[Contribution from the Research Station, The British Petroleum Company Limited]

Preparation and Physical Properties of Sulfur Compounds Related to Petroleum. VI. *endo*-4,7-Methano-*cis*-2-thiahydrindan and *endo*-4,7-Ethano-*cis*-2-thiahydrindan

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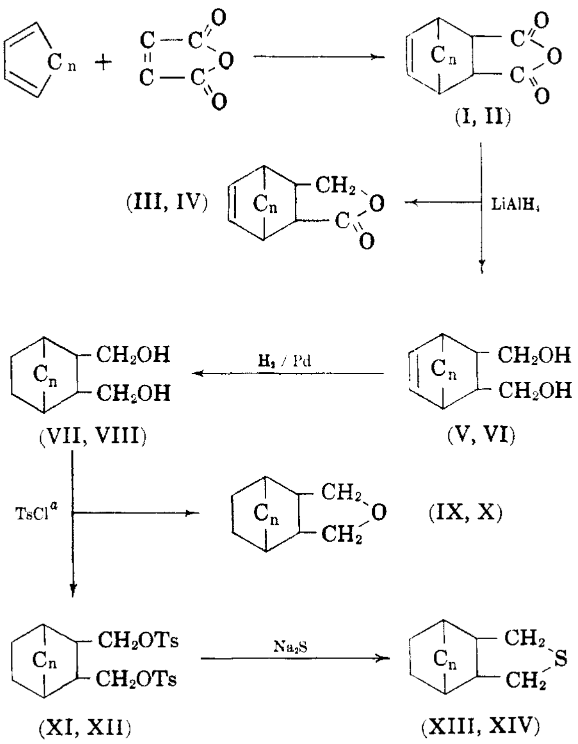
endo-4,7-Methano-*cis*-2-thiahydrindan and *endo*-4,7-ethano-*cis*-2-thiahydrindan have been synthesized and their physical properties have been recorded. The sulfides have been characterized by the preparation of derivatives.

As part of a program of research into the nature of sulfur compounds related to petroleum, a number of dialkyl, monocyclic, and bicyclic sulfides have been synthesized in these laboratories and their preparation and physical properties have been described in the previous papers of this series.[1–5] The isolation of thiadamantane from a kerosine extract tar oil[6] has shown that tricyclic sulfides, a class of compounds about which little is known, are also present in petroleum. The preparation of two compounds of this type, *viz.* *endo*-4,7-methano-*cis*-2-thiahydrindan ·(XIII) and *endo*-4,7-ethano-*cis*-2-thiahydrindan (XIV), is now reported.

The syntheses involved the preparation of the diols VII and VIII and their conversion to the cyclic sulfides *via* their ditosates as shown in the reaction scheme.

The unsaturated anhydrides I and II were obtained by the Diels-Alder condensation of maleic anhydride and the appropriate cyclic dienes. Reduction of I and II with lithium aluminum hydride gave the unsaturated diols V and VI but considerable quantities of by-products resulting from partial reduction were also obtained and only about 50% of the theoretical yields of the pure diols could be isolated from the reaction products. Hydrogenation of the unsaturated diols proceeded smoothly to give the required compounds VII and VIII in quantitative yields. (Since the completion of this work, the lithium aluminum hydride reduction of I has been described by Bailey and Lawson.[7] These authors also describe the preparation of VII by esterification of I followed by two stage reduction of the unsaturated diester, *cf.* Alder and Roth.[8] This method gives VII in rather better overall yield than the method involving direct reduction of the anhydride which was employed by us).

Treatment of the diols VII and VIII with *p*-toluenesulfonyl chloride gave the ditosates XI and XII together with the corresponding cyclic oxides IX and X. The pure ditosates were obtained in 41 and 63% yields respectively by crystallization of the crude solid products from ethanol; small quantities of the oxides were isolated from the reaction liquors and purified by crystallization from methanol. The formation of *endo*-4,7-methano-*cis*-hexahydrophthalan (IX) on tosylation of the methanodiol VII has previously been reported by Alder and Roth.[9]



^{a} Ts = p-$CH_3C_6H_4SO_2$
I, III, V, VII, IX, XI, XIII n = 1
II, IV, VI, VIII, X, XII, XIV n = 2

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[1] McAllan, Cullum, Dean, and Fidler, *J. Am. Chem. Soc.*, **73**, 3627 (1951).

