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REACTION OF ARYLFURANES WITH HYDROGOEN SULFIDE AND HYDROGEN SELENIDE UNDER CONDITIONS OF ACID CATALYSIS

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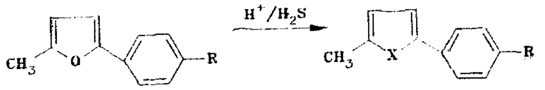
For the first time arylsubstituted furanes have been reacted with hydrogen sulfide and hydrogen selenide under the influence of proton acids. The respective arylthiophenes and arylselenophenes were obtained.

We have previously reported a new addition reaction of furanes with hydrogen sulfide and hydrogen selenide under conditions of acid catalysis, by which dialkylfuranes and furanes containing various functional-group substituents are converted to the respectively theophene and selenophene analogs [1-3].

The present work is a study of the application of this reaction to a new group of furanes, viz., arylfuranes of various structures. According to our data, arylfuranes I-V react with hydrogen sulfide and hydrogen selenide under conditions of acid catalysis to form the respective thiophenes and selenophenes:



I–V

VI–XIV

I, VI, XI R=H; II, VII, XII R=CH_3; III, VIII R=OCH_3; IV, IX, XIII R=Cl; V, X, XIV R=Br; VI—X X=S; XI—XIV X=Se

When the reaction is carried out in a medium of concentrated acid (HCl, $HClO_4$, CF_3COOH), in addition to the desired products, the products of the hydrolytic cleavage of the furanes are also separated from the reaction mixture, viz., the respective 1,4-dicarbonyl compounds [2, 3]. Therefore in this work we used as acid component a 2-3.2 M solution of dry hydrogen chloride in absolute ethyl alcohol.

With the reaction of 2-methyl-5-p-tolylfurane with hydrogen sulfide as an example, the optimum process conditions were developed. The results are shown in Table 1. The best yields of desired product were obtained at 50° and 3.2 M hydrogen chloride.

Conversion of arylfuranes I-V to the respective arylthiophenes VI-X and arylselenophenes XI-XIV was carried out under similar conditions. The yields of desired products were 50-75%. We established that conversion of I-V requires 10-50 h, as compared with 1-1.5 h for the 2,5-dialkylfuranes. This is probably related to the different electron densities in the heterocycle due to the substituents.

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TABLE 1. Dependence of Conversion of II on Acid Concentration and Reaction Temperature (duration of reaction 10 h)

Hydrogen chloride concn. in ethanol, M	Temp., °C	Conversion of II, % (by GLC)
2	25	8
	40	18
	50	25
2,5	25	20
	40	32
	50	55
3,2	25	48
	40	85
	50	100

TABLE 2. Dependence of Reaction Time on Nature of R Substituent and Heteroatom in VI-XIV

Compound	X	R	Reaction time,* h
VI	S	H	13
XI	Se	H	14
VII	S	CH_3	10
XII	Se	CH_3	9
VIII	S	OCH_3	8
IX	S	Cl	48,5
XIII	Se	Cl	50
X	S	Br	36
XIV	Se	Br	35

*The end of the reaction was monitored by the disappearance of the GLC peak of the starting arylfurane.

Study of the reaction showed that the time required for completion of the process is independent of the nature of the nucleophile. This is probably evidence that the limiting step of the process is the opening of the furane ring under the influence of the protonic acid. It was established that reaction time is significantly influenced by the nature of the substituent in the aryl segment. With respect to reactivity, furanes I-V fall in the following sequence: III > II > I > V > IV; i.e., there is a definite dependence of reaction rate on the Hammett σ-constant of the phenyl segment (Table 2). Quantitative estimation of this dependence will be considered in subsequent communications.

The IR spectra of VI-XIV contain a series of absorption bands that are typical of the phenyl ring (740, 1500, 1605 cm^{-1}), and thiophene or selenophene rings (800, 1040, 1240, 1380, 1450 cm^{-1}); the latter correspond to skeletal vibrations [4, 5]. The νCH absorption band appears at 3030 cm^{-1} in thiophenes and at 3015 cm^{-1} for selenophenes.

PMR data for I-XIV are shown in Table 3. There is a definite dependence of the chemical shifts of the methyl protons and the heterocycle β-protons on the nature of the heteroatom. In going from furane to thiophene and selenophene, the signals of the above protons shift toward the weaker field; this agrees with the data of [6].

