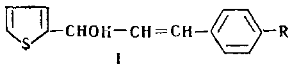
SYNTHESIS AND ABSORPTION SPECTRA OF THIENYLPHENYLPROPENOL DERIVATIVES

V. F. Lavrushin, R. I. Pogonina,
N. S. Pivnenko, and V. P. Izvekov

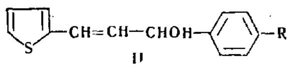
UDC 542.91+547.732+535.34

Fourteen thienylphenylpropenol derivatives containing substituents of varying electronic nature were synthesized. IR and NMR spectroscopy established that the α, β-unsaturated alcohols obtained belong to the trans series. The electronic and PMR spectra of the alcohols in neutral and acidic solutions were studied. A correlation was found between the chemical shifts of the proton of the alcohol hydroxyl group and the shifts of the wave numbers of the long-wave absorption maxima, and the Hammett σ constants.

We have previously studied the spectra and halochromism of vinylogs of thienylphenyl- and dithienylpropenols [1,2]. In order to study the effect of substituents on the fundamental and halochromic spectra of thienylphenylpropenol it was of interest to investigate the behavior of isomeric alcohols of the I and II type, where R are different electron-donating and electron-accepting substituents (Table 1). These compounds were synthesized from the corresponding α, β-unsaturated ketones by reduction with sodium borohydride.



I



II

The IR spectra of the alcohols do not contain a band for the valence vibrations of the carbonyl group but have a broad intense absorption band for the valence vibrations of an associated hydroxyl group (3200-3500 cm^{-1}, in KBr pellets) or a free hydroxyl group (3605-3630 cm^{-1}, in CCl_4). The aliphatic double bonds can be detected from the $\nu_{CH\,=\,CH}$ valence vibration band at 1591-1625 cm^{-1}. All of the α, β-unsaturated alcohols have an intense absorption band at 950-980 cm^{-1}, which is due to the out-of-plane deformational vibrations of the hydrogen atoms of the vinylene group with trans orientation of the substituents ($\gamma_{CH\,=\,CH}$) [3]. The trans configuration of the alcohols is also confirmed by their PMR spectra (Fig. 1), where the spin interaction constants of the α and β protons are 15.6-16.2 Hz (see [4,5]).

Data on the measurement of the electronic absorption spectra of neutral and acidic solutions of the unsaturated alcohols are presented in Table 1. The introduction of substituents into the benzene ring of the thienylphenylpropenol when it is situated next to the hydroxyl group has almost no effect on the absorption maximum. However, the introduction of a substituent into the benzene ring when it is removed from the hydroxyl group causes a shift in the absorption maximum. Moreover, the magnitude of the shift increases with an increase in both the electron-donating and electron-accepting effect of the substituent (Table 1). It is interesting that for electron-donating substituents, the values of this shift, expressed in wave numbers (cm^{-1}), correlate with the Hammett σ constants (r = 0.99, ρ = 15.85) [6] according to the equation [7]

$$(1/\lambda_R - 1/\lambda_H)\frac{Nhc}{2.3RT} = \rho\sigma.$$

A. M. Gorki Kharkov State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1605-1608, December, 1970. Original article submitted September 29, 1969.

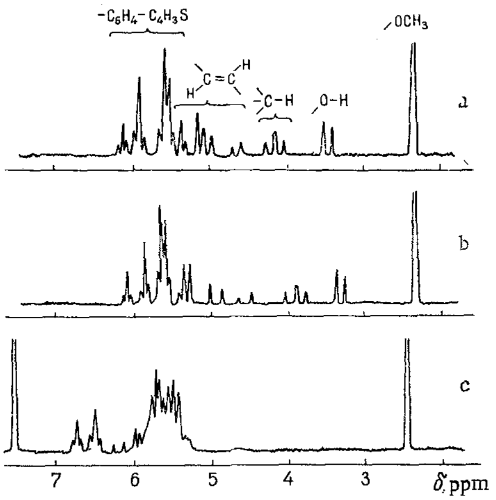


Fig. 1

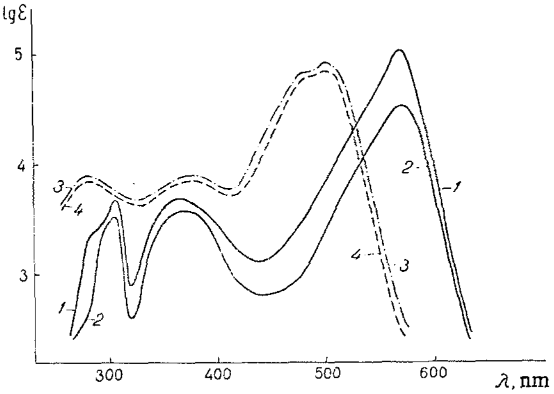


Fig. 2

Fig. 1. PMR spectra (40 MHz): 1-(2-thienyl)-3-(4-methoxyphenyl)-2-propen-1-ol in acetone (a) and in 10% CF_3COOH in dichloroethane (b); 1-(2-thienyl)-3-(4-methoxyphenyl)-1-propen-3-ol in acetone (c).

Fig. 2. Absorption spectra in 10% CF_3COOH in dichloroethane: 1) and 2) 1-(2-thienyl)-3-(4-methoxyphenyl)-2-propene-1-ol and its isomer; 3) and 4) 1-(2-thienyl)-3-(4-nitrophenyl)-2-propen-1-ol and its isomer.

