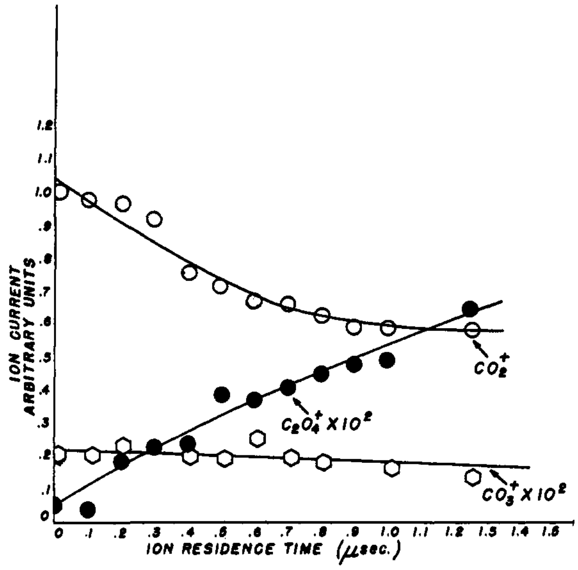

Figure 1. Relative concentrations [corrected for thermal drift: J. J. DeCorpo and F. W. Lampe, *J. Chem. Phys.*, **51**, 943 (1969)] of CO_2^+, CO_3^+, and $C_2O_4^+$ as a function of ion residence time.

chemiluminescent reactions, we have repeated this study.

As in the previous work, the gaseous products of hydrogen peroxide–oxalate ester reaction were allowed to flow directly into a Bendix Model 12 mass spectrometer. In the work reproduced in this laboratory, however, the products were not isolated behind a needle valve but were allowed to flow directly from the reaction vessel into the ionization region. This was made possible by fast differential pumping of the ion source in our mass spectrometer. This technique prevents any possible fractionation of the sample by the needle valve.

Another alteration effected in the study performed in this laboratory was the installation of a variable time-delay circuit. This circuit allows a variable time delay from 0 to 10 μsec between the end of the pulsed electron beam and the onset of the drawout pulse. The reaction or residence time is the sum of time delay and the time necessary for the ion to be withdrawn from the ionization chamber. The addition of the time-delay circuit permitted a study of the ions as a function of their residence time in the ion source. A Baratron Model 100A capacitance manometer was used to monitor the ion source pressure over a range of 0–50 μ and to study the ion current as a function of pressure.

With zero delay time, the data cited by Cordes, *et al.*,[1] were reproduced. The major reaction product was CO_2; the ions at *m/e* 88 or 60 were also observed as reported previously. However, when either of the major components (ester or hydrogen peroxide) was not present in the reaction vessel the ion currents at *m/e* 88 and 60 were not observed. When the ion currents at *m/e* 88 ($C_2O_4^+$), 60 (CO_3^+), and 44 (CO_2^+) were investigated as a function of ion source residence time or pressure, it became apparent that $C_2O_4^+$ is a secondary ion formed by an ion–molecule reaction in the ion source itself and not as a product of the H_2O_2–oxalate ester reaction.

Examination of a plot of the relative concentration of $C_2O_4^+$, CO_2^+, CO_3^+ as a function of ion residence time, which is shown in Figure 1, reveals that simultaneously in the ion source the $C_2O_4^+$ ion is formed while the CO_2^+ ion is consumed. Thus, the ion observed at *m/e* 88 cannot be formed from the agent producing chemiluminescence as proposed earlier.[1] It should be noted that the ion current observed at *m/e* 60 (CO_3^+) exhibited the behavior of a species formed from the reaction mixture and thus its precursor is a possible chemiluminescent agent. When CO_2 was studied under similar conditions, *i.e.*, the same pressures and delay times used in these experiments, no *m/e* 88 was observed. This suggests that the ion–molecule reaction which produced *m/e* 88 in the chemiluminescent study was not between a CO_2 ion and a neutral CO_2 molecule. Two other possibilities exist: a reaction between CO_2^+ and some organic species (*e.g.*, the ester), or between $RCOO^+$ and CO_2. The first reaction is more likely and is supported by the decrease in the *m/e* 44 ion current shown in Figure 1. A comprehensive study of the formation of the *m/e* 88 ion current will be reported in a future publication.

