# I. The Action of Sulfur on Terpenes. The Limonene Sulfides

BY A. W. WEITKAMP

The volatile products of the reaction of sulfur with three isomeric terpenes were studied to gain insight into the reaction mechanism. Besides the complex mixture of non-volatile polysulfides obtained in each instance, terpinolene and α-terpinene gave large yields of p-cymene. The volatile products from d-limonene contained some aromatic hydrocarbons but consisted mainly of sulfur compounds. Three sulfur compounds have been isolated and identified as cyclic thioethers with sulfide bridges joining the 1,8- and 2,8-positions. A trace of 3,6-dimethylbenzothiophene was also found.

Introduction

Many terpenes have been heated with sulfur to prepare non-volatile polysulfides. The mechanism of the reaction is not fully understood because the molecular structures of the products were not determined. Even the volatile by-products have been largely neglected. The dehydrogenating action of sulfur on terpenes was recognized long ago by Ruzicka[1] who obtained p-cymene from limonene by this means. The formation of some volatile sulfur compounds by direct action of sulfur on limonene was noted by Nakatsuchi.[2,3]

We have studied the sulfurization of three isomeric terpenes—limonene (I), terpinolene (II) and α-terpinene (III)—and have identified the

I   II   III
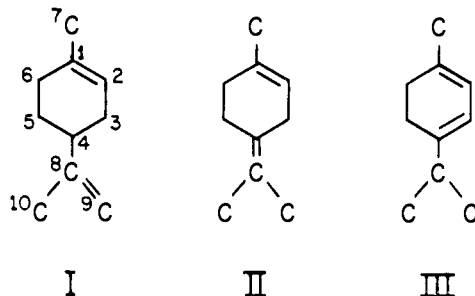
hydrocarbons and volatile sulfur compounds in the products. Only limonene gave substantial yields of volatile sulfur compounds.

Experimental

Materials.—Terpinolene and α-terpinene were used as obtained from Hercules Powder Co. The terpinolene was found to be homogeneous by gas-liquid chromatographic analysis. The α-terpinene contained about 12% p-cymene as the only detectible impurity. It was not further purified because p-cymene is not reactive enough to interfere in the sulfurizations. dl-Limonene of 99.+% purity was obtained from commercial dipentene by silica-gel percolation and fractional distillation through an 80-plate column.

d-Limonene, originating from orange peel, was obtained from Onyx Oils and Resins, Inc. The purity was about 95%, $\alpha^{25}D$ +98.8°, $n^{20}D$ 1.4710. The "best" fraction obtained by fractional distillation had a purity of 99.6%, estimated from the relative slopes of the melting and warming curves taken in a melting point apparatus similar to that described by Glasgow.[4] Its properties were m.p. −74.35°, $n^{20}D$ 1.4723, d^{20}_4 0.8611, $\alpha^{25}D$ +103.9°. Trends in the properties of adjacent fractions suggested that the remaining impurity differed slightly in volatility. Hence the optical purity of orange peel d-limonene is probably greater than 99.6%, i.e., the content of l-limonene is less than 0.4%.

(1) L. Ruzicka, Jules Meyer and M. Mingazzini, Helv. Chim. Acta, 5, 356 (1922).

(2) Akira Nakatsuchi, J. Soc. Chem. Ind. Japan (Suppl. Binding), 33, 408 (1930).

(3) Akira Nakatsuchi, ibid., 35, 376 (1932).

(4) A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, J. Research Natl. Bur. Standards, 35, 355 (1945).

