SPIROPYRANS BASED ON 5,10-DIMETHYL-4, 9-DIAZAPYRENE

É. R. Zakhs, R. P. Polyakova and L. S. Éfros

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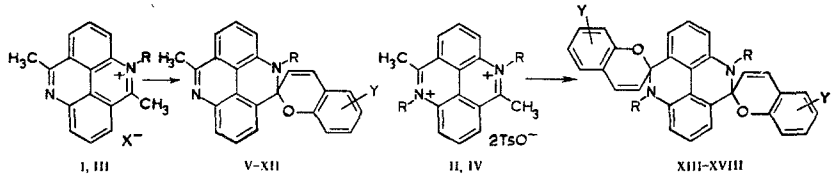
The corresponding mono- and dispiropyrans, the cyclic forms of which are more stable than the analogous compounds of the phenanthridine series, were obtained by condensation of mono- and diquaternary salts of 5,10-dimethyl-4,9-diazapyrene with aromatic o-hydroxy aldehydes. Successive opening of the pyran rings of the dispiropyrans occurs in acetic acid solutions, whereas the monospiropyrans, after opening of the pyran ring, are protonated at the nitrogen atom in the 9 position.

Colorless spiropyrans with properties similar to those of spirans based on phenanthridine [1] are formed in the condensation of mono- and diquaternary salts (I, II) of 5,10-dimethyl-4,9-diazapyrene with salicylaldehyde. In the present paper we describe the synthesis and properties of substituted diazapyrene spiropyrans (V-XVIII, Table 1). They were also obtained by reaction of mono- and diquaternary salts (I-IV) with salicylaldehyde derivatives by heating in ethanol or dimethylformamide (DMF) with the addition of piperidine.



I, III V-XII II, IV XIII-XVIII

I, II, V-VII, IX-XIV, XVI, XVII R = CH_3; III, IV, VIII, XV, XVIII R = C_2H_5; I X = CH_3SO_4; III X = I

The products of the reaction of salicylaldehyde derivatives with monoquaternary salts I, III, viz., V-XII, including the 6',8'-dibromo and 6'-nitro derivatives (X-XII), were isolated from the reaction mixture in the form of almost colorless spiropyrans. The presence of absorption bands at 1520-1530 (apparently the pyridine ring), 1230-1250 (C—O—C), and 950-980 cm^{-1} is characteristic for the IR spectra of these compounds. We were unable to obtain the colored merocyanine forms of X-XII, as was done in the case of the analogous phenanthridine derivatives [2, 3]. The nitro-substituted compounds (XI, XII) are partially converted to merocyanines only in alcohol solutions, as evidenced by the appearance in the absorption spectra of a band at 520-560 nm. As compared with the phenanthridine analogs, this band is shifted bathochromically by 30-40 nm, but its intensity referred to the total concentration (the "apparent extinction coefficient, ε") is approximately one order of magnitude lower than the values observed for the completely open analogous compounds. These results show that the cyclic forms of monospiropyrans of 5,10-dimethyl-4,9-diazapyrene are more stable than phenanthridine, as one should have expected in accordance with quantum-chemical calculations [1].

The products (XIII-XVIII) of the reaction of the diquaternary salts of 5,10-dimethyl-4,9-diazapyrene (II, IV) with aldehydes were also isolated from the reaction mixtures in their colorless forms. The absorption band at 1520-1530 cm^{-1} characteristic for monospirans is absent in the IR spectra of dispiropyrans XIII-XVIII, and bands are observed at 1230-1250 and 950-980 cm^{-1}. In conformity with the higher energy of localization of the C_5 and C_{10} atoms in the double salts of diazapyrene as compared with the single salts [1], the second spiropyran grouping in the dispiropyrans could be more labile than in the monospirans but more stable than in the phenanthridine derivatives. In fact, compounds XV-XVIII can be isolated in their deeply colored merocyanine forms by neutralization of acetic acid solutions of these compounds, in which they exist in the form of salts of the cyanine type. However, the merocyanines thus obtained are rapidly decolorized when they are dissolved in

