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STEREOCHEMICAL SPECIFICITY OF THE PALLADIUM-CATALYZED HYDROGENATION OF CYCLOHEXA[b]THIOPYRANS AND THEIR DERIVATIVES

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Conformationally and configurationally homogeneous 2α-R^1-4α-R^2-cis-1-thiadecalins with an equatorial orientation of the substituents attached to the $C_{(2)}$ and $C_{(4)}$ atoms were isolated as the final reduction products in the catalytic hydrogenation on palladium of 2-R^1-4-R^2-4H(6H)-cyclohexa[b]thiopyrans, cis-3-R^1-5-R^2-2-thiabicyclo[4.4.0]-$\Delta^{1,6}$-decenes, and 2-R^1-4-R^2-cyclohexa[b]thiopyrylium tetrafluoroborates and trifluoroacetates. cis-3-R^1-5-R^2-2-Thiabicyclo[4.4.0]-$\Delta^{1,6}$-decenes were obtained as intermediates in the incomplete reduction of 2-phenyl- and 2,4-diphenyl-4H-cyclohexa[b]thiopyrans and 2-(4-methoxyphenyl)-4-R^2-cyclohexa[b]thiopyrylium salts; 2-R^1-4-R^2-6H-cyclohexa[b]thiopyrans undergo complete reduction of the double bonds of the heteroring. The hydrogenation products were oxidized to sulfoxides and sulfones.

The liquid-phase hydrogenation on palladium of some two-ring thiopyran [1], dihydrothiopyrans [1], and thiopyrylium salts [2] has been previously accomplished for preparative purposes; however, structural studies of the hydrogenation products were not made. The only exception was 2α,4α-diphenyl-cis-1-thiadecalin, which was obtained in the hydrogenation of 2,4-diphenyl-6H-cyclohexa[b]thiopyran; the structure of this product was established via a combined study of the ^{1}H NMR spectra of the sulfide, its 3D,10D derivative, and the S-oxide [3].

We have carried out the hydrogenation of known and new 4H(6H)-cyclohexa[b]thiopyrans I-VII on 10% palladium on carbon under the previously described conditions at 100°C and an initial hydrogen pressure of 50 atm [1] (Table 1).

As a result of hydrogenation, 2,4-diaryl-6H-cyclohexa[b]thiopyrans IV-VII form 2α,4α-diaryl-cis-1-thiadecalins XX and XXII-XXIV in 83-86% yields. Dihydro products could not be isolated in the experiments with sulfides IV-VII; this is possibly associated with the β position of the double bond in the heteroring, which is sterically less hindered than the angular double bond in dihydrothiopyrans VIII-XIII.

After 6-7 h, sulfides I and II undergo reduction of both double bonds of the heteroring and form the corresponding 2α-phenyl- and 2α,4α-diphenyl-cis-1-thiadecalins (XIX, XX) (Table 1). Shortening the reaction time by one half in the experiment with 2,4-diphenyl-4H-cyclohexa[b]thiopyran (II) leads to reduction of the sterically less hindered double bond and to the formation of chiefly cis-3,5-diphenyl-2-thiabicyclo[4.4.0]-$\Delta^{1,6}$-decene (VIII) [4] (60%) and a small amount of 2α,4α-diphenyl-cis-1-thiadecalin (XX); the latter was detected by thin-layer chromatography (TLC).

The hydrogenation of 2-(4-methoxyphenyl)-4-phenyl-4H-cyclohexa[b]thiopyran (III) proceeds anomalously: not only are the double bonds of the heteroring reduced, but skeletal isomerization also occurs, and 2α-(4-methoxyphenyl)-4α-phenyl-cis-1-thiadecalin (XXI) and 2α-(4-methoxyphenyl)-3-benzyl-cis-1-thiahydrindan (XXVI) are formed in a ratio of 1:1. Compound XXVI was not isolated in the individual state and was characterized through sulfone XXVII.

