The Stereochemistry of 2-Oxazoline Formation from Epoxides

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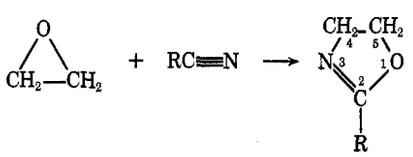
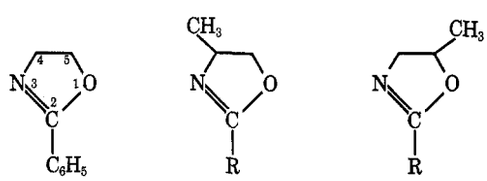
The stereochemistry of the ring-enlargement reaction of epoxides with nitriles in the presence of strong acids to give 2-oxazolines has been investigated. It is shown, mainly by nmr data, that the reaction proceeds with inversion and is 100% stereospecific; *e.g.*, *cis*- and *trans*-2,3-epoxybutane (**4** and **5**) with benzonitrile give exclusively *trans*-4,5-dimethyl-2-phenyl-2-oxazoline (**6b**) and *cis*-4,5-dimethyl-2-phenyl-2-oxazoline (**7b**), respectively. A number of new 2-oxazolines have been prepared, and their physical constants, derivatives, and nmr spectra are reported. The mechanism of the formation of the 2-oxazolines is discussed.

This paper deals with the acid-catalyzed ring opening of epoxides with nitriles to give 2-oxazolines[1] according to the following scheme (eq 1). Oda and



(1)

coworkers were the first to report this reaction.[2] Using ethylene oxide and benzonitrile with concentrated sulfuric acid as catalyst they obtained 2-phenyl-2-oxazoline (**1**) in 19% yield. Using propylene oxide and acetonitrile they obtained in 8% yield a mixture of the two positional isomers, consisting of 70% 2,4-dimethyl-2-oxazoline (**2a**) and 30% 2,5-dimethyl-2-oxazoline (**3a**). Using benzonitrile and propylene oxide a similar 70:30 mixture of 4-methyl-2-phenyl-2-oxazoline (**2b**) and 5-methyl-2-phenyl-2-oxazoline (**3b**)



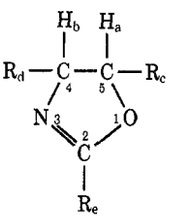
1 **2a**, R = CH_3; **b**, R = C_6H_5 **3a**, R = CH_3; **b**, R = C_6H_5

was obtained. Yields in all these and similar reactions were low, between 5 and 21%.

Temnikova and coworkers performed additions to substituted styrene oxides with benzonitrile and acetonitrile using $SnCl_4$ as a catalyst.[3] Since none of these workers had investigated the stereochemistry and mechanism of this type of epoxide reaction, we undertook the present work.

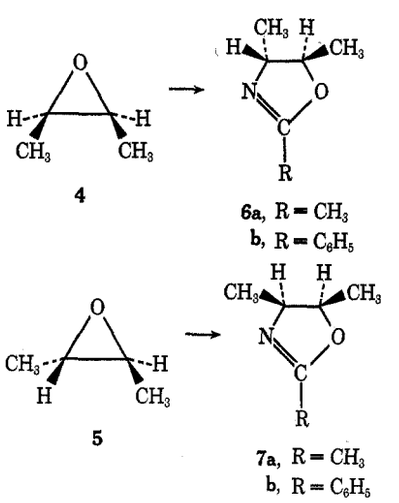
Results

Acetonitrile and benzonitrile were added to *cis*- and *trans*-2,3-epoxybutane (**4** and **5**, respectively) in the presence of concentrated sulfuric acid. In all cases the corresponding 2-oxazolines according to



eq 1 were obtained, although generally in disappointingly low yield, as already found by Oda and coworkers.[2] The results are summarized in Table I.

Thus in the reaction of *cis*-2,3-epoxybutane (**4**) with acetonitrile, the oxazoline formed was *trans*-2,4,5-trimethyl-2-oxazoline (**6a**) exclusively. *trans*-2,3-Epoxybutane (**5**) on reaction with acetonitrile gave *cis*-2,4,5-trimethyl-2-oxazoline (**7a**) as the sole oxazoline isomer.



