SYNTHESIS AND ABSORPTION SPECTRA OF VINYLOGS OF 2-THIENYLPHENYL- AND BIS(2-THIENYL)CARBINOLS

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Eleven α,β-unsaturated alcohols and their fluoborate salts were synthesized by the selective reduction with sodium borohydride of vinylogs of thiophene chalcones. On the basis of the IR and NMR spectra it was established that these alcohols are the trans isomers with respect to the orientation of the hydrogen atoms on the aliphatic double bond. The absorption spectra of the alcohols and their fluoborates in neutral and acid solvents were studied. The isomeric alcohols form cations of the same structure with acids. A linear dependence between the absorption maxima of the polymethine salt and the number of methine groups in the cations was established. Deviations were noted for acid solutions of alcohols with unsymmetrical structures.

We have previously studied the spectra and halochromism of diphenyl-, 2-thienylphenyl- (I), and bis-(2-thienyl)carbinols (IX) [1]. It is well known [1-3] that these carbinols form deeply colored solutions on reaction with acids. It was of interest to study the effect of the halochromism of vinylogs of 2-thienylphenyl- and bis(2-thienyl)carbinols. With this end in mind we synthesized 11 previously undescribed α,β-unsaturated alcohols. The compositions and structures of these compounds were confirmed by analysis

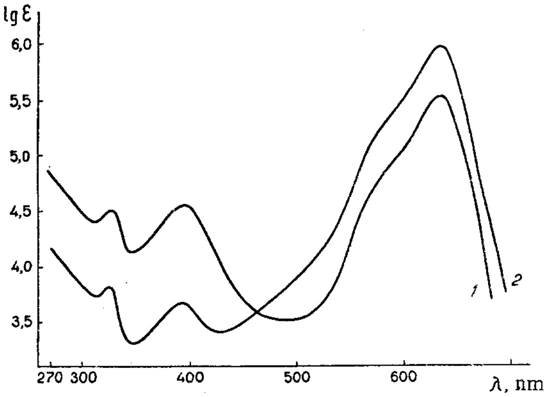

Fig. 1

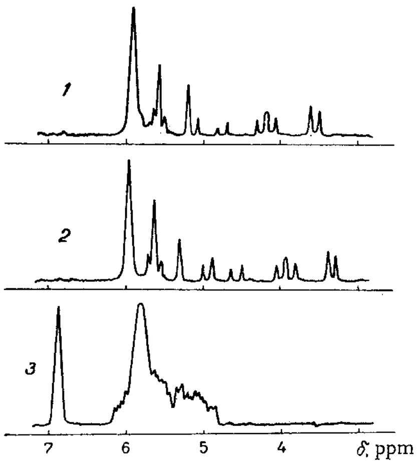

Fig. 2

Fig. 1. Absorption spectra of vinylogs of dithienylcarbinol (IX) in 10% CF_3COOH in $C_2H_4Cl_2$: 1) 1,5-bis(2-thienyl)-1,4-pentadien-3-ol (XI); 2) 1,5-bis(2-thienyl)-2,4-pentadien-1-ol (XII).

Fig. 2. PMR spectra: 1) 1-(2-thienyl)-3-phenyl-2-propenol (III) in acetone; 2) 1-phenyl-3-(2-thienyl)-2-propenol (II) in acetone; 3) II and III in 10% CF_3COOH in $C_2H_4Cl_2$.

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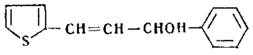
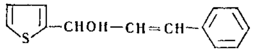
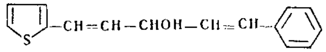
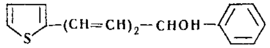
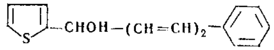
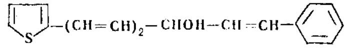
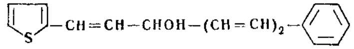
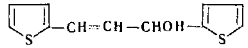
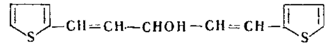
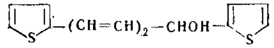
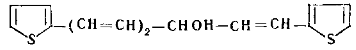
TABLE 1. 2-Thienylphenyl- and Bis(2-thienyl)carbinols and Their Vinylogs

Compound	Structural formula	mp	λ_{max}, nm *				IR spectrum, cm^{-1}			Empirical formula	Found		S calc., %	Yield, %
			ethanol	30% H_2SO_4 in CH_3COOH	10% CF_3COOH in $C_2H_4Cl_2$	Fluoborates in $C_2H_4Cl_2$	ν_{OH} in KBr	ν_{OH} in CCl_4	$\gamma_{CH=CH}$ (trans)		S, %	No. of active H		
II		39—40	282	505 †	520	523	3360	3630	970	$C_{13}H_{12}OS$	14,78	0,90	14,79	75
III		69—70	255	505	520	520	3370	3630	978	$C_{13}H_{12}OS$	14,84	0,92	14,79	70
IV		51—52	285	575	593	595	3320	3633	977	$C_{15}H_{14}OS$	12,94	1,10	13,23	70
V		80—81	310	570	593	597	3350	3630	990	$C_{15}H_{14}OS$	13,34	0,96	13,23	90
VI		94—95	290	570	593	597	3390	3630	990	$C_{15}H_{14}OS$	13,28	0,98	13,23	80
VII		80—81	310	638	658	676	3370	3608	970	$C_{17}H_{16}OS$	12,08	1,13	11,94	50
VIII		107—108	287	638	658	676	3375	3600	972	$C_{17}H_{16}OS$	12,07	1,11	11,94	60
X		59—60	283	550	560	560	3465	3625	970	$C_{11}H_{10}OS_2$	29,05	1,12	28,87	70
XI		61—62	292	620	635	643	3310	3632	970	$C_{13}H_{12}OS_2$	25,80	1,10	25,80	50
XII		92—93	312	622	635	642	3340	3628	990	$C_{13}H_{12}OS_2$	25,70	1,12	25,80	60
XIII		63—64	328	694	702	702	3310	3633	987	$C_{15}H_{14}OS_2$	23,10	0,98	23,35	50

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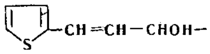
*λ_{max} in concentrated H_2SO_4: 468 nm for 2-thienylphenylcarbinol (I), 487 nm for bis(2-thienyl)carbinol; λ_{max} 236 nm in ethanol for I and IX.

