SYNTHESIS OF 2-METHYL-1-THIADECALIN, 2-METHYL- AND 2,6,8-TRIMETHYL-1-THIABICYCLO [4.3.0] NONANES*

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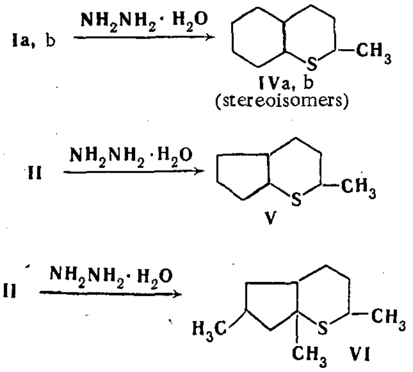
2-Methyl- and 2, 6, 8-trimethyl-1-thiabicyclo [4.3.0] nonan-4-one, 2-methyl-1-thiadecalin, 2-methyl- and 2, 6, 8-trimethyl-1-thiabicyclo [4.3.0] nonane are synthesized and characterized for the first time. Conditions are found for thin-layer chromatographic separation of some geometric isomers of the compounds synthesized.

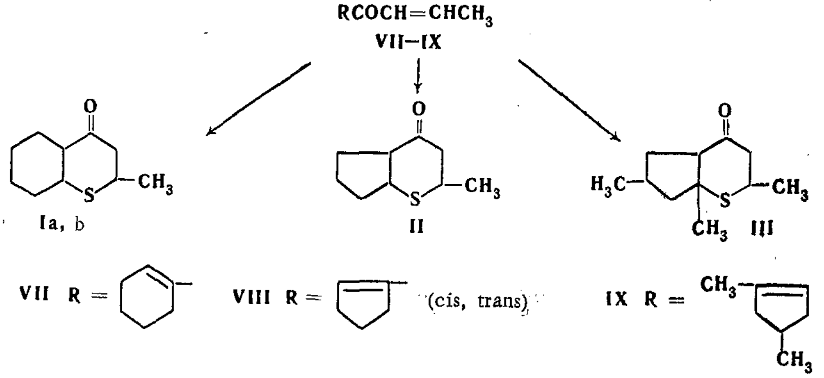
In connection with studies of the structures of sulfides in middle cuts of petroleum [1–4], we are undertaking synthesis of some mono- and tri-substituted thiabicyclanes, which simulate groups of compounds found in petroleum. A number of unsubstituted thiabicyclanes have been synthesized by Birch et al., [5–7], either by condensing dienes with sulfur dioxide and then reducing the resultant sulfones, or by condensing the appropriate dibromides or tosylates with sodium sulfide.

Hitherto thiabicyclanes have not been obtained.

We used condensation of ketodienes with hydrogen sulfide, a reaction developed by Nazarov and coworkers [8,9] to synthesize thiabicyclanes with CH_3 groups α to the sulfur atom. They synthesized monocyclic thiapyranones, as well as stereoisomeric 2-methyl-1-thiadecalones. The same authors showed [10] that the keto group in thiapyran-4-one can be reduced by the Huang-Minlon method [12] to CH_2.

We prepared 2-methyl-1-thiadecal-4-one (Ia,b), 2-methyl-1-thiabicyclo [4.3.0] nonan-4-one (II), 2,6,8-trimethyl-1-thiabicyclo [4.3.0] nonan-4-one and the corresponding thiabicyclanes (IV–VI) by the following reactions:





Tables 2 and 3 give the properties of the thiabicyclanes and their derivatives, now prepared for the first time.

From the stereochemical relationships it might have been expected that the closure of dienes with a flat cyclopentane ring would proceed with greater difficulty than with a 6-membered ring, and that introduction of a methyl group into the 5-membered ring would give rise to further steric hindrance. Actually reaction could be successfully effected only by considerably raising the hydrogen sulfide concentration above that obtained when carrying out the reaction in the liquid phase (see Table 1). Under those conditions the cyclization of propenylcyclohexenyl ketone made it possible to effect a real cut in reaction time as compared with [11], with simultaneous increase in product yield. The results in Table 1 show the relationship between extent of conversion of ketodienes to ketosulfides, and the structures of the starting ketodienes.

