TO THE THIOPHENE ANALOGS

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On reaction with hydrogen sulfide in strongly acidic media, difurylalkyl-(aryl)methanes are converted to furylthienylalkyl(aryl)- or dithienylalkyl-(aryl)methanes, depending on the conditions.

When furan compounds react with hydrogen sulfide or selenide under conditions of acid catalysis, they are converted into the corresponding thiophenes or selenophenes [1-5]. In order to further study the reaction, we have considered the recyclization of difurylalkyl-(aryl)methanes I-V:



I, VI, XI R=CH₃; II, VII, XII R=C₂H₅; III, VIII, XIII R=C₆H₅; IV, IX, XIV R= =C₆H₄OCH₃-p; V, X R=C₆H₄Br-p

A study of their conversions at room temperature in ethyl alcohol solution saturated with hydrogen chloride up to concentrations of 2.5 to 3.5 N has shown that recyclization of one furan ring to form 1-(5-methylfuryl-2)-1-R-1-(5-methylthienyl-2)-methanes (VI-X) takes place. The optimum concentration of the acid component is 2.8 N.

The use of propyl alcohol allowed us to obtain both the compounds with one thiophene ring (VI-X) and dithienylalkyl(aryl)methanes (XI-XIV) (Table 1). The reaction of alkylcontaining compounds I and II with hydrogen sulfide in propanol takes place with the formation of two kinds of products: 1-(5-methylthienyl-2)alkanes (VI, VII) and 1,1-di(5-methylthienyl-2)alkanes (XI, XII). Difurylarylmethanes III and IV react with hydrogen sulfide in propanol to form only dithienylarylmethanes XIII and XIV. When the reaction is carried out with 1,1-di(5-methylfuryl-2)-1-(4-bromophenyl)methane under these same conditions, only monothienyl substituted compound XIV is obtained. It was established that the optimum concentration for compounds III and IV is 3.5 N. The dependence of the yield of products on the nature of the solvent is presented in Table 2. Under uniform reaction conditions (Table 2), the degree of recyclization of furan compounds III and IV is greater than that of compounds I and II.

We have also determined the solubility of hydrogen sulfide in ethanol and propanol that are 3.0 N in hydrogen chloride (Table 3). The greater degree of recyclization of furans I-IV in propanol can be explained by the greater solubility of hydrogen sulfide in propanol.

The IR spectra of compounds VI-X contain absorption bands at 780 (C-O-C) and 795 cm^{-1} (C-S-C), and the spectra of compounds XI-XIV contain an intense absorption band at 795 cm^{-1} (C-S-C). The PMR spectra of compounds III, VIII, and XIII are presented in Table 4.

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Compound	Empirical formula	T _{bp} , °C (mm Hg)	n _D ²⁰
VI VII VIII IX X XI XII XIII XIV	$\begin{array}{c} C_{12}H_{14}OS\\ C_{13}H_{16}OS\\ C_{17}H_{16}OS\\ C_{18}H_{18}O_2S\\ C_{17}H_{15}OSBr\\ C_{12}H_{14}S_2\\ C_{13}H_{16}S_2\\ C_{17}H_{16}S_2\\ C_{18}H_{18}S_2 \end{array}$	$\begin{array}{c} 130 \dots 135 & (4) \\ 135 \dots 140 & (4) \\ & 85^* \\ 130 \dots 132 & (2) \\ 190 \dots 193 & (2) \\ 136 \dots 140 & (4) \\ 140 \dots 145 & (4) \\ 174 \dots 175 & (2) \\ & 89^* \end{array}$	1,5480 1,5370

TABLE 1. Characteristics of the Compounds Synthesized

*Melting point.

