SYNTHESIS AND SOME TRANSFORMATIONS OF THIOESTERS OF THIENYLACRYLIC ACID

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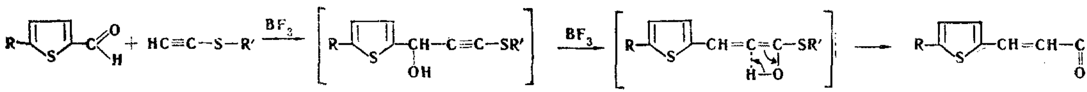
A number of thioesters of thienylacrylic acid were obtained by the condensation of 2-formylthiophene and 5-bromo-2-formylthiophene with acetylenic thioethers in the presence of boron trifluoride etherate. The reaction of the condensation products with hydrazine hydrate is accompanied by intramolecular cyclization to form the corresponding pyrazolines. The IR spectra of the synthesized compounds are discussed.

The condensation of acetylenic ethers and thioethers with aliphatic and aromatic aldehydes is one of the most convenient methods for the synthesis of α,β-unsaturated esters [1,2]. In this study, the difficult-to-obtain thioesters of thienylacrylic acid were obtained by the condensation of 2-formylthiophene and 5-bromo-2-formylthiophene with acetylenic thioethers in the presence of a catalyst – boron trifluoride etherate. The reaction was accomplished under mild conditions with cooling (to −10°) in a solution of dry diethyl ether in 1 h. The vinyl ketones obtained were isolated by vacuum distillation and were yellow, viscous oils that solidified in the cold.

The mechanism of this reaction can be represented as follows:



I–VIII

I R=H, R'=CH_3; II R=H, R'=C_2H_5; III R=H, R'=C_3H_7; IV R=H, R'=C_4H_9;
V R=H, R'=C_6H_{13}; VI R=Br, R'=C_2H_5; VII R=H, R'=C_6H_5; VIII R=Br, R'=C_6H_5

TABLE 1. Thioesters of 2-Thienylacrylic Acid

Comp.	R	R'	Bp, °C (mm)	Mp, °C	Empirical formula	Found, %			Calc. %			Yield, %
						C	H	S	C	H	S	
I	H	CH_3	126—128(2)	34—35	$C_8H_8OS_2$	52,55	4,41	34,57	52,17	4,35	34,78	53
II	H	C_2H_5	116—118(1)	—	$C_9H_{10}OS_2$	54,74	5,07	32,18	54,55	5,05	32,32	63
III	H	C_3H_7	127—128(1)	—	$C_{10}H_{12}OS_2$	56,73	5,71	30,20	56,60	5,66	30,19	48
IV	H	C_4H_9	139—141(1)	—	$C_{11}H_{14}OS_2$	58,70	6,18	28,37	58,41	6,19	28,32	50
V	H	C_6H_{13}	—	—	$C_{13}H_{18}OS_2$	61,39	7,18	25,37	61,42	7,09	25,20	38
VI	Br	C_2H_5	145—147(1)	—	$C_9H_9BrOS_2$[a]	—	—	23,31	—	—	23,40	48
VII	H	C_6H_5	—	73—75	$C_{13}H_{10}OS_2$	63,28	4,12	25,80	63,41	4,07	26,02	44
VIII	Br	C_6H_5	—	94—96	$C_{13}H_9BrOS_2$[b]	—	—	19,53	—	—	19,69	72

[a] Found: Br 28.69%. Calculated: Br 28.88%.
[b] Found: Br 24.81%. Calculated: Br 24.62%

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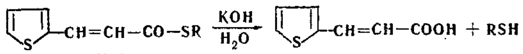
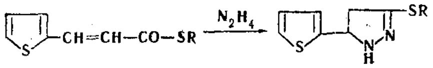
Secondary thioacetylenic alcohols, which, under the influence of an acid catalyst (BF_3), undergo allylic isomerization with 1,3-migration of the oxygen atom, are probably initially formed as a result of the condensation of 2-formylthiophene with acetylenic thioethers. A similar type of isomerization was previously observed in phenylethynylcarbinol under the influence of sulfuric acid [3].