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Table 1
Reaction of Ketodienes with Hydrogen Sulfide at 0°

Compound Number	Name	Hydrogen sulfide (state of aggregation)	Reaction time, hr	Ketosulfide fraction yield, %	% ketosulfide in the ketosulfide fraction
VII	Propenylcyclohexenyl ketone	Gas*	13.5	64.5	**
	the same	Liquid	1.0	78	
VIII-cis	Propenylcyclopentenyl ketone	"	1.5	24	37
VIII-cis	the same	"	3.0	23	89
VIII-cis	the same	"	5.0	69	96
VIII-trans	Propenylcyclopentenyl ketone	"	3.0	70	99
IX	Propenyl-2, 4-dimethyl-cyclopentenyl ketone	Gas	22	49	83
	the same	Liquid	3.0	19.5	89
	the same	"	7.0	50.5	97

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*The reaction temperature was held in the limits 0 to −2°.

**Bp 2-methyl-1-thiadecal-4-one 123–125° (7 mm), n_D^{20} 1.5208; the literature gives [11] 117–125° (7 mm), n_D^{20} 1.5190.

When Nazarov, Kuznetsova, and Gurvich synthesized Ia and Ib [11], they regarded them as cis and trans isomers, analogs of the decalones, differing by the positions of the hydrogens relative to the angular C–C group. The presence of hetero atoms and of angular and peripheral substituents in the molecules of the heterobicyclanes offers additional possibilities of geometrical isomerism. The following nomenclature rules for substituted thiabicycloanes have consequently to be introduced, to clearly denote and represent possible stereoisomers.

1. When giving the number of members in the rings (figures in square brackets), the chain containing the hetero atom is placed first.

2. In drawing the structural formulas, the heteratom is put in the lower part of the right ring.

3. Starting at the heteroatom, the substituents are numbered counter-clockwise.

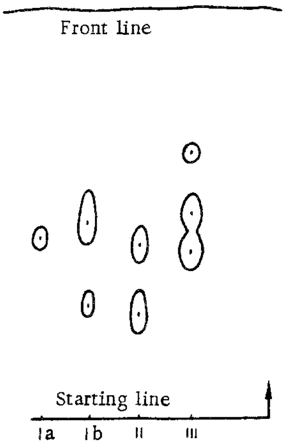

Fig. 1. Chromatogram of thiobicyclanes. Eluent isoPr$_2$O-isooctane, 9:1. Rf for the spots of compounds Ia, Ib, II, and III are respectively 0.45; 0.28 and 0.44; 0.25 and 0.42; 0.40, 0.50, and 0.65.

4. The angular substituent nearest the heteroatom lies in the direction nearest the observer. The positions of all the other substituents are determined relative to that one, firstly the second angular substituent, and then the peripheral ones.

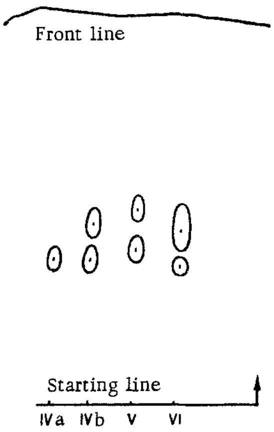

Fig. 2. Chromatogram of thiabicyclanes. Eluent IsoPr$_2$O-isooctane, 1:50. Rf for the spots of compounds (Table 2) IVa, IVb, V, and VI are respectively 0.36, 0.36, and 0.47; 0.40 and 0.51; 0.63 and 0.73.

5. In naming the compound, the peripheral substituents are first enumerated, as indicated in ¶3 above, spatial position being indicated with reference to the substituent nearest the heteroatom, then follows the layout of the angular substituents, which determine whether the thiabicyclanes belong to the cis or trans series.

Inspection of the Stuart-Brigleb stereo models of the ketosulfides for the cases of 2-methyl-1-thiadecal-4-one (I), 2-methyl-1-thiabicyclo [4.3.0] nonan-4-one (II), and 2,6,8-trimethyl-1-thiabicyclo [4.3.0] nonan-4-one (III), leads to the conclusion that the probability of formation of geometric isomers is not equal.