TABLE 1. Thienylphenylpropenols I and II and Their Derivatives

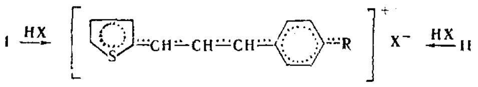
Compound	R	Mp, °C	S, %		No. of active H atoms	ν_{OH}, cm^{-1}		$\nu_{CH=CH_2}$, cm^{-1}	δ_{OH}, ppm	λ_{max}, nm		
			Found	Calc.		In KBr pellets	In CCl_4	In KBr pellets	In Acetone	C_2H_5OH	10% CF_3COOH in $C_2H_4Cl_2$	30% H_2SO_4 in CH_3COOH
I	H^2								3,55	255	521	505
II	H^2								3,39	282	520	505*
I	CH_3	63—64	13,9	13,9	0,9	3300	3620	978	3,53	258	541	526
II	CH_3	†	13,8	13,9	1,0	3335	3605	954	3,31	282	543	530
I	C_6H_5	123—124	10,8	10,9	1,2	3385	3627	980	—	280	584	560
II	C_6H_5	97—98	10,9	10,9	1,0	3380	3630	970	—	285	584	562
I	OCH_3	61—62	13,2	13,0	1,0	3340	3625	970	3,48	267	573	558
II	OCH_3	38—39	13,2	13,0	1,1	3520	3630	985	3,30	282	575	558
I	$(OCH_3)_2$-2,4	91—92	11,5	11,6	0,9	3410	3628	978	—	305	577	568
II	$(OCH_3)_2$-2,4	76—77	11,5	11,6	0,9	3350	3625	970	—	285	575	570
I	$N(CH_3)_2$	115—116	12,3	12,3	1,1	3210	3629	975	3,33	300	574	560
II	$N(CH_3)_2$	35—36	12,3	12,3	0,9	3330	3612	955	3,02	287	574	560
I	Cl	66—67	10,2	10,3	1,0	3400	3628	978	3,65	260	535	517
II	Cl	24—25	10,2	10,3	1,1	3440	3614	956	3,51	282	537	516
I	NO_2	97—98	12,0	12,2	0,9	3500	3630	960	3,85	310	504	506
II	NO_2	81—82	12,1	12,2	0,9	3500	3630	958	3,82	275	503	506

*2% H_2SO_4 in CH_3COOH.

†Bp 134°C (8 mm).

The chemical shifts of the hydroxyl proton of the substituted and unsubstituted alcohols (Table 1) also correlate with the Hammett σ constants: $r = 0.98$ and $\rho = 0.31$ for 1-phenyl-3-(2-thienyl)-1-propen-3-ol derivatives; $r = 0.97$ and $\rho = 0.50$ for 1-phenyl-3-(2-thienyl)-2-propen-1-ol derivatives.

It is well known that aromatic carbinols form colored cations in acidic solutions [8]. It is apparent from the data presented in Table 1 and Figs. 1 and 2 that acidic solutions of the isomeric alcohols have practically the same electronic and PMR spectra. This is associated with the fact that isomeric alcohols I and II form the same cation on reaction with acid:



Electron-donating groups deepen the color in the electronic absorption of acidic solutions. It is interesting that the introduction of a chloro group leads to a bathochromic effect, as in a previously noted case [9], while a nitro group either has no effect at all or gives a hypsochromic shift. The substantial effect of a phenyl substituent is apparently associated with lengthening of the conjugation chain. Moreover, in a series of 1-phenyl-3-(2-thienyl)-1-propen-3-ol derivatives with electron-donating substituents the shifts in the frequencies of the long-wave absorption maxima correlate with the σ substituent constants ($r = 0.91$, $\rho = 3.62$).

EXPERIMENTAL

The α,β-unsaturated alcohols were synthesized as described in [2]. The products were purified by crystallization from hexane or hexane–benzene. The IR spectra in $1 \cdot 10^{-2}$ M CCl_4 solutions or KBr pellets (2 mg of compound per 200 mg of KBr) were obtained with a UR-20M spectrometer. The electronic absorption spectra for concentrations of 2 to $5 \cdot 10^{-5}$ M and 1 to $9 \cdot 10^{-6}$ M were obtained with SF-4 and SF-10 spectrophotometers, respectively. The PMR spectra were obtained with a YaMR-5535 spectrometer (40 MHz), the chemical shifts (δ scale) were measured relative to a cyclohexane internal standard [$\delta = -1.44$ ppm relative to TMS (tetramethylsilane)].

LITERATURE CITED

1. L. M. Grin, R. I. Pogonina, N. S. Pivnenko, L. M. Kutsenko, V. P. Izvekov, and V. F. Lavrushin, Dokl. Akad. Nauk Ukr. SSR, Ser. B, 1009 (1969).
2. R. I. Pogonina, N. S. Pivnenko, V. P. Izvekov, and V. F. Lavrushin, Khim. Geterotsikl. Soedin., (1971) (in press).
3. L. Bellamy, Infrared Spectra of Complex Molecules, Methuen (1958).
4. M. Karplus, J. Chem. Phys., 30, 11 (1959); 33, 1942 (1960).
5. M. Karplus, J. Phys. Chem., 64, 1793 (1960).
6. V. A. Pal'm, Usp. Khim., 30, 1069 (1965).
7. R. Campbell and H. M. Gilow, J. Am. Chem. Soc., 82, 5426 (1960).
8. L. P. Hammett, Physical Organic Chemistry, New York (1940), p. 54.
9. G. Hesse and P. Thieme, Ann., 686, 64 (1965).