TABLE I

INDOLE ACIDS OBTAINED BY THE ALKALINE HYDROLYSIS OF SOME 3′-INDOLYL-2-OXOALKYLPYRIDINIUM SALTS

Pyridinium salt used	Acid obtained	M.p.,* °C.	Yield, %	Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
2-3′-Indolyl-2-oxoethyl-	Indole-3-carboxylic acid	220[a]	87	$C_9H_7NO_2$	67.1	4.4	8.7	67.5	4.8	8.6
2-1′-Methyl-3′-indolyl-2-oxoethyl-	1-Methylindole-3-carboxylic acid	214[b]	90	$C_{10}H_9NO_2$	68.6	5.2	8.0	68.7	5.0	7.8
2-2′-Methyl-3′-indolyl-2-oxoethyl-	2-Methylindole-3-carboxylic acid	180[c]	90	$C_{10}H_9NO_2$	68.6	5.2	8.0	68.9	5.3	8.5
4-3′-Indolyl-2-oxobutyl-	Indole-3-propionic acid	134[d]	93	$C_{11}H_{11}NO_2$	69.8	5.9	7.4	69.4	5.9	7.3
4-1′-Methyl-3′-indolyl-2-oxobutyl	1-Methylindole-3-propionic acid	125[e]	20[f]	$C_{12}H_{13}NO_2$	70.9	6.45	6.9	70.5	6.6	6.8

* *In vacuo.* [a] Lit.,[22] m.p. 218°. [b] Lit.,[21] m.p. 212° dec. [c] Lit.,[23] m.p. 176–177°. [d] Lit.,[24] m.p. 134°. [e] Lit.,[20] m.p. 125.5–126°. [f] Hydrolysis effected without purification of the pyridinium salt.

gave a pure product identical with that prepared by method (a).

Alkaline Hydrolysis of the Pyridinium Salts. General Procedure.—The pyridinium salt (0.01 mole) was dissolved in aqueous ethanol (60 ml. of 50%) and the solution was warmed gently with sodium hydroxide (3 g.) for 10 min. (30 min. with the propionic acids). After cooling and acidification with hydrochloric acid, the solution was extracted with ether (3 × 50 ml.) and the ether extract was dried (sodium sulfate) and evaporated to dryness. Crystallization of the solid residue from water or acetone–water (charcoal) usually afforded the acid as white crystals. Identification was established by analytical data, mixed m.p. determinations, and comparison of infrared spectra with those of authentic specimens.

1-Methylindole-3-propionic Acid.—1-Methylindole (2.6 g., 0.02 mole), acetic acid (12 ml.), acetic anhydride (4 ml.), and commercial acrylic acid (4.3 g., 0.06 mole) were heated on a boiling water bath for 3 hr. The volatile material was then removed and the thick, blue residue added to a solution of sodium hydroxide (2.5 g.) in water (20 ml.). After cooling, the solution was filtered and the filtrate acidified with 2 *N* hydrochloric acid. The precipitated acid was collected, washed well with water, and recrystallized from water (charcoal) whence it separated as long, white needles, 2.4 g., 60%, m.p. 125° (lit.,[20] m.p. 125.5–126°.)

Anal. Calcd. for $C_{12}H_{13}NO_2$: C, 70.9; H, 6.45; N, 6.9. Found: C, 70.7; H, 6.3; N, 7.4.

1-Methylindole-3-carboxylic Acid.—A sample of this acid was prepared in good yield by oxidation of 1-methylindole-3-aldehyde with alkaline potassium permanganate at 60° and isolation of the product in the usual way for this type of reaction. Crystallization from acetone–water gave pale cream plates, m.p. 214° (*in vacuo*) (lit.,[21] m.p. 212° dec.).