Acknowledgment. We wish to thank Dr. A. B. Harvey for calling our attention to this problem and to Dr. T. Hall of the Naval Ordnance Laboratory for the chemical used in the reaction.

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Facile Conversion of Oxiranes to Thiiranes by Phosphine Sulfides. Scope, Stereochemistry, and Mechanism

Sir:

We wish to report that thiiranes may be conveniently and rapidly synthesized from the corresponding oxiranes with phosphine sulfides.

In general, oxiranes can be converted to thiiranes by the use of thiocyanate ion, thiourea, or thioamides and related compounds.[1–4] Recently, it was reported that 2-hydroxyethyl disulfide reacted with triphenylphosphine to give ethylene sulfide and triphenylphosphine oxide.[5] A pentavalent phosphorus species I was proposed as the intermediate[5,6] (I, L_{1-3} = Ph; R_{1-4} = H). We reasoned that a thiophosphoryl compound might well react with an oxirane to form such an intermediate which would proceed to give a phosphoryl compound and a thiirane.[7] Formation of the phos-

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[1] General reviews on thiiranes: D. D. Reynolds and D. L. Fields in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part I, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, p 576; L. Goodman and E. J. Reist in "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, New York, N. Y., 1966, p 93; M. Sander, *Chem. Rev.*, **66**, 297 (1966).

[2] F. Lautenschlaeger and N. V. Schwartz, *J. Org. Chem.*, **34**, 3991 (1969).

[3] D. L. Clason and L. E. Coleman, U. S. Patent 3,560,528 (1970); *Chem. Abstr.*, **75**, 20171*h* (1971).

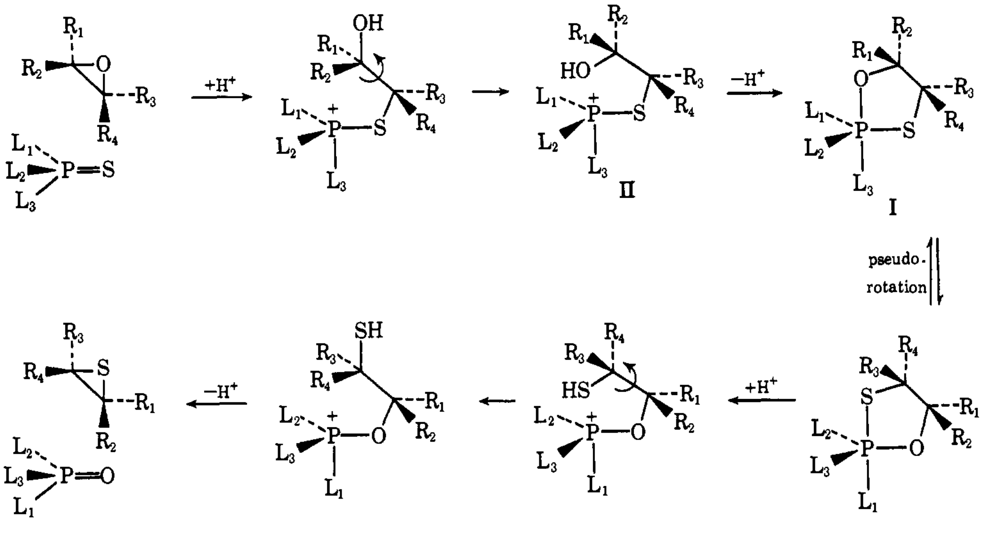
[4] R. C. Vander Linden, J. M. Salva, and P. A. C. Smith, U. S. Patent 3,542,808 (1970); *Chem. Abstr.*, **74**, 53498*c* (1971).

[5] M. Grayson and C. E. Farley, *Chem. Commun.*, 831 (1967).

[6] K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7031 (1969).

[7] An isolated example was provided by G. Schrader and W. Lorenz, German Patent 1,082,915 (1960); *Chem. Abstr.*, **55**, 25983 (1961), who reported the generation of thioglycidyl thiophosphate by conversion of epichlorohydrin with 2 mol of potassium dialkyl thiophosphate.

