1-Cyclohexyl-2-cyclohexylamino-4,5-dihydro-5-imidazolone (4). A mixture of 13.8 g of HBr-*H*-Gly-ONP and 10.3 g of DCC in 150 ml of acetonitrile was stirred vigorously at room temperature (25°). After 2.5 hr the 2115-cm^{-1} peak had disappeared. After 1 hr at 0° a precipitate separated, 7.3 g, mp 168–171° dec. A second crop, 2.6 g, mp 255–260°, was obtained from the residue by solution in acetonitrile and precipitation with ether. Recrystallization from acetonitrile gave colorless plates, mp 274–276° dec, in 50% recovery. This is the hydrobromide salt.

Anal. Calcd for $C_{15}H_{26}H_3OBr$: C, 52.32; H, 7.61; N, 12.20; O, 4.65; Br, 23.21. Found: C, 52.89; H, 7.66; N, 12.23; O, 4.89; Br, 22.85.

The infrared spectrum (137, KBr) showed 3250–2880 (broad, complex), 1785, 1670, 1565, 987, 960, 700, 683 cm^{-1}, and other smaller peaks; the nmr spectrum (CF_3COOH) showed 480 (one proton), 426 (doublet, J = 8 cps, one proton), 266 (two protons), 200–255 (broad, maximum at 233, two protons), 50–150 (broad, complex, peaks at 117, 92, 83, 20 protons; ($CDCl_3$) 578 (one proton), 540 (doublet, J = 8 cps one proton), 264–300 (broad, maximum at 280, one proton), 243 (two protons), 190–260 (broad, one proton), 50–150 (broad, maximum at 103, 20 protons).

The free base was obtained by dissolving the hydrobromide salt in chloroform, adding triethylamine, and extracting with water. After drying, hexane was added and the solution cooled to give colorless needles, mp 152–153° (lit.[37] mp 156°).

Anal. Calcd for $C_{15}H_{25}N_3O$: C, 68.40; H, 9.57; N, 15.95; O, 6.08. Found: C, 68.49; H, 9.55; N, 15.86; O, 6.31.

The infrared spectrum (137, KBr) showed 3250, 3000, 2900, 2840, 1720, 1605, 1535, 1085, 760, 750 cm^{-1}, and other smaller peaks; the nmr spectrum (CF_3COOH) showed the same as for the salt.

A General, Stereospecific Synthetic Route to Δ^2-Thiazolines

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Abstract: A new route to Δ^2-thiazolines is presented, consisting of treatment of an episulfide with a nitrile in the presence of a strong acid. The stereospecificity of the reaction is shown by production of isomeric thiazolines from *cis*- and *trans*-2-butene episulfides. The reaction is successful with either alkyl or aryl nitriles and gives moderate yields even with hindered nitriles. Polymerization of the episulfide is a competing reaction and predominates in the case of ethylene sulfide. Use of the nitrile as solvent has been found to produce the best yields. Reduced yields result if the product thiazoline is highly strained. A number of new thiazolines have been prepared, and their physical constants and derivatives are reported.

Thiazolines (Δ^2) have been obtained from β-bromoalkylamine salts and thioamides (43–80% yields),[1] from β-mercaptoamines and nitriles (52–89% yields),[2] from the N-thiobenzoyl derivatives of 1,2-amino alcohols (50–78% yields),[3] from diacyl-1,2-amino alcohols and phosphorus pentasulfide (7–36% yields),[4] and from N-alkenylthioamides and aluminum chloride (1.5–60% yields).[5] Some of these earlier reactions have shown limitations such as low yields, stereochemical barriers to reaction, or lack of stereospecificity. The method reported here avoids these problems and is also attractive from the standpoint of availability of starting materials. Further investigations of the stereochemistry of this reaction will be reported in a later paper.

Addition of a solution of an episulfide to a mixture of a nitrile and a strong acid results in the formation of the appropriate thiazoline in yields up to 80%. This reaction constitutes a new synthesis of Δ^2-thiazolines which is widely applicable for rings with substituents in the 2-, 4-, and 5-positions, and which permits stereochemical control of products.

