three-membered ring and the formation of 30-80% of the corresponding methyl Z- and E-4-phenoxy-3-alkylbut-3-enoates.

2. 2,4-Dinitrophenol, butyl mercaptan, and 4-methylcyclohex-4-ene-1,2-dicarboximide on reaction with methyl 1-methylcyclopropene-3-carboxylate in the presence of 20-100 mole% of $CuCl \cdot 2MeC{\equiv}CSiMe_3$ do not give addition products, functioning merely as proton donors to give the methyl Z- and E-4-chloro-3-methylbut-3-enoates in yields of up to 60%.

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SYNTHESIS OF 2-ALKYL(ARYL)-cis-1-THIAHYDRINDANES

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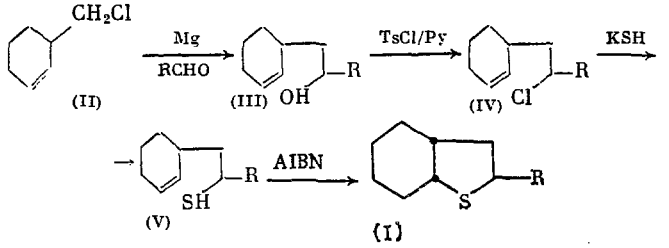
UDC 542.91:547.665

We have previously proposed [1, 2] a method of synthesis of 2-alkyl(aryl)-cis-1-thiahydrindanes (I), which affords (I) containing structural isomers as impurities. The reason for this was the presence in the starting 3-chloromethylcyclohexene (II) of 4-chlorocycloheptene, formed in the preparation of (II) from 3-hydroxymethyl cyclohexene and thionyl chloride. The later development [3] of a single-step tosylate method for the synthesis of the pure chlorides from alcohols prone to isomerization on chlorination with thionyl chloride enables (II) to be obtained very simply, without contamination by the structural isomer. This made it possible to synthesize 2-alkyl(aryl)-cis-1-thiahydrindanes (I) uncontaminated by bridged sulfides.



When R = H or Ph, the chlorination of the alcohol (III) is more conveniently carried out using thionyl chloride.

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2352-2357, October, 1988. Original article submitted May 18, 1987.

0568-5230/88/3710-2118$12.50

TABLE 1. 3-(2-Hydroxyalkyl)cyclohexenes (III) and 3-(2-Chloroalkyl)cyclohexenes (IV)

Compound	R	Yield, %	Bp, °C (p, mm)	n_D^{20}	d_4^{20}	Empirical formula	Found/Calculated, % C	H	Cl	Notes
(III)	H	57	110(23)	1.4840	0.9568	$C_8H_{14}O$	76.27 76.14	11.12 11.18		Pure (GC), cf. [4]
(III)	Me	52	86(6)	1.4828	0.9439	$C_9H_{16}O$	77.13 77.08	11.40 11.50		Pure (GC)
(III)	Pr	56	95(3)	1.4760	0.9168	$C_{11}H_{20}O$	78.52 78.51	11.75 11.98		Pure (GC)
(III)	Ph	62	132(2)	1.5490	1.0299	$C_{14}H_{18}O$	83.64 83.12	8.95 8.97		–
(IV)	H	78	85(23)	1.4850	1.0048	$C_8H_{13}Cl$			24.60 24.51	Pure (GC); obtained by reaction of (III) (R = H) with $SOCl_2$
(IV)	Me	61	63(5)	1.4786	0.9764	$C_9H_{15}Cl$			22.00 22.35	Pure (GC)
(IV)	Pr	70	91(5)	1.4777	0.9542	$C_{11}H_{19}Cl$			18.90 18.99	Pure (GC)
(IV)	Ph	64	132(3)	1.5493	1.0596	$C_{14}H_{17}Cl$			15.90 16.06	Obtained by treatment of (III) (R = Ph) with $SOCl_2$ at 5-7°C

TABLE 2. cis-1-Thiahydrindane and its 2-Substituted Derivatives (I)

R	Yield, %	Bp, °C (p, mm) (mp, °C)	n_D^{20}	d_4^{20}	Empirical formula
H	93	103(23)	1.5303	1.0379	$C_8H_{14}S$
Me (mixture of cis- and trans-isomers)	77	79(5)	1.5155	0.9969	$C_9H_{16}S$
Me (trans-isomer) (peak 1)	–	–	1.5148	0.9977	$C_9H_{16}S$
Me (cis-isomer) (peak 2)	–	–	1.5165	0.9963	$C_9H_{16}S$
Pr (mixture of cis- and trans-isomers)	87	94(5)	1.5077	0.9707	$C_{11}H_{20}S$
Pr (trans-isomer) (peak 1)	–	–	1.5070	0.97	$C_{11}H_{20}S$
Pr (cis-isomer) (peak 2)	–	–	1.5085	0.97	$C_{11}H_{20}S$
Ph (mixture of cis- and trans-isomers)	64	144(2)	–	–	$C_{14}H_{18}S$
Ph (trans-isomer)	–	(99)	–	–	$C_{14}H_{18}S$
Ph (cis-isomer)	–	(67)	–	–	$C_{14}H_{18}S$

