for 20 min, after which it was cooled and diluted with 20 ml of absolute ether, and the crystalline precipitate was removed by filtration and recrystallized from 15 ml of glacial acetic acid to give 1.4 g (75%) of double salt VI in the form of black crystals with mp 225-226°C. UV spectrum (chloroform), λ_{max} (log ε): 565 (3.54) and 655 nm (3.57). Found: C 65.1; H 4.0; Cl 9.4%. $C_{41}H_{28}Cl_2O_{10}$. Calculated: C 65.5; H 3.8; Cl 9.4%.

2,6-Diphenyl-4H-pyran (VII). This compound was isolated by the method in [4] in the form of colorless crystals with mp 89-90°C.

2,6-Diphenyl-4-(1,2-diphenylbenzo[b]cyclopenta[e]-3-pyrania)pyrylium Perchlorate (VIII). A mixture of 0.75 g (1 mmole) of double salt VI, 0.08 g (1 mmole) of sodium acetate, and 10 ml of glacial acetic acid was heated to the boiling point, after which it was cooled, diluted with 10 ml of absolute ether, and worked up to give 0.59 g (91%) of perchlorate VIII in the form of black crystals with mp 204-205°C. UV spectrum (chloroform), λ_{max} (log ε): 532 (3.89), 566 (4.07), 653 (3.87), and 714 nm (3.98). Found: C 75.3; H 4.4; Cl 5.6%. $C_{41}H_{27}ClO_6$. Calculated: C 75.6; H 4.2; Cl 5.5%.

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NEW METHOD FOR THE SYNTHESIS OF cis-2-THIAHYDRINDANE DERIVATIVES*

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A new method was worked out for the stereospecific synthesis of derivatives of cis-1,3-disubstituted cis-2-thiahydrindanes; the method is based on the reaction of sulfur dichloride with cis-1,2-divinylcyclohexane and is distinguished by its simplicity and high yields. It was established that two stereoisomeric sulfoxides that differ only with respect to the orientation of the sulfoxide oxygen atom are formed in the oxidation of cis-1,3-dichloromethyl-2-thiahydrindane. The structures of cis-1,3-dichloromethyl-cis-2-thiahydrindane and its oxidation products were studied by ^{1}H NMR spectroscopy, ^{1}H NMR spectroscopy with the addition of a shift reagent [tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)europium], and ^{13}C NMR spectroscopy.

Thiahydrindane derivatives are difficult to obtain [2, 3]. The available literature data make it possible to arrive at the judgement that the methods for the synthesis of thiahydrindanes are extremely laborious and inadequate.

We have developed a new method for the synthesis of 1,3-disubstituted cis-2-thiahydrindane that is distinguished by its simplicity, high yields, and stereospecificity. The method is based on the reaction of SCl_2 with cis-1,2-divinylcyclohexane, which is a completely

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accessible compound [4]. The addition of SCl_2 to divinylcyclohexane takes place exceptionally readily in dichloromethane at —50 to —60°C and gives cis-1,3-bis(chloromethyl)-2-thiahydrindane (I) in ~70% yield.

In the discussion of the stereochemistry of the new compound one must note that the sufficiently substantiated conclusion that the rings are cis-fused follows from the very fact of the use of cis-1,2-divinylcyclohexane as the starting compound; however, the definitive solution of the problem requires additional data.

The PMR spectrum is not very informative, since the protons of the HCS and HCCl fragments form a system with a high degree of coupling (at 3.23-3.67 ppm). The ^{13}C NMR spectrum contains five groups of signals corresponding to the paired carbon atoms 5-C and 6-C (23.17 ppm), 4-C and 7-C (25.89 ppm), 9-C and 8-C (44.82 ppm), and 1-C and 3-C (52.17 ppm), and two carbon atoms of the chloromethyl groups (47.22 ppm). It is apparent that the spectrum corresponds to the proposed symmetrical structure.

