[Contribution from the Research Station, Anglo-Iranian Oil Company Limited]

PREPARATION AND PHYSICAL PROPERTIES OF SULFUR COMPOUNDS RELATED TO PETROLEUM. IV. *cis*- AND *trans*-2-THIAHYDRINDAN AND 2-THIADECALIN

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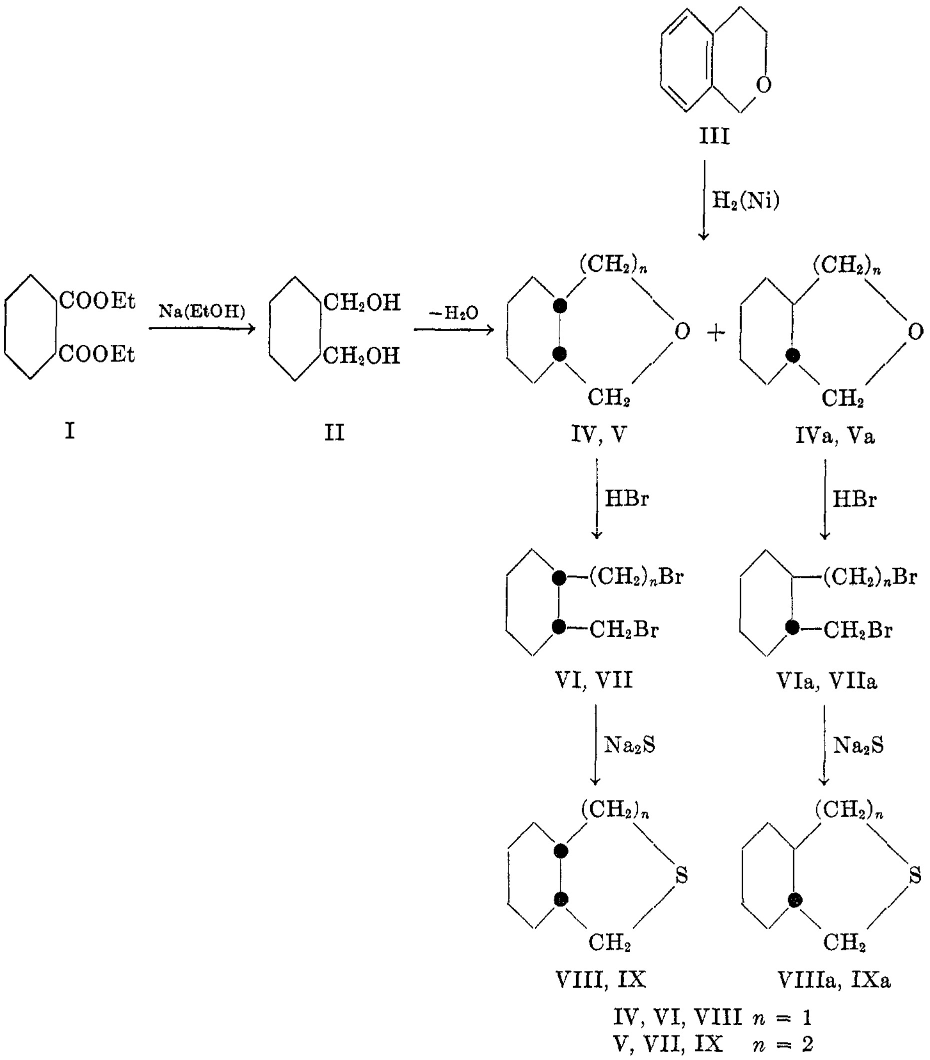
The presence of bicyclic sulfides has been reported in certain oils of West Texas origin (1) and in the sulfur compounds obtained by the acid treatment of an aromatic kerosine extract derived from Agha Jari (S. Persia) crude oil (2). From their properties, these sulfides resemble the thia-derivatives of bicyclo[3.3.0]octane, hydrindan, and decalin rather than semi-aromatic compounds derived from hydrindene or tetralin. This is consistent with the presence of thiacyclopentane and thiacyclohexane derivatives in the corresponding distillates of the gasoline boiling range (2, 3).

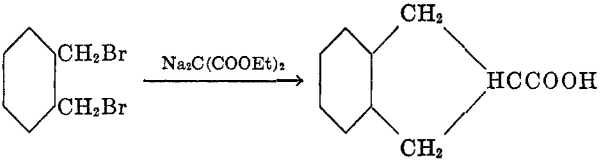
No account of the physical or chemical properties of compounds of this type is to be found in the literature and accordingly, as part of the investigation into the nature of petroleum sulfur bodies in progress in these laboratories, the preparation of a number of simple bicyclic sulfides was undertaken. Since from knowledge of the cyclic sulfides in the lower-boiling ranges those with fused five- and six-membered rings appeared to be most likely, compounds of this type were chosen for investigation. In the present account the syntheses of the geometrical isomers of 2-thiahydrindan (VIII, VIIIA) and 2-thiadecalin (IX, IXA) are described and some of their more important physical properties are recorded.

The preparation of sulfides of this type is complicated since each can exist in two stereoisomeric forms. It was therefore essential to employ a stereospecific synthesis and to determine the configuration at an intermediate stage since no way of proving the structure of the final sulfide could be found. When the pure sulfides became available it was shown that the hydrocarbon produced by Raney nickel desulfurization (4) had in fact retained the stereochemical identity of the sulfide and that this method may therefore be used to determine configuration.

The scale of each preparation was sufficient to allow for purification prior to the determination of physical constants and absorption spectra. The synthesis of both sulfides involved the preparation of the appropriate glycol or cyclic oxide, separation of the stereoisomers, and conversion of these *via* the corresponding dibromide to the cyclic sulfide as shown schematically below as follows:



Although reduction of the pure diethyl cyclohexane-1,2-dicarboxylates with lithium aluminum hydride would have given the pure glycols as has since been described by Haggis and Owen (6) this reagent was not available to us at the time the work was carried out. Diethyl phthalate was accordingly hydrogenated and the resulting diethyl cyclohexane-1,2-dicarboxylates (I) were reduced by the Bouveault-Blanc method to give a mixture of *cis*- and *trans*-1,2-bishydroxymethylcyclohexanes (II) which were used as the starting materials in the preparation of the 2-thiahydrindans. Separation of the isomers was attempted by fractionation of the glycol but this proved only partially successful and the separation was completed by repeated fractionation of the cyclic oxides (IV, IVA), prepared from the glycol fractions by dehydration with dilute sulfuric acid. The identities of the individual oxides were not known with any certainty at the time of preparation and since there was a possibility of loss of configuration during the hydrobromination step, the configurations of the dibromides (VI, VIA) were determined by the method used by Wislicenus for establishing the configuration of the 2,5-dibromohexanes (7). This comprised reaction of the dibromides with diethyl malonate and isolation of the monocarboxylic acids.