(20) H. R. Snyder and E. L. Eliel, *J. Am. Chem. Soc.*, **71**, 663 (1949).
(21) W. B. Whalley, *J. Chem. Soc.*, 1651 (1954).
(22) C. Zatti and A. Furante, *Ber.*, **23**, 2296 (1890).
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Desulfurization of Thiiranes with Iodine

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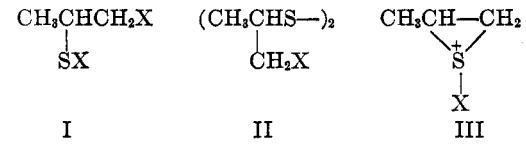
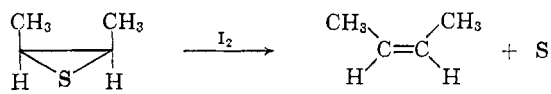
The reaction of chlorine and bromine with propylene sulfide has been shown to result in ring opening with the formation of a β-halosulfenyl halide, I, or the corresponding disulfide, II, depending on the conditions employed.[1] An *S*-halo



I II III

intermediate, III, was postulated for the reactions. In a more recent investigation equilibrium constants were determined for the formation of iodine complexes of cyclic sulfides,[2] and it was observed that thiacyclobutane polymerized readily in carbon tetrachloride solutions of iodine. However, in neither instance was there any report of the iodine–thiirane system. The possibility of an interaction or reaction between iodine and 2,3-dimethylthiirane was of interest to us because the desulfurization of the latter with methyl iodide led under certain conditions to the formation of molecular iodine.[3]

We wish to report that iodine reacts with *meso*- and DL-2,3-dimethylthiirane in solvents such as refluxing acetone or benzene with stereospecific loss of sulfur to yield butene and elementary sulfur in moderate yield. Although some molecular iodine is consumed in the process, an iodine/sulfide molar ratio of less than 0.5 is sufficient to carry out the desulfurization.



Thiirane isomers were prepared from *cis*- and *trans*-2-butene by the thiourea method[4] as reported previously.[3] The initial alkenes contained less than 0.6% of the contaminating stereoisomer, and the composition of the butene products, determined on a silicone or dimethyl sulfolane chromatographic column, is given in Table I. No C-4 isomers other than *cis*- and *trans*-2-butene were detected.

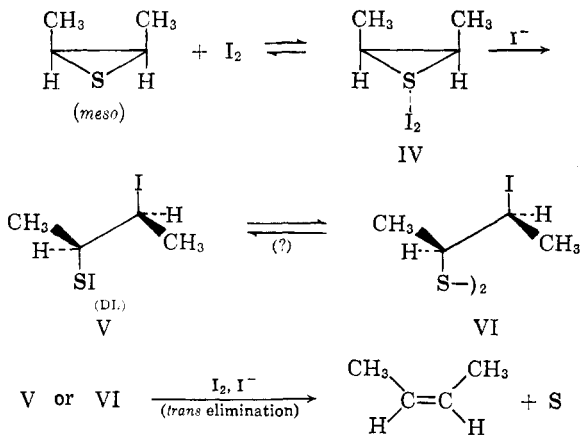
(1) J. M. Stewart and H. P. Cordts, *J. Am. Chem. Soc.*, **74**, 5880 (1952).
(2) J. D. McCullough and D. Mulvey, *ibid.*, **81**, 1291 (1959).
(3) G. K. Helmkamp and D. J. Pettitt, *J. Org. Chem.*, **25**, 1754 (1960).
(4) F. G. Bordwell and H. M. Andersen, *J. Am. Chem. Soc.*, **75**, 4959 (1953).

TABLE I
BUTENE ISOMER COMPOSITION IN IODINE DESULFURIZATION OF THIIRANES

2,3-Dimethylthiirane	Solvent	% *cis*	% *trans*
meso	Acetone	99.1	0.9
meso	Benzene	98.2	1.8
DL	Acetone	0.4	99.6
DL	Benzene	1.1	98.9

The yield of butenes was 40–50% in acetone solvent and about 80% in benzene solvent. The yield of sulfur, determined spectrophotometrically after isolation by chromatography on neutral alumina, was about 60%, a value slightly lower than that for butene.