[2] Whitehead, Dean, and Fidler, *J. Am. Chem. Soc.*, **73**, 3632 (1951).

[3] Birch, Dean, and Whitehead, *J. Inst. Petroleum*, **40**, 76 (1954).

[4] Birch, Dean, and Whitehead, *J. Org. Chem.*, **19**, 1449 (1954).

[5] Birch, Dean, Hunter, and Whitehead, *J. Org. Chem.*, **20**, 1178 (1955).

[6] Birch, Cullum, Dean, and Denyer, *Ind. Eng. Chem.*, **47**, 240 (1955).

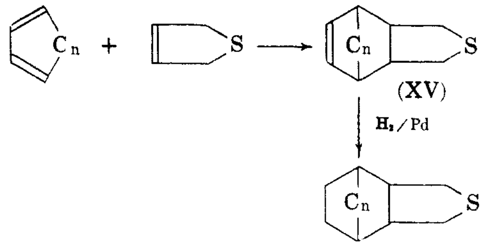
[7] Bailey and Lawson, *J. Am. Chem. Soc.*, **77**, 1606 (1955).

[8] Alder and Roth, *Ber.*, **87**, 161 (1954).

[9] Alder and Roth, *Ber.*, **88**, 407 (1955).

The sulfides XIII and XIV obtained by treatment of the ditosates with sodium sulfide were, like thiadamantane, solids with strong camphoraceous odors. The yields (18 and 47% respectively) were rather poorer than expected on the basis of the results of previous cyclizations of this type,[5] considerable quantities of polymeric materials being obtained. The sulfides were, as usual, purified through their mercuric chloride complexes.

From the work of Alder, Rickert, and Windemuth[10,11] and Mozingo and his co-workers[12] it appeared that the sulfides might also be obtained by condensation of 2,5-dihydrothiophene[13] with the appropriate cyclic diene and hydrogenation of the resultant unsaturated sulfide, as indicated below.



In an investigation into the possibilities of this method, cyclopentadiene was heated with 2,5-dihydrothiophene and it was found that a fraction consisting largely of *endo*-4,7-methano-*cis*-1,3,3a,-4,7,7a-hexahydroisothianaphthene (XV, n = 1) could be isolated from the complex condensation product. It was also found possible to hydrogenate the crude unsaturated sulfide using a large amount of catalyst; the sulfide isolated from the hydrogenation product through its mercuric chloride complex was shown by comparison of infrared spectra to be identical with XIII obtained by the method previously described. The over-all yield of XIII was about 5%.

Derivatives of the sulfides XIII, XIV, and XV were prepared and their melting points and analyses are recorded in Table I. The infrared absorption spectra in the range 2–15 μ of the sulfides XIII and XIV and the oxides IX and X have been obtained using a Grubb Parsons double beam spectrometer and they are recorded in Figures 1–4.

EXPERIMENTAL

Melting points are uncorrected. Microanalyses by Dr. Ing A. Schoeller, Kronach/Oberfranken, Germany.

endo-4,7-METHANO-*cis*-2-THIAHYDRINDAN

(*A*) *From the Diels-Alder adduct* (I) *of cyclopentadiene and maleic anhydride. endo-2,3-Dimethylolbicyclo*[*2.2.1*]*hept-5-ene* (V). *endo*-Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (I) (82 g.) was reduced with lithium aluminum hydride by the method of Nystrom and Brown.[14] Four crystallizations of the crude product from ether at −20° were necessary to remove the by-products and obtain material (40 g., 50%) melting constantly at 82–83°. Reported m.p. 82.8–83.4°[7] and 86°.[8] A total of 120 g. of pure diol was prepared in this way.

