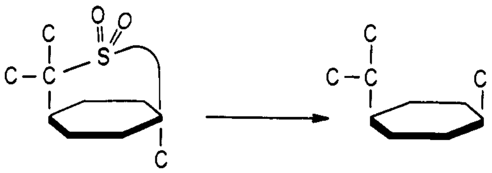
sulfides, increasingly favored reaction by the olefin route. However, at very low concentrations of nickel the proportion of the thermodynamically unfavored *cis*-*p*-menthane increased remarkably. Thus, from the standpoint of mechanism, the olefin, 1-*p*-menthene, may have to scavenge for scarce hydrogen and does so more effectively if the bulky isopropyl group is on the opposite side of the ring from the nickel surface. These effects are magnified in the case of 1,8-*p*-menthylene sulfide. Its resistance to desulfurization suggests that it exerts strong "poisoning" effect by being adsorbed without immediately reacting. The high olefin yield and high *cis:trans* ratio reflect a low "effective" nickel concentration as if each adsorbed molecule covered many active sites.

Desulfurization of Sulfones

The sulfones were prepared by oxidation of the corresponding sulfides with hydrogen peroxide in glacial acetic acid. Mass spectrometry showed that the molecular weight was increased from 170 for the sulfides to 202 for the sulfones, consistent with the addition of two atoms of oxygen. The sulfones, like the sulfides, exhibited differences in reactivity toward Raney nickel, but in the reverse order. The 1,8-sulfone V reacted smoothly in boiling 1-propanol to give a good yield of *cis*-*p*-menthane with no trace of the *trans* isomer. Clearly, inversion had occurred, probably by an S$_N$2 mechanism.



The isomeric 2,8-sulfone VI gave a small yield of a mixed product with the *p*-menthane portion consisting of about 6% *trans* and 94% *cis* isomers. Evidently, the mechanism whereby this sulfone group is eliminated is not a simple displacement. A backside attack may have been prevented by the considerable shielding of the back side of position 2 by the *trans*-methyl group at position 1.

Conclusion

The free-radical reductive desulfurization of sulfides proceeds, in part, by way of an olefin intermediate. Sulfones are desulfurized by an ionic mechanism when the backside approach is unhindered.

WHITING, IND.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL CO. (INDIANA)]

III. Mechanism of the Formation of Limonene Sulfides

BY A. W. WEITKAMP

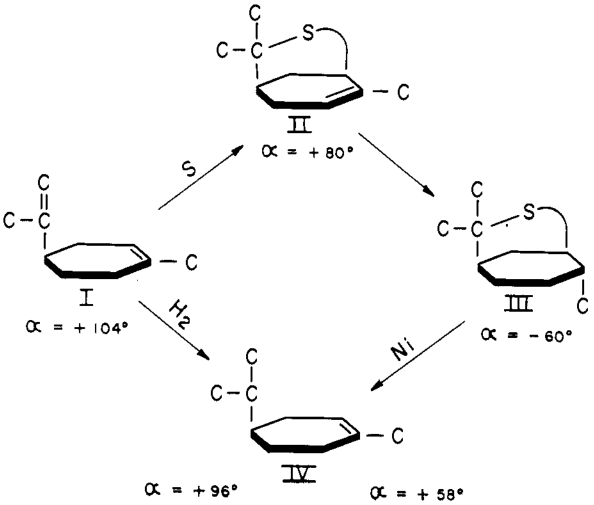
RECEIVED NOVEMBER 10, 1958

The time and temperature variables of the sulfurization of *d*-limonene and the stereochemical relationships of the volatile products have been studied. Introduction of sulfur seems to occur by way of a free-radical attack on the ring double bond, accompanied by an allylic shift. Saturation of the shifted double bond is stereospecific with respect to formation of the *trans* isomer. Attack on the side chain appears to be ionic. These findings should help in understanding the sulfurization of olefins having structures that do not reveal the stereochemical path of reaction.

