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SYNTHESIS OF 2- AND 3-ALKYL(ARYL)-CIS-1-THIADECALINS

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2-Alkyl(aryl)- (I) and 3-alkyl(aryl)-cis-1-thiadecalins (II), which are of interest for identification of sulfides of petroleum origin, have been little studied. Also, cis-1-thiadecalin is difficult to obtain and its synthesis [1] includes nine steps and allows no possibility of introducing a substituent into position 2. The method of [2] affords only 2-methyl substituted thiadecalins and a mixture of isomers is formed with both orientations of the substituent (predominantly cis) as well as both ring junctures (a mixture of cis- and trans-1-thiadecalins in a ratio of 1.5:1). By the method of [3] only cis-2-phenyl-cis-1-thiahydrindane is formed. 3-Alkyl(aryl)-cis-1-thiadecalins have been studied even less. In [1] only the preparation of 3-methyl-cis-1-thiadecalin (9 steps) from cyclohexanone and methyl methacrylate is presented. Introduction of other substituents is limited by the absence of α-substituted acrylic acids.

We have worked out simpler preparative methods for synthesis of 2- and 3-substituted cis-1-thiadecalins starting from 3-chloromethylcyclohexene (III) [4].

Heating of unsaturated thiols (VIII) and (XIII) with azobisisobutyronitrile (AIBN) led to sulfides (I) and (II) with high yields. The solvent plays an essential role. Thus, thiol (VIII, R = H) upon heating with AIBN in benzene is cyclized to cis-1-thiadecalin (I, R = H) and upon standing for 2 days without solvent it is transformed into a viscous polymer. This indicates preferential intermolecular addition, which is explained by steric hindrance in the thiabicyclic system formed by intramolecular cyclization. Purification of sulfides (I) and (II) was carried out according to [5]. Due to possible instability of alcohols {(VI) and (XI), R = Ph} and chlorides {(VII) and (XII), R = Ph} they were used without purification, which apparently explains the presence of impurities in the 2- and 3-phenyl-cis-1-thiadecalin.

The yields and properties of the intermediate and final products are shown in Tables 1-4. Alcohols (IV) and (IX) and chlorides (V) and (X) are described in [6]. The configurations of the 2- and 3-substituted cis-1-thiadecalins were assigned by ^{13}C NMR spectroscopy (Tables 5, 6). In the spectra of 2-alkyl-cis-1-thiadecalins signal assignments were based on their multiplicity and $^1J_{^{13}C-^1H}$ coupling constants (signals of C^2, C^9, C^{10} and CH_3 groups), by comparison of the spectra of 2-methyl- and 2-propyl substituted cis-1-thiadecalins (signals of C^2, C^3, and C^9), and by comparison of experimental and theoretical spectra. In the calculations chemical shifts of cis-1-thiadecalins [9] and increments of the Me groups in methylcyclohexanes [10] were used. Also, the spectral parameters of 2-alkyl-cis-1-thia- (I) and 2-methyl-cis-decalins [11] were compared. cis-1-Thiadecalins (I) and (II) exist in con-

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TABLE 1. 3-(3-Hydroxyalkyl)cyclohexenes (VI) and 3(3-Chloroalkyl)cyclohexenes (VII)

Compound*	Yield, %	Bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	Molecular formula	Found/calculated, %		
						C	H	Cl
(VI, R=H)	72	95(5)	1,4830	0,9442	$C_9H_{16}O$	76.75 / 77.09	11.35 / 11,50	–
(VI, R=Me)	68	95(5)	1.4806	0.9322	$C_{10}H_{18}O$	77,40 / 77,86	11.40 / 11.76	–
(VI, R=Pr)	62	109(3,5)	1,4767	0,9134	$C_{12}H_{22}O$	79,00 / 79,06	12.20 / 12,17	–
(VII, R=H) **	86	92–93(14)	1,4844	0.9903	$C_9H_{15}Cl$	–	–	22.2 / 22,35
(VII, R=Me)	67	80(5)	1,4790	0,9655	$C_{10}H_{17}Cl$	–	–	20.4 / 20.53
(VII, R=Pr)	75	108(5)	1,4809	0,9596	$C_{12}H_{21}Cl$	–	–	17,8 / 17,66

*GLC analysis: one peak.
**Obtained by action of $SOCl_2$ on primary alcohol (VI, R = H).