4 **6a**, R = CH_3; **b**, R = C_6H_5

5 **7a**, R = CH_3; **b**, R = C_6H_5

The stereospecificity of the reaction was best demonstrated by examination of the low-field part of the nmr spectra corresponding to the absorption bands of the 4 and 5 protons. For the crude reaction product from the cis epoxide **4**, namely the trans 2-oxazoline **6a**, absence of peaks in the region 4.16–4.75 ppm indicated that the cis 2-oxazoline **7a** was not present. Similarly, for cis 2-oxazoline **7a**, the product from the trans epoxide **5**, the absence of peaks in the region 3.18–3.68 ppm indicated that the trans 2-oxazoline **6a** was not present.

It was likewise shown that the cis epoxide **4**, when treated with benzonitrile, gave exclusively *trans*-4,5-dimethyl-2-phenyl-2-oxazoline (**6b**). This compound seems, on the basis of the melting point of its picrate salt, to be identical with a compound pre-

(1) For a recent review of oxazoline chemistry see J. A. Frump, *Chem. Rev.*, **71**, 483 (1971).

(2) R. Oda, M. Okano, S. Tokiura, and F. Mismui, *Bull. Chem. Soc. Jap.*, **35**, 1219 (1962).

(3) T. I. Temnikova and V. N. Yandovskii, *Zh. Org. Khim.*, **4**, 178 (1968); *Chem. Abstr.*, **68**, 78176 (1968); T. I. Temnikova and T. E. Zhesko, *Zh. Obshch. Khim.*, **33**, 3436 (1963); *Chem. Abstr.*, **60**, 1738c (1964).

TABLE I.—PHYSICAL PROPERTIES AND NMR SPECTRA OF 2-OXAZOLINES

Oxazoline	Yield, %	Bp, °C (mm)	Mp of picrate, °C	Chemical shifts, δ in CCl4[a]				
				H_a	H_b	H_c	H_d	H_e
trans-2,4,5-Trimethyl-2-oxazoline (**6a**)	10	115–116	152–153	3.74–4.16 (pent) J_{ac} = 5.9 J_{ab} = 6.0	3.18–3.68 (m) J_{bd} = 6.0 J_{ba} = 6.0 J_{bc} = 1.5	1.27 (d)	1.15 (d)	1.83 (d) J_{eb} = 1.5
trans-4,5-Dimethyl-2-phenyl-2-oxazoline (**6b**)	5	116–118 (11)	133–134	3.91–4.23 (pent) J_{ac} = 5.5 J_{ab} = 6.0	3.41–3.86 (pent) J_{bd} = 6.0 J_{ba} = 6.0	1.35[b] (d)	1.21[b] (d)	7.55 + 7.83 (m)
cis-2,4,5-Trimethyl-2-oxazoline (**7a**)	17	120–122	136–137	4.28–4.75 (m) J_{ac} = 6.2 J_{ab} = 9.0	3.68–4.21 (m) J_{bd} = 6.6 J_{ba} = 9.0 J_{bc} = 1.5	1.16 (d)	1.03 (d)	1.81 (d) J_{eb} = 1.5
cis-4,5-Dimethyl-2-phenyl-2-oxazoline (**7b**)	3	142–144 (29)	205–207	4.41–4.91 (oct) J_{ac} = 6.0 J_{ab} = 9.0	3.89–4.38 (oct) J_{bd} = 6.5 J_{ba} = 9.0	1.25[b] (d)	1.14[b] (d)	7.25 + 7.83 (m)
2,4-Dimethyl-2-oxazoline (**2a**) and 2,5-Dimethyl-2-oxazoline (**3a**)	10	129–130 (**2a** only) 112–114 (mixture)		2.98–4.75 including H_d (m) J_{ac} = 5.8	3.49–4.41 (m) J_{bd} = 6.0 J_{bc} = 1.5 J_{ba} = 1.5	1.28 (d)	1.16 (d) See H_a + H_b	1.86 (d) J_{eb} = 1.5 1.85 (t) J_{eb} = 1.5

[a] With respect to tetramethylsilane as internal standard. J values are observed splitting values in hertz. [b] Two doublets superimposed into an unsymmetrical triplet.

pared by Strauss.[4] No mention of the stereochemical aspects of the compound was made, however. Similarly, the trans epoxide **5** gave the new compound *cis*-4,5-dimethyl-2-phenyl-2-oxazoline (**7b**) as the exclusive oxazoline.

Thus all reactions examined were found to proceed 100% stereospecifically with inversion to give the corresponding 2-oxazoline of inverted configuration.

Nmr Spectra.—All nmr data of the 2-oxazolines are summarized in Table I.

