hr. and to 100° for 10 min. After cooling, the greenish-violet 5-nitroso derivative was filtered and, while still wet, was added portionwise with stirring to 80 ml. of water, kept at 60–70°. Alternating with the nitroso compound, portions of sodium hydrosulfite were added in such a manner that complete reduction of each charge was effected before introduction of a fresh lot of nitroso derivative. Upon cooling, the yellowish diamine (Id) crystallized in polyhedric prisms, m.p. 278–280°; yield 3.5 g. (76%).

1,2-Dihydro-1-methyl-2,4-dithio-5,6-diaminopyrimidine (IId). Thiation of Id (2.0 g.) with phosphorus pentasulfide (7.0 g.) in pyridine (100 ml.) was carried out by the method described above. IId was obtained in yellow, prismatic needles, which decomposed above 300°; yield 1.9 g. (87%).

Anal. Calcd. for $C_5H_8N_4S_2$: C, 31.9; H, 4.3. Found: C, 32.4; H, 4.5.

3-Methyl-2,6-dithiouric acid (IIId). Ring closure with urea was carried out as described above. By reprecipitation with 5% sodium hydroxide and acetic acid, yellow plates decomposing above 300° were obtained; yield 85%.

Anal. Calcd. for $C_6H_6N_4OS_2$: N, 26.2. Found: N, 26.1.

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[CONTRIBUTION FROM THE DIVISION OF PHYSICAL SCIENCES, UNIVERSITY OF CALIFORNIA AT RIVERSIDE]

Stereochemistry of the Desulfurization of Thiiranes with Methyl Iodide[1]

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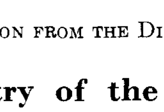
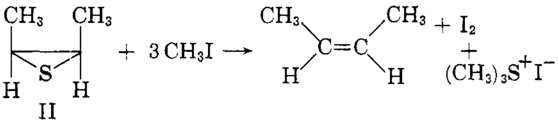
The reaction of isomers of 2,3-dimethylthiirane with methyl iodide results in the formation of 2-butene, with greater than 97% stereoselective desulfurization.

The reaction of thiiranes with methyl iodide leads to the formation of trimethylsulfonium iodide,[3,4] but little information has been given in literature concerning the olefin formed in the reaction.[5] This desulfurization has been investigated with regard to its stereochemistry, since a probable cyclic sulfonium intermediate (I) was of interest for studying generalized thiirane ring-openings.



I

When *cis*-2,3-dimethylthiirane (II) was treated with methyl iodide in refluxing acetone, *cis*-2-butene, iodine, and trimethylsulfonium iodide were formed in approximately equivalent amounts. The progress of such reactions was usually determined by gravimetric analysis of the sulfonium halide which precipitated from solution. Although yields of butene and iodine were occasionally higher than that of the salt, measurements of butene were limited to volume estimations, and titration or photometric methods for iodine were somewhat unsatisfactory because of chemical instability of the acetone solutions. Yields of sulfonium iodide varied from about 15% to 40%, the higher values arising from low methyl iodide/thiirane ratios in the reaction mixtures.



II

The entire reaction sequence involved the conversions *cis*-2-butene→*meso*-2,3-dimethyloxirane (*meso*-2,3-epoxybutane)→*cis*-2,3-dimethylthiirane →*cis*-2-butene. Trace chromatographic analysis showed less than 0.2% *trans*-2-butene in the starting olefin and only 1.6% in the final product. In a somewhat parallel synthetic sequence, the *meso*-epoxide was prepared from recrystallized *meso*-2,3-butanediol, and the final olefin was found to contain 3.0% *trans*-2-butene. The results of reactions of *meso*- and DL-isomers are given in Table I. The processes appear to have a high degree of stereospecificity, for the small amount of con-

TABLE I

PRODUCTS OF DESULFURIZATION OF 2,3-DIMETHYLTHIIRANES

Thiirane Isomer	Source of Thiirane	Composition of Butenes, %[a]		
		1-	*cis*-2-	*trans*-2-
meso	*cis*-2-Butene	0	98.4	1.6
meso	*meso*-2,3-Butanediol	0	97.0	3.0
DL	Epoxide distilled from mixed isomers[b]	1.0	0.6	98.4

[a] Infrared spectra of the butenes showed no trace of isobutylene. [b] Low-boiling fraction of Dow Chemical Co's Butylene Oxides S.

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(1) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

(2) Taken in part from the B.A. thesis of David J. Pettitt, University of California at Riverside.

(3) M. Delépine and P. Jaffeux, *Compt. rend.*, **172**, 158 (1921).

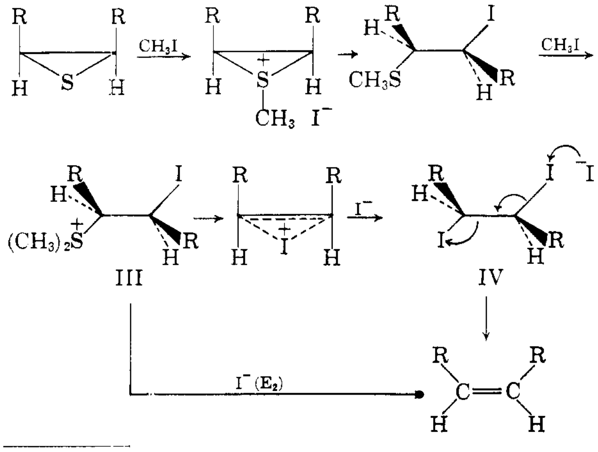
(4) C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, **1949,** 284.