TABLE 2. cis-1-Thiadecalin and Its 2-R-Substituted Derivatives (I)

R	GLC elution order	Yield, %	Bp (mp), °C (p, mm Hg)	n_D^{20}	d_4^{20}	Molecular formula	Found/calculated, %		
							C	H	S
H*	–	67	86(5)	1,5295	1,0250	$C_9H_{16}S$	–	–	20,4 / 20,51
cis-Me:trans-Me mixture, 1.5:1	–	74	84(3)	–	–	$C_{10}H_{18}S$	–	–	18,7 / 18,82
cis-Me**	Peak 1	–	(4,5)	1.5168	0.9926	»	–	–	18,7 / 18,82
trans-Me**	Peak 2	–	(–78 glass)	1,5200	1,0000	»	–	–	18,5 / 18,82
cis-Pr:trans-Pr mixture, 1:1		60	103(3)	–	–	$C_{12}H_{22}S$	–	–	16.1 / 16,16
cis-Pr	Peak 1	–	(–1)	1,5110	0,9734	»	72,71 / 72,66	11.23 / 11,18	16,1 / 16,16
trans-Pr	Peak 2	–	(–78 glass)	1,5121	0,9771	»	72,68 / 72,66	11.16 / 11,18	16.0 / 16,16
cis-Ph***	–	–	156(3)	–	–	–	–	–	—

*GLC analysis: one peak; see [1].
**See [2, 7].
***According to ^{13}C NMR it contains ≈50% of an unidentified compound. According to [8] mp is 58–59°C.

formations A and B [9]. Calculations were carried out for each conformation (Table 5). Visible broadening of signals is not observed in the spectra of the Me-substituted thiadecalins, indicating no ring inversion at ~20°C. The data obtained, especially the positions of the C^2 and C^3 signals, allow unambiguous identification of the first 2-methyl-cis-1-thiadecalin peak (I, R = Me) as the cis-2-Me-isomer and the second peak as the trans-2-Me-isomer. The first isomer at ~20°C is mainly in conformation A and the second one in conformation B.

Assignment of signals in the ^{13}C NMR spectra of 2-propyl-cis-1-thiadecalins (I, R = Pr) was done analogously with calculation of "hydrocarbon" increments [12] for the C^2, C^3, and C^4 ring signals and the C_α- and C_β-propyl groups. The ^{13}C NMR spectrum of the 2-phenyl-cis-1-thiadecalins coincides with the chemical shifts reported in [8] for cis-2-phenyl-cis-1-thia decalin and also shows the presence of ≈50% of an unidentified compound. The data obtained confirm the conclusions about the GLC elution order and the configuration of 2-methyl-cis-1-thiadecalins made in [7].

TABLE 3. 3-(3-Hydroxy-2-alkylpropyl)cyclohexenes (XI) and 3(3-Chloro-2-alkylpropyl)cyclohexenes (XII)

