mine-free product, 3,4-dinitrothiophene (III), if it were formed we prepared a sample of the material by the reaction between the bromodinitrothiophene II and copper in boiling butyric acid.[8] 3,4-Dinitrothiophene, which has already been prepared in similar fashion from the dinitrodibromothiophene I by Dr. Ellis Brown and which will be described in detail by him later, melts at 94–95° and mixtures of the monobromodinitrothiophene II and the dinitrothiophene III melt below 75°.

2-Bromo-3,4,5-trinitrothiophene (IV). Twenty grams (0.08 mole) of the crude bromodinitrothiophene II was added with stirring during 5 min. to a mixture of 100 ml. of concentrated sulfuric acid and 100 ml. of fuming nitric acid (d. 1.59–1.60). The solid dissolved in the nitrating acid, which was at room temperature, without an appreciable evolution of heat. In about 0.5 hr. the trinitro compound began to precipitate. Stirring was continued for 2 hr., after which time the reaction mixture was left overnight before it was poured onto 300 g. of ice. The yield of crude nitration product, melting at 123–125°, was 21.5 g. (90%).

2-Bromo-3,4,5-trinitrothiophene is a pale yellow solid which is soluble in the common solvents, but apparently with solvolysis; the solutions develop much color and the solute crystallizes poorly or not at all. The only satisfactory procedure for purification is to dissolve the trinitrobromothiophene in concentrated nitric acid (10 ml./g.) by heating on the steam bath. On cooling the filtered solution, the product is obtained with an 80% recovery as lemon yellow crystals melting at 130–131°.

Anal. Calcd. for $C_4BrN_3O_6S$: C, 16.10; H, 0.0; Br, 26.8. Found: C, 16.16; H, 0.0; Br, 26.7.

The trinitrobromothiophene furnishes only intractable material on treatment with potassium acetate in acetic acid. With aniline in methanol it yields a dianilino derivative (V), which is obtained as orange needles melting at 196–196.5° after crystallization from acetone-methanol.

Anal. Calcd. for $C_{16}H_{12}N_4O_4S$: C, 53.9; H, 3.39. Found: C, 54.05; H, 3.46.

2,3,4-Trinitrothiophene (VI). A solution of 5.0 g. (0.017 mole) of the crude bromotrinitrothiophene IV in 100 ml. of acetone was cooled to about 10° and 10 ml. (0.85 mole) of 50% hypophosphorous acid was added. An orange-red color developed at once. The solution was kept at room temperature by immersing the flask in cold water from time to time. After 1 hr. the solution was poured into 800 ml. of water and the tan precipitate was filtered; yield, 2.8 g. (76%), m.p. 138–141°. The product was purified by crystallization from ether (30 ml./g.) and an equal volume of 30–60° petroleum ether. The recovery was 70%.

Anal. Calcd. for $C_4HN_3O_6S$: C, 21.90; H, 0.46. Found: C, 21.93; H, 0.60.

2,3,4-Trinitrothiophene is a colorless solid which melts at 143°. When a small sample of the material in a sealed melting point tube is heated in a free flame it explodes vigorously. The material, which analyzes satisfactorily for carbon and hydrogen, gives low values for nitrogen and sulfur. The trinitrothiophene is unaffected by the ordinary nitric acid–sulfuric acid nitrating mixtures at steam bath temperatures. When one gram of the material was heated at 130° for 1.5 hr. with 10 ml. of concentrated sulfuric acid and 2 g. of potassium nitrate or for 4 hr. with 5 ml. of nitrating acid of the composition 82.3% H_2SO_4–17.6% HNO_3–0.1% H_2O, there was no indication that nitration had taken place and 60% of essentially pure starting material was recovered.

FLUSHING 67, N. Y.

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

Preparation and Physical Properties of Sulfur Compounds Related to Petroleum. VII. 2-, 6- and 8-Thiabicyclo[3.2.1]octane and 2-Thiabicyclo[2.2.2]octane

STANLEY F. BIRCH, RONALD A. DEAN, NEVILLE J. HUNTER, AND EDMUND V. WHITEHEAD

Received April 8, 1957

2-, 6-, and 8-Thiabicyclo[3.2.1]octane and 2-thiabicyclo[2.2.2]octane have been synthesized and their physical properties have been recorded. Each sulfide has been characterized by the preparation of derivatives.