There are 4 possible isomers of I, but 3 of them would be most likely to be formed: trans-2-methyl-cis-1-thiadecal-4-one; cis-2-methyl-trans-1-thiadecal-4-one, and trans-2-methyl-trans-1-thiadecal-4-one.

Consideration of the space relationships for ketosulfides II and III leads to the important conclusion that formation of trans series compounds by the angular substituents is practically impossible in such cases. Hence in the case of II only 2 isomers would be expected to be formed: trans-2-methyl-cis-1-thiabicyclo [4.3.0] nonan-4-one and cis-2-methyl-cis-1-thiabicyclo [4.3.0] nonan-4-one, while in the case of III, 4 would be expected: trans-trans-cis-, trans-cis-cis, cis-trans-cis-, and cis-cis-cis-2,6,8-trimethyl-1-thiabicyclo [4.3.0] nonan-4-ones. The formation of the last two isomers is less probable, since it requires considerable steric approach of the CH_3 groups at positions 2 and 8. The same stereochemical relationships are valid for the sulfides IV–VI as hold for the corresponding ketosulfides I–III. On converting compounds I–VI to sulfoxides, the number of geometric isomers is to be expected to be doubled as compared with the unoxidized thiabicyclanes and thiabicyclanones.

The results of thin-layer chromatography of compounds I–VI (see Figs. 1 and 2) and of their isomerization products are in full accord with the stereochemical views enunciated above. Thus the liquid isomer Ib is a mixture of at least two stereoisomers, one of which is the "solid" isomer Ia. When isomerized with sodium methoxide the mixed isomers Ib are converted to Ia, to which obviously the structure of trans-2-methyl-trans-1-thiadecal-4-one is to be assigned.

Unlike Ib, the corresponding sulfides IVb are not isomerized under those conditions, thus confirming the keto-enol mechanism put forward in [11] for cis-trans isomerization of ketosulfides, taking place with involvement of angular substituents. Ketosulfides II and III also do not undergo isomerization, since formation of trans isomers by angular substituents is sterically impossible for them, as was mentioned above.

Determination of sulfide sulfur in IV–VI by potentiometric iodometry [13] gives quite high values (see Table 2). This must be mentioned because this method of determining sulfides quantitatively, at present widely used in investigating the compositions of middle cuts of petroleum was developed using model sulfides differing greatly in structure from the sulfides of middle petroleum cuts. Elucidation of the mechanism of oxidation of IV–VI under the conditions of [13], and specification for determining sulfides of the newly obtained structure types by iodometry, requires special investigation.

EXPERIMENTAL

Synthesis of ketodienes. The starting unsaturated cyclanols, vinylethynyl-cyclohexan-1-ol (X), vinylethynylcyclopentan-1-ol (XI), and vinylethynyl-2, 4-dimethylcyclopentan-1-ol (XII), were prepared for the first time in satisfactory yields by using the Grignard compounds*.

Preparation of X (also by reacting vinylacetylene with acetone [14]). 13 g (1.2 mole) ethyl bromide was dropped into dry ether covering 1.16 g Mg turnings at such a rate that the ether boiled, after which the mixture was stirred for 1 hr longer. 79.6 g (1.53 mole) vinylacetylene (prepared according to [15]) was added in 4 lots at 20 min intervals, at 0–4°, after which the mixture was stirred for 2 hr at room temperature. Then 99.5 g (1.07 mole) cyclohexanone in an equal volume of dry ether was added gradually at such a rate that the mixture boiled steadily; after addition was complete, stirring was continued for 1 hr 30 min at room temperature, and the products then decomposed with ice-water. After working up in the usual way the bulked ether extracts were dried over $MgSO_4$, the ether distilled off in a current of nitrogen, and the residue vacuum-distilled, to give an 85.5% yield of X, bp 82–88° (5 mm), n_D^{20} 1.5118. The literature gives [16] 95–97° (8 mm), n_D^{20} 1.5168.