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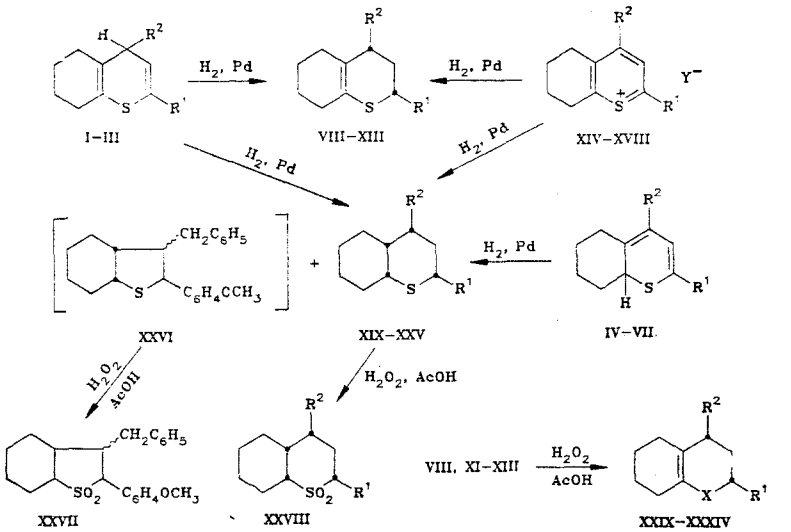
TABLE 1. Hydrogenation of Cyclohexa[b]thiopyrans, 2-Thiabicyclo[4.4.0]decenes, and Cyclohexa[b]thiopyrylium Salts on 10% Palladium on Carbon

Starting compound	Initial hydrogen pressure, atm	Time, h	Reaction product*	mp, °C	Yield of chief product, %**
I	50	6	XIX	58—59 [5]	78
II	50	7	(XX)	125—126,5 [3]	80
II	50	3.5	VIII (XX)	106—108 [4]	60 (80)
III	50	6.5	XXI, XXVI	197—198 (XXVIII)*** 263—265 (XXVII)***	88
IV	50	5	XX	125—126,5 [3,5]	83
V	50	5	XXII	121—122 [5]	86
VI	50	5	XXIII	142—143 [5]	85
VII	50	5	XXIV	99—100	84
VIII	50	3.5	XX	125—126,5 [3]	80
IX	50	3.5	XXII	121—122	77
X	50	3.5	XXIII	142—143 [6]	72
XI	50	3.5	XXIV	99—100	82
XII	50	4	XXI	126—127 [5]	80
XIII	50	4	XXV	77—79	85
XIV	100	12—14	XXIV	99—100	56
XV	100	14	XXIV	99—100	45
XIV	100	7—8	XI (XXIV)	101—102	38 (58)
XV	100	7—8	XI (XXIV)	101—102	32 (45)
XVI	100	12—14	XXI	126—127 [5]	53
XVII	100	12—14	XXI	126—127 [5]	42
XVI	100	7—8	XII (XXI)	103—104	48 (54)
XVII	100	7—8	XII (XXI)	103—104	40 (45)
XVIII	100	7—8	XIII (XXV)	71—72	45 (60)
XVIII	100	14	XXV	77—79	55

*The reaction products that are present in insignificant amounts are indicated in parentheses.

**The overall yield of a mixture of sulfides is presented in parentheses.

***Identified through sulfones XXVIII and XXVII.



I XIX $R^1=C_6H_5$, $R^2=H$; II, IV, VIII, XX, XXXII $R^1=R^2=C_6H_5$; III, XII, XVI, XVII, XXI, XXVIII, XXIX $R^1=C_6H_4OCH_3$-4, $R^2=C_6H_5$; V, IX, XXII $R^1=C_6H_5$, $R^2=C_6H_4OCH_3$-4; VI, X, XXIII $R^1=C_6H_5$, $R^2=C_6H_3(OCH_3)_2$-3,4; VII, XI, XIV, XV, XXIV, XXX, XXXIII $R^1=R^2=C_6H_4OCH_3$-4; XIII, XVIII, XXV, XXXI, XXXIV $R^1=C_6H_4OCH_3$-4, $R^2=H$; XIV, XVI, XVIII $Y=BF_4^-$; XV, XVIII $Y=CF_3COO^-$; XXIX—XXXI $X=SO_2$; XXXII—XXXIV $X=SO$

