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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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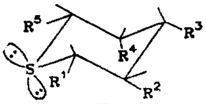
A conclusion regarding a diequatorial orientation of the aryl substituents was drawn on the basis of a study of the ^{1}H and ^{13}C NMR spectra of 2,6-diarylthiacyclohexanes. A trans structure of the complexes with an equatorial S→metal bond was established by a comparative analysis of the ^{13}C NMR 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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TABLE 1. PMR Spectra of 2,6-Diarylthiacyclohexanes ($CDCl_3$)

Compound	δ, ppm				$^3J_{2a3e}$, $^3J_{2a3a}$, Hz
	2(6)-H (d.d)	3(5)-H	4-H (m)	C_6H_5	
I	4,15	2,25 m	2,75	7,20 м	3,6; 10,4
II	4,10	1,02 d	1,88	7,26 м	2,7; 10,5
III	3,96		1,95	7,25 м	2.6; 10.2
IV	4,33	1,06 d	2,14	7,33 с	3,0; 7,1
V	4,57	2.00 m	2,76	7,26 м	3,5; 6,6
VI*	4,14	2,25 m	2,75	7,21 с, 7,01 д.д	3,2; 10,6

*δ 3.63 ppm (CH_3O).

TABLE 2. ^{13}C NMR Spectra of 2,6-Diarylthiacyclohexanes I-VI

Compound	Carbon atoms in the heteroring, δ, ppm				
	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$
I	49,1	41,7	45,3	41,7	49,1
II	49,0	42,7	33,8	42,7	49,0
III	48,9	34,0	27,3	34,0	48.9
IV	54.9	34,2	41,1	34,2	54.9
V	55,1	41,3	49,1	32,2	48.9
VI	48,3	41,9	45,4	41,9	48.3

Compound	Carbon atoms in the substituents, δ, ppm							
	$R^1=R^5$				R^3			
	$C'_{(1)}$	*o*	m	*n*	$C'_{(1)}$	*o*	m	*n*
I	141,4	127,2	128,4	127,2	145,7	128,3	126,6	126,3
II[a]	141,9	127,3	128,4	127,2	—	—	—	—
III	141,9	127,2	128,2	127,0	—	—	—	—
IV[b]	141,4	127,5	128,0	126,7	—	—	—	—
V[c]	141,9	127,6		126,8				
			128,0	127,4	144,3	128,5	127,4	126,0
	140,8	127,2		127,4				
VI[d]	133,6	128,3	113,7	158,6	145,8	128,4	126,6	126,2

[a] δ 22.8 ppm (CH_3 in R^3). [b] δ 15.8 ppm (R^2, R^4). [c] δ 6.3 ppm (R^2). [d] δ 54.9 ppm (OCH_3).

tutes evidence for the equatorial character of the C_6H_5 group attached to $C_{(2)}$ and $C_{(6)}$ and for a cis structure.

In the case of thiacyclohexane II the problem of the steric orientation of the CH_3 group cannot be resolved only on the basis of the PMR spectral data. In the PMR spectrum of sulfide II a doublet of protons of a methyl group is located at δ 1.02 ppm (J_{HH}^{vic} = 5.2 Hz). Assuming that the 4-CH_3 group in this case is axially oriented, one might have expected changes in the chemical shifts of the 2- and 6-H protons as a consequence of a strong 1,3-diaxial interaction. However, only a slight change in the chemical shift for 2- and 6-H is observed when one compares the PMR spectra of thiacyclohexane I, in which the phenyl groups attached to $C_{(2)}$ and $C_{(6)}$ are equatorial (Table 1), and sulfide II.

The most nearly complete information regarding the structures of 2,6-diarylthiacyclohexanes I-VI can be obtained on the basis of data from their ^{13}C NMR spectra (Table 2). The assignments of the signals in the spectra of the sulfides were made in conformity with [5, 6]; the results in [7, 8] were used in the assignment of the signals of the alkyl and aryl substituents.

