4,8-Dihalo-2-selenaadamantanes (IIIa,b). A solution of 0.002 mole of IIa or IIb in 15 ml of acetone was refluxed for 30 min, after which the solvent was removed by vacuum evaporation, and the crystals were removed by filtration, dried in a vacuum desiccator, and purified by recrystallization.

Bis(3-chlorobicyclo[3.3.1]non-6-en-2-yl)selenium Dichloride (IV). A 1.1-g (0.005 mole) sample of tetrachloroselenium was added with stirring to a solution of 1.2 g (0.01 mole) of bicyclo[3.3.1]nona-2,6-diene in 50 ml of ether, after which the ether layer was separated and dried over anhydrous calcium chloride. The solvent was removed in vacuo to give 1.1 g (47.8%) of IV with mp 106° (from acetonitrile). PMR spectrum: 1.30 (4H, t, J = 3 Hz, 9-H, 9'-H), 1.57 (4H, m, 4-H, 4'-H), 2.28 (4H, m, 8-H, 8'-H), 2.44 (2H, m, 5-H, 5'-H), 2.60 (2H, m, 1-H, 1'-H), 3.02 (2H, t, J = 2 Hz, 2-H, 2'-H), 3.17 (2H, m, 7-H, 7'-H), 3.78 (2H, q, J = 3.5 Hz, 6-H, 6'-H), 5.12 (2H, m, 7-H, 7'-H). Found, %: C 46.6; H 5.2. $C_{18}H_{24}Cl_4Se$. Calculated, %: C 46.8; H 5.2.

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FREE-RADICAL ADDITION OF ALKANETHIOLS TO 1-VINYLPYRROLES

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In the presence of 2,2'-azobisisobutyronitrile or in the absence of an initiator alkanethiols add to 1-vinylpyrroles exclusively counter to Markovnikov's rule to give 1-(2'-alkylthioethyl)pyrroles (in yields up to 94%).

A new reaction of acetylene with ketoximes, which made it possible in one step to synthesize 1-vinylpyrroles with a variety of substituents in the 4 and 5 positions, was recently discovered [1, 2]. In the present research we investigated the addition of alkanethiols to these 1-vinylpyrroles in the presence and absence of free-radical initiators. The literature contains rather contradictory data on the order of addition of hydrogen sulfide and mercaptans to N-vinyl compounds. It is known that cyclic enamines [3, 4] add mercaptans in accordance with Markovnikov's rule (the thiiyl radical is directed to the α-carbon atom of the vinyl group) under the influence of radical initiators and under noncatalytic conditions. There are data [5] that indicate that hydrogen sulfide and thiols add to N-vinyl compounds of the pyrrole series counter to Markovnikov's rule. Thus β-addition products were obtained [6, 7] when hydrogen sulfide was passed through a heated alcoholic alkali solution of N-vinylcarbazole and also when heated N-vinylindole containing potassium metal was treated with hydrogen sulfide. Refluxing N-vinylcarbazole with thiocresol and 2-mercaptoanthraquinone without a catalyst led to β-addition products [6, 7]. The free-radical addition of thiols to N-vinylindole and N-vinylimidazole under the influence of 2,2'-azobisisobutyronitrile (AIBN) proceeds with the formation of a mixture containing α- and β-addition products [8]. According to the data in [8], thiols do not add to N-vinylindole in the absence of initiators.

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TABLE 1. Characteristics of the 1-(2'-Alkylthioethyl)pyrroles

