American Chemical Society, for their support of this research.

Registry No.—2-Thiophenecarboxaldehyde, 98-03-3; methyl 2-thienyl ketone, 88-15-3; ethyl 2-thienyl ketone, 13679-75-9; isopropyl 2-thienyl ketone, 36448-60-9; *tert*-butyl 2-thienyl ketone, 20409-48-7; malononitrile, 109-77-3.

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(3) Thiophenecarboxaldehyde, methyl 2-thienyl ketone, and phenyl 2-thienyl ketone were available from Aldrich Chemical Co., whereas ethyl 2-thienyl ketone was obtained from Columbia Organic Chemicals Co. Isopropyl 2-thienyl ketone[4] and *tert*-butyl 2-thienyl ketone[5] were prepared by the method of J. R. Johnson and G. E. May, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 8.
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(6) D. A. Templer, Ph.D. Thesis, Indiana University, Bloomington, Ind., Aug 1968.
(7) Compound **2** (R′ = H) was a single isomer by TLC. However, to date it has not been possible to assign the exact geometrical stereochemistry for **2** (R′ = H) and the representation given here is arbitrary but is believed to be correct based on data accrued in ref 6 for a similar benzene system.
(8) The stereochemistry of **4** (obtained as a single isomer by TLC) was not crucial to this aspect of the problem and has not been established. However, the condensation between thiophenecarboxaldehyde and methyl 2-thienyl ketone and cyanoacetamide is apparently stereospecific, since only the product (by TLC) corresponding to **4** was produced in quantitative yield.
(9) Several less functionalized, and therefore less versatile, derivatives of the cyclopenta[*b*]thiophene ring system have been reported. For example, see (a) O. Meth-Conn and S. Gronowitz, *Acta Chem. Scand.*, **20**, 1577 (1966); (b) K. Aparajithan, A. C. Thompson, and J. Sam, *J. Heterocycl. Chem.*, **3**, 466 (1966); (c) J. Skramstad, *Acta Chem. Scand.*, **25**, 1287 (1971).
(10) Melting points were taken on a Mel-Temp capillary melting point apparatus and are uncorrected. The NMR spectra were obtained on a Varian A-60 spectrometer using Me_4Si as an internal standard. Ir spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. The microanalyses were performed by Het-Chem-Co., Harrisonville, Mo.

Stereochemical Course of Sulfolane Fragmentation

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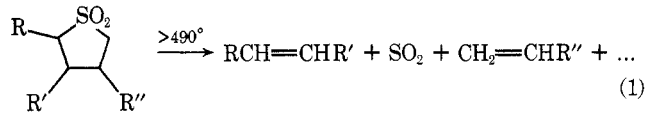
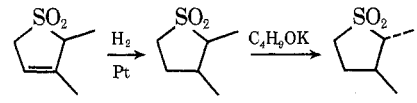
At elevated temperatures, simple sulfolanes (tetrahydrothiophene 1,1-dioxides) are pyrolyzed to sulfur dioxide and olefins (eq 1: R, R′, R″ = H; R = CH_3, R′, R″ = H; R′ = CH_3, R, R″ = H; R′, R″ = CH_3, R = H; R, R″ = CH_3, R′ = H, etc).[1] We have now examined the stereochemistry of this reaction (R, R′ = CH_3; R″ = H), with a view to detecting possible concertedness.



(1)

Results

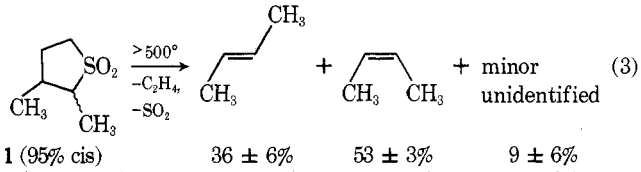
The requisite sulfones were obtained (eq 2) via 2,3-dimethylsulfolene (adduct from 3-methyl-1,3-pentadiene plus SO_2).[2] Catalytic hydrogenation (PtO_2) gave an inseparable mixture of sulfolanes (ca. 95:5) of which the major isomer was assigned the cis configuration (**1**) on the basis of steric considerations and subsequent results. Epimerization of this mixture with potassium *tert*-butylate in *tert*-butyl alcohol (eq 2) gave a new mixture (ca. 10:90), enriched in the trans isomer (**2**). Isomer ratios were estimated by NMR analysis.