endo-2,3-Dimethylolbicyclo[*2.2.1*]*heptane* (VII). The diol (V) (120 g.) in methanol (600 ml.) was hydrogenated at room temperature and atmospheric pressure using Schmidt's catalyst[15] (10 g.). The saturated diol, which was obtained in quantitative yield, distilled at 145–150°/1 mm. and melted at 60°. Reported m.p. 60–61°[7] and 62°.[8]

TABLE I

Melting Points and Analyses of the Derivatives of the Sulfides

Sulfide	Formula of Derivative	M.P., °C. (uncorrected)	Analyses Calc'd C	Calc'd H	Calc'd S	Found C	Found H	Found S
endo-4,7-Methano-*cis*-1,3,3a,4,7,7a-hexahydro-isothianaphthene	$C_9H_{12}Cl_2HgS$	200–201	25.5	2.8	7.6	25.8	2.8	7.8
	$C_{10}H_{15}IS$	144–144.5[a]	40.8	5.1	10.9	41.1	5.0	11.0
	$C_9H_{12}O_2S$	114–116	58.7	6.6	17.4	58.4	6.6	17.7
endo-4,7-Methano-*cis*-2-thiahydrindan	$C_9H_{14}Cl_2HgS$	219–220	25.4	3.3	7.5	25.2	3.3	7.5
	$C_{10}H_{17}IS$	167–168.5[a]	40.5	5.8	10.8	40.7	6.2	11.0
	$C_9H_{14}O_2S$	102–104	58.0	7.6	17.2	58.3	7.9	17.4
endo-4,7-Ethano-*cis*-2-thiahydrindan	$C_{10}H_{16}Cl_2HgS$	212–213	27.3	3.7	7.3	27.4	3.8	7.4
	$C_{11}H_{19}IS$	185–187.5[a]	42.6	6.2	10.3	42.6	6.1	10.4
	$C_{10}H_{16}O_2S$	97–98	60.0	8.1	16.0	60.0	8.2	16.3

All the mercuric chloride complexes and methiodides melted with decomposition

[a] Sealed tube

Ditosate of endo-2,3-dimethylolbicyclo[*2.2.1*]*heptane* (XI). The ditosate was prepared from the diol (VII) (70 g.) by the method given in *Organic Syntheses*[16] and the product was crystallized from ethanol to give the pure material (85 g., 41%) melting at 129.5–130.5°. Reported m.p. 131°.[8] Ether extraction of the steam-distillate of the aqueous reaction liquors yielded a small quantity (3 g., 5%) of *endo*-4,7-methano-*cis*-hexahydrophthalan (IX) which, after crystallization from methanol and sublimation *in vacuo*, melted at 109.5–111.5°. Reported m.p. 110°.[9]

endo-4,7-Methano-cis-2-thiahydrindan (XIII) was pre-

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[10] Alder, Rickert, and Windemuth, *Ber.*, **71**, 2451 (1938).

[11] Alder and Windemuth, *Ber.*, **71**, 373 (1938).

[12] Mozingo, Harris, Wolf, Hoffhine, Easton, and Folkers, *J. Am. Chem. Soc.*, **67**, 2092 (1945).

[13] Birch and McAllan, *J. Chem. Soc.*, 2556 (1951).

[14] Nystrom and Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).

[15] Schmidt, *Ber.*, **52**, 400 (1919).

[16] Marvel and Sekera, *Org. Syntheses*, **20**, 50 (1940).