The *cis-* dibromide should give two acids whereas the *trans* should give only one. One of our dibromides gave as sole product a pure hydrindan-2-carboxylic acid, thus definitely proving it to be the *trans* form. The product from the other yielded only a small amount of a second solid hydrindan-2-carboxylic acid and a quantity of an oily acid which could not be induced to crystallize. That this was the *cis*-dibromide was confirmed in later stages of the preparation. Each dibromide gave a sulfide the purity of which was estimated from its freezing point (8). The *trans-* compound was 99.87 mole-per cent pure and the *cis-* compound 99.88 mole-per cent pure. No change of configuration was expected to occur on ring closure of the dibromide with sodium sulfide which was confirmed by the purity of the sulfides and by the fact that each isomer gave the expected hydrocarbon on desulfurization. The *trans-* isomer was the major product obtained by this method and a further quantity of the *cis*-isomer was subsequently prepared from *cis*-1,2-bishydroxymethylcyclohexane by reduction of diethyl *cis*-cyclohexane-1,2-dicarboxylate with lithium aluminum hydride (6). This preparation not only gave a further quantity of the *cis-* sulfide but also established the configuration of the cyclic oxides and showed that no change of configuration had occurred in the preparation of the dibromides from the oxides.

In addition to the pure individual sulfides a quantity of mixed isomers was obtained from intermediate fractions of the hexahydrophthalans. Since the quantity was insufficient for fractionation in the 100-plate column available, separation was achieved by azeotropic fractionation using Methyl Carbitol[1] as the third component. In this way a further quantity of both isomers was obtained. The *cis-* compound formed an azeotrope b.p. 92°/20.5 mm., n_D^{20} 1.4580, containing *ca.* 30% of sulfide; the *trans-* compound an azeotrope b.p. 90.9°/21 mm., n_D^{20} 1.4610, containing *ca.* 35% of sulfide.

Catalytic hydrogenation of isochroman (III) (9) provided a mixture of *cis-* and *trans-* hexahydrochromans (V, VA) which was separated into the individual isomers by careful fractionation. These were converted to the *cis-* and *trans*-2-thiadecalins of purity 99.87 and 99.89 mole-per cent respectively, and their

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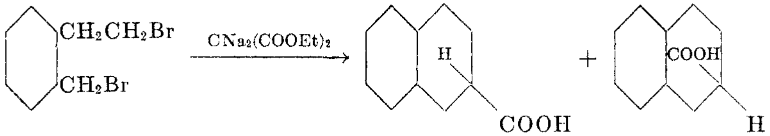
[1] The monomethyl ether of diethylene glycol.

configuration established by determining that of the dibromides (VII, VIIA). The reaction with diethyl disodiomalonate was used for this purpose but with the bromomethyl-2-(β-bromoethyl)cyclohexanes each dibromide is capable of giving two decalin-2-carboxylic acids although we succeeded in isolating only one pure acid from each.



One melting at 81° was shown to be identical with that obtained by hydrogenation of β-naphthoic acid at room temperature, which Dauben and Hoerger (10) have shown possesses an all *cis*-configuration, thus establishing the configuration of the dibromide. The other acid (m.p. 106°) was similar in melting point to a decalin-2-carboxylic acid described by Tsatsas (11) who prepared it by carbonation of the Grignard compound from *trans*-2-decalol, m.p. 75°. Although this reaction may produce inversion at the 2-carbon atom it does not affect the stereochemistry of the 9- and 10- carbon atoms (10) and, accordingly the acid prepared by Tsatsas must be one of the *trans*-decalin-2-carboxylic acids. We repeated his preparation and obtained an acid m.p. 106° identical with that from the dibromide, which must therefore have a *trans*- configuration. The configuration of the oxides also follows since the conversion of the oxides to the dibromides has been shown to proceed with retention of configuration (*vide supra*).

Infrared absorption spectra were obtained for all four sulfides in the range 2–15 μ using a Grubb-Parsons double beam spectrometer (Figures 1–4). The physical properties of the sulfides and their intermediates are given in Tables I and II. The four pure sulfides in ethanol solution were desulfurized to the hydrocarbons using Raney nickel (4). In each instance the hydrocarbon had the same configuration as the sulfide as shown by physical properties and the infrared absorption spectra. The absence of hydrindan in the product from the desulfurization of *trans*-2-thiadecalin indicated that no cyclization reaction had taken place as had been shown to occur with 3-thiabicyclo[3.2.1]octane and thiacyclohexane (12).

The spectra of *cis*- and *trans*-methyl-2-ethylcyclohexane were not available and these compounds were prepared by catalytic hydrogenation of *o*-ethyltoluene in the presence of a Raney nickel catalyst, the isomers of the cyclohexane being separated by azeotropic fractionation using Cellosolve[2] as the third component. To determine the configuration a small quantity of the *cis*- compound was also prepared by hydrogenation of *o*-ethyltoluene at room temperature with a platinum catalyst (13). The physical properties of *cis*- and *trans*-methyl-2-ethylcyclohexane and their azeotropes are given in Table III and the spectra of the hydrocarbons in Figures 5–6.

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[2] The monoethyl ether of ethylene glycol.

