STUDY OF CERTAIN CONDENSATION PRODUCTS IN THE 2,2'-DITHIENYL SERIES. III

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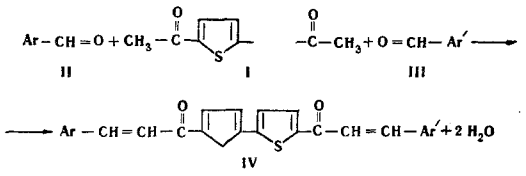
Bis-α, β-unsaturated diketones of 2,2'-dithienyl, which had not been previously described in the literature, were synthesized by means of a crotonic condensation of 5,5'-diacetyl-2,2'-dithienyl with certain aromatic and heterocyclic aldehydes. These compounds form halochromic solutions in sulfuric acid. The IR and UV spectra were determined.

The synthesis of the so-called n-dichalcones and their heterocyclic analogs containing thiophene and furan rings has been described in the literature [1,2]. There is no information concerning the products of condensation between 5,5'-diacetyl-2,2'-dithienyl and aldehydes. As a continuation of our previous studies [3, 4], this work describes certain bis-α,β-unsaturated diketones of the order 2,2'-dithienyl (IV), obtained by a crotonic condensation of 5,5'-diacetyl-2,2'-dithienyl (I) with aromatic and heterocyclic aldehydes (II, III) according to the scheme:



Benzaldehyde, furfurol, 2-thiophenaldehyde, 5-formyl-2,2'-dithienyl, and a mixture of these aldehydes (II), (III) were introduced into the condensation reaction with compound I. When the condensation was conducted in boiling alcohol in the presence of NaOH, it was possible to obtain compound IV (V–XI, table). In addition to compound IV, side products of polymerization of an unestablished structure were obtained. Synthesized compounds IV are crystalline substances, yellow and brown in color, soluble in dioxane and conc H_2SO_4, poorly soluble in benzene and alcohol, and insoluble in water. They all possess characteristic halochromic properties and in a solution of H_2SO_4 they darken to a violet color.

With the object of confirming the structure and determining additional characteristics of the synthesized compounds, spectrophotometrical measurements were conducted in the IKS-14, SF-4, and SF-10 spectrophotometers. All diketones studied have a sharply pronounced absorption maximum in the 1650 cm^{-1} region, which is characteristic for valency oscillations of the carbonyl group. The main spectral data for UV spectra are presented in the table.

EXPERIMENTAL

5,5'-Diacetyl-2,2'-dithienyl was obtained by acetylation of 2,2'-dithienyl acetic anhydride in the presence of 85% H_3PO_4 [5]. Yield, 87%; mp 231–232° C (from dioxane). According to data in the literature [5] mp 233.5–234° C (from dioxane).

Bisdiketones (V–XI, table). A 3.2 g quantity of solid NaOH was gradually added to a solution of 0.0012 mole of compound I and the corresponding quantity of compounds II or III or a mixture of II and III in 200 ml of boiling alcohol. The reaction mixture was boiled in a water bath for 30 min. The resulting precipitate was removed by filtration, washed with acidified water, and then with water and alcohol. The diketone was extracted with boiling dioxane and crystallized from a mixture of dioxane and alcohol.

IR and UV Absorption Spectra. Measurements of IR spectra were conducted with the IKS-14 spectrophotometer in a prism of NaCl in vaseline oil. Measurements of UV spectra were conducted in the SF-4 spectrophotometer in DMFA with the concentration of the solutions equivalent to $1 \cdot 10^{-5}$ M and in the SF-10 recording spectrophotometer in 96% H_2SO_4 when the concentration of the solutions was from $0.2 \cdot 10^{-4}$ to $1 \cdot 10^{-4}$ M. IR and UV spectra were measured in collaberation with R. A. Bakulinii.

REFERENCES

1. W. Davey and D. H. Maass, J. Chem. Soc., 4386, 1963.

2. M. Vaysse and P. Pastour, C. r., 259, 2865, 1964.

3. A. E. Lipkin and N. I. Putokhin, KhGS [Chemistry of Heterocyclic Compounds], 519, 1966.

4. A. E. Lipkin and N. I. Putokhin, KhGS [Chemistry of Heterocyclic Compounds], 243, 1967.

5. H. Wynberg and A. Logothetis, J. Am. Chem. Soc., 78, 1960, 1956.

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Characteristics of the Compounds Obtained

Compound	Ar	Ar′	Mp, °C	λ_{max}, nm (log ε)		Empirical formula	S, %		Yield, %
				DMFA	96% H_2SO_4		found	calculated	
V	Phenyl	Phenyl	260—263	385 (4.38); 298 (3.85)	557 (4.44)	$C_{26}H_{18}O_2S_2$	15.28	15.03	27.4
VI	2-Furyl	2-Furyl	Nonliquefiable powder (decomposition)	385 (4.27); 304 (3.99); 266 (4.05)	543 (2.73)	$C_{22}H_{14}O_4S_2$	15.91	15.77	46.8
VII	2-Thienyl	2-Thienyl	209—213	380 (4.44); 285 (3.94);	570 (4.07); 463 (4.05)	$C_{22}H_{14}O_2S_4$	29.26	29.24	16.0
VIII	2,2′-Dithienyl-5-yl	2,2′-Dithienyl-5-yl	224—228	400 (4.02)	678 (4.34); 443 (4.39)	$C_{30}H_{18}O_2S_6$	31.84	31.91	12.0
IX	Phenyl	2-Furyl	Nonliquefiable powder (decomposition)	380 (4.34); 288 (4.07)	531 (2.86)	$C_{24}H_{16}O_3S_2$	15.59	15.39	44.0
X	Phenyl	2-Thienyl	290—295 (decomposition)	370 (4.36); 281 (3.87)	556 (4.19); 464 (4.26) 440 (4.25)	$C_{24}H_{16}O_2S_3$	22.41	22.23	31.0
XI	2-Furyl	2-Thienyl	Nonliquefiable powder (decomposition)	380 (4.51)	560 (3.01)	$C_{22}H_{14}O_3S_3$	22.43	22.76	14.0

*The diketones were recrystallized from a dioxane–alcohol mixture.