In an earlier paper[1], Birch *et al.* reported the isolation from an Agha Jari (S. Persia) kerosine of a sulfide which was apparently 8-thiabicyclo[3.2.1]-octane and suggested that other thiabicyclooctanes were also present in this kerosine. It has previously been found possible to identify certain other sulfides as constituents of the kerosine, by comparison of the infrared spectra of the isolated sulfides or sulfide mixtures with those of synthetic compounds which have been prepared in these laboratories.[2] Consequently, the synthesis of 2-, 6- and 8-thiabicyclo[3.2.1]octane (IX, XIII and IV) and 2-thiabicyclo[2.2.2]octane (XVII) was carried out, as reported in the present paper. 3-Thiabicyclo-[3.2.1]octane, the fifth member of the group of thiabicyclooctanes containing only five- and six-membered rings and having an atomic bridge, has already been described.[3] The stereochemistry of the thiabicyclo[3.2.1]- and thiabicyclo[2.2.2]octane systems is such that the *trans*- forms would be extremely strained and, as with the corresponding hydrocarbons, it is probable that only one form having a *cis*- configuration can exist.[4] As recently

---

(1) S. F. Birch, T. V. Cullum, R. A. Dean, and R. L. Denyer, *Ind. Eng. Chem.*, **47**, 240 (1955).

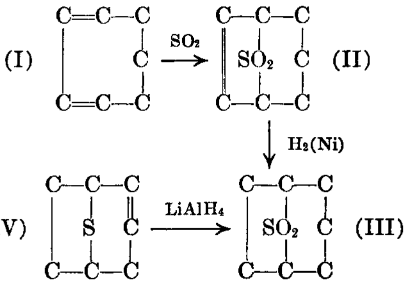
(2) S. F. Birch, R. A. Dean, N. J. Hunter, and E. V. Whitehead, *J. Org. Chem.*, 20, 1178 (1955).

(3) S. F. Birch and R. A. Dean, *Chem. Ber.*, **585**, 234 (1954) in which this sulfide is referred to as 6-thiabicyclo-[1.2.3]octane.

(4) H. Gilman, *Organic Chemistry*, 2nd. Ed., John Wiley and Sons, Inc., New York, 1948, Vol. 1, p. 485.

reported,[5] it has been confirmed that all five of the above thiabicyclooctanes are in fact present in the kerosine under investigation.

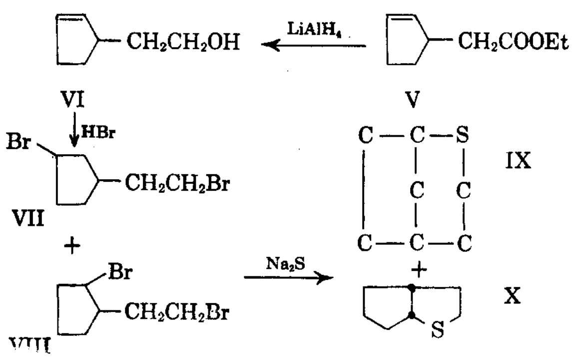
These "atomic-bridge" bicyclic sulfides have not been synthesized previously, although the corresponding hydrocarbons and certain nitrogen and oxygen analogues have been prepared. In common with other bicyclic sulfides which we have synthesized[2,6] they were obtained by two general methods: (*a*) hydrogenation and reduction of the unsaturated sulfones obtained by condensation of sulfur dioxide and the appropriate diene and (*b*) cyclization of the appropriate dibromide or ditosylate[7] with sodium sulfide. The yields obtained by method (*b*) were rather poor but method (*a*), which gives better yields, can be used only for compounds in which the sulfur atom is part of a five-membered ring, and then only when the structure of the intermediate unsaturated sulfone would not violate Bredt's Rule.[8] Accordingly, of the required sulfides, only 8-thiabicyclo[3.2.1]octane (IV) was prepared by method (*a*); the reaction route is shown schematically (I-IV).



