for 15 h. After filtration the solvent was removed and the substance isolated analogously to compound IVe. Yield 0.65 g (36.0%), mp 30-31°C (pentane). PMR spectrum: 2.88 (1H, s, OH); 4.50 (2H, s, CH_2O); 7.00-7.75 (5H, m, aromatic protons). Compound IV*l* was produced analogously. In the PMR spectrum the signals of the two methyl groups in position 6 of the ring appear at 1.50 ppm.

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CONFIGURATIONALLY AND CONFORMATIONALLY HOMOGENEOUS ARYL-cis-1-THIADECALINS

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The structure of aryl-substituted cis-1-thiadecalins formed together with 5,6-tetramethylenethiopyrylium salts in disproportionation reactions of condensed 4H-, 6H-thiopyrans and dihydrothiopyrans with CF_3COOH, as well as in the ionic reduction of the latter by the ion pair trifluoroacetic acid—triethylsilane, was studied. It was shown that the reduction proceeds stereospecifically with the formation of configurationally and conformationally homogeneous aryl-cis-1-thiadecalins possessing 2α-R^1- and 2α-R^1-4α-R^2-configurations. The configurational and conformational assignments were made by the ^{13}C NMR method.

Intermolecular hydride transfer in such an acid-catalyzed reaction as the disproportionation of chromenes, thiochromenes, and dihydroquinolines leads to the formation not only of salts but also of products of reduction of the double bond in the heterocycle [1-6]. The stereochemical direction of the processes of reduction of heterocyclic compounds during disproportionation have been rather widely discussed in the literature [1-6]. 3,4-Diaklyl-2H-thiochromenes and N-methyl-1,2-dihydroquinolines are reduced predominantly to cis-isomers under the conditions of the reaction described, while O-analogs form cis- and trans-isomers in equal amounts under analogous conditions [1-6]. Derivatives of 3,4-trimethylene-1,2-dihydroquinoline give only cis-3,4-trimethylenetetrahydroquinoline [2], while 3,4-tetramethylene-2H-thiochromene and chromene are converted in this case 77 and 65%, respectively, to the cis-isomers [3]. Up to 83% cis-isomers are also obtained in the disproportionation of N-methyl-2,3-trimethylene-1,4-dihydroquinolines [5]. Only cis-2,4-diphenylchroman was isolated in disproportionation of 2,4-diphenyl-4H-chromene with CF_3COOH, CF_3COOD, or $HClO_4$ [6]. On the contrary, N-methyl-2,3-$(CH_2)_n$-1,4-dihydroquinolines (n = 4-6) are reduced exclusively or predominantly to trans-N-methyl-2,3-$(CH_2)_n$-1,2,3,4-tetrahydroquinolines [5]. We have shown that in the disproportionation of 2-diphenyl-5,6-tetramethylene-4H-thiopyran or -6H-thiopyran with trifluoroacetic adid, 2,4-diphenyl-cis-1-thiadecalin, which has a cis-cis-cis-configuration, are formed [7-9].

The present investigation was undertaken in order to establish the configuration and conformation of aryl-substituted 1-thiadecalins, which, together with the salt, are disproportionation products of 5,6-tetramethylene-4H(6H)-thiopyrans and dihydrothiopyrans [10-14]. This seems especially important since in the disproportionation of the objects described, two

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TABLE 1. Results of the Disproportionation of 5,6-Tetramethylene-4H-thiopyrans (I-III), 5,6-Tetramethylene-6H-thiopyrans (VII-IX), and 2-Thiabicyclo[4,4,0]decanes-$\Delta^{1,6}$(IV-VII) with Trichloroacetic Acid

