[CONTRIBUTION FROM THE RESEARCH STATION, THE BRITISH PETROLEUM COMPANY LIMITED]

PREPARATION AND PHYSICAL PROPERTIES OF SULFUR COMPOUNDS RELATED TO PETROLEUM. V. *cis*- AND *trans*-1-THIAHYDRINDAN AND 3-THIABICYCLO[3.3.0]OCTANE, AND *cis*-2-THIABICYCLO[3.3.0]OCTANE

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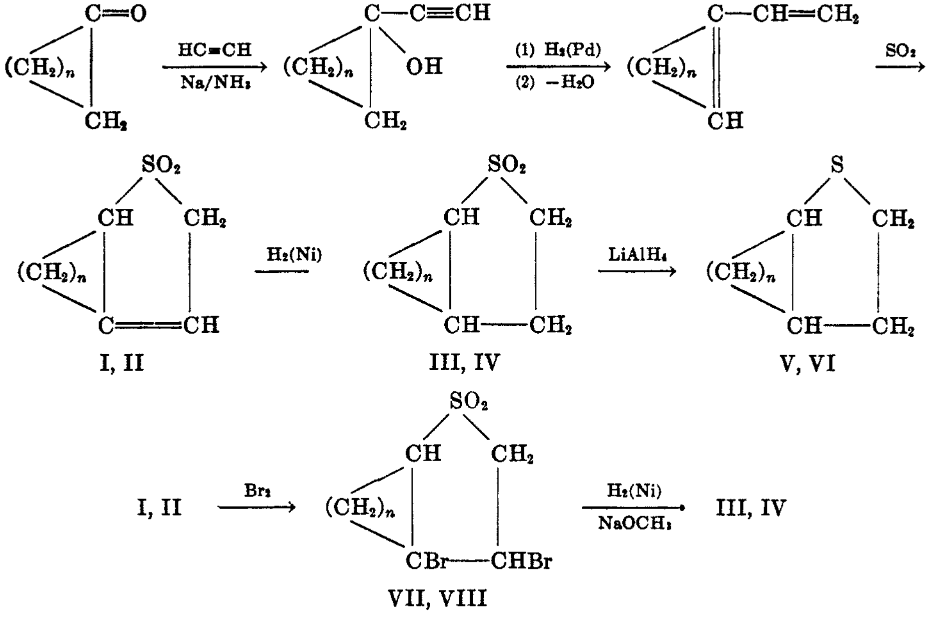
In continuation of the program of research into the nature of sulfur compounds associated with petroleum, the preparation of a number of typical bicyclic sulfides has been undertaken. In the previous paper of this series (1) the *cis*- and *trans*- isomers of both 2-thiahydrindan and 2-thiadecalin were described. The present account records the synthesis of the *cis*- and *trans*- isomers of 1-thiahydrindan[1] and three of the four possible thiabicyclooctanes containing two condensed five-membered rings, *viz.* the *cis*- and *trans*- isomers of 3-thiabicyclo[3.3.0]octane and *cis*-2-thiabicyclo[3.3.0]octane. Attempts to prepare the *trans*-2-thiabicyclo[3.3.0]octane by isomerization of the corresponding *cis*-sulfone have so far proved unsuccessful; this method was successfully used for the preparation of *trans*-1-thiahydrindan.

cis-2-Thiabicyclo[3.3.0]octane (V) and *cis*-1-thiahydrindan (VI) were prepared from the appropriate cycloalkanones *via* the diolefins and sulfones as indicated in the reaction scheme.



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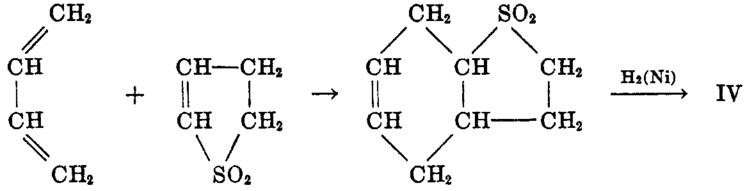
[1] The isolation of these sulfides in a kerosine distillate from an Agha Jari (S. Persia) crude oil has recently been reported by Birch, Cullum, Dean, and Denyer [*Ind. Eng. Chem.*, **47**, 240 (1955)].



IX

I, III, V, VII n = 3
II, IV, VI, VIII n = 4

The unsaturated sulfones (I, II), previously prepared by Backer and Bij (2), were obtained by us in good yields using the conditions of Grummitt and Splitter (3). Hydrogenation of these (4) was, however, a very erratic operation. The Adams platinum catalyst appeared to be completely ineffective but one portion of I was successfully hydrogenated with the aid of a palladium on barium sulfate catalyst (5). Raney nickel proved the most reliable catalyst for I although to obtain complete hydrogenation the addition of fresh catalyst generally was necessary. Acidification of the used catalyst from this sulfone with hydrochloric acid invariably produced hydrogen sulfide indicating that desulfurization had occurred to some extent. The hydrogenation of II, even with Raney nickel, was more erratic, although in this instance the used catalyst contained no sulfide. On some occasions only part (30–50%) of the theoretical amount of hydrogen was absorbed in spite of the addition of fresh catalyst. The unreduced sulfone (II) was accordingly converted to the saturated compound (IV) by hydrogenation of the dibromide (VIII) in the presence of Raney nickel and sodium methoxide (6).