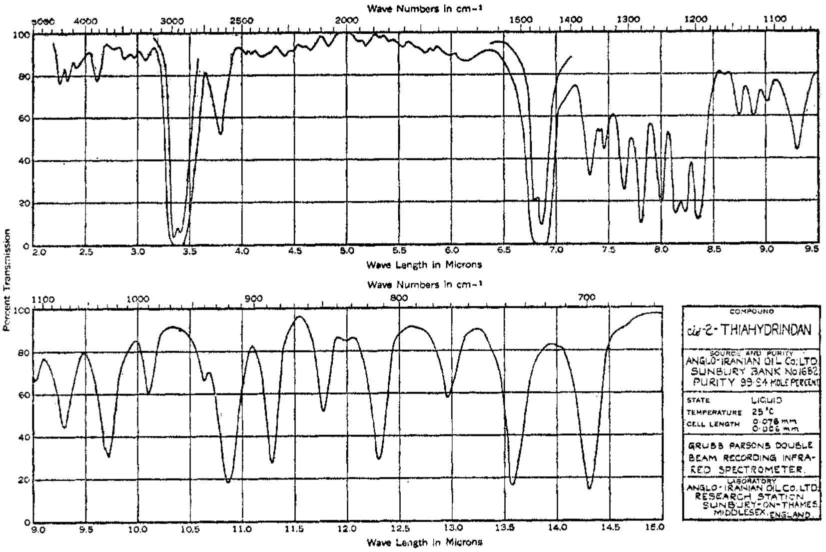

FIG. 1

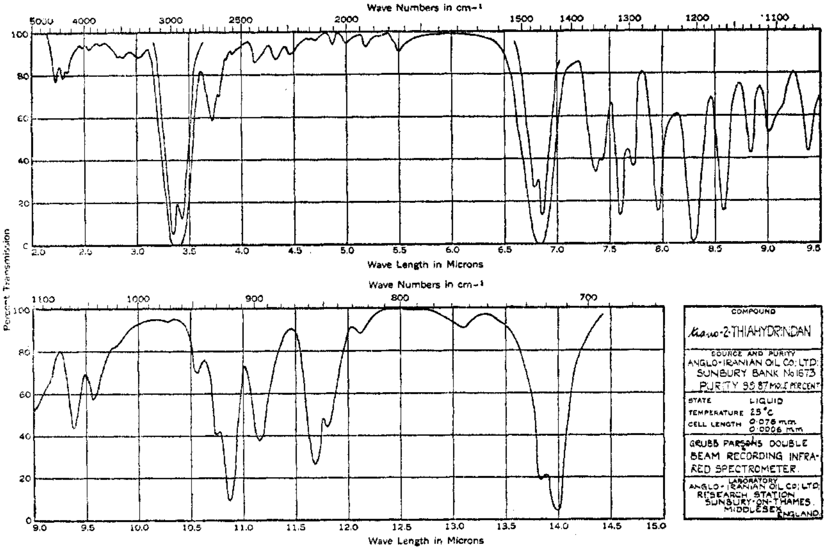

FIG. 2

FIG. 1 AND 2. INFRARED SPECTRA OF 2-THIAHYDRINDANS

All four sulfur compounds formed water-soluble derivatives when extracted with saturated mercuric acetate solution (14) the parent sulfide being recoverable from the extracts by heating with hydrochloric acid. The methiodides, sulfones, and mercuric chloride derivatives were prepared and were crystallized to constant melting point by the methods previously described (15); unlike those

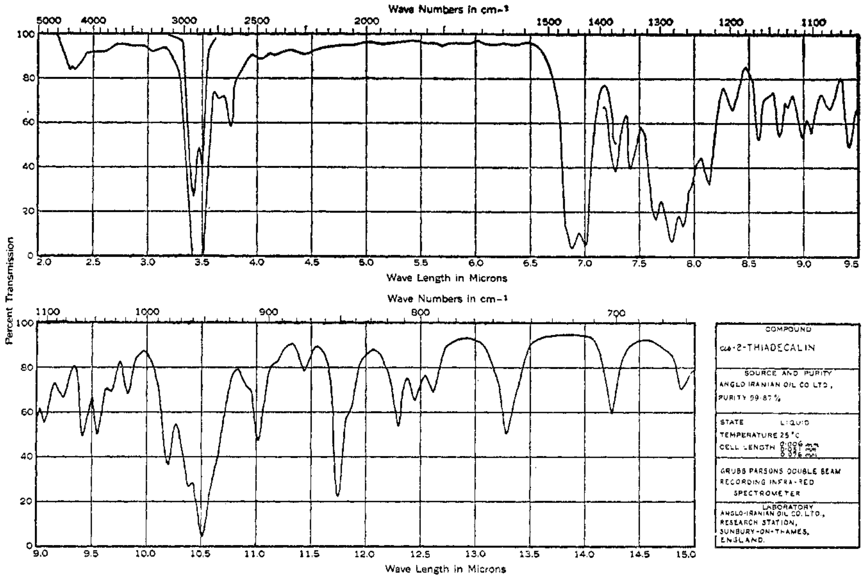

FIG. 3

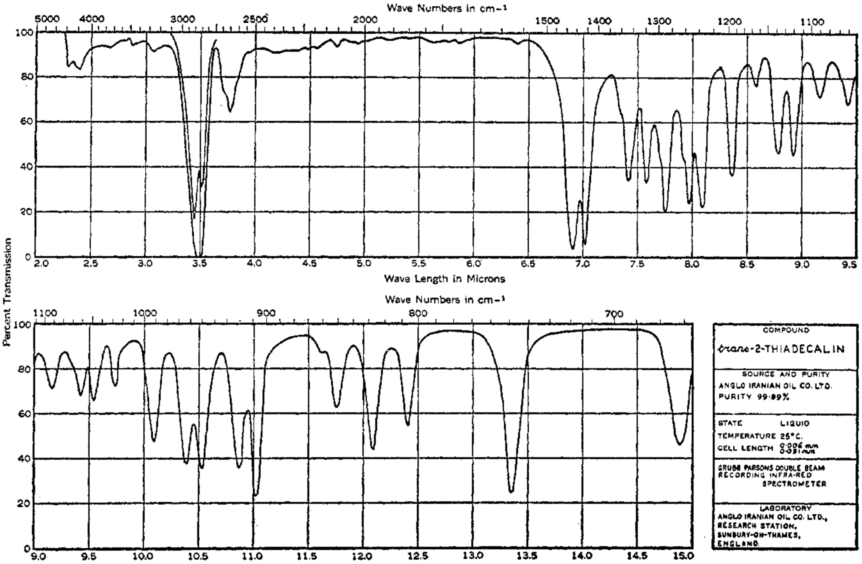

FIG. 4

FIG. 3 AND 4. INFRARED SPECTRA OF 2-THIADECALINS

of the monocyclic sulfides, the mercuric chloride complexes were all stable compounds. The sulfoxides were prepared by oxidation of the sulfide in glacial acetic acid with *tert*-butyl hydroperoxide. Although *trans*-2-thiahydrindan can give only one sulfoxide, the *cis*-sulfide should give a mixture of two stereoisomeric