Scheme I



phoryl bond should provide the driving force for the reaction. This has now been reduced to practice and the reaction was found to be competitive with or superior to existing methods of thiirane synthesis.

A typical reaction was carried out as follows. A solution of 10 mmol each of the oxirane and phosphine sulfide was prepared in 35 ml of dry benzene. To the solution, an equivalent amount of trifluoroacetic acid in 5 ml of benzene was added with stirring. The reaction was usually carried out at ambient or slightly higher temperature. The progress of the reaction can be followed by glpc analysis. At the end of the reaction, solid sodium bicarbonate was added and stirred for 15 min. Thiirane[8] can then be isolated by column chromatography on silica gel eluting with benzene. Some typical results are presented in Table I. Perhaps the most striking feature of the reaction is its rapidity. In many cases, the conversion is essentially complete in 5 min.[10]

Table I

Oxirane (1 mol)	Phosphine sulfide (mol)	Reaction temp, °C	Reaction time, min	Thiirane yields,[a] %	Lit. ref
Cyclohexene oxide	$Ph_3P{=}S$ (1)	20	5	50 (62)	*d*, *e*
1-Octene oxide	$Ph_3P{=}S$ (1)	20	20	58 (70)	*b*
	$Ph_3P{=}S$ (1.5)	20	145	(83)	
Cyclopentene oxide	$Ph_3P{=}S$ (1)	60	55	35 (44)	*d*, *f*
Styrene oxide	*n*-$Bu_3P{=}S$ (1)	20	85	62	*c*, *d*
	n-$Bu_3P{=}S$ (4)	20	50	(71)	
Cyclooctene oxide	*n*-$Bu_3P{=}S$ (1)	60	1260	64 (69)	*g*

[a] Yields were determined on isolated pure products except those numbers in parentheses which were determined by glpc on a 6-ft SE-30 ultraphase column. [b] C. G. Moore and M. Porter, *J. Chem. Soc.*, 2062 (1958). [c] C. O. Guss and D. L. Chamberlain, Jr., *J. Amer. Chem. Soc.*, **74**, 1382 (1952). [d] Reference 2. [e] Reference 14. [f] Reference 12. [g] Reference 9.

With cyclohexene oxide as the standard substrate, it was found that triphenylphosphine and tri-*n*-butylphosphine sulfides are comparable in their efficacy. Tris(diethylamino)phosphine sulfide effected the conversion poorly and many side products were formed in addition to the thiirane, whereas triethyl thiophosphate was not effective at all. The presence of acid is mandatory in this reaction since a mixture of cyclohexene oxide and triphenylphosphine sulfide in benzene remained unchanged after 4.5 hr at reflux. One mole equivalent of trifluoroacetic acid was required to give optimal yields. While the role of the acid is probably a simple catalyst, its effect seems to be neutralized by the phosphine oxide that is formed. It is known that both phosphine oxide and sulfide complex with acid.[11] *p*-Toluenesulfonic acid monohydrate also enabled formation of thiirane but in poor yield.

The utility of this reaction was indicated by the conversion of cyclopentene and cyclooctene oxides to the corresponding episulfides. The conventional methods using thiocyanate or thiourea were either difficult or unsuccessful.[9,12]

Reasonable yields were realized for each thiirane and, in general, the yield can be impoved by using excess phosphine sulfide.

In analogy to the thiocyanate[13–15] and thiourea[16] reactions, we propose that the present reaction follows the general mechanism shown in Scheme I. A stereochemical consequence of this mechanism is that two Walden inversions must take place in the overall reaction. In support of this, it was found that *cis*-stilbene oxide was converted by excess tri-*n*-butylphosphine sulfide in $CDCl_3$ into a 90% yield of exclusively *cis*-stilbene sulfide[8,16,17] (nmr) in 2 hr. As further proof of its structure, the sulfide was desulfur-

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[8] Thiiranes were identified by comparison with authentic samples with the exception of cyclocotene sulfide which was identified by its ir and nmr spectra.[9]

[9] D. J. Pettit and G. K. Helmkamp, *J. Org. Chem.*, 29, 2702 (1964).