It was anticipated that the sulfones (III, IV) would have a *cis*-configuration and this was confirmed in the case of *cis*-1-thiahydrindan sulfone (IV) by comparing it with the product formed on hydrogenation of the Diels-Adler adduct (IX) from 2,3-dihydrothiophene sulfone and butadiene. By the Alder rule (7), the condensation product (IX) will have a *cis*-configuration and this will be unaffected by hydrogenation. The sulfone (IX) was prepared by the method of Alder, Rickert, and Windemuth (8). These authors do not report a yield but using their conditions only *ca.* 20% of the product was obtained. This figure was increased to 43% by extending the heating period from 25 to 66 hours, but even with this time none of the required product could be isolated when the scale of the reaction was increased either four- or six-fold.

The reduction of the sulfones to sulfides was carried out using lithium aluminum hydride as described by Bordwell and McKellin (9). Diethyl ether was used as the solvent after it had been shown that refluxing tetrahydropyran caused appreciable mercaptan formation. Although the reaction mixture contained excess hydride, unreduced sulfone was always present in the product. It was shown that an increase in reaction time beyond four hours had little effect on the extent of reduction and that an increase in the hydride/sulfone ratio did not produce reduction of all the sulfone (Table I). The formation of a

TABLE I

REDUCTION OF *cis*-1-THIAHYDRINDAN-1,1-DIOXIDE

Molar Ratio $LiAlH_4$/Sulfone	Yield of Sulfide, % (on Sulfone used)	Unreduced Sulfone, %
1:1	42	55
2:1	54	44
3:1	58	37
5:1	62	32

precipitate during the reaction suggests that the incomplete reduction of the sulfone results from the existence of an insoluble, and therefore slowly reduced, complex between the sulfone and the hydride. It was anticipated that any sulfone recovered from this complex would contain both stereoisomers and *trans*-1-thiahydrindan sulfone was in fact isolated from the sulfone recovered from the reduction of IV. *cis*-2-Thiabicyclo[3.3.0]octane (V) was purified through its mercuric chloride complex and by fractional distillation, and *cis*-1-thiahydrindan (VI) by repeated crystallization of its mercuric chloride complex. When the *trans*-1-thiahydrindan became available it was shown by infrared spectroscopic analysis that the *cis*-1-thiahydrindan, before purification, contained *ca.* 8% of the *trans*- isomer. It is believed that the reduction is stereospecific and that the *trans*-sulfide results from reduction of the *trans*-sulfone, formed by isomerization.

trans-1-Thiahydrindan was prepared by reduction of the *trans*-sulfone obtained by isomerization of the *cis*-sulfone with alcoholic alkali. This isomerization, further details of which will be given in a subsequent publication, is believed to result from activation of the hydrogen atoms on the adjacent carbon atoms by the sulfone group. The sulfide was purified by crystallization of the mercuric chloride complex.

The two stereoisomers of 3-thiabicyclo[3.3.0]octane were prepared from the corresponding isomers of cyclopentane-1,2-dicarboxylic acid, *via* the glycol and ditosate,[2] by the method previously described for the preparation of 3-thiabicyclo[3.2.1]octane from *cis*-cyclopentane-1,3-dicarboxylic acid (10). Since the completion of the present work Owen and Peto (11) have described the preparation of these two sulfides from the corresponding ditosates. These workers also prepared the *cis*- and *trans*-3-oxabicyclo[3.3.0]octanes from the dimethanesulfonates by alkaline hydrolysis. The *cis*-oxide was obtained by us as a by-product (12) in the preparation of the ditosate of *cis*-1,2-bishydroxymethylcyclopentane and also by dehydration of the corresponding glycol with aqueous sulfuric acid.

Since cyclopentane-1,2-dicarboxylic acid for these preparations was required in comparatively large amounts, Perkin's method (13), involving the condensation of malonic ester and trimethylene dibromide was considered unsuitable as Halford and Weissmann (14) have reported it to give a low yield.[3] An alternative

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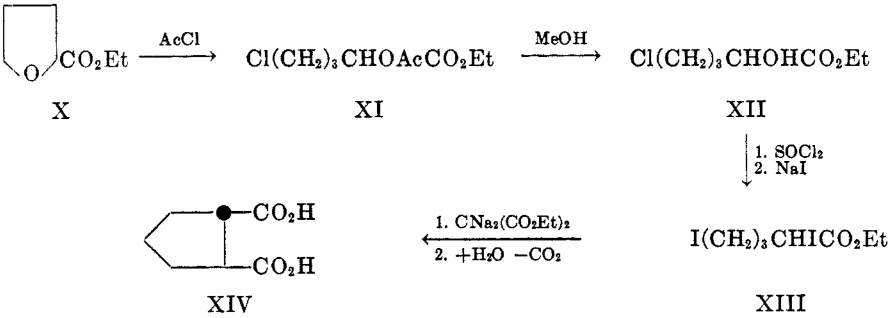
[2] Di-*p*-toluene sulfonate.

[3] Bailey and Sorenson [*J. Am. Chem. Soc.*, **76**, 5421 (1954)], have recently modified Perkins method and obtained good yields.

route described by Fuson, *et al.* (15) suffers from the disadvantage that it starts from pimelic acid which was not readily available to us. Investigations showed that condensation of ethyl α,δ-dichlorovalerate with diethyl disodiomalonate, followed by hydrolysis and decarboxylation of the product in acid solution, gave the *trans-* acid (XIV), but the yield (30–40%) was poor. Conversion of the dichloro- to the diiodo-ester (XIII) and reaction of the latter with malonate, however, gave good yields (70–80%) of the required acid, and this method was finally adopted. In this condensation the mode of addition of the reactants was found to influence the yield materially and concurrent addition of sodium ethoxide solution and a mixture of the malonate and diiodoester was found to give the highest yield. The dichloro- ester was obtained, using the method of Paul (16), from ethyl tetrahydrofuroate (X).