In the spectra of trisubstituted thiacyclohexanes the changes in the $C_{(2)}$ and $C_{(6)}$ signals may be indicators of the spatial orientation of the radical attached to $C_{(4)}$ by virtue of a 1,3 interaction – the axial γ effect, which is clearly expressed for cyclic systems; a strong-field shift of the signals to 6 ppm is observed [9]. It is apparent from Table 2 that the chemical shifts of $C_{(2)}$ and $C_{(6)}$ in sulfide II and the others do not change substantially. Thus it may be concluded that the CH_3 group attached to $C_{(4)}$ in thiacyclohexane

TABLE 3. ^{13}C NMR Spectra of Complexes VII-XII

Compound	Ligand (L)	Metal (M)	Carbon atoms in the heteroring, δ, ppm				
			$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$
VII	II	Pt	52,4	42,7	32,6	42,7	52,4
VIII	III	Pt	52,7	34,3	26,1	34,3	52,7
IX[a]	V	Pt	58,3 58,0	42,5	52,6	32,2 31,5	47,3
X	II	Pd	52,8	42,9	32,6	42,9	52,8
XI	III	Pd	53,0	34,9	26,1	34,4	51,0
XII[a]	V	Pd	58,6 58,2	42,6	52,9	32,3 31,7	47,3
XIII	VI	Pd	52,3	41,7	43,7	41,7	52,3

Compound	Carbon atoms in the substituents, δ, ppm								
	$R^1=R^5$				R^2	R^3			
	$C'_{(1)}$	o	m	n		$C'_{(1)}$	o	m	n
VII[b]	138,9	128,0	128,5	127,7	—	—	—	—	—
VIII	139,1	128,0	128,4	127,6	—	—	—	—	—
IX[a]	138,7 138,4 137,8 137,6	127,7 127,1	128,0	126,3 127,8	6,6	142,8	128,4	127,9	126,0
X[c]	138,9	127,6	128,6	127,8	—	—	—	—	—
XI	139,0 138,6 138,3 137,7 137,4	127,9 127,4 127,1	128,5 128,1	127,8 126,2 128,6	6,5 6,3	142,7	128,6	127,8	126,3
XIII[d]	130,4	128,3	113,7	158,9	—	144,0	128,3	126,3	126,2

[a]These are tentative assignments. [b]δ 22.0 ppm (R^4). [c]δ 21.9 ppm (R^4). [d]δ 54.8 ppm [CH_3O in R^1 (R^5)].

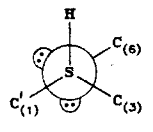
II is equatorially oriented; this confirms the cis structure of this compound, as well as of trisubstituted thiacyclohexanes I and III.

The strong field shift of the signal of the carbon atom of the methyl group in the spectrum of thiacyclohexane V (Table 2) as compared with the spectrum of IV is probably associated with the shielding effect of the bulky (C_6H_5) substituent attached to $C_{(4)}$ [8, 10, 11]. In addition, a γ effect of the axial methyl groups is clearly manifested in the spectra of sulfides IV and V. Thus in the spectrum of V the $C_{(5)}$ signal was shifted 9.6 ppm to strong field as compared with the signal of $C_{(5)}$ in I (Table 2).

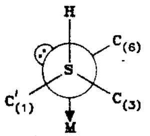
The ^{13}C NMR spectra of substituted thiacyclohexanes I-VI, obtained by catalytic reduction of the corresponding thiopyrylium salts, confirm their configuration with equatorial aryl substituents.

We made a comparative analysis of the ^{13}C NMR spectra of 2,6-diarylthiacyclohexanes (Table 2) and some of their trans complexes with Pt(II) and Pd(II) (Table 3) dissolved in $CDCl_3$.