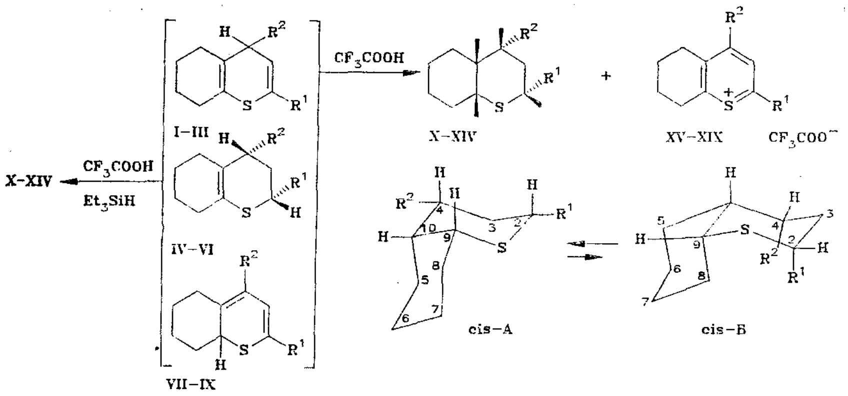
Compound	R¹	R²	Time of reaction, h	Reaction products					
				1 thiadecalin	mp, °C	yield, %	salt*	mp, °C	yield, %
I	C_6H_5	H	6	X	58—59	28	XV	213—215	61
II	C_6H_5	C_6H_5	12	XI	126—127,5	30	XVI	183—184 (168—170)	60
III	$C_6H_4OCH_3$-4	C_6H_5	12	XII	126—127	25	XVII	151—153 (70—71)	59
IV	C_6H_5	C_6H_5	12	XI	126,5—127,5	60	XVI	183—184 (168—170)	30
V	C_6H_5	$C_6H_4OCH_3$-4	3	XIII	121—122	57	XVIII	169—171	29
VI	C_6H_5	$C_6H_3(OCH_3)_2$-3,4	0,5	XIV	142—143	56	XIX	182—184	27
VII	C_6H_5	C_6H_5	6	XI	126,5—127,5	27	XVI	183—184 (168—170)	62
VIII	C_6H_5	$C_6H_4OCH_3$-4	3	XIII	121—122	29	XVIII	169—171	59
IX	C_6H_5	$C_6H_3(OCH_3)_2$-3,4	0,5	XIV	142—143	26	XIX	182—184	57

*Mp of the corresponding perchlorate; in parentheses: mp of trifluoroacetates. The yields of the salt are given converted to the corresponding perchlorate.

double bonds of the heterocycle are reduced, while the presence of aryl substituents in the 2- or 2,4-position should impose rigid steric limitations on the system.

Table 1 generalizes the data on the disproportionation of aryl-substituted condensed bicyclic 4H-, 6H-thiopyrans and dihydrothiopyrans I-IX. In all cases a salt and a sulfide are formed from the thiopyrans I-III, VII-IX in a 2:1 ratio and from dihydrothiopyrans IV-VI in a 1:2 ratio (Table 1).

All the 1-thiadecalins X-XIV obtained, as will be shown in the discussion of the ^{13}C NMR spectra, belong to the cis-series and are also characterized by the same orientation of the aryl substituents, i.e., they are configurationally and conformationally homogeneous. Thus, regardless of the position of the double bond in the heterocycle and the degree of its unsaturation, the same isomers arise.

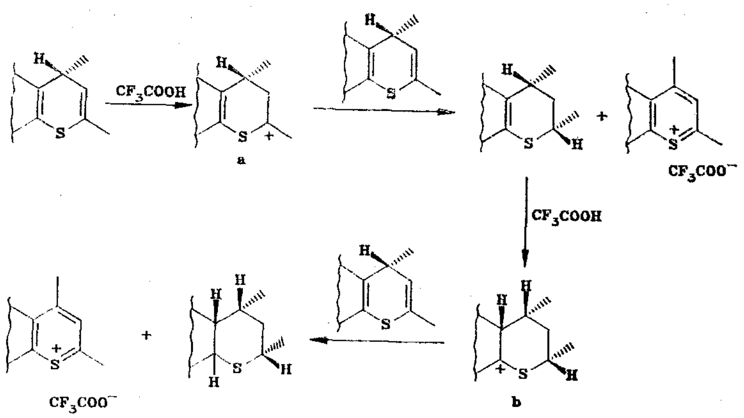


The formation of aryl-cis-1-thiadecalins in the reaction under consideration occurs with the participation of the carbocations *a*, b, c, d, as can be seen from schemes 1-3. Moreover, 4H-thiopyrans and dihydrothiopyrans disproportionate through the same ions *a* and b. The structure of the carbocations mentioned was established in reactions with D-trifluoroacetic acid [7].