Our original assignment of the 4- and 5-methyl groups and protons was based on the use of the corresponding monomethyl compounds, 2,4-dimethyl-2-oxazoline (**2a**) and 2,5-dimethyl-2-oxazoline (**3a**). A 70:30 mixture of these compounds was prepared, using the method of Oda and coworkers,[2] and separated by gas chromatography. The structure of these two compounds was ascertained by independent synthesis.[2] It was found that the 4-methyl group in compound **2a** appeared clearly upfield in comparison with the 5-methyl group of oxazoline **3a**. Therefore, in the cases of the 4,5-dimethyl-2-oxazolines **6a**, **6b**, **7a**, and **7b** the upfield doublet was assigned to the 4-methyl group and the lower field doublet to the 5-methyl group. Similarly, the 4-methine proton absorbs at higher field than the 5 proton in all cases. All coupling constants are consistent with this assignment and the assignment agrees with the data reported for other 2-oxazolines.[5-8] All spectra were analyzed as X_3ABY_3 systems with $J_{AY} = J_{BX} = 0$.

In all examples studied the coupling constant $^3J_{HH}$ between the methyl group and the geminal proton was somewhat larger for the 4 position than for the 5 position. It has been found for other compounds that a neighboring π bond can decrease geminal coupling constants.[9] It is likely that the same effect, in our case the C=N double bond, can also decrease the doupling constant between geminal methyl group and proton.

Assignment of the Cis or Trans Configuration.—The assignment of the cis or trans configuration is based mainly upon the 4-H,5-H coupling constant. From Table I it is seen that the two cis compounds, **7a** and **7b**, have a 4-H,5-H coupling constant of 9.0 cps, whereas the corresponding two trans compounds, **6a** and **6b**, have a coupling constant of 6.0 cps. These values agree well with the values observed in other cis and trans 2-oxazolines of established structure. Generally, cis proton coupling is larger than trans proton coupling in five-membered rings, which cannot deviate appreciably from planarity as expected from the Karplus rule.[5,7,8,11,12]

(4) E. Strauss, *Chem. Ber.*, **33**, 2825 (1900).
(5) R. F. Lambert and C. E. Kristofferson, *J. Org. Chem.*, **30**, 3938 (1965).
(6) T. Nishiguchi, H. Tochio, A. Nebeya, and Y. Iwakura, *J. Amer. Chem. Soc.*, **91**, 5835 (1969); J. R. Carson, G. I. Poos, and H. R. Almond, *J. Org. Chem.*, **30**, 2225 (1965).
(7) T. A. Foglia, L. M. Gregory, and G. Maerker, *J. Org. Chem.*, **35**, 3779 (1970); T. A. Foglia and D. Swern, *ibid.*, **34**, 1680 (1969).
(8) M. A. Weinberger and R. Greenhalgh, *Can. J. Chem.*, **41**, 1038 (1963).
(9) Reference 10, p 273.
(10) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969.
(11) T. A. Foglia, L. M. Gregory, G. Maerker, and S. F. Osman, *J. Org. Chem.*, **36**, 1068 (1971).
(12) S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969); ref 10, p 286 ff.

Further support for the assignment of the cis and trans configuration comes from a comparison of the chemical shifts at the 4 and 5 positions. The 4- and 5-methyl groups in all compounds examined absorb at *ca.* 0.1 ppm higher field in the cis isomers than in the corresponding trans isomers. On the other hand, the 4- and 5-methine protons absorb at *ca.* 0.5 ppm lower field in the cis 2-oxazolines than in the trans isomers. This effect can be attributed mainly to the diamagnetic anisotropy of the *C*-methyl bond and is found in many cis–trans isomer pairs of planar three- to five-membered ring compounds.[13] A methyl group has the tendency to shield a neighboring substituent in the cis position and to deshield a neighboring substituent in trans orientation. Thus, trans 4,5-methyl groups will mutually deshield each other so as to shift both methyl bands to lower field. At the same time the 4 and 5 protons will be shielded by the neighboring methyl groups and therefore shift upfield.[13]

Likewise, cis 4,5-methyl groups will mutually shield each other, causing the methyl bands to appear at higher field. The 4,5 protons will now be deshielded and therefore move to lower field. A more accurate treatment has to take into account the diamagnetic anisotropy of the C–H bonds of the methine protons[14] and the C–H bonds of the methyl groups as well as the rotation of the methyl groups.[15] This does not substantially change, however, the above conclusions.

