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 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.

WHITING, IND.

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

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

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

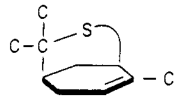
BY A. W. WEITKAMP

RECEIVED NOVEMBER 10, 1958

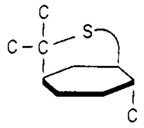
Reductive desulfurization of the three limonene sulfides by Raney nickel was studied over a range of conditions to obtain maximum structural information. Fourfold differences in reactivity due to structure were observed. Products ranging from diolefins to naphthenes were obtained and their distributions 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

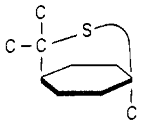
The three sulfides (I, II, III) obtained by the direct sulfurization[1] of *d*-limonene (IV) and the corresponding sulfones V, VI provide interesting three-dimensional structures for the study of the stereochemical paths of reductive desulfurization with Raney nickel. This reaction is widely used as 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 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.



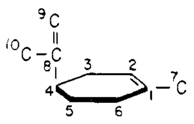
I



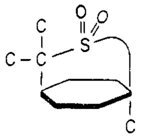
II



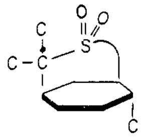
III



IV



V



VI

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

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

[2] H. Hauptmann and B. Wladislaw, *ibid.*, **72**, 707, 711 (1950).

[3] Wm. A. Bonner, *ibid.*, **74**, 1033 (1952).

[4] Wm. A. Bonner, *ibid.*, **74**, 1034 (1952).

purity above 99%, but optical purity was only about 87%. W-5 Raney nickel was prepared according to the directions of Billica and Adkins[5] except that either methanol or 1-propanol was used in place of ethanol in the finished slurry.

Hydrogenolysis.—The reaction mixture, ranging from 0.8 g. of nickel with 1.0 g. of reactant to as much as 5 g. of nickel with 0.1 g. of reactant, was refluxed in 5–10 ml. of alcohol. The sulfides and *d*-limonene were hydrogenolyzed for 40 minutes in methanol; the sulfones, for 20 hours in 1-propanol. After the reaction mixture had been diluted with water, the product was extracted with isopentane. Analysis was by gas–liquid partition chromatography in columns containing dinonyl phthalate or silicone oil on Celite. Each component was identified at least once by isolation and infrared analysis.

Desulfurization of Sulfides

Results.—The sulfides I, II, III were much more reactive toward Raney nickel than the sulfones V, VI, but differed widely in their individual reactivities. Figure 1 shows that 8, 32 and 128 atoms of nickel desulfurized about 0.7 mole of I, II and III, respectively. These amounts of nickel reflect about fourfold differences in reactivity. The extent of desulfurization of each sulfide was proportional to the amount of nickel used.

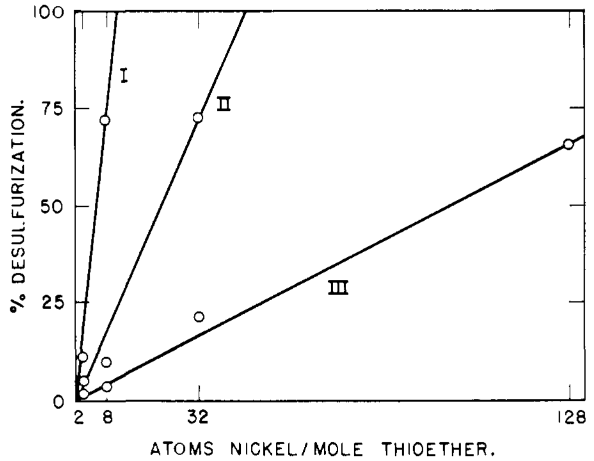

Fig. 1.—Extent of desulfurization of (+)-1-*p*-menthen-6,8-ylene sulfide, curve I, (−)-2,8-*trans*-*p*-menthylene sulfide, curve II, 1,8-*p*-menthylene sulfide, curve III.

