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THREE-DIMENSIONAL STRUCTURES OF DIHYDROPYRANS

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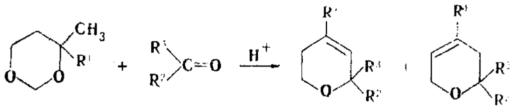
The three-dimensional structures of alkyl- and aryldihydropyrans were studied by means of PMR spectroscopy. It is shown that the investigated compounds exist primarily in the half-chair conformation.

Six-membered saturated and unsaturated heterocycles constitute the prevalent fragments of natural and biologically active compounds and in many respects determine their structures and properties. Owing to the presence of an unsaturated bond in the ring, dihydropyrans are, in addition, convenient substrates for the synthesis of analogs of natural compounds. However, the literature does not contain information regarding the determination of the position of the double bond by NMR methods, the spin–spin coupling constants (SSCC), the effect of substituents on the conformations, etc.

We synthesized alkyl- and aryl-substituted dihydropyrans I and II by the reaction of 4, 4-dimethyl- and 4-methyl-4-phenyl-1,3-dioxanes with aldehydes and ketones:



I–II a, IV–VI a, IX–XII a   I–VIII b, Xb, XII b

I $R^1=C_6H_5$, $R^2=R^3=H$; II $R^1=C_6H_5$, $R^2=H$, $R^3=i\text{-}C_3H_7$; III $R^1=C_6H_5$, $R^2=H$, $R^3=n\text{-}C_4H_9$; IV $R^1=C_6H_5$, $R^2=CH_3$, $R^3=C_2H_5$; V $R^1=CH_3$, $R^2=R^3=H$; VI $R^1=CH_3$, $R^2=H$, $R^3=i\text{-}C_3H_7$; VII $R^1=CH_3$, $R^2=H$, $R^3=n\text{-}C_4H_9$; VIII $R^1=CH_3$, $R^2=H$, $R^3=C_6H_5$; IX $R^1=CH_3$, $R^2=R^3=C_2H_5$; X $R^1=CH_3$, $R^2=CH_3$, $R^3=C_2H_5$; XI $R^1=CH_3$, $R^2=CH_3$, $R^3=n\text{-}C_3H_7$; XII $R^1=CH_3$, $R^2=CH_3$, $R^3=n\text{-}C_4H_9$

The three-dimensional structures of these compounds were studied by PMR spectroscopy. The SSCC were determined by means of double homonuclear resonance. The chemical shift and the structure of the signal of the 6-H methylene protons are most informative for the determination of the position of the double bond in the ring (Table 1). In the case of 4-methyl-5,6-dihydro-2H-pyran (Va) the 6-H signal is a triplet with δ 3.60 ppm and $^3J_{65} = 5.5$ Hz. The absence of geminal splitting of the 5- and 6-H methylene protons constitutes evidence for their equivalence. This is possibly a consequence of rapid (on the NMR time scale) ring inversion. The 5-H protons in 2-substituted dihydropyrans Xa–XIIa are nonequivalent if $R^2 \neq R^3$, and the 6-H signal is a doublet of doublets with $^3J_{5a6} = 6.0$ Hz and $^3J_{5e6} = 4.6$ Hz. The $^3J_{56}$ values are virtually independent of the structure of the alkyl substituents attached to C_2. However, if $R^2 = R^3$, the signal of the 5-H protons is simplified to a triplet.

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TABLE 1. Chemical Shifts and SSCC's in the PMR Spectra of 5, 6-Dihydro-2H-pyrans

Compound	δ, ppm						SSCC, Hz							
	3-H	5-H	6-H	R¹	R²	R⁴	$^3J_{23}$	$^5J_{25}$	$^3J_{56}$	$^4J_{53}$	$^4J_{54}$	$^4J_{43}$	$^5J_{24}$	$^3J_{R^4}$
Ia	5,94	2,33	3,72	7,17	4,01	4,01	2,8	2,8	5,3	1,45	—	—	—	—
IIa	6,18	2,70	4,35	7,30	3,50	1,63 0,92 0,87			6,0	1,5	—	—	—	6,2 6,8
IVa	5,82	2,22	3,74	7,20	1,13	1,50 0,83	—	—	5,5	1,5	—	—	—	7,0
Va	5,28	1,88	3,60	1,62	3,90	3,90	2,4	2,6	5,5	1,4	0,9	1,4	2,0	—
XIIIa*	5,17	1,73	3,65 1,10	1,60	4,00	1,05	1,4	3,0	8,0 5,8	1,4	1,0	1,4	2,0	6,8
IXa	5,14	1,82	3,61	1,65	1,40 0,73	1,40 0,73	—	—	5,5	1,4	0,9	1,4	—	7,0
Xa	5,13	1,78	3,60	1,60	1,01	1,38 0,73	—	—	6,0 4,6	1,4	1,0	1,4	—	7,0
XIa	5,15	1,80	3,61	1,62	1,02	1,30 0,75	—	—	6,2 4,8	1,6	1,0	1,4	—	
XIIa	5,12	1,65	3,57	1,62	1,04	1,30 0,83	—	—	6,2 4,8	1,6	1,0	1,4	—	

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*2,4,6-Trimethyl-5,6-dihydro-2H-pyran; $^3J_{6\text{-H},\ CH_3}$ = 6.2 Hz.