Compound	Name	bp, °C (mm)	d_4^{20}	n_D^{20}	Found, %				Empirical formula	Calc., %				Yield, %
					C	H	N	S		C	H	N	S	
I	1-(2'-Ethylthioethyl)-4,5,6,7-tetrahydroindole	111—112	1,0402	1,5475	69,27	9,17	—	15,37	$C_{12}H_{19}NS$	68,84	9,15	—	15,32	83
II	1-(2'-Propylthioethyl)-4,5,6,7-tetrahydroindole	128—129	1,0313	1,5410	70,03	9,69	6,33	14,15	$C_{13}H_{21}NS$	69,90	9,48	6,27	14,36	82
III	1-(2'-Isopropylthioethyl)-4,5,6,7-tetrahydroindole	116—117	1,0166	1,5390	69,95	9,34	6,16	14,40	$C_{13}H_{21}NS$	69,90	9,48	6,27	14,36	77
IV	1-(2'-Butylthioethyl)-4,5,6,7-tetrahydroindole	150—151	1,0336	1,5350	70,39	9,57	5,54	—	$C_{14}H_{23}NS$	70,78	9,68	5,89	—	89
V	1-(2'-Isobutylthioethyl)-4,5,6,7-tetrahydroindole	142—143	1,0321	1,5330	—	—	5,83	13,21	$C_{14}H_{23}NS$	—	—	5,89	13,48	75
VI	1-(2'-Ethylthioethyl)7-methyl-4,5,6,-7-tetrahydroindole	125—126	1,0632	1,5375	70,07	9,40	5,87	14,40	$C_{13}H_{21}NS$	69,90	9,47	6,28	14,35	80
VII	1-(2'-Propylthioethyl)-7-methyl-4,5,-6,7-tetrahydroindole	128—129	0,9991	1,5340	70,97	9,57	6,15	13,45	$C_{14}H_{23}NS$	70,83	9,76	5,90	13,50	82
VIII	1-(2'-Isopropylthioethyl)-7-methyl-4,5,6,7-tetrahydroindole	110—111	0,9844	1,5335	70,94	9,73	5,92	13,77	$C_{14}H_{23}NS$	70,83	9,76	5,90	13,50	76
IX	1-(2'-Butylthioethyl)-7-methyl-4,5,-6,7-tetrahydroindole	139—140	1,0014	1,5290	71,61	9,98	5,47	12,89	$C_{15}H_{25}NS$	71,65	10,02	5,58	12,75	80
X	1-(2'-Isobutylthioethyl-7-methyl-4,5,6,7-tetrahydroindole	128—129	1,0128	1,5280	71,60	9,77	5,71	12,37	$C_{15}H_{25}NS$	71,65	10,02	5,58	12,75	73
XI	1-(2'-Ethylthioethyl)-2-phenylpyrrole	144—145	1,0766	1,5955	72,36	7,36	5,92	13,61	$C_{14}H_{17}NS$	72,50	7,40	6,11	13,90	93
XII	1-(2'-Propylthioethyl)-2-phenylpyrrole	158—160	1,0550	1,5826	73,64	7,81	5,95	12,64	$C_{15}H_{19}NS$	73,50	7,82	5,71	13,10	94
XIII	1-(2'-Butylthioethyl)-2-phenylpyrrole	166—167	1,0450	1,5757	—	—	—	—	$C_{16}H_{21}NS$	—	—	—	—	70

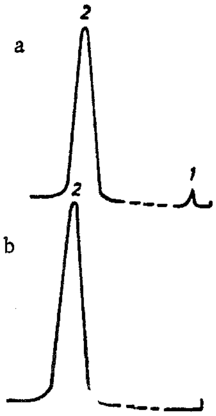


Fig. 1

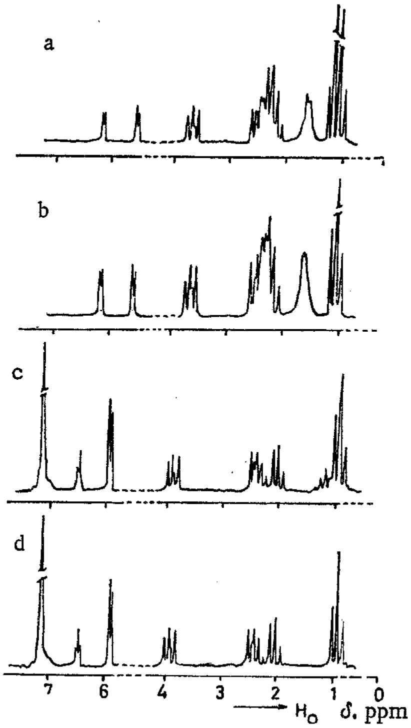


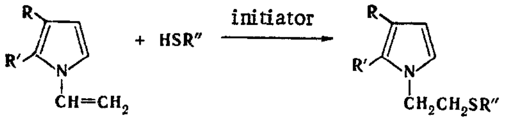
Fig. 2

Fig. 1. Chromatograms of the reaction mixture (a) and of the distillate (b) obtained in the addition of ethanethiol to 1-vinyl-4,5,6,7-tetrahydroindole: 1) ethanethiol; 2) I (obtained by heating a mixture of 2.6 g of 1-vinyl-4,5,6,7-tetrahydroindole, 2.0 g of ethanethiol, and 0.01 g of initiator in an ampule at 80°C for 20 h).

Fig. 2. PMR spectra of the undistilled reaction mixtures and distillates obtained by the addition of ethanethiol to 1-vinyl-4,5,6,7-tetrahydroindole (a,b) and 1-vinyl-2-phenylpyrrole (c,d).