Preparation of XI. Similarly to X, from 150 g (1.88 mole) cyclopentanone. Yield 72%, 75–77° (4 mm), n_D^{20} 1.5160.

Preparation of XII. From 140 g 2, 4-dimethylcyclopentan-1-one, (synthesized as described in [18]) similarly to X. Bp 92–95° (10mm), n_D^{20} 1.4949, yield 73%. The literature gives [19] bp 74–75° (3 mm), n_D^{20} 1.5490.

Vinylethynylcyclohexene (XIII). Prepared as described in [16], from 210 g (1.46 mole X, yield 78%, bp 71–75° (7 mm), n_D^{20} 1.5490.

Vinylethynylcyclopent-1-ene (XIV). Prepared as described in [17] from 177 g (1.34 mole) yield 80%, bp 65–68° (13 mm), n_D^{20} 1.5498. The literature gives bp 57–59° (10 mm), n_D^{20} 1.5490.

1-Vinylethynyl-2, 4-dimethylcyclopent-1-ene (XV). Prepared from XII as described in [19], 85% yield, bp 66–69° (3 mm), n_D^{20} 1.5211. The literature gives [19] bp 103–103° (7 mm), n_D^{20} 1.5158.

Propenylcyclohexenyl ketone (VII). This was prepared as described in [16], from 155 g (1.2 mole) XIII. Yield 70%, 103–104° (7 mm), n_D^{20} 1.5158. The literature [16] gives 101–103° (7 mm), n_D^{15} 1.5155.

Propenylcyclpentenyl ketone (VIII). Prepared as described in [17], from 76 g (0.61 mole) XIV, yield 62%, bp 78–88° (7 mm), n_D^{20} 1.5030. On cooling there crystallized out 33 g trans-propenylcyclopentenyl ketone, mp (after recrystallizing from MeOH) 31–32.5°. The mother liquors were vacuum-distilled through a column**, to give 4.8 cis-propenylcyclopentenyl ketone, bp 87-93° (7.5 mm), n_D^{20} 1.5050–1.5065, and 5.1 g trans-propenylcyclopentenyl ketone bp 93° (7.5 mm), n_D^{20} 1.5038 and mp 31–31.5°. The literature gives [17] for cis-propenylcyclopentenyl ketone bp 82–84° (7 mm), n_D^{20} 1.5030, for trans-propenylcyclopentenyl ketone mp 31–31.5°.

Propenyl-2, 4-dimethylcyclopentenyl ketone (IX) was prepared as described in [19], from 180 g (1.31 mole), XV, yield 36.4%, bp 95–96° (4 mm), n_D^{20} 1.5000. The literature gives [19] bp 92–94° (4 mm), n_D^{20} 1.5012. Distillation of 50 g product through the column gave 23.4 g ketone bp 105° (4 mm), n_D^{20} 1.5010.

2-Methyl-1-thiadecal-4-one (Ia and Ib). a) Modification of the method described in [11]. A solution of 0.12 g (1.5 mmole) fused NaOAc in 445 ml ethanol at –5° was saturated in 20 min with hydrogen sulfide, then 60 g (0.4 mole) VII added over a period of 1 hr 30 min at the same temperature. Hydrogen sulfide was again passed in for 12 hr at 0 to –2°. Then the reaction products were refluxed for some hours, and worked up as described in [11] to give 48.9 g ketosulfide cut bp 123–126° (7 mm), n_D^{20} 1.5208, yield 64.5%.

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*Nazarov and Burmistrova's [19] method of condensing vinylacetylene using powdered KOH gave XII in half the yield recorded by them.