The episulfide reaction was discovered during a study of the alkylation of episulfides with *t*-butyl 2,4,6-trinitrobenzenesulfonate. The *t*-butyl ester was prepared *in situ* from *t*-butyl chloride or bromide and the acetonitrile complex of silver 2,4,6-trinitrobenzenesulfonate in nitromethane–methylene chloride solution. When a solution of cyclohexene sulfide in methylene chloride was added to the freshly prepared ester solution, *trans*-2-methyl-3a,4,5,6,7,7a-hexahydrobenzthiazolium 2,4,6-trinitrobenzenesulfonate was isolated in 59% yield by precipitation with ether–pentane. The equivalent weight, by osmometry, was 230 (calcd 224). Infrared absorption bands at 3.15 (N–H), 9.73 and 9.43 (ionic sulfonate), and 6.23 μ (C=N), and the elemental analysis suggested the above structure, which was later confirmed by preparation of the same salt from the free base. In similar fashion, the trinitrobenzenesulfonate salts of *trans*- and *cis*-2,4,5-trimethylthiazoline were prepared in 29 and 40% yields, respectively, from *cis*- and *trans*-2-butene episulfide.

A plausible explanation for these unexpected results was elimination of 2,4,6-trinitrobenzenesulfonic acid from the *t*-butyl ester, followed by protonation of the episulfide and ring opening by acetonitrile. Thus it followed that strong acids should bring about the same reaction. This proved to be the case. When *trans*-2-butene episulfide was added to a solution of 2,4,6-trinitrobenzenesulfonic acid in acetonitrile, *cis*-2,4,5-trimethyl-Δ^2-thiazolinium 2,4,6-trinitrobenzenesul-

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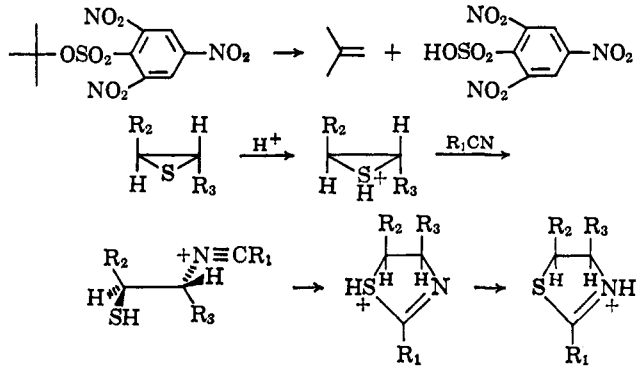

fonate was obtained in 80% yield, identical with the same salt obtained previously. The free base, however, could be isolated in only 26% yield from the salt, reducing the over-all yield to 20%. Use of 60% perchloric acid instead resulted in yields of the free base which ranged from 6.7 to 37%. When concentrated sulfuric acid was employed, the yields generally ranged up to 79% for product isolated as the free base. This last procedure has since been used to prepare a number of alkyl- and aryl-substituted thiazolines.

The stereospecificity of this reaction is evident from the isolation of isomeric thiazolines fom the reaction of *cis*- and *trans*-2-butene episulfide with either acetonitrile or benzonitrile, and by preparation of an optically active thiazoline from an optically active episulfide (the assignment of the stereochemistry of the thiazolines and preparation of the optically active thiazoline will be described in a following paper).

Assignment of the Δ^2-thiazoline structure to the bases obtained from this reaction was on the basis of spectral data and elemental analyses. The infrared spectra of these compounds showed C=N absorption at 6.13–6.19 μ in the case of the 2-alkyl derivatives, and 6.22–6.25μ in the case of the 2-aryl derivatives, consistent with the values reported for 2-substituted Δ^2-thiazolines by Otting and Drawert.[6]

The nmr spectra were completely consistent with the assigned structures. The protons on the 2-alkyl groups showed coupling with the 4-protons, with coupling constants in the 1–2-cps range, as reported by Roggero and Metzger.[7] Evidence supporting the assignment in Table III of chemical shifts of the 4- and 5-methyl and 4- and 5-H will be presented in a following paper on stereochemistry.

