

Continuing our study of the properties of 2-trichloromethyl-4-methylene-1,3-diololanes [1, 2], we have made a more detailed study of their PMR spectra and for the first time have examined the ¹³C NMR spectra of a number of representatives of this class of cyclic vinyl ethers in order to obtain information regarding their electronic and three-dimensional structures. The ¹H and ¹³C chemical shifts (CS) for dioxolanes I-VI (the atoms are designated in conformity with the formula presented below) are presented in Table 1. Since the assignment of the signals in the ¹H and, particularly, the ¹³C NMR spectra is not a trivial matter, we will examine this problem in the case of the spectra of I. (See scheme on following page.)

The PMR spectrum of dioxolane I consists of a broad 1-H singlet and a complex multiplet at 4-5 ppm of all of the remaining protons. We were able to analyze the spectrum by using a solvent ($C_6H_6$, 70 mole%) that "simplifies" the PMR spectrum of I and the method of

TABLE 1. ¹H and ¹³C Chemical Shifts (ppm) of I-VI

| Compound | R | R' | 1-H | 2-H | 3-H | R-H | R'-H | 1-C | 2-C | 3-C | 4-C | 5-C | R—C | R'—C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I | H | H | 5,61 | 4,56 | 4,05 | 4,82 | 4,64 | 99,16 | 108,25 | 154,71 | 80,41 | 68,34 | — | — |
| II | CH₃ | H | 5,53 | 4,47 | 3,94 | 1,49 | 4,83 | 98,14 | 105,99 | 159,01 | 80,15 | 75,80 | 18,71 | — |
| III | H | CH₃ | 5,61 | 4,50 | 3,96 | 5,08 | 1,42 | 99,35 | 106,98 | 159,82 | 80,06 | 75,80 | — | 20,63 |
| IV | CH₃ | CH₃ | 5,54 | 4,38 | 3,91 | 1,54 | 1,45 | 98,43 | 105,12 | 162,67 | 79,12 | 83,30 | 26,36 | 28,05 |
| V | C₂H₅ | CH₃ | 5,50 | 4,39 | 3,86 | 1,82*/1,03 | 1,39 | 98,11 | 104,94 | 161,65 | 79,79 | 85,63 | 32,08*/8,13 | 29,23 |
| VI | CH₃ | C₂H₅ | 5,52 | 4,44 | 3,86 | 1,51 | 1,70*/0,96 | 98,82 | 106,31 | 161,86 | 79,25 | 86,77 | 24,94 | 34,50*/8,20 |

*The chemical shifts are indicated for the nuclei of the $CH_2$ and $CH_3$ fragments.
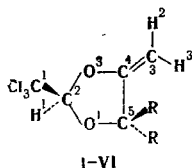


I $R = R' = H$; II $R = CH_3$, $R' = H$;
III $R = H$, $R' = CH_3$; IV $R = R' = CH_3$;
V $R = C_2H_5$, $R' = CH_3$; VI $R = CH_3$, $R' = C_2H_5$

I-VI

¹H-{¹H} double NMR. The PMR spectrum of this compound without irradiation (a) and with irradiation with a secondary ratio-frequency field (b) of the 1-H signal, the assignment of which raises no doubt proceeding from the previously examined model 1,3-dioxolanes [3], is presented in Fig. 1. The signals of the protons in the 5 position can be identified on the basis of the fact that they should correspond to a spin system of the AB type with a spin-spin coupling constant (SSCC) on the order of 8-12 Hz [4]. In the case of I, $^2J_{RR'} = -11.2$ Hz. The assignment of R(H₄) and R'(H₅) presented in Fig. 1b was based on the previously reliably established deshielding effect of the $CCl_3$ group (an average of 0.2 ppm) on the protons attached to 4,5-C in the cis position relative to it. The 2-H and 3-H signals in the spectrum are 0.5 ppm from one another; this is due to the somewhat lower shielding of the proton in the cis position relative to the oxygen atom that is characteristic for vinyl-oxy compounds [5]. Additional confirmations of this assignment follow from the SSCC, which will be examined below, and also from a comparison of the ¹H CS in the spectra of I and II-VI (see Table 1).

The ¹³C NMR spectrum contains five signals. The number of protons attached to each carbon atom was found by double NMR with incomplete ¹³C-{¹H} spin-spin decoupling. The assignment of the signals was made on the basis of the identified ¹H spectrum and experiments on selective ¹³C-{¹H} double resonance. It is confirmed by the known (for example, see [6]) ¹³C CS of the individual fragments entering into the composition of I. The ¹³C NMR spectra of dioxolanes II-VI were similarly analyzed.