Sulfurization.—Small-scale sulfurizations were carried out by heating 0.2 mole of terpene with 0.23 gram atom of sulfur in a flask immersed in an oil-bath at the desired temperature for the required time. With terpinolene and α-terpinene, the initial reaction was so vigorous that external cooling was necessary. The volatile products were evaporated off under vacuum and analyzed by gas-liquid partition chromatography.
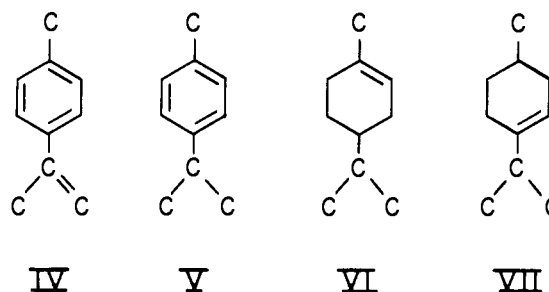
Large-scale sulfurizations of d-limonene and dl-limonene were carried out to obtain quantities of the volatile sulfur compounds for further study. Ten moles of limonene were heated with 15 gram atoms of sulfur at reflux temperature for one hour. The reaction was started by melting the sulfur in the presence of one-half mole of limonene and adding the remainder of the limonene through a dropping funnel as rapidly as the heat evolution permitted.

Gas–Liquid Partition Chromatography.—The chromatographic column was filled with dinonyl phthalate[5] supported on Celite and was heated to 150° in a vapor bath. The sensing device was a gas density balance.[6] Nitrogen was the eluent.

Thiourea Adduction.—The ability of a compound to form a thiourea adduct[7] was shown by the formation of a copious precipitate when a small amount of the compound was added to a saturated solution of thiourea in methanol. Formation of adducts on a preparative scale was done by contacting the compound with a slurry of powdered thiourea in isopentane to which a little methanol had been added.

Hydrocarbon Products

The sulfur-free part of the reaction product consisted of hydrocarbons that had either gained or lost hydrogen by hydrogen transfer. The four hydrocarbons that were isolated in significant amounts were identified as p-isopropenyltoluene (IV), p-cymene (V), 1-p-menthene (VI) and 3-p-menthene (VII) by comparison of their infrared spectra with reference spectra.[8,9]

IV   V   VI   VII

Yields of individual hydrocarbons and sulfurized products obtained in small-scale sulfurizations of limonene (I), terpinolene (II) and α-terpinene (III) at a bath temperature of 170° for two hours are shown in Table I.

Limonene reacted less rapidly than terpinolene and α-terpinene. The double bond in the 8:9-position of limonene

(5) N. H. Ray, J. Applied Chem., 4, 21 (1954).

(6) A. J. P. Martin and A. T. James, Biochem. J. (London), 63, 138 (1956).

(7) R. W. Schiessler and D. Flitter, THIS JOURNAL, 74, 1720 (1952).

(8) p-Isopropenyltoluene; M. J. Murray and W. S. Gallaway, ibid., 70, 3867 (1948).

(9) "Catalog of Infrared Spectral Data" of the A.P.I. Res. Proj. 44; p-cymene, Serial No. 1848; 1-p-menthene, Serial No. 1777; 3-p-menthene, Serial No. 1779.

TABLE I

PRODUCTS OF TERPENE SULFURIZATION

Terpene	% not con- verted	Mole % terpene converted to:				Volatile sulfur com- pounds	Poly- sul- fides
		IV	V	VI	VII		
Limonene	6	4	10	0	<0.1	36	44
Terpinolene	0	2	47	4	12	Trace	35
α-Terpinene	0	0	50	4	6	Trace	40

survived to give a significant yield of p-isopropenyltoluene (IV). The 4:8-double bond of terpinolene disappeared completely into the side chain and the ring but preferentially into the ring since the product distribution more closely resembles that from α-terpinene than from limonene. However, the high yield of 3-p-menthene (VII) suggests that terpinolene was not preisomerized to α-terpinene but that a common intermediate was involved. The failure to obtain either of the cyclohexenes VI, VII from limonene suggests that the disappearance of the 8:9-double bond to yield p-cymene (V) is not by way of stepwise migration into the ring but must involve saturation *in situ* by a hydrogen-transfer process.