TABLE I

PHYSICAL PROPERTIES OF THE *cis*- AND *trans*-BICYCLIC SULFIDES

Sulfide	Refractive Index†								B.P., °C.	Density g./ml.		Estimated Purity, mole-%	Estimated m.p. for zero impurity, °C.	Cryoscopic constant, mole-% per deg. C.
	Temp., °C.	Wavelength Ångstrom Units												
		6678	6563	5893	5461	5016	4861	4358		20°	25°			
cis-2-Thiahydrindan	20	1.52854	1.52899	1.53215	1.53487	1.53851	1.54003	1.54630	108.5 at 21 mm.	1.0430	1.0388	99.88	−8.90	0.20*
	25	1.52622	1.52667	1.52983	1.53255	1.53618	1.53770	1.54396						
	30	1.52396	1.52440	1.52755	1.53025	1.53386	1.53537	1.54160						
trans-2-Thiahydrindan	20	1.52115	1.52160	1.52481	1.52755	1.53121	1.53273	1.53901	104.6–105.6 at 20 mm.	1.0203	1.0162	99.87	+4.28	1.2*
	25	1.51890	1.51935	1.52255	1.52528	1.52893	1.53045	1.53671						
	30	1.51667	1.51712	1.52029	1.52300	1.52662	1.52813	1.53434						
cis - 2 - Thia - decalin	20	1.52984	1.53029	1.53346	1.53619	1.53983	1.54136	1.54767	122.5–123.25 at 20 mm.	1.0350	1.0312	99.87	−3.61	1.5*
	25	1.52766	1.52811	1.53128	1.53401	1.53765	1.53918	1.54548						
	30	1.52558	1.52602	1.52917	1.53188	1.53549	1.53701	1.54327						
trans - 2-Thia-decalin	20	1.51812	1.51857	1.52173	1.52444	1.52806	1.52957	1.53580	115.5–116.5 at 20 mm.	1.0058	1.0020	99.89	+9.38	1.5*
	25	1.51601	1.51645	1.51960	1.52230	1.52591	1.52742	1.53363						
	30	1.51402	1.51445	1.51758	1.52024	1.52385	1.52535	1.53151						

* Determined. † These values have been smoothed by the method of Forziati (5).

TABLE II

PHYSICAL PROPERTIES OF INTERMEDIATE COMPOUNDS USED IN THE SYNTHESIS OF THE *cis*-AND *trans*-BICYCLIC SULFIDES

Compound	B.P., °C.	mm.	n_D^{20}	d^{20}	Purity, mole-%	M.P., °C.	Cryoscopic constant, mole-% per deg. C.
cis-1,2-Bis-hydroxymethylcyclohexane	129.6	1.5	—	—	97	42.4	2.0*
trans-1,2-Bis-hydroxymethylcyclohexane	128	0.5	1.4870†	—	—	51.16 and 48.76	—
cis-Hexahydrophthalan	179.5	779	1.4700	—	96.3	−4.8	1.0*
trans-Hexahydrophthalan	80	31	1.4675	0.9634	>99	−70.54	0.4*
cis-1,2-Bis-bromomethylcyclohexane	110–112	0.75	1.5435	1.6365	Would not freeze		
trans-1,2-Bis-bromomethylcyclohexane	100–110	2–3	1.5390	1.6298	99.46	17.73	1.8
cis-Hexahydroisochroman	93–94	28	1.4761	0.9682	99.5	−19.99	2.5*
trans-Hexahydroisochroman	85	24	1.4675	0.9449	95 ± 1.0	−41.4	2.5
cis-Bromomethyl-2-(β-bromoethyl)-cyclohexane	90–100	0.1	1.5381	1.5658	Would not freeze		
trans-Bromomethyl-2-(β-bromoethyl)-cyclohexane	104–106	0.8	1.5350	1.5590	99.7	0.58	2.1

* Estimated. † Determined on the supercooled liquid.

TABLE III

PHYSICAL PROPERTIES OF *cis*- AND *trans*-METHYL-2-ETHYLCYCLOHEXANE AND OF THEIR AZEOTROPES WITH CELLOSOLVE

Hydrocarbon and Azeotrope	B.P., °C./760 mm.	n_D^{20}	n_D^{25}	d^{20}	d^{25}	Hydrocarbon in azeotrope, wt.-%
cis-Methyl-2-ethylcyclohexane......	155.97	1.4432	1.4410	0.8094	0.8056	—
Azeotrope with Cellosolve..........	130.0	1.4202	—	—	—	40
trans-Methyl-2-ethylcyclohexane....	151.69	1.4382	1.4359	.7972	.7934	—
Azeotrope with Cellosolve..........	128.8	1.4199	—	—	—	45

sulfoxides; the products from both isomers were however extremely hygroscopic and no pure compounds were isolated. With 2-thiadecalin each isomer can give two sulfoxides but only one isomer of the *cis*-sulfoxide could be isolated in a pure state, it not being possible to obtain constant melting samples for any of the other three isomers.

The physical properties and analyses of all these derivatives are given in Table IV.