Additional evidence for the thiazoline structure was provided by synthesis of *trans*-2,4,5-trimethyl-Δ^2-thiazoline from *cis*-2,3-dimethylaziridine and thioacetamide, after the method of Kuhn and Drawert.[8] These workers had treated ethylenimine with 2-phenylthioacetamide, obtaining 2-phenylthiazoline in 64% yield. Since stereoisomerism is impossible in the latter, the stereochemistry of this reaction is not demonstrated by their results. The product from *cis*-2,3-dimethylaziridine and thioacetamide, obtained in 10% yield, was identical with the product from *cis*-2-butene episulfide and acetonitrile, establishing the latter product as a 2,4,5-trimethyl-Δ^2-thiazoline. Identity was established by vpc analysis and melting points and mixture melting points of the picrate and 2,4,6-trinitrobenzenesulfonate salts.

The scope and limitations of the reaction were investigated by preparation of a number of thiazolines bearing methyl groups on the 4- and 5-positions and alkyl or aryl substituents on the 2-position. Three factors appeared to greatly influence the yields obtained. The first of these was the degree of substitution on the episulfide. In the case of either *cis*- or *trans*-2-butene episulfide, and with tetramethylethylene sulfide, yields as high as 79% were obtained. With ethylene sulfide, however, polymerization predominated, and reaction with acetonitrile produced only a trace of 2-methyl-Δ^2-thiazoline. A sterically hindered nitrile, 2,2-dimethylpropionitrile, also gave a lower yield of the corresponding thiazoline (31%).

The second important factor influencing the yield of this reaction was the solvent. The reactions in which a solvent other than the reactant nitrile was used invariably gave lower yields. In one case a direct comparison was made, and it was found that the yield of *cis*-2,4,5-trimethyl-Δ^2-thiazoline was reduced from 79 to 38.5% when carried out in 1,2-dimethoxyethane. Similarly, the yield of *trans*-2-anisyl-4,5-dimethyl-Δ^2-thiazoline, prepared from *p*-anisonitrile (a solid) in dimethoxyethane, was only 11.5%. Little difference in yield was found between acetonitrile, benzonitrile, and phenylacetonitrile when these were used as solvent in conjunction with sulfuric acid.

A third important consideration is the influence of steric factors on product stability. The reaction of cyclohexene sulfide with acetonitrile gave only a 36% yield of the corresponding thiazoline. Models show that the product, with the thiazoline ring fused *trans* to a cyclohexane ring, is quite strained. Thus the low yield in this case may be due either to steric inhibition of the ring closure, or to steric acceleration of hydrolysis.

Experimental Section

Practical grade acetonitrile was dried over anhydrous magnesium sulfate and distilled from phosphorus pentoxide, bp 80.3–81° (737 mm). Practical grade phenylacetonitrile was distilled at atmospheric pressure through a 10-cm Vigreux column, bp 231–233.5° (737 mm). Both *cis*- and *trans*-2-butene episulfide were synthesized by the method of Bordwell and Andersen[9] and distilled through a 45-cm Vigreux column. The *cis* isomer boiled at 101–102° (737 mm), and the *trans* isomer boiled at 89–91° (737 mm). Tetramethylethylene sulfide was prepared by the method of Youtz and Perkins,[10] mp 75.5–77°. *cis*-2,3-Dimethylaziridine was prepared *via* the epoxide by the reported method,[11] bp 82.5–83.5° (737 mm). Other materials were reagent grade and were used without purification.