Since we did not have other samples of 2-(4-methoxyphenyl)-4-R-4H-cyclohexa[b]thiopyrans at our disposal, it seemed of interest to study the behavior of the corresponding salts, viz., 2-(4-methoxyphenyl)-4-R-cyclohexa[b]thiopyrylium tetrafluoroborates and trifluoroacetates XIV-XVIII, under liquid-phase hydrogenation conditions. One might have expected that skeletal isomerization of the intermediate 2-(4-methoxyphenyl)-4-R-4H-cyclohexa[b]thiopyrans (R = H, C_6H_5, $C_6H_4OCH_3$-4) would also be observed in the liquid-phase hydrogenation of salts XIV-XVIII with a 4-methoxyphenyl group attached to $C_{(2)}$. Thus it has been shown [2] by TLC that the hydrogenation of 2-phenyl- and 2,4-diphenylcyclohexa[b]thiopyrylium tetrafluoroborates occurs through the intermediate formation of the corresponding 4H-thiopyrans.

However, the reduction of salts XIV-XVIII on 10% Pd/C under previously described [2] conditions (100°C, 100 atm) leads to the formation of either dihydrothiopyrans XI-XIII with a cis configuration or 2α-aryl- and 2α,4α-diaryl-cis-1-thiadecalins XXI, XXIV, and XXV (Table 1), i.e., skeletal isomerization is not observed in the reduction process. It is apparent from Table 1 that the yields of the cited products from salts XIV-XVIII are, on the whole, lower (42-60%) than from 4H(6H)-cyclohexa[b]thiopyrans I-VII and that the reaction times and catalyst consumption are 2-2.5 times greater. Dihydrothiopyrans XI-XIII were isolated 7-8 h after the start of the reaction, and saturated sulfides XXI, XXIV, and XXV are present in small amounts as impurities. Dihydrothiopyrans XI-XIII were isolated in the individual state by fractional crystallization from ethanol.

A possible reason for the different behavior of 4H-thiopyran III and salts XIV-XVIII in the hydrogenation process is the presence in the latter case of acid, which protonates the double bond of the heteroring primarily at the $C_{(3)}$ atom, which hinders isomerization.

Thus dihydrothiopyrans VIII and XI-XIII with a cis configuration were isolated for the first time as intermediates in the palladium-catalyzed hydrogenation of 4H-cycloalka[b]-thiopyran II and cycloalka[b]thiopyrylium salts XIV-XVIII. The hydrogenation of cis-3,5-diaryl-2-thiabicyclo[4.4.0]-$\Delta^{1,6}$-decenes VIII-XIII on palladium also proceeds as cis addition of hydrogen to the angular double bond.

The same 2α-aryl- and 2α,4α-diaryl-cis-1-thiadecalins XIX-XXV are formed in the hydrogenation of cyclohexa[b]thiopyrans I-VII, cyclohexa[b]thiopyrylium salts XIV-XVIII, and dihydrothiopyrans VIII-XIII, i.e., their hydrogenation proceeds stereospecifically. The only example of skeletal isomerization observed in the reduction of 4H-thiopyran III with a 4-methoxyphenyl group attached to $C_{(2)}$ does not make it possible to deal with the reasons for it.

Dihydrothiopyran VIII was identical to a sample of cis-3,5-diphenyl-2-thiabicyclo-[4.4.0]-$\Delta^{1,6}$-decene obtained previously from 2,4-diphenyl-1-thiadecalin 1-oxide in the Pummerer reaction [4], and thiadecalins XIX-XXIII were identical to the 2α-R^1- and 2α-R^1-4α-R^2-cis-1-thiadecalins formed in the case of disproportionation in trifluoroacetic acid and in the ionic hydrogenation of thiopyrans I-VII and dihydrothiopyrans VIII-X [5].

Dihydrothiopyrans VIII and XI-XIII were oxidized with hydrogen peroxide in acetic acid to sulfones XXIX-XXXI and sulfoxides XXXII-XXXIV.

The ^{13}C NMR spectra of the previously undescribed compounds are presented in Table 3. It is apparent from Table 3 that XI and XII are structural analogs of cis-3,5-diphenyl-2-thiabicyclo[4.4.0]-$\Delta^{1,6}$-decene (VIII). The assignments for cis-1-thiadecalins XXIV and XXV were confirmed in each case by comparison of the theoretical and experimental spectra [5].

The substituents in the heteroring give signals that are characteristic for mono- and disubstituted benzenes in the spectra of all of the investigated compounds.