The aim of the present study was to develop a convenient method for the synthesis of a new group of sulfur-containing pyrroles — namely, 1-(2'-alkylthioethyl)pyrroles — by the addition of alkanethiols to 1-vinylpyrroles and to clear up the controversial question regarding the structural specificity of this reaction.

We established that heating 1-vinylpyrroles with alkanethiols both in the presence of an initiator and without an initiator leads to β-addition products — 1-(2'-alkylthioethyl)-pyrroles:



I-XIII

I-V R—R'=$(CH_2)_4$; VI-X R—R'=$(CH_2)_3CHCH_3$; XI-XIII R=H, R'=C_6H_5;
R"=C_2H_5, C_3H_7, i-C_3H_7, C_4H_9, i-C_4H_9

Addition proceeds readily at 70-80°C and is complete in 18-25 h. When AIBN is used, I-XIII are obtained in 70-94% preparative yields* (Table 1). Under comparable conditions without an initiator the yields of adducts fall to 20-30%. The individuality and structures of the synthesized compounds were proved by gas—liquid chromatography (GLC) and IR and PMR spectroscopy and by determination of the elementary compositions. A peculiarity of the reaction is its high selectivity: even traces of side products, including polymeric products, cannot be detected in the reaction mixtures at any point in the transformations. It is seen from Fig. 1 that the chromatograms of the undistilled reaction mixture (the crude product)

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*Here and subsequently, the yields are based on the amount of vinylpyrrole.

and of the product isolated by distillation are practically identical. The PMR spectra of the undistilled products differ from the PMR spectra of the distillates (Fig. 2) only with respect to weak additional signals of protons of CH_2 and CH_3 groups belonging to ethanethiol, which was used in a small excess amount, and (in one case) diethyl disulfide (an impurity in the starting ethanethiol). The PMR spectra of chromatographically pure adducts I, III, and XI-XIII do not contain signals of protons of the $RSCH{-}CH_3$ grouping, and the character and integral intensities of the signals are in complete agreement with the 1-(2'-alkylthioethyl)pyrrole structure; this indicates addition of the thiiyl radical only in the β position of the vinyl group. A comparison of the IR spectra of the starting 1-vinylpyrroles and their adducts with alkanethiols makes it possible to reliably isolate the bands of the vinyl group (which vanish after thiiylation): 485, 520, 585, 850, 970, 1180, 1320, 1550, 1600, 1650, 3020, and 3070 cm^{-1}. The disappearance of the intense triplet in the region of C=C stretching vibrations (1550, 1600, and 1650 cm^{-1}) is particularly interesting. Only a very weak band at 1580 cm^{-1} and a broad, diffuse, and equally weak absorption at 1630-1670 cm^{-1} remain in the spectra of the adducts in this region. It may be assumed that the triplet that vanishes during thiiylation is related to different rotational isomers of 1-vinylpyrroles (relative to the $N{-}C_{sp^2}$ bond).

Thus the previously unknown 1-(2'-alkylthioethyl)pyrroles were synthesized by reaction of 1-vinyl-4,5,6,7-tetrahydroindole, 1-vinyl-7-methyl-4,5,6,7-tetrahydroindole, and 1-vinyl-2-phenylpyrrole with alkanethiols. The reaction proceeds regiospecifically to give β-addition products.

EXPERIMENTAL

The PMR spectra of 10% solutions of the compounds were recorded with a BS-487B spectrometer (80 MHz). The internal standard for solutions in CCl_4 was hexamethyldisiloxane. The IR spectra of liquid films of the compounds were obtained with a UR-20 spectrometer. Chromatographic analysis was accomplished with a Khrom-4 chromatograph. The detector was a katharometer, the column length was 2.5 m, the diameter was 3 mm, the solid phase was Chromaton N-AW-DMCS, the liquid phase was 15% DS 550 silicone, the thermostat temperature was 170°C, and the carrier gas was helium.

The starting 1-vinylpyrroles were obtained by the methods in [1, 2].

1-(2'-Butylthioethyl)-4,5,6,7-tetrahydroindole (IV). A mixture of 2.6 g (0.012 mole) of 1-vinyl-4,5,6,7-tetrahydroindole and 1.8 g (0.02 mole) of butanethiol was heated in a sealed ampule in the presence of 0.02 g of AIBN at 70-80°C for 20 h, after which it was subjected to vacuum distillation to give 4.2 g (89%) of tetrahydroindole IV. Compounds I-III and V were similarly synthesized.