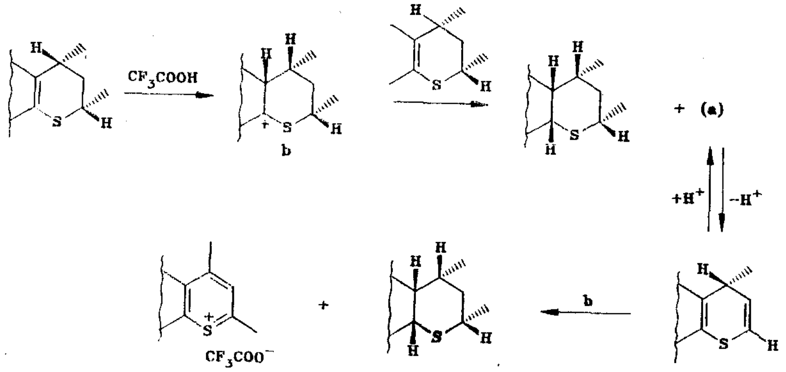
It is known [15] that in the ionic reduction of the tetrasubstituted double bond in 1,2-dimethylcyclopentane and 1,2-dimethylcyclohexane by the ion pair trifluoroacetic acid—triethylsilane, mixtures of cis- and trans-isomers are formed, with the trans-isomer predominating.

We conducted the ionic reduction of a series of condensed 4H-, 6H-thiopyrans and dihydrothiopyrans I-IX. The results are presented in Table 2. The presence of trans-isomers is not

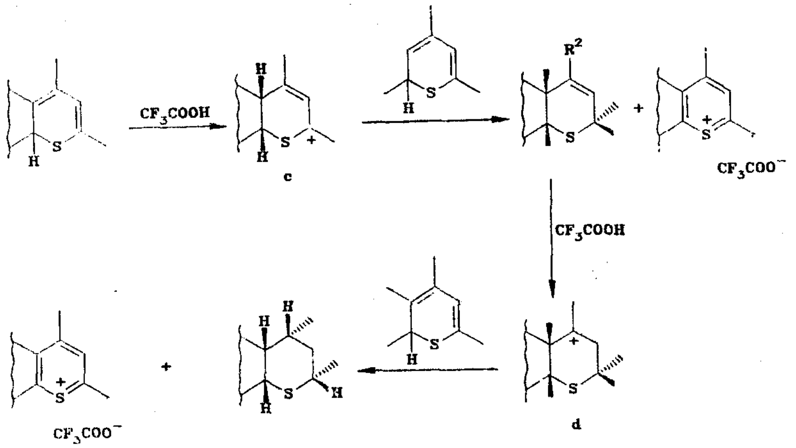
Scheme 1



Scheme 2



Scheme 3



detected even in the crude reaction products. The products of ionic hydrogenation — aryl-cis-1-thiadecalins — are identical with the samples isolated in disproportionation reactions (Tables 1 and 2). The ionic reduction of the ion pair triethylsilane—trifluoroacetic acid simulates the reduction in the disproportionation process and evidently proceeds with the participation of the same carbonium ions *a* and c, b and d.