A material balance on transferred hydrogen shows that each molecule of terpinolene or α-terpinene that was converted to polysulfide must also have absorbed an average of two atoms of hydrogen. In the case of limonene, the yield of monosulfides was more than enough to absorb all of the hydrogen that was transferred from hydrocarbons; the extra hydrogen for the saturation of the monosulfides could only be supplied at the expense of the polysulfide fraction. This apparent difference in saturation may account for the pale honey color of the polysulfides of terpinolene and α-terpinene, compared with the molasses color of limonene polysulfides.
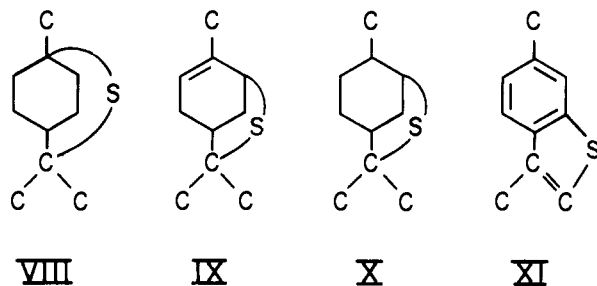
Analytical separation by precise fractional distillation was adequate for all components except p-cymene and unreacted limonene; the latter were estimated from the refractive index of the mixture. Yields and properties of the products from d-limonene or dl-limonene were the same except for the optical rotations and cryoscopic properties of compounds IX and X. Yields and properties of the products from a typical large-scale sulfurization of d-limonene are shown in Table II.
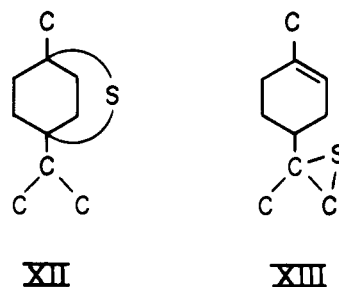
Because of the higher ratio of sulfur used in the large-scale runs conversion was more nearly complete than in the small-scale runs under otherwise similar conditions, but the yields of volatile products were lower. Mercaptans were not present in significant amounts.

Nakatsuchi proposed structures XII and XIII for the volatile sulfur compounds, but his efforts to isolate and identify them were not entirely successful. That his saturated compound, $C_{10}H_{18}S$, obtained from dl-limonene,[3] was the same as our compound X is shown by the comparison in Table III, but the symmetry of the structure XII proposed for this compound is inconsistent with its optical activity when prepared from d-limonene.

The unsaturated material obtained from d-limonene and assigned the episulfide structure XIII and empirical formula,

TABLE III

PROPERTIES OF dl-2,8-trans-p-MENTHYLENE SULFIDE (X)

	Nakatsuchi[3]	This study
B.p., °C. (mm.)	223 (759)	224 (745)
		79 (5)
M.p., °C.	−23	−23
$n^{20}D$	1.52045 (15.3°)	1.51798
d^{20}_4	1.033 (27.6°)	1.0016
Sulfone, m.p., °C.	65.5	65.5

TABLE II

PRODUCTS FROM THE SULFURIZATION OF d-LIMONENE

Component	Wt. % of reaction product	Mole % of d-limonene converted	B.p., °C. (5 mm.)	$n^{20}D$	$\alpha^{25}D$	d^{20}_4
d-Limonene (I)[a]	3.7	... }	46.5	1.4822	...	....
p-Cymene (V)	4.1	5.8 }				
p-Isopropenyltoluene (IV)	1.7	2.4	59	1.5350	0	....
$C_{10}H_{18}S$ (VIII)[b]	2.2	2.5	72	1.5050	0	0.9732
$C_{10}H_{16}S$ (IX)	6.0	6.8	79.5	1.5250	+79.9°	1.0057
$C_{10}H_{18}S$ (cis) (X)	Trace	Trace	79–80	1.509	−54°	
$C_{10}H_{18}S$ (trans) (X)[c]	20.2	22.9	84	1.5180	−59.9°[e]	1.0016
3,6-Dimethylbenzothiophene (XI)[d]	0.4	0.5	110	....	0	....
Polysulfides	61.7	59.1				
	100.0	100.0				

[a] Conversion was 95 mole %. [b] M.p. of sulfone 60°. [c] M.p. of sulfone: dl, 65.5°; optically active, 106°. [d] M.p. 40.5°. [e] $\alpha^{25}D$ of optically pure compound −69.1°.