1,3-Cycloheptadiene (I) reacted with sulfur dioxide at a lower temperature (20°) and gave a better yield (95%) of the corresponding unsaturated sulfone than did 1-vinylcyclopentene in the analogous preparation of *cis*-2-thiabicyclo[3.3.0]-octane.[2] Reduction of the unsaturated sulfone (II) proceeded smoothly and no poisoning of the catalyst was experienced during this reaction. In common with other saturated bycyclic sulfones[2]; 8-thiabicyclo[3.2.1]octane-8,8-dioxide (III) was incompletely reduced by lithium aluminum hydride (2 moles) and gave only 65% of the expected sulfide together with 30% of unreduced sulfone. No isomerization[2] occurred during this reduction, since the degree of strain required in the *trans*-isomer of the sulfone precludes its formation. The sulfide was purified by crystallization and sublimation.

The other three sulfides were obtained by method (*b*). The replacement of the secondary bromide or tosylate group of the intermediates used in this method, is accompanied by Walden inversion.[9,10] Accordingly, on reaction with sodium sulfide, a *cis*-intermediate should give a *trans*-sulfide, and a *trans*-intermediate a *cis*-sulfide. Since the formation of a *trans*-sulfide is prohibited the *cis*-intermediates actually give entirely polymeric material. Moreover, even with the *trans*-isomers, the formation of the required sulfides is hindered by the tendency for the secondary bromide or tosylate groups to eliminate with a neighboring ring hydrogen atom[11,12] and, possibly, by the difference in the reactivities of the primary and secondary bromide or tosylate groups[9,10] which may favor intermolecular reaction. It is thus not surprising that poor yields were obtained in these preparations.

The dibromides and ditosylates required as intermediates in method (*b*) are, in general, most conveniently obtained from the corresponding diols by hydrobromination and treatment with *p*-toluenesulfonyl chloride respectively. Rearrangements usually occur during hydrobromination of secondary alcohols[13,14] resulting in the formation of mixtures of isomeric dibromides. Consequently, in the dibromide route tedious separation processes may be required at either the dibromide or sulfide stage and/or there may be some uncertainty as to the structure of the pure sulfide finally isolated. On the other hand, tosylation of secondary alcohols takes place without isomerization[15] and with retention of configuration,[9,10] and the structure of a sulfide obtained *via* the ditosylate is thus unambiguous. However, this advantage may be offset if the parent diol of the required ditosylate is not easily prepared while the corresponding dibromide can be obtained from another compound. In addition, better yields are obtained by the dibromide



---

[5] S. F. Birch, T. V. Cullum, and R. A. Dean. Paper presented before the Division of Petroleum Chemistry, 130th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1956.

[6] S. F. Birch, R. A. Dean, and E. V. Whitehead, *J. Org. Chem.*, **19**, 1449 (1954).

[7] Di-*p*-toluenesulfonate.

[8] F. S. Fawcett, *Chem. Revs.*, **47**, 219 (1950).

(9) M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 2108 (1950).

(10) L. N. Owen and P. A. Robins, *J. Chem. Soc.*, 326 (1949).

(11) L. N. Owen and P. A. Robins, *J. Chem. Soc.*, 320 (1949).

(12) M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 2103 (1950).