When the reaction of thiiranes with iodine was carried out in the cold in methylene chloride, two moles of sulfide were required per mole of iodine. No butene was produced, and on evaporation of the solvent at reduced pressure a clear liquid was obtained which was unstable to heat and could not be isolated in sufficiently pure form for elemental analysis. When the liquid was treated with iodine in refluxing benzene the appropriate butene isomer (related to the starting thiirane) was obtained in fair yield. It is proposed that the liquid is an iodine analog of compound II, for then the stoichiometric relationship of the reaction would be satisfied and a substitution–elimination process proceeding *via* a sulfenyl halide (V) or disulfide (VI) would predict the proper stereochemical result.



The coördination of iodine with sulfur in the thiirane (intermediate IV) should facilitate subsequent nucleophilic ring-opening by iodide, and a corresponding coördination with the sulfur atom in V or VI followed by iodide attack on iodine and resulting in a *trans* elimination is consistent with the nature of the products.

Experimental

Desulfurization of 2,3-Dimethylthiirane.—A solution of 1.0 g. (0.004 mole) of iodine in 8 ml. of reagent grade benzene was introduced into a 50-ml. two-necked flask fitted with a dropping funnel and condenser. The end of the condenser was fitted with a delivery tube leading to a trap at Dry Ice–acetone temperature. The mixture was brought to reflux and 0.9 g. (0.010 mole) of DL-2,3-dimethylthiirane was added over a period of 1 hr. Heating was continued for an additional hour. The yield of butene was 0.45 g., 80% (see Table I for isomer distribution). The reaction mixture was evaporated to near dryness, added to a chromatographic column packed with 30 g. of neutral alumina, and eluted with carbon disulfide. The carbon disulfide was evaporated and the residual sulfur was dissolved in ethanol and determined spectrophotometrically[5]; yield, 62%.

Acknowledgment.—This investigation was supported by an intramural research grant by the University of California.

(5) J. E. Baer and M. Carmack, *J. Am. Chem. Soc.*, **71**, 1215 (1949).

The Isomerization of Aziridine Derivatives. VI. The Rearrangement of Some 2-(1-Aziridinyl)quinoxalines[1]

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Earlier communications in this series described the isomerization of 1-(*N*-arylbenzimidoyl)aziridines into 1,2-diaryl-2-imidazolines,[2] 2,4,6-tris-(1-aziridinyl)-*s*-triazine into 2,3,6,7,10,11-hexahydrotrisimidazo[1,2-*a*; 1′,2′-*c*; 1″, 2″-*e*]-*s*-triazine,[3] and 1-(arylazo) aziridines into 1-aryl-Δ^2-1,2,3-triazolines.[4] In each of these examples the aziridinyl moiety could be converted by a suitable nucleophile into an effective alkylating agent for a neighboring nitrogen. It would appear that this reaction might be quite general and could be employed for the synthesis of novel heterocyclic compounds. We now wish to report the isomerization of some 2-(1-aziridinyl)quinoxalines to 1,2-dihydroimidazo[1,2-*a*]quinoxalines, a new heterocyclic ring system.[5]

Results

The starting materials used for the isomerization studies were 2-(1-aziridinyl)-3-chloroquinoxaline (Ia) and 2-(1-aziridinyl)-3-methoxyquinoxaline (Ib). These compounds are readily prepared by reaction of aziridine with 2,3-dichloroquinoxaline and 2-chloro-3-methoxyquinoxaline in benzene containing triethylamine. The 2-(1-aziridinyl)-3-methoxyquinoxaline was also readily available by treatment of Ia with sodium methoxide.

(1) Aided by Grant No. T-143A from the American Cancer Society.
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(3) H. W. Heine, W. G. Kenyon, and E. M. Johnson, *J. Am. Chem. Soc.*, **83**, 2570 (1961).
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(5) We wish to thank Leonard T. Capell of The Chemical Abstracts Service for the naming and numbering of this new heterocyclic system.