TABLE 3. PMR Spectra of 2-Methyl-5-arylfuranes I-V, Arylthiophenes VI-X, and Arylselenophenes XI-XIV

Compound	Chemical shift, δ, ppm						Spin-spin coupling constant, Hz	
	$2\text{-}CH_3$, d	3-H, m	4-H, d	$H_3C\text{—}Ar$, s	$H_3CO\text{—}Ar$, s	Ar, m	$^4J_{2\text{-}CH_3, 3H}$	$^3J_{3,4}$
I	2,33	5,93	6,40			7,59—7,08	0,8	3,2
II	2,33	5,88	6,34	2,30		7,50—6,95	0,8	3,1
III	2,31	5,89	6,24		3,73	7,49—6,70	0,8	3,1
IV	2,32	5,94	6,38			7,51—7,16	1,0	3,2
V	2,32	5,96	6,42			7,41, c	1,0	3,2
VI	2,47	6,58	6,97			7,47—7,15	1,0	3,5
VII	2,46	6,55	6,92	2,31		7,37—6,98	0,9	3,8
VIII	2,46	6,56	6,71		3,75	7,40—6,78	1,0	2,11
IX	2,47	6,61	6,95			7,45—7,16	1,0	3,5
X	2,48	6,62	6,96			7,43—7,28	1,1	3,5
XI	2,56	6,78	—*			7,43—7,09	1,2	—*
XII	2,55	6,75	7,05	2,31		7,33—6,97	1,1	3,6
XIII	2,58	6,79	7,10			7,31—7,16	1,2	3,8
XIV	2,53	6,75	7,15			7,42—7,16	1,2	3,9

*Masked by signals of phenyl protons.

TABLE 4. 2-Methyl-5-arylthiophenes and Selenophenes

Compound	mp, °C	Found, %				Empirical found	Calculated, %				Yield, %
		C	H	Br (Cl)	S		C	H	Br (Cl)	S	
VI	43—44	76,2	6,0	—	18,7	$C_{11}H_{10}S$	75,8	5,8	—	18,4	76
VII	38	76,8	6,3	—	16,7	$C_{12}H_{12}S$	76,6	6,4	—	17,0	55
VIII	91	70,2	5,8	—	15,1	$C_{12}H_{12}OS$	70,6	5,9	—	15,7	61
IX	108—109	63,6	4,7	(16,5)	14,9	$C_{11}H_9ClS$	63,3	4,4	(17,0)	15,4	54
X	128—129	52,3	3,9	31,1	12,0	$C_{11}H_9BrS$	52,2	3,6	31,6	12,7	51
XI	57,5—58	60,0	4,7	—	—	$C_{11}H_{10}Se$	59,7	4,6	—	—	65
XII	61,5	61,5	5,4	—	—	$C_{12}H_{12}Se$	61,3	5,1	—	—	68
XIII	123—124	51,9	4,0	(13,4)	—	$C_{11}H_9ClSe$	51,7	3,6	(13,9)	—	62
XIV	135,5—136,5	44,5	3,5	26,3	—	$C_{11}H_9BrSe$	44,0	3,0	26,6	—	54

EXPERIMENTAL

IR spectra were obtained in mineral oil and hexachlorobutadiene on a UR-20 instrument. PMR spectra were obtained on a Varian FT-80A in CCl_4, HMDS internal standard. Synthesized compounds were analyzed by GLC on a Tsvet 101 instrument with flame ionization detector, steel column 1000 × 3 mm, with 15% Apiezon L on Chromatone N-AW, helium carrier gas at 3.5 liter/h, 220°C.

Arylfuranes I-V were synthesized by the procedures of [7, 8].

Properties of the synthesized compounds VI-XIV are shown in Table 4.

General Procedure for Synthesis of Arylthiophenes VI-X. A solution of 3.2 N hydrogen chloride in absolute ethyl alcohol is placed in a thermostated reactor provided with a gas feed tube, a reflux condenser, and a magnetic stirrer, and is saturated with hydrogen sulfide for 1.5 h. Then 5 mmole of starting arylfuran is added. The reaction is finished when according to GLC the starting compound has disappeared. The reaction mixture is neutralized with a saturated sodium bicarbonate solution. After removal of ether [sic] the material is recrystallized from ethanol.

General Procedure for Synthesis of Arylselenophenes XI-XIV. The synthesis is analogous to that just described; the alcoholic solution of hydrogen chloride is previously purged with argon for 1 h.

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