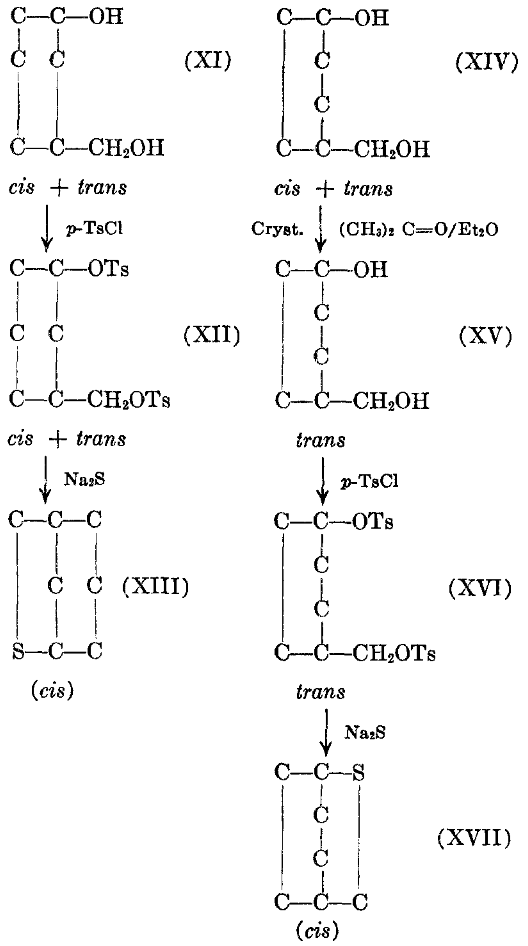
(13) B. Rothstein, *Ann. Chem.*, **14**, 461 (1930).

(14) H. Pines, A. Rudin, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **74**, 4063 (1952).

(15) H. Phillips, *J. Chem. Soc.*, 2552 (1925).

route and for these reasons, 2-thiabicyclo[3.2.1]-octane (IX) was prepared by this route, as shown in the reaction scheme (V-X).

The alcohol VI was obtained in good yield when the ester V (prepared by the method of Noller and Adams[16]) was reduced with lithium aluminum hydride. v. Braun *et al.*[17] reported that on hydrobromination of VI they obtained 1-bromo-3-(2-bromoethyl)cyclopentane (VII) and not the corresponding 2-(2-bromoethyl) compound (VIII). However, even if isomerization did not occur under the conditions employed by these workers, it seems unlikely that VII was the only addition product, and certainly their identification of their dibromide as this compound does not appear conclusive. We anticipated that the corresponding 1- and 2-(2-bromoethyl) compounds would accompany 1-bromo-3-(2-bromoethyl)cyclopentane in our preparation, and the decomposition, accompanied by evolution of hydrogen bromide, which occurred on distillation of our hydrobromination product, and the occurrence of 2-thiabicyclo[3.3.0]octane in addition to the required 2-thiabicyclo[3.2.1]octane in the product obtained on treatment of the distilled dibromide with sodium sulfide, confirmed our expectations. Fractional distillation of the mixture of bicyclic sulfides (34% yield) separated from the polymeric portion of the product, followed by fractional crystallization of the mercuric chloride complexes of the liquid and solid fractions so obtained, gave a quantity of the 2-thiabicyclo[3.2.1]-octane complex, and the sulfide regenerated from this was purified by crystallization and sublimation. The sulfide regenerated from the combined residual complexes was shown by spectroscopic examination to contain *cis*-2-thiabicyclo[3.3.0]-octane; no *trans*-2-thiabicyclo[3.3.0]octane[18] could be detected, however, and it seems that the amount of the *cis*-isomer of VIII in the hydrobromination product was very small.



The diols required for the synthesis of 6-thiabicyclo[3.2.1]octane (XIII) and 2-thiabicyclo[2.2.2]-octane (XVII), *viz*, the 3- and 4-hydroxycyclohexanemethanols (XI and XIV), are readily obtainable, and XIII and XVII were therefore synthesized by the ditosylate route as indicated schematically (XI-XVII). These diols were prepared, in average yields of 69 and 63% respectively, as described by Owen *et al.*[9,10] Neither *trans*-3-hydroxycyclohexanemethanol nor its ditosylate can readily be separated from their respective admixtures with the corresponding *cis*-compounds,[9] so that a mixture of *cis*- and *trans*-ditosylates, obtained in almost theoretical yield by the usual method,[19] had to be used for the preparation of XIII. The *trans*- isomer of 4-hydroxycyclohexanemethanol is easily separated from its admixture with the *cis*- isomer[10] however, so that the pure *trans*-ditosylate (XVI) was used for the preparation of XVII. Only a poor yield of XVI was obtained in a preliminary preparation carried out in the usual way,[19] and, following a suggestion by Haggis and Owen,[20] the majority of this ditosylate was prepared by reverse addition of the reactants.