In the spectrum of sulfone XXVII, as compared with the spectrum of 2α-(4-methoxyphenyl)-4α-phenyl-cis-1-thiadecalin 1,1-dioxide, one's attention is directed to the signals of the 4-methoxyphenyl group, which virtually coincide in the spectra of both samples; this serves as a confirmation of the isomerization pathway.

EXPERIMENTAL

The electronic spectra of solutions (10^{-3} M) of the compounds in methylene chloride in cuvettes with a thickness of 0.1 cm were obtained with a Specord M-40 spectrometer. The IR spectra of suspensions in mineral oil were recorded with a UR-20 spectrometer. The ^1H and ^{13}C NMR spectra were obtained with a Varian FT-80A spectrometer at 30°C with hexamethyldisiloxane (HMDS) and $CDCl_3$ as the internal standards for the ^1H and ^{13}C spectra, respectively. The frequencies for the ^{13}C and ^1H nuclei were 20 and 80 MHz, respectively.

TABLE 2. Characteristics of 2α-R^1-4α-R^2-cis-1-Thiadecalins XXIV and XXV, cis-3-R^1-5-R^2-2-Thiabicyclo[4.4.0]-$\Delta^{1,6}$-decenes XI-XIII, and Their Oxidation Products XXXIX-XXXIV

Compound	mp, °C	IR spectrum, cm^{-1}		Found, %			Empirical formula	Calculated, %			Yield, %
		C=C	S→O	C	H	S		C	H	S	
XI	101—102	1650	—	75.1	7.3	8.8	$C_{23}H_{26}O_2S$	75.4	7.2	8.8	38
XII	103—104	1640	—	78.3	7.5	9.2	$C_{22}H_{24}OS$	78.5	7.2	9.5	48
XIII	71— 72	1640	—	74.0	7.8	12.5	$C_{16}H_{20}OS$	73.8	7.7	12.3	45
XXIV	99—100	—	—	74.9	7.5	9.0	$C_{23}H_{28}O_2S$	75.0	7.6	8.7	56
XXV	76— 77	—	—	72.9	8.1	12.2	$C_{16}H_{22}OS$	73.3	8.5	12.2	55
XXIX	213—215	1645	1295, 1135	71.9	6.7	8.8	$C_{22}H_{24}O_3S$	71.7	6.6	8.7	88
XXX	204—204.5	1640	1300, 1130	68.8	6.9	8.0	$C_{22}H_{26}O_4S$	69.3	6.6	8.2	84
XXXI	163—164	1645	1290, 1130	66.0	6.7	10.6	$C_{16}H_{20}O_3S$	65.7	6.9	11.0	81
XXXII	129—130	1640	1060	78.1	6.8	9.9	$C_{21}H_{22}OS$	78.2	6.9	9.9	60
XXXIII	113—115	1645	1060	72.2	7.2	8.6	$C_{23}H_{26}O_3S$	72.2	6.9	8.4	56
XXXIV	113—114	1630	1045	69.4	7.5	11.4	$C_{16}H_{20}O_2S$	69.5	7.3	11.6	54

*Compounds XI-XIII were recrystallized from ethanol, and XXIV and XXV were recrystallized from ethanol—acetone.

The starting 4H-cyclohexa[b]thiopyrans I-III were obtained by the method in [5, 7], 6H-cyclohexa[b]thiopyrans IV-VI were obtained by the method in [8], 3,5-diaryl-2-thiabicyclo-[4.4.0]-$\Delta^{1,6}$-decenes IX and X were obtained by the method in [9], and trifluoroacetate XV was obtained by the method in [10].

2,4-Bis(4-methoxyphenyl)-6H-cyclohexa[b]thiopyrine (VII). This compound was obtained by the reduction of 11.43 g (24 mmole) of trifluoroacetate XV [10] with lithium aluminum hydride by the method in [8]. This procedure gave 5.67 g (65%) of a product with mp 106-108°C (ethanol—ether). UV spectrum, λ_{max} (log ε): 271 (4.36), 361 nm (3.70). IR spectrum: 1605, 1580, 1540, 1505 cm^{-1} (C=C). PMR spectrum: 1.59-1.94 (8H, m, alicyclic protons); 3.73 and 3.75 (3H and 3H, s, OCH_3); 3.95 (1H, t, $C_{(6)}$—H); 6.18 (1H, s, $C_{(3)}$—H); 6.72-7.49 ppm (8H, m, aromatic protons). Found: C 75.8; H 6.6; S 8.5%. $C_{23}H_{24}O_2S$. Calculated: C 75.9; H 6.7; S 8.8%.