R	Found/Calculated, % C	H	S	Notes
H			22.60 22.54	Pure (GLC); cf. [5]
Me (mixture of cis- and trans-isomers)			20.30 20.52	GLC; two peaks (1:1)
Me (trans-isomer) (peak 1)			20.60 20.52	Contains ≈ 10% Me (cis) (from ^{13}C NMR)
Me (cis-isomer) (peak 2)			20.40 20.52	Pure (GLC and ^{13}C NMR)
Pr (mixture of cis- and trans-isomers)			17.30 17.39	GLC; two peaks (1:1)
Pr (trans-isomer) (peak 1)				Contains ≈ 15 % of Pr (cis) (from ^{13}C NMR)
Pr (cis-isomer) (peak 2)				Contains ≈ 25% Pr (trans) (from ^{13}C NMR)
Ph (mixture of cis- and trans-isomers)				–
Ph (trans-isomer)	77.24 77.01	8.34 8.31	14.50 14.68	Pure (^{13}C NMR)
Ph (cis-isomer)	76.86 77.01	8.06 8.31	14.80 14.68	Contains ≈ 10% (trans) (^{13}C NMR)

TABLE 3. Chemical Shifts in PMR Spectra of 2-Alkyl(aryl)-cis-1-thiahydrindanes (I), δ, ppm*

R	H^2	H^3_e	H^3_a	H^4	H^5	CH_3
trans-Me (peak 1)	3.56	2.00	≈1.50	2,22	3.62	1.27
cis-Me (peak 2)	3.50	1.92	1.69	2,35	3.13	1.35
trans-Ph (mp 99°C)	4.65	2.26	1.98	2,40	3.96	–

*Internal standard TMS, solvent $CDCl_3$.

TABLE 4. Coupling Constants in the PMR Spectra of 2-Alkyl(aryl) cis-1-thiahydrindanes (I) (J, Hz)

R	$H^2-H^3_e$	$H^2-H^3_a$	$H^4-H^3_e$	$H^4-H^3_a$	H^4-H^9	$H^4-H^5_e$	$H^4 H^5_a$	$H^9-H^8_e$	$H^9 H^8_a$	$H^3_e H^3_a$	$H^{Me}-H^2$
trans-Me	7,1	7.1	5,0	5	5	5	8,5	4.5–5,0	4.5–5.0	12,5	6,6
cis-Me	6,6	10.0	5.4	12,8	6.5	3,0	5–6	5,4	11.2	12,8	6,6
trans-Ph	7,3	8,9	3,7	5,1	4,5	4,5	9	4–5	4–5	12,7	–

TABLE 5. ^{13}C NMR Chemical Shifts of cis-1-Thiahydrindane and 2-Alkyl(aryl)-cis-1-thiahydrindanes (I), δ*

R in (I)	C²**	C³	C⁴	C⁵	C⁶
H (calculated)	33	35	41	23.0	26.0
H (found)	29.00	33.68	42.23	22.99	25.46
trans-Me	40.62	43,22	42.26	23,19	25.88
trans-Pr	46.54	41,62	42,22	23.56	25.99
trans-Ph***	50.65	45.37	43.14	23.75	25.99
cis-Me	42.19	40,05	43.79	34,09	21.12
cis-Pr	46.47	37,61	43,94	33,70	20,82
cis-Ph***	51,75	41.01	43,76	34,21	20.94
1-Thiadecalin (form A) [5]	–	–	–	24,4	26.7
1-Thiadecalin (form B) [5]	–	–	–	34,2	19,6

R in (I)	C⁷	C⁸	C⁹**	C (substituent)
H (calculated)	21.0	28.5	47	
H (found)	21.45	29.10	46.94	
trans-Me	20.82	28.58	48.00	23,19
trans-Pr	20.64	28.43	47.24	C_α 40,65, C_β 21,62, C_γ 13,38
trans-Ph***	20.54	28.21	49.28	
cis-Me	27,38	25.65	47.93	23.26
cis-Pr	27,15	25,37	47.40	C_α 40,61, C_β 21,85, C_γ 13,31
cis-Ph***	27,28	25.86	47,98	
1-Thiadecalin (form A) [5]	20.9	31.9	–	–
1-Thiadecalin (form B) [5]	28,3	27.3	–	–

*The chemical shifts were measured relative to the signal of the solvent ($CDCl_3$), and recalculated in the δ-scale relative to TMS using the relationship $\delta_{TMS} = \delta_{CDCl_3} + 76.90$ ppm.