The changing nature of the products as the severity of the hydrogenolysis was varied is shown by the plots of product distribution in Fig. 2. At all concentrations of nickel, each of the three sulfides was more or less reductively desulfurized to *p*-menthane. The proportions of the *cis* and *trans* isomers differed according to the structure of the sulfur compound. At lower concentrations, not only was desulfurization less complete but less complete reduction was evidenced by significant yields of the olefins 1-*p*-menthene and limonene.

In order to evaluate the effect of secondary saturation of first-formed olefins on the product distribution, a study was made of the saturation of limonene. The product distribution plotted in Fig. 3 shows that with a deficiency of hydrogen only the side chain was saturated. No trace of the ring-saturated product *p*-isopropenylcyclohexane was found. With excess nickel, complete disappearance of olefins gave the *cis*- and *trans*-*p*-menthanes in a characteristic ratio of 37:63.

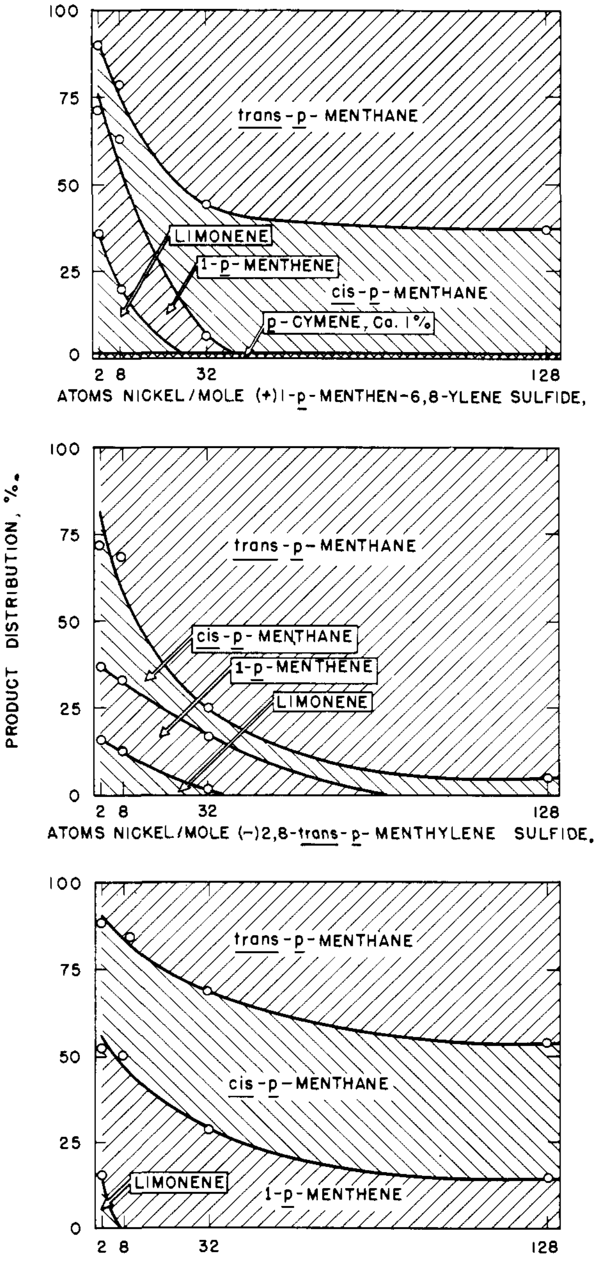

Fig. 2.— Desulfurization of thioethers.

The 3 to 10% yield of *p*-cymene unexpectedly showed that desaturation accompanied saturation, with transfer of hydrogen either to nickel or some other acceptor. The conversion of limonene, with increasing severity in this series of experiments, was 35, 69, 100 and 100%.

Discussion.—*p*-Menthane is evidently formed by two routes: direct hydrogenolysis of C–S bonds and saturation of intermediate olefins. The observed *cis*:*trans* ratios reflect the relative importance of the two processes. Data showing the relative proportions of *cis*- and *trans*-*p*-menthane from limonene and the three sulfides over the range of nickel concentrations are plotted in Fig. 4.