**Here and below the column used had 10 theoretical plates.

Table 2

Constants of Thiabicyclanes Synthesized

Compound no.	Name	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_{found}	I_s	Formula	Found, %				Calculated, %			Yield, %
								C	H	S_{total}	$S_{sulfide}$	C	H	S	
II	2-Methyl-1-thiabicyclo[4.3.0]nonan-4-one	117 (7)	1.5242	1.0916	47.81	8.5	$C_9H_{14}OS$	63.4	8.5	18.8	17.9	63.5	8.3	18.8	70
III	2, 6, 8-Trimethyl-1-thiabicyclo[4.3.0]nonan-4-one	110 (4)	1.5038	1.0561	54.9	8.6	$C_{11}H_{18}OS$	66.9	9.1	15.5	13.4	66.7	9.1	16.1	50.5
IVa	2-Methyl-1-thiadecalin	90 (7)	1.5081	0.9734	52.1	8.2	$C_{10}H_{18}S$	70.3	10.7	19.0	27.3	70.6	10.7	18.8	78
IVb	2-Methyl-1-thiadecalin	85 (7)	1.5138	0.9882	51.9	7.7	$C_{10}H_{18}S$	70.5	10.6	18.7	30.5	70.6	10.7	18.8	78
V	2-Methyl-1-thiabicyclo[4.3.0]nonane	91—92 (7)	1.5110	0.9845	47.5	8.2	$C_9H_{16}S$	69.2	10.3	20.6	24.5	69.2	10.3	20.5	61
VI	2, 6, 8-Trimethyl-1-thiabicyclo[4.3.0] nonane	72—74 (2)	1.4961	0.9772	54.5	8.2	$C_{11}H_{20}S$	71.5	10.6	17.7	25.4	71.8	10.9	17.4	36

Table 3

Derivatives of Thiabicyclanes

Compound no.	Derivative	Mp, °C bp, °C (pressure, mm)	Bp, °C (pressure, mm) n_D^{20}	Formula	Found, %		Calculated, %		Yield, %
					C	H	C	H	
Ib	$HgCl_2$ complex*	146 —147	—	—	—	—	—	—	80
II	Semicarbazone	168.5—170	—	$C_{10}H_{17}N_3OS$	N 18.1		N 18.5		80
	Sulfone	110 —112	—	$C_9H_{14}O_3S$	53.6	6.9	53.4	7.0	38
	$HgCl_2$ complex	122 —123	—	—	—	—	—	—	61
III	Semicarbazone	164 —165.5	—	$C_{12}H_{21}N_3OS$	N 12.4		N 12.5		43
	$HgCl_2$ complex	78 — 79.5	—	—	—	—	—	—	50
	Sulfone	103 —103.5	—	$C_{11}H_{12}O_3S$	57.3	7.8	57.6	7.8	36
IVa	$HgCl_2$ complex	147	—	—	—	—	—	—	76
	Sulfone	96 — 97	—	$C_{10}H_{18}SO_2$	59.6	9.0	59.5	8.9	81
IVb	$HgCl_2$ complex	132 —133.5	—	—	—	—	—	—	69
	Sulfone	97 — 97.5**	—	$C_{10}H_{18}SO_2$	59.8	9.1	59.5	8.9	11.9
		—	149—152 (1.5); 1.5114		59.9	9.2	59.5	8.9	41.6
	Sulfoxide***	—		$C_{10}H_{18}SO$	63.3	10.1	64.5	9.7	93.5
V	$HgCl_2$ complex	119 —120	—	—	—	—	—	—	87
	Sulfone	—	194—196 (2); 1.5042	$C_9H_{16}O_2S$	57.6	8.6	57.5	8.6	50.1
VI	Sulfoxide	151 —153	—	—	—	—	—	—	55
	Sulfone	—	192—195 (2); 1.4993	$C_{11}H_{20}O_2S$	60.7	9.2	61.1	9.3	41

*Yields of all $HgCl_2$ complexes, except **VI**, calculated based on a composition $R_2S \cdot HgCl_2$; composition of **VI** $R_2S \cdot 2HgCl_2$.

The **IVa and **IVb** sulfones gave an undepressed mixed mp. This in conjunction with the thin-layer chromatography results, indicates that **IVb** was contaminated with **IVa**.