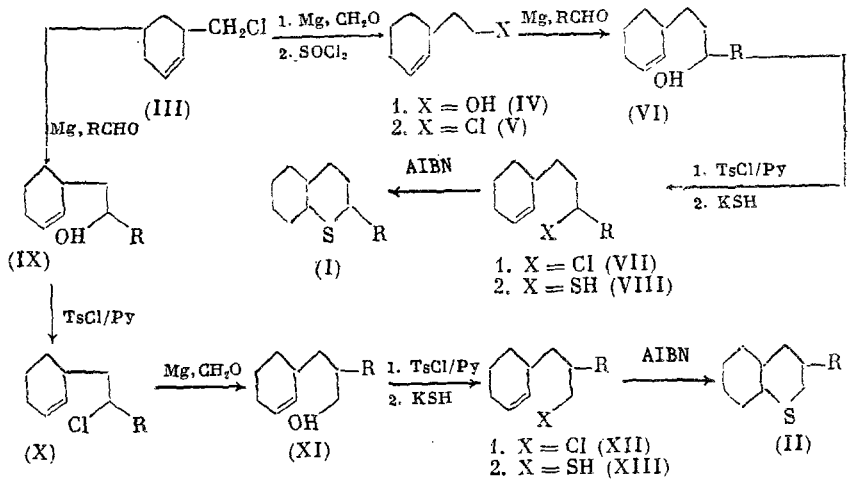
Compound	Yield, %	Bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	Molecular formula	Found/calculated, %		
						C	H	Cl
(XI, R=Me)	47	98(5)	1,4823	0.9325	$C_{10}H_{18}O$	77.74 77,86	11,72 11,76	–
(XI, R=Pr)	26	92(1,5)	1,4823	0.9229	$C_{12}H_{22}O$	79,27 79,05	12,19 12,17	–
(XII, R=Me) *	80	84(5)	1,4830	0.9779	$C_{10}H_{17}Cl$	–	–	20.6 20,53
(XII, R=Pr) *	72	97(3)	1,4835	0,9608	$C_{12}H_{21}Cl$	–	–	17,7 17,66

*GLC analysis: one peak.

TABLE 4. 3-R-Substituted cis-1-Thiadecalins (II)

R	GLC elution order	Yield, %	Bp (mp), °C (p, mm Hg)	n_D^{20}	d_4^{20}	Molecular formula	Found/Calculated, %		
							C	H	S
trans-Me: cis-Me mixture, 6:1*	–	69	85(3)	–	–	$C_{10}H_{18}S$	–	–	18.6 18.82
trans-Me*	Peak1	–	(10)	1.5165	0.9945	»	70.78 70,52	10,75 10,65	18.7 18.82
cis-Me*	Peak2	–	(32–33)	1.5168 **	0.9936 **	»	70.98 70,52	10.49 10.65	18.4 18.82
trans-Pr: cis-Pr mixture, 5:1	–	60	104–107(3)	–	–	$C_{12}H_{22}S$	–	–	15,6 16.16
Ph ***	–	–	137–145(2)	–	–	–	–	–	–

*See [1] for GLC elution order of isomers.
**At 32°C.
***Not isolated in pure state.



The 3-methyl-cis-1-thiadecalin chemical shifts coincide with known values from [9] (Table 6). From Table 2 it is seen that cis-2-methyl-cis-1-thiadecalin (I, R = cis-Me) has a lower boiling point, but a higher melting point, than the trans-2-Me-isomer. This, however, does confirm the assumption in [7] of applicability of the von Auwers-Skita rule to 2-alkyl-1-thiadecalins (I), according to which the cis-2-Me-isomer should have a lower boiling point than the 1,3-disubstituted cyclohexane.

TABLE 5. Values of ^{13}C NMR Chemical Shifts for 2-R-Substituted cis-1-Thiadecalins (I) and 2-Methyl-cis-decalins (δ, ppm)

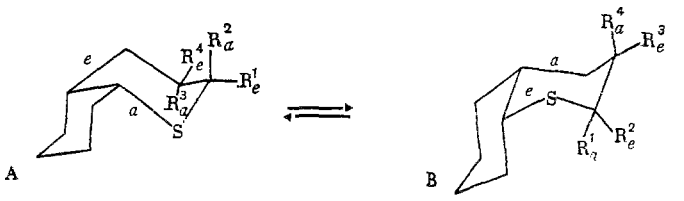
R, compound	Conformation	C² *	C³	C⁴	C⁵	C⁶	C⁷	C⁸	C⁹ *	C¹⁰	C (substituent)
cis-2-Methyl-cis-decalin [11]		33,9	30,2	32,9	26,3	27,5	21,4	32,9	36,6	36,1	23,1 (CH_3–)
cis-Me	A, Me-*e* (calculation)	35,5	30,0	32,5	24,4	26,7	20,9	31,9	43,1	35,7	
(peak 1)	A, Me-*e* (experiment)	38,46	30,32	32,77	24,35	26,54	20,67	31,50	43,54	35,25	21,35 (CH_3–)
cis-Pr	A, Pr-*e* (experiment)	43,36	28,63	32,73	24,40	26,52	20,69	31,64	43,63	35,87	C_α 38,28, C_β 19,55, C_γ 13,59
trans-2-Methyl-cis-decalin [11]		27,3	36,3	27,3	32,4	21,6	27,5	26,3	36,9	36,0	22,0 (CH_3–)
trans-Me	A, Me-*a* (calculation)	31,0	26,3	27,1	24,4	26,7	20,9	31,9	37,7	35,9	
"	B, Me-*e* (calculation)	29,2	37,2	24,9	34,2	19,6	28,3	27,3	40,4	36,4	
"	B, Me-*e* (experiment)	32,02	36,53	26,01	32,64	20,32	29,56	26,72	41,51	36,28	21,01 (CH_3–)
(peak 2)											
trans-Pr (peak 2)	B, Pr-*e* (experiment)	37,23	34,46	26,15	32,61	20,60	29,74	26,67	41,40	36,94	C_α 37,71; C_β 19,98; C_γ 13,80