All of the SSCC in the spectra of dioxolanes I were found from the ¹H-{¹H} double NMR spectrum (Fig. 1b), which was analyzed as an ABMX four-spin system. The SSCC with participation of 1-H were found from the contraction of the appropriate lines under double-resonance conditions; their signs were not determined:

$$^2J_{2,3} = -2.9 \text{ Hz}, \quad ^2J_{RR'} = -11.2 \text{ Hz}, \quad ^4J_{2,R} = -2.3 \text{ Hz}, \quad ^4J_{2,R'} = -2.2 \text{ Hz},$$
$$^4J_{3,R} = -2.0 \text{ Hz}, \quad ^4J_{3,R'} = -1.8 \text{ Hz}, \quad ^4J_{1,R} = \pm0.5 \text{ Hz}, \quad ^4J_{1,R'} = \pm0.2 \text{ Hz},$$
$$^5J_{1,2} = \pm0.1 \text{ Hz}, \quad ^5J_{1,3} = \pm0.2 \text{ Hz}.$$

The presence of an exocyclic double bond reduces the conformational lability of I-VI. This makes it possible to consider as most likely "envelope" conformations with deviation of either the 1-O or 2-C atom from the plane of the ring and "half-chair" conformations in which both of these atoms deviate from the plane of the ring. The choice between them was based on an examination of the ¹H-¹H SSCC. The geminal SSCC of the terminal methylene group in the vinyloxy compounds may serve as a measure of the delocalization of the electron density from oxygen to the β-carbon atom [3, 7]. Thus, it is -2.2 Hz in the spectrum of $CH_3OCH=CH_2$ (VII), -1.5 Hz in the spectrum of $PhOCH=CH_2$, $\pm0.1$ Hz in the spectrum of $(CH_3)_3COCH=CH_2$, etc. Thus, steric hindrance or competitive conjugation of oxygen with another unsaturated fragment leads to a decrease in this SSCC. The large and almost equal negative $J_{2,3}$ SSCC in the spectra of dioxolanes I-VI (from -2.8 to -3.0 Hz) provide evidence that the exocyclic methylene group is in p—π conjugation with oxygen and that all of the examined compounds are sufficiently conformationally homogeneous. This is also confirmed by the considerable 3-C shielding in I-VI (CS of 3-C ≈ 80 ppm), which exceeds the
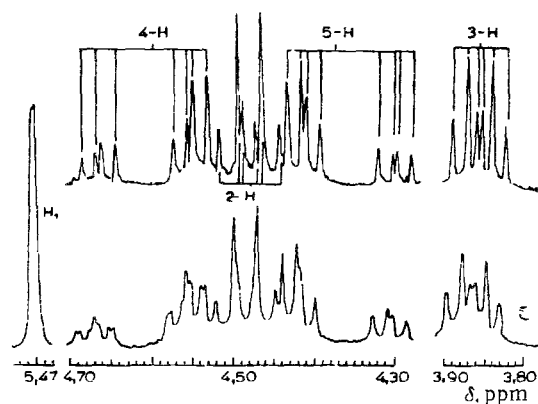
Fig. 1. PMR spectrum of dioxolane I:
a) single resonance; b) double reson-
ance with irradiation of 1-H.

$C_\beta$ shielding (CS ≈ 85 ppm) in ether VII, which has a preferred s-cis conformation [8].
Since the coplanarity of the vinyloxy fragment is a necessary condition for the most effec-
tive p–π interaction [9], it is logical to exclude conformational models of the "half-
chair" and "envelope" type with a "cleavage" axis passing through the 1-O and 3-O atoms
from further examination of the question of the three-dimensional structure of I-VI, i.e.,
only the 1-O atom can evidently deviate from the plane of the ring. The allyl SSCC in the
spectrum of dioxolane I presented above contain information regarding the conformational
mobility of the heteroring. It should be noted that the well-known stereochemical depend-
ence of the allyl SSCC [4] cannot be used in our case for quantitative estimates of the di-
hedral angles, since all of the corresponding constants are subjected to the effect of the
adjacent heteroatoms and are also distorted due to a certain amount of ring strain. How-
ever, the effect of the indicated reasons on the difference in the SSCC ($^4J_{2,R}$–$^4J_2,R'$ and
$^4J_{3,R}$–$^4J_3,R'$) is small and can be disregarded; this makes it possible to establish the posi-
tion of the conformational equilibrium. The mutual orientation of the substituents in di-
oxolanes I-VI can be schematically represented as follows (the horizontal dash line coin-
cides with the plane of the vinyloxy group):
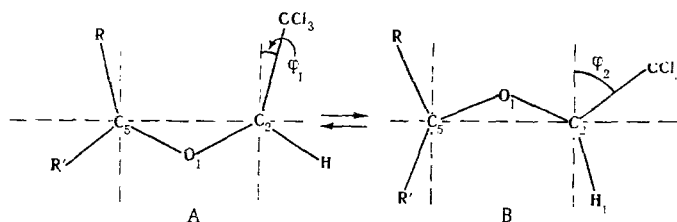


The primary population of one of the conformations presented above should be responsible
for the considerable (up to ∿3 Hz with $\varphi_1=0°$) magnitude of the differences in the allyl
SSCC. On the other hand, the equal populations of conformers A and B or the existence of
the examined heterocycles in a planar conformation will level off this difference in the
SSCC. The small difference in the SSCC (0.1 Hz) observed in the spectrum of dioxolane I is
in agreement with the last models.

