HALOCHROMISM OF THIOPHENE-CONTAINING ANALOGS OF CHALCONES AND THEIR DERIVATIVES

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The formation of hydroxy-, acyloxy-, chloro-, and tetrachlorophosphoroxycarbonium ions was established on the basis of the electronic absorption spectra of thiophene-containing analogs of chalcones and their derivatives in concentrated sulfuric acid, in dilute solutions of sulfuric acid in acetic and trichloroacetic anhydrides, and in acetonitrile benzene, dichloroethane, and nitromethane in the presence of phosphorous pentachloride.

Considerations favoring a hydroxycarbonium structure for the cation were previously expressed in a study of acid solutions of unsaturated ketones [1,2]. This sort of structure for the cations is also considered to be more likely in [3-5]. In our preliminary communication [6], we used a spectrophotometric method to demonstrate the conversion of hydroxycarbonium ions to acyloxycarbonium ions. The formation of acetoxycarbonium ions of ketones in acid media containing acetic anhydride was proposed in [7, 8].

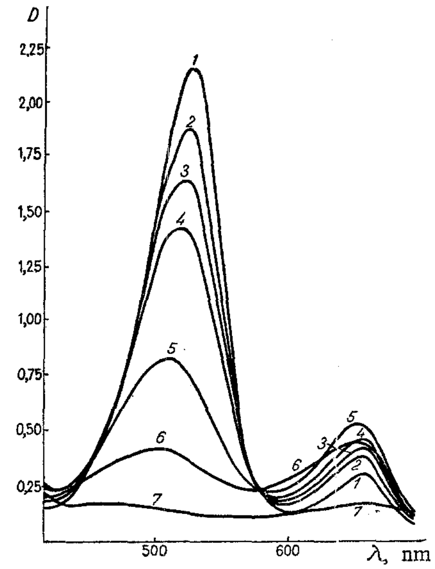

Fig. 1

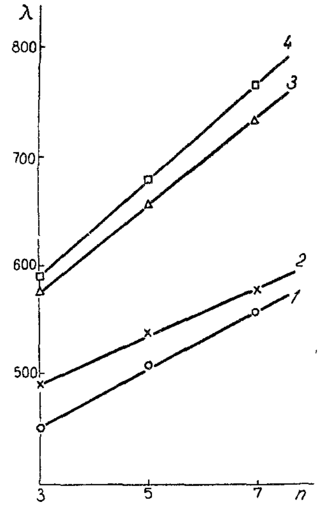

Fig. 2

Fig. 1. Absorption spectra of 1,5-di(2-thienyl)-1,4-pentadien-3-one in 0.55% H_2SO_4 in $(CCl_3CO)_2O$ as a function of time: 1) 10 min; 2) 20 min; 3) 30 min; 4) 1 h; 5) 2 h 40 min; 6) 5 h 50 min; 7) 12 h.

Fig. 2. Dependence of the absorption maxima of vinylogs of the thiophenol analog of chalcone on the number of methine groups: 1) 3% PCl_5 in CH_3CN; 2) 60% H_2SO_4; 3) 1.63% CCl_3COOH in $(CCl_3CO)_2O$; 4) 3% PCl_5 in C_6H_6.

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TABLE 1. Electronic Absorption Spectra of Thiophene-Containing Analogs of Chalcones and Their Derivatives

Compound*	λ_{max}, nm							
	60% H_2SO_4	0,55% H_2SO_4 in $(CH_3CO)_2O$		0,55% H_2SO_4 in $(CCl_3CO)_2O$		1,63% CCl_3COOH in $(CCl_3CO)_2O$	3% PCl_5 in C_6H_6	3% PCl_5 in CH_3CN
		I	II	I	II			
$R-CO-CH=CH-R_1$	428	438	515	420	536	—	—	—
$R-CH=CH-CO-R_1$	450	442	510	460	534	—	—	—
$R-CO-(CH=CH)_2-R_1$	480	483	582	480	610	610	630	450
$R-(CH=CH)_2-CO-R_1$	528	540	586	540	610	615	620	490
$R-CH=CH-CO-CH=CH-R_1$	495	494	585	490	614	620	650	490
$R-(CH=CH)_2-CO-CH=CH-R_1$	555	528	646	550	678	678	698	515
$R-CH=CH-CO-(CH=CH)_2-R_1$	532	530	652	525	687	688	698	515
$R-CO-CH=CH-R_2-CH_3$	468	446	533	450	558	—	—	—
$R-CH=CH-CO-R_2-CH_3$	450	465	535	450	555	555	—	—
$R-CO-(CH=CH)_2-R_2-CH_3$	546	506	604	—	640	644	—	—
$R-(CH=CH)_2-CO-R_2-CH_3$	490	—	598	490	620	622	633	480
$R-CH=CH-CO-CH=$ $=CH-R_2-CH_3$	512	510	618	500	640	640	656	487
$R-CO-CH=CH-R_2-OCH_3$	479	494	572	480	598	600	610	466
$R-CH=CH-CO-R_2-OCH_3$	475	484	565	465	594	592	630	466
$R-CO-(CH=CH)_2-R_2-OCH_3$	562	—	638	—	647	659	674	520
$R-(CH=CH)_2-CO-R_2-OCH_3$	524	—	574	—	660	666	676	500
$R-CH=CH-CO-CH=$ $=CH-R_2-OCH_3$	521	520	656	517	685	682	700	514
$R-CO-CH=CH-R_3-(OCH_3)_2-2,4$	510	480	573	480	589	570	615	505
$R-CH=CH-CO-R_3-(OCH_3)_2-2,4$	477	488	573	460	598	597	614	477
$R-CO-(CH=CH)_3-R_3-(OCH_3)_2-2,4$	578	—	655	—	—	—	—	—
$R-(CH=CH)_2-CO-R_3-(OCH_3)_2-2,4$	515	510	644	526	677	—	689	515
$R-CH=CH-CO-CH=$ $=CH-R_3-(OCH_3)_2-2,4$	543	540	654	530	670	685	704	538
$R-CO-CH=CH-R_2-N(CH_3)_2$	415	412	527	526	570	—	564	—
$R-CH=CH-CO-R_2-N(CH_3)_2$	460	430	527	462	580	620	590	520
$R-(CH=CH)_2-CO-R_2-N(CH_3)_2$	490	—	562	544	610	—	668	—
$R-CH=CH-CO-CH=$ $=CH-R_2-N(CH_3)_2$	488	405	525	405	590	590	620	472
$R-CO-CH=CH-R_2-R_1$	450	475	575	470	615	615	—	—
$R-CH=CH-CO-R_2-R_1$	470	483	566	480	605	605	—	—
$R-(CH=CH)_2-CO-R_2-R_1$	516	—	625	650	678	—	670	510
$R-CH=CH-CO-CH=CH-R_2-R_1$	516	525	638	525	685	686	690	498
$R-CH=CH-CO-R$	475	475	550	460	574	574	587	450
$R-CO-(CH=CH)_2-R$	535	500	624	510	650	650	665	507
$R-CH=CH-CO-CH=CH-R$	520	522	630	513	655	658	675	520
$R-(CH=CH)_2-CO-CH=CH-R$	575	540	698	540	710	732	760	555