All 2-methyl-2-oxazolines show a long-range coupling between the 2-methyl group and the 4 proton(s) of *ca.* 1.5 Hz, as has been reported for other 2-methyl-2-oxazolines and the similar 2-thiazolines.[8,16,17]

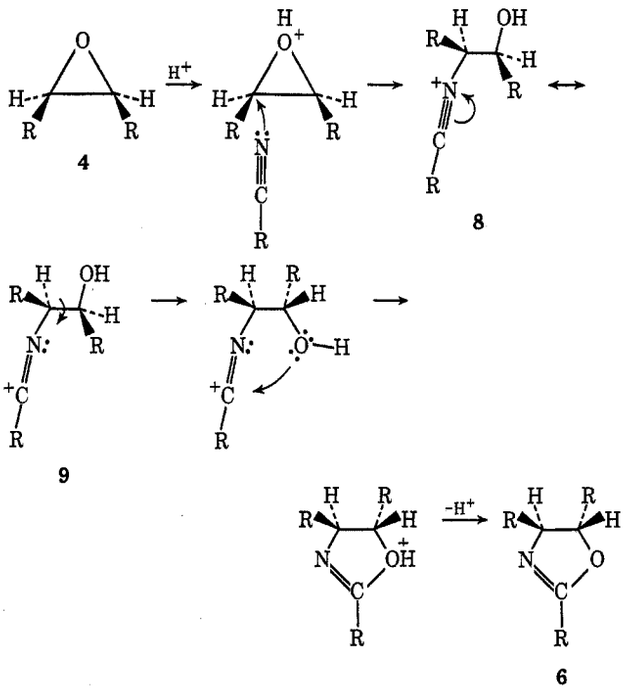
Infrared Spectra.—All 2-oxazolines show the strong band around 1665 cm^{-1} characteristic of the C=N stretch[6–8,18,19] and a strong band around 1040 cm^{-1} which can be assigned to one of the C–O–C stretching modes in agreement with Lundquist and Ruby.[19]

Discussion

The following general mechanism, illustrated by the reaction of the cis epoxide **4** to give the trans 2-oxazoline **6**, seems to account best for the observed results.

Thus the reaction involves one inversion on opening of the protonated epoxide ring by the nitrile to give the corresponding nitrilium ion **8**. This is followed by rotation around the C–C bond of the former epoxide ring and ring closure to give the 2-oxazoline of inverted configuration.

The above mechanism is completely analogous to the mechanism proposed by Helmkamp and coworkers[16] for the acid-catalyzed ring expansion of episulfides with nitriles to give 2-thiazolines (scheme below, O replaced by S). Here also complete stereospecificity



was found in all cases, with *cis*- and *trans*-2-butene episulfide (**4** and **5**, with O replaced by S) giving exclusively *trans*-2,4,5-trimethyl-2-thiazoline and *cis*-2,4,5-trimethyl-2-thiazoline, respectively (**6a** and **7a**, O replaced by S), upon reaction with acetonitrile in the presence of strong acids.

With respect to ring-expansion reactions of epoxides, the example best investigated with respect to the stereochemistry seems to be the reaction with xanthates to give 1,3-dithiolane-2-thiones ("cyclic trithiocarbonates"). Here Overberger and Drucker found also complete stereospecificity with Walden inversion in all examples studied.[20] All other ring expansions of epoxides[21] seem to proceed with predominant, if not exclusive, inversion, as do practically all epoxide ring-opening reactions.[22]

Experimental Section

General Procedures.—Infrared spectra were taken on a Perkin-Elmer 137 sodium chloride spectrophotometer. Methylene chloride was used as solvent.

Gas chromatography was done on a Varian Model 90P gas chromatograph. Most of the work was done with a 6-ft column of 15% Carbowax 20M on Gas-Chrom R.

Nmr spectra were taken on a Varian A-60 nuclear magnetic resonance spectrometer. Carbon tetrachloride was used as solvent and tetramethylsilane as internal standard.

The microanalyses were performed by the Hoffmann-La Roche Corp., Nutley, N. J., to whom we would like to extend our thanks.

