RING INVERSION IN 5,5-DISUBSTITUTED 1,3-DIOXANES

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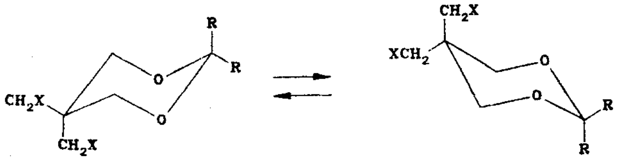
The conformational mobility was studied by dynamic PMR and the free energies of activation of the conformational transitions of 5,5-bis(chloromethyl)-, 5,5-bis(iodomethyl)- and 2,3-pentamethylene-bis-5,5-bis(chloromethyl)-1,3-dioxanes were determined.

Extensive information is available on the geometry and dynamic stereochemistry of 1,3-dioxanes [1-5]. Along with this, quantitative data on the influence of different substituents at the 5-position on the rate of inversion of the 1,3-dioxane ring are scanty [6-8]. In the present work, we studied the conformational mobility of 5,5-bis(chloromethyl)-, 5,5-bis(iodomethyl)- and 2,2-pentamethylene-5,5-bis-(chloromethyl)-1,3-dioxanes (I-III) by the dynamic PMR method.

The PMR spectra of compounds I-III in toluene were studied over the temperature range of 20 to −70°C. In the PMR spectra of dioxanes I-III, at room temperature, the resonance lines of the geminal protons of all the groups of the dioxane ring are in the form of fairly narrow singlets (Fig. 1), which indicates a rapid chair-chair type inversion on the NMR time scale that is known for six-membered heterocycles [3, 4].



R=H, X=Cl; II R=H, X=I; III R-R=-$(CH_2)_5$-, X=Cl

With decrease in temperature, the rate of the ring inversion decreases, and this is evidenced in the spectrum by broadening of the signals of methylene protons at the 2 and 4 positions, and also of the halomethyl groups at the 5-position.

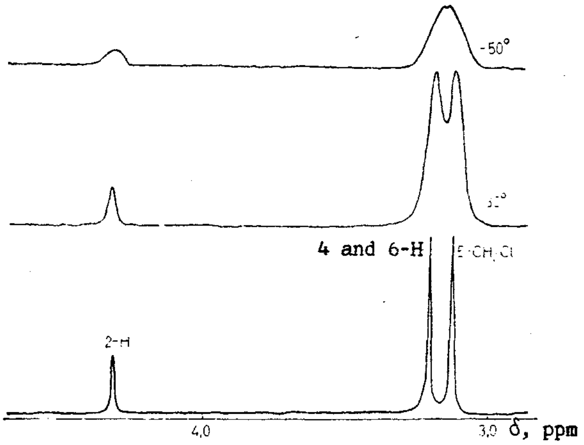


Fig. 1. PMR spectra of compound 1 at temperatures 0°C, −30°C, −50°C.

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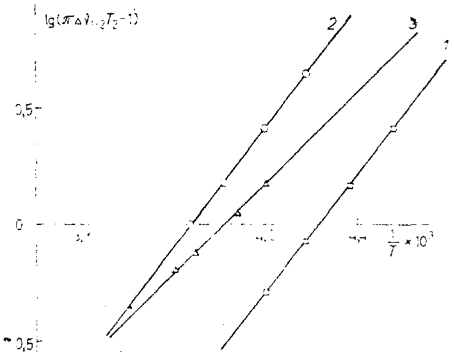

Fig. 2. Dependence of the value of log ($\pi\Delta\nu_{1/2}T_2 - 1$) on 1/T: 1) 5,5-bis(chloromethyl)-1,3-dioxane; 2) 5,5-bis(iodomethyl)-1,3-dioxane; 3) pentamethylene-5,5-bis(chloromethyl)-1,3-dioxane.

TABLE 1. Inversion Barriers in 1,3-Dioxanes

Compound	$\Delta G^{\neq}$, kJ/mole
I	47,5±0,8
II	50,0±0,8
III	42,4±0,8
5,5-Dimethyl-1,3-dioxane*	43,3—46,1
1,3-Dioxane*	37,1—41,6

*Data from [6-8] are given.

Under conditions giving rapid conformational transitions, the free energy of activation $\Delta G^{\neq}$ (the inversion barrier) is determined according to equation [5]:

$$\lg(\pi\Delta\nu_{1/2}T_2 - 1) = \lg(2A/\nabla T_2) + \Delta G^{\neq}/2.303RT,$$

where $\Delta\nu_{1/2}$ is line width (Hz) of the CH_2X group signals at its halfwidth; T_2 is the time of spin-spin relaxation (sec), determined from the line width at the halfwidth in the absence of conformational transitions; ∇ is the second moment of the resonance line.

For acetals I-III, the linear dependences of the value of log ($\pi\Delta\nu_{1/2}T_2 - 1$) on 1/T could be used to determine $\Delta G^{\neq}$ (Table 1). The inversion barriers in cyclic formals I and II are close to and higher than in 5,5-dimethyl-1,3-dioxane [6-8], which is clearly due to increase in the size of the geminal substituents. Lowering of the inversion barrier on transition from formal I to the ketal III is due to increase in the 1,3-syn-axial interactions.