The product from the acetic anhydride treatment (17) of the *trans-* acid appeared to be a mixture of mono- and poly-meric anhydrides but since the latter depolymerized on strong heating the distillate was essentially monomeric anhydride and on redistillation it boiled over a narrow range. Hydrolysis gave almost pure *cis*-cyclopentane-1,2-dicarboxylic acid although several crystallizations of the anhydride were required to give pure material.

The *cis-* and *trans*-3-thiabicyclo[3.3.0]octanes were purified by crystallization of their mercuric chloride complexes.

Derivatives of the five sulfides were prepared as described previously (1, 18); their physical properties and those of the sulfides are given in Tables III and II. The infrared absorption spectra were obtained for these sulfides in the range 2–15μ using a Grubb-Parsons double beam spectrometer (Figures 1–5).

EXPERIMENTAL

All melting points are corrected. Purities were estimated by the freezing point method of Mair, Glasgow, and Rossini (20). Cryoscopic constants were estimated from the freezing time. Microanalyses are by Dr. Ing. A. Schoeller of Kronach/Oberfranken, Bambergerstrasse 20, Germany. All hydrogenations were carried out at room temperature and atmospheric pressure.

cis- AND *trans*-3-THIABICYCLO[3.3.0]OCTANE

Ethyl α-acetoxy-δ-chlorovalerate (XI). Acetyl chloride (950 g., 12.1 moles) was added (1 hr.) to ethyl tetrahydrofuroate (n_D^{20} 1.4365, 875 g., 6.1 moles) and freshly fused zinc chloride (1 g.) at 65–70°, an additional quantity (1 g.) of zinc chloride was added and the

TABLE II

Physical Properties of the *cis*- and *trans*- Bicyclic Sulfides

Sulfide	Temp., °C.	Refractive Index[b]							B. P., °C.	Density, g./ml.		Estimated Purity, mole-%	Estimated m.p. for zero impurity, °C.	Cryoscopic constant, mole-% per deg. C.
		Wavelength Ångstrom Units								20°	25°			
		6678	6563	5893	5461	5016	4861	4358						
cis-1-Thiahydrindan	20	1.52716	1.52762	1.53078	1.53352	1.53717	1.53871	1.54506	102.0–102.5	1.0383	1.0341	*ca.* 99.0	−44.1	2.5[d]
	25	1.52490	1.52535	1.52850	1.53122	1.53485	1.53638	1.54270	at 20 mm.					
	30	1.52266	1.52311	1.52624	1.52894	1.53255	1.53407	1.54035						
trans-1-Thiahydrindan	20	1.52115	1.52161	1.52478	1.52753	1.53119	1.53273	1.53910	102.7–103.7	1.0209	1.0167	*ca.* 99.6	−11.50[c]	1.2[a]
	25	1.51889	1.51934	1.52249	1.52521	1.52284	1.53037	1.53669	at 21 mm.					
	30	1.51657	1.51702	1.52016	1.52288	1.52650	1.52802	1.53433						
cis-2-Thiabicyclo[3.3.0]-octane	20	1.52424	1.52470	1.52791	1.53067	1.54337	1.53592	1.54236	87.7–88.0	1.0419	1.0379	—	*ca.* −33	—
	25	1.52185	1.52230	1.52551	1.52827	1.53197	1.53352	1.53995	at 25 mm.					
	30	1.51959	1.52003	1.52322	1.52596	1.52963	1.53117	1.53756						
cis-3-Thiabicyclo[3.3.0]-octane	20	1.52388	1.52434	1.52757	1.53034	1.53404	1.53559	1.54199	88.3–88.5	1.0427	1.0386	99.9	−17.16	0.11[a]
	25	1.52159	1.52205	1.52528	1.52805	1.53175	1.53330	1.53970	at 25 mm.					
	30	1.51939	1.51985	1.52306	1.52581	1.52949	1.53103	1.53739						
trans-3-Thiabicyclo-[3.3.0]octane	30	1.52099	1.52144	1.52464	1.52740	1.53110	1.53266	1.53911	95.5–96.0	1.0294	—	99.8	28.05	1.6[a]
									at 28 mm.	at 30°				

[a] Determined by measuring the latent heat of fusion.

[b] These values have been smoothed by the method of Forziati (19).

[c] Actual melting point of the sample—no freezing point for zero impurity could be estimated.

[d] A second crystalline modification melted at *ca.* −47.3°; thus no latent heat of fusion could be determined.