To prove the structure of the synthesized compounds, II-IV were subjected to alkaline hydrolysis, as a result of which 2-thienylacrylic acid was isolated; the unpleasant odor indicated the presence of mercaptans.



II-IV

The thioesters of thienylacrylic acid readily react with hydrazine hydrate in aqueous methanol, thereby undergoing intramolecular cyclization to form 5-(2-thienyl)-3-alkylthiopyrazolines (IX-XI).



IX-XI

IX R=CH_3; X R=C_2H_5; XI R=C_3H_7

The IR spectra of I-VIII contain absorption bands at 1660-1672 and 1598-1603 cm^{-1}, which correspond to a conjugated carbonyl group and a double bond. The absorption band at 600-605 cm^{-1} corresponds to the C—S bond. The absorption band at 965 cm^{-1} indicates a trans orientation of the hydrogen atoms attached to the double bond of I-VIII.

The IR spectra of IX-XI contain absorption bands at 3200-3210 cm^{-1} from the associated N—H bond and at 1660 cm^{-1} from the C=N bond.

EXPERIMENTAL

1-(2-Thienyl)-3-methylthio-2-propen-3-one (I). A 1.77-g (0.0125 mole) sample of boron trifluoride etherate in absolute ether and 0.9 g (0.125 mole) of methylthioacetylene were added at −10° to a solution of 2.8 g (0.025 mole) of 2-formylthiophene in 10 ml of absolute ether, and the mixture was stirred for 1 h. It was then decomposed with 15% sodium acetate and extracted with ether. The extract was dried with calcined magnesium sulfate, the ether was evaporated, and the residue was vacuum-distilled to give 1.22 g (53% based on methylthioacetylene) of product.

Compounds II-VIII were similarly obtained. Compound V was isolated by chromatography on Al_2O_3 with elution by benzene—diethyl ether (4 : 1). Compounds VII and VIII were isolated by recrystallization from diethyl ether in the cold. The physical constants and yields of I-VIII are presented in Table 1.

Alkaline Hydrolysis of 1-(2-Thienyl)-3-ethylthio-2-propen-3-one (II). A 1-g (0.005 mole) sample of II was refluxed with 10 ml of 25% KOH in ethanol for 5 h. The solution was neutralized with 5% HCl, and the crystals of 2-thienylacrylic acid were removed by filtration and washed on the filter with water to give 0.72 g (92%) of a product with mp 182-184° (from ethanol). Found: S 20.65%. $C_7H_6O_2S$. Calculated: S 20.78%.

Compounds III and IV were similarly hydrolyzed. The yields of 2-thienylacrylic acid were 91% and 94%, respectively.

5-(2-Thienyl)-3-methylthiopyrazoline (IX). A total of 0.24 g (0.005 mole) of 96% hydrazine hydrate was added slowly to a solution of 0.48 g (0.0026 mole) of I in 20 ml of methanol under reflux. The mixture was refluxed for 1.5 h and cooled. The water, alcohol, and excess hydrazine hydrate were vacuum-evaporated in a stream of nitrogen at 100°. The residue [0.46 g (88%)] was a yellow, viscous mass (IX) that decomposed on distillation. Found: N 14.01; S 32.52%. $C_8H_{10}N_2S_2$. Calculated: N 14.14; S 32.32%.

5-(2-Thienyl)-3-ethylthiopyrazoline (X). This compound was similarly obtained in 91% yield. Found: N 13.50; S 30.41%. $C_9H_{12}N_2S_2$. Calculated: N 13.21; S 30.19%.

5-(2-Thienyl)-3-propylthiopyrazoline (XI). This compound was similarly obtained in 82% yield. Found: N 12.05; S 28.38%. $C_{10}H_{14}N_2S_2$. Calculated: N 12.39; S 28.32%.

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3. J. Jawai, J. Soc. Org. Synthetic Chem. Japan, 23, 304 (1965).