The proof of the structures of the products of the oxidation of I is a separate problem, since instances of rearrangement of the carbon skeleton have been noted in the case of the oxidation of chloro sulfides [1, 5]. Two isomeric sulfoxides (II and III) in a ratio of 10:1 were obtained in the oxidation of I with tert-amyl hydroperoxide (V) in the presence of $MoCl_5$ by the method in [6]. The isomers differ with respect to their polarities during chromatography in a thin layer of Al_2O_3 [elution with benzene—ethanol (9:1)]. The subsequent oxidation of both compounds gives the same sulfone — cis-1,3-bis(chloromethyl)-2-thiahydrindane-2,2-dioxide (IV) — a fact that indicates that the sulfoxides are stereoisomers that differ only with respect to the orientation of the sulfoxide oxygen atom.

Sulfoxide III was also obtained in quantitative yield by inversion of sulfoxide II by means of triethyloxonium tetrafluoroborate by the method in [7]. The PMR spectra of both sulfoxides completely definitively indicate a cis-disubstituted thiahydrindane structure: The two-proton signal corresponds to the HCS fragment, and the four-proton signal corresponds to the HCCl fragment (Fig. 1, spectra b and c). The same conclusion also follows from an examination of sulfone IV (Fig. 1, spectrum e). A comparison of the spectra shows that the protons of the CH_2Cl group of the sulfoxides are not equivalent, whereas they are equivalent in the sulfide and sulfone.

In the spectrum of the sulfone these signals appear in the form of one doublet with J_{AX} = 7 Hz. The signals of the 1-H and 3-H protons in the spectrum of sulfone IV form an AX_2Y system with $J_{AX} \approx J_{AY} \approx$ 6-7 Hz.

The 1-H and 3-H signals and the signal of the CH_2Cl groups in the PMR spectrum of sulfoxide II form an AA'X system that is difficult to analyze. When a shift reagent (tris(1,1-1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)europium [Eu(fod)$_3$]) is added, the pattern of the signals is simplified and is an ABX system, from which it is easy to determine the spin—spin coupling constants (SSCC) ($J_{AA'}$ = 12 Hz, J_{AX} = 5.5 Hz, $J_{A'X}$ = 5 Hz, δ_A 3.69 ppm, and δ_B 3.88 ppm) (Fig. 1, spectrum d). The chemical shifts of the A and B nuclei ($\Delta\delta$ 0.19 ppm) are determined by extrapolation of the shift reagent concentration to zero. The 1-H and 3-H signals and the signal of the CH_2Cl groups are shifted at different rates with retention of the SSCC. In the final analysis, when the ratio of Eu(fod)$_3$ to II is 0.2, the shifts of the A and B protons correspond to δ_A 4.80 ppm and δ_B 4.42 ppm ($\Delta\delta$ 0.4 ppm). The difference in the chemical shifts of these protons and the different rates of shift of their signals prove the nonequivalence of the AB protons.

It can be seen from the graph in Fig. 2 that the rate of shift of the signals of the angular protons of sulfoxide II is comparable to the rate of shift of the signals of the protons of the CH_2Cl groups. The angular hydrogen atoms and the protons of the CH_2Cl groups consequently are located on the same side of the cyclopentane ring. The signals of both angular protons are shifted at the same rate — a fact that confirms cis fusion of the rings. Since the signals of the 1-H and 3-H protons are shifted identically, one may conclude that the CH_2Cl groups are cis-oriented. It follows from the slopes of the lines corresponding to the shift of the signals of CH_2Cl and the 3-H and 1-H protons that the 1-H and 3-H protons are located on the same side as the SO group, whereas the CH_2Cl groups are located on the other side with respect to the "plane" of the cyclopentane ring. In addition, of the group of cyclohexane protons, two are shifted at a rate comparable to the rate of shift of the