***Found: $S_{sulfoxide}$ 16.5%; calculated $S_{sulfoxide} = S_{total} = 17.2\%$.

Repeated freezing and subsequent recrystallization from MeOH gave 9 g Ia, yield 12%, bp 75–78°. The mother liquors were distilled through the column to give 18.1 g Ib, yield 44.1%, bp 110–111° (12 mm), n_D^{20} 1.5259. The literature [11] gives mp of Ia 77.5°, bp Ib 111° (5 mm), n_D^{20} 1.5270.

b) 3 g (0.02 mole VII, 0.4 g (0.005 mole) fused NaOAc, and 10 ml EtOH were placed together in a glass pressure vessel with 2 outlets, and holding 250 ml. Hydrogen sulfide was introduced through one opening by means of a capillary, and using liquid nitrogen cooling, about 2 g (0.06 mole) was condensed. At the same temperature the vessel was evacuated to 2 mm, then sealed and kept at 0°, for 1 hr, excess hydrogen sulfide allowed to evaporated under ambient conditions, and the reaction products worked up as described in [11] to give a 78% yield of ketosulfide cut.

2-Methyl-1-thiabicyclo [4.3.0] nonan-4-one (II). a) In a way similar to that described above, 3.5 g (0.026) trans VIII and 6 ml EtOH plus 0.6 g (0.007 mole) fused NaOAc was condensed with 3.4 g (0.1 mole) liquid hydrogen sulfide, reaction time 3 hr.

b) In the way described above, 4.8 g (0.04 mole) cis-VIII, with reaction time 5 hr, gave a 69% yield of II. Table 2 gives the properties of II as well as of other newly-synthesized thiabicyclanes.

2, 6, 8-Trimethyl-1-thiabicyclo [4.3.0] nonan-4-one (III). In the way described above, 7 g (0.045 mole) IX was condensed with liquid H_2S, reaction time 7 hr. The reaction products from 4 runs were bulked, and fractionated through the column. Yield of III 50.8%.

Semicarbazones II and III. 1 g semicarbazide hydrochloride and 1 g NaOAc were dissolved in 6 ml water, with slight heating, the solution cooled, and to it added 0.1 g II in an equal volume of EtOH; the precipitate formed was filtered off, washed with water, and vacuum-dried, after which it was twice recrystallized from MeOH, to give 0.12 g substance mp 168.5–170° (see table 3). The semicarbazone III was prepared similarly.

Thin-layer chromatography of 2-methyl-1-thiadecalones, 2-methyl-, and 2, 6, 8-1-thiabicyclo [4.3.0] nonan-4-ones. Ia, Ib, II and III were chromatographed by ascending thin-layer chromatography on a non-stabilized layer of absorbent (Brockman grade II activity, alumina). Layer thickness 0.5 mm, eluent 10% (by volume) isooctane in isopropyl ether. 0.05 mg substance was introduced on to the plate as a 1% solution in isooctane. Iodine was the visualizer, and the visualizing time 30 min (Fig. 1).

Isomerization of the ketosulfides. a) Isomerization of Ib to Ia, according to [11]. 12.3 g (0.067 mole) Ib was added to a solution of 0.18 g (0.008 g at) Na metal in 60 ml MeOH, the mixture refluxed for 2 hr, the MeOH distilled off, and the residue treated with water and ether. The ether layer was separated and neutralized with 10% HCl, dried over $MgSO_4$, the ether evaporated off, and the residue recrystallized from MeOH, to give 6.8 g Ia, R_f 0.45.

b) Under the conditions of the above experiment II and III are not isomerized, and thin-layer chromatography shows that their structures are unchanged.

2-Methyl-1-thiadecalins (IV). a) 0.55 g (0.003 mole) Ib was dissolved in 30 ml triethyleneglycol, bp 49° (26 mm) added. The mixture was quickly heated to 150° under nitrogen, and after 1 hr at that temperature 5 ml distillate had come over. The distillate was returned to the reaction mixture, and heating continued at the same temperature until distillate ceased to come over, after which heating was continued for 2 hr more at the same temperature, then finally for 1 hr at 165°. 6.1 g (0.11 mole) fused KOH was added with cooling, and the mixture heated, at 130° there was vigorous evolution of nitrogen. When reaction ceased, the mixture was heated for 30 min at 150°, then at 165° for 15 min. After cooling the mixture was extracted with ether, the extract neutralized with 15% HCl, and dried over $MgSO_4$. The ether was distilled off, and the residue vacuum-distilled. Repeated distillation gave IVb, yield 78%, for properties see Table 2.

b) 7.7 g (0.42 mole) Ia was reduced as above, yield of IVa 78%. For properties, see Table 2.