Limonene Sulfides

Isolation.—Products from large-scale sulfurization of limonene were worked up by vacuum fractional distillation to isolate quantities of the monosulfur derivatives (VIII, IX, X, XI) for characterization. Compound XI is 3,6-dimethyl-

VIII   IX   X   XI

benzothiophene. The naming of the three cyclic thioethers is covered by two official systems.[10]

(10) The cyclic thioether derivatives of limonene can be named either by a special system for terpenes (Advances in Chemistry Series

XII   XIII

No. 14, "Nomenclature for Terpene Hydrocarbons," American Chemical Society, Washington, D. C., 1955) or by the general ring index system (A. M. Patterson and L. T. Capell, "The Ring Index," ACS Monograph No. 84, The Reinhold Publishing Corp., New York, N. Y., 1940). Thus, compound VIII can be named either 1,8-p-menthylene sulfide or 1,3,3-trimethyl-2-thiabicyclo[2.2.2]octane. The optically active form of compound IX is (+)-1-p-menthen-6,8-ylene sulfide or (+)-4,7,7-trimethyl-Δ³-6-thiabicyclo[3.2.1]octene. Compound X, in its optically active form, is (−)-2,8-trans-p-menthylene sulfide or (−)-4-exomethyl-7,7-dimethyl-6-thiabicyclo[3.2.1]octane.
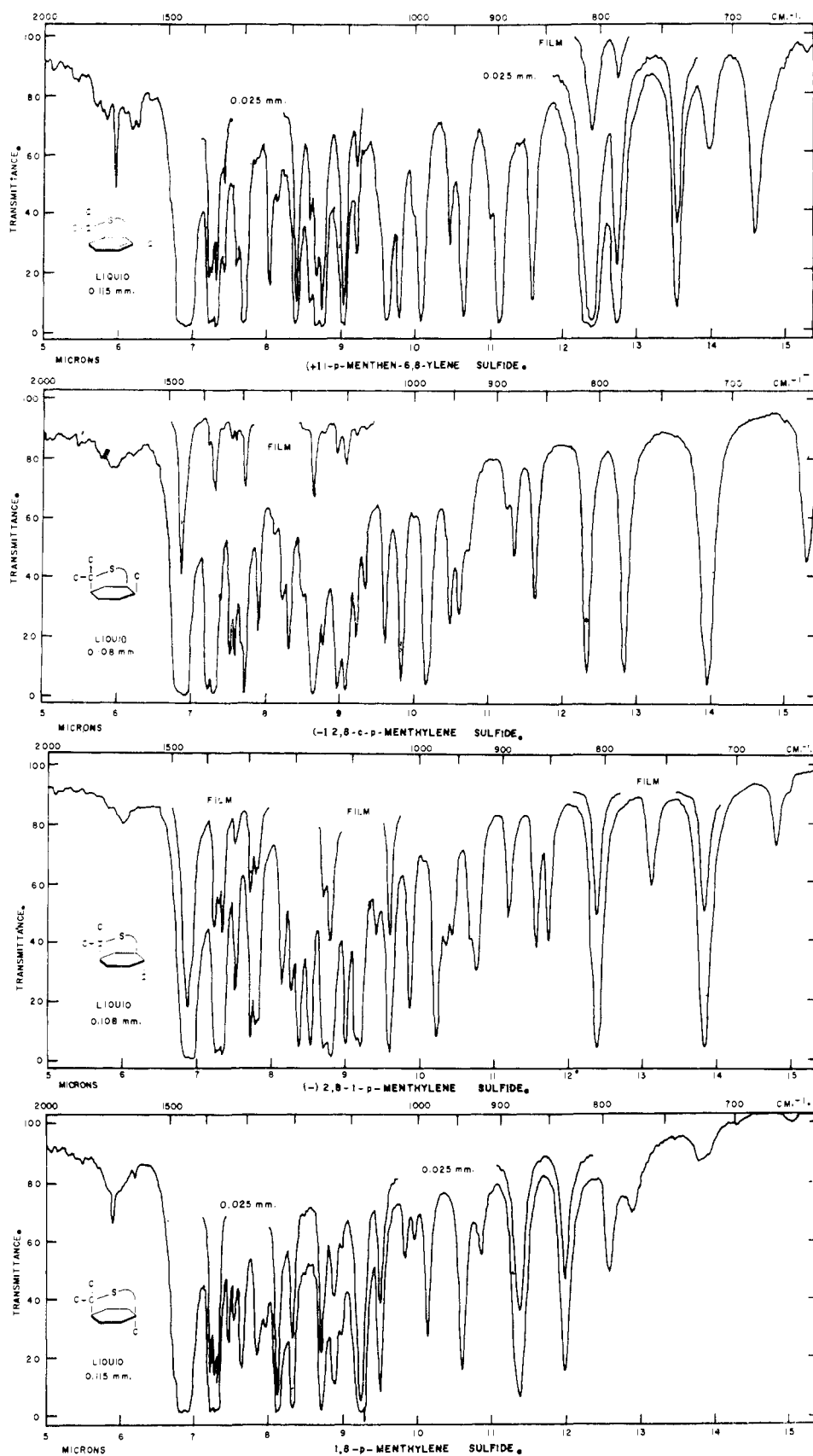
Fig. 1.—Infrared spectra of limonene sulfides.