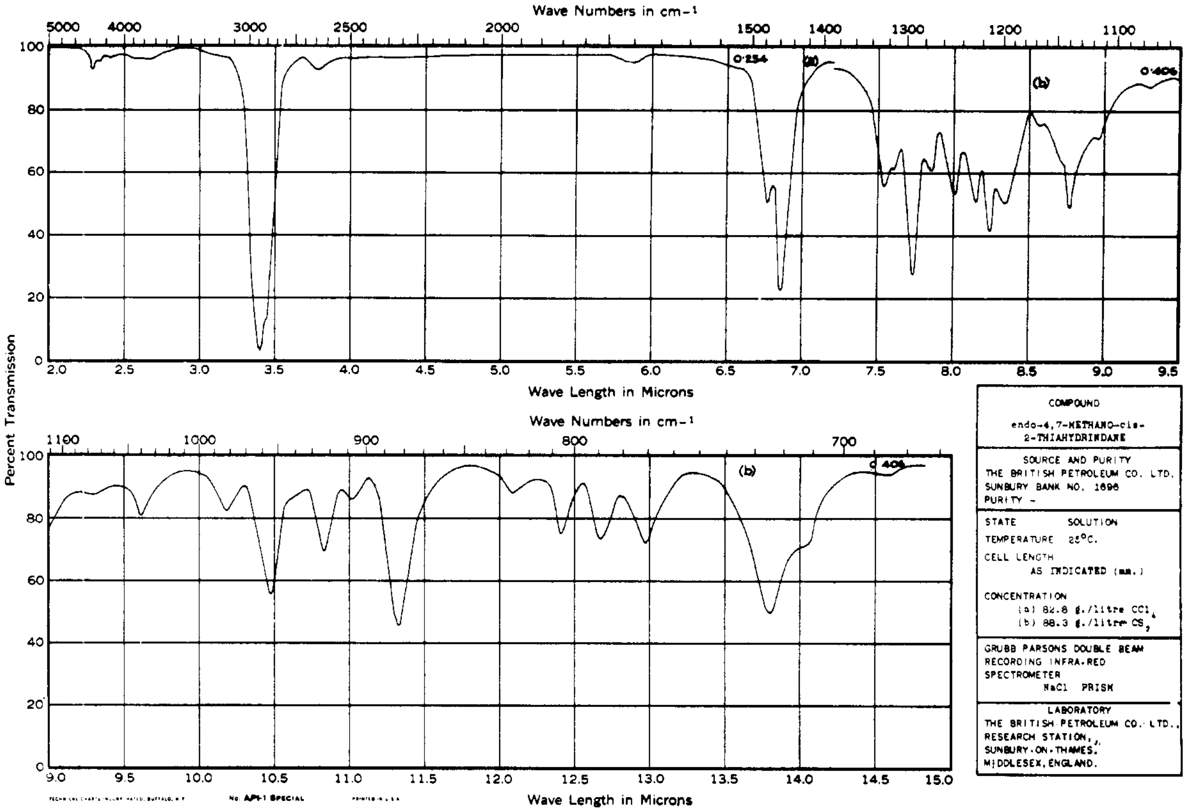


FIGURE 1.

