ADDITION OF HYDROHALIC ACIDS TO ACETYLENIC KETONES OF THE THIOPHENE SERIES

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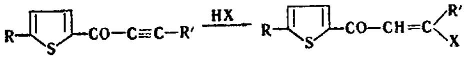
The synthesis of β-chloro(bromo)vinyl ketones of the thiophene series was accomplished by the addition of hydrogen chloride and hydrogen bromide to acetylenic ketones of the thiophene series. The sequence of addition of the hydrogen halide was proved by alternative synthesis.

The addition of hydrogen chloride and hydrogen bromide to a number of aryl- and alkylacetylenic ketones has been previously studied, and it was demonstrated that in all cases the halogen adds to the β-carbon atom relative to the carbonyl group [1-4].

In a continuation of our investigations of the synthesis and study of the reactivities of thienyl ethynyl ketones [5,6], we have studied the addition of hydrogen halides to the latter in the presence of a catalyst – cuprous chloride. As a result of the reaction, we obtained good yields of β-chloro(bromo)vinyl ketones of the thiophene series, the physical constants and yields of which are presented in Table 1.



I-X

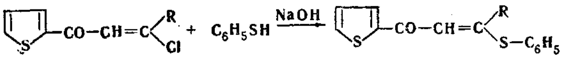
The reaction of ethynyl ketones of the thiophene series with hydrohalic acids was carried out at room temperature (I, IV, VII-X) or at lower temperatures (II, III, V, VI) in chloroform or carbon tetrachloride.

A thioalkyl substituent attached to the acetylenic bond in the starting ketone hinders the reaction, and the β-chlorovinyl ketone formed (VI) is an unstable compound; it was isolated by chromatography on aluminum oxide.

To prove the structures, β-chlorovinyl ketones II, III, and VI were obtained by alternative synthesis by the condensation of thiophene-2-carboxylic acid chloride with the appropriate alkylacetylenes in the presence of aluminum chloride [7] and with propylthioacetylene in the presence of stannic chloride.

II $R=CH_3$; III $R=C_4H_9$; VI $R=S-C_3H_7$

It is known that β-chlorovinyl ketones have a very labile chlorine atom that can be substituted by various functional groups. We obtained high yields of the corresponding phenylthiovinyl ketones (XI-XIII) (Table 1) by the reaction of II, III, and VI with thiophenol in the presence of alkali.



XI-XIII

The IR spectra of I-X contain absorption bands at 1660 and 1670 cm^{-1} and 1588-1600 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 in XI-XIII.

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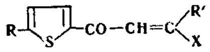
TABLE 1



Comp.	R	R′	X	Bp, °C (mm)	Mp, °C	Empirical formula	Found, %				Calc., %				Yield, %
							C	H	Cl (Br)	S	C	H	Cl (Br)	S	
I	H	H	Cl	95(2)	28	C_7H_5ClOS	—	—	20,34	18,19	—	—	20,58	18,55	72
II	H	CH_3	Cl	—	35	C_8H_7ClOS	—	—	19,10	17,25	—	—	19,03	17,16	37
III	H	C_4H_9	Cl	131—133(2)	—	$C_{11}H_{13}ClOS$	—	—	15,42	13,93	—	—	15,53	14,02	52
IV	H	C_6H_5	Cl	193—195(1)	oil	$C_{13}H_9ClOS$	—	—	14,84	13,35	—	—	14,28	12,88	60
V	Br	C_6H_5	Cl	—	49—50	$C_{13}H_8BrClOS$	47,47	2,51	—	9,36	47,56	2,44	—	9,76	60
VI	H	S—C_3H_7	Cl	—	oil	$C_{10}H_{11}ClOS_2$	—	—	13,96	26,14	—	—	14,40	25,96	25
VII	H	H	Br	114—116(1)	—	C_7H_5BrOS a	—	—	36,57	14,81	—	—	36,86	14,74	50
VIII	H	CH_3	Br	—	48—49	C_8H_7BrOS	—	—	34,30	13,65	—	—	34,63	13,80	61
IX	H	C_4H_9	Br	145—147(1)	—	$C_{11}H_{13}BrOS$ b	—	—	29,18	11,64	—	—	29,30	11,72	66
X	H	C_6H_5	Br	203—205(4)	oil	$C_{13}H_9BrOS$	—	—	27,03	10,88	—	—	27,30	10,92	65
XI	H	CH_3	S—C_6H_5	166—168(1)	121—123	$C_{14}H_{12}OS_2$	64,42	4,58	—	24,59	64,62	4,62	—	24,62	83
XII	H	C_4H_9	S—C_6H_5	140—142(1)	—	$C_{17}H_{18}OS_2$	67,61	6,02	—	21,05	67,55	5,96	—	21,19	68
XIII	H	S—C_3H_7	S—C_6H_5	—	72—75	$C_{16}H_{16}OS_3$	60,21	4,92	—	29,84	60,00	5,00	—	30,00	75