EXPERIMENTAL

All melting points are corrected. Purities were estimated by the freezing point method of Mair, Glasgow, and Rossini (8). Cryoscopic constants were either estimated from the

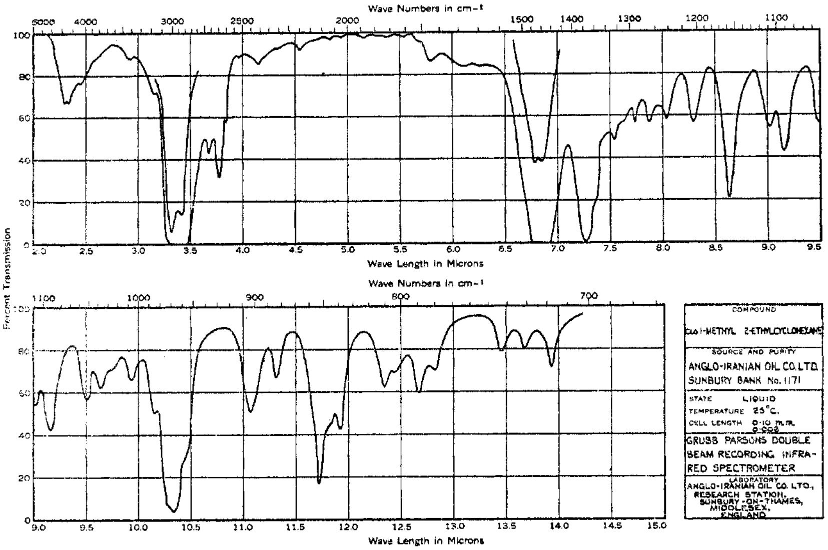

FIG. 5

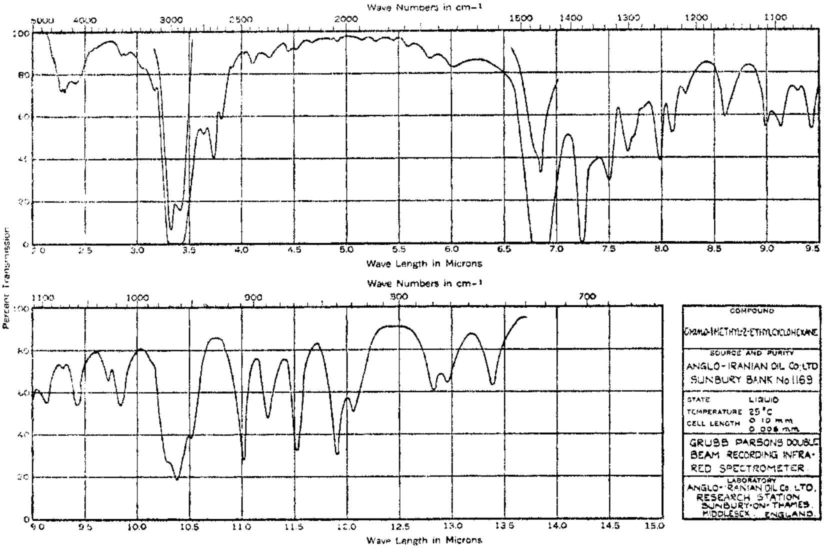

FIG. 6

FIG. 5 AND 6. INFRARED SPECTRA OF METHYLETHYLCYCLOHEXANES

freezing time or were determined by measuring the latent heat of fusion. Microanalyses are by Dr. Weiler and Dr. Strauss of Oxford, England.

cis- AND *trans-*2-THIAHYDRINDAN

cis-1,2-Bishydroxymethylcyclohexane. Diethyl *cis*-cyclohexane-1,2-dicarboxylate was prepared by the method of Cope and Herrick (16) in 91% yield, b.p. 88–94°/0.5 mm., from *cis*-Δ^4-tetrahydrophthalic anhydride. The ester (95 g., 0.41 mole) dissolved in diethyl ether (800 ml.) was reduced by addition to a stirred refluxing solution of lithium aluminum

TABLE IV

MELTING POINTS AND ANALYSES OF THE DERIVATIVES OF THE *cis* AND *trans* BICYCLIC SULFIDES

Compound	Formula of Derivative	m.p., °C. (corrected)	Analyses							
			Calc'd				Found			
			C	H	S	Halogen	C	H	S	Halogen
cis-2-Thiahydrindan	$C_8H_{14}Cl_2HgS$	187.2–187.7	23.2	3.4	7.7	17.1	23.4	3.3	7.7	17.5
	$C_8H_{14}O_2S$	39.5–41.0	55.2	8.1	18.3	—	55.7	8.6	18.1	—
trans-2-Thiahydrindan	$C_9H_{17}IS$	142.5–144.0*	38.0	6.0	11.3	44.7	38.2	6.1	11.5	44.3
	$C_8H_{14}Cl_2HgS$	212.5–213.5	23.2	3.4	7.7	17.1	23.2	3.1	7.9	17.4
	$C_8H_{14}O_2S$	105.0–105.5	55.2	8.1	18.3	—	55.4	8.2	17.9	—
	$C_9H_{17}IS$	164.5–166.0*	38.0	6.0	11.3	44.7	38.3	6.1	11.3	44.7
cis-2-Thiadecalin	$C_9H_{16}Cl_2HgS$	148.5–151.5	25.3	3.8	7.4	16.5	26.0	3.9	7.0	16.0
	$C_9H_{16}O_2S$	86.0–87.4	57.4	8.6	17.0	—	57.6	8.5	17.0	—
	$C_{10}H_{19}IS$	159.6–161.6*	40.3	6.4	10.7	42.6	40.6	6.4	10.4	42.5
	$C_9H_{16}OS$	104.5–105.5	62.7	9.4	18.6	—	62.6	9.4	18.5	—
trans-2-Thiadecalin	$C_9H_{16}Cl_2HgS$	149.8–150.4	25.3	3.8	7.4	16.5	25.7	3.9	7.3	16.5
	$C_9H_{16}O_2S$	91.0–92.8	57.4	8.6	17.0	—	57.7	8.6	16.9	—
	$C_{10}H_{19}IS$	173.5–174.5*	40.3	6.4	10.7	42.6	40.9	5.9	10.8	42.9

The methiodides all melted with decomposition. * Sealed tube.

hydride (40 g., 1.05 moles) in diethyl ether (1.5 l.). The reaction mixture was worked up in the usual manner with dilute sulphuric acid and the glycol, which solidified on cooling, was obtained in 94% yield by continuous extraction of the aqueous layer with ether. After two crystallizations from ether and redistillation under reduced pressure to remove traces of solvent, it had the following properties: b.p. 129.6°/1.5 mm.; m.p. 42.4°; purity 97 mole-%; cryoscopic constant 2.0 mole-% per deg.; Haggis and Owen (6) give m.p. 42–43°.