The yields of XIII and XVII obtained on reaction of these ditosylates with sodium sulfide were very low (*ca.* 5%), the majority of the product being di- or poly-meric material. Consequently, since it appeared likely that the dibromide corresponding to the structure of the original diol would be the main hydrobromination product, it was considered worthwhile to investigate whether, despite the disadvantages already mentioned, the dibromide route might not prove to be on the whole more satisfactory than the ditosylate route. The yields of bicyclic sulfide were certainly increased to 15 and 12% based on the dibromides obtained from XI and XIV respectively, but surprisingly, this sulfide consisted in both instances almost entirely

---

[16] C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, **48**, 2444 (1926).

[17] J. v. Braun, E. Kamp, and J. Kopp, *Ber.*, **70**, 1750 (1937).

[18] S. F. Birch, R. A. Dean, and E. V. Whitehead, *Chemistry & Industry* (London), 409 (1956) and a future publication in this series.

[19] E. C. Horning, *Org. Syntheses*, **Coll. Vol. 3**, 366 (1955).

[20] G. A. Haggis and L. N. Owen, *J. Chem. Soc.*, 389 (1953).

TABLE I

MELTING POINTS AND ANALYSES OF THE DERIVATIVES OF THE SULFIDES

Compound	Formula of derivative	M.P., °C., (corrected)	Analyses					
			Calcd.			Found		
			C	H	S	C	H	S
2-Thiabicyclo[3.2.1]octane	$C_7H_{12}Cl_2HgS$	193–194[a]	21.0	3.0	8.0	21.3	3.0	8.1
	$C_7H_{12}O_2S$	257[a]	52.5	7.6	20.0	52.3	7.7	20.1
	$C_8H_{15}IS$	210–211[a,b]	35.6	5.6	11.9	35.7	5.8	12.0
6-Thiabicyclo[3.2.1]octane	$C_7H_{12}Cl_2HgS$	157–157.5[a]	21.0	3.0	8.0	21.1	3.3	8.2
	$C_7H_{12}O_2S$	236–237	52.5	7.6	20.0	52.8	7.8	20.4
	$C_8H_{15}IS$	162.5–163.5[a,b]	35.6	5.6	11.9	35.7	5.6	12.4
8-Thiabicyclo[3.2.1]octane	$C_7H_{12}Cl_2HgS$	226[a]	21.0	3.0	8.0	20.9	3.0	8.0
	$C_7H_{12}O_2S$	281.5–282	52.5	7.6	20.0	52.3	7.8	20.2
	$C_8H_{15}IS$	242.5–243[a,b]	35.6	5.6	11.9	35.6	5.8	12.0
2-Thiabicyclo[2.2.2]octane	$C_7H_{12}Cl_2HgS$	185–187[a]	21.0	3.0	8.0	21.3	3.2	7.9
	$C_7H_{12}O_2S$	*ca.* 310	52.5	7.6	20.0	52.6	7.7	20.1
	$C_8H_{15}IS$	225–226[a,b]	35.6	5.6	11.9	34.9	5.3	12.3

[a] With decomposition. [b] Sealed tube plunged into bath at *ca.* 10° below m.p.

of XIII, and XVII was not present in detectable quantities in either product. This would seem to show that while with XI the hydrobromination complexes and reaction products do not tend to rearrange in such a way that *trans*-1-bromo-4-(bromomethyl)cyclohexane is formed, with XIV extensive rearrangements occur such that *trans*-1-bromo-3-(bromomethyl)cyclohexane is a major end product. Thus, while a quantity of XIII was obtained by this dibromide route, further amounts of XVII had to be prepared *via* the ditosylate. Specimens of XIII and XVII were purified by crystallization of their mercuric chloride complexes, followed by crystallization and sublimation of the regenerated sulfides.