The ions *a* and c were more stable (stabilization on account of the free electron pair of the heteroatom and the aryl) in comparison with b and d. However, the relative stability of the tertiary carbonium ions under discussion should not differ significantly, and, in our opinion, cannot be the controlling factor. At the same time, if the transfer of a hydride ion occurs in a bimolecular process, it should be sensitive to steric hindrances created primarily by the aryl substituents at $C_{(2)}$ and $C_{(4)}$. In our case the addition of a hydride ion to the carbocation *a* occurs on the part of the hydrogen at $C_{(4)}$ and leads to dihydrothiopyrans

TABLE 2. Ionic Hydrogenation of Condensed 4H-, 6H-Thiopyrans and Dihydrothiopyrans by the Ion Pair Triethylsilane—Trifluoroacetic Acid (Sulfide—Silane—Acid Ratio 1:3:5)*

Compound	R^1	R^2	cis 1 thiadecalin	mp, °C	Yield, %
I	C_6H_5	H	X	58—59	69
II	C_6H_5	C_6H_5	XI	125,5—127	85
III	$C_6H_4OCH_3$-4	C_6H_5	XII	126—127	78
IV	C_6H_5	C_6H_5	XI	125,5—127	79
V	C_6H_5	$C_6H_4OCH_3$-4	XIII	121—122	70
VI	C_6H_5	$C_6H_3(OCH_3)_2$-3,4	XIV	142,5—143,5	69
VII	C_6H_5	C_6H_5		125,5—127	83
VIII	C_6H_5	$C_6H_4OCH_3$-4	XIII	121—122	87
IX	C_6H_5	$C_6H_3(OCH_3)_2$-3,4	XIV	142,5—143	80

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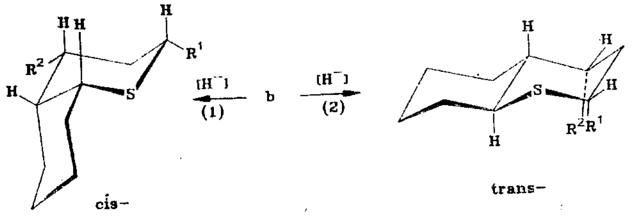
*The sulfides were recrystallized from ethanol or from a 1:1 ethanol—acetone mixture.

IV-VI with cis-configuration. As shown in [9], the thiacyclohexane ring represents a distorted half-chair with aryl substituents in a pseudoequatorial position. It is easy to note that in dihydrothiopyrans of the structure described, 1,3-interactions between the substituents are reduced to a minimum. The relative stability of the end products is evidently the deciding factor responsible for stereochemical control (see Scheme 1).

The further conversion of dihydrothiopyrans IV-VI proceeds through the carbocation (b) and provides the possibility of cis- and trans-addition of a hydride ion. Of the two possible directions of attack, direction (1) is preferential. In this case cis-1-thiadecalins with substituents in the equatorial position are formed, which distorts the syn-axial interactions, which should be very strong in the trans-isomer.



Reduction in the process of disproportionation of the 6H-isomers proceeds successively through the carbocations c and d and also leads to cis-1-thiadecalins with the same orientation of the aryl substituents at $C_{(2)}$ and $C_{(4)}$, which confirms our hypotheses on the determining role of the relative stability of the end products in providing for stereocontrol in the reaction under consideration.

To establish the configuration and preferential conformation we studied the ^{13}C NMR spectra at room temperature of 2-aryl- and 2,4-diaryl-1-thiadecalins X-XIV, obtained in reactions of disproportionation and ionic hydrogenation of condensed 2-aryl- and 2,4-diaryl-5,6-tetramethylene-4H(6H)-thiopyrans and dihydrothiopyrans I-IX. The assignment of the signals was made according to the data of the spectra with incomplete unbinding from protons and a comparison of the experimental and theoretical spectra, which were considered using the known parameters of the ^{13}C NMR spectra of the unsubstituted cis- and trans-1-thiadecalins [16] and the increments of the equatorial phenyl group in substituted cyclohexane [17]. As an example, Table 3 presents the experimental and theoretical ^{13}C NMR spectra of 2-phenyl-1-thiadecalin (X) and the data of [16] for unsubstituted cis- and trans-1-thiadecalins.

