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RESEARCHES ON CONDENSATION PRODUCTS OF SOME 2, 2'-DITHIENYL COMPOUNDS. I

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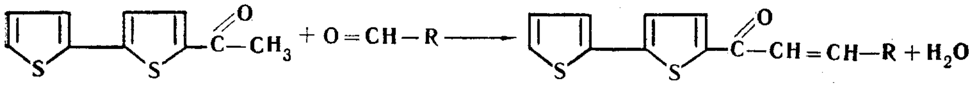
Crotonaldehyde-type condensation of 5-acetyl-2, 2'-dithienyl with some aromatic and heterotyclic aldehydes and nitroaldehydes in the presence of alkali is used to synthesize a number of hitherto undescribed unsaturated 2, 2'-dithienyl ketones. The visible and UV absorption spectra of these compounds of the ketones synthesized are measured in ethanol and 96% sulfuric acid solutions. In sulfuric acid all the compounds investigated form intensely colored halochromic solutions. Comparison of the spectral characteristics of the compounds prepared shows that replacement of the benzene ring by furan and thiophene rings gives rise to a bathochromic effect which is significantly greater in acid solution than in neutral solution. For the neutral solution, introduction of a single nitro group into the benzene or thiophene ring gives rise to a K-band bathchromic shift, while in acid solution there is a hypsochromic effect.

There is comparatively little published research on 2, 2'-dithienyl condensation products. More particularly, 2, 2'-dithienyl aldehydes have been condensed with arylacetonitriles [1]. The present work aimed to prepare unsaturated 2, 2'-dithienyl aldehydes by crotonaldehyde-type condensation of 5-acetyl-2, 2'-dithienyl with aromatic and heterocyclic aldehydes, according to the equation



The following were brought to react with 5-acetyl-2, 2'-dithienyl: benzaldehyde, p-nitrobenzaldehyde, m-nitrobenzaldehyde, furfural, 2-thiophene aldehyde, and 5-nitro-2-thiophenealdehyde. When the reaction was carried out at room temperature with 20% sodium hydroxide solution as catalyst, it proceeded readily and gave acceptable yields of 2, 2'-dithienyl α, β-unsaturated ketones (I-VI, table).

Attempts to effect crotonaldehyde-type condensation of 5-acetyl-2, 2'-dithienyl with 5-nitrofurfural using an alkaline or acid catalyst [2] were unsuccessful.

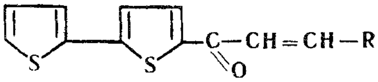
The unsaturated ketones which we have synthesized were yellow and yellowish-orange crystalline compounds, soluble in benzene, ether, and dioxane; less soluble in ethanol, and insoluble in water. Introduction of a nitro group into the molecule of the unsaturated ketones sharply diminished their solubilities, particularly in ethanol and ether, and raised their melting points. They all exhibit characteristic halochromic properties, and, in sulfuric acid solution, their colors are deepened to purplish-violet. To compare the spectroscopic characteristics of the compounds synthesized in the UV and visible regions, spectrophotometric measurements were made in 95% ethanol and 96% sulfuric acid. The table gives the basic spectroscopic data for the ketones investigated.

The data show that the UV spectra of 2, 2'-dithienyl unsaturated ketones are characterized by the same regularity as analogous thiophene compounds [3].

To ascertain the effects of electron-accepting groups on the UV spectra and halochromic properties of the 2, 2'-dithienyl ketones, we inserted a nitro group in the benzene and thiophene rings (table, compounds IV-VI). As was to be expected, when a chromophoric group able to participate in the general conjugated chain was introduced, a bathochromic shift of the K-band was observed. It should be mentioned that when the nitro group is at a meta position in the benzene ring, the bathochromic shift of the K-band is less than when it is in the para position. It was also of interest to exhibit the difference between the halochromic coloring of 2, 2'-dithienyl ketones in solution in 96% sulfuric acid. The data in the table show clearly that the maximum absorption of the longwave band in the acid solvent is displaced 120-147 mμ towards the red region, as compared with the same in ethanol. Here it is to be emphasized that with ketones containing a nitro group (IV-VI), as compared with ketones I-III, there is a hypsochromic shift in the longwave band region, in agreement with the qualitative theory of the effect of solvent and dissolved substance on absorption spectrum [4]. The theory states that shift of absorption bands towards the shortwave region occurs when both dissolved substance and solvent are polar.

Finally, it should be mentioned that each of the 2, 2'-dithienyl ketones investigated has a characteristic absorption curve which can serve for identification, together with the other constants given.

α, β Unsaturated Ketones



Keystone number	R	T. Mp °C	Formula	S, %		UV spectra			Yield, %
				Found	Calculated	95% спирт		96% H_2SO_4	
						λ_{max} mμ/lg ε	λ_{min} mμ/lg ε	λ_{max} mμ/lg ε	
I	C_6H_5	115—117	$C_{17}H_{12}OS_2$	21.50	21.63	380 4.34 225 3.92	244 3.61	516 4.54	77.4
II	α-Furyl	130—132	$C_{15}H_{10}O_2S_2$	22.41	22.39	393 4.35 263 3.86	300 3.65 242 3.54	544 4.17	77.0
III	α-Thienyl	116—118	$C_{15}H_{10}OS_3$	32.07	31.80	394 4.35 270 3.68	306 3.55 242 3.38	530 4.39	65.3
IV	*m*-$NO_2C_6H_4$	172—175	$C_{17}H_{11}NO_3S_2$	18.93	18.78	381 4.15 272 4.04 228 4.00	330 3.89 254 3.97	496 4.36	84.0
V	*p*-$NO_2C_6H_4$	204—208	$C_{17}H_{11}NO_3S_2$	18.74	18.78	382 4.08 324 4.09	350 4.04 245 3.80	500 4.27	76.3
VI	α-(α'-Nitro-thienyl	162—167	$C_{15}H_9NO_3S_3$	27.72	27.68	397 3.99 275 3.74	288 3.74 239 3.73	527 3.81 428 3.56	34.5

Experimental

5-Acetyl-2, 2'-dithienyl. Prepared by acetylating 2, 2'-dithienyl with AcOCl in the presence of $SnCl_4$. Yield 70%, mp 114–115° (ex EtOH).

Ketones I–IV. (table). A 20% aqueous solution of sodium hydroxide (0.3–0.6 g) was added dropwise to solution of equimolecular amounts (0.0024 mole) 5-acetyl-2, 2'-dithienyl and the appropriate aromatic or heterocyclic aldehyde in a small amount of ethanol (10–11 ml). The reaction mixture was left overnight, the precipitate filtered off washed with aqueous EtOH, then with water, and recrystallized from EtOH to constant mp.

UV absorption spectra (table). The absorption spectra were measured with a SF-4 spectrophotometer and self-recording SF-10 spectrophotometer, using solutions of concentration 1×10^{-4} to 1×10^{-5} M. The ethanol for optical purposes was purified as stated in [6].

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