Limonene (IV) and the unsaturated sulfide I gave identical *cis*-*trans* distributions as would be ex-

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(5) H. B. Billica and H. Adkins, THIS JOURNAL, **70**, 695 (1948).

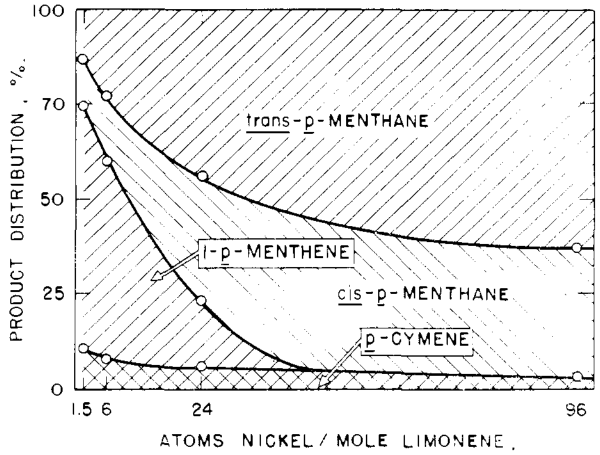
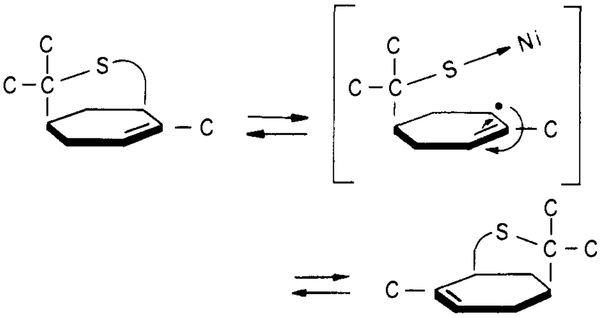


Fig. 3.—Saturation of limonene.

pected if hydrogenolysis of the carbon–sulfur bond at position 6 preceded saturation of the ring double bond. That such is the case was shown by complete racemization of both the left-over sulfide I and the olefins formed by mild desulfurization. A likely mechanism for racemization involves an



allylic free-radical intermediate in which the odd electron oscillates between positions 1 and 6 and the C–S bond is broken and reformed randomly at positions 1 and 6, while the C–S bond at position 8 remains intact.

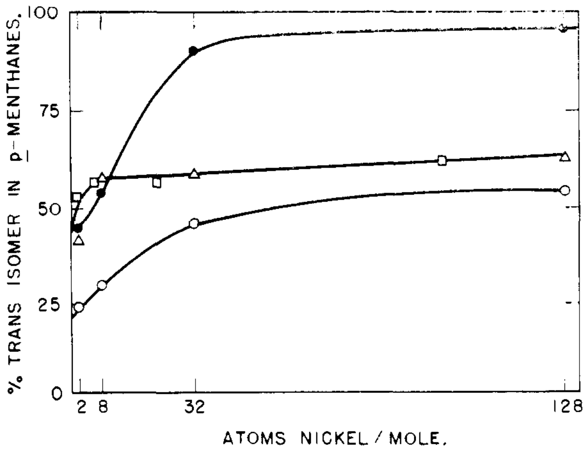
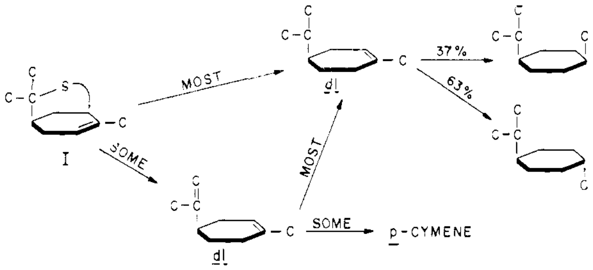
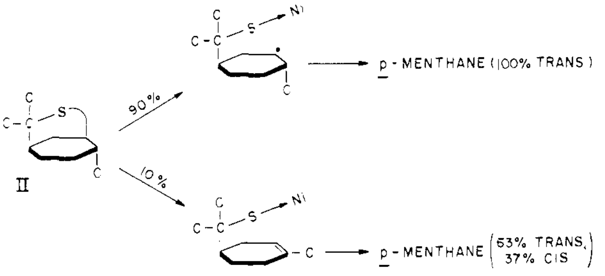


Fig. 4.—Distribution of *cis* and *trans* isomers of *p*-menthane from hydrogenolysis of: ●, (−)2,8-*trans*-*p*-menthylene sulfide; ○, 1,8-*p*-menthylene sulfide; △, (+)-1-*p*-menthen-6,8-ylene sulfide; □, *d*-limonene.