An analysis of the data cited in Table 3 permitted us to make a selection in favor of cis-coupling of the rings, which suggests the presence of a strongly polar signal. Actually, in the spectrum of compound X we find a signal at 20.87 ppm. It is known [16] that unsubstituted cis-1-thiadecalin (R^1=R^2=H) exists in the form of a mixture of two conformers A and B (58:42, respectively, at −70°C). In the spectra of all the investigated sulfides X-XIV, nine sharp signals of saturated carbon atoms of the heterocycle and alicycle were recorded, which is an indication of the absence of ring inversion at room temperature. The most weakly polar signals in the aliphatic portion of the spectrum of 2-phenyl-cis-1-thiadecalin appear as doublets in the spectrum with incomplete unbinding from protons and were identified as $C_{(2)}$,

TABLE 3. Comparative Characteristics of the Experimental and Theoretical Spectra of 2-Phenyl-1-thiadecalin

R^1*	Configuration and conformation	Nature of data	Temperature, °C	Chemical shifts of ^{13}C, δ, ppm								
				$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$
2α-C_6H_5	cis-A	exp.	30	48,62	28,77	33,32	24,64	26,79	20,87	31,64	45,06	35,46
	cis-A	calc.	—	47,42	28,40	32,30	24,40	26,69	20,88	31,86	43,11	36,01
	cis-B	calc.	—	41,09	35,58	24,72	34,22	19,61	28,28	27,34	40,41	36,75
2β-C_6H_5	trans-	calc.	—	47,54	35,53	34,20	34,36	26,34	26,76	32,58	47,01	44,27
H	cis-A	lit. [16]	−70	29,92	21,10	32,50	24,40	26,69	20,88	31,86	43,11	36,01
	cis-B	lit. [16]	−70	23,59	28,28	24,92	34,22	19,61	28,28	27,34	40,41	36,75
	trans-	lit. [16]	30	30,04	28,23	34,40	34,56	26,34	26,76	32,58	47,01	44,27

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*The notation of the position of the substituents by the symbol "α" was taken from the nomenclature of the steroids and used in the same sense as in [16].

$C_{(9)}$, $C_{(10)}$. The signals of the $C_{(4)}$ and $C_{(9)}$ atoms, which are found in the γ-position to the phenyl group, differ negligibly from the corresponding signals in cis-1-thiadecalin, by −0.72 and 0.22 ppm, which is an indication of an equatorial position of the substituent. At $C_{(2)}$ a small weak-field shift of 18.7 ppm is noted, as a result of the α-effect of the phenyl group. The signals of $C_{(9)}$ and $C_{(10)}$ do not undergo any significant changes in comparison with cis-1-thiadecalin (Table 3). The signals at 33.32, 31.64, and 28.77 ppm were assigned to $C_{(4)}$, $C_{(8)}$, and $C_{(3)}$; moreover, a weakly polar shift of the signal of the $C_{(3)}$ atom in the β-position relative to the substituent is noted. The chemical shifts of the atoms $C_{(5)}$, $C_{(6)}$, and $C_{(7)}$ virtually coincide with the analogous signals in cis-1-thiadecalin. As can be seen from Table 3, for compound X the best agreement of the experimental and theoretical spectra is observed for conformation A.

Table 4 presents the ^{13}C NMR spectra of compounds X-XIV, which indicate that 2-R^1-4-R^2-1-thiadecalins XI-XIV are structural analogs of compound X and of cis-1-thiadecalin. In the spectra of the compounds XI-XIV, as a result of the α- and β-effects of the substituents at $C_{(4)}$, the signals of the $C_{(4)}$ and $C_{(10)}$ atoms experience a weak-field shift (Table 4).

Aryl substituents at $C_{(2)}$ and $C_{(4)}$ give signals characteristic of mono-, di-, and trisubstituted benzenes in the spectra of compounds X-XIV and are of no interest for the purposes of our investigation.