2-(4-Methoxyphenyl)-4-phenylcyclohexa[b]thiopyrylium Trifluoroacetate (XVII). The reaction of 30 mmole of 1-(4-methoxyphenyl)-3-phenyl-3-(2-oxocyclohexyl)-1-propanone via the method in [10] gave 6.96 g (52%) of trifluoroacetate XVII with mp 70-71°C (chloroform—hexane). IR spectrum: 1700-1790 (CF_3COO^-), 1610, 1575, 1525 cm^{-1} (C=C). Found: C 64.4; H 4.5; S 7.4%. $C_{24}H_{21}F_3O_3S$. Calculated: C 64.6; H 4.8; S 7.2%.

General Method for Obtaining Cyclohexa[b]thiopyrylium Tetrafluoroborates XIV, XVI, and XVIII. A suspension of 50 mmole of the corresponding 1-R^1-3-R^2-3-(2-oxocyclohexyl)-1-propanone in 70 ml of glacial acetic acid was saturated with hydrogen sulfide for 2 h at 20°C, after which 40 ml of freshly distilled boron trifluoride etherate was added dropwise in the course of 1.5 h without stopping the flow of hydrogen sulfide. The reaction mixture was then saturated with hydrogen sulfide for another 6 h and maintained at 20°C for 3 days. At the end of the reaction, the mixture was poured into 350 ml of ether, and the crystalline tetrafluoroborate was removed by filtration and washed with ether.

2,4-Bis(4-methoxyphenyl)cyclohexa[b]thiopyrylium Tetrafluoroborate (XIV). This compound, which had mp 155-156°C (chloroform—ether), was obtained in a yield of 7.87 g (35%). UV spectrum, λ_{max}, nm (log ε): 267 (4.18), 298 (4.06), 436 nm (4.41). IR spectrum: 1600, 1570, 1560, 1500 (C=C), 1060 cm^{-1} (BF_4^-). Found: C 61.1; H 5.3; S 7.1%. $C_{23}H_{23}BF_4O_2S$. Calculated: C 61.4; H 5.2; S 7.1%.

2-(4-Methoxyphenyl)-4-phenylcyclohexa[b]thiopyrylium Tetrafluoroborate (XVI). This compound, which had mp 128-129°C (acetonitrile—ether), was obtained in a yield of 8.82 g (42%). UV spectrum, λ_{max}, nm (log ε): 264 (4.11), 304 (4.17), 358 (4.01), 451 nm (4.46). IR spectrum: 1605, 1568, 1510 (C=C), 1060 cm^{-1} (BF_4^-). Found: 63.2; H 5.2; S 7.3%. $C_{22}H_{21}BF_4OS$. Calculated: C 62.9; H 5.0; S 7.6%.

2-(4-Methoxyphenyl)cyclohexa[b]thiopyrylium Tetrafluoroborate (XVIII). This compound, which had mp 189-190°C (chloroform—ether), was obtained in a yield of 8.43 g (49%). UV spectrum, λ_{max}, nm (log ε): 264 (4.00), 301 (3.98), 450 nm (4.28). IR spectrum: 1605, 1580, 1540, 1500 (C=C), 1060 cm^{-1} (BF_4^-). Found: C 55.7; H 4.9; S 9.2%. $C_{16}H_{17}BF_4OS$. Calculated: C 55.9; H 5.0; S 9.3%.