TABLE III

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 C	Calc'd H	Calc'd S	Found C	Found H	Found S
cis-1-Thiahydrindan	$C_8H_{14}Cl_2HgS$	135.0–136.0	23.2	3.4	7.7	23.3	3.7	—
	$C_8H_{14}O_2S$	38.24	55.1	8.1	18.4	55.1	8.1	18.4
	$C_9H_{17}IS$	142.4–142.7	38.0	6.0	11.3	38.0	5.9	11.1
trans-1-Thiahydrindan	$C_8H_{14}Cl_2HgS$	143.5–144.5	23.2	3.4	7.7	23.3	3.6	7.7
	$C_8H_{14}O_2S$	92.8– 93.5	55.1	8.1	18.4	55.2	8.1	18.4
	$C_9H_{17}IS$	163.2–163.7	38.0	6.0	11.3	38.3	6.2	11.2
cis-2-Thiabicyclo-[3.3.0]octane	$C_7H_{12}Cl_2HgS$	93.5– 94.0	21.0	3.0	8.0	21.3	3.2	7.7
	$C_7H_{12}O_2S$	36.65	52.5	7.6	20.0	52.5	7.7	19.9
	$C_8H_{15}IS$	142.0–143.0	35.6	5.6	11.9	35.7	5.7	11.8
cis-3-Thiabicyclo-[3.3.0]octane	$C_7H_{12}Cl_2HgS$	163.5–164.0	21.0	3.0	8.0	21.1	3.0	8.3
	$C_7H_{12}O_2S$	72.0– 72.5	52.5	7.6	20.0	52.7	7.8	20.0
	$C_8H_{15}IS$	174.0–174.5	35.6	5.6	11.9	35.6	5.5	11.9
trans-3-Thiabicyclo-[3.3.0]octane	$C_7H_{12}Cl_2HgS$	185.5–186.0	21.0	3.0	8.0	21.2	3.2	8.0
	$C_7H_{12}O_2S$	119.7–120.2	52.5	7.6	20.0	52.5	7.7	20.0
	$C_8H_{15}IS$	119.7–120.7[a]	35.6	5.6	11.9	35.6	5.6	11.9
	$C_7H_{12}OS$	87.5– 88.5	58.3	8.4	22.2	58.5	8.6	22.2

The methiodides all melted with decomposition. [a] Sealed tube.

solution was refluxed for five hours. After removal of excess acetyl chloride the residual oil was distilled to give (a) a fraction (120 g.) b.p. 80°/10 mm.–120°/7 mm. and (b) the required ester (1100 g.) b.p. 120–132°/7 mm.; n_D^{20} 1.4428. The yield of ethyl α-acetoxy-δ-chlorovalerate was increased to 91% (1228 g.) by treating the low-boiling material with acetyl chloride.

Ethyl α,δ-diiodovalerate[4] (XIII). A solution of ethyl α-acetoxy-δ-chlorovalerate (824 g.) in methanol (1400 g.) and concentrated hydrochloric acid (14 ml.) was refluxed (19 hr.) through a short glass-packed column and the methyl acetate/methanol azeotrope (b.p. 54°/760 mm.) was removed as it was formed. Removal of the solvent left the required ester (XII). Yield almost theoretical. Thionyl chloride (640 g.) was added to a stirred solution of this material (600 g.) in cyclohexane (1200 ml.) and pyridine (360 g.) at 15° after which it was slowly (30 min.) heated to 70° and maintained at this temperature for 30 minutes. The cooled product was poured in to ice/water (1 l.), and the cyclohexane layer was distilled to give the dichloro-ester in 70% yield; b.p. 77–79°/2 mm.; n_D^{20} 1.4610. Conversion of the dichloro-ester to the diiodo-ester was effected by refluxing the former (437 g.) for 16 hours with a solution of sodium iodide (900 g.) in acetone (5 l.). The crude diiodo-ester (92% yield) was freed from traces of iodine by treatment with aqueous sodium thiosulfate and used without further treatment.

trans-Cyclopentane-1,2-dicarboxylic acid (XIV). A mixture of diethyl malonate (261 g., 1.63 moles) and ethyl α,δ-diiodovalerate (540 g., 1.41 moles) and a solution of sodium ethoxide (sodium 75 g., 3.26 g.-atoms) in anhydrous ethanol (1.4 l.) were added concurrently to a stirred solution of the diiodo-ester (60 g., 0.16 mole) in anhydrous ethanol (200 ml.), at such a rate that the addition of the two solutions was completed in the same time

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[4] From the method of preparation the ester is believed to be mainly ethyl but some methyl may be present.

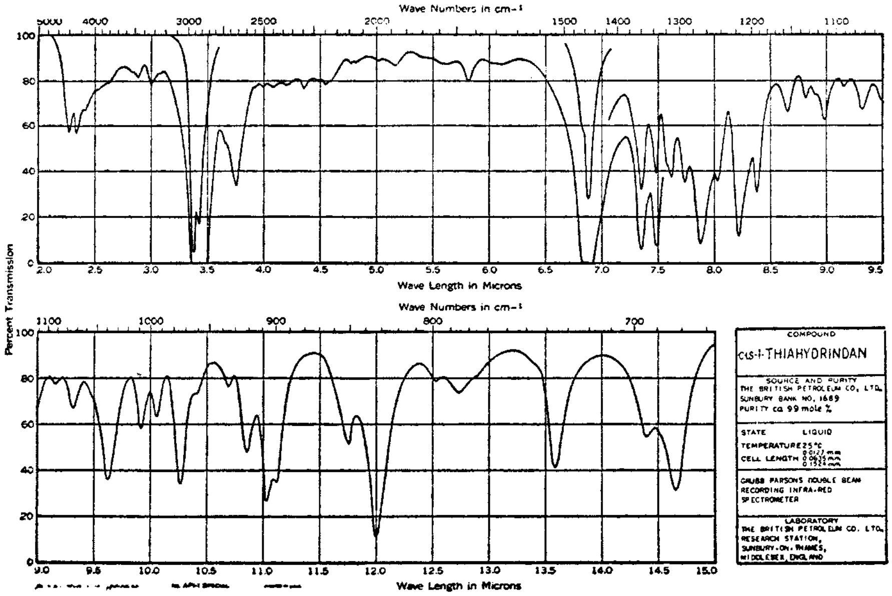

FIG. 1.

