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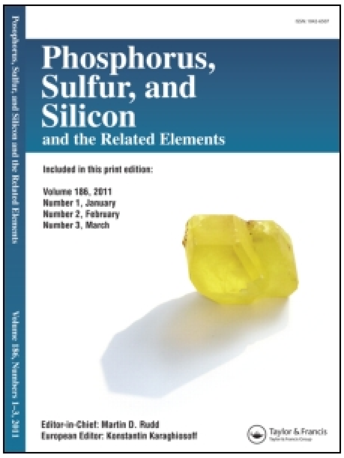

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CIRCUMAMBULATORY REARRANGEMENTS OF O-, S-, Se-, AND Te- CENTRED GROUPS AROUND THE CYCLOPENTADIENE RING

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O-, S-, Se- and Te-centred migrants circumambulate the cyclopentadiene ring in the corresponding derivatives of substituted cyclopentadienes by surmounting the activation barriers falling into the range of 13.4-34.8 kcal/mol.

Key words: thio-, seleno-, telluro- cyclopentadienes, rearrangements

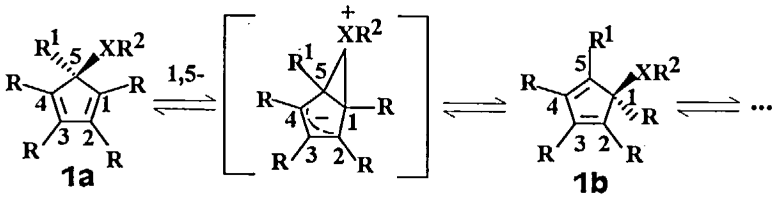
INTRODUCTION

The fluxional cyclopentadienes with organometallic migrants discovered in 1956 received widespread attention due to both theoretical (origin of the low-energy barrier reactions, unusual multicentre character of bonding in the intermediate and transition state structures) and practical (application in important catalytical systems, useful thermo- and solvatochromic properties, etc.) reasons [1]. Starting from the 70th an extensive study of the circumambulatory rearrangements of main group 13,14 elements (B, Si, Ge, Sn) has been undertaken that was later supplemented by study of the migratory aptitude of P-centred groups[2]. Our study of the rearrangemens of main group element centred migrants in substituted cyclopentadienes [3-9] started in the beginning of 80th has been directed to investigation into the migratory ability of main group 15-17 migrants.

First Sample

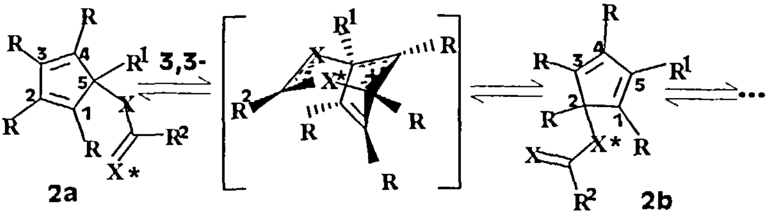
Synthesis of O-, S-, Se-, and Te-derivatives of cyclopentadienes **1, 2** substituted in the ring positions and study of kinetics and mechanisms of their circumambulatory rearrangements around the cyclopentadiene ring were carried out using methods of dynamic 1D, 2D ^{1}H, ^{13}C NMR spectroscopy, X-ray diffraction studies, mass-spectroscopy, and quantum chemical calculations of critical parts of the reaction paths. It has been demonstrated that O-, S-, Se- and Te-centred migrants circumambulate the cyclopentadiene ring in compounds **1, 2** by surmounting the activation barriers falling into the range of 13.4-34.8 kcal/mol. By contrast with transition metal groups, the ligand environment of the main group 16 centres was found to exert significant influence on the rates and even the very capability of the compounds **1, 2** of sufficiently fast migrations.

Whereas the principal reaction mechanism that governs migration of the above groups was determined as the sequence of 1,5-sigmatropic shifts (**1a**⇌**1b**⇌...),



R=CO_2Me, Ar, Me; R^1=CO_2Me, Ar, Me, Bz; XR^2= OAr, SAr, SePh, SeAlk, SeCN, $TeC_6H_4(CHO)$-2, $TeC_6H_4(CH{=}NAr)$-2

earlier unidentified reaction pathway was revealed: 3,3-sigmatropic shift mechanism (hetero-Cope rearrangement) for the case of acyloxy and dithioacyloxy (2a⇌2b⇌...) groups.



R=Ph, R^1=Ar, Bz; X=O, S; R^2=Alk, OAlk

The free energies of activation ($\Delta G^{\neq}_{298}$) for the circumambulatory degenerate and nondegenerate rearrangements calculated by line shape analysis of dynamic NMR ^{1}H spectra of the compound **1**, **2** or by studying the time dependence of intensities of isomers signals in the NMR ^{1}H spectra are given in Table.

TABLE Activation parameters of circumambulations of main group 16 element centered migrants in the compounds **1**, **2**

Compound		$\Delta G^{\neq}_{298}$, kcal/mol
1, R=Ph, R^1=4-MeC_6H_4 or Bz;	XR^2=O(4-$OAlkC_6H_4$),	24.6-25.5
	XR^2= O[4-NO_2(or Hal)C_6H_4]	25.0-28.4
1, R= R^1=CO_2Me;	XR^2=S(4-$OAlkC_6H_4$), SPh,	16.0-17.5
	XR^2=S[$(NO_2)_nC_6H_{5-n}$]	17.8-20.7

1, R= R^1=Ph;	XR^2=SeCN		16.7
1, R= R^1= Me;	XR^2=SePh		20.1
1, R= R^1=CO_2Me;	XR^2= Te[C_6H_4(CHO)-2],		13.4
	XR^2=Te[C_6H_4(CHNAr)-2]		≤10
2, R=Ph, R^1=4-MeC_6H_4;	X=O;	R^2=Me,	34.8
R=Ph, R^1= Bz;	X=O;	R^2=$CHal_3$,	26.6-28.1
2, R=Ph, R^1=Bz;	X=S;	R^2=OEt	23.9-24.3

The table shows that in the structurally equivalent environment the rate of the rearrangements increases in proportion to the increase in the atomic number of element X (Te>Se>S>O). Besides,the electron-withdrawing substituents in the element-centered groups slow down the process (**1a**⇌**1b**⇌...), while the electron-donating ones speed it up. The influence of substituents in migrants on the rate of the process (**2a**⇌**2b**⇌...) are opposite.

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