TABLE 3. ^{13}C NMR Chemical Shifts of VIII, XI-XIII, XXIV, XXV, XXXI, and XXXIV

Compound*	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	$C_{(10)}$	R^1/R^2				OCH_3
										quaternary	ortho	meta	para	
VIII	45,42	43,53	49,33	29,97	23,08	23,08	30,92	126,63	126,05	140,48/144,60	127,37/128,10	128,44/128,34	127,37/126,19	—
XI	44,79	43,67	48,53	29,95	23,09	23,09	30,88	126,41	126,34	133,17/136,66	128,39/128,95	113,75/113,86	158,71/158,00	55,04
XII	44,60	43,55	49,26	29,82	23,94	23,94	30,75	126,59	125,82	132,95/144,56	128,25/127,96	113,71/128,95	158,64/126,06	55,87
XIII	45,01	31,55	31,55	29,92	23,19	22,99	30,70	123,32	123,32	134,06	128,55	113,85	159,72	55,11
XXIV	47,76	33,50	47,58	21,06	26,46	19,03	31,58	46,43	43,02	134,52/136,37	128,18/128,18	113,67/113,23	158,49/157,58	54,91
XXV	47,76	28,78	33,26	24,52	26,72	18,79	31,52	44,93	35,28	134,91	128,14	113,59	158,39	54,99
XXXI	63,52	25,79	31,59	31,15	21,32	21,26	19,78	141,40	133,59	122,06	130,79	113,82	159,81	55,02
XXXIV	63,62	24,31	30,83	31,40	22,91	21,56	23,97	137,20	129,53	129,53	128,94	113,86	159,16	54,89

*The same numbering of the condensed system as for cis-1-thiadecalins XXIV and XXV was used for VIII, XI-XIII, XXXI, and XXXIV in Table 3.

The acetic acid–ether solutions remaining after separation of tetrafluoroborates XIV, XVI, and XVIII were washed with water until the wash waters were neutral and dried with magnesium sulfate, and the ether was partially evaporated in vacuo. 2-Thiabicyclo[4.4.0]-$\Delta^{1,6}$-decenes XI-XIII crystallized from the residues after the addition of 2-3 ml of ethanol and cooling with dry ice; sulfides XI and XII were identified by melting of mixtures with samples obtained by hydrogenation (Table 1). The yields of the sulfides were 30-36% (based on the purified products). Sulfide XIII was identified through sulfone XXXI with mp 163-164°C (Table 2).

Hydrogenation of Sulfides (I-XIII). Hydrogenation was carried out in an autoclave by the method in [1] at an initial hydrogen pressure of 50 atm at 100°C with the use of 50 ml of ethanol and 1 g of 10% palladium on carbon per gram of the substrate. The yields of cis-1-thiadecalins XIX-XXV were 72-85%, and the yield of cis-3,5-diphenyl-2-thiabicyclo-[4.4.0]-$\Delta^{1,6}$-decene was 60% (Tables 1 and 2).

A mixture of sulfides XXI and XXVI in a ratio of 1:1 (according to ^{13}C NMR data) was obtained in an experiment with 4H-thiopyran III. For identification, 0.8 g of a mixture of sulfides XXI and XXVI was oxidized with hydrogen peroxide in acetic acid as described in [1] to give the corresponding sulfones XXVIII and XXVII, which were separated by fractional crystallization from alcohol and acetone.

2α-(4-Methoxyphenyl)-3-benzyl-cis-1-thiahydrindan 1,1-Dioxide (XXVII). This compound had mp 263-265°C. IR spectrum: 1295, 1130-1140 cm^{-1} (S–O). ^{13}C NMR spectrum: 62.59 ($C_{(2)}$); 38.46; 38.97 ($C_{(3)}$, $C_{(9)}$); 28.38 ($C_{(4)}$); 25.44 ($C_{(5)}$); 19.14 ($C_{(6)}$); 22.61 ($C_{(7)}$); 60.55 ($C_{(8)}$); 40.33; 141.99; 128.70; 128.70; 126.79 ($CH_2C_6H_5$); 121.24; 130.73; 113.82; 159.92; 54.94 ppm ($C_6H_4OCH_3$-4). Found: C 71.3; H 7.0; S 8.2%. $C_{22}H_{26}O_3S$. Calculated: C 71.3; H 7.1; S 8.7%.

2α-(4-Methoxyphenyl)-4α-phenyl-cis-1-thiadecalin 1,1-Dioxide (XXVIII). This compound had mp 197-198°C. IR spectrum: 1300, 1135 cm^{-1} (S–O). ^{13}C NMR spectrum: 66.46($C_{(2)}$); 30.60 ($C_{(3)}$); 46.63 ($C_{(4)}$); 20.97 ($C_{(5)}$); 25.05 ($C_{(6)}$); 19.31 ($C_{(7)}$); 23.49 ($C_{(8)}$); 60.40 ($C_{(9)}$); 44.58 ($C_{(10)}$); 122.07; 130.79; 113.37; 159.84; 54.90 ($C_6H_4OCH_3$–4); 141.80; 127.20; 128.04; 126.32 ppm (C_6H_5). Found: C 71.7; H 7.2; S 8.8%. $C_{22}H_{28}O_3S$. Calculated: C 71.3; H 7.1; S 8.7%.