(5) R. D. Schuetz and R. L. Jacobs, Abstracts of Papers of the Division of Organic Chemistry, April, 1960. Mention is made of the fact that 2-alkoxymethylthiiranes react with methyl iodide to yield an olefinic compound corresponding to the thiirane employed.

taminating isomer has arisen through an accumulation of racemized materials of a reasonably long series of synthetic intermediates. In the case of the DL-thiirane, the commercial mixed epoxide isomers used as starting materials contained major amounts of 1,2-epoxide and *cis*-2,3-epoxide, and distillation processes were ineffective for complete separation.

The low yields in the reactions can be accounted for by side reactions, the principal one probably involving molecular iodine and the thiirane, for iodine reacted quite rapidly with the thiirane in hydroxylated solvents such as ethanol or in acetone containing water.[6] In these same solvents the desulfurization took place reasonably well, as indicated by formation of trimethylsulfonium iodide precipitate, but no iodine color developed until after prolonged reaction times. In very poor reaction solvents, such as saturated hydrocarbons, color again failed to develop. In this instance, it is proposed that the iodine never attained sufficient concentration for detection, as the rate of its reaction with thiirane, although low, was considerably greater than its rate of formation.

A series of reaction intermediates proposed by Culvenor, Davies, and Heath[4] accounts satisfactorily for the steric course of the desulfurization process if their diiodo compound (IV) is formed from its sulfonium precursor (III) with net retention of configuration, and this is followed by a *trans*-elimination. However, it is unnecessary to proceed as far as the dihalide, for the sulfonium precursor itself can lead directly to the appropriate alkene by an elimination reaction initiated by iodide ion attack on the secondary iodine atom.[8,9]



EXPERIMENTAL

meso-2,3-Epoxybutane. *cis*-2-Butene containing less than 0.2% of other butene isomers was converted by way of the chlorohydrin to *cis*-2,3-epoxybutane according to the method of Wilson and Lucas[10]: yield, 30%; b.p. 58–60°, 735 mm.

In an alternate procedure, the *meso*-epoxide was prepared from recrystallized *meso*-2,3-butanediol, m.p. 33.5–34.0°, by the same sequence of reactions previously used for the active isomer.[11]

DL-*2,3-Epoxybutane.* This epoxide isomer pair was isolated by fractional distillation of straight-chain butylene oxide isomers[12] in a 2-meter column packed with glass helices: b.p. 53–54° (735 mm.). The original mixture of isomers contained about 40% each of *meso*-2,3-epoxybutane and 1,2-epoxybutane. As the desulfurization took place stereospecifically, the product composition (Table I) was considered sufficient criterion of isomer purity. The conversion to thiiranes and treatment with methyl iodide actually served as a convenient tool for determining isomer distribution in the epoxides.

2,3-Dimethylthiiranes. The *cis* and *trans* isomers were prepared from the corresponding epoxides by the thiourea method of Bordwell and Andersen.[13] Yield and physical constants of the *trans* isomer were similar to those previously reported for optically active 2,3-dimethylthiirane.[14] Redistilled *cis* isomer gave the following constants: b.p. 98.5° (735 mm.); n_D^{25} 1.4684 (lit.,[15] b.p. 51.0–51.5° at 130 mm.; n_D^{20} 1.4765).

Desulfurization. Although the reaction between thiirane and methyl iodide could be carried out in the absence of solvent, the yields were low. Ordinarily, the two reactants were added to acetone and the mixture was allowed to stand at room temperature, or the solution was refluxed in an apparatus designed for butene collection. In a typical reaction, to 20 ml. of dry acetone were added 5.0 g. of 2,3-dimethylthiirane and 24.5 g. of methyl iodide. The mixture was refluxed, and after 10–15 min. iodine color began to appear. The yield after 24 hr. of trimethylsulfonium iodide was obtained gravimetrically, of butenes volumetrically, and of iodine spectrophotometrically: trimethylsulfonium iodide, 16% (1.9 g.); butenes, 41% (2.0 ml.); iodine, 36%. After the trimethylsulfonium iodide had been recrystallized three times from ethanol, it decomposed smoothly and completely at 204–210° without any discoloration. Infrared and NMR spectra were consistent with the structure of the salt. Butene analyses were made on an Aerograph vapor phase fractometer.

When an identical reaction was carried out at room temperature, iodine color began to appear after 0.5 hr., and the yield of iodine after 24 hr. was only 7.4%. Under these conditions, the sulfonium salt, formed in 19% yield, showed traces of impurities, for some decomposition took place at 100°. The bulk of the precipitate, however, exhibited the same features of decomposition as the trimethylsulfonium iodide.

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(6) Although bromine and chlorine have been shown to react with thiiranes,[7] no mention is made of iodine.

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(12) The authors are indebted to the Dow Chemical Co., Midland, Mich., for a generous sample of the mixed epoxide isomers.

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