Infrared spectra were determined on a Perkin-Elmer Model 421 infrared spectrophotometer and were calibrated against a polystyrene standard. Nuclear magnetic resonance (nmr) spectra were determined in carbon tetrachloride solution on a Varian Model A-60 spectrometer, using tetramethylsilane as the internal standard. Melting points were determined on a Thomas Hoover capillary melting point apparatus, in evacuated capillary tubes; melting and boiling points are uncorrected. Vapor phase chromatographic (vpc) analyses were performed on an Aerograph Model A-90-C instrument, using 5- and 8-ft × 0.25-in columns of silicone (GE SF 96) on Fluoropak or firebrick. Elemental analyses were performed by Mr. C. F. Geiger, Ontario, Calif., and by Elek Microanalytical Laboratories, Torrance, Calif. Tables I–III

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Table I. Substituted Δ^2-Thiazolines

	Δ^2-Thiazoline	Mp or bp (mm), °C	$n^{25}D$	Procedure[a]	Yield, %	Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
I	*cis*-2-Phenyl-4,5-dimethyl[b]	107 (2)	1.5837	C	37	69.06	6.85	7.32	69.35	6.52	7.25
II	*trans*-2-Phenyl-4,5-dimethyl	281 (736)[c,d]	1.5780	C	16	69.06	6.85	7.32	69.43	6.65	7.33
III	2-Phenyl-4,4,5,5-tetramethyl	293 (736)[c]	1.5638	D	73	71.18	7.81	6.39	70.99	7.91	5.92
				C	44						
IV	*cis*-2-Benzyl-4,5-dimethyl	123.5 (0.5)	1.5582	D	76	70.20	7.36	6.82	70.26	7.41	6.55
V	*trans*-2-*p*-Anisyl-4,5-dimethyl	33–35		E	11.5	65.12	6.83	6.33	65.20	6.91	6.42
VI	2-Methyl		1.5129	D	Trace						
VII	*cis*-2,4,5-Trimethyl[b]	69 (25)	1.4926	D	79	55.77	8.58		55.30	8.66	
				A[e]	40						
				B[e]	80						
				C	9.2						
				E	38.5						
VIII	*trans*-2,4,5-Trimethyl	158 (735)[c,f]	1.4798	C	6.7	55.77	8.58		55.37	8.77	
				A[e]	29						
IX	*trans*-2-*t*-Butyl-4,5-dimethyl	69–70 (14)	1.4699	D	31	63.10	10.00		62.99	9.92	
X	*trans*-2-Methyl-3a,4,5,6,7,7a-hexahydrobenzthiazole	89–90 (9)	1.5221	D	36	61.89	8.44		61.90	8.44	
				A[e]	59						

[a] Procedure as defined in the description of experimental results. [b] Mixtures of I and II and of VII and VIII were analyzed by vpc. Both mixtures exhibited two distinct but incompletely separated peaks. [c] Micro boiling point determination: R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 32. [d] Farkas and Sicher[3] report bp 155–158° (15 mm); Bach and Zahn[4] report bp 280–284°, stereochemistry not stated. [e] Isolated as the TNBS salt. In the case of VII, the TNBS salt was later converted to the free base, but only in 26% yield. [f] Smith and Sullivan[5] report bp 55–56 (25 mm), stereochemistry not stated.

Table II. Derivatives of Substituted Δ^2-Thiazolines

Thiazoline	Picrate Mp, °C	Picrate Calcd C	Picrate Calcd H	Picrate Found C	Picrate Found H	TNBS salt Mp, °C	TNBS salt Calcd C	TNBS salt Calcd H	TNBS salt Found C	TNBS salt Found H
I	140–141	48.57	3.84	48.98	3.76	193.5–195	42.14	3.33	42.07	3.16
II	139–140[a]	48.57	3.84	48.78	4.10	215–217	42.14	3.33	42.25	3.58
III	143–144	50.88	4.50	51.10	4.78	206–208	44.52	3.93	44.78	4.01
IV	127–128.5	49.76	4.18	49.95	4.37	174–175	43.37	3.64	43.18	3.64
V	177–179	48.00	4.03	48.08	4.22	205.5–207	42.02	3.53	42.00	3.69
VI	171–172[b]					217–218				
VII	151.5–152.5[c]	40.22	3.94	40.21	4.16	151.5–152.5[d,e]	34.12	3.34	34.36	3.57
						169–170				
VIII	174–175.5[f]	40.22	3.94	39.91	4.18	153–155[g]	34.12	3.34	34.12	3.57
IX	133–134	44.99	5.03	45.33	5.25	199–201	38.79	4.34	38.99	4.34
X	169.5–170.5					194–196[h]	37.50	3.52	37.86	3.90