Hydrogenation of 2-R^1-4-R^2-Cyclohexa[b]thiopyrylium Tetrafluoroborates and Trifluoroacetates XIV-XVIII. Hydrogenation was accomplished as described in [2] with the use of 2-2.5 g of 10% palladium on carbon per gram of substrate at an initial hydrogen pressure of 100 atm and a temperature of 100°C. This procedure gave 2-thiabicyclo[4.4.0]-$\Delta^{1,6}$-decenes XI-XIII or cis-1-thiadecalines XXI, XXIV, and XXV (Tables 1-3). The known 2α-R^1-4α-R^2-cis-1-thiadecalines XIX-XXIII [3, 5, 6] and cis-3,5-diphenyl-2-thiabicyclo[4.4.0]-$\Delta^{1,6}$-decene (VIII) were identified by melting of mixtures with genuine samples [3-6].

cis-3-R^1-5-R^2-2-Thiabicyclo[4.4.0]-$\Delta^{1,6}$-decene 1,1-Dioxides XXIX-XXX. These compounds were obtained by the method in [1].

cis-3-R^1-5-R^2-Thiabicyclo[4.4.0]-$\Delta^{1,6}$-decene 1-Oxides XXXII-XXXIV. These compounds were obtained by the method in [10].

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QUANTUM-CHEMICAL INTERPRETATION OF THE MASS SPECTRA OF PYRROLE, FURAN, AND THIOPHENE

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A simple quantum-chemical interpretation of the mass-spectrometric fragmentation of organic molecules in which the probability of the cleavage of the bonds under the influence of electron impact is related to their self-consistent π-electron orders and the possible rearrangement processes are described on the basis of the long-range bond orders is proposed. This approach was tested in the case of pyrrole, furan, and thiophene.

In the modern literature there are several approaches to the theoretical description of mass spectra: a statistical approach [1] in which the intensity of an ion peak is assumed to be higher, the greater the number of fragments of a given mass that can be obtained as a result of cleavage of the various bonds of the starting molecule; the charge-localization approximation [2-6] in which bond cleavage depends on the site of the primary location of the positive charge in the molecular ion; taking into account the bond orders [4] and energies [7, 8] (calculated, as a rule, by the Nückel method); application of the Dewar theory of perturbed MO [9] and the method of potential surfaces [10, 11]. In some of these models, which are based on quasi-equilibrium theory, identity of the structures of the molecular ion and the neutral molecule is assumed without substantiation [12]; this clearly does not correspond to the physical pattern of the phenomenon. Other methods, for example, the method of potential surfaces, while being physically correct, are extremely laborious from a computational point of view, and this substantially limits their range of application. Virtually all of the theoretical schemes (except for the method of potential surfaces) do not take into account the role of rearrangement processes, which are intimately associated with the stabilities of the resulting fragments and, consequently [13], with the intensities of their peaks in the mass spectra. Let us note that some isomerization processes of this sort have been observed [with the use of the MIKES (DADI) [14] and CID/MIKE [15] methods with devices with "inverse" geometry] experimentally (see [16]).

We assume that the pathways of the fragmentation of a molecular ion are due to its electronic structure and that the pattern of the mass spectrum is determined to a significant degree by rearrangements of the corresponding cation radicals or cations. As in [17, 18], we describe cyclizations by means of the long-range bond orders, which, moreover, are a measure of the aromatic character [19], i.e., the thermodynamic stabilities of the resulting rearrangement ions. We determine the probability of bond cleavage in the fragmentation of conjugated systems from the corresponding self-consistent π-electron bond orders; we assume that the ion undergoing fragmentation exists in the ground state. In contrast to [17, 18], in which the mass-spectrometric recyclizations of cations with a closed electron shell were examined, the rearrangements and fragmentation of pyrrole, furan, and thiophene cation radicals were studied here. The parameters of the π-electron Hamiltonian are the same as in [20-22].

The bond orders of pyrrole (Ia), furan (Ib), and thiophene (Ic) cation radicals, as well as their π-open forms II-IV, calculated by the unrestricted Hartree–Fock method are presented in Table 1.

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