(2)

1 **2**

Thermolyses were carried out by injection of the enriched mixtures of **1** and **2** into a hot (>500°) bed of silicon carbide chips. The effluent gases were collected in a cold trap, and the butenes were subsequently analyzed by GLC. The results are summarized in eq 3.



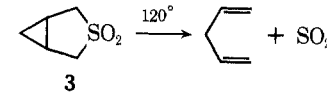
(3)

1 (95% cis)	36 ± 6%	53 ± 3%	9 ± 6%
2 (90% trans)	51 ± 6%	40 ± 3%	9 ± 6%

In the appropriate control experiments, it was found that from a partial pyrolysis **1** could be recovered unchanged (no appreciable epimerization to **2**). Furthermore, authentic *cis*-2-butene when passed through the reactor suffered less than 2% isomerization to *trans*-2-butene. In view of the substantial crossover in the thermolysis of **1** and **2** it was felt that attempts to refine the experiment by further purification of **1** and **2** or by improving the GLC resolution of the products were unwarranted.

Discussion

It has previously been demonstrated that pericyclic [$_\sigma 2_s + {}_\sigma 2_s + {}_\sigma 2_s$] fragmentation in the strained system **3** (eq 4)



(4)

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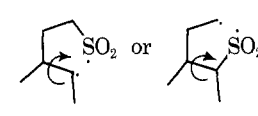
proceeds concertedly by tests of stereospecificity and kinetic facility.[3] Although equivalent thermolysis of simple sulfolanes requires temperatures more than 200° higher than for **3**, it was considered plausible that **1** and **2** might dissociate with retention of methyl group stereochemistry in view of the fully synchronous nature of the *sulfolene* reaction.[4] The experimental results indicate otherwise. From either sulfolane (**1** or **2**) mixtures of 2-butenes were obtained (uncorrected trans/cis ratios 0.7 *E*:1.0 *Z* and 1.0 *E*:0.8 *Z*, respectively). We suggest that the results are best accommodated by a multistep mechanism, in which diradical (or zwitterionic) intermediates exist for appreciable lifetimes. It is sufficient that internal rotation within such an intermediate (**4**) be competitive with bond scission. In



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spite of our control experiments the possibility cannot rigorously be excluded that fragmentation is in fact concerted, but that isomerization occurs subsequently (SO_2 catalysis). However, it is difficult to envision such a latter mechanism which would not in actuality be available to the incipient reaction products in the primary step.

The low residual stereospecificity is reminiscent of other recently reported extrusion reactions.[5] We would only comment that concepts of diradical chemistry should be adjusted to accommodate what appears to be a pattern of partial stereochemical retention.

Experimental Section

Synthesis. 2,3-Dimethylsulfolene was prepared essentially as previously described.[2] The crude product was purified by column chromatography (silicic acid, benzene eluent) rather than distillation, in order to avoid decomposition. Of several hydrogenation catalysts tried, platinum oxide (Adams) in ethyl acetate afforded the greatest stereoselectivity (ca. 95%) for the reduction to **1**. Refluxing a *t*-BuOK–*t*-BuOH solution of **1** for several hours followed by work-up yielded a mixture enriched in **2** (ratio 2:1 9:1). Isomer percentages were estimated from resolved NMR resonances in the methyl region ($CDCl_3$ solution).

Anal. (for enriched **1**). Calcd for $C_6H_{12}O_2S$: C, 48.64; H, 8.16. Found: C, 48.54; H, 8.25.

Thermolysis. As previously indicated, ca. 0.5-g portions of **1** or **2** were injected slowly via syringe into a heated reservoir (SiC chips at >500°) connected to a cold trap. Some refluxing was noted. Subsequently, the butenes were allowed to vaporize and were sampled by GLC [column, 15 ft of 25% $AgNO_3$–propylene glycol (1:2) on Chromosorb W, 25°]. Comparison was made to authentic 2-butenes. A minor, unidentified pyrolysate component was eluted shortly after (and overlapping) *trans*-butene. It has previously been asserted that sulfolane thermolysis affords 9–19% of "saturated hydrocarbon".[1] In the present case a complete analysis of product balance was not undertaken, since our interest only extended to alkene geometry.

Acknowledgment. One of us (I.M.) thanks the Rotary Foundation for a Graduate Fellowship. This work was partially supported by the National Science Foundation.

Registry No.—**1**, 54910-40-6; **2**, 54910-39-3; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 2,3-dimethylsulfolene, 10033-87-1.