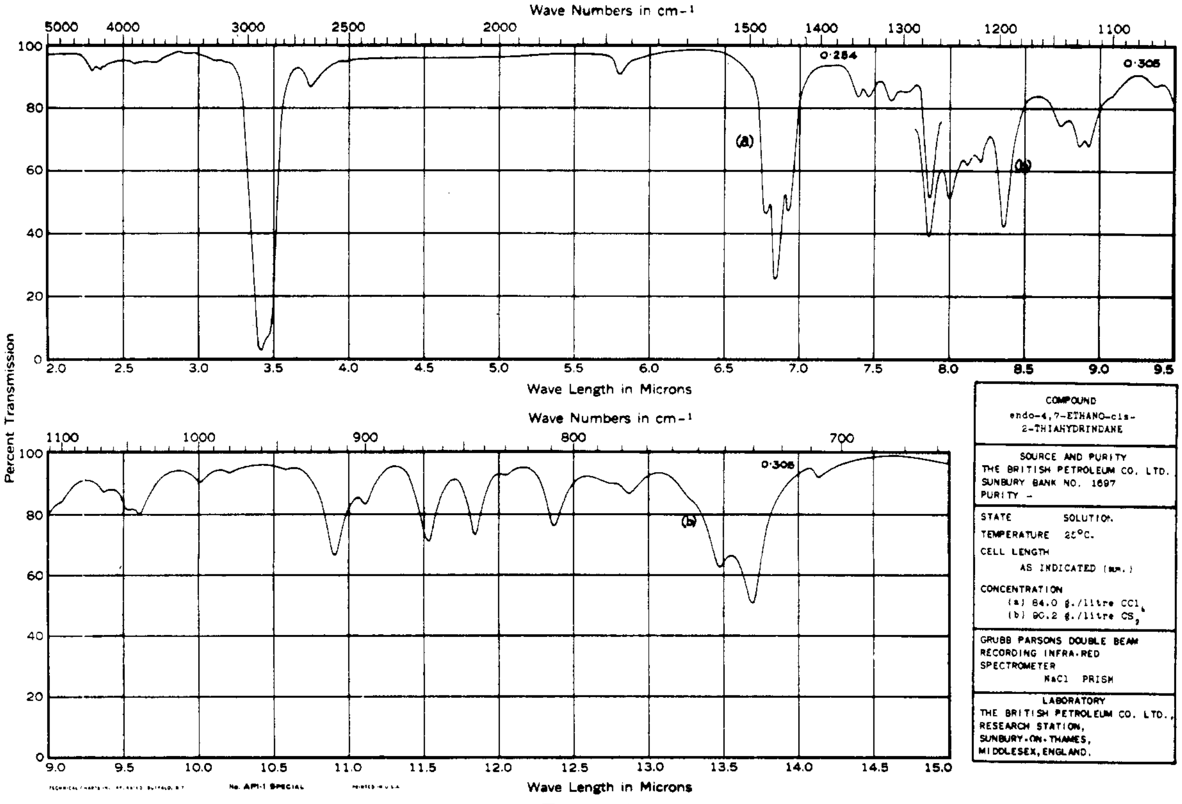
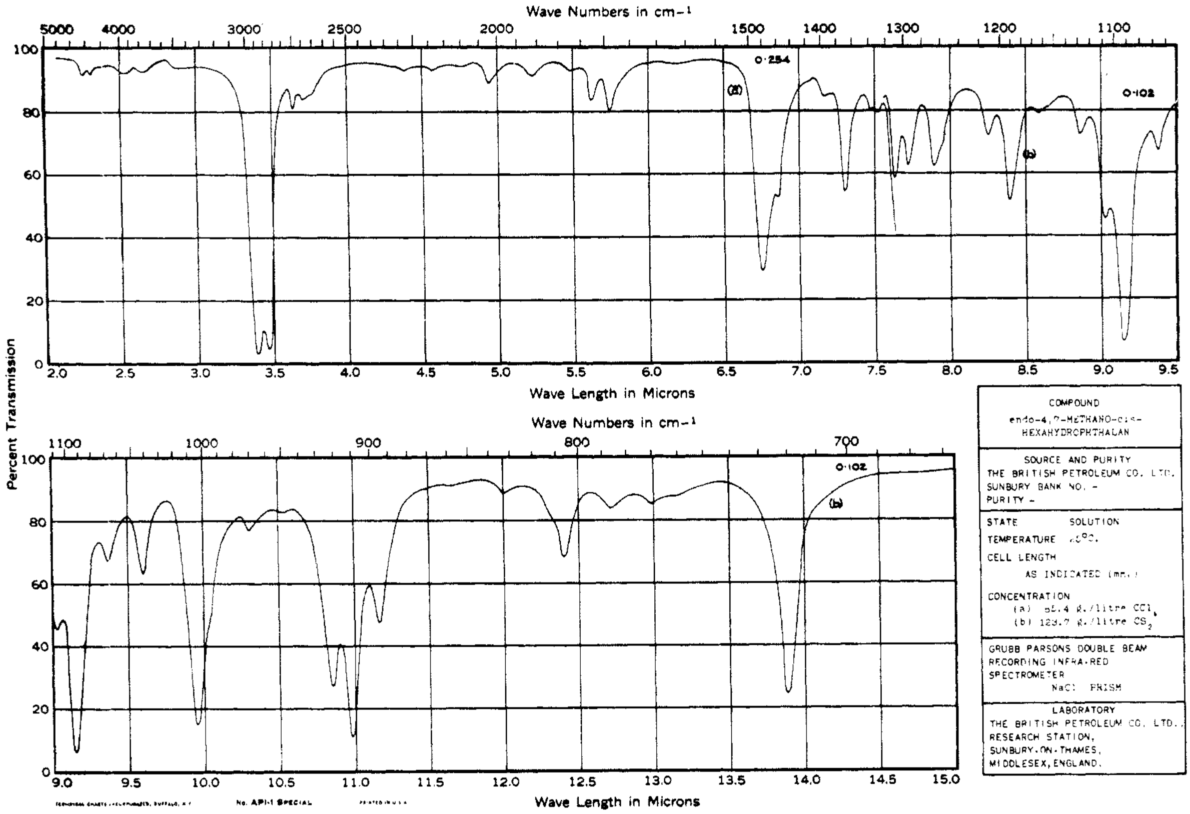