[a] Farkas and Sicher[3] report mp 133°; Bach and Zahn[4] report mp 181–182°, stereochemistry not stated. [b] Gabriel and von Hirsch[1] report mp 171–172°. [c] Recrystallized from benzene–petroleum ether. [d] Double melting point; melted, resolidified, and melted again. [e] Osmometric equiv wt (in nitromethane), 218 (calcd 211). [f] Smith and Sullivan[5] report mp 170–172°, stereochemistry not stated. [g] Osmometric equiv wt (in nitromethane), 228 (calcd 211). [h] Osmometric equiv wt (in nitromethane), 230 (calcd 224).

summarize the procedures and analytical data for the Δ^2-thiazolines.

A. ***t*-Butyl 2,4,6-Trinitrobenzenesulfonate Procedure.** This method is illustrated by the preparation of *trans*-2-methyl-3a,4,5,6,7a-hexahydrobenzthiazole from cyclohexene sulfide and *t*-butyl 2,4,6-trinitrobenzenesulfonate (TNBS). A solution of *t*-butyl TNBS was prepared by dissolving 5.0 g (0.0095 mole) of silver TNBS trisacetonitrile solvate in 20 ml of nitromethane, adding 25 ml of methylene chloride, and adding a solution of 1.8 g (0.013 mole) of *t*-butyl bromide in 25 ml of methylene chloride with swirling. After 5 min the solution was decanted from the precipitated silver bromide, and the precipitate was washed with 5 ml of nitromethane. To the solution of *t*-butyl ester thus obtained a solution of 1.14 g (0.010 mole) of cyclohexene sulfide in 25 ml of methylene chloride was added with vigorous magnetic stirring. After stirring for 15 min, the reaction mixture was evaporated under vacuum to one-fourth its original volume. The product was precipitated by adding 100 ml each of ether and pentane, and cooling in an ice bath. The solid was isolated by filtration, washed with ether and pentane, and dried under vacuum. The solid, 2.50 g (59%), melted at 192–194°. After one recrystallization from warm nitromethane–ether the melting point was raised to 193–195°.

B. **2,4,6-Trinitrobenzenesulfonic Acid Procedure.** This procedure is shown by the preparation of *cis*-2,4,5-trimethyl-Δ^2-thiazoline *via* its TNBS salt. The **TNBS salt** was obtained by adding a solution of 0.88 g (0.01 mole) of *trans*-2-butene episulfide in 100 ml of 50% acetonitrile–methylene chloride to a solution of 3.2 g (0.011 mole) of trinitrobenzenesulfonic acid in 50 ml of 50% acetonitrile–methylene chloride, with vigorous stirring. After stirring 20 hr, the solvents were evaporated under vacuum to a few milliliters, and 75 ml each of ether and hexane were added. A yellow oil separated which partially crystallized in the freezer. After separating 0.55 g of crystals, additional crude material was obtained by evaporation of the solvent, giving a total of 3.35 g, 79.5%. After recrystallization from 95% ethanol, the salt melted at 150–151.5° without depression by mixture with the TNBS salt prepared from the free base. A solution of 2.00 g of the salt in 20 ml of 25% aqueous acetonitrile was made basic with 10% sodium hydroxide and extracted with ether. The ether extracts were washed with distilled water and dried over anhydrous potassium carbonate. Removal of ether under vacuum gave 0.16 g (26% from the salt) of *cis*-2,4,5-trimethyl-Δ^2-thiazoline, identified as the picrate.

C. **Perchloric Acid Procedure.** An example of this method is the synthesis of *cis*-2-phenyl-4,5-dimethyl-Δ^2-thiazoline. Benzonitrile (50 ml) was cooled in an ice bath, and 30 ml of 60% perchloric acid was added slowly with stirring. The solution was allowed to warm to room temperature, and a solution of 4.48 g (0.05 mole) of *trans*-2-butene episulfide in 10 ml of benzonitrile and 40 ml of methylene chloride was added slowly with vigorous stirring over a period of 1 hr. After addition was complete, the reaction mixture was stirred for an additional hour.