Mixed isomers of 1,2-bishydroxymethylcyclohexane. The mixture of isomeric diethyl cyclohexane-1,2-dicarboxylates, obtained by the hydrogenation of diethyl phthalate in the presence of a Raney nickel catalyst at 160–215° and a hydrogen pressure of 1800 p.s.i., was fractionated under reduced pressure through a 50-plate column. No separation of the isomers was obtained and the material boiling at 130–131°/6.5 mm.; n_D^{20} 1.4520, was reduced to the corresponding glycol by the Bouveault-Blanc procedure using 9 g.-atoms of sodium and 2.4 l. of dry ethanol per mole of ester with an average yield of 75%. The total product (1284 g.) was fractionated under reduced pressure using a 100-plate column. The material boiling between 133–137°/2.5 mm. was substantially one isomer which exhibited two crystalline modifications m.p. 51.2° and 48.8° respectively. This was later shown to be the *trans*-isomer for which Haggis and Owen (6) give a melting point of 57°. Although higher-boiling fractions contained mainly the *cis*- isomer no complete separation was obtained.

cis- and trans-Hexahydrophthalan. The oxides were prepared from the glycols as follows: The glycol (2 moles) was dissolved in water (1.5 l.) and was refluxed gently through a modified form (Figure 7) of the oil-water separator described by Human and Mills (17). Concentrated sulfuric acid (10 ml.) was then slowly added after which the oxide commenced to collect in the receiver. The addition of acid was continued until no more oxide was formed (*ca.* 300 ml. was required); yield 94%. The fractions from the distillation of the mixed glycols were combined according to their refractive indices, converted to the oxides, and the separation of the isomers was completed by fractionation. The glycol obtained from the pure *cis*-cyclohexane-1,2-dicarboxylate was similarly converted to the oxide. The physical properties of the oxides were as follows: *trans*- b.p. 80°/31 mm.; 178°/760 mm.; n_D^{20} 1.4675; f.p. $-70.54°$; purity >99 mole-%; cryoscopic constant 0.4 mole-% per deg.;

cis- b.p. 80°/28 mm.; 179.5°/760 mm.; n_D^{20} 1.4700; m.p. −4.8°; purity 96.3 mole-%; cryoscopic constant 1.0 mole-% per deg.

cis- and trans-1,2-Bisbromomethylcyclohexane. A mixture of the appropriate cyclic oxide and water (10% by weight) was saturated with anhydrous hydrogen bromide (18) at 110–120° until no further increase in weight occurred (10 hr.). The product was dissolved in light petroleum (40–60°), excess hydrogen bromide was removed, and the extract was washed with concentrated sulfuric acid, sodium bicarbonate solution, and water. The solvent was removed after drying ($CaCl_2$) and the residue was distilled under reduced pressure. *trans*-1,2-Bisbromomethylcyclohexane, obtained in 95% yield, was purified by crystallization from light petroleum at −15°; m.p. 17.73°; b.p. 100°/2 mm.–110°/3 mm.; n_D^{20} 1.5390; d^{20} 1.6298; purity 99.5 mole-%; cryoscopic constant 1.80 mole-% per deg.

Anal. Calc'd for $C_8H_{14}Br_2$: Br, 59.2. Found: Br, 59.2.

cis-1,2-Bisbromomethylcyclohexane was obtained in 78% yield; b.p. 103–106°/2 mm.; n_D^{20} 1.5435; d^{20} 1.6365. No purity estimation was possible as the compound set to a glass on cooling.

Anal. Calc'd for $C_8H_{14}Br_2$: Br, 59.2. Found: Br, 59.3.

cis- and trans-2-Thiahydrindan. One half of a solution of sodium sulfide nonahydrate (2.0 moles) in aqueous ethanol (water 450 ml. and ethanol 500 ml.) was brought to reflux, and the second half and the appropriate dibromide (1.0 mole) were added to the refluxing solution concurrently. Refluxing was continued for a further 12 hr. after addition was complete; then the alcohol was removed and the bicyclic sulfide was recovered using the

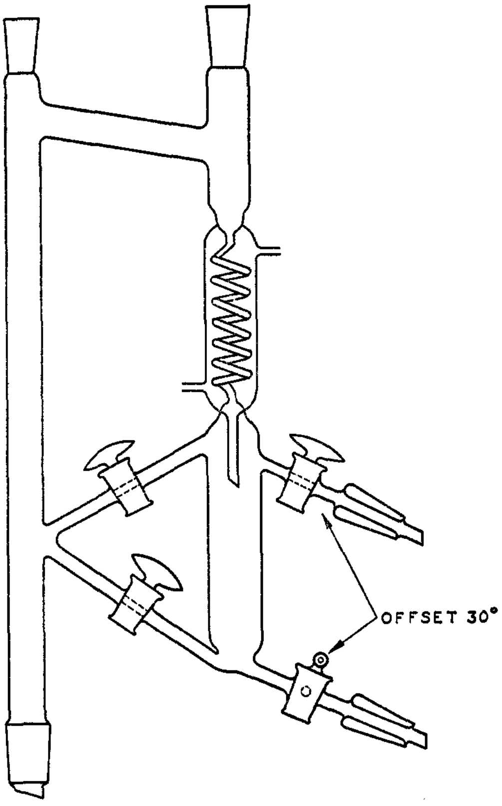

FIG. 7. MODIFIED OIL-WATER SEPARATOR

improved oil-water separator mentioned above. The recovered alcohol and sulfide were combined and treated with an alcoholic solution of mercuric chloride (2 moles in ethanol, 1630 ml.) giving a crystalline mercuric chloride complex which was filtered off, crystallized to constant melting point, dried, and regenerated by steam-distillation with 15% hydrochloric acid. The sulfide after washing and drying was distilled under reduced pressure and finally fractionated. The *cis-* isomer was obtained in 75% yield and the *trans-* in 91% yield. Their physical properties are given in Table 1.

Anal. Calc'd for $C_8H_{14}S$: C, 67.5; H, 9.9; S, 22.5.

Found for *cis*-2-thiahydrindan: C, 67.6; H, 10.0; S, 22.2.