*$^1J_{^{13}C-^1H}$ = 133-135 Hz; for the remaining signals: 124-127 Hz.

TABLE 6. ^{13}C NMR Chemical Shifts for 3-Methyl-cis-1-thiadecalins (II, R = CH_3) (δ, ppm)

Configuration	Conformation	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	CH_3
trans	A, Me-*e* [9]	36.63	27.07	41,43	26,01	26,74	21.40	31.45	42.78	37.42	22,50
trans (peak 1)	A, Me-*e* (experiment)	36,43	26,90	41,25	25,87	26,57	21,25	31.28	42.57	37.27	22,27
cis	B, Me-*e* [9]	30,70	34.85	(34.28)	(34,46)	19,93	28,56	27,50	40,01	37.81	23.10
cis (peak 2)	B, Me-*e* experiment)	30,60	34,72	(34,38)	(34,15)	19.82	28.44	27.37	39,91	37,77	22,96

For 3-methyl-cis-1-thiadecalin (II, R = Me) the trans-3-Me-isomer has the lower boiling and melting points {Table 4, (II, R = trans-Me)}. If we ignore the presence of a sulfur atom, which is assumed in [7], then the analog in both cases is the same 2-methyl-cis-decalin, and



(I): cis-R^1 (R^2, R^3, R^4=H); (I), trans-R^2 (R^1, R^3, R^4=H);
(II): cis-R^3 (R^1, R^2, R^4=H); (II), trans-R^4, (R^1, R^2, R^3=H)

the GLC elution order of the 2- and 3-substituted cis-1-thiadecalins should be the same. Since cis-2-methyl-cis-decalin [13] is lower boiling, both cis-2-Me- and cis-3-Me-cis-1-thiadecalin should elute first, which contradicts the facts. Assignments based on the von Auwers–Skita law in [7] turned out to be correct only by chance.

EXPERIMENTAL

^{13}C NMR spectra were recorded on Bruker WP-80 DS spectrometer with working frequency of 20.1 MHz in $CDCl_3$. Chemical shift values were converted to the δ-scale relative to TMS by the relation $\delta_{TMS} = \delta_{CDCl_3} + 76.90$ (ppm). Preparative GLC was carried out on a PAKhV-05 chromatograph with a series of 11 m long columns of from 25 to 6 mm diameter with 15% PEGA on INZ-600 as stationary phase and He as carrier gas. Purification of isomers from stationary phase impurities was carried out by freezing them out in a closed system consisting of two 5 ml glass vessels.

3-(3-Hydroxybutyl)cyclohexene (VI, R = Me). To the Grignard reagent obtained according to [14] from 115 g (0.8 mole) of 3-(2-chloroethyl)cyclohexene [6] and 24 g (1 g-atom) of Mg in 300 ml of abs. ether, a solution of 35 g (0.8 mole) of freshly prepared MeCHO in 50 ml of abs. ether was added over 10 min at 0°C. By the usual treatment there was obtained 83.6 g (68%) of alcohol (VI, R = Me) (Table 1).