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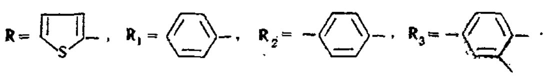


In order to study the structure of the halochromic salts, we undertook a spectrophotometric investigation of various thiophene-containing unsaturated ketones.

As seen from Table 1, the absorption maxima for solutions of the ketones in concentrated sulfuric acid lie at 428-578 nm. However, two bands, the first of which is found in the region of the absorption maxima of sulfuric acid solutions, the second of which is situated at longer wavelengths, were obtained for acid solutions of the ketones in acetic and trichloroacetic anhydrides in the visible region of the spectrum. The position of the first halochromic band of the same ketone remains virtually unchanged on passing from concentrated sulfuric acid to acid solutions in acid anhydrides. At the same time, the position of the second absorption maximum changes appreciably on passing from acetic to trichloroacetic anhydride (Table 1). These investigations of the absorption spectra of acid solutions of the ketones in trichloroacetic anhydride as a function of the time and acid concentration demonstrated that the transformations that occur are reversible in several hours (Fig. 1).

It can therefore be assumed that the first halochromic band is related to the hydroxycarbonium ion, while the second band pertains to its acyl derivative:

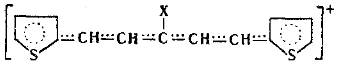
$$>C=O \overset{H^+}{\rightleftharpoons} >\overset{+}{C}-OH \overset{(RCO)_2O}{\rightleftharpoons} >\overset{+}{C}-O-C\overset{O}{\underset{R}{\lessdot}} \qquad R = CH_3,\ CCl_3$$

Because of the electron-acceptor effect of the acetyl and trichloroacetyl groups, the absorption maximum of the second halochromic band of acid solutions in acetic anhydride and, particularly, in trichloroacetic anhydride is considerably higher than the absorption maxima of the first halochromic band, and its magnitude approaches that of the corresponding carbonium ion [9, 10].

The intermediate formation of carbonium ions of the $>\overset{+}{C}-O-PCl_4$ and $>\overset{+}{C}-Cl$ structures during the reaction of ketones with phosphorus pentachloride is proposed in [11]. We found that most of the ketones that we investigated form two types of colored solutions in solvents containing phosphorus pentachloride – orange to red-brown in acetonitrile and blue to green in benzene, dichloroethane, and nitromethane. As seen from Table 1, the absorption maxima of solutions of the ketones in acetonitrile containing phosphorus pentachloride are close to those for solutions of the ketone in concentrated sulfuric acid. This is apparently associated with the formation of chlorocarbonium ions under the influence of phosphorus pentachloride, since their absorption spectra differ little from the spectra of the hydroxycarbonium ion [5]. Higher absorption maxima that were close to the absorption maxima of acid solutions of the ketones and trichloroacetic anhydride were obtained for solutions of the ketones in benzene containing phosphorus pentachloride.

It can therefore be assumed that carbonium ions of the $>C-OPCl_4$. structure are formed in benzene solutions containing phosphorus pentachloride.

There is a linear dependence for all of the thiophene-containing unsaturated ketones between their λ_{max} values and the number of methine groups (Fig. 2). This serves as an additional confirmation of the similarity of the salts



(X=OH, $OCOCH_3$, $OCOCCl_3$, Cl, $OPCl_4$)

to cyanine dyes, for which a similar regularity was noted [12, 13].

The position of the long-wave maximum depends on the electronic effect of X, and, as is apparent from the data in Table 1, the tetrachlorophosphoroxy group ($-O-PCl_4$) has a particularly strong electron-acceptor effect.

EXPERIMENTAL

The α,β-unsaturated ketones were synthesized by the crotonic condensation of the appropriate aldehydes and methyl ketones of the aromatic and thiophene series by the methods in [14, 15].

The electronic absorption spectra of $5 \cdot 10^{-4}$–$1 \cdot 10^{-5}$ M solutions were measured with SF-4 and SF-10 spectrophotometers.

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