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TABLE 1. Spiropyrans V-XVIII

Compound	Y	Dec. temp., °C	Empirical formula	Found, %			Calc., %			λ_{max}, nm (log ε or log ε')*		Yield, %
				C	H	N	C	H	N	in alcohol	in other solvents	
V	6′-OCH_3	196—197	$C_{25}H_{20}N_2O_2$	78,9	5,5	7,5	78,9	5,3	7,4	217 (4,63); 231 (4,57), 253 (4,45), 285 (4,06)*, 320 (3,80), 360—380 (3,7)		48
VI	8′-OCH_3	190—191	$C_{25}H_{20}N_2O_2$	78,7	5,6	7,6	78,9	5,3	7,4	220 (4,76), 230 (4,72)*, 253 (4,52), 275 (4,29)*, 315 (3,88)*, 378 (3,78)		50
VII	5′,6′-Benzo	271—272	$C_{28}H_{20}N_2O$	84,5	5,4	7,3	84,0	5,0	7,0	D: 242 (4,80), 255 (4,64)*, 310 (4,11)*, 362 (4,00)	AcOH: 293 (4,13), 342 (4,02), 390 (3,97), 470 (3,98)	42
VIII	5′,6′-Benzo	218—220	$C_{29}H_{22}N_2O$	83.9	5,7	6,8	84,0	5,3	6,8	241 (4,79), 255 (4,59)*, 285 (4,22)*, 314 (4,02), 362 (3,92), 380 (3,75)*	AcOH: 295 (4,22), 344 (4,08), 393 (4,03), 475 (4,05)	57
IX	6′-Br	231—232	$C_{24}H_{17}BrN_2O$†	—	—	6,8	—	—	6,5	225—230 (4,78)*, 253 (4,58), 285 (4,22)*, 307—315 (3,95)*, 378 (3,80)	DCE: 256 (4,56), 285 (4,27)*, 305 (3,98)*, 360—370 (3,8)*, 375 (3,81)	55
X	6′,8′-Br_2	215—220	$C_{24}H_{16}Br_2N_2O$†	—	—	5,7	—	—	5,5	230 (4,85), 255 (4,62)*, 315 (3,98), 370 (3,85)	DCE: 255 (4,5)*, 285 (4,24)*, 305 (3,93)*, 320 (3,9)*, 330 (3,87)*, 340 (3,86)*, 360 (3,8), 375 (3,79)	35
XI	6′-NO_2-8′-OCH_3	200—205	$C_{25}H_{19}N_3O_4$	70,9	5,0	10,0	70,6	4,5	9,9	232 (4,61), 250—255 (4,49)*, 315—320 (4,01)*, 360 (4,10), 376 (4,10), 555 (3,03)	DCE: 256 (4,58), 300 (4,14)*, 305 (4,11)*, 315—320 (4,03)*, 340 (4,02)*, 360 (4,16), 376 (4,17)	42