The assignments made in Table 4 were confirmed in each case by a comparison of the theoretical and experimental spectra. Compounds XI-XIV are configurationally and conformationally homogeneous and exist in conformation A. The other conformation is excluded on account of strong syn-axial interactions of the aryl groups with $C_{(8)}$ in compound X and $C_{(6)}$, $C_{(8)}$ in compounds XI-XIV.

EXPERIMENTAL

The ^{13}C NMR spectra were recorded on a Varian FT-80A Fourier spectrometer with complete suppression of spin—spin interaction with protons. The frequency for the ^{13}C nuclei was 20 mHz. The spectra were calibrated according to the signals of a secondary standard, as which the signal of the solvent $CDCl_3$ is used.

The IR spectra were recorded on a UR-20 spectrometer in liquid petrolatum. The electronic spectra were recorded on an SF-4A instrument for 10^{-2} M solutions in methylene chloride at a thickness of the absorbing layer $22 \cdot 10^{-4}$ cm.

2-(4-Methoxyphenyl)-4-phenyl-5,6-tetramethylene-4H-thiopyran (III). A suspension of 6.56 g (0.019 mole) 1-(4-methoxyphenyl)-3-phenyl-3-(2-oxocyclohexyl)-1-propane in 50 ml of absolute ethanol was saturated with hydrogen sulfide for 1 h, then with a mixture of dry HCl/H_2S and exposed at the temperature 18°C for 48 h. The crystals that precipitated were filtered off and precipitated from a 10:1 ether—ethanol mixture. The sulfide III was obtained in an amount of 3.48 g (53%), mp 107-108°C. IR spectrum: 1610, 1657 cm^{-1} (C=C). UV spectrum: λ_{max} (log ε): 257 (4.20), 300 nm (3.25). PMR spectrum ($CDCl_3$): 5.81 (d, 3-H), 3.95 ppm (d, 4-H), $^3J_{34}$ = 5.8 Hz. Found: C 79.3; H 6.4; S 9.6%. $C_{22}H_{22}OS$. Calculated: C 79.1; H 6.6; S 9.6%.

TABLE 4. Chemical Shifts of ^{13}C of 2-Aryl- and 2,4-Diarylsubstituted cis-1-Thiadecalins (X-XIV)

Compound	2α-R¹	4α-R²	Chemical shifts of ^{13}C, δ, ppm									
			$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	OCH_3
X	C_6H_5	H	48,62	28,77	33,32	24,64	26,79	20,87	31,64	45,06	35,46	—
XI	C_6H_5	C_6H_5	48,70	33,23	48,70	21,17	26,53	19,20	31,71	46,62	43,06	—
XII	$C_6H_4OCH_3$	C_6H_5	47,05	33,37	48,73	21,16	26,53	19,17	31,69	46,60	43,03	55,05
XIII	C_6H_5	$C_6H_5OCH_3$-4	48,75	33,46	47,87	21,21	26,56	19,16	31,70	46,60	43,18	55,04
XIV	C_6H_5	$C_6H_3(OCH_3)_2$-3,4	48,70	33,50	48,20	21,10	26,50	19,20	31,60	46,50	43,10	55,59; 55,68

Ionic Hydrogenation of Condensed 4H- 6H-Thiopyrans and Dihydrothiopyrans. A mixture of 0.006 mole of the sulfide I-IX, 0.018 mole triethylsilane, and 0.3 mole trifluoroacetic acid was boiled for 5-8 h and extracted with ether. The extracts were washed with water, dried with anhydrous magnesium sulfate, and evaporated under vacuum. The precipitate was crystallized with an addition of alcohol or acetone. A 69-85% yield of the sulfide X-XIV was obtained after recrystallization.

Disproportionation of Condensed 4H-, 6H-Thiopyrans and Dihydrothiopyrans with Trifluoroacetic Acid was conducted by boiling 0.01-0.02 mole of the sulfide I-IX in a 10-fold excess of absolute trifluoroacetic acid, as described in [7, 14].

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