[10] Under these mild conditions acid-catalyzed rearrangement of oxirane to ketone or aldehyde was not significant to any detectable extent.

[11] R. A. Zingaro and R. E. McGlothlin, *J. Org. Chem.*, **26**, 5205 (1961).

[12] L. Goodman and B. R. Baker, *J. Amer. Chem. Soc.*, **81**, 4924 (1959).

[13] M. G. Ettlinger, *ibid.*, 72, 4792 (1950).

[14] E. E. van Tamelen, *ibid.*, 73, 3444 (1951).

[15] C. C. Price and P. F. Kirk, *ibid.*, 75, 2396 (1953).

[16] R. Ketcham and V. P. Shah, *J. Org. Chem.*, 28, 229 (1963).

[17] Strictly speaking, this experiment does not give conclusive evidence. Compare with Price and Kirk who used optically active 2,3-epoxybutane with thiocyanate.[15]

ized *in situ* with triphenylphosphine to *cis*-stilbene.[18]

Further insight on the mechanism of this reaction can be gained from the use of optically active phosphine sulfide. Apical intramolecular nucleophilic attack at phophorus by the hydroxy group in the chiral phosphonium salt II may lead to the phosphorane I. Recent analysis by Mislow, *et al.*, on the stereochemical consequences of similar systems indicated that retention of configuration at phosphorus is expected when the phosphorus atom is incorporated in a small ring.[6] Thus, we found that (*S*)-(−)-methylphenyl-*n*-propylphosphine sulfide ($[\alpha]_D$ −5.6°),[19] on reaction with a twofold excess of cyclohexene oxide and trifluoroacetic acid, was converted to (*S*)-(−)-oxide, in greater than 89% yield, with $[\alpha]_D$ −3.8° after purification by chromatography on silica gel followed by molecular distillation. The reaction thus proceeds with retention of configuration.[20]

Acknowledgments. We thank the National Research Council of Canada for financial support of this work. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial financial support.

[18] D. B. Denney and M. J. Boskin, *J. Amer. Chem. Soc.*, **82**, 4736 (1960); *Chem. Ind.* (*London*), 330 (1959).

[19] G. Zon, K. E. DeBruin, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7023 (1969).

[20] For a facile oxidation of phosphinothioates with either retention or inversion at phosphorus, see A. W. Herriott, *ibid.*, **93**, 3304 (1971).

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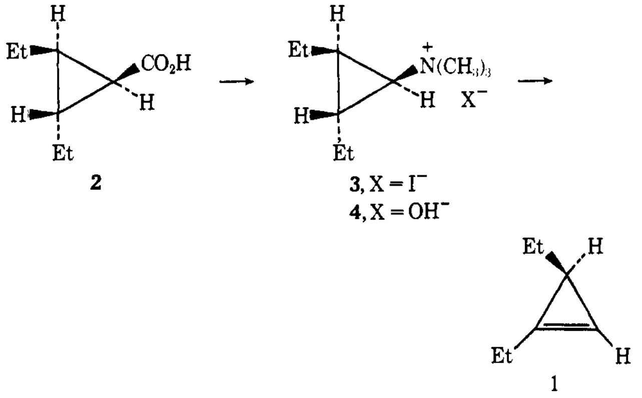
Rapid Racemization of an Optically Active Cyclopropene Derivative *via* Ring Opening, Bond Rotation, and Ring Closure

Sir:

We wish to report that optically active 1,3-diethylcyclopropene (**1**) undergoes thermal racemization in the gas phase at a rate more rapid than that associated with structural isomerization. This observation indicates that despite the high strain energy (53 kcal/mol[1]) of **1**, a ring-opened species is formed on its pyrolysis which recyclizes surprisingly easily.