All four sulfides are, like 3-thiabicyclo[3.2.1]-octane, wax-like solids with strong camphoraceous odors. 6- and 8-Thiabicyclo[3.2.1]octane melt at about the same temperature as 3-thiabicyclo[3.2.1]-octane (174–175°) and the melting point of 2-thiabicyclo [3.2.1] octane is only about 10° lower, while the melting point of 2-thiabicyclo[2.2.2]-octane is as high as 210–212°. Melting points of mixtures of the sulfides are indefinite, but are intermediate between those of the components of the mixtures, *i.e.* there is no true depression of the melting point. All five sulfides of the group have boiling points[21] within two or three degrees of 195° at atmospheric pressure. (The boiling points of 3-thiabicyclo[3.2.1]octane and 2-thiabicyclo-[2.2.2]octane[21] have not actually been determined, but their values can be deduced from data on the occurrence of the sulfides in fractions obtained on distillation of sulfide concentrates isolated from crude kerosene[5].)

Derivatives of the four sulfides described in this paper were prepared by methods described previously[6,22] and their melting points are given in Table I; the high melting points of the sulfones, especially that of 2-thiabicyclo[2.2.2]octane, are noteworthy. The infrared spectra[23] of these sulfides and of 3-thiabicyclo[3.2.1]octane have been obtained in the range 2–15 μ using a Grubb Parsons double beam spectrometer.

EXPERIMENTAL

All melting points are corrected. Microanalyses are by Dr. Ing. A. Schoeller of Kronach/Oberfranken, Bambergerstrasse 20, Germany.

3-Thiabicyclo[3.2.1]-6-octene-3,3-dioxide (II) was obtained in 90–95% yield when 1,3-cycloheptadiene (I) (25 g.) (b.p. 120–121°/770 mm., n_D^{20} 1.4960), phenyl-β-naphthylamine (0.2 g.), and sulfur dioxide (86 g.) were reacted[2] at room temperature for 40 hr. The product, worked up in the usual way[2] and crystallized from ethanol, melted at 160.5–162°.

Anal. Calcd. for $C_7H_{10}SO_2$: C, 53.1; H, 6.4; S, 20.3. Found: C, 53.2; H, 6.5; S, 20.3.

8-Thiabicyclo[3.2.1]octane-3,3-dioxide (III) was obtained in theoretical yield by hydrogenating[2] II. The product was not distilled, but was crystallized from ether or benzene/cyclohexane. It melted at 281.5–282°.

3-Thiabicyclo[3.2.1]octane (IV). Reduction[2] of the sulfone (III) (1 mole) with lithium aluminum hydride (2 moles) gave 66% of the sulfide (IV) and 30% of unreduced sulfone (III). Crystallized to constant melting point from *n*-pentane and sublimed at 0.4 mm., 8-thiabicyclo[3.2.1]octane melted (sealed tube) at 176.5–178.5°, b.p. 194.5°/769 mm.

Anal. Calcd. for $C_7H_{12}S$: C, 65.6; H, 9.4; S, 25.0. Found: C, 65.6; H, 9.5; S, 25.0.

2-Cyclopentene-1-acetic acid was obtained in 65% yield by the method of Noller and Adams.[16] The diester was not isolated but was hydrolyzed and decarboxylated to give the required acid (b.p. 90°/2 mm.-90°1.2 mm., n_D^{20} 1.4682). The ester (V) obtained in 82% yield by continuous esterification of the acid, boiled at 95°/29 mm.-96°/27 mm., n_D^{20} 1.4480.

2-Cyclopentene-1-ethanol (VI) was prepared by reducing the ester (V) (258 g.) with lithium aluminum hydride (38 g.), yield 87%, b.p. 98°/30 mm., n_D^{20} 1.4722. (Hydrogenation of a portion of VI with a platinum black catalyst gave cyclopentanethanol in 87% yield, b.p. 96°/25 mm., n_D^{20} 1.4577).

Bromo-(2-bromoethyl)cyclopentanes (VII, VIII). Anhydrous hydrogen bromide was passed into a mixture of the alcohol (VI) (108 g.) and water (1 g.), at a maximum tem-

---

(21) Boiling point defined as temperature at which vapor pressure is 760 mm. 2-Thiabicyclo[2.2.2]octane sublimes when heated at atmospheric pressure and has no normal boiling point.

(22) E. V. Whitehead, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.* **73**, 3632 (1951).

