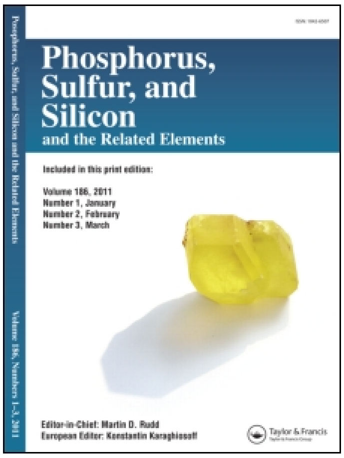

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^{1}H NMR STUDY ON THE ISOMERIZATION OF 2,4,6-TRIPHENYL-4H-SELENO(THIO)PYRANS

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It is shown using ^{1}H NMR spectroscopy that 2,4,6-triphenyl-4H-seleno(thio)pyrans can be isomerized into 2H-isomers by the action of lithium perchlorate or lithium chloride in DMF or only by DMF. The reaction time is found to depend on the Lewis acidity of used salt. It is supposed that isomerization in presence of Lewis acids proceeds as endocyclic 1,3-proton transfer or as a series of two 1,2-hydride shifts.

Keywords: 4H-selenopyran; 4H-thiopyran; isomerization.

INTRODUCTION

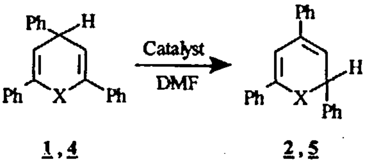
It is known that 2,4,6-triphenyl-4H-thiopyran 1 can be isomerized into 2H-thiopyran 2 in presence of 2,4,6-triphenylthiopyrylium perchlorate 3[1,2]. The reaction was supposed to proceed by bimolecular mechanism involving a hydride transfer from 4H-thiopyran to C-2 atom of the salt giving molecule of 2H-thiopyran 2 and molecule of the catalyst 3. The results of further study of this isomerization allowed to calculate K_{eq} of this reaction[3].

Here we report a ^{1}H NMR study on the isomerization of 2,4,6-triphenyl-4H-selenopyran 4 and thiopyran 1 in DMF in presence of Lewis acids such as lithium perchlorate and lithium chloride as well as in presence of the corresponding chalcogenopyrylium salts.

Although the isomerization of 4H-thiopyran 1 by the action of thiopyrylium salt has been studied previously[1,2] we performed this reaction for comparison with the same reaction of 4H-selenopyran 4.

RESULTS AND DISCUSSION

The reaction of substrates 1 and 4 was carried out in $[^2H_7]$DMF at 60°C. It is found that isomerization of 4H-selenopyran into 2H-isomer 5 can proceed not only by the action of 2,4,6-triphenylselenopyrylium perchlorate 6 but also by the action of lithium perchlorate, lithium chloride or DMF, whereas 4H-thiopyran 1 forms 2H-isomer 2 with a distinct rate only in presence of thiopyrylium salt 3 or lithium perchlorate (Scheme 1).



X=Se (4,5,6):
Catalyst=$LiClO_4$, LiCl, 6 ;
X=S (1,2,3):
Catalyst=$LiClO_4$, 3

SCHEME 1

It is established that isomerization of compounds 4 and 1 completely proceeds within 6 h if catalyst is salt 6 or 3. Continuous heating of compounds 1 and 3 at 60°C is found to lead to their partial destruction, so reaction was being carried out for 1.5 h for the purpose to obtain more correct data. The molar isomer ratios determined within 1.5 h by ^{1}H NMR are presented in the Table I.