The $^4J_2,R$–$^4J_3,R$ and $^4J_2,R'$–$^4J_3,R'$ differences (≈ 0.3 and 0.4 Hz, respectively), with
allowance for the known stereochemical dependence [4], constitute evidence in favor of al-
most equal populations of forms A and B, with $\varphi_1 ≈ 15°$, and $\varphi_2 ≈ 45°$. The conformational dis-
advantageousness of the pseudoaxial orientation of the $CCl_3$ group in the A form, which fol-
lows from an examination of molecular models of stereoisomers of II-III and V-VI, is pos-
sibly compensated to a certain degree by the effect of the syn-axial H..... $Cl_3C$ attrac-
tion, which is similar to that previously noted [10] for 2-chloro-1,3,2-dioxaarsenanes. The
considerable difference in the allyl SSCC in the spectra of dioxolanes II($^4J_2,R'$ = —2.2 Hz,
$^4J_3,R'$ = —1.9 Hz), III($^4J_2,R$ = —2.1 Hz, $^4J_3,R$ = —1.7 Hz), and I confirms the conformational
homogeneity of the investigated series.

The difference in the geometry of the examined compounds and saturated 1,3-dioxolanes
is responsible for the certain peculiarities in their PMR spectra. One of them is disrup-
tion of the additivity of the contributions [3] to shielding of 1-H when methyl groups are

introduced at 5-C. Moreover, the deshielding of this proton due to the cis-alkyl group is generally absent, whereas a trans-alkyl group has a nontypical (for 1,3-dioxolanes) appreciable shielding effect (0.1 ppm). This sort of effect of alkyl substituents on the shielding of 1-H follows from an examination of the PMR spectra of the isomeric 2-trichloromethyl-5-methyl-1,3-dioxolan-4-ones [11]. It may be assumed that the same conformations as in the case of I-VI are characteristic for the latter.

Another peculiarity of the PMR spectra of dioxolanes I-VI is the presence of a long-range spin-spin coupling (SSC) between the cis and trans protons attached to 2-C and 4,5-C. As we have previously assumed in [12] the dominant mechanism of long-range SSC through the 4 and 5 bonds in the case of dioxolanes containing $sp^2$ carbons in the ring is $\sigma$—$2p$—$\pi$—$\sigma$ conjugation due to overlapping of the orbitals of the $\sigma$-C-H bonds with the orbitals of the $\pi$ electrons and the unshared electron pairs of the oxygen atoms. The extent of this interaction is undoubtedly determined by the ring conformation. This sort of long-range SSCC is observed for all I-VI. Thus, $^5J_{1,R} = 0.3$ Hz and $^5J_{1,R'} = 0.1$ Hz in the spectrum of dioxolane IV, i.e., trans coupling is somewhat greater [3].

The $^{13}$C CS in the spectra of I-VI confirm the stronger shielding of the $^{13}$C nuclei in the cis isomers that is characteristic for the $^{13}$C NMR spectra of cis-trans-isomeric compounds [6]. In dioxolanes II and VI, the $CCl_3$ group of which and the bulkier substituent attached to 5-C are in the cis configuration, the 1-C, 2-C, 3-C, and R CS are lower than in the spectra of the corresponding trans isomers of III and V. In the spectrum of IV, which contains two identical substituents attached to 5-C, the change in the 1-C CS as compared with dioxolane I(-0.73 ppm) is close to the additive sum of the increments (-0.83 ppm) obtained for 1-C on passing from I to II(-1.02 ppm) and from I to III(+0.19 ppm). This also indirectly confirms the conformational homogeneity of the representatives of the series under consideration here.

Thus, the $^{13}$C chemical shifts can be used both for reliable assignment of the configuration of the isomers and in the examination of the problem of the conformational structure of substituted 1,3-dioxolanes.

EXPERIMENTAL

The methods used to synthesize and purify dioxolanes I-VI were described in [13]. The NMR spectra were recorded with a Varian XL-100/12 high-resolution spectrometer equipped with a second frequency synthesizer for experiments involving homonuclear and heteronuclear double resonance. The samples were the pure liquids containing ∿5 mole % of the internal standard (tetramethylsilane); the spectra were recorded at 25°.

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