1-(2'-Ethylthioethyl)-4,5,6,7-tetrahydroindole (I). A mixture of 2.6 g (0.012 mole) of 1-vinyl-4,5,6,7-tetrahydroindole and 2.0 g (0.031 mole) of ethanethiol was heated in a sealed ampule at 70-80°C for 20 h, after which it was subjected to vacuum distillation to give 1.0 g (24%) of tetrahydroindole I.

In an experiment to verify the reproducibility of the results the reaction of 2.6 g of 1-vinyl-4,5,6,7-tetrahydroindole and 2.0 g of ethanethiol in the presence of 0.01 g of initiator gave 2.1 g (83.5%) of tetrahydroindole I with bp 136-137°C (3 mm), n_D^{20} 1.5480, and d_4^{20} 1.0406. The chromatograms of the undistilled reaction mixture and the distillate are presented in Fig. 1, and the PMR spectra* are presented in Fig. 2.

1-(2'-Propylthioethyl)-7-methyl-4,5,6,7-tetrahydroindole (VII). A mixture of 2.6 g (0.02 mole) of 1-vinyl-7-methyl-4,5,6,7-tetrahydroindole and 1.2 g (0.031 mole) of propanethiol was heated in a sealed ampule at 70-80°C for 18 h in the presence of 0.01 g of initiator. Vacuum distillation of the contents gave 1.9 g (82%) of tetrahydroindole VII. Compounds VI and VIII-X were similarly synthesized.

1-(2'-Propylthioethyl)-2-phenylpyrrole (XII). A mixture of 2.5 g (0.015 mole) of 1-vinyl-2-phenylpyrrole, 1.2 g (0.017 mole) of propanethiol, and 0.015 g of AIBN was heated in a sealed ampule at 70°C for 24 h, after which it was subjected to vacuum distillation to give 3.4 g (94%) of phenylpyrrole XII. The yield of XII fell to 72% at 80°C, all other conditions being equal. Compounds XI and XIII were similarly obtained.

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In a repeat experiment the reaction of 6.23 g (0.037 mole) of 1-vinyl-2-phenylpyrrole and 4.7 g of ethanethiol in the presence of an initiator (in an ampule at 70°C for 24 h) gave 7.9 g (92.7%) of phenylpyrrole XI with bp 144-145°C (1 mm), n_D^{20} 1.5955, and d_4^{20} 1.0766. The PMR spectra of the undistilled mixture and the distillate are shown in Fig. 2.

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PHOTOCHROMIC PROPERTIES OF SOME N-SUBSTITUTED 3,3-DIMETHYL-6'-NITRO-INDOLINE-2-SPIRO-2'-2H-CHROMENES

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543.422.6

A number of photochromic 1-carbethoxymethyl-3,3-dimethyl-6'-nitroindoline-2-spiro-2'-2H-chromenes were synthesized. The introduction of a carbethoxymethyl substituent at the nitrogen atom instead of a methyl group somewhat increases the rate of dark decolorization of the photomerocyanines without appreciably affecting the spectral characteristics. The results are compared with the analogous spectral-kinetic characteristics of 1-phenyl-substituted compounds.

The interest in indolinespirochromenes as a class of photochromic compounds is due to the extensive possibilities of variation of the structure; this makes it possible to change their spectral-kinetic properties in a desired direction. From the point of view of the most widely accepted concepts, the rate of decolorization of spirochromenes is determined by the charges on the reaction centers [1], the magnitudes of which are particularly strongly affected by the substituents attached to the nitrogen atom. In this connection, it seemed of interest to compare the effect of a phenyl substituent attached to the nitrogen atom and of a substituent similar to it with respect to its inductive effect on the spectral-kinetic properties of spirochromenes in order to draw a conclusion regarding the effect of structural factors on the individual steps in the thermal decolorization of photomerocyanine molecules.

We synthesized the unstable 1-carbethoxymethyl-3,3-dimethyl-2-methyleneindoline by alkylation of 2,3,3-trimethylindolenine [2] with ethyl bromoacetate and subsequent treatment of the resulting 1-carbethoxymethyl-2,2,3-trimethylindoleninium bromide with sodium hydroxide; reaction of the product with 5-nitro-, 3-methoxy-5-nitro-, 3-bromo-5-nitro-, and 3,5-dinitrosalicylaldehydes gave the corresponding spirochomenes I-IV.

We investigated the kinetics of dark decolorization and the spectral properties of the compounds obtained and the corresponding series of N-phenyl-substituted spirochromenes V-VIII by the methods described in [3, 4]. The results are presented in Tables 1 and 2.

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