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a n_D^{20} 1.6254.

b n_D^{20} 1.5385.

EXPERIMENTAL

1-(2-Thienyl)-3-chloro-2-propen-1-one (I). Dry hydrogen chloride was bubbled through a solution of 2 g (0.014 mole) of 1-(2-thienyl)-2-propyn-1-one in 8 ml of dry chloroform in the presence of 0.15 g (0.0015 mole) of cuprous chloride at room temperature for 5-6 h. The chloroform was removed by distillation, and the residue was vacuum-distilled to give 1.83 g (72%) of I.

Compound IV was similarly obtained.

1-(2-Thienyl)-3-chloro-2-buten-1-one (II). Cuprous chloride [0.26 g (0.0026 mole)] was added to a solution of 3 g (0.02 mole) of 1-(2-thienyl)-2-butyn-1-one in 10 ml of dry chloroform, the reaction mixture was cooled to −40°, and 50 ml of a saturated solution of hydrogen chloride in dry chloroform was added dropwise. The mixture was stirred for 20 min, the catalyst was removed by filtration, and the chloroform was evaporated. The residue was vacuum-distilled to give 1.5 g (37%) of II. The reaction was accompanied by considerable resinification.

Compounds III, V, and VI were similarly obtained.

1-(2-Thienyl)-3-bromo-2-buten-1-one (VIII). A total of 0.83 ml of a saturated aqueous solution (65%) of hydrobromic acid was added dropwise to a solution of 1 g (0.007 mole) of 1-(2-thienyl)-2-butyn-1-one in 20 ml of carbon tetrachloride containing 0.1 g (0.001 mole) of cuprous chloride. The mixture was stirred for 15 h at room temperature and poured into water. The aqueous layer was extracted with ether. The ether extracts were dried with calcined magnesium sulfate, the ether was evaporated, and the crystals that precipitated in the cold were recrystallized from ethanol to give 0.96 g (61%) of VIII with mp 48-49°.

Compounds VII, IX, and X were similarly obtained.

Condensation of Thiophene-2-carboxylic Acid Chloride with Methyl- and Butylacetylenes. The reaction was carried out in the presence of aluminum chloride as described in [7]. The yields of β-chlorovinyl ketones II and III were 56 and 64%, respectively.

Condensation of Thiophene-2-carboxylic Acid Chloride with Propylthioacetylene. Propylthioacetylene [1.4 g (0.014 mole)] was added dropwise to a solution of 2 g (0.014 mole) of thiophene-2-carboxylic acid chloride and 3.5 g (0.014 mole) of stannic chloride in 20 ml of dichloroethane, cooled to −25°. The mixture was stirred for 30 min and decomposed with water while cooling. The organic layer was separated, and the aqueous layer was neutralized with sodium carbonate and extracted with chloroform. The extracts were dried with calcined magnesium sulfate, and the solution was evaporated. The residue was chromatographed on aluminum oxide with elution by benzene–ether–hexane (3 : 1 : 1) to give 1.8 g (55%) of VI.

1-(2-Thienyl)-3-phenylthio-2-buten-1-one (XI). A 0.3-g (0.002 mole) sample of II was added with stirring to a solution of 0.2 g (0.002 mole) of thiophenol and 0.2 g (0.005 mole) of sodium hydroxide in 1 ml of water. The mixture was stirred for 5 h at room temperature and extracted with ether. The ether extracts were dried with sodium sulfate, the ether was evaporated, and the resulting crystals were recrystallized from ethanol to give 0.35 g (83%) of XI.

Compounds XII and XIII were similarly obtained.

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