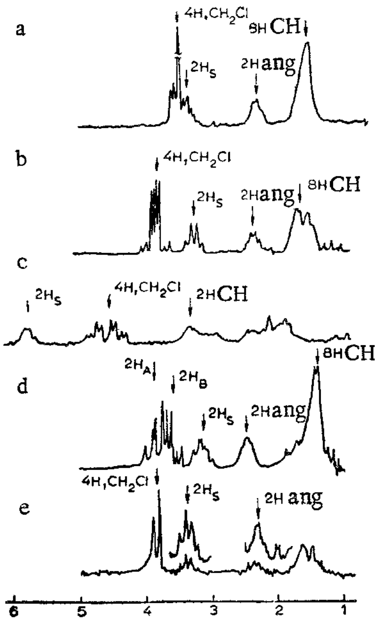


Fig. 1

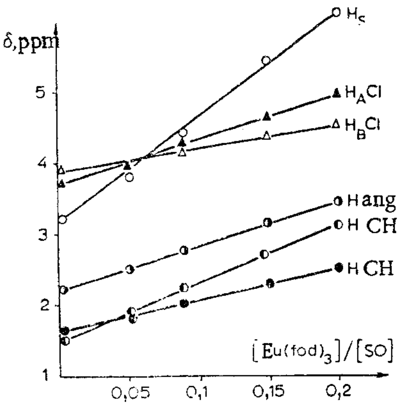
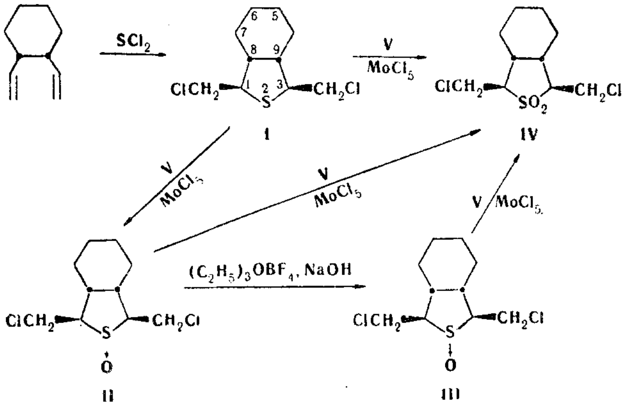


Fig. 2

Fig. 1. PMR spectra: a) cis-1,3-bis(chloromethyl)-2-thiahydrindane (I); b) cis-1,3-bis(chloromethyl)-2-thiahydrindane 2-oxide (II); c) cis-1,3-bis(chloromethyl)-2-thiahydrindane 2-oxide (II) in the presence of $Eu(fod)_3$; d) cis-1,3-bis-(chloromethyl)-2-thiahydrindane 2-oxide (III); e) cis-1,3-bis(chloromethyl)-2-thiahydrindane 2,2-dioxide (IV).

Fig. 2. Dependence of the chemical shifts (δ) of the protons of cis-1,3-bis(chloromethyl)-2-thiahydrindane 2-oxide (II) on the ratio of the $Eu(fod)_3$ concentration to the sulfoxide concentration.

angular protons. This fact, together with the data from the ^{13}C NMR spectra, indicates high symmetrical character of 2-thiahydrindane derivatives.



It is apparent from Fig. 3 that the SO group in the III molecule is located on the same side as the chloromethyl substituents, since the rate of shift of the signals of the protons of the CH_2Cl groups is greater than the rate of shift of the protons attached to the sulfur atom. In addition, this finds confirmation in the fact that the signals of the angular protons (8-C—9-C) are well resolved in the spectrum of sulfoxide II, whereas the signals of the protons of the CH_2Cl groups are well-resolved in the spectrum of sulfoxide III. The latter signals in the spectrum of sulfoxide III, even without the addition of the shift reagent, appear as a well-resolved AB portion of an ABX system with δ_A 3.85 ppm and δ_B 3.57 ppm (J_{AB} = 24 Hz, J_{AX} = 9 Hz, and J_{BX} = 5.5 Hz). The ^{13}C spectra of both sulfoxides, which each contain five groups of signals (Table 1), not only indicate high symmetrical character of the