(23) These spectra have been submitted to the A.P.I. Research Project 44 for inclusion in their catalog of spectral data.

perature of 70° until no further increase in weight occurred. After working up the product in the usual way[6] it was distilled under reduced pressure when partial decomposition accompanied by evolution of hydrogen bromide took place. The following fractions were obtained: 1. b.p. <110°/5 mm., 44 g.; 2. b.p. 110°/5 mm.–112°/2.5 mm., 47 g., n_D^{20} 1.524; 3. b.p. 112°/2.5 mm.–98°/0.4 mm., 124 g., n_D^{20} 1.5332; residue 7 g. The third fraction was used for cyclization, a total of 264 g. being prepared. Hydrobromination of VI in the presence of ascaridole and under irradiation by ultraviolet light gave a similar product.

2-Thiabicyclo[3.2.1]octane (IX). The mixture of dibromides (VII, VIII) was reacted with sodium sulfide in the usual way[6] except that the reaction mixture was refluxed for 16 hr. The product was steam distilled and the distillate extracted with *n*-pentane; mercaptans present in the extract were oxidized with 10% aqueous potash and iodine, and after removal of the solvent the residue was distilled to give a semi solid product, b.p. 82–86°/19 mm., in 34% yield. Fractionation of this material under reduced pressure through a Bower and Cooke column[24] gave partial separation into liquid and solid fractions. These fractions were converted separately into their mercuric chloride complexes and fractional crystallization of these from ethanol yielded a constant melting derivative. The sulfide (6.8 g.) was regenerated from this complex with 15% hydrochloric acid: it melted at 165–166° (sealed tube), and after crystallization from acetic acid and sublimation the melting point was unchanged; b.p. 197°/774 mm.

Anal. Calcd. for $C_7H_{12}S$: C, 65.6; H, 9.4; S, 25.0. Found: C, 65.4; H, 9.4; S, 24.7.

The sulfide obtained from the remaining mercuric chloride complex was shown spectroscopically to consist of a mixture of 2-thiabicyclo[3.2.1]octane and *cis*-2-thiabicyclo[3.3.0]octane; *trans*-2-thiabicyclo[3.3.0]octane could not be detected in the sample.

3-Hydroxycyclohexanemethanol (XI), (306 g., b.p. 117–119°/0.6 mm., n_D^{20} 1.4935) was prepared in average overall yield of 69% from ethyl *m*-hydroxybenzoate (564 g.), as described by Clarke and Owen.[9]

6-Thiabicyclo[3.2.1]octane (XIII). (a) *By the ditosylate[7] route.* A mixture of the ditosylates of *cis*- and *trans*-3-hydroxycyclohexanemethanol was obtained in almost theoretical yield by reaction of the diol (100 g.) with *p*-toluenesulfonyl chloride as described in *Organic Syntheses*,[19] except that the reaction mixture was allowed to stand overnight. The crude product, (which failed to solidify) was dried azeotropically by distilling off the solvent from its benzene solution, and dissolved in ethanol and reacted with sodium sulfide nonahydrate by the usual method.[3] The material steam distilled from the crude reaction product was dissolved in *n*-pentane and the solution was exhaustively extracted with 10 ml. portions of aqueous mercuric acetate (1 mole/liter), the extracts were added to excess aqueous sodium chloride and the sulfide was regenerated from the mercuric chloride complex by refluxing with 15% hydrochloric acid. Sublimation gave 4.5 g. (5%) of sulfide, the pure mercuric chloride complex of which melted at 157.5°.

(b) *By the dibromide route. cis*- and *trans*-3-Hydroxycyclohexanemethanol (85 g.) was hydrobrominated and the resultant dibromide (145 g., 87%, b.p. 84–89°/0.8 mm., n_D^{20} 1.5444) reacted with sodium sulfide by the general method described in an earlier paper.[6] The crude mercuric chloride complex of the sulfide gave pure material (49 g., m.p. 157.5°) after two crystallizations from ethanol. A *n*-pentane solution of the sulfide regenerated from this pure complex with 15% hydrochloric acid was washed with iodine in 10% aqueous caustic potash until mercaptan free and then with aqueous sodium thiosulfate until colorless. Sublimation of the residue from evaporation gave 6-thiabicyclo[3.2.1]octane (10.8 g., 15%) which, after three crystallizations from acetic acid, melted (constantly) at 172.5–174° and boiled at 197°/769 mm.