***cis*- and *trans*-2,3-epoxybutane, 4 and 5,** respectively, were prepared essentially according to the method of Winstein and Lucas,[23] by addition of HOBr with *N*-bromosuccinimide to *cis*- and *trans*-2-butene, respectively, and elimination of HBr with aqueous NaOH, using, however, *N*-bromosuccinimide in place of *N*-bromoacetamide. The epoxides were found to be >99% pure

(13) Reference 10, p 234 ff.
(14) Reference 10, p 78 ff.
(15) J. Elguero and A. Fruchier, *Bull. Soc. Chim. Fr.*, 496 (1970).
(16) G. K. Helmkamp, P. J. Pettitt, J. R. Lowell, Jr., W. R. Inabey and R. G. Wolcott, *J. Amer. Chem. Soc.*, **88**, 1030 (1966); J. R. Lowell, Jr., and G. K. Helmkamp, *ibid.*, **88**, 768 (1966).
(17) J. Roggero and J. Metzger, *Bull. Soc. Chim. Fr.*, 1715 (1964).
(18) A. R. Katritzky and A. P. Aubler, "Physical Methods in Heterocyclic Chemistry," Vol. 2, Academic Press, New York, N. Y., 1963, p 218; J. R. Carson, G. I. Poos, and H. R. Almond, Jr., *J. Org. Chem.*, **30**, 2225 (1965); H. L. Wehrmeister, *ibid.*, **26**, 3821 (1961); Stadtler Standard Infrared Spectra 21053-55.
(19) R. T. Lundquist and A. Ruby, *Appl. Spectrosc.*, **20**, 258 (1966).
(20) C. G. Overberger and A. Drucker, *J. Org. Chem.*, **29**, 360 (1964).
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(22) A. Rosowsky in A. Weissberger, Ed., "Heterocyclic Compounds with Three- and Four-Membered Rings," Part 1, Interscience, New York, N. Y., 1964; R. J. Gritter in S. Patai, Ed., "The Chemistry of the Ether Linkage," Interscience, New York, N. Y., 1967, pp 381–411; R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).
(23) S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, **61**, 1576 (1939).

on the base of ir and nmr data and gas chromatographic analysis as originally assumed by Winstein and Lucas. *cis*- and *trans*-2,3-epoxybutane, **4** and **5**, each gave only one peak on gas chromatography on a 6-ft 15% Carbowax 20M on Gas-Chrom R column. A mixture of the two compounds was easily separated at 65°, the compounds having retention times of 4.8 and 3.6 min, respectively.

cis-**2,3-Epoxybutane** (**4**) had nmr $X_3AA'X_3'$ system; H_A = 2.60–2.94 (two overlapping octets); H_X = 1.19 (multiplet with predominating doublet); J_{AX} = 5.4 Hz (first-order analysis).[24]

trans-**2,3-Epoxybutane** (**5**) had nmr $X_3AA'X_3'$ system; H_A = 2.32–2.66 (multiplet); H_X = 1.21 (doublet); J_{AX} = 4.5 Hz (first-order analysis).

General Procedure for Reaction of Epoxides with Nitriles Similar to Procedure of Oda and Coworkers.[1]—A 30-ml portion of nitrile (distilled over phosphorus pentoxide) was added to a round-bottom flask and cooled in an ice bath; 15 ml of concentrated sulfuric acid was added slowly with stirring. A mixture of *ca.* 0.15 mol of the epoxide in 30 ml of the nitrile was added through the reflux condenser over a period of 1 hr. The mixture was then stirred for a period of 3 hr with the ice bath being allowed to melt at its own rate and then poured into 100 ml of ice water. This mixture was then extracted three times with 100 ml of ether and the ether was discarded. The aqueous phase was then neutralized with concentrated NaOH and filtered. Next it was made strongly basic with NaOH and extracted three times with 100 ml of ether. The three ether fractions were combined, dried over anhydrous magnesium sulfate, filtered, and distilled. The oxazoline was isolated by distillation through a short Vigreux column.

A number of attempts were made to seek conditions to improve the yield. These include the use of 60% perchloric acid, trifluoroacetic acid, and *p*-toluenesulfonic acid in place of the concentrated sulfuric acid, as well as no acid at all. All attempts, including the use of inverse addition, did not produce better yields.

2,4- and 2,5-Dimethyl-2-oxazolines (**2a and 3a**).—The general procedure was followed using propylene oxide and acetonitrile. The mixture boiling at 112–114° was collected and separated by gas chromatography using a 6-ft column of 15% Carbowax 20M on Gas-Chrom R. Quantitative analysis showed the two isomers **2a** and **3a** to be in 70:30 proportion. The melting point of the picrate of the 2,4 isomer **2a** was 130° (lit.[2] mp 130–131°).

trans-**2,4,5-Trimethyl-2-oxazoline** (**6a**).—The general procedure was followed using 12.0 g (0.166 mol) of *cis*-2,3-epoxybutane (**4**). The reaction yielded 1.90 g (10%) of *trans*-2,4,5-trimethyl-2-oxazoline (**6a**), bp 115–116°, mp of picrate 152–153°.