† In 2% H_2SO_4 in CH_3COOH.

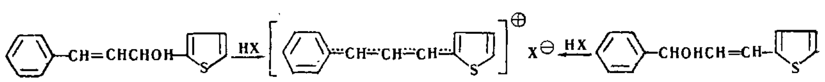
and by the UV, IR, and PMR spectra. The analytical data, measurements of the absorption spectra of neutral and acidic solutions of the alcohols and solutions of the fluoborates, and the frequencies of the valence vibrations of the hydroxyl group (ν_{OH}) and the out-of-plane deformation vibrations of the hydrogen atoms of the vinylene group ($\gamma_{CH=CH}$) are presented in Table 1.

The IR spectrograms of KBr pellets of all of the alcohols contain a broad intense band from 3300-3500 cm^{-1} from the valence vibrations of the hydroxyl group associated by an intermolecular hydrogen bond. This bond is apparently weak since the band of the associated hydroxyl group of the alcohol vanishes in 10^{-2} M carbon tetrachloride solutions, and one observed only the absorption band of the free hydroxyl group (3600-3640 cm^{-1}). The intense absorption at 960-990 cm^{-1} is due to out-of-plane deformation vibrations of the hydrogens of the vinyl group with trans orientation of the substituents [4]. In [5] it was established that the thiophene analogs of chalcone and its vinylogs are the trans isomers with respect to the position of the substituents on the aliphatic double bond. Consequently, reduction of the carbonyl group of the α,β-unsaturated ketones does not change their trans configuration. Our investigation of the PMR spectra of the alcohols confirms this conclusion. The measured spin-spin interaction constants of the α and β protons are found at 15.6 to 16.2 Hz, which is convincing proof of their trans orientation with respect to the double bonds [6, 7].

As seen from Table 1, the α,β-unsaturated alcohols in ethanol absorb from 230 to 330 nm. Replacement of the phenyl radical by the more electron-donating thienyl radical (σ −0.21) [8] in I, II, and V does not change the position of the long-wave absorption maximum, while the same substitution in III causes a bathochromic shift in λ_{max} by 28 nm (compare III with X). This may serve as a confirmation of the fact that the atomic grouping responsible for the long-wave absorption of the alcohols is



In a comparison of λ_{max} for neutral and acid solutions it turned out that the latter absorbed in a considerably longer-wave region. As is apparent from the data for acid solutions of the alcohols, replacement of the phenyl ring by a thiophene ring leads to a red shift in the maximum by ~40 nm (II, III, and X; IV, V, VI, XI, and XII; VII, VIII, and XIII). As in the case of neutral solutions of the alcohols, the accumulation of vinylene groups causes a deepening in the color, during which a linear dependence of the absorption maximum on the number of methine groups is observed for each series of acid solutions of the polymethine salts. A similar dependence was noted in the cyanin dye series [9, 10]. It is interesting that the absorption maximum of isomeric alcohols (II and III, IV, V, and VI: VII and VIII; XI and XII; Fig. 1) have the same values. This sort of regularity was also observed in [11] for several isomeric distyrylcarbinols. This indicates the formation of cations with the same structure and also confirms the identical character of the PMR spectra of acid solutions of the isomeric unsaturated alcohols (Fig. 2). The signals of the protons of vinylene groups and of the methine proton of the carbinol are markedly shifted to weak field in comparison with neutral solutions and are virtually the same as the signals of the ring protons of the aromatic and heterocyclic rings [12, 13]. This indicates that the positive charge is delocalized over the entire molecule, including the aromatic and heterocyclic radicals.



A comparison of the long-wave absorption maxima of the polymethine salts of both symmetrical and unsymmetrical structures (II, IV, and VII) indicates that λ_{max} of the unsymmetrical salt is shifted somewhat (5-12 nm) to the short-wave region relative to the half-sum of the absorption maxima of the corresponding symmetrical compounds [13].

EXPERIMENTAL

α,β-Unsaturated Alcohols. These were synthesized as follows. Sodium borohydride (0.025 mole) was added gradually with stirring and cooling to 0.05 mole of the ketone in 20-40 ml of methanol. The mixture was allowed to stand for 2 h at room temperature, cooled, and a cold 5% solution of sodium hydroxide was added to it. The resulting precipitate was filtered, washed with alkali and water until it gave a neutral reaction, and dried in vacuo. The compounds obtained are solid crystalline substances and, like unsaturated aromatic alcohols [14, 15], are thermally unstable and gradually oxidized in air.

Fluoborate Salts. These were obtained by mixing a 0.05-mole ether solution of the unsaturated alcohol and 0.5 mole of a 32% solution of fluoboric acid. The salt that resulted on cooling was filtered, washed repeatedly with absolute ether, and dried.

The IR spectra of carbon tetrachloride solutions (c $1 \cdot 10^{-2}$ M) and KBr pellets (2 mg of compound per 200 mg of KBr) were obtained with a UR-20M spectrometer. The PMR spectra were obtained with a YaMR-5535 spectrometer with an operating frequency of 40 MHz. The absorption spectra were measured with Hitachi SF-4 and SF-10 spectrophotometers.

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