This gave rise to paramagnetic particles the EPR spectra of which differed from the EPR spectra of the anion radicals of piazthiole and piazselenole. The extensions of the EPR spectra of the anion radicals from β- and α-chloropiazselenoles were the same at 31 G. This agrees with the equivalence of the hfs constants from the β and α protons in the anion radical from unsubstituted piazselenole recorded in the literature [1,2]. According to Atherton and Ockwell [3], in the benzfurazan, piazthiole, and piazselenole series, the difference in the splitting constants $[a_{H\alpha} - a_{H\beta}]$ is least for the anion radical of piazselenole.

The EPR spectra of the anion radicals from piazthiole, β-chloropiazthiole (I, X = S, Y = β-Cl) and α-chloropiazthiole (I, X = S, Y = α-Cl) are shown in the figure. Without yet going into details of the analysis of the complex hyperfine structure of the spectra, we may point out the successive decrease in their total extension from 31.3 to 29.04 to 27.94 G, respectively. This decrease is connected with the replacement of the β or α hydrogen atom in the anion radical of piazthiole, which have different α_H constants, by a chlorine atom. As a result, the spectra of the chloro derivatives become narrower, this contraction being approximately equal to the values of the hyperfine splittings of the corresponding hydrogen atoms in the anion radical of piazthiole mentioned previously ($a_{H\beta} = 1.6$; $a_{H\alpha} = 2.9$ G) [1]. The result obtained independently confirms the conclusion drawn previously that an inequality of the type $\rho_\alpha > \rho_\beta$ is valid for the anion radical of piazthiole. Thus, we have succeeded in eliminating the indefiniteness mentioned above in the conclusion concerning the participation of the sulfur atom of piazthiole in the creation of a system of electrons delocalized over the molecule.

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SYNTHESIS OF ESTERS OF THE FURAN SERIES

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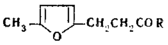
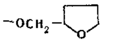
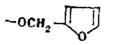
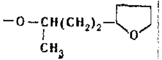
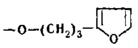
Five new esters of the furan series have been synthesized by the reaction of β-(5-methyl-2-furyl)propionyl chloride with 2-(3'-hydroxypropyl)-furan, 2-(3'-hydroxybutyl)tetrahydrofuran, and furfuryl, tetrahydrofurfuryl, and allyl alcohols in the presence of pyridine.

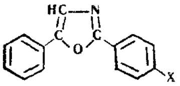
On being heated with saturated monohydric or polyhydric aliphatic alcohols or their alkoxides, the chlorides of furylalkanecarboxylic acids form the corresponding esters or chloro esters [1,2]. Tetrahydrofuran and, particularly, furan derivatives in which the nuclei are not stabilized by electronegative substituents, are extremely sensitive to the action of acidic agents at high temperatures [3].

For this reason, in the reaction of β-(5-methyl-2-furyl) propionyl chloride (I) with furfuryl and tetrahydrofurfuryl alcohols and with their alkoxides, instead of the formation of the corresponding esters complete resinification of the reaction products takes place.

We have found that esters of the furan series can be obtained from I and acidophobic alcohols with a yield of ~70% if this reaction is carried out in pyridine.

Esters of the Furan Series 

R	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Empirical formula	Found, % C	Found, % H	Calculated, % C	Calculated, % H	Yield, %
	145—146 (3)	1.4850	1.1025	61.93	61.84	$C_{13}H_{18}O_4$	65.59 65.84	7.84 7.67	65.52	7.61	66
	124—124.5 (3)	1.5018	1.1385	60.69	60.90	$C_{13}H_{14}O_4$	67.02 66.91	6.13 6.13	66.65	6.02	73
	182 (7)	1.4761	1.0470	75.55	75.69	$C_{16}H_{24}O_4$	68.66 68.58	8.96 9.00	68.54	8.63	70
	139—140 (3)	1.4915	1.0958	71.89	71.67	$C_{15}H_{18}O_4$	68.86 68.67	7.11 7.19	68.68	6.92	68
$-OCH_2CH=CH_2$	103—104 (7)	1.4780	1.0397	52.87	52.69	$C_{11}H_{14}O_3$	68.12 68.19	7.31 7.42	68.02	7.27	79



EXPERIMENTAL

The furan esters obtained by the method described [1, 2] are colorless or pale yellow liquids with a characteristic odor. Their physical constants and analytical results are given in the table.

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DIPOLE MOMENTS AND STRUCTURE OF THE MOLECULES OF SOME OXAZOLE DERIVATIVES

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The values of the dipole moments of 15 substituted, 1,3-oxazoles are given. The electron density distribution in the molecules of 2,5-, 2,4-, and 4,5-diphenyl-1,3-oxazoles has been calculated by the LCAO MO method. Their heterocycle does not contain a single π-electron system with the participation in conjugation of the π-electrons of the C=N and C=C bonds and the p-electron pair of the oxygen. A vector calculation permits the detection of a considerable conjugation between substituents and the π-electrons of the heterocycle through phenyl.

An analysis of various properties of the molecules of phenyl-substituted isoxazoles has led to the conclusion that the aromaticity of the isoxazole ring is low and its interaction with the π-electron system of the phenyl rings is very weak [1]. It was desirable to confirm this for phenyl-substituted 1,3-oxazoles. Table 1 gives the results of measurements of the dipole moments (μ) of a number of substituted 1,3-oxazoles in benzene as solvent. For some of them (2,5-, 2,4-, and 4,5-diphenyloxazoles) the molecular diagrams and π moments (μ_π) have been calculated by the LCAO MO method in Hückel's approximation; for the compounds with para substituents in the phenyl rings, the observed moment has been compared with that calculated by simple vector combination of the moments of the individual functional groups of the molecule. Calculation of the electron density distribution by the MO method was carried out using Orgel's parameters [3], namely: $\alpha_{(-N=)} = \alpha_C + \beta$; $\alpha_{(-O)} = \alpha_C + 3{,}2\beta$; $\beta_{(C-O)} = 1{,}4\beta$; $\beta_{(C-N)} = 1{,}2\beta$; $\beta_{(N-N)} = \beta$. The inductive influence of the heteroatoms on the carbon atom connected to them was taken into account by