Analysis of the data obtained from the study of the ring inversion kinetics of compounds I-III shows that introduction of gem-substituents into the 5- position of the dioxane ring leads to inhibition of the inversion, in comparison with the inversion of 1,3-dioxane.

EXPERIMENTAL

The PMR spectra of solutions of compounds I-III in toluene were recorded on a Tesla BS-497 spectrometer (100 MHz) in the temperature range of from 20 to −70°C, at 5°C intervals. The accuracy of establishing the temperature of the sample was ±2.5°C. Toluene was used as the internal standard.

LITERATURE CITED

1. Yu. Yu. Samitov, Atlas of Nuclear Magnetic Resonance Spectra of Steric Isomers [in Russian], Vol. 1, Izd-vo-Kazan'sk. Univ. Kazan' (1978).

2. N. S. Zefirov and I. V. Kazimirchik, Usp. Khim., 43, 252 (1974).
3. E. L. Eliel and R. J. Enanoza, J. Am. Chem. Soc., 94, 8072 (1972).
4. L. H. Piette and W. A. Anderson, J. Chem. Soc., No. 3, 899 (1959).
5. I. E. Anderson and I. C. Brand, Trans. Faraday Soc., 62, 39 (1966).
6. H. Friebolin, S. Kabyss, and W. Maier, Tetrahedron Lett., No. 16, 683 (1962).
7. H. Friebolin and H. G. Schmid, Org. Magn. Reson., 1, 67 (1969).
8. E. Goene and M. Anteunis, Bull. Soc. Chim. Belges, 79, 37 (1970).

INVESTIGATION OF 2,6-DIARYLTHIACYCLOHEXANES AND THEIR COMPLEXES WITH Pt(II) AND Pd(II) BY ^{1}H AND ^{13}C NMR SPECTROSCOPY

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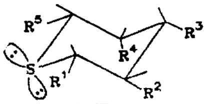
A conclusion regarding a diequatorial orientation of the aryl substituents was drawn on the basis of a study of the ^{1}H and ^{13}C NMR spectra of 2,6-diarylthiacyclohexanes. A trans structure of the complexes with an equatorial S→metal bond was established by a comparative analysis of the ^{13}C NMR spectra of 2,6-diarylthiacyclohexanes and their complexes with Pt(II) and Pd(II).

We have previously reported obtaining substituted thiacyclohexanes by catalytic reduction of the corresponding thiopyrylium salts [1] and the synthesis of trans complexes of these saturated sulfides with Pt(II) and Pd(II) with the composition ML_2Cl_2, where M is the metal and L is the sulfide [2].

To establish the fine structures of 2,6-diarylthiacyclohexanes and their complexes we made a comparative study of the ^{13}C NMR spectra of some of these compounds, obtained by hydrogenation of thiopyrylium salts in the presence of Pd/C:



I–VI

I $R^1=R^3=R^5=C_6H_5$, $R^2=R^4=H$; II $R^1=R^5=C_6H_5$, $R^2=R^4=H$, $R^3=CH_3$; III $R^1=R^5=C_6H_5$, $R^2=R^3=R^4=H$; IV $R^1=R^5=C_6H_5$, $R^2=R^4=CH_3$, $R^3=H$; V $R^1=R^3=R^5=C_6H_5$, $R^2=CH_3$, $R^4=H$; VI $R^1=R^5=C_6H_4OCH_3$-4, $R^2=R^4=H$, $R^3=C_6H_5$

An examination of the PMR spectra of thiacyclohexanes I-VI (Table 1), which were obtained by catalytic reduction of thiopyrylium salts, showed that the spectra of thiacyclohexanes I, IV, and V are identical to the spectra of the corresponding sulfides obtained by disproportionation and catalytic reduction of the corresponding thiopyrans [3, 4]. As regards 4-methyl-2,6-diphenyl- (II), 2,6-diphenyl- (III), and 2,6-di(p-methoxyphenyl)thiacyclohexane (VI), structural assignments were not made for them in the literature, and the PMR spectrum of VI has not been described at all.

We observed agreement between the data from the PMR spectra of sulfide VI (Table 1) and the known 2,4,6-triphenylthiacyclohexane [5, 6] with allowance for the effect of the electronegative OCH_3 group in the para position of the phenyl substituent on the shift of the proton signals. On the basis of this we concluded that thiacyclohexane VI has a configurationally rigid structure ($J_{HH}^{vic} \approx 11$ Hz) with an equatorial orientation of the bulky anisyl substituents.

Similarly, for sulfides II and III it may be assumed from the double-doublet signals of the 2- and 6-H protons that they are axially oriented (Table 1), since $^3J_{2a3a} = {}^3J_{5a6a} \approx 10.5$ Hz. In addition, $^3J_{2a3e} = {}^3J_{5e6a} \approx 2.5$-$3.5$ Hz for thiacyclohexane III; this consti-

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