TABLE 2. Dependence of the Yield of Reaction Products on the Solvent

		HCl con-	Yield, %		
Com- pound	Solvent	tion g-eq/	mono- thienyl substit- uted	dithieny: substi- tuted	
I	Ethanol Propanol	2,8 3,5	26 (VI) 24 (VI)	50 (XI)	
II	Ethanol Propanol	2.8 3,5	20 (VII) - 24 (VII)	49 (XII)	
III	Ethanol Propanol	2,8 3,5	26 (VIII)	41 (XIII)	
IV	Ethanol Propanol	2.8 3,5	19 (IX)	6 (XIV) 50 (XIV)	
v	Éthanol Propanol	2,8 3,5	20 (X) 53 (X)		

TABLE 3. Solubility of Hydrogen Sulfide in Alcohols*

Solvent	Concentration, g-eq/liter		ura- n e, h
	H ₂ S HCl		tio tin
Ethanol	0.181 0.229 0.290 0.298 0.282	 3,0 3,0 3,0	$ \begin{array}{c} 1 \\ 2 \\ 2 \\ 3 \\ 4 \end{array} $
Abs. ethanol	0,305 0,325	 3,0	4 4
Propanol	0,339 0,345 0,397 0,383	3,0 3,0 3,0	2 2 3 4
Abs. pro- panol	0.353 0,360	3,0	4 4

*Determined by iodometric titration.

TABLE 4. PMR Spectra, ppm

Compound	Furyl	Pheny1	Thienyl.	СН	Substituent
HI VIII	5,68 (s. 4H) 5,78 (s. 2H)	7.08 (s. 5H) 7,17 (s. 5H)	6.48 (s, 2H)	5,16 5,25	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$
XIII	_	7.19 (s , 5H)	6,48 (s, 4H)	5,28	2,31 (s,6H)

EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument in a film; the PMR spectra, on a Varian-80A (80 MHz) in $CDCl_3$ with HMDS as an internal standard. The course of the reaction was followed and the individuality of the compounds obtained was checked by TLC on Silufol UV-254B plates in a hexane/ether system (10:1) developed with iodine vapor.

Compounds I and II were obtained by the condensation of sylvan with the corresponding aldehyde [6]; difurylarylmethanes, by the procedure in [7]. The characteristics of compounds VI-XIV are presented in Table 1. The elementary analyses for C, H, and S for compounds VI-XIV agree with the calculated values.

<u>The General Method of Preparing Thiophene Compounds VI-XIV.</u> Twenty milliliters of a 2.8-3.5 N solution of dry HCl in absolute ethyl or propyl alcohol is placed in an

agitatable reactor of the long necked hydrogenation flask type that is thermostated at 40° C and saturated with hydrogen sulfide for two hours. Then, 3 mmoles of the appropriate furan is added to the reaction mixture. The course of the reaction is followed with the help of TLC, and when it has ended, the mixture is neutralized with a saturated NaOH solution to a weakly alkaline reaction and extracted with ether. The ethereal extract is washed with water and dried with calcined MgSO₄. After removal of the ether, the residue is sub-limed in vacuum.

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KINETICS OF IONIZATION OF CH BONDS OF FIVE-MEMBERED HETEROCYCLES AND

THEIR BENZO DERIVATIVES AND MECHANISM OF THE ELEMENTARY ACT OF PROTON

TRANSFER.

1. QUANTUM-CHEMICAL CALCULATION OF GEOMETRICAL AND ELECTRON STRUCTURES OF THE MOLECULES AND CARBANIONS

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The heats of formation and the parameters of the geometrical and electron structures of the molecules and carbanions of furan, thiophene, N-methylpyrrole, N-methylimidazole, benzofuran, benzothiophene, N-methylindole, benzene, and naphthalene were calculated by the self-consistent-field (SCF) MO LCAO method within the MNDO and CNDO/2 approximations. According to the calculations, the deprotonation of the indicated CH acids leads to relatively small changes in the geometrical structures of the anionic fragments. The charge on the deprotonated carbon atom changes most markedly in the formation of the carbanions.

The proposed series of studies continues systematic investigations to ascertain the interrelationship between the mechanism of the elementary act of proton transfer in reactions involving the ionization of CH acids and the structures of the reagents [1, p. 128; 2-4].

Data on the geometrical and electron structures of the molecules and carbanions are necessary to obtain information regarding the peculiarities of the structural reorganization of the anionic fragments of five-membered heterocycles in ionization reactions. In the proposed research the geometrical and electron structures of furan (I), thiophene (II),

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