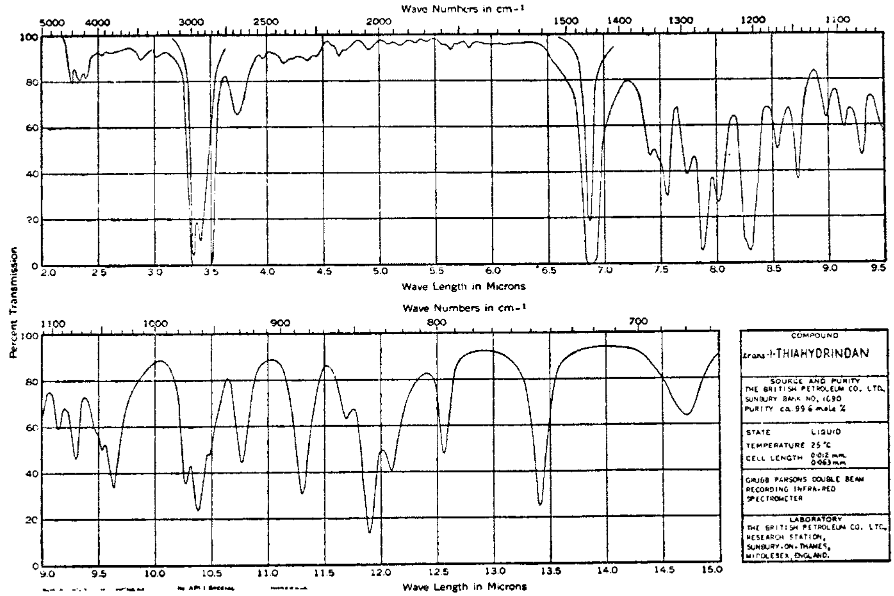

FIG. 2.

FIGS. 1 and 2. INFRARED SPECTRA OF THIAHYDRINDANS.

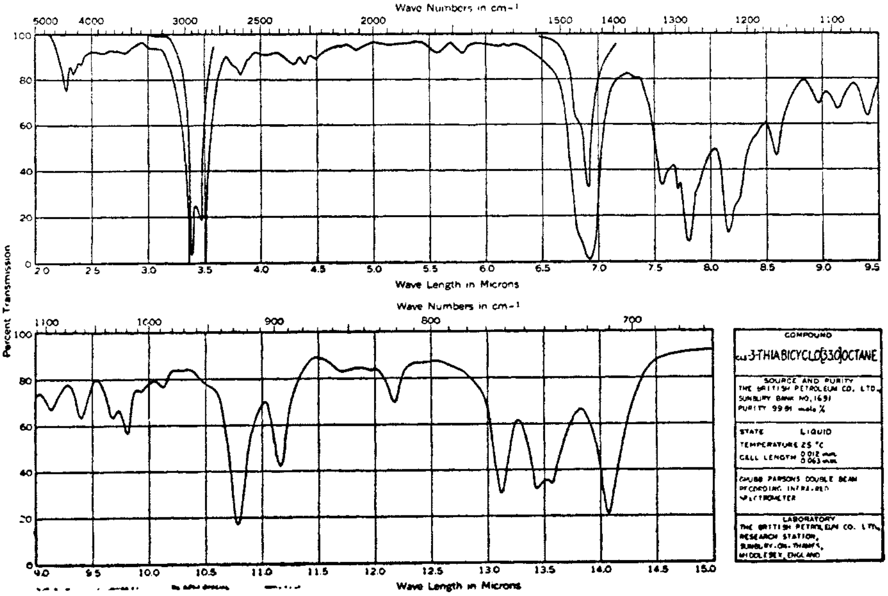

FIG. 3.

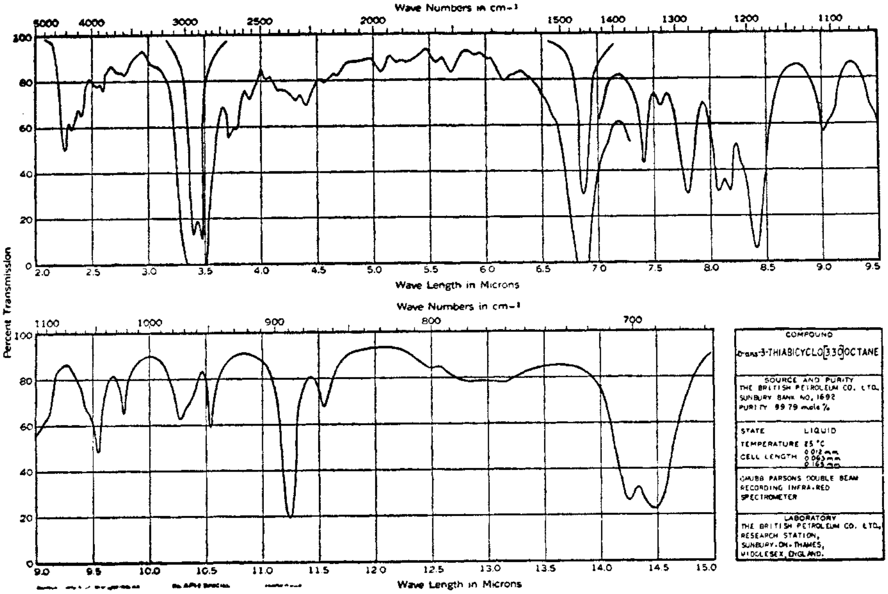

FIG. 4.