TABLE IV

RELATIVE ION INTENSITIES IN THE PARENT MASS REGION OF THE MASS SPECTRUM

m/e	Found[a] XI	Theory for $C_{10}H_{10}S$	m/e	Found[b] IX	Theory for $C_{10}H_{16}S$	m/e	Found			Theory for	
							XIII	X (trans)	X (cis)	$C_{10}H_{18}S$	$C_8H_{10}S_2$
162	100	100	168	100	100	170	100	100	100	100	100
163	11.5	11.8	169	12.2	11.9	171	12.4	12.4	12.4	11.9	10.4
164	5.0	5.1	170	5.1	5.1	172	6.0	5.1	5.2	5.1	9.4
165	0.5	0.5	171	0.5	0.5	173	0.7	0.5	0.5	0.5	0.9

[a] The methylated aromatic compound, 3,6-dimethylbenzothiophene, under electron impact dissociates in part by the loss of one or two hydrogens. Corrections were made for the contributions of the isotopic $C_{10}H_9S^+$ and $C_{10}H_8S^+$ ions to the $C_{10}H_{10}S^+$ peaks. [b] Corrections were made for saturated impurities of 170 molecular weight consisting of 1.3% X (*trans* isomer) and 7.3% X (*cis* isomer). The *cis* isomer is inseparable from IX by distillation or gas chromatography. Its occurrence here as a minor component is the only evidence that any was formed in the sulfurization reaction.

$C_{10}H_{16}S,^2$ may have contained some of our compound IX ($\alpha^{25}D$ +79.9°), but is judged on the basis of the sign and magnitude of its rotation (−12.3°) to be badly contaminated with the saturated compound X ($C_{10}H_{18}S$, $\alpha^{25}D$ −59.9°).

Identification.—Each of the four sulfur compounds isolated from the reaction product has been assigned a structure consistent with its chemical and physical properties. Raney nickel desulfurization[11] showed that the carbon skeleton of *d*-limonene was intact. Complete proof of structures involved the determination of the empirical formulae, the location of both C–S bonds and in compound IX the position of unsaturation. Absolute configurations of the optically active compounds IX and X were also worked out.[12]