Table III. Nmr Spectra of Substituted Δ^2-Thiazolines

Thiazoline	Chem shift[a] (δ)	Splitting (J), cps	Area	Assignment
I	1.18	Doublet[b] (7)	6[c]	5-Methyl
	1.35	Doublet[b] (7)		4-Methyl
	3.81	Quintet	1	5-H
	4.37	Quintet	1	4-H
	7.2–7.5	Multiplet	3	Arom H
	7.7–8.0	Multiplet	2	Arom H
II	1.29	Doublet[b] (7)	6[c]	5-Methyl
	1.36	Doublet[b] (7)	..	4-Methyl
	3.48	Multiplet	1	5-H
	4.28	Multiplet	1	4-H
	7.2–7.5	Multiplet	3	Arom H
	7.7–8.0	Multiplet	2	Arom H
III	1.22	Singlet	6	5-Methyl
	1.35	Singlet	6	4-Methyl
	7.2–7.5	Multiplet	3	Arom H
	7.7–8.0	Multiplet	2	Arom H
IV	1.12	Doublet (7)	3	5-Methyl
	1.27	Doublet (7)	3	4-Methyl
	3.70	Doublet[b] (1.5)	3[c]	2-Methylene
	3.72	Multiplet[b]	..	5-H
	4.19	Multiplet	1	4-H
	7.22	Singlet	5	Arom H
V	1.28	Doublet[b] (7)	6[c]	5-Methyl
	1.38	Doublet[b] (7)	..	4-Methyl
	3.49	Multiplet	1	5-H
	3.76	Singlet	3	*p*-Methoxyl
	4.23	Multiplet	1	4-H
	6.82	Doublet (8.5)	2	Arom H
	7.75	Doublet (8.5)	2	Arom H
VII	1.18	Doublet[b] (6.5)	6[c]	5-Methyl
	1.27	Doublet[b] (6.5)	..	4-Methyl
	2.13	Doublet (2)	3	2-Methyl
	3.83	Multiplet[b]	2[c]	5-H
	4.18	Multiplet[b]	..	4-H
VIII	1.18	Doublet[b] (6.5)	6[c]	5-Methyl
	1.33	Doublet[b] (6.5)	..	4-Methyl
	2.12	Doublet (1.5)	3	2-Methyl
	3.42	Multiplet	1	5-H
	4.00	Multiplet	1	4-H
IX	1.18	Multiplet[d]	15	2-*t*-butyl, 4- and 5-methyl
	3.33	Multiplet	1	5-H
	4.03	Multiplet	1	4-H
X	1.2–2.8	Broad multiplet	8	4,5,6,7-H
	2.16	Doublet (1)	3	2-Methyl
	3.3	Multiplet	2	3a- and 7a-H

[a] In parts per million downfield from an internal tetramethylsilane standard; all spectra determined in carbon tetrachloride solution. [b] Overlapping peaks. [c] Total area of overlapping peaks. [d] This peak appears to be a singlet of large area superimposed on a peak of smaller area and greater splitting, possibly the overlapping doublets generally observed for the 4- and 5-methyl groups.

The reaction mixture was poured onto 200 g of ice, and 100 ml of ether was added. The layers were separated, and the organic layer was extracted three times with 100-ml portions of 10% aqueous hydrochloric acid. The combined acid extracts were made strongly basic with 50% aqueous sodium hydroxide, and the product was extracted with three 100-ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate. Removal of the ether under aspirator vacuum left 3.90 g of colorless oil. This was shown by vpc analysis to contain 91.5% thiazoline derivative and 8.5% benzonitrile. Distillation through a 10-cm Vigreux column gave a colorless liquid, bp 106.8–107.2° (2 mm).