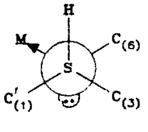
Weak-field shifts of the signals of the $C_{(2)}$ and $C_{(6)}$ atoms to 3.5-5.0 ppm relative to the spectra of the ligands (Table 2) are observed in the spectra of the complexes with Pt(II) (VII-IX) and Pd(II) (X-XIII) (Table 3); this is probably a consequence of the manifestation of the inductive effect of the coordinated sulfur atom. At the same time, the slight changes in the chemical shifts of the carbon atoms of the heteroring on passing from the platinum complexes to the palladium complexes are evidently due to the existence of a heavy-atom effect [12]. One should also note the strong-field shift (3 ppm) of the carbon atom of the phenyl substituent attached to $C_{(2)}$ and $C_{(6)}$ [$C'_{(1)}$] in the spectra of the complexes as compared with the spectra of the ligands. The latter circumstance can be explained by means of Newman projections:



a (ligand)

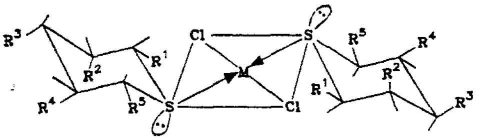


b (complex)



c (complex)

Ligand–metal coordination can be realized in two ways: either the S → M bond is axial to the plane of the heteroring (projection b), or the S → M bond is equatorial (projection c). A similar phenomenon is observed in the formation fo the S=O bond in sulfoxides [13] and is examined in a review [14] in the case of complexing of metals with cyclic thioethers. In the formation of an S → M bond in both cases (b and c) the $C_{(2)}$—$C'_{(1)}$ [$C_{(6)}$—$C'_{(1)}$] bond is in a skewed orientation relative to the free electron pair of the sulfur atom and the S → M bond; this is reponsible for the hsift of the signals of the $C'_{(1)}$ atoms of the phenyl groups to strong field as compared with the ligand (projection a). The signals of the $C_{(3)}$ atoms in the complex and in the ligand are identical; this is possible only in the case of an equatorial orientation of the S → M bond:



Thus the results of a study of the ^1H and ^{13}C NMR spectra of 2,6-diphenylthiacyclohexanes showed that hydrogenation of the corresponding thiopyrylium salts in the presence of Pd/C leads to saturated sulfides with a 2r,3c,4c,6c configuration with equatorial aryl substituents, i.e., with the same configuration as in the disproportionation of thiopyrans under the influence of acids or in the case of their catalytic reduction.

EXPERIMENTAL

The ^{13}C NMR spectra of solutions of the compounds in $CDCl_3$ were recorded at 35°C with a Varian FT-80A (20 MHz) spectrometer. The spectra were calibrated with respect to the signal of the solvent – the middle peak at 76.9 ppm relative to tetramethylsilane (TMS).

2,6-Diarylthiacyclohexanes I-VI were obtained by the method in [1]. Compounds V and VI were synthesized at substrate:metal ratios of 10:3 (for V) and 10:3.5 (for VI). Compound V was obtained in 69% yield and had mp 117-118.5°C (from ethanol). Found: C 83.6; H 7.1; S 9.0%. $C_{24}H_{24}S$. Calculated: C 83.7; H 7.0; S 9.3%. Compound VI was obtained in 71% yield and had mp 148-149°C (from ethanol). Found: C 77.2; H 7.0; S 7.8%. $C_{25}H_{26}O_2S$. Calculated: C 76.9; H 6.7; S 8.2%.

Complexes VII-XIII were synthesized by the method in [2]. Complex IX was obtained in 79% yield and had mp 250°C (dec.). Found: C 59.9; H 5.1; S 6.7%. Complex XII was obtained in 91% yield and had mp 240°C (dec.). Found: C 66.5; H 6.6; S 7.3%. $C_{48}H_{48}S_2 \cdot PdCl_2$. Calculated: C 66.6; H 5.6; S 7.4%. Complex XIII was obtained in 83% yield and had mp 230°C (dec.). Found: C 63.3; H 5.6; S 6.5%. $C_{50}H_{52}S_2 \cdot PdCl_2$. Calculated: C 62.7; H 5.4; S 6.7%.