Introduction

The problem of the mechanism by which olefins are sulfurized was clearly stated by Farmer and Shipley[1] as: "It is necessary to envisage that a radical reagent may in general attack an olefin either by replacing an α-methylenic hydrogen or by adding to the double bond." Just as polar addition to unsymmetrical olefins follows the rule of Markovnikov, radical addition is anti-Markovnikov.[2] The optically active sulfur compounds derived from *d*-limonene[3] have the structural characteristics necessary to resolve this problem, providing their optical configurations can be related to *d*-limonene (I). Such a possibility arose in consequence of a detailed study of reductive desulfurization with Raney nickel.

The problem was to determine whether or not the double bond in (+)-1-*p*-menthen-6,8-ylene sulfide (II) was in the same absolute position as in *d*-limonene. Pines[4] had shown that the selective saturation of the side chain of *d*-limonene left the sign of rotation unchanged and had little effect on the magnitude of rotation. Thus, the thioether could equally well be correlated with *d*-limonene or the stereochemically equivalent *d*-1-*p*-menthene (IV). The key to the configurational relationship between II and IV proved to be (−)-2,8-*trans*-*p*-menthylene sulfide (III). The successful line of attack involved establishing the relationships



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[1] E. H. Farmer and F. W. Shipley, *J. Chem. Soc.*, 1519 (1947).

[2] E. H. Farmer, *J. Soc. Chem. Ind.*, **66**, 86 (1947).

[3] A. W. Weitkamp, THIS JOURNAL, **81**, 3430 (1959).

[4] H. Pines, *ibid.*, **72**, 4260 (1950).

TABLE I

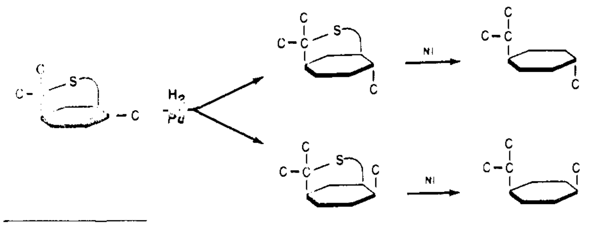
RESULTS OF TIME AND TEMPERATURE STUDIES

Reaction temperature, °C.	140	140	150	140	150	160	160	170
Reaction time, hours	2	4	2	8	4	2	4	2
Limonene, converted, %	28	52	65	79	80	78	94	94
Distribution of converted limonene, mole %								
To hydrocarbons	9	8	10	12	12	12	13	16
To thioethers	10	10	18	19	23	30	23	38
To polysulfides	81	82	72	70	65	58	64	46
Distribution of volatile components, mole %								
p-Cymene	27.1	31.9	21.7	30.0	25.2	20.9	27.2	20.8
p-Isopropenyltoluene	19.3	13.0	12.2	10.0	8.7	7.8	8.9	8.1
1,8-*p*-Menthylene sulfide	3.2	3.5	3.8	3.5	3.6	3.8	4.2	3.9
(+)-1-*p*-Menthen-6,8-ylene sulfide	30.5	23.4	23.9	13.7	15.9	19.7	12.4	17.4
(−)-2,8-*trans*-*p*-Methylene sulfide	19.9	28.2	38.4	42.8	46.6	47.8	47.3	49.8

Results

Small Scale Sulfurizations.—The time and temperature variables of sulfurization were studied in order to distinguish between the primary products of sulfurization and products of secondary conversions. In a series of small-scale experiments, 0.2 mole of optically pure *d*-limonene was heated with 0.23 gram atom of sulfur. The volatile portion of the product was analyzed by gas–liquid partition chromatography. The conditions, conversions and product distributions are detailed in Table I.