XII	6′-NO_2	220—225	$C_{24}H_{17}N_3O_3$	73,2	4,4	10,4	72,9	4,3	10,6	250 (4,6)*, 340 (4,18), 520 (2,53)	DCE: 250 (4,57), 355 (4,17), 370 (4,09)*	45
XIII	6′,6″-$(OCH_3)_2$	269—270	$C_{34}H_{28}N_2O_4$	77,3	5,5	5,3	77,3	5,3	5,3	$CHCl_3$: 255 (4,78), 350 (4,05)	AcOH: 265—270 (4,41)*, 276 (4,44), 342 (4,24), 386 (4,12)*, 403 (4,26), 450 (3,57)*	41
XIV	8′,8″-$(OCH_3)_2$	253—255	$C_{34}H_{28}N_2O_4$	77,6	5,9	5,6	77,3	5,3	5,3		D: 227 (4,84), 252 (4,71), 275 (4,38)*, 330 (3,88), 365 (3,95)	54
XV	5′,6′,5″,6″-Dibenzo	308—310	$C_{42}H_{32}N_2O_2$	84,3	5,7	4,9	84,4	5,4	4,7	DCE: 259 (4,97), 305 (4,19), 316 (4,20), 350 (4,20)*, 362 (4,21)	AcOH: 270 (4,38)*, 308 (4,30), 338 (4,27), 352 (4,28), 375 (4,19), 394 (4,22), 520 (4,30)	45
XVI	6′,6″-Br_2	284—285	$C_{32}H_{22}Br_2N_2O_2$†	—	—	4,6	—	—	4,5		D: 255 (4,90), 323 (4,00), 365 (3,99)	35
XVII	6′,8′,6″,8″-Br_4	264—265	$C_{32}H_{20}Br_4N_2O_2$†	—	—	3,8	—	—	3,6	D: 230 (4,93), 258 (4,82), 335 (4,09), 350—365 (4,00)	AcOH: 267 (4,41)*, 276 (4,44), 340 (4,20), 390 (4,09)*, 404 (4,24)	35
XVIII	6′,8′,6″,8″-Br_4	279—280	$C_{34}H_{24}Br_4N_2O_2$†	—	—	3,4	—	—	3,4		D: 230 (4,85), 260 (4,78), 330 (4,06), 366 (3,97)	40

*The shoulders and inflection points are noted. In addition to alcohol, dioxane (D), dichloroethane (DCE), and 50% aqueous acetic acid (AcOH) were used as the solvents. The spectra of solutions of XIII and XVII in 50% aqueous CH_3COOH containing 10% H_2SO_4 are presented. The log ε 'values are indicated for XI and XII in alcohol, whereas the log ε values are indicated for the remaining compounds.

† The compositions of IX, X, and XVI-XVIII were also confirmed by determination of their bromine content.

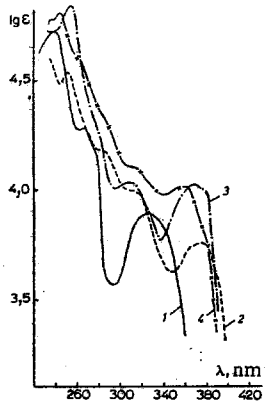


Fig. 1

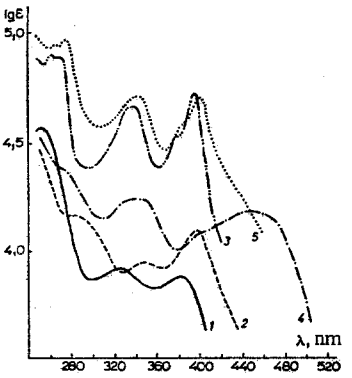


Fig. 2

Fig. 1. Absorption spectra of spiropyrans in dioxane: 1) 5-methylspiro-(5,6-dihydrophenanthridine-6,2'-[2H]chromene); 2) 4,10-dimethylspiro-(4,5-dihydro-4,9-diazapyrene-5,2'-[2H]-chromene) (XIX, in alcohol); 3) 4,9-dimethyldispiro(4,5,9,10-tetrahydro-4,9-diazapyrene-5,10,2',2''-bis [2H]chromene) (XX); 4) 4,10-dimethylspiro(4,5-dihydro-4,9-diazapyrene-5,5'-[3H]-benzo[f]chromene) (VII).

Fig. 2. Absorption spectra of spiropyrans in 50% aqueous CH_3COOH: 1) 5-methylspiro(5,6-dihydrophenanthridine-6,2'-[2H]chromene) (with the addition of 10% H_2SO_4); 2) XIX; 3) XIX with the addition of 10% H_2SO_4; 4) XX; 5) XX with the addition of 10% H_2SO_4 (the log ε +0.5 values are plotted along the axis of ordinates for curves 3 and 5).