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Complete Resolution of *cis*-1-Benzyl-3-methyl-1-phenylphospholanium Iodide. Use of the Optically Active Salt in Stereochemical Studies

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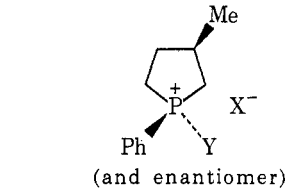
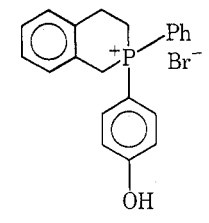
The literature records no total resolutions of heterocyclic phosphonium salts containing an asymmetric phosphorus atom. We report herein the first such instance, the complete resolution of racemic *cis*-1-benzyl-3-methyl-1-phenylphospholanium iodide (**1**) with the aid of silver (+)-10-camphorsulfonate. Compounds **2**,[1] **3**,[2] and **4**[3] have been partially resolved, although the resolution of **2** could not be reproduced and details of the resolution of **4** have not yet been disclosed. The spiro salt (**5**), which has been totally resolved, owes its optical activity to molecular dissymmetry rather than to an asymmetric phosphorus atom of the $R^1R^2R^3R^4P^+X^-$ type.[4]



(and enantiomer)
1, Y = CH_2Ph; X = I
6, Y = O^-; X = nil
7, Y = CH_2Ph; X = (+)-10-camphorsulfonate
8, Y = lone pair; X = nil
9, Y = CH_2Ph; X = Br
12, Y = OMe; X = PF_6



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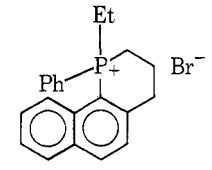

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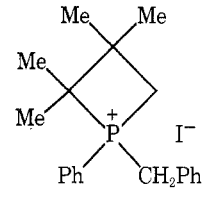

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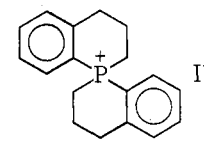

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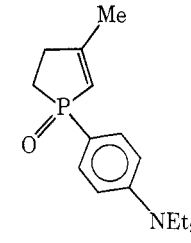

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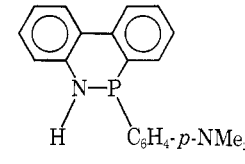

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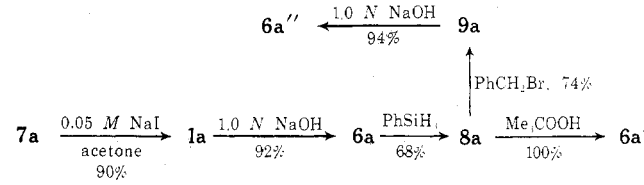
With the optically active phosphonium salts (**1**) available, we wished to verify earlier conclusions[5,6] that hydroxide cleavage of **1** occurs with complete retention of configuration at phosphorus. The NMR analyses leading to these conclusions were possibly subject to considerable error, although predominant retention had been rigorously proved. Within experimental error, the results shown in Scheme I are compatible with complete retention of configuration for base cleavage and phenylsilane reduction as previously reported.[5,6] This is true only if the oxide epimeric at phosphorus, produced by inversion of configuration at phosphorus, does not have a rotation comparable to that for the (+)

Scheme I[a]



Compd	Mp or bp, °C (mm)	$[\alpha]^{22}D$, deg (*c*)
7a	244–246	+28.09 ± 0.49 (2.980, EtOH)
1a	184.5–185.5	+2.16 ± 0.09 (15.57, $CDCl_3$)
6a	130 (0.5)	+23.52 ± 0.67 (7.590, $CDCl_3$)
8a	90 (0.5)	+22.18 ± 0.42 (6.710, MeOH)
6a′	132 (0.6)	+22.53 ± 0.59 (7.395, $CDCl_3$)
6a″	135 (0.6)	+22.59 ± 0.63 (6.505, $CDCl_3$)

[a] **9a** was not recrystallized prior to cleavage. *tert*-Butyl hydroperoxide oxidations of phosphines occur with retention of configuration: D. B. Denney and J. W. Hanifin, Jr., *Tetrahedron Lett.*, 2177 (1963). Phenylsilane has been found to reduce phosphine oxides with retention of configuration: K. L. Marsi, *J. Org. Chem.*, **39**, 265 (1974). Distillations were accomplished by use of a Kugelrohr.