Mass spectral data aided in the derivation of empirical formulas. The integrity of the *d*-limonene carbon skeleton eliminated all possible formulas that did not contain ten or a multiple of ten carbon atoms. Molecular weights, determined as the mass of the most abundant molecule ion, were 168 for IX, 170 for VIII, X (*trans*) and X (*cis*) and 162 for XI. These values can only be satisfied by molecules consisting of ten carbons, one sulfur and an appropriate number of hydrogens. Further evidence that the molecules contained one and only one atom of sulfur was derived from the yields of molecule ions containing heavy isotopes of carbon, hydrogen and sulfur. The yields shown in Table IV of ions heavier by one unit were appropriate for the contribution of natural C^{13}, H^2 and S^{33} and those heavier by two units reflected principally the contribution of the S^{34} isotope. By comparing the observed molecule ion distributions with the statistical calculations of McAdams[13] the empirical formulas shown in Table II were uniquely established. From chemical evidence that these compounds were thioethers and the observed molecular weights it appeared that IX was an unsaturated bicyclic sulfide; VIII and X were saturated bicyclic sulfides and XI was a benzothiophene. A fragment ion that had a mass corresponding to the loss of C_3H_7S+ occurred prominently in the spectra of compounds VIII, IX and X and indicated that one of the C–S bonds involved the isopropyl group.

The infrared spectra of compounds VIII, IX and X in Fig. 1 have bands at 7.25 to 7.35 μ that are attributed to methyl deformation. The occurrence of three bands in this region is explained as follows: the central band is due to the single methyl attached to the ring. The bands on either side are due to the two methyls attached to the central carbon of the isopropyl group. Accordingly, these positions are not involved in C–S linkages and sulfur must be joined to the isopropyl group at the central carbon. In contrast, the spectrum[14] of compound XI has a single methyl deformation band at 7.26 μ because the isopropyl group is joined to sulfur at a terminal carbon, and a strong band at 12.36 μ is evidence for 1,2,4-aromatic substitution. In the region beyond 15 μ (KBr prism) compound VIII had a single strong band at 17 μ. Absorption in this region is associated with the tertiary sulfide structure. The presence of several bands in the spectra of IX and X in the region of 15 to 20 μ

suggested that both tertiary and secondary sulfide linkages might be present, although correlations are not as firm.

The ultraviolet spectrum of compound IX resembled that of allyl sulfide and confirmed that unsaturation was present. The unsaturation must necessarily be in the ring to be consistent with the infrared evidence that neither the methyl nor isopropyl groups were involved. The ultraviolet spectrum[14] of compound XI resembled that of benzothiophene.
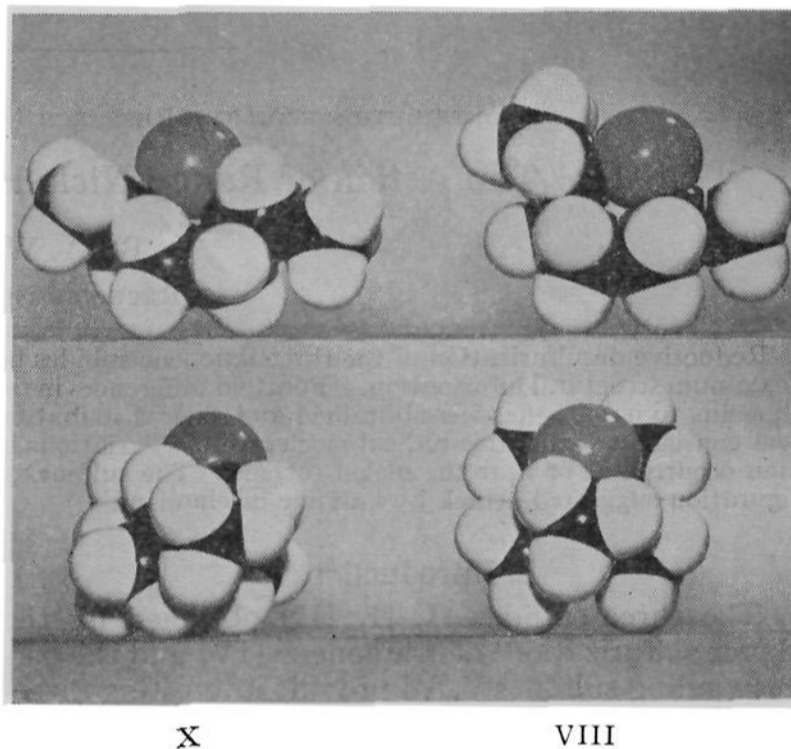

X   VIII

Fig. 2.—Left, (−)-2,8-*trans-p*-menthylene sulfide; right, 1,8-*p*-menthylene sulfide.