Found for *trans*-2-thiahydrindan: C, 67.3; H, 9.9; S, 22.7.

trans-Hydrindan-2-carboxylic acid. trans-1,2-Bisbromomethylcyclohexane (11 g., m.p. 17.6°) was added to a refluxing solution of diethyl disodiomalonate [prepared from sodium (1.8 g.), diethyl malonate (6.2 g.), and ethanol (23 ml.)] and refluxed for 4 hr. Water was added to the residue and the alcohol was distilled off; the oily diethyl ester (11.1 g.) of the dicarboxylic acid was separated by extraction with ether and then hydrolyzed with alcoholic potassium hydroxide. The acid product worked up in the usual manner gave a white waxy solid, which was decarboxylated by heating at 180–185° to give the monocarboxylic acid which was distilled under reduced pressure, b.p. 108°/0.3 mm.; yield 4.75 g. (75%); m.p. 37–38°. Recrystallization from *n*-hexane raised the melting point to 40–41°.

Anal. Calc'd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6; Neut. equiv., 168.

Found: C, 71.3; H, 9.5; Neut. equiv., 175.

Evaporation of the mother liquors from the crystallization gave an acid, m.p. 35–36°, from which only the original acid could be separated.

cis-Hydrindan-2-carboxylic acid. cis-1,2-Bisbromomethylcyclohexane (10.1 g.) similarly treated gave, after decarboxylation, a product which distilled at 120–125°/0.5 mm.; yield 2.33 g. (40%). It could not be induced to solidify. After standing for several months it deposited a small quantity of solid, which was recrystallized to constant melting point from *n*-hexane, m.p. 71–73°.

Anal. Calc'd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6; Neut. equiv., 168.

Found: C, 71.1; H, 9.6; Neut. equiv., 175.

No further quantity of this or the isomeric *cis*-hydrindan-2-carboxylic acid could be isolated from the residual oil.

Desulfurization of the cis- and trans-2-thiahydrindans. The sulfide (0.035 mole) in ethanol (350 ml.) was refluxed with Raney nickel (19) (100 g.) through a short glass-helix packed fractionating column. The hydrocarbon/alcohol azeotrope was diluted with water and the hydrocarbon was separated, water-washed, dried, and distilled. The refractive index and infrared adsorption spectrum were then recorded and compared with those of the pure hydrocarbon.

trans-2-Thiahydrindan gave a 66% yield of hydrocarbon; b.p. 124°/760 mm.; n_D^{20} 1.4273. Ref. (20) gives b.p. 123.419°/760 mm.; n_D^{20} 1.42695 for *trans*-1,2-dimethylcyclohexane. The infrared spectrum confirmed that the hydrocarbon was *trans*-1,2-dimethylcyclohexane. *cis*-2-Thiahydrindan gave a 43% yield of hydrocarbon; b.p. 130°/760 mm.; n_D^{20} 1.4352. Ref. (20) gives; b.p. 129.728°/760 mm.; n_D^{20} 1.43596 for *cis*-1,2-dimethylcyclohexane. The infrared spectrum confirmed that the hydrocarbon was *cis*-1,2-dimethylcyclohexane.

cis- AND *trans*-2-THIADECALIN

cis- and trans-Hexahydroisochroman. Isochroman (9) (1000 g.) was hydrogenated at 200–230° using a Raney nickel catalyst and a hydrogen pressure of 1800 p.s.i., the product was fractionated under reduced pressure through a 100-plate column. The first portion of the distillate (182 g.) b.p. 68.4°/135 mm.–90.4°/28 mm. consisted of hydrogenolysis products which were shown by spectroscopic analysis to contain the *cis-* and *trans*-1,2-dimethylcyclohexanes and methylethylcyclohexanes, *o*-xylene, and *o*-ethyltoluene. The second portion b.p. 90.4°/28 mm.–96.4°/31 mm. (166 g.) was mainly the *trans-* isomer, and the third b.p. 96.4°/31 mm.–88.9°/23 mm. (458 g.) mainly the *cis*-isomer. There was a higher-boiling residue of 85 g. Refractionation of the second and third portions in a 50-plate column gave the pure isomers; the *cis*- in 30% yield on the isochroman and the *trans*- in 10% yield with the following properties:

trans- b.p. 85°/24 mm.; n_D^{20} 1.4675; d^{20} 0.9449; f.p. −41.4°; purity 95 ± 1.0 mole-%; cryoscopic constant 2.5 mole-% per deg.

cis- b.p. 93–94°/28 mm.; n_D^{20} 1.4761; d^{20} 0.9682; f.p. −19.99°; purity 99.5 mole-%; cryoscopic constant 2.5 mole-% per deg.

trans-Bromomethyl-2-(β-bromoethyl)cyclohexane was prepared from *trans*-hexahydroisochroman by the method given for the 1,2-bisbromomethylcyclohexanes and was purified by crystallization from light petroleum at −30°; yield 65%; b.p. 104–106°/0.8 mm.; n_D^{20} 1.5350; d^{20} 1.5590; m.p. 0.58°; purity 99.7 mole-%; cryoscopic constant 2.1 mole-% per deg.

Anal. Calc'd for $C_9H_{16}Br_2$: Br, 56.3. Found: Br, 56.3.

cis-Bromomethyl-2-(β-bromoethyl)cyclohexane was similarly prepared from *cis*-hexahydroisochroman in 85% yield; b.p. 90–100°/0.1 mm.; n_D^{20} 1.5381; d^{20} 1.5658; no purity estimation was possible as this compound set to a glass on cooling.

Anal. Calc'd for $C_9H_{16}Br_2$: Br, 56.3. Found: Br, 56.0.

cis- and trans-2-Thiadecalin were prepared by the method described for the thiahydrindans in yields of 83.5 and 86.5% respectively. The boiling point of the *cis*-sulfide was determined using a modified Swietoslowski apparatus (21), Antoine constants; A = 7.2610; B = 2035.6; C = 218.76, giving an extrapolated boiling point of 246.0°/760 mm. The *trans*-sulfide boiled at 115.5–116.5°/20 mm.