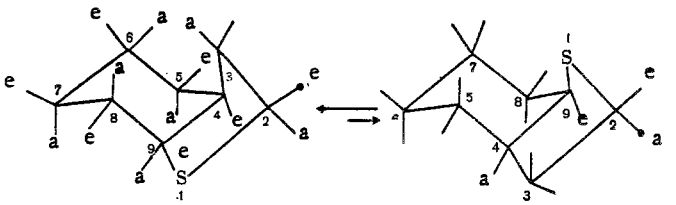
**$^1J_{^{13}C,^1H} \geq 135$ Hz (measured from the means of the multiplets).

***The ^{13}C chemical shifts in the aromatic ring are not given.

The use of azobisisobutyronitrile (AIBN) in benzene facilitates the cyclization of the thiol (V), prevents intermolecular addition, and increases the yields of the required sulfide (I) to 64-93%. The yields and properties of the intermediates are given in Table 1, and those of the final sulfides in Table 2. Separation of the sulfides isomeric in the positions of the substituent R was carried out by preparative GLC.

The isomers of the high-boiling 2-phenyl-cis-1-thiahydrindane were separated by fractional crystallization from methanol and hexane.

The configurations of the new 2-alkyl(aryl)-cis-1-thiahydrindanes (I) were established by ^1H (Tables 3 and 4) and ^{13}C NMR (Table 5). Partial assignment of the signals in the PMR spectra of both isomers (I, R = Me) and the higher-melting isomer of (I, R = Ph) were made from the chemical shifts and double homonuclear resonance experiments. In the higher-melting isomer of the sulfide (I, R = Me), H^9 in the cyclohexane ring is axial, with $^3J_{H^9,H_a^8} = 11.2$ Hz, and H^4 is equatorial, with $^3J_{H^9,H^4} = 6.5$ and $^3J_{H^4,H_a^5} \leq 6$ Hz, confirming the cis-fusion of the rings and the fixed conformation of the cis-2-methyl-cis-1-thiahydrindane (I, R = Me) molecule, which is present in solution in form B:



B A

The absence of broadening of the signals in the PMR spectra indicates the absence of ring inversion at ~20°C. The coupling constants of H^4 with H_a^3 and of H^2 with H_a^3 show that H^4 and H^2 are oriented pseudoaxially in the cyclopentane ring. Similar consideration of the other two compounds showed that the lower-boiling (peak 1) sulfide (I, R = Me) is trans-2-methyl-cis-1-thiahydrindane, and the higher-melting sulfide (I, R = Ph) is trans-2-phenyl-cis-1-thiahydrindane, both of these compounds existing preferentially in form A, and no ring inversion was observed under the conditions of recording the spectra.

Assignment of the signals for C^2, C^3, C^4, and C^9 in the ^{13}C NMR spectra of the sulfides (I) (Table 5) was made from the multiplicity and coupling constants $^1J_{^{13}C,^1H}$, and by comparing the chemical shifts of all the compounds examined taking into account increments for the phenyl group [6] and 'hydrocarbon' increments [7]. Assignment of the remaining signals was carried out from information on the ^{13}C chemical shifts of the hydrocarbon ring in 1-thiadecalins taking into account PMR data on the conformation of the rings [8]. The presence in all the spectra of signals for the CH_2 group at δ around 21 ppm confirms the cis-coupling of the rings.

The orientation of the substituents was established by comparing the chemical shifts of the signals for C^3 and C^4 in the spectra of the propyl- and phenyl-substituted thiahydrindanes (I, R = Pr or Ph) with the spectra of the 2-methyl-cis-1-thiahydrindanes (I, R = Me). It will be seen from Table 5 that all the trans-2-R-isomers exist in solution preferentially in form A, and the cis-isomers in form B [8].

In the PMR spectrum of cis-2-phenyl-cis-1-thiahydrindane (I, R = cis-Ph), the broadening of the signals indicates ring inversion at ~20°C, whereas the ^{13}C NMR spectrum of this isomer shows only slight broadening of the signal for C^5.