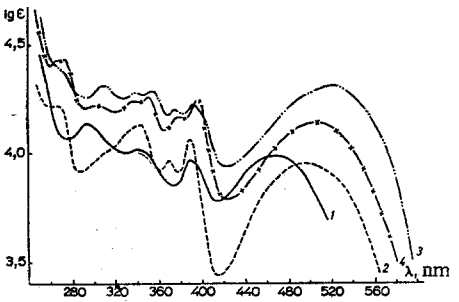


Fig. 3. Absorption spectra of spirobenzo[f]chromenes (VII, XV) in 50% CH_3COOH: 1) VII; 2) VII with the addition of 10% H_2SO_4; 3) 4,9-diethyldispiro(4,5,9,10-tetrahydro-4,9-diazapyrene-5,10,3',3''-bis [3H]benzo[f]-chromene) (XV); 4) XV with the addition of 10% H_2SO_4.

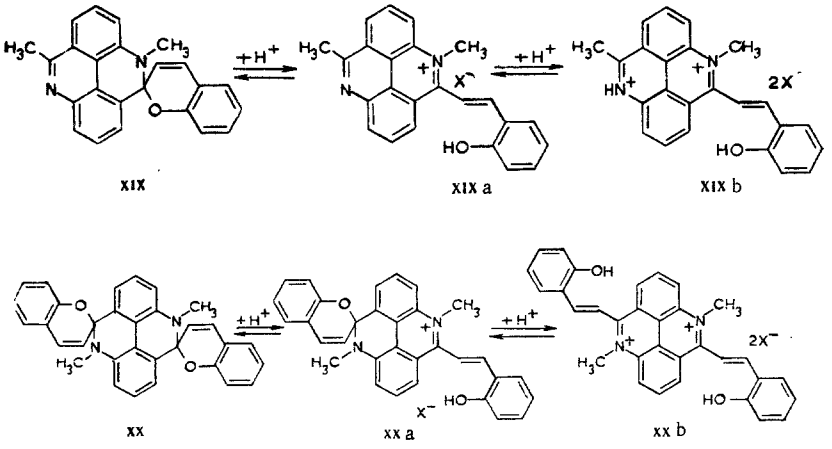
organic solvents, particularly low-polarity solvents. The crystallization of these compounds in the merocyanine form from aqueous solutions is apparently explained by their hydrophobic character, owing to which they are more rapidly precipitated than they are isomerized to spiropyrans. When aqueous suspensions of them are heated they are rapidly decolorized to give the spiropyrans.

The absorption spectra of the mono- and dispiropyrans are similar and differ primarily only with respect to the intensity of the absorption of the longwave (~370 nm) and shortwave (~250 nm) bands (Fig. 1, Table 1). The longwave band is shifted bathochromically by 40 nm relative to the analogous absorption band of the spiropyrans of the phenanthridine series. The spectra of the colorless forms change only slightly on passing from dioxane to alcohol.

Like the spiropyrans of the phenanthridine series [3], diazapyrene spiropyrans are converted to salts of the open forms on dissolving in 20-50% acetic acid. In contrast to the phenanthridine derivatives, the absorption spectra of these salts depend on the acidity of the solution. In the case of monospiropyrans XIX and VII, the addition of the first proton in 50% CH_3COOH (Figs. 2 and 3) leads to the formation of a monosalt (XIXa, VIIIa), the color of which is considerably deeper in the case of the benzo derivative (VIIa). The longwave absorption band (470 nm) in the spectrum of VIIa is evidently due to excitation of the cyanine chromophore. However, in the spectrum of XIXa it is probably overlapped by the band of excitation of

the condensed portion of the molecule (395 nm). New absorption maxima at 270 and 340 nm appear when sulfuric acid is added, and the longwave maximum of VIIa is shifted bathochromically by 30 nm. This shift, as in the case of cyanine dyes [4], should occur when the acceptor properties of the second nitrogen atom are intensified due to its protonation (the formation of diquaternary salts XIXb and VIIb).