Anal. Calc'd for $C_9H_{16}S$: C, 69.2; H, 10.3; S, 20.5.
Found for *cis*-2-thiadecalin: C, 69.3; H, 10.2; S, 20.4.
Found for *trans*-2-thiadecalin: C, 69.0; H, 10.3; S, 20.6.

trans-Decalin-2-carboxylic acid. (*a*). A mixture of monocarboxylic acids was obtained by the method described for the hydrindan-2-carboxylic acids, from the reaction of *trans*-bromomethyl-2-(β-bromoethyl)cyclohexane (11.36 g.) with diethyl disodiomalonate; b.p. 128–130°/1 mm.; yield 4.3 g. (56%). After standing for 10 days the distillate solidified to a waxy solid m.p. 52–57° from which an acid, m.p. 105.5–106.8°, was obtained by crystallization from *n*-hexane.

Anal. Calc'd for $C_{11}H_{18}O_2$: C, 72.5; H, 10.0; Neut. equiv., 182.
Found: C, 72.4; H, 9.9; Neut. equiv., 181.

The *amide*, prepared by the method of Dauben and Hoerger (10) had m.p. 205–206° from aqueous ethanol.

Anal. Calc'd for $C_{11}H_{19}NO$: C, 72.9; H, 10.6; N, 7.7.
Found: C, 73.0; H, 10.6; N, 7.3.

(*b*). *trans*-2-Decalol, m.p. 75°, on hydrobromination (18) at 100–110° gave *trans*-2-bromodecalin, b.p. 86°/1.6 mm.; m.p. 3.0–4.0°; n_D^{20} 1.5619; yield 91.5%. Carbonation of the magnesium bromide by the method of Hussey (22) gave a 52% yield of *trans*-decalin-2-carboxylic acid, m.p. 106–107° from *n*-hexane, amide m.p. 205–206°. Mixture melting points with the acid and amide prepared above, showed no depression.

cis-Decalin-2-carboxylic acid. (*a*). *cis*-Bromomethyl-2-(β-bromoethyl)cyclohexane (17.04 g.) was reacted with diethyl disodiomalonate as described above to give a monocarboxylic acid product, b.p. 130–136°/0.6 mm., yield 7.9 g. (73%). The viscous distillate solidified on standing for a week giving a mixture of acids, m.p. 43–50° from which a pure *cis*-decalin-2-carboxylic acid, m.p. 81.9–82.7° was isolated by crystallization from *n*-hexane.

Anal. Calc'd for $C_{11}H_{18}O_2$: C, 72.5; H, 10.0; Neut. equiv., 182.
Found: C, 72.5; H, 10.0; Neut. equiv., 183.

The *amide* prepared as above and recrystallized from aqueous ethanol melted at 179.7–180.7°.

Anal. Calc'd for $C_{11}H_{19}NO$: C, 72.9; H, 10.6; N, 7.7.
Found: C, 72.6; H, 10.4; N, 7.9.

(*b*). 2-Naphthoic acid was hydrogenated using a platinum catalyst as described by Dauben and Hoerger (10). The melting points of this *cis*-decalin-2-carboxylic acid and its amide were identical with those of the acid above and mixture melting points showed no depression.

cis- and trans-2-Thiadecalin-2-oxide. The sulfoxides were prepared by the addition of *tert*-butylhydroperoxide (slight excess) to a cooled solution of the sulfide (0.02 mole) in glacial acetic acid (0.08 mole). After standing at room temperature for 24 hr. acetic acid and excess peroxide were separated from the product by distillation under reduced pressure. The distilled sulfoxide (*ca.* 75% yield) was crystallized from *n*-hexane/benzene or *n*-hexane/ether solution.

trans-2-Thiadecalin gave a product m.p. 45–60° which was a mixture from which only a very small amount of almost pure material m.p. 69–70° was obtained. The product from *cis*-2-thiadecalin was also a mixture, m.p. 67–83°, but a small quantity of pure *cis*-2-thiadecalin-2-oxide, m.p. 104.5–105.5°, was obtained.

Anal. Calc'd for $C_9H_{16}OS$: C, 62.7; H, 9.4; S, 18.6.
Found: C, 62.6; H, 9.4; S, 18.5.

Desulfurization of cis- and trans-2-thiadecalin. By the method described for the thiahydrindans, *trans*-2-thiadecalin gave a 56% yield of a hydrocarbon b.p. 140–150°, the infrared spectrum of which was identical with that of *trans*-methyl-2-ethylcyclohexane. *cis*-2-Thiadecalin gave a 64% yield of hydrocarbon b.p. 151°, n_D^{20} 1.4431 the infrared spectrum of which was identical with that of *cis*-methyl-2-ethylcyclohexane.

cis- and trans-Methyl-2-ethylcyclohexane. (*a*). *o*-Ethyltoluene (500 g., purity 99.7 mole-%) was hydrogenated using a Raney nickel catalyst at 180–250° and a hydrogen pressure of 1800 p.s.i. Traces of high- and low-boiling materials were removed by a preliminary distillation and the main portion was azeotropically fractionated through a 100-plate column using Cellosolve[2] as entrainer. The fractions were washed with water and then refractive indices were determined. Two well-defined plateaux were apparent and fractions on these plateaux were combined and the products finally were purified by percolation over silica gel. In spite of repeated fractionation no purity determination was possible as both hydrocarbons set to a glass on cooling. The physical properties of the hydrocarbons and their azeotropes are given in Table 3 and their infrared spectra in Figures 5 and 6. The boiling points of these hydrocarbons, determined using a modified Swietoslowski apparatus (21), were: for the *cis*-isomer 155.97° ± 0.5°/760 mm.; Antoine constants; A = 6.8764; B = 1460.9; C = 209.65; for the *trans*-isomer 151.60° ± 0.5°/760 mm.; Antoine constants; A = 6.8595; B = 1439.2; C = 210.04.

(*b*). *o*-Ethyltoluene (40 g.) was hydrogenated at room temperature and 44 p.s.i. pressure of hydrogen using an Adams catalyst (23). The product was percolated through silica gel to remove aromatics and was fractionated in a 30-plate column containing packing of the Bower and Cooke (24) type. Both isomers were present but the higher-boiling isomer (n_D^{20} 1.4432) was the greater part (77%) of the distillate. This was accordingly designated the *cis*- compound; it was identical with that obtained from *cis*-2-thiadecalin.

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SUMMARY

The *cis*- and *trans*- isomers of 2-thiahydrindan and 2-thiadecalin have been synthesized by an unambiguous route and their physical properties have been recorded.

Each sulfide has been characterised by the preparation of derivatives.

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