FIGURE 2.



COMPOUND
endo-4,7-METHANO-cis-
HEXAHYDROPHTHALAN

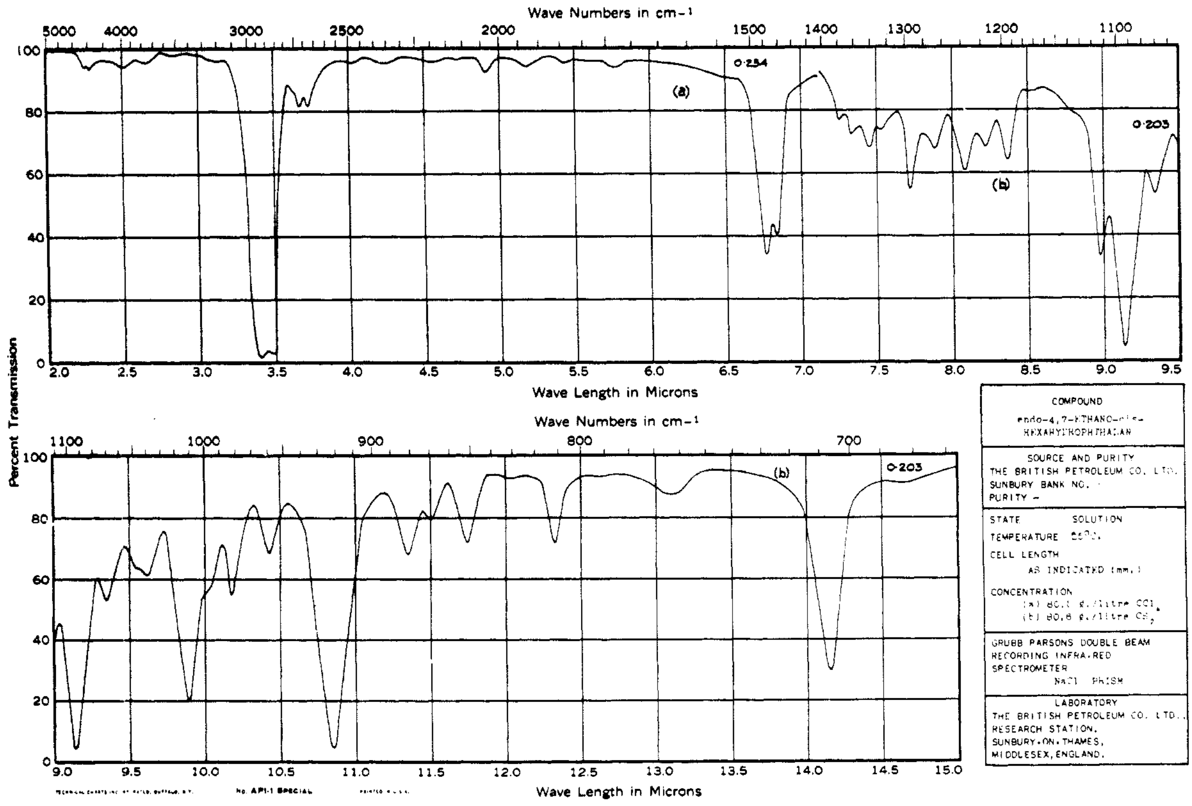
SOURCE AND PURITY
THE BRITISH PETROLEUM CO. LTD.
SUNBURY BANK NO. -
PURITY -

STATE SOLUTION
TEMPERATURE 25°C.
CELL LENGTH
AS INDICATED (mm.)
CONCENTRATION
(a) 55.4 g./litre CCl_4
(b) 123.7 g./litre CS_2