In the PMR spectrum of cis-1-thiahydrindane (I, R = H), the coupling constants of H^9 with H^4 and of H_a^8 with H_e^8 are approximately the same (~5 Hz). Hence, cis-1-thiahydrindane exists preferentially in form A (H^9 is equatorial in the cyclohexane ring), so that the chemical shifts in its ^{13}C NMR spectra can be calculated from the data for trans-2-methyl-cis-1-thiahydrindane and the 'methyl' increments for cyclopentanes [9] (Table 5). Comparison of the observed values of the chemical shifts with the calculated values, together with the multiplicity and $^1J_{^{13}C,^1H}$ coupling constants, enables the assignment of signals given in Table 5 to be carried out. The considerable departure of the measured value of δ for C^2 from the calculated value is similar to that found on comparing the calculated with the measured values for the chemical shifts for C^2 in thianes, if the increments for methyl groups in cyclohexanes are used [10]. The synthesis of cis- and trans-2-methyl-cis-1-thiahydrindanes is described in the Experimental. The other sulfides were obtained similarly.

EXPERIMENTAL

PMR spectra were recorded on a Bruker WM-400 spectrometer, operating frequency 400 MHz, and ^3C NMR spectra on a Bruker WP-80DS, operating frequency 20.1 MHz. Preparative GC

was carried out on a PAKhV-05 chromatograph with a set of tubes with diameters from 25 to 6 mm, and an overall length of 11 m, stationary phase 15% PEGA on IN3-600, carrier gas helium.

3-(2-Hydroxypropyl)cyclohexene (III, R = Me). To 42 g (1.75 g·atom) of magnesium turnings in 200 ml of dry ether was added, following activation with 2 ml of methyl iodide, over 20 min a solution of 200 g (1.54 moles) of 3-chloromethylcyclohexene (II) [3] in 200 ml of dry ether, with periodic cooling of the mixture with ice-salt. When spontaneous boiling of the mixture ceased (30 min), it was heated for 15 min, cooled to 0°C, and a solution of 68 g (1.54 moles) of freshly-redistilled acetaldehyde in 50 ml of dry ether added over 20 min. The mixture was stirred for 5 min, and decomposed with dilute (1:1) HCl. Working up in the usual way gave 123 g (57%) of (III, R = Me) (Table 1).

3-(2-Chloropropyl)cyclohexene (IV, R = Me). To 124 g (0.65 mole) of toluene-p-sulfonyl chloride was added at 80°C over 2 min with stirring a mixture of 77 g (0.55 mole) of (III, R = Me) and 47.5 g of dry pyridine. The reaction was slightly exothermic. Eight minutes after mixing the reactants, an oil separated (pyridinium toluene-p-sulfonate). The mixture was held at 100°C for 80 min, then cooled to 80°C, 50 ml of water added immediately, and cooled. The upper organic layer was separated, and the aqueous layer washed with hexane. Fractionation through a column (8 theor. plates) gave 53 g (61%) of the chloride (IV, R = Me), bp 63°C (5 mm). It was purified by dissolving in an equal volume of acetone, followed by the addition of two volumes of conc. HCl (Table 1).

2-Methyl-cis-1-thiahydrindane (I, R = Me). To an alcoholic solution of KSH, obtained by saturating 23 g (0.41 mole) of KOH in 130 ml of ethanol with H_2S at −4°C, was added 43.3 g (0.27 mole) of the chloride (IV, R = Me), and the mixture kept for 1 h at 100°C, then for 1 h at 125°C in a stainless steel autoclave. The mixture was then cooled, treated with water, the organic layer separated, and the aqueous-organic layer extracted wtih pentane (3 × 10 ml). Fractionation gave 35 g of product, bp 95-97°C (15 mm). A solution of this (27 g) in 60 ml of benzene was treated with 2.7 g of AIBN, and the mixture heated for 4 h at 88°C. Fractionation gave 25 g (77%) of the sulfide (I, R = Me), bp 94°C (15 mm) or 79°C (5 mm). Purification was carried out by the uniform addition of 5 ml of conc. HBr over 40 min to a mixture of the sulfide with 5 ml of PBr_3 at 120°C. On cooling, the organic layer was separated and the product distilled in vacuo. Final purification was effected by heating with sodium at 120°C until the mirror surface of the sodium persisted. The product was decanted from the sodium, the slurry mixed with hexane, and the hexane solution added to the main portion of the sulfide and fractionated (Table 2).

The authors thank I. I. Chervin for help in obtaining and interpreting the spectra.

CONCLUSIONS

1. cis- and trans-2-Alkyl(aryl)-cis-1-thiahydrindanes have been obtained for the first time free from traces of structural isomers.

2. cis-1-Thiahydrindane and trans-2-alkyl(aryl)-cis-1-thiahydrindanes are present in solution predominantly in conformations in which H^9 is equatorial in the cyclohexane ring, whereas cis-2-alkyl(aryl)-cis-1-thiahydrindanes have the conformation in which H^9 is axial.

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