trans-**4,5-Dimethyl-2-phenyl-2-oxazoline** (**6b**).—The general procedure was followed using 12.0 g (0.166 mol) of the cis epoxide **4** and benzonitrile as solvent. The reaction yielded 0.95 g (5%) of *trans*-4,5-dimethyl-2-phenyl-2-oxazoline, bp 116–118° (11 mm), mp of picrate 133–134°. *Anal.* Calcd for $C_{17}H_{16}N_4O_8$: C, 50.5; H, 3.99; N, 13.86. Found: C, 50.40; H, 4.18; N, 13.68.

cis-**2,4,5-Trimethyl-2-oxazoline** (**7a**).—This compound was prepared according to the general procedure using 12.0 g (0.166 mol) of *trans*-2,3-epoxybutane (**5**).

Distillation of the product yielded 3.30 g (17%) of *cis*-2,4,5-trimethyl-2-oxazone (**7a**), bp 120–122°, mp of picrate 136–137°. *Anal.* Calcd for $C_{12}H_{14}N_4O_8$: C, 42.11; H, 4.14; N, 16.37. Found: C, 42.19; H, 4.31; N, 16.29.

cis-**4,5-Dimethyl-2-phenyl-2-oxazoline** (**7b**).—The general procedure was followed using 12.0 g (0.166 mol) of *trans*-2,3-epoxybutane (**5**) and benzonitrile as solvent. The reaction yielded 0.60 g (3%) of *cis*-4,5-dimethyl-2-phenyl-2-oxazoline (**7b**), bp 142–144° (29 mm), mp of picrate 205–207°.

Registry No.—**2a**, 6159-23-5; **3a**, 6159-22-4; **4**, 1758-33-4; **5**, 21490-63-1; **6a**, 23336-75-6; **6a** picrate, 38898-94-1; **6b**, 38898-95-2; **6b** picrate, 38898-96-3; **7a**, 23236-41-1; **7a** picrate, 38898-98-5; **7b**, 36746-57-3; **7b** picrate, 38899-00-2; propylene oxide, 75-56-9.

Acknowledgments.—The authors wish to thank the Rutgers Research Council for financial support.

(24) Compare ref 10, p 224.

2,3-Dimethylcyclopropanecarboxylic Acids from 2,3-Dimethyloxiranes *via* the Wittig Reaction. Stereochemistry and Mechanism

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Triethyl phosphonoacetate anion reacted with (+)-(2*R*,3*R*)-2,3-dimethyloxirane to give predominantly (+)-(2*S*,3*S*)-2,3-dimethylcyclopropanecarboxylic acid and with *cis*-2,3-dimethyloxirane to give predominantly *cis*-2,3-dimethylcyclopropane-*trans*-carboxylic acid. Inversion of configuration must have occurred at both carbon atoms to account for these products. In each case minor amounts of stereoisomeric acids were produced. The results are discussed in terms of the overall mechanistic scheme.

The reaction of Wittig type reagents with epoxides to form cyclopropanecarboxylic acid derivatives has been well documented. Both carboethoxymethylenephosphoranes[1,2] and phosphonate anions[3-7] have been successfully utilized. Although certain aspects of the reaction pathway are well understood, there remains some disagreement concerning the overall mechanistic scheme.

Denney[1] postulated a stepwise decomposition of the intermediate **4** (process Y in Scheme I) to give **6** *via* an intramolecular SN2 displacement. This proposal was based on the observation that carboethoxymethylenetriphenylphosphorane reacted at 200° with cyclohexene oxide to form ethyl 7-norcaranecarboxylate and with optically active styrene oxide to form optically active *trans*-2-phenylcyclopropanecarboxylate. Denney's inversion mechanism has been supported by Tomoskozi[4] and Walborsky,[8] who established the absolute configuration of optically active *trans*-2-phenylcyclopropanecarboxylic acid.

In addition to the inversion mechanism the possibility of a competitive direct collapse of **4** (process X) either through a concerted process or through a zwit-

(1) D. B. Denney, J. J. Vill, and M. J. Boskin, *J. Amer. Chem. Soc.*, **84**, 3944 (1962).
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(4) I. Tomoskozi, *Tetrahedron*, **19**, 1969 (1963).
(5) I. Tomoskozi, *Tetrahedron*, **22**, 179 (1966).
(6) I. Tomoskozi, *Chem. Ind. (London)*, 689 (1965).
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