GRUBB PARSONS DOUBLE BEAM
RECORDING INFRA-RED
SPECTROMETER
NaCl PRISM

LABORATORY
THE BRITISH PETROLEUM CO. LTD.,
RESEARCH STATION,
SUNBURY-ON-THAMES,
MIDDLESEX, ENGLAND.

FIGURE 3.



COMPOUND
endo-4,7-ETHANO-cis-
HEXAHYDROPHTHALAN

SOURCE AND PURITY
THE BRITISH PETROLEUM CO. LTD.
SUNBURY BANK NO. -
PURITY -

STATE SOLUTION
TEMPERATURE 25°C.
CELL LENGTH
AS INDICATED (mm.)
CONCENTRATION
(a) 80.1 g./litre CCl_4
(b) 80.6 g./litre CS_2

GRUBB PARSONS DOUBLE BEAM
RECORDING INFRA-RED
SPECTROMETER
NaCl PRISM

LABORATORY
THE BRITISH PETROLEUM CO. LTD.,
RESEARCH STATION,
SUNBURY-ON-THAMES,
MIDDLESEX, ENGLAND.

FIGURE 4.

pared by treatment of the ditosate (XI) (82 g.) with sodium sulfide as described by Birch and Dean.[17] The crude product in *n*-pentane solution was shaken with iodine in the presence of aqueous caustic potash to oxidize traces of mercaptan; the sulfide recovered from this treatment was sublimed *in vacuo* and the sublimate (5 g., 18%) was converted to its mercuric chloride complex. The latter, crystallized to constant melting point from ethanol, melted at 219–220° with decomposition. The sulfide (3 g.) regenerated from the pure complex (9 g.) by refluxing with 15% hydrochloric acid (50 ml.) melted at 123.5–125° after sublimation *in vacuo*. Recrystallization from glacial acetic acid followed by sublimation failed to alter its melting point.

Anal. Calc'd for $C_9H_{14}S$: C, 70.1; H, 9.1; S, 20.8. Found: C, 70.3; H, 9.3; S, 20.5.

The boiling point of the sulfide as determined by a capillary tube method was 247 ± 2°/770 mm.

Derivatives. The mercuric chloride complex, methiodide, and sulfone of XIII were prepared by the usual methods.[2] Their melting points and analyses are recorded in Table I.

(*B*) *From cyclopentadiene and 2,5-dihydrothiophene. endo-4,7-Methano-cis-1,3,3a,4,7,7a-hexahydroisothianaphthene* (XV). A mixture of 2,5-dihydrothiophene (20 g.), cyclopentadiene (13 g.) and toluene (5 g.) was heated for 10 hours in a steel bomb immersed in an oil-bath at 200°. Distillation of the reaction mixture gave a fraction (8 g.) of b.p. 116–120°/18 mm. and n_D^{20} 1.5550, consisting largely of the required unsaturated sulfide XV.

The sulfide was not purified but was characterized by the preparation of three derivatives the melting points and analyses of which are recorded in Table I. The mercuric chloride complex was prepared by the usual method[2] and the methiodide by allowing equimolar amounts of the sulfide and methyl iodide in ethanol to stand at 0° for three days. The sulfone was prepared by the usual method[2] but an excess of only 50% of the peroxide required for sulfone formation was used in order to avoid addition at the double bond.