3-(3-Chlorobutyl)cyclohexene (VII, R = Me). To 105 g (0.55 mole) of p-toluenesulfonyl chloride at 80°C was added with stirring a mixture of 77 g (0.5 mole) of alcohol (VI, R = Me) and 43 ml (0.55 mole) of dry Py [4] over 2 min. The reaction mixture was kept at 100°C for 80 min, cooled to 80°C, 50 ml of water was added at once, and cooled to ~20°C. The organic layer was separated and the water layer was extracted with hexane. By distillation on a column there was obtained 58 g (67%) of chloride (VII, R = Me) with bp of 120-125°C. Purification was carried out by heating with $NaHCO_3$ solution, washing with conc. HCl, and a second distillation (Table 1).

2-Methyl-cis-1-thiadecalin (I, R = Me). To a KSH solution, obtained by saturation with H_2S of an alcohol solution of 28 g (0.5 mole) of KOH at −4°C, 57 g (0.33 mole) of chloride (VII, R = Me) was added and the mixture was heated at 100°C for 1 h and then at 115°C for 1 h

in a stainless steel autoclave. After cooling the mixture was treated with water and the organic layer was separated, and the water–alcohol layer extracted with pentane (3 times by 10 ml). By distillation on a column there was obtained 50.5 g of a liquid with bp of 73-85°C (3 mm). The product was dissolved in 200 ml of benzene, 4 g of AIBN was added, and the mixture was heated for 4 h at 88°C in a stainless steel autoclave. By distillation on a column (8 theoretical plates) there was obtained 41.2 g (74%) of crude sulfide (I, R = Me) with bp of 78-81°C (3 mm). Purification was carried out according to [5] (Table 2).

3-(3-Mercaptopropyl)cyclohexene (VIII, R = H). 45 g (0.285 mole) of chloride (VII, R = H) and KSH solution, obtained by saturation with H_2S at −4°C of a solution of 24 g (0.43 mole) of KOH in 130 ml of ethanol, were placed in a stainless steel autoclave. The mixture was heated for 1 h at 100°C and then for 3 h at 125°C. After cooling the autoclave contents were treated with water, the organic layer was removed with hexane and distilled. There was obtained 40 g (90%) of crude thiol (VIII, R = H). In order to rid this of the cis-1-thiadecalin (I, R = H) impurity the product was treated with Na, the solid was washed with hexane, dissolved in methanol, acidified with HCl (1:1), extracted with hexane, and distilled. Thiol (VIII, R = H) is a liquid with bp of 85°C (5 mm), n_D^{20} 1.5105, d_4^{20} 0.9594. Found, S 20.2%. $C_9H_{16}S$. Calculated: S 20.51%.

cis-1-Thiadecalin (I, R = H). A solution of 21 g (0.13 mole) of thiol (VIII, R = H) and 2 g of AIBN in 60 ml of benzene was heated at 88-90°C for 4 h. After cooling the benzene was distilled off. To the residue 50 ml of heptane and 1.5 g of Na was added, and the mixture was heated for 1 h at 100°C. The solution was decanted from the precipitate, washed with heptane, the solvent was distilled off, and the residue was distilled under vacuum. After purification [5], there was obtained 12 g (57%) of cis-1-thiadecalin (I, R = H) (Table 2).

3-(3-Hydroxy-2-methylpropyl)cyclohexene (XI, Re = Me). Through the Grignard reagent obtained according to [14] from 73 g (0.46 mole) of chloride (X, R = Me) [4] and 16 g (0.67 g-atom) of Mg in 200 ml of abs. ether, anhydrous formaldehyde was passed at 0°C with vigorous stirring by heating 14 g (0.47 mole) of $(CH_2O)_x$ in a flask attached to the reaction flask. After the usual treatment and distillation of ether methanolysis of the resultant formal was carried out. By distillation under vacuum there was obtained 33.5 g (47%) of alcohol (XI, R = Me) (Table 3).

3-(3-Chloro-2-methylpropyl)cyclohexene (XII, R = Me). A mixture of 32 g (0.207 mole) of alcohol (XI, R = Me) and 18 ml (0.22 mole) of Py was added to 43 g (0.22 mole) of p-toluenesulfonyl chloride analogously to the described procedure for chloride (VII, R = Me). There was obtained 28.7 g (80%) of chloride (XII, R = Me) (Table 3).