Thiourea readily formed a crystalline adduct with compound X, but not with the isomeric compound VIII or with any other of the reaction products. Scale models of structures VIII and X, shown in Fig. 2, were constructed from Stuart and Briegleb atom models. Measurements on the scale models (1.5 cm. = 1 Å.) showed that the cross section of VIII (6.5 × 6.6 Å.) was a little too large to enter the 5.8 × 6.8 channels of the thiourea adduct lattice.[7] The cross section of X (5.7 × 6.5 Å.) was favorable for adduct formation.

Optical activity of compounds IX and X, when prepared from *d*-limonene, required that the structures be unsymmetrical and excluded a ditertiary structure for X. The optical inactivity of VIII was consistent with the symmetrical ditertiary structure but *per se* did not preclude the possibility that it might be racemic.

Compound X was obtained in sufficient quantity to study its optical purity. Thiourea adduction proved to be a very effective means of eliminating traces of close-boiling impurities but did not alter the optical purity. The maximum rotation obtainable by repeated adduction was −59.9°. The melting point was −7.85° and the cryoscopic behavior indicated a purity of 87 ± 5%. Four recrystallizations from isopentane increased the rotation to −69.1°, the melting point to −3.88°, and the purity to 99+%. The thiourea-purified product therefore contained

(11) A. W. Weitkamp, THIS JOURNAL, **81**, 3434 (1959).

(12) A. W. Weitkamp, *Ibid.* **81**, 3437 (1959).

(13) D. R. McAdams, "Isotope Correction Factors for Mass Spectra of Petroleum Fractions," Oct. 7, 1957, issued by ASTM Committee E-14, Sub-Committee III.

(14) A. W. Weitkamp, "Catalog of Infrared Spectral Data" of the A.P.I. Res. Proj. 44, Serial No. 1854; "Catalog of Ultraviolet Spectral Data," Serial No. 667.

about 6.5% of the dextrorotatory isomer or 13% of the racemate.

A direct relationship between the skeletons of IX and X was established by hydrogenation of IX over 5% Pd-on-charcoal.[12] The saturated product was a mixture of cis and trans isomers, one of which was shown by the infrared spectrum of the mixture to be the trans isomer identical with compound X obtained from the sulfurization reaction mixture. Pure cis isomer was separated from the mixture by percolation over alumina. Its infrared spectrum is included in Fig. 1.

Reductive desulfurization with excess Raney nickel yielded roughly equal amounts of cis- and trans-p-menthane from compound VIII, consistent with a 1-p-menthyl free-radical intermediate. Reduction of the corresponding sulfone yielded cis-p-menthane by inversion of configuration at the 1-position. Compound IX yielded a 37:63 cis:trans ratio of isomers consistent with saturation of a double bond in the 1:2-position. Compound X yielded trans-p-menthane and the corresponding cis isomer[15] separated from the

(15) During review it was suggested that trans-p-menthane might result from equilibration and therefore not necessarily reflect a trans-structure in the sulfur compound identified as 2,8-trans-p-menthylene sulfide. To clarify this point it was urged that the epimer, 2,8-cis-p-menthylene sulfide be isolated and studied. This has been done and

hydrogenation products of compound IX yielded cis-p-menthane consistent with a 2-p-menthyl free-radical intermediate. Additional evidence was obtained by desulfurization with a deficiency of nickel to yield olefins of known structure. The details are presented separately.[11] Compound XI yielded p-cymene consistent with its identification as 3,6-dimethylbenzothiophene.