endo-4,7-Methano-cis-2-thiahydrindan (XIII). A quantity (6 g.) of the crude unsaturated sulfide in methanol (250 ml.) was hydrogenated at room temperature and atmospheric pressure using a palladium chloride on charcoal catalyst[12] (20 g.) and the saturated sulfide was isolated as its mercuric chloride complex (6 g.). The complex was crystallized to constant melting point from ethanol and the sulfide (1.1 g.) was regenerated by refluxing the pure complex with 15% hydrochloric acid. Infrared spectroscopic examination showed this sulfide to be identical with that obtained by route (*A*) above.

endo-4,7-ETHANO-*cis*-2-THIAHYDRINDAN

endo-2,3-Dimethylolbicyclo[2.2.2]oct-5-ene (VI). The diol VI was prepared from *endo*-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride (II) (295 g.) by the method employed for the preparation of the corresponding methano-compound (V). In this instance, however, the alkali-soluble byproducts were removed by washing the ether extract with excess 10% aqueous caustic potash. A single crystallization at −20° then gave almost pure diol (130 g., 47%). An analytical specimen (m.p. 104–106°) was obtained by a further crystallization from ether.

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

Acidification of the alkaline wash-liquors gave an oil (88 g.) which rapidly solidified. After several crystallizations from ether/*n*-pentane, the solid melted constantly at 91–92.5°. This compound is probably the lactone (IV) of *endo*-2-methylolbicyclo[2.2.2]oct-5-ene-3-carboxylic acid.

Anal. Calc'd for $C_{10}H_{12}O_2$: C, 73.1; H, 7.4. Found: C, 73.2; H, 7.4.

endo-2,3-Dimethylolbicyclo[2.2.2]octane (VIII). An almost quantitative yield of the diol VIII was obtained on hydrogenation of the diol VI (123 g.). Crystallization from ether gave the pure compound melting at 90.5–91.5°.

Anal. Calc'd for $C_{10}H_{18}O_2$: C, 70.5; H, 10.7. Found: C, 70.6; H, 10.6.

Ditosate of endo-2,3-dimethylolbicyclo[2.2.2]octane (XII). The diol VIII (87 g.) on treatment with *p*-toluenesulfonyl chloride gave a product from which pure ditosate (m.p. 121.5–122.5°) was obtained in 63% yield.

Anal. Calc'd for $C_{24}H_{30}O_6S_2$: C, 60.2; H, 6.3; S, 13.4. Found: C, 60.5; H, 6.4; S, 13.6.

endo-4,7-Ethano-*cis*-hexahydrophthalan (X) (3.3 g., 4%) isolated from the reaction liquors, on crystallization from methanol, melted constantly at 112.5–113.5°.

Anal. Calc'd for $C_{10}H_{16}O$: 78.9; H, 10.6. Found: C, 78.9; H, 10.7.

endo-4,7-Ethano-cis-2-thiahydrindan (XIV). The crude sulfide XIV (21 g., 47%) obtained from the ditosate XII by the method employed for the preparation of the corresponding methano-compound (XIII) was converted to its mercuric chloride complex. The sulfide regenerated by addition of the purified complex (30 g., m.p. 212–213°, decomp.) suspended in Carbitol[18] (100 ml.) to a refluxing aqueous sodium sulfide solution (100 g. of $Na_2S{\cdot}9H_2O$/200 ml. H_2O) melted at 56–58° after sublimation *in vacuo*. Crystallization from *n*-pentane at low temperature followed by sublimation failed to alter its melting point.

Anal. Calc'd for $C_{10}H_{16}S$: C, 71.4; H, 9.6; S, 19.1. Found: C, 71.3; H, 9.6; S, 19.1.

The boiling point of the sulfide as determined by a capillary tube method was 277 ± 2°/770 mm.

Derivatives. The mercuric chloride complex, methiodide, and sulfone of XIV were prepared by the usual methods.[2] Their melting points and analyses are recorded in Table I.

Acknowledgment. The authors wish to thank the Chairman of the British Petroleum Company Limited for permission to publish these results and Messrs. N. G. McTaggart and A. R. West for the determination of the absorption spectra.

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[17] Birch and Dean, *Ann.*, **585**, 234 (1954).

[18] Carbide and Carbon Chemical Co. trade name; Carbitol is the monoethyl ether of diethylene glycol.