Anal. Calcd. for $C_7H_{12}S$: C, 65.6; H, 9.4; S, 25.0. Found: C, 65.6; H, 9.6; S, 24.8.

This sulfide was shown by comparison of infrared spectra to be identical with the sulfide obtained from the ditosylate as described in section (a) above. Spectroscopic examination of the sulfide regenerated from the mercuric chloride complex recovered from the recrystallization mother liquors failed to detect the presence of any 2-thiabicyclo[2.2.2]octane in this material.

4-Hydroxycyclohexanemethanol (XIV) (925 g., b.p. 120–122°/1.3 mm., n_D^{20} 1.4932) was prepared, in average overall yield of 63%, from ethyl *p*-hydroxybenzoate (1868 g.) as described by Owen and Robins.[10] A quantity (380 g.) of the *trans*-diol (XV) (m.p. 105–108°) was isolated from a portion (815 g.) of this *cis-trans* mixture, also as described by these authors.[10]

2-Thiabicyclo[2.2.2]octane (XVII). (a) *By the ditosylate route. trans*-4-Hydroxycyclohexanemethanol (165 g.) was added portionwise with stirring to a cooled solution of *p*-toluenesulfonyl chloride (5% excess) in pyridine and the mixture was allowed to stand overnight. The ditosylate was isolated in the usual way[19] and, crystallized twice from ethanol, it melted constantly at 94–95° (reported[10] m.p. 94–95°). A total of 932 g. of pure ditosylate was prepared in this way from 380 g. of diol.

A *n*-pentane solution of the product obtained on treatment of the pure ditosylate (300 g.) with sodium sulfide[3] was washed with iodine and 10% aqueous caustic potash until mercaptan free and then with aqueous sodium thiosulfate until colorless. The solution was evaporated and the solid sulfide (4 g., 5%) sublimed from the residue was converted to the mercuric chloride complex and crystallized to constant melting point (185–187.5°) from ethanol. 2-Thiabicyclo[2.2.2]octane (2.2 g., m.p. 208–210°) was regenerated by addition of this complex (7.5 g.) suspended in Carbitol[25] (30 ml.) to a refluxing solution of sodium sulfide nonahydrate (33 g.) in water (50 ml.). This was combined with the sulfide (4.5 g.) obtained from 2 further 300 g. batches of ditosylate and the whole was crystallized from acetic acid and sublimed to give pure 2-thiabicyclo[2.2.2]octane melting at 210–212°.

Anal. Calcd. for $C_7H_{12}S$: C, 65.6; H, 9.4; S, 25.0. Found: C, 65.4; H, 9.4; S, 24.9.

(b) *Attempted preparation by the dibromide route.* The sulfide obtained by sodium sulfide treatment[6] of the dibromide (199 g., 92%, b.p. 100–104°/2.5 mm., n_D^{20} 1.5446) resulting from hydrobromination[6] of *cis*- and *trans*-4-hydroxycyclohexanemethanol (110 g.), was converted to the crude mercuric chloride complex and the material (12 g., 12%) regenerated by refluxing this complex with 15% hydrochloric acid was purified by crystallization from acetic acid. The pure sulfide proved to be identical (m.p. and infrared spectrum) with 6-thiabicyclo[3.2.1]octane and even the sulfide recovered from the recrystallization mother liquors did not contain sufficient 2-thiabicyclo[2.2.2]octane to be detectable by infrared spectroscopy.

Derivatives of the Sulfides. The mercuric chloride complexes, methiodides, and sulfones of all four sulfides were prepared by the usual methods, and their melting points and analyses are recorded in Table I.

Acknowledgment. The authors wish to thank the chairman and directors 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.

SUNBURY-ON-THAMES, ENGLAND

---

(24) J. R. Bower and L. M. Cooke, *Ind. Eng. Chem., Anal. Ed.*, 15, 290 (1943).

(25) Union Carbide Chemicals Co. trade name; Carbitol is the monoethyl ether of diethylene glycol.