3-Methyl-cis-1-thiadecalin (II, R = Me). 26.2 g (0.152 mole) of chloride (XII, R = Me) was heated with KSH in alcohol solution as described for sulfide (I, R = Me). After cyclization with AIBN there was obtained 17.8 g (69%) of sulfide with bp of 84°C (3 mm). After purification according to [5] there was obtained 14.8 g of 3-methyl-cis-1-thiadecalin (II, R = Me) (Table 4).

CONCLUSIONS

For the first time cis- and trans-2- and 3-alkyl-cis-1-thiadecalins were synthesized and some of their physical constants were examined.

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ACTIVATION OF CS_2 IN REACTION WITH BUTADIENE CATALYZED BY PALLADIUM COMPLEXES

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Recently we realized the catalytic activation of elemental sulfur using metal complex catalysts in reactions with 1,3-dienes. This allowed us to produce, in a single stage, unsaturated linear and cyclic sulfides [1-3].

Continuing our investigations of catalytic reactions taking place with the participation of small molecules and aiming at the preparation of difficult to obtain organic sulfur compounds, we carried out for the first time the heterocyclization of CS_2 with butadiene, a reaction catalyzed by palladium phosphine complexes. These complexes are widely used to activate CO_2, NH_3, H_2O, S, and SO_2 [1-10]. To prepare the catalyst, we used the $Pd(acac)_2$–PPh_3–$AlEt_3$ system.

We established that butadiene and CS_2, taken in a ratio 1:1 in toluene at 130°C, in the presence of the indicated catalytic system were converted to 1,3E,7Z-octatriene and $Ph_3P{=}S$. When this reaction was carried out in DMF, we obtained dicrotyl sulfide, whose yield was over 8% [10]. All our attempts to increase the yield by varying the reaction conditions as well as by using different activating ligands proved futile.

When we introduced into the reaction mass simultaneously CO_2 and NH_3 and when we substituted 1,2-bis(diphenylphosphino)ethane for Ph_3P (molar ratio Pd:diphos:CO_2:NH_3 = 1:1:300:500), we were able to obtain a mixture of saturated, six-membered 1,4-bis-sulfides and 1,4-bis-sulfoxides (I)-(IV) with an overall yield of 93% (DMF; 150°C; 20 h). In addition to (I)-(IV), whose ^{13}C NMR spectra are given in Table 1, we observed the formation of linear saturated sulfides (V)-(VI). The ratio (I)-(III):(IV):(V):(VI) = 25:67:1.5:6.5.

As can be seen, only three (Ia-c) of the theoretically possible eight stereoisomers of 2,3,5,6-tetramethyl-1,4-dithiocyclohexane were obtained in the conditions of our experiments. As concerns 2-ethyl-5,6-dimethyl-1,4-dithiocyclohexanes, they were represented by all four possible stereoisomers (IIa-d), and 2,5-diethyl-1,4-dithiocyclohexanes were identified as cis and trans isomers (IIIa) and (IIIb).

What attracted our attention was the circumstance that in all our experiments we observed the formation of saturated 1,4-dithianes, sulfides, and 1,4-bis-sulfoxides from butadiene and CS_2. Apparently, the NH_3 used in the reaction under heterocyclization conditions acted as a source of hydrogen atoms, and the formed unsaturated sulfides were reduced to the corresponding saturated compounds (I)-(VI) in the presence of palladium complexes. Concerning the formation of sulfoxides, it can be assumed that an oxidation reaction of 1,4-bis-sulfides (I) by CO_2 took place in our experiments under the influence of Pd complexes. These results can be explained if we take into consideration publications [10, 11], where it was shown that under mild conditions, CO_2 oxidized quantitatively Ph_3P to $Ph_3P{=}O$ in the presence of Pd complexes.

One question still remained unclear: it related to an increase in the catalytic activity of Pd complexes in the heterocyclization reaction when CO_2 and NH_3 were introduced simul-

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