Donor substituents cause an even more pronounced deepening of the color in the case of the cyanines [4]. In fact, an absorption band at 450 nm, the appearance of which can be explained only by the formation of a mono salt (XXa) with one cyanine chromophore and a tertiary nitrogen atom, is observed in the spectrum of an acetic acid solution of dispiropyran XX. When the acidity is raised further (up to 10% H_2SO_4), this absorption band vanishes because of secondary protonation and opening of the second pyran ring, and this leads to conversion of the tertiary nitrogen atom to a quaternary nitrogen atom (XXb). As a result, the spectra of strongly acidic solutions of XX and XIX become very similar (Fig. 2). Similar changes are observed in the spectra of XV. It should be noted that, judging from the spectra of XX and XV in 50% CH_3COOH, diquaternary salts XXb and XVb are, in contrast to monospirans XIX and VII, present in considerable but not predominant amounts. This is in agreement with the assumption of the lower stability of one of the spiropyran rings in the dispiropyrans as compared with monospiropyrans, an assumption that was expressed above on the basis of a comparison of the localization energies.



XIX XIX a XIX b

XX XX a XX b

All of the spiropyrans obtained in this study display thermochromic properties when they are heated in hydroquinone dimethyl ether. The photochromic properties of these compounds in low-polarity solvents are observed only during flash photolysis, inasmuch as the dark conversion of the colored forms to colorless form occurs very rapidly.

EXPERIMENTAL

5,10-Dimethyl-4,9-diethyl-4,9-diazapyrenium Ditoluenesulfonate (IV). A mixture of 2 g (8.6 mmole) of 5,10-dimethyl-4,9-diazapyrene and 16 g (80 mmole) of ethyl p-toluenesulfonate was heated at 190° for 1 h, after which the melt was triturated with ethanol to give 2.9 g (53%) of ditoluenesulfonate IV with mp 285-290° (dec.). Crystallization from 75% alcohol (1 : 10) gave 1.77g of light-yellow crystals of IV with mp 295-300° (dec.). The salt was quite soluble in water but insoluble in ether and benzene and was crystallized from alcohol (1 : 150). UV spectrum in alcohol (c $1.58 \cdot 10^{-5}$ M), λ_{max}, nm ($\log \varepsilon$): 225 (4.76), 267 (4.40), 332 (3.93), and 500 (3.35). Found: C 64.7; H 6.1; N 4.6; S 10.8%. $C_{34}H_{36}N_2O_6S_2$. Calculated: C 64.5; H 5.7; N 4.4; S 10.1%.

5,10-Dimethyl-4-ethyl-4,9-diazapyrenium Iodide (III).* A mixture of 0.5 g (2.2 mmole) of 5.10-dimethyl-4,9-diazapyrene and 2 g (11 mmole) of ethyl p-toluenesulfonate was heated at 140° for 1 h, after which 1 ml of alcohol was added, and the mixture was triturated. The dark-gray solid IV was removed by filtration and washed with 1 ml of alcohol and 25 ml of ether to give 0.3 g of ditoluenesulfonate IV with mp 280-283° (dec.). The combined filtrates was evaporated, and the residue was triturated with 25 ml of ether. The solid was separated and dissolved by heating in 6 ml of alcohol. The solution was treated with char-

*The conditions under which II was isolated along with IV are indicated. The optimum conditions for the preparation of II were not determined.

coal and filtered, 0.15 g of KI was added to the filtrate, and the precipitate was separated and washed with ether to give 0.49 g (58%) of greenish-yellow crystals of III [mp 248-251° (dec.)], which were dissolved by refluxing in a mixture of 50 ml of alcohol and 6 ml of water. The solution was treated with charcoal and filtered, and the filtrate was evaporated to half its original volume to give 0.41 g of II with mp 248-249° (dec.). Found: I 32.6%. $C_{18}H_{17}IN_2$. Calculated: I 32.8%.

