SYNTHESIS OF CARBONYL DERIVATIVES OF 3-PHENYLTHIOPHENE

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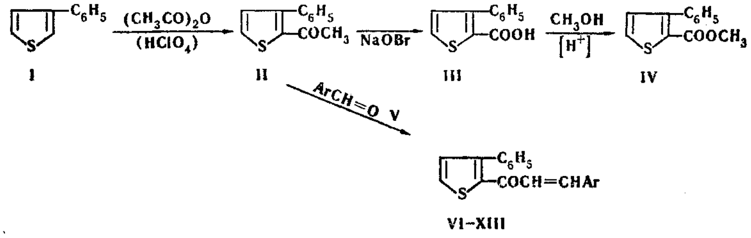
3-Phenyl-2-acetylthiophene was synthesized by the acetylation of 3-phenylthiophene with acetic anhydride in the presence of 56% perchloric acid. Previously undescribed α,β-unsaturated ketones were synthesized by the crotonic condensation of 3-phenyl-2-acetylthiophene with several aromatic and heterocyclic aldehydes.

We have obtained 3-phenyl-2-acetylthiophene (II) by the acetylation of 3-phenylthiophene (I) with acetic anhydride in the presence of 56% perchloric acid via the method described in [1]. The structure of II was proved by its oxidation to the known 3-phenylthiophene-2-carboxylic acid (III) [2] with aqueous sodium hypobromite and by the preparation of its methyl ester (IV). Traces of other isomers were not detected in the acetylation of I. We have obtained α,β-unsaturated ketones (VI-XIII) by the crotonic condensation of II with some aromatic and heterocyclic aldehydes (V).



The ketones obtained (VI-XIII) (see Table 1) are crystalline, slightly yellow substances that are soluble in acetone, benzene, and ether, slightly soluble in alcohol, and insoluble in water.

Colored solutions are formed in concentrated sulfuric acid. Absorption bands corresponding to the stretching vibrations of the C=O group of α,β-unsaturated ketones [3] (1634-1646 cm^{-1}) and NO_2 group vibrations are noted in the IR spectra of VI-XIII.

EXPERIMENTAL

3-Phenylthiophene (I). This compound was obtained in 10.2% yield by the method in [4] and melted at 90-91° (from alcohol).

3-Phenyl-2-acetylthiophene (II). An 18.0-g (0.11 mole) sample of I was dissolved at 60° in 18 ml (0.19 mole) of acetic anhydride, and eight to ten drops of 56% perchloric acid were added with stirring, during which the reaction mixture heated up to 100-120°. The mixture was heated on a boiling-water bath for 1 h, cooled, and poured into water. The resulting oil was extracted with benzene. The benzene extract was washed with saturated $NaHCO_3$ solution and dried over Na_2SO_4, and the benzene was removed by distillation. The residue was vacuum-distilled to give 16.86 g (76%) of a fraction with bp 165-175° (7-8 mm) and mp 64-65° (from alcohol). Found: C 71.5; H 5.0; S 15.8%. $C_{12}H_{10}OS$. Calculated: C 71.2; H 5.0; S 15.8%. The 2,4-dinitrophenylhydrazone was obtained as red crystals with mp 166° (from n-propyl alcohol). Found: N 14.43%. $C_{18}H_{13}N_4O_4S$. Calculated: N 14.66%.

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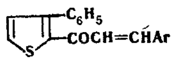
TABLE 1. 1-(3-Phenyl-2-thienyl)-3-Ar-2-propen-1-one



Comp.	Ar	Mp, °C	Empirical formula	Found, %			Calc., %			2,4-Dinitrophenylhydrazones				Yield, %
				C	H	S	C	H	S	empirical formula	Mp, °C	S, % found	S, % calc.	
VI	Phenyl	82	$C_{19}H_{14}OS$	78,9	4,8	11,3	78,6	4,8	11,0	$C_{25}H_{18}N_4O_4S$	239,5	6,5	6,8	92
VII	4-Nitrophenyl	155	$C_{19}H_{13}NO_3S$	67,8	4,1	9,9	68,1	3,9	9,6	$C_{20}H_{14}N_4O_3S$*	247	8,0	8,0	87
VIII	3-Nitrophenyl	120	$C_{19}H_{13}NO_3S$	68,2	4,0	9,5	68,1	3,9	9,6	$C_{25}H_{17}N_5O_6S$	245	6,5	6,2	85
IX	2-Nitrophenyl	116	$C_{19}H_{13}NO_3S$	68,3	4,1	9,5	68,1	3,9	9,6	$C_{25}H_{17}N_5O_6S$	174	6,4	6,2	72
X	4-N,N-Dimethyl-aminophenyl	104	$C_{21}H_{19}NOS$	75,7	5,8	9,8	75,7	5,7	9,6	$C_{27}H_{23}N_5O_4S$	239	6,7	6,4	52
XI	2-Furyl	86	$C_{17}H_{12}O_2S$	70,3	4,2	10,1	70,3	4,3	10,4	$C_{23}H_{16}N_4O_5S$	202	7,2	7,0	93
XII	2-Thienyl	115	$C_{17}H_{12}OS_2$	69,3	4,2	21,7	69,0	4,1	21,6	$C_{23}H_{16}N_4O_4S_2$	215	13,7	13,5	83
XIII	5-Nitro-2-thienyl	187	$C_{17}H_{11}NO_3S_2$	59,9	3,4	18,6	59,8	3,2	18,8	$C_{18}H_{12}N_4O_3S_2$*	251	15,8	16,1	43

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*Semicarbazone.

3-Phenylthiophene-2-carboxylic Acid (III). Bromine [3.6 g (0.023 mole)] was added dropwise with cooling to an aqueous solution of 4.35 g (0.0054 mole) of sodium hydroxide, and 1 g (0.005 mole) of II (ground to a powder) was added to the resulting solution. The suspension was stirred for 3 h at room temperature. The solid was removed by filtration and washed with water. The combined aqueous filtrate was acidified with hydrochloric acid, and the precipitate was removed by filtration and air-dried to give 0.6 g (60%) of 3-phenylthiophene-2-carboxylic acid with mp 204-205° (from alcohol) (mp 205-207° [2]). The methyl ester (IV) of this acid was obtained by esterification and had mp 120-120.5° (mp 119-120° [2]).

Ketones (VI-XIII). Several drops of 20% aqueous sodium hydroxide were added with stirring to a solution of equimolecular amounts (0.025 mole) of II and the appropriate aromatic or heterocyclic aldehyde (V) in the minimum amount of ethanol. The reaction mixture was allowed to stand for several hours, and the resulting precipitate was removed by filtration, washed with alcohol and water, and recrystallized from alcohol.

The IR spectra of KBr pellets of VI-XIII were measured with an IKS-14 spectrophotometer.

LITERATURE CITED

1. G. N. Dorofeenko, V. I. Karban, L. V. Dulenko, and V. N. Novikov, Izv. Vuzov, Ser. Khim., 7, 432 (1964).
2. N. Gjos and S. Gronowitz, Ark. Kemi, 30, 225 (1969).
3. P. S. Kalsi, Perfumes and Essent. Oil Res., 60, 316 (1969).
4. A. S. Broun and M. G. Voronkov, Zh. Obshch. Khim., 17, 1162 (1947).