Hydrogenation of (+)-1-*p*-Menthen-6,8-ylene Sulfide (II).—Hydrogenation of a double bond in a sulfur compound was shown by Mozingo[5] to be catalyzed by 5% palladium-on-charcoal. At ambient temperature 1.5 g. of II in methanol was hydrogenated under 1700 lb. pressure over 6.5 g. of catalyst for three hours in a magnetically stirred vessel. The rotation changed from +80 to −40°. Analysis by gas chromatography revealed two nicely resolved peaks of about equal area. The elution time of the first peak overlapped that of the original unsaturated sulfur compound. The elution time of the second peak corresponded to 2,8-*trans*-*p*-menthylene sulfide (III). The infrared spectrum contained all of the bands characteristic of III but none of the bands characteristic of II. Thus hydrogenation was complete and the first eluting component was a new substance, presumably the *cis* isomer of 2,8-*p*-menthylene sulfide. Additional hydrogenation experiments showed that different shipments of palladium-on-charcoal varied widely in activity. In another experiment 4.25 g. of II was hydrogenated in methanol over 10 g. of catalyst under 1700 lb. pressure. Saturation was about 95% complete in 80 hours. The rotation changed from +80 to −42°. The isomers were successfully separated on a 16 ft. × 0.5 in. column of Alcoa F-20 alumina by elution with pentane. The order of elution was *cis* isomer, *trans* isomer III and unhydrogenated feed II. The rotations of the separated isomers were: *cis*, α^{25}/D −54°; *trans*, α^{25}/D −26°. The quantity of *cis* isomer isolated was insufficient for a study of optical purity. Comparison of the rotation of the separated trans isomer with the rotation of optically pure material (α^{25}D −69.1°) suggests that considerable racemization may have occurred during hydrogenation.



Desulfurization of the *cis* and *trans* isomers with excess Raney nickel yielded the corresponding *cis*- and *trans*-*p*-menthanes in 87 and 93% purity, respectively. Thus, desulfurization did not produce "equilibrium" *p*-menthane but faithfully reflected the *cis* and *trans* structures of the sulfur compounds.

Discussion

The series of small-scale batch experiments did not constitute a rate study. However, trends were revealed that permit some generalizations to be made. The rate of disappearance of *d*-limonene was such that a 10° decrease in temperature roughly doubled the time required for a given conversion. In general, the yield of hydrocarbons increased with increasing degree of conversion irrespective of time or temperature. The yield of thioethers increased at the expense of polysulfides as a function of the temperature rather than the extent of conversion.

The distributions of the hydrocarbons and the thioethers in the volatile portion of the product are also shown in the table relative to each other. It is not known to what extent secondary breakdown of polysulfides may have contributed to the formation of volatile products. Farmer[1] suggested that such was the case in the sulfurization of geraniolene and dihydromyrcene. At any rate, there is no definite trend in the relative yields of *p*-cymene. The experimental error is large because *p*-cymene and *d*-limonene are not as completely separated as the other components in the gas-liquid chromatographic analysis. *p*-Isopropenyltoluene is significantly more abundant at the mildest conditions, but tends to disappear under more drastic conditions by further attack on the olefinic double bond.

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(5) R. Mozingo, S. A. Harris, D. E. Wolf, C. E. Hoffhine, Jr., N. R. Easton and K. Folkers, THIS JOURNAL, **67**, 2092 (1945).

The thioethers are formed in reactions such that the net change is represented by

$$C_{10}H_{16} + S \longrightarrow C_{10}H_{16}S$$
$$C_{10}H_{16} + H_2S \longrightarrow C_{10}H_{18}S$$

A plot of thioether distribution as a function of *d*-limonene conversion in Fig. 1, extrapolated to zero conversion, suggests that (+)-1-*p*-menthen-6,8-ylene sulfide is a primary product. Hence it may be formed by the direct addition of sulfur to *d*-limonene. A small but remarkably constant proportion of 1,8-*p*-menthylene sulfide suggests that it also may be a primary product formed by the direct addition of hydrogen sulfide to both double bonds of *d*-limonene, according to Markovnikov's rule.

The other saturated thioether, (−)-2,8-*trans*-*p*-menthylene sulfide, is probably not a primary product. Direct formation by hydrogen sulfide addition would have required the unlikely anti-Markovnikov addition to the ring double bond. Its appearance at higher conversions suggests that it is a secondary product, possibly involving sulfur addition and saturation by hydrogen transfer in two discrete steps. The unsaturated sulfide may be its precursor, requiring only the stereospecific addition of hydrogen to yield exclusively the *trans* isomer; if so, the stereochemical identity of the two structures would be established.