4,10-Dimethyl-6'-bromospiro(4,5-dihydro-4,9-diazapyrene-5,2'-[2H]chromene) (IX). A solution of 1 g (2.8 mmole) of I, 0.6 g (3.0 mmole) of 5-bromosalicylaldehyde, and 0.9 ml (9 mmole) of piperidine in 100 ml of alcohol was refluxed for 1.5 h, after which the solid material [0.95 g, mp 216-217° (dec.)] was removed by filtration, washed with water, and crystallized once from a mixture of 300 ml of alcohol and 20 ml of dioxane and twice from alcohol to give colorless IX with mp 231-232° (dec.).

Compounds V-VII (Table 1) were similarly obtained. Spiropyran V was isolated from the reaction mixture by evaporation to half its original volume and was crystallized twice from alcohol (1:60). Compound VI was isolated by dilution of the reaction mixture with an equal volume of water and was crystallized from alcohol (1:60); VII was crystallized twice from 70% aqueous dioxane (1:120).

Spiropyrans VIII and X-XII (Table 1) were obtained by heating a solution of equimolecular amounts of the monoquaternary salt of the diazapyrene (I or III), the appropriate aldehyde, and piperidine in DMF (25 ml per gram of the salt) at 95-98° for 30 min. The reaction mixture was diluted to twice its original volume with water, and the resulting precipitate was removed by filtration and washed with water. Compound VIII was purified by crystallization from 85% aqueous dioxane (1:36) and alcohol–dioxane (4:1; 1:70); X was reprecipitated from benzene (1:60) and twice from CCl_4 (1:30) by means of equal volumes of petroleum ether and was crystallized from alcohol–dioxane (4:1; 1:125). Compound XI was reprecipitated three times from benzene (1:90) by means of petroleum ether, after which it was dissolved by boiling in CCl_4 (1:190), and the solution was treated with charcoal and evaporated to half its original volume prior to crystallization. Compound XII was extracted four times with boiling benzene (1:40), and the filtrates were evaporated to one-fourth their original volume; XII was precipitated by the addition of an equal volume of petroleum ether, after which it was crystallized from CCl_4 (1:60).

4,9-Dimethyl-6',8',6'',8''-tetrabromodispiro(4,5,9,10-tetrahydro-4,9-diazapyrene-5,10,2',2'-bis-[2H]chromene (XVII) and the Merocyanine Form (XVIIA). A solution of 0.6 g (1 mmole) of II, 0.6 g (2.1 mmole) of 3,5-dibromosalicylaldehyde, and 1.2 ml (12 mmole) of piperidine in 45 ml of 70% alcohol was refluxed for 1 h, and the resulting dark-green precipitate [0.5 g, mp 255-260° (dec.)] was washed with water and alcohol and crystallized twice from chlorobenzene (1:50).

For the preparation of the merocyanine form (XVIIA), 50 mg of spiropyran XVII, with mp 264-265° (dec.), was dissolved in 3 ml of acetic acid, the solution was filtered, and the filtrate was poured into a saturated solution of $NaHCO_3$. The resulting blue precipitate was separated, washed with water and ether, and vacuum dried to give 40 mg of XVIIA with mp 245-246° (dec.). A solution of XVIIA in alcohol was violet at room temperature but decolorized on heating and in light. A green coloration, which changed immediately to yellow, was observed in chloroform only when the compound was dissolved. Solutions in acetone and acetonitrile were yellow. Found: Br 40.9; N 3.3%. $C_{32}H_{20}Br_4N_2O_2$. Calculated: Br 40.8; N 3.6%.

