IONIC DEHYDROGENATION AND ISOMERIZATION OF CYCLIC SULFIDES

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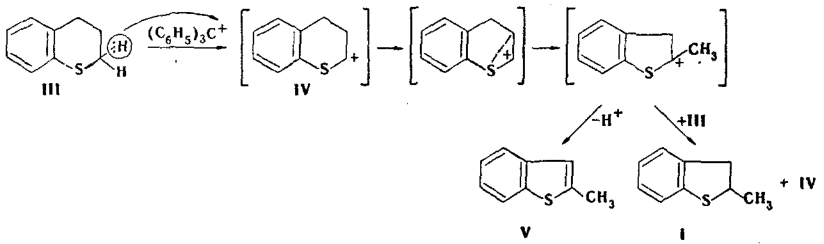
One of us [1] has demonstrated the possibility of dehydrogenation of 2,3-dihydrobenzofurans to benzofurans during reaction with hydride ion acceptors. Under similar conditions, chromans underwent isomerization and dehydroisomerization, respectively, to 2,3-dihydrobenzofurans and benzofurans. Transformations of this sort are also characteristic for cyclic sulfides – 2-methyl-2,3-dihydrobenzothiophene (I), thiacyclohexane (II), and thiochroman (III). In the presence of a mixture of stannic chloride and triphenylchloromethane (see Table 1), 2-methyl-2,3-dihydrobenzothiophene is dehydrogenated to 2-methylbenzothiophene (V), while thiochroman and thiacyclohexane under the same conditions undergo contraction of the heterocyclic ring and dehydrogenation of it.

Taking the structures of the sulfides cited above into account, one can propose a scheme including stripping of a hydride ion from the 2 position for these transformations:



2-Methyl-2,3-dihydrobenzothiophene, thiochroman, and thiacyclohexane with purities of 98-99% were used in the experiments. The reaction products were analyzed by gas-liquid chromatography using standard samples. All of the experiments were carried out under nitrogen with recrystallized (from hexane) triphenylchloromethane and freshly distilled stannic chloride. The sulfide–triphenylchloromethane–stannic chloride molar ratios were 1 : 1 : 1. A 1.5-2-g sample of the sulfide was used in each experiment, and the overall yield of liquid products after the reaction was ~ 85%.

TABLE 1. Results of Experiments on the Transformations of Cyclic Sulfides

Substance	Solvent	Exptl. temp., °C	Expt. time, h	Yield of reaction products, %		
				I	V	2-methylthiophene
2-Methyl-2,3-dihydrobenzothiophene (I)	Nitromethane	100	1	—	87	—
	Benzene	80	1	—	87	—
Thiochroman (III)	Nitromethane	100	4	11	6	—
	Benzene	80	4	—	13	—
	Methylene chloride	40	4	7	6	—
Thiacyclohexane (II)	Nitromethane	100	4	—	—	31

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