Mechanism.—As pointed out earlier, one way to resolve the key question as to whether or not the ring double bond of *d*-limonene had shifted was to determine the absolute configuration of (+)-1-*p*-menthen-6,8-ylene sulfide (II). The direct approach, by partial desulfurization with Raney nickel, failed because the resulting olefins were optically inactive due to complete racemization of the unsaturated thioether during desulfurization.[6]

The saturated thioether, (−)2,8-*trans*-*p*-menthylene sulfide (III), was desulfurized without further racemization. A small yield of optically active olefin, identified by the sign and magnitude of rotation (α^{25}/D +58) as partially racemic *d*-1-*p*-menthene (IV), was obtained. Thus, to a large extent, the sulfur was joined to the ring where the double bond had been originally. The complications leading to a partially racemic olefin could only have arisen in the sulfurization and desulfurization steps, since the original *d*-limonene was optically pure.

After (−)-2,8-*trans*-*p*-menthylene sulfide, obtained by sulfurization, was carefully purified by thiourea adduction to preserve the original stereoisomer distribution, its optical rotation, $\alpha^{25}\mathrm{D}$ was −59.9°. The content of dextrorotatory isomer was about 6.5%, based on a rotation of −69.1° for the optically pure compound.[3] Thus, either the α-methylenic hydrogens were attacked by sulfur to the extent of 6.5% or partial racemization occurred by another route.

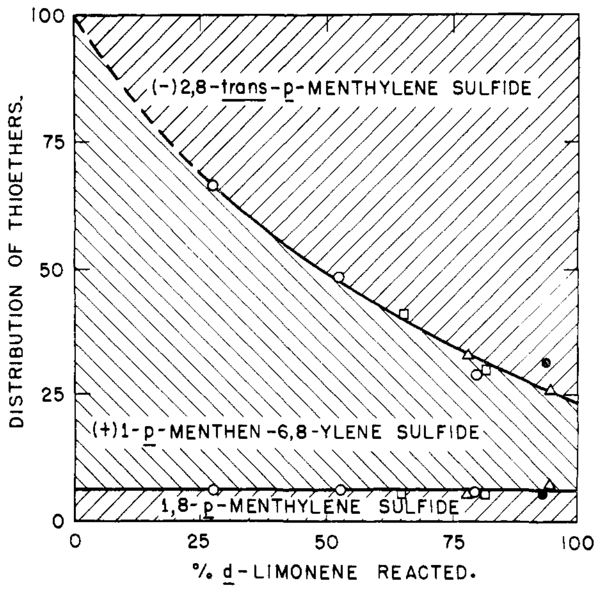

Fig. 1.—Distribution of thioethers as a function of *d*-limonene conversion: ○, 140°, 2, 4, 8 hr.; □, 150°, 2, 4 hr.; △, 160°, 2, 4 hr.; ●, 170°, 2 hr.

There remained the matter of establishing the stereochemical relationship of (+)-1-*p*-menthen-6,8-ylene sulfide (II) to the saturated analog (−)-2,8-*trans*-*p*-menthylene sulfide (III). The key experiment of saturation of the double bond over a catalyst consisting of 5% palladium-on-charcoal yielded an epimeric pair, one of which had the same structure as III and the other was shown to be the *cis* isomer. Both isomers from the hydrogenation had negative rotations. It follows that hydrogenation gave the same enantiomorph as sulfurization, although of a lower optical purity.

Thus, the sulfur is on the same side of the ring in the unsaturated sulfide II as in the structurally related saturated sulfide III. Consequently, the double bond in the unsaturated sulfide is on the opposite side from the double bond in the *d*-limonene ring, and an allylic shift must have occurred when sulfur was introduced.

The experimental results at hand do not reveal whether the sequence of reactions was free-radical addition to the ring followed by closure of the thioether ring by ionic addition to the side chain or the reverse. The argument for a free radical step in the mechanism rests largely on the evidence for homolytic rupture of the S_8 ring at elevated temperatures.[7] More recently Bateman[8] has proposed a polar mechanism for olefin sulfurization that assumes a heterolytic rupture of the S_8 ring at about 140°.

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[6] A. W. Weitkamp, THIS JOURNAL, **81**, 3434 (1959).

[7] D. M. Gardner and Geo. K. Fraenkel, *ibid.*, **75**, 4115 (1953); **76**, 5891 (1954); **78**, 3279 (1956).

[8] L. Bateman, C. G. Moore and M. Porter, *J. Chem. Soc.*, 2866 (1958).