FIGS. 3 and 4. INFRARED SPECTRA OF 3-THIABICYCLO[3.3.0]OCTANES.

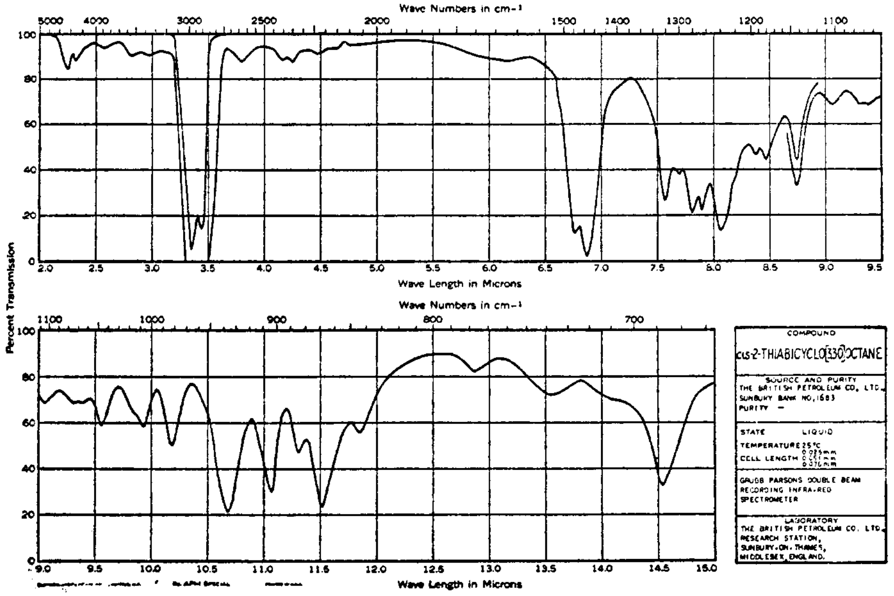

FIG. 5. INFRARED SPECTRA OF *cis*-2-THIABICYCLO[3.3.0]OCTANE.

(1.5 hr.). After refluxing overnight, water (1.5 l.) was added and the ethanol was removed by distillation. The cyclopentane-1,1,2-tricarboxylic ester, isolated by extraction with ether, was hydrolyzed and decarboxylated by refluxing (96 hr.) with concentrated hydrochloric acid (1.5 l.). After decolorizing with charcoal the *trans-* acid (m.p. 161–162°) crystallized on cooling. Yield 65–70%. A further quantity was obtained from the mother liquors. Total yield 80%. Recrystallized from acetone it melted at 162–163°.

cis-Cyclopentane-1,2-dicarboxylic acid anhydride was obtained by refluxing *trans*-cyclopentane-1,2-dicarboxylic acid (640 g.) for 10 hours with acetic anhydride (3.2 l.) and distilling the product in 150-g. portions after removal of acetic anhydride. The material b.p. 110–180°/2 mm. on redistillation gave the *cis*-anhydride, b.p. 110–120°/2 mm. Yield 81%. A portion recrystallized 6 times from ether melted at 73.5–74°.

cis-Cyclopentane-1,2-dicarboxylic acid. The anhydride (447 g.) was hydrolyzed by refluxing with an aqueous potassium hydroxide solution (13.5%, 3000 g.). Cooling and acidification with concentrated hydrochloric acid (1 l.) yielded crude *cis*-acid. On dissolving the latter in water (1 l.), cooling to 0°, and adding concentrated hydrochloric acid (450 ml.), the pure *cis*-acid crystallized, m.p. 139–140°. Extraction of the combined mother liquors with ether and crystallization of the extract gave an additional quantity of pure acid. Total yield 73%.

cis- and trans-3-Thiabicyclo[3.3.0]octane. The yields and physical properties of the intermediate *cis-* and *trans-* esters, glycols, and ditosates are given in Table IV.

The sulfides were obtained by treatment of the appropriate ditosate with sodium sulfide and were purified as previously described by Birch and Dean (10). The *cis-* isomer was obtained in 79% yield and the *trans-* in 76% yield; their physical properties are given in Table II.

Anal. Calc'd for $C_7H_{12}S$: C, 65.6; H, 9.4; S, 25.0.

Found for *cis*-3-thiabicyclo[3.3.0]octane: C, 65.8; H, 9.7; S, 24.7.