Synthesis and optical resolution of *trans,trans*-2,3-diethylcyclopropanecarboxylic acid (**2**, $[\alpha]^{25}_D$ −4.80°, $[\alpha]^{25}_{365}$ −6.45°) were performed essentially as described by Walbrick, Wilson, and Jones.[2] The acid was transformed[3] *via* acyl azide, isocyanate, methylamine, and dimethylamine to the corresponding trimethylammonium iodide **3** and thence to the quaternary hydroxide **4**. Pyrolysis (355°) of **4** in an evacuated flask containing platinized asbestos[3a] and connected to a cold trap gave optically active 1,3-diethylcyclopropene[4] (**1**, $[\alpha]^{25}_D$ +34.0°, $[\alpha]^{25}_{365}$ +119°) in 18% yield based on dialkylated amine (corrected for recovered amine).



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3, X = I⁻
4, X = OH⁻

1

Thermolysis of cyclopropene **1** was carried out in a conventional well-conditioned static reactor[5] in the temperature range 160–190°. Products **5**, **6**, **7a**, and **7b** were formed[4] in essentially quantitative yield in the ratio 33:34:29:4. The first-order rate constants for total loss of optical activity (k_α) and product formation (k_i) are reported in Table I.

Table I. Rate Constants and Arrhenius Parameters for Gas-Phase Thermal Racemization and Structural Isomerization of Optically Active 1,3-Diethylcyclopropene (**1**)

Rate constants[a,b] (× 10⁵), sec⁻¹	Temp, °C 161.1	175.6	190.4	Arrhenius parameters[c,d] Log *A*	E_a
k_α	2.69	8.04	29.6	11.8	32.6
$k_i = k_P$	0.151	0.415	1.61	10.4	32.2
k_{DL}	1.27	3.81	14.0	11.5	32.7
k_{DL}/k_P	8.4	9.2	8.7		

[a] For a definition of rate constant symbols, see the text. [b] Error limits in the reported rate constants are generally ±3%. [c] Error in log *A* is ±1 log unit; error in E_a is ±1.5 kcal/mol. [d] $\Delta H^\ddagger$ (see text) calculated using the equation $\Delta H^\ddagger = E_a - nRT$ with $n = 1$ and $T = 448$°K. Energy units are kcal/mol.

Assuming racemization does not occur by unprecedented,[6] orbital-symmetry–forbidden[7] 1,3-hydrogen shift, it must be produced by 180° rotation about the C_1–C_3 and/or C_2–C_3 bonds in **1**. We cannot rule out a completely concerted process for this motion; however, it is informative to discuss our results in terms of the formal stepwise mechanism outlined in Scheme I. Simple ring cleavage[8] in **1** could lead to "diradical" **8**. In order to produce racemization, 90° rotation must take place leading to **9**, which contains a plane of symmetry; this species is perhaps best described as a sub-

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[1] R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968).

[2] J. M. Walbrick, J. W. Wilson, and W. M. Jones, *ibid.*, **90**, 2897 (1968). Drawings are not intended to reflect actual absolute configurations.

[3] (a) M. J. Schlatter, *ibid.*, **63**, 1733 (1941); (b) J. Weinstock, *J. Org. Chem.*, **26**, 3511 (1961); (c) W. H. de Wolfe and F. Bickelhaupt, *Recl. Trav. Chim. Pays-Bas*, **90**, 150 (1971).

[4] Analytical data on all new compounds reported are consistent with their assigned structures. Details of the preparative work will be reported in a full paper.

[5] Techniques used were similar to those described earlier: R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969).

[6] For example, 1- and 3-methylcyclopropene do *not* interconvert on pyrolysis. That 1,3-alkyl shift is not responsible for racemization is suggested by the observation that 1,3- and 3,3-dimethylcyclopropene also do not interconvert thermally: *cf.* (a) R. Srinivasan, *ibid.*, **91**, 6250 (1969); (b) R. Srinivasan, *J. Chem. Soc. D*, 1041 (1971).

[7] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970, Chapter 7.

[8] Although the C_1–C_3 bond is the most highly substituted, we believe that cleavage of both C_1–C_3 and C_2–C_3 in **1** may be occurring simultaneously (see ref 6b); racemization may therefore be the result of both processes. Our data also provide no information concerning the hybridization at C_1 in **9**, and the stereochemistry at C_3 is probably a mixture of cis and trans. For reasons of space and clarity, only one pathway is explicitly illustrated in Scheme I. The symbol X in Scheme II refers to the total set of reaction intermediates.