Conclusion

The position of the double bonds in isomeric terpenes determines the course of the reaction with sulfur. Terpinolene and α-terpinene were easily dehydrogenated by a hydrogen transfer process in which the donor molecules became p-cymene and the acceptor molecules were largely converted to polysulfides. d-Limonene was dehydrogenated less readily and the transferred hydrogen seems to have been used in the formation of saturated cyclic monosulfides.

the originally assigned structures have been confirmed. The infrared spectrum is included in Fig. 1; other data are in ref. 12.

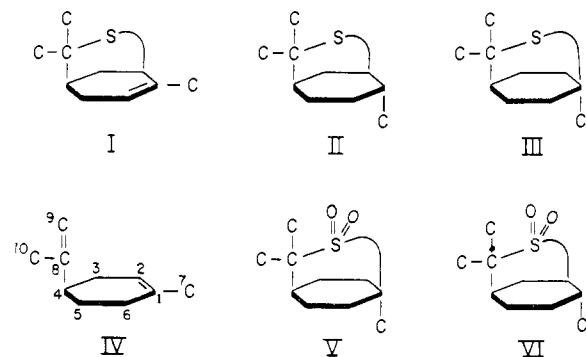WHITING, IND.

II. The Action of Raney Nickel on Limonene Sulfides and Sulfones

BY A. W. WEITKAMP

Reductive desulfurization of the three limonene sulfides by Raney nickel was studied over a range of conditions to obtain maximum structural information. Fourfold differences in reactivity due to structure were observed. Products ranging from diolefins to naphthenes were obtained and their distributions depended on conditions. Retention or loss of configuration was consistent with a free radical mechanism. Variations in the distribution of cis and trans isomers suggested that reduction occurred at or near the nickel surface. The sulfones were much more resistant to desulfurization; inversion of configuration suggested attack by an ionic mechanism.

Introduction

The three sulfides (I, II, III) obtained by the direct sulfurization[1] of d-limonene (IV) and the corresponding sulfones V, VI provide interesting three-

dimensional structures for the study of the stereochemical paths of reductive desulfurization with Raney nickel. This reaction is widely used as an aid in elucidating the structures of organic molecules. Usually, an excess of nickel is used to push hydrogenolysis to completion. However, Hauptmann and Wladislaw[2] used "hydrogen-free" and "hydrogen-poor" nickel in xylene solvent on certain aromatic sulfur compounds and observed

(1) A. W. Weitkamp, THIS JOURNAL, **81**, 3430 (1959).
(2) H. Hauptmann and B. Wladislaw, ibid., **72**, 707, 711 (1950).

that hydrogenolysis to the parent aromatic hydrocarbon occurred only so long as hydrogen was present. In the absence of hydrogen a Wurtz-like coupling reaction occurred.

Bonner[3] examined the possibility that hydrogen for the hydrogenolysis reaction might be donated by a solvent such as alcohol and showed by experiment that the nickel, rather than the solvent, provided the necessary hydrogen for reductive desulfurization. With sulfides and sulfoxides, he[4] postulated a free-radical intermediate that would racemize during the replacement of sulfur by hydrogen. On the other hand, elimination of the sulfone group was thought to be an ionic reaction accompanied by inversion of configuration.

In the present work reductive desulfurization was studied over a range of conditions to obtain maximum structural information. Our approach differed from that of Hauptmann and Wladislaw in the use of a polar solvent—methanol or 1-propanol—and hydrogen-rich Raney nickel in amounts varying from a large excess to a definite deficiency of available hydrogen.

Experimental

Materials.—The sulfur compounds, (+)-1-p-menthen-6,8-ylene sulfide (I) and 1,8-p-menthylene sulfide (III), had purities of 97 to 98%. (−)-2,8-trans-p-Menthylene sulfide (II) was purified by adduction with thiourea to a chemical

(3) Wm. A. Bonner, ibid., **74**, 1033 (1952).
(4) Wm. A. Bonner, ibid., **74**, 1034 (1952).