Found for *trans*-3-thiabicyclo[3.3.0]octane: C, 65.5; H, 9.6; S, 24.9.

cis-3-Oxabicyclo[3.3.0]octane. (*a*). The aqueous mother liquors from the preparation of the *cis-* ditosate were distilled through a short glass-packed column until the distillate

TABLE IV

PHYSICAL PROPERTIES OF INTERMEDIATE COMPOUNDS USED IN THE SYNTHESIS OF *cis*- AND *trans*- 3-THIABICYCLO[3.3.0]OCTANE AND *cis*-1-THIAHYDRINDAN

Compound	B.P.		n_D^{20}	d^{20}	Estimated Purity, mole-%	M.P.,°C	Cryoscopic constant,[b] mole-% per deg. C.	Yield, %
	°C.	mm.						
Diethyl *cis*-cyclopentane-1,2-dicarboxylate	119–122	6.0	1.4490	1.0630	98.9	−30.51	1.5	94
Diethyl *trans*-cyclopentane-1,2-dicarboxylate	111–113	7.0	1.4435	1.0480	99.4	−32.13	4.0	95
cis-1,2-Bis-hydroxymethylcyclopentane	117–119	1.6	1.4851	1.059	99.7	6.70	1.0	98
trans-1,2-Bis-hydroxymethylcyclopentane	102–106	0.4	1.4798	1.045	Would not freeze		—	96
cis-1,2-Bis-*p*-toluenesulfonoxymethyl cyclopentane	—	—	—	—	—	80.0–80.5	—	65
trans-1,2-Bis-*p*-toluenesulfonoxymethylcyclopentane	—	—	—	—	—	73.5–74.0	—	96
1-Ethynylcyclohexanol	81.5–82.5	20	1.4803[c]	—	98.7	30.41	3.0	74[a]
1-Vinylcyclohexanol	84.5–86.0	30	1.4777	—	—	—	—	73
1-Vinylcyclohexene	139–144	760	1.4952	—	—	—	—	89
2,4,5,6,7,7a-Hexahydrothianaphthene-1,1-dioxide (II)	Decomp.		—	—	Would not freeze		—	74

[a] Taking into account recovered cyclohexanone (18%). [b] Estimated from freezing time. [c] n_D^{30}.

became homogeneous. Extraction of the distillate with ether gave the oxide, b.p. 146–149°/764 mm.; n_D^{20} 1.4603. Yield, based on the glycol, 12%.

(*b*). The oxide was also obtained, in 70% yield, by dehydration of the *cis*- glycol with sulfuric acid using the method described previously for the preparation of hexahydrophthalan (1).

Anal. Calc'd for $C_7H_{12}O$: C, 75.0; H, 10.8.
Found: C, 74.7; H, 10.9.

cis-2-THIABICYCLO[3.3.0]OCTANE AND *cis*-1-THIAHYDRINDAN

1-Ethynylcyclopentanol was prepared from cyclopentanone by the method given in Organic Syntheses (21), fractionation of the product through a 50-plate column giving the required alcohol, b.p. 60–61°/12 mm.; n_D^{25} 1.4725; d^{25} 0.9698; f.p. 25.28°; purity 98.9 mole-%; cryoscopic constant 4.0 mole-% per deg. Yield 52% taking into account recovered ketone (10%).

1-Vinylcyclopentanol. 1-Ethynylcyclopentanol (330 g.) in methanol (1 l.) was hydrogenated over a palladium on calcium carbonate catalyst (22) until the theoretical amount of hydrogen had been absorbed. The product, after removal of catalyst and solvent, was fractionated in a 50-plate column giving 1-vinylcyclopentanol, yield 75%; b.p. 45°/6.5 mm.; n_D^{20} 1.4711; d^{20} 0.9399; f.p. −11.20°; purity 98.8 mole-%; cryoscopic constant 4.0 mole-% per deg.

1-Vinylcyclopentene was obtained by dehydrating 1-vinylcyclopentanol with potassium bisulfate at 160° under nitrogen. Redistillation of the dried product through a short glass-packed column in an atmosphere of nitrogen gave the diolefin in 74% yield; b.p. 109–112°/760 mm.; n_D^{20} 1.4863; d^{20} 0.8267; f.p. −105.12°; purity 98.4 mole-%; cryoscopic constant 4.0 mole-% per deg.

2-Thiabicyclo[3.3.0]-(4,5)-octene-2,2-dioxide (I). A stainless steel pressure vessel, charged with a mixture of freshly distilled 1-vinylcyclopentene (18.8 g.), liquid sulfur dioxide (96 g.), and phenyl-β-naphthylamine (0.2 g.), was heated at 68–70° for 2.5 hours. On removal of sulfur dioxide the product was obtained in theoretical yield. Crystallized from chloroform it melted at 75–76° dec.

Anal. Calc'd for $C_7H_{10}SO_2$: S, 20.3. Found: S, 19.9.

cis-2-Thiabicyclo[3.3.0]octane-2,2-dioxide (III). (*a*). The unsaturated sulfone (I) (68 g.) in ethanol (600 ml.) was hydrogenated over a Raney nickel catalyst (23) (6 g.) absorbing 9.05 l. of hydrogen in three hours (theoretical 9.6 l.). After distillation, the product, b.p. 133–135°/1.5 mm. was crystallized from diethyl ether; m.p. 36.65°; purity 99.1 mole-%; cryoscopic constant 3.0 mole-% per deg.