D. Sulfuric Acid Procedure (Reactant Nitrile as Solvent). This procedure is demonstrated by the preparation of *cis*-2-benzyl-4,5-dimethyl-Δ^2-thiazoline. To 30 ml of phenylacetonitrile which had been cooled in an ice bath was added 20 ml of concentrated sulfuric acid with stirring (Caution: if the nitrile is not well cooled before adding the acid, an exothermic reaction may occur which results in a viscous reddish oil.) The solution was allowed to warm to room temperature, and a solution of 2.69 g (0.031 mole) of *trans*-2-butene episulfide was added slowly with vigorous stirring over a period of 1 hr. Isolation of the product was essentially the same as in C, except for removing 10.0 g of phenylacetamide which precipitated on neutralization of the acid extract. The pale yellow oil (6.01 g) remaining after removal of the ether was shown to contain 79% thiazoline derivative by vpc analysis. Distillation through a 10-cm Vigreux column gave, after a small forerun of phenylacetonitrile, a pure product, bp 123.2–123.8° (0.5 mm).

E. Sulfuric Acid Procedure (Dimethoxyethane as Solvent). This method is illustrated by the preparation of *trans*-2-*p*-anisyl-4,5-dimethyl-Δ^2-thiazoline. To 30 ml of 1,2-dimethoxyethane (DME), cooled in an ice bath, was added 15 ml of concentrated sulfuric acid slowly with stirring. After adding 10.0 g (0.07 mole) of *p*-anisonitrile, the solution was allowed to warm to room temperature, and a solution of 2.7 g (0.031 mole) of *cis*-2-butene episulfide in 10 ml of DME was added slowly with vigorous stirring over a period of 30 min. After stirring 15 min more, the mixture was cooled in an ice bath, and 30 ml of 50% aqueous sodium hydroxide was added, followed by 50 ml of distilled water. After filtering, the base was extracted with three 100-ml portions of hexane, the hexane solution was extracted three times with 10% aqueous hydrochloric acid, and the acid extracts were made strongly basic with 50% aqueous sodium hydroxide. Extraction with three 100-ml portions of hexane and removal of hexane under vacuum gave 0.94 g of white oil, shown by vpc to contain 83.5% thiazoline. Thus the yield was 0.79 g (11.5%). Microdistillation at 121–125° (1 mm) did not separate the base from remaining nitrile, but this was accomplished by vpc. The collected sample was sublimed twice at 74–79° (2 mm), giving a white powder, mp 33–35°.

trans-**2,4,5-Trimethyl-Δ^2-thiazoline.** A sample for comparison with the trimethylthiazolines from the episulfide reaction was prepared from thioacetamide and *cis*-2,3-dimethylaziridine. To 1.00 g (0.014 mole) of the freshly distilled imine in 15 ml of benzene was added 1.06 g (0.014 mole) of thioacetamide, and the mixture was refluxed 2.5 hr. Extraction with 10% aqueous hydrochloric acid, neutralization of the acid with excess 50% sodium hydroxide, and extracting the free base with ether gave, after removal of the ether under vacuum, 0.18 g (10%) of colorless liquid. This was identical with the *trans*-2,4,5-trimethyl-Δ^2-thiazoline obtained from the *cis*-2-butene episulfide, as shown by identical vpc retention times and no melting point depression between samples of the respective picrate and TNBS salts.

Thiazoline Salts. The picrates were prepared by adding an ether solution of the thiazoline to an excess of a saturated ether solution of picric acid. The precipitated salts were washed with ether and recrystallized four times from 95% ethanol.

The TNBS salts were prepared by adding a solution of the thiazoline in 95% ethanol to a solution of excess 2,4,6-trinitrobenzenesulfonic acid in 95% ethanol. The resulting solutions were heated to boiling, and the TNBS salts crystallized on cooling. The TNBS salts were recrystallized four times from 95% ethanol.

Acknowledgment. This work was supported in part by Grant GM-08185 from the National Institutes of Health, U. S. Public Health Service, and in part by a Public Health Service Fellowship, GM-20,764, to J. R. L. from the National Institute of General Medical Sciences.