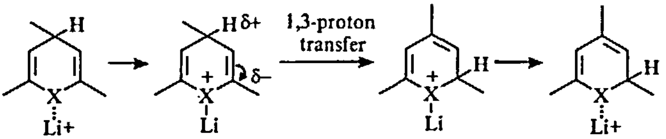
TABLE I. Molar ratios (2H/4H) determined by ^{1}H NMR at 60°C

Substrate	Catalyst	Ratio
4	6	8,0
4	$LiClO_4$	10,0
4	LiCl	2,2
4	without catalyst	2,0
1	3	8,0
1	$LiClO_4$	0,1
1	LiCl	<0,05*
1	without catalyst	<0,05*

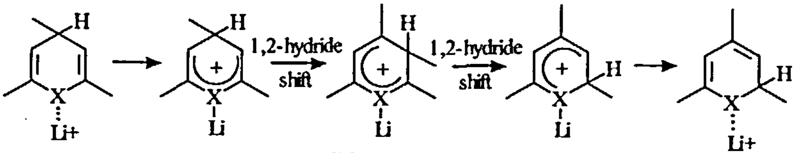
*The ratio 2H/4H is quoted as <0.05 when only trace amount of 2H-isomer is detected.

The results show that the efficiency of used catalysts is increased in the order $LiCl < LiClO_4$ It is to be noted that isomerization of selenopyran 4 proceeds also at it heating in pure DMF without catalyst. Lithium chloride does not accelerate isomerization in comparison with the control, so its catalytic action is approximately same as it is of DMF.

The increase of negative charge density in the anions in order $ClO_4^- < Cl^-$ leads to the decrease of Lewis acidity of salts in order $LiClO_4 > LiCl$ [4]. Comparison of this fact with the data on isomerization (Table I) shows that the increase of Lewis acidity of catalyst results in the increase of catalytic effect. Two possible intramolecular reaction pathways may be suggested. Isomerization by the action of Lewis acid can proceed as endocyclic 1,3-proton transfer (Scheme 2) or as a series of two 1,2-hydride shifts in carbocation (Scheme 3). Both pathways are facilitated by interaction between Lewis acid and heteroatom of 4H-(thio)selenopyran.



SCHEME 2



SCHEME 3

DMF probably also takes part in this reaction as very soft Lewis acid, that explains the isomerization observed at heating of selenopyran 4 with pure DMF. In this connection less isomerization rate for 4H-thiopyran compared with the rate for 4H-selenopyran may be explained by more effective interaction between selenium atom and Lewis acid that leads to higher positive charge on carbocation in Scheme 3 or to more effective stabilization of carbanion-like intermediate in Scheme 2. It has to be noted that trace amounts of 2H-isomer 2 are registered also in the reactions of thiopyran 1 with LiCl and pure DMF. No distinctions are observed between thiopyran and selenopyran when catalyst is chalcogenopyrylium salt. This fact witnesses that isomerization pathway when catalyst is salt 3 or 6 is differed from pathway by the action of Lewis acids.

The following conclusions may be drawn from this study: the isomerization of 4H-thio- and selenopyrans into 2H-isomers can proceed by two different pathways. Intermolecular pathway involving hydride transfer is realized when catalyst is thio- or selenopyrylium salt, whereas intramolecular isomerization proceeds by the action of Lewis acid.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded at 80 MHz on Varian FT-80A spectrometer using tetramethylsilane as internal reference.

Typical Procedure for Isomerization of Chalcogenopyrans 1 and 4

The mixture of 4H-chalcogenopyran (1.6 mmol) and lithium perchlorate (1.6 mmol), chloride or chalcogenopyrylium perchlorate in 20 mL of [$^2H_7$]DMF is stirred at 60°C. ^{1}H NMR spectra is recorded after 1.5 h of stirring.

The reaction mixture of 4H-selenopyran 4 with lithium perchlorate after 6 h of stirring was cooled and diluted with the water. The produced solid 2H-selenopyran 5 was collected by filtration, washed with water and reprecipitated by methanol from benzene. Yield 0.538 g (90%), m.p. 72-74°C.

^{1}H NMR data for 4H- and 2H-selenopyrans (δ, ppm (J, Hz)): 4: 4.19 t (4.2) 1H, H-4; 6.12 d (4.2) 2H, H-3,5; 7.05-7.52 m 15H, Ph; 5: 5.09 d (5.6) 1H, H-2; 5.83 d (5.6) 1H, H-3; 6.98 s 1H, H-5; 7.04-7.52 m 15H, Ph. The ^{1}H NMR spectroscopy data obtained for thiopyrans 1 and 2 were the same as described[1,2].

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