The relatively low yield of about 1% *p*-cymene from I, compared with the 3 to 10% from limonene, suggests that limonene, as such, was not formed in large quantities as an intermediate but that most of the reaction went by way of the monoölefin.

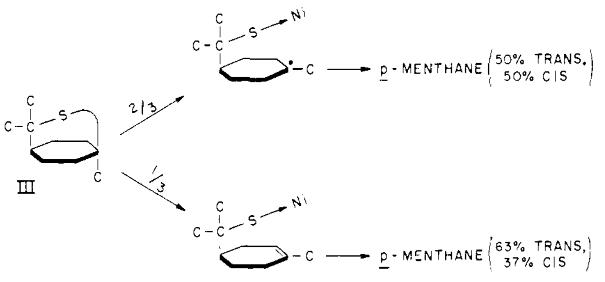


2,8-*trans*-*p*-Menthylene sulfide (II) yielded *p*-menthane that never contained more than 96% of the *trans* isomer even though the purity of the thioether was better than 99%. The spectrum of products showed that some *p*-menthane was always produced by way of the olefin intermediate, regardless of the excess of nickel present. However, under conditions of incomplete hydrogenolysis, neither the left-over sulfur compound nor the olefin product was racemized. No direct evidence



was found as to whether the secondary C–S bond at position 2 was opened more easily than the tertiary bond at position 8. However, the relative ease of desulfurization of the 2,8-sulfide, compared with 1,8-*p*-menthylene sulfide, showed that the secondary bond was more easily opened than the tertiary bond at position 1.

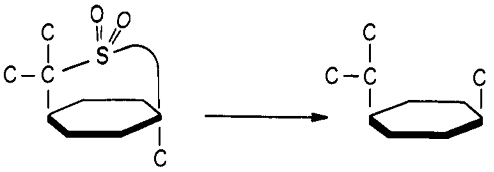
From 1,8-*p*-menthylene sulfide (III), the maximum yield of *trans*-*p*-menthane was 54% and 1-*p*-menthene was very prominent in the spectrum of products. If saturation of the symmetrical free-radical intermediate is assumed to yield a random mixture of *cis*- and *trans*-*p*-menthanes, the 54% yield of *trans* isomer would suggest that about one-third was produced by the olefin-intermediate route.



Lower concentrations of nickel, with all three 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_N2 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

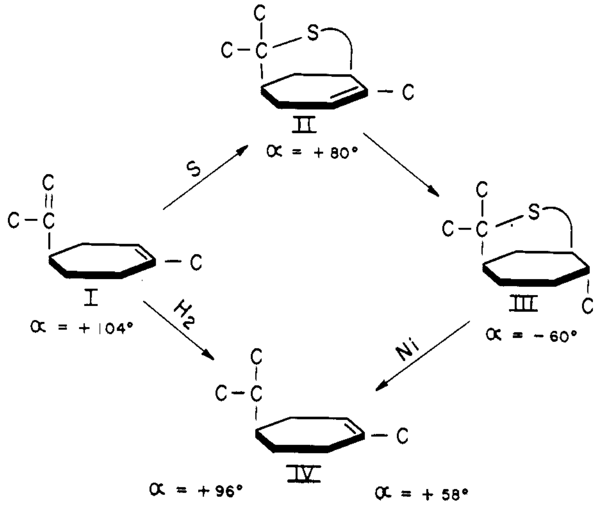
RECEIVED NOVEMBER 10, 1958

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).