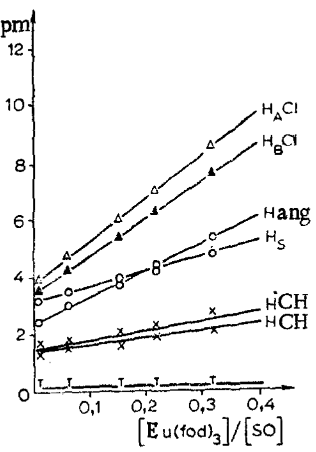


Fig. 3

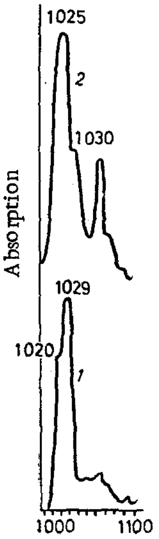


Fig. 4

Fig. 3. Dependence of the chemical shifts (δ) of the protons of cis-1,3-bis(chloromethyl)-2-thiahydrindane 2-oxide (III) on the ratio of the $Eu(fod)_3$ concentration to the sulfoxide concentration.

Fig. 4. IR spectra in the region of the absorption of the SO group: 1) cis-1,3-bis(chloromethyl)-2-thiahydrindane 2-oxide (II); 2) cis-1,3-bis(chloromethyl)-2-thiahydrindane 2-oxide (III).

molecule but also make it possible to assign the structure unambigously. Thus in the spectrum of sulfoxide II the 3-C and 1-C atoms resonate at weaker field; this may be associated with the effect of the closely located sulfoxide oxygen atom. It is interesting to note that differences in the IR spectra of the sulfoxides that are displayed distinctly in the region of the stretching vibrations of the SO group (Fig. 4), as well as the unusually low-frequency position of the SO band.

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a Tesla BS-478-B spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The ^{13}C NMR spectra were recorded with a Bruker WH-90 spectrometer (22.63 MHz). The mass spectra were recorded with an MKh-1303 spectrometer with electron energies up to 70 eV. The course of the reactions was monitored by thin-layer chromatography (TLC) on activity II Al_2O_3 in a benzene–ethanol system (9:1).

cis-1,3-Bis(chloromethyl)-cis-2-thiahydrindane (I). A solution of 41.2 g (0.4 mole) of SCl_2 in 150 ml of CH_2Cl_2 was added dropwise with stirring at −50 to −60°C in the course of 1.5 h to a solution of 54.4 g (0.4 mole) of cis-1,2-divinylcyclohexane in 750 ml of anhydrous CH_2Cl_2, after which the reaction mixture was maintained at −50 to −30°C for 1-1.5 h. The solvent was then removed by vacuum evaporation, and the residue was crystallized from anhydrous hexane to give 67 g (70%) of I with mp 82-82.5°C. Found: C 50.4; H 6.6; Cl 30.0; S 13.2%; M^+ 238. $C_{10}H_{16}Cl_2S$. Calculated: C 50.2; H 6.7; Cl 29.7; S 13.4%; M 239. IR spectrum: 725 (C—Cl) and 690 cm^{-1} (C—S). PMR spectrum (CCl_4): 1.37-1.83 (m, 8H, CH_2), 2.32 (m, 2H, angular), and 3.76 ppm (m, 6H, HCS, CH_2Cl).

cis-1,3-Bis(chloromethyl)-cis-2-thiahydrindane 2-Oxides (II, III). A solution of 6.62 ml (0.063 mole) of a 92% solution of V in 50 ml of benzene containing a catalytic $MoCl_5$ additive was added slowly dropwise to a solution of 1.5 g (0.063 mole) of I in 100 ml of anhydrous benzene, after which the benzene was removed gradually by distillation. At the end of the reaction, the benzene solution was washed with water and dried with magnesium sulfate. The benzene was partially removed, and the residual mixture was worked up to give 14.1 g (85%) of sulfoxide II. The residue (2 g) was a mixture of sulfoxides II and III, from which pure