2-Methyl-1-thiabicyclo [4.3.0] nonane (V), prepared from 5.8 g (~0.035 mole) II, similarly to Ib, yield 61%, properties given in Table 2.

2, 6, 8-Trimethyl-1-thiabicyclo [4.3.0] nonane (VI). 9.7 g (0.05 mole) III was reduced as discribed above, yield 36%, for properties see Table 2. Reduction was accompanied by appreciable resinification.

Thin-layer chromatography of 2-methyl-1-thiadecalins, 2-methyl- and 2, 6, 8-trimethyl-1-thiabicyclo [4.3.0] nonanes. IVa, IVb, V, and VI were chromatographed under the conditions used for the ketosulfides, but the eluent was a 1.96% (by volume) solution of isopropyl ether in isooctane. Iodine was the visualizer, and the visualizing time 10 min (see Fig. 2). Comparison of the chromatogram of the ketosulfides with that of their reduction products leads to the conclusion that reduction leaves the number and ratios of isomers unchanged. This indicates that the reaction takes place without change in configuration.

Attempt to isomerize IVb. 1 g IVb was heated with sodium methoxide solution as described for Ib, to give 0.79 g compound bp 91–93° (7 mm), n_D^{20} 1.5140, R_f 0.37 and 0.49. Practically no isomerization was detected.

Oxidation of 2-methyl-1-thiadecalin (IVb). a) 1.28 g (7.5 mmole) IV was dissolved in 4 ml Ac_2O, and after 15 min, 0.9 g (7.5 mmole) 28% H_2O_2 added at ≤ 25°. After 1 hr 15 min a sample gave a negative reaction for peroxide. The solvents were vacuum-distilled off at ≤ 30°. The residue contained sulfoxide IVb, yield 93%. It was purified by chromatographing on ASK silica gel [20], the eluent for removing the unoxidized impurities was benzene, while the eluent for sulfoxide was ethanol. Table 3 gives the constants of the purified compounds.

b) 9.7 g (0.08 mole) 28% H_2O_2 was added to a stirred solution of 3.74 g (0.022 mole) IVb in 15 ml AcOH, when the temperature rose to about 70°. The mixture was heated at 100° for 1 hr. After cooling, the unreacted hydrogen peroxide was decomposed by adding manganese dioxide, the solution filtered, and the filtrate vacuum-concentrated. The residue partly crystallized, giving 0.49 g sulfone IVb. After recrystallizing from EtOH the sulfone weighed 0.42 g, mp 95–97°. The mother liquors gave a further 0.09 g sulfone, mp 94–97°, and two distillations gave 1.51 g sulfone bp 149–152° (1.5 mm). The sulfones of II, III, IVa, V, and VI were prepared similarly (see Table 3).

Mercuric chloride complexes of thiabicyclanones and thiabicyclanes. 0.08 g (0.5 mmole) IVa was added to 3 ml saturated $HgCl_2$ solution, the precipitate of complex filtered off, washed with ethanol, and then twice recrystallized from ethanol. Yield 0.19 g, mp 147°. Complexes were similarly prepared from Ib, III, IVa, IVb, V, and VI (see Table 3).

Note. Up to the time of publication there were doubts about the correctness of the position of the double bond in the ring of ketone IX, as found in [19]. Cyclization of the ketone with the double bond in the alternative position viz 2, 4-dimethylcyclopentene-5-isopropenyl ketone, by hydrogen sulfide, should give not 2, 6, 8-, but 2, 5, 7-tri-methyl-1-thiabicyclo [4.3.0] nonan-4-one. Further research is needed to finally place the methyl groups in the cyclopentane ring of ketone III, and correspondingly of sulfide VI.

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