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STEREOCHEMICAL SPECIFICITY OF THE PALLADIUM-CATALYZED HYDROGENATION OF CYCLOHEXA[b]THIOPYRANS AND THEIR DERIVATIVES

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Conformationally and configurationally homogeneous 2α-R^1-4α-R^2-cis-1-thiadecalins with an equatorial orientation of the substituents attached to the $C_{(2)}$ and $C_{(4)}$ atoms were isolated as the final reduction products in the catalytic hydrogenation on palladium of 2-R^1-4-R^2-4H(6H)-cyclohexa[b]thiopyrans, cis-3-R^1-5-R^2-2-thiabicyclo[4.4.0]-$\Delta^{1,6}$-decenes, and 2-R^1-4-R^2-cyclohexa[b]thiopyrylium tetrafluoroborates and trifluoroacetates. cis-3-R^1-5-R^2-2-Thiabicyclo[4.4.0]-$\Delta^{1,6}$-decenes were obtained as intermediates in the incomplete reduction of 2-phenyl- and 2,4-diphenyl-4H-cyclohexa[b]thiopyrans and 2-(4-methoxyphenyl)-4-R^2-cyclohexa[b]thiopyrylium salts; 2-R^1-4-R^2-6H-cyclohexa[b]thiopyrans undergo complete reduction of the double bonds of the heteroring. The hydrogenation products were oxidized to sulfoxides and sulfones.

The liquid-phase hydrogenation on palladium of some two-ring thiopyran [1], dihydrothiopyrans [1], and thiopyrylium salts [2] has been previously accomplished for preparative purposes; however, structural studies of the hydrogenation products were not made. The only exception was 2α,4α-diphenyl-cis-1-thiadecalin, which was obtained in the hydrogenation of 2,4-diphenyl-6H-cyclohexa[b]thiopyran; the structure of this product was established via a combined study of the ^1H NMR spectra of the sulfide, its 3D,10D derivative, and the S-oxide [3].

We have carried out the hydrogenation of known and new 4H(6H)-cyclohexa[b]thiopyrans I-VII on 10% palladium on carbon under the previously described conditions at 100°C and an initial hydrogen pressure of 50 atm [1] (Table 1).

As a result of hydrogenation, 2,4-diaryl-6H-cyclohexa[b]thiopyrans IV-VII form 2α,4α-diaryl-cis-1-thiadecalins XX and XXII-XXIV in 83-86% yields. Dihydro products could not be isolated in the experiments with sulfides IV-VII; this is possibly associated with the β position of the double bond in the heteroring, which is sterically less hindered than the angular double bond in dihydrothiopyrans VIII-XIII.

After 6-7 h, sulfides I and II undergo reduction of both double bonds of the heteroring and form the corresponding 2α-phenyl- and 2α,4α-diphenyl-cis-1-thiadecalins (XIX, XX) (Table 1). Shortening the reaction time by one half in the experiment with 2,4-diphenyl-4H-cyclohexa[b]thiopyran (II) leads to reduction of the sterically less hindered double bond and to the formation of chiefly cis-3,5-diphenyl-2-thiabicyclo[4.4.0]-$\Delta^{1,6}$-decene (VIII) [4] (60%) and a small amount of 2α,4α-diphenyl-cis-1-thiadecalin (XX); the latter was detected by thin-layer chromatography (TLC).

The hydrogenation of 2-(4-methoxyphenyl)-4-phenyl-4H-cyclohexa[b]thiopyran (III) proceeds anomalously: not only are the double bonds of the heteroring reduced, but skeletal isomerization also occurs, and 2α-(4-methoxyphenyl)-4α-phenyl-cis-1-thiadecalin (XXI) and 2α-(4-methoxyphenyl)-3-benzyl-cis-1-thiahydrindan (XXVI) are formed in a ratio of 1:1. Compound XXVI was not isolated in the individual state and was characterized through sulfone XXVII.

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