(*b*). 4,5-Dibromo-2-thiabicyclo[3.3.0]octane-2,2-dioxide (VII), prepared from I, when hydrogenated in a sodium methoxide/methanol solution (6) over Raney nickel gave a product, m.p. 37.5–38°. The sulfones prepared by both of these methods were identical (mixture m.p.).

cis-2-Thiabicyclo[3.3.0]octane (V). A solution of *cis*-2-thiabicyclo[3.3.0]octane-2,2-dioxide (107 g., 0.67 mole) in ether (700 ml.) was slowly added (2.5 hr.) to a refluxing solution of lithium aluminum hydride (102 g., 2.7 moles) in ether (2 l.), and the mixture was refluxed for a further four hours. The product, after cautious decomposition with water (500 ml.) and acidification with 15% hydrochloric acid (2.8 l.), was continuously extracted with ether. Removal of the solvent from the dried extract left an oil which on distillation gave the sulfide, b.p. 78°/14 mm. (yield 63% based on sulfone used) and unreacted sulfone (29 g.). The crude sulfide after removal of traces of mercaptan by treatment with alkaline hydrogen peroxide, was fractionated through a 30-plate column containing Bower and Cooke type packing (24). Fractions of constant refractive index, b.p. 87.7–88°/25 mm., were combined as the pure sulfide. (The sulfone obtained by oxidation of a sample of this sulfide was identical (mixture m.p.) with the sulfone from which the sulfide was obtained.) No accurate purity of the sulfide could be determined due to its poor freezing characteristics but since crystallization of the mercuric chloride complex failed to bring about any significant change in the refractive index it was assumed to be pure. The physical properties of *cis*-2-thiabicyclo[3.3.0]octane are given in Table II.

Anal. Calc'd for $C_7H_{12}S$: C, 65.6; H, 9.4; S, 25.0.
Found: C, 65.5; H, 9.4; S, 24.8.

cis-1-Thiahydrindan-1,1-dioxide (IV). The yields and physical properties of the intermediates used in the preparation of IV are given in Table IV.

(*a*). Hydrogenations of II (by the method used for I) which went to completion gave a 96% yield of the saturated sulfone. The products from incomplete hydrogenations were brominated in methanol at 0° (using the equivalent quantity of bromine as indicated by the bromine number of the mixture), sodium methoxide (equivalent to the bromine used) was added, and the resulting solution was hydrogenated using Raney nickel. Distillation of the product gave the saturated sulfone, b.p. 139–141°/1.4 mm., in 81% yield, identical (m.p. and mixture m.p.) with that above, and a high-boiling residue. The sulfone was purified by crystallization from diethyl ether; m.p. 38.24°; purity 98.4 mole-%; cryoscopic constant 3.0 mole-% per deg.

(*b*). A mixture of butadiene (12 ml.), 2,3-dihydrothiophene-1,1-dioxide (5 g.) (25), and phenyl-β-naphthylamine (0.1 g.) was heated in a pressure vessel at 180° for 66 hours and the product was distilled. The fraction b.p. 110–140°/0.5 mm. (5.9 g.) on crystallization from ethyl acetate gave the sulfone (IX), m.p. 95° (3.12 g.). This was hydrogenated using Raney nickel and the product, crystallized from ether, melted at 38.5–40°, undepressed on admixture with the product from (*a*).

cis-1-Thiahydrindan (VI) was prepared by reduction of IV with a 1:2 molar ratio of lithium aluminum hydride using the method described previously. The sulfide was obtained in 54% yield (95% based on sulfone converted). Reduction of the recovered sulfone gave an additional quantity of sulfide (retained as second quality material) and unreduced sulfone. Fractional crystallization of the latter yielded a small quantity of material, m.p. 92°, subsequently identified as the *trans*- isomer of 1-thiahydrindan-1,1-dioxide.

The sulfide was purified through its mercuric chloride complex, its physical properties are given in Table II.

Anal. Calc'd for $C_8H_{14}S$: C, 67.5; H, 9.9; S, 22.5.
Found: C, 67.6; H, 10.2; S, 22.2.

trans-1-THIAHYDRINDAN

trans-1-Thiahydrindan-1,1-dioxide. *cis*-1-Thiahydrindan-1,1-dioxide (232 g.) was refluxed (1.5 hr.) with a solution of caustic potash (200 g.) in ethanol (2 l.). The cooled solution was neutralized with carbon dioxide and filtered to remove potassium carbonate. Removal of alcohol from the filtrate by distillation left a residue which on crystallization from ether gave a solid sulfone (89 g.) m.p. 81–85°. Repeated isomerization of the residual oil obtained from the crystallization mother liquors gave successive quantities of this solid. Recrystallization to constant melting point from ether gave pure *trans*-1-thiahydrindan-1,1-dioxide (160 g.) melting at 92.8–93.5°.

trans-1-Thiahydrindan was obtained in 55% yield (on sulfone used) by reduction of the *trans*-sulfone (1:2 molar ratio) as described for III, and it was purified by recrystallization of the mercuric chloride complex. The physical properties of the pure *trans*- sulfide are given in Table II.

Anal. Calc'd for $C_8H_{14}S$: C, 67.5; H, 9.9; S. 22.5.
Found: C, 67.6; H, 10.1; S, 22.0.

The sulfones obtained by oxidation of the pure *cis*- and *trans*-1-thiahydrindans were identical (mixture m.p.) with the sulfones from which the sulfides were obtained.

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SUMMARY

The *cis*- and *trans*- isomers of 1-thiahydrindan and 3-thiabicyclo[3.3.0]octane, and *cis*-2-thiabicyclo[3.3.0]octane have been synthesized and their physical properties have been recorded.

Alcoholic alkali has been shown to produce *cis-trans* isomerization of the 1-thiahydrindan-1,1-dioxides.

Each sulfide has been characterized by the preparation of derivatives.

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On and after September 1, 1955, the Journal will accept *Notes*; the Journal will accept *Communications to the Editor* received on or after November 1, 1955 for publication in Volume 21. See revised Notice to Authors for details.

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