Merocyanine XVIIIA. This compound, with mp 258-260° (dec.), was obtained by the method used to prepare XVIIA. Alcohol solutions of XVIIIA underwent color changes similar to those observed for solutions of XVIIA. A rapidly vanishing green coloration was observed when it was dissolved in acetone and chloroform. Found: Br 39.6; N 3.8%. $C_{34}H_{24}Br_4N_2O_2$. Calculated: Br 39.4; N 3.5%

Dispiropyrans XIII, XIV, XVI, and XVIII (Table 1). These compounds were obtained by the method used to prepare XVII. They were practically insoluble in alcohol and were crystallized from large amounts of low-polarity solvents. Compound XIII was crystallized from dioxane (1:80), XIV was crystallized from benzene (1:140), XVI was crystallized from 65% aqueous dioxane (1:450), and XVIII was crystallized from chlorobenzene (1:200).

Compound XV (Table 1) was obtained by heating a solution of 0.64 g (1 mmole) of IV, 0.36 g (2.1 mmole) of 2-hydroxynaphthaldehyde, and 0.6 ml (6 mmole) of piperidine in 15 ml of DMF at 95-98° for 1 h, after which the solid material was separated, washed with water and alcohol, crystallized from nitrobenzene (1:65), and washed with alcohol and ether.

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HYDRIDE SHIFT REACTIONS WITH THE PARTICIPATION OF TWO-RING SULFIDES

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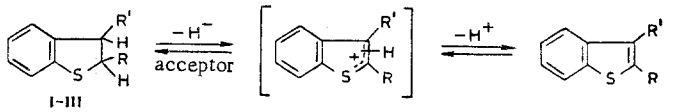
2,3-Dihydrobenzothiophenes are dehydrogenated to the corresponding benzothiophenes on reaction with the hydride-ion acceptors triphenylmethyl tetrafluoroborate and chloranil. Thiochroman reacts with chloranil to give 2-methyl-2,3-dihydrobenzothiophene and 2-methylbenzothiophene and reacts with triphenylmethyl tetrafluoroborate to give a thiochromenylium salt.

The dehydrogenation and isomerization reactions of two-ring sulfides in the presence of catalysts based on aluminum oxide apparently proceed through a step involving detachment of a hydride ion under the influence of the aprotic centers of the catalysts [1, 2], and dehydrogenation takes place without hydrogen evolution into the gas phase. In this connection, we investigated the dehydrogenation of 2,3-dihydrobenzothiophene (I), 2-methyl-2,3-dihydrobenzothiophene (II), and 3-methyl-2,3-dihydrobenzothiophene (III) on reaction with triphenylmethyl tetrafluoroborate and chloranil (tetrachloro-1,4-benzoquinone). The reaction gives high yields of the corresponding benzothiophene in aprotic solvents with high polarities (Table 1). At 80° in acetonitrile the dehydrogenation of II gives the product in yields up to 93%, whereas the yield at 20° after 1 h was only 29%. The character of the effect of the solvents and the absence of reaction products with doubled molecular weights make it possible to suppose that the reaction proceeds via an ionic scheme:

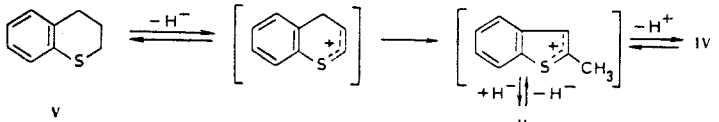


I-III (1)

I R = R′ = H; II R = CH₃, R′ = H; III R = H, R′ = CH₃

As compared with triphenylmethyl tetrafluoroborate, the use of chloranil requires an increase in the temperature and reaction time. Thus the yield of 2-methylbenzothiophene (IV) did not exceed 32% in the dehydrogenation of II in o-xylene at 100° for 15 h. The relative rates of dehydrogenation for I, II, and III, which were found to be, respectively, 1.5 : 2.4 : 1, were calculated on the basis of the dependence of the yields of the reaction products on the time.

Under the influence of chloranil, thiochroman (V) undergoes isomerization to give small amounts of II (2%) and its dehydrogenation product IV (3%):



V II (2)

M. V. Lomonosov Moscow State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 328-330, March, 1976. Original article submitted January 3, 1975.