TABLE 2. Chemical Shifts and SSCC's in the PMR Spectra of 3, 6-Dihydro-2H-pyrans

Compound	δ, ppm						SSCC, Hz								
	3-H	5-H	6-H	R¹	R²	R³	$^3J_{65}$	$^5J_{64}$	$^5J_{63}$	$^3J_{23}$	$^4J_{53}$	$^4J_{34}$	$^4J_{54}$	$^2J_{2H,\ R^3}$	$^3J_{R^3}$
Ib	2,33	5,94	4,01	7,17	3,72	3,72	2,8	—	2,8	5,3	1,45	—	—	—	—
IIb	2,25	5,93	3,91	7,20	3,10	1,63 0,92 0,87	2,6	—	3,0	6,6	2,0	—	—	6,6	6,2 6,8
IIIb	—	5,92	4,15	7,15	3,40	2,45 1,43 0,85	2,7	—	2,8	6,0	2,0	—	—	6,0	7,0
IVb	2,25	5,95	4,18	7,18	1,05	1,45 0,83	2,7	—	2,7	—	1,4	—	—	—	—
Vb	1,88	5,28	3,90	1,62	3,60	3,60	2,4	2,4	2,6	5,5	1,4	0,9	1,4	—	—
VIb	1,70	5,26	3,93	1,58	3,00	1,45 0,87 0,80	2,4	2,2	2,5	8,8 4,8	2,2	1,0	1,4	6,2	6,8
VIIb	1,70	5,25	3,95	1,60	3,40	1,34 0,83	2,4	2,4	2,4	8,8 4,8	1,4	1,0	1,4	5,8	—
VIIIb	1,88	5,22	4,07	1,50	4,30	7,15	2,4	2,2	2,6	8,6 5,0	1,8	1,0	1,4	—	—
Xb	1,70	5,27	3,90	1,55	1,17	1,37 0,80	2,4	2,4	2,4	—	1,2	1,0	1,4	—	7,0
XIIb	1,75	5,27	3,88	1,60	1,01	1,30 0,83	2,4	2,4	2,4	—	1,3	1,0	1,4	—	—

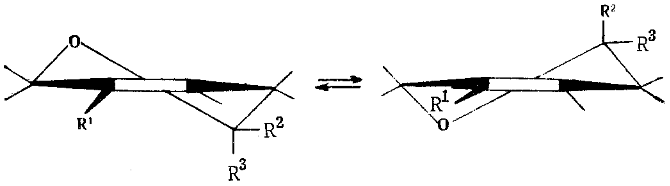
In the spectra of 4-phenyldihydropyrans I-IV as compared with 4-methyldihydropyrans V-XIII the resonance signal of the band of the 6-H protons is shifted 0.15-0.20 ppm to weak field. The triplet structure of the signal of the 6-H protons is also retained for 2-substituted dihydropyrans. The effect of a phenyl substituent is evidently due to a change in the properties of the double bond as a result of conjugation with the aromatic system. Deshielding of the olefin protons ($\Delta\delta_{I-IV}$ 0.66 ppm) also indicates the coplanar orientation of the phenyl substituent and the double bond [1, 2]. This assumption is confirmed by the UV spectroscopic data. The absorption of the ring C=C bond of 4-methyl-5,6-dihydro-2H-pyran appears in the far-UV region (below 200 nm), which is characteristic for olefins with an unconjugated double bond [3]. Two maxima at 248 and 204 nm, which are due to the absorption of the phenyl substituent and the C=C bond, respectively, are observed in the spectrum of 4-phenyl-5,6-dihydro-2H-pyran. A shift of the absorption band of the unsaturated bond to the longwave region occurs as a result of the effect of the phenyl substituent, and its intensity is characteristic for a C=C bond conjugated with an aromatic ring [3].

The signals of the 5-H, 4-CH_3, and 3-H protons are multiplets as a consequence of allylic and homoallylic spin–spin couplings.

The resonance of the 6-H protons in the spectra of Ib-XIIb is observed at weaker (0.3-0.4 ppm) field than in the case of Ia-XIIIa (Table 2). The form of the signal is a quartet when $R^1 = C_6H_5$ and a septet when $R^1 = CH_3$. The more complex structure of the signals of the 6-H protons in the spectra of Ib-XIIb than in the case of Ia-XIIa is due to allylic and homoallylic spin–spin coupling. These effects also determine the complex structure of the 5-H, 4-CH_3, and 3- and 2-H signals. The chemical shifts of the protons of these groups are virtually independent of the structure of the substituent attached to C_2. An increase in the length of the alkyl substituent in Ia-XIIIa leads to a small shift of the signal of the olefin proton to strong field.

Dihydropyran is the heteroanalog of cyclohexene. A half-chair conformation is preferred for cyclohexene [4, 5] and its derivatives [6]. The allylic and homoallylic SSCC that characterize the conformations of the synthesized compounds are close to the corresponding SSCC for cyclohexenes [6, 7]. From this it may be concluded that a half-chair conformation is preferred for alkyl(aryl)-substituted dihydropyrans.

The manifestation of nonequivalence of the signals of the 3-H protons is characteristic for the spectra of VIb-VIIIb. The SSCC of the vicinal protons (J_{23}) are 8.8 and 4.8 Hz; this is characteristic for axial–axial and axial–equatorial interactions [8]. It may be assumed that a half-chair conformation with an equatorial orientation of R^3 is the dominant conformation in dihydropyrans VIb-VIIIb. Rapid inversion of the "half-chair–half-chair" type with an approximately equal ratio of the conformers is characteristic for all of the other investigated compounds:



EXPERIMENTAL

The PMR spectra of solutions of the investigated compounds in carbon tetrachloride were recorded at room temperature with a Tesla BS-467 spectrometer (60 MHz) and hexamethyldisiloxane as the internal standard. The UV spectra of solutions of I and V in methanol were recorded with a Specord UV-vis spectrophotometer. The synthesis of alkyl(aryl)-substituted dihydropyrans was described in [9].

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