TABLE 1. ^{13}C NMR Spectra of I-IV (δ, ppm)

Compound	C—S	C—H ang	CH_2(C-4, C-7)	CH_2(C-5, C-6)	CH_2Cl
I[a]	52,17 d	44,82 d	25,89 t	23,17 t	47,22 t
II[b]	66,22 d	39,52 d	27,51 t	22,85 t	41,85 t
III[b]	72,99 d	41,53 d	26,97 t	22,95 t	41,53 t
IV[c]	66,70 d	38,14 d	26,61 t	22,21 t	40,86 t

a) In CCl_4. b) In $CDCl_3$. c) In DMF.

II or III could not be isolated by crystallization. Sulfoxide II, with mp 92-93°C and R_f 0.58, was hygroscopic. Found: C 47.0; H 6.2; Cl 27.9; S 12.4%; M^+ 254. $C_{10}H_{16}Cl_2OS$. Calculated: C 47.0; H 6.3; Cl 27.8; S 12.5%; M 255. IR spectrum: 732 (C—Cl), 680 (C—S), and 1020-1029 cm^{-1} (SO). PMR spectrum ($CDCl_3$): 1.30-1.87 (m, 8H, CH_2), 2.17 (m, 2H, angular), 3.30 (m, 2H, HCS), and 3.70-3.84 ppm (m, 4H, CH_2Cl).

Inversion of Sulfoxide II to Isomer III. An 8-g (0.031 mole) sample of II was dissolved in 50 ml of anhydrous CH_2Cl_2, 5.96 g (0.031 mole) of triethyloxonium tetrafluoroborate [8] was added, and the mixture was allowed to stand at room temperature for 24 h. The solvent was then removed by evaporation, and the residue was crystallized from diethyl ether to give 9.9 g (91%) of the product of alkylation of sulfoxide II with mp 95-98°C. A 9.8-g sample of this product was dissolved in 19 ml of dioxane, and 34 ml of a 5% aqueous solution of NaOH was added dropwise with stirring. The resulting crystals were washed with cold water and recrystallized from benzene to give 5.9 g (74%) of sulfoxide III with mp 98.5-99.5°C and R_f 0.69. The product was not hygroscopic. Found: C 47.1; H 6.2; Cl 28.0; S 12.5%; M^+ 254. $C_{10}H_{16}Cl_2OS$. Calculated: C 47.0; H 6.3; Cl 27.8; S 12.5%; M 255. IR spectrum: 730 (C—Cl), 655 (C—S); 1025 and 1030 cm^{-1} (SO). PMR spectrum ($CDCl_3$): 1.25-1.80 (m, 8H, CH_2), 2.44 (m, 2H, angular), 3.13 (m, 2H, HCS), and 3.57-3.87 ppm (m, 4H, CH_2Cl).

cis-1,3-Bis(chloromethyl)-cis-2-thiahydrindane 2,2-Dioxide (IV). A solution of 11 ml (0.10 mole) of a 92% solution of V in 50 ml of anhydrous benzene containing a catalytic $MoCl_5$ additive was added dropwise to a solution of 12 g (0.05 mole) of I in 100 ml of anhydrous benzene, after which the benzene solution was washed with water and dried over magnesium sulfate. The solvent was removed by vacuum evaporation, and the residue was crystallized from benzene to give 12.65 g (93%) of sulfone IV with mp 160-160.5°C and R_f 0.77. Found: C 44.4; H 5.9; Cl 25.9; S 11.8%; M^+ 270. $C_{10}H_{16}Cl_2O_2S$. Calculated: C 44.3; H 5.9; Cl 26.2; S 11.8%; M 271. IR spectrum: 730 (C—Cl), 690 (C—S), and 1310 and 1120 cm^{-1} (SO_2). PMR spectrum (DMF): 1.42-1.87 (m, 8H, CH_2), 2.36 (m, 2H, angular), 3.43 (m, 2H, CHS), and 3.82-4.20 ppm (m, 4H, CH_2Cl).

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