

hours with 2 g. of bromoacetone. The crude quaternary salt XVI was precipitated by the addition of ether, the filtrate concentrated, and more product precipitated by addition of ethyl acetate. The quaternary salt XVII recrystallized from ethanol and ether yielded 0.8 g., m.p. 202–205°. By continuing the reflux period for an additional 46 hours it was possible to obtain another 0.35 g. of the salt XVII, making the total yield 1.15 g. (62%). The analytical sample was obtained from ethanol–ether as colorless plates, m.p. 204.5–207.5°.

*Anal.* Calcd. for  $C_{14}H_{14}BrNO_2 \cdot \frac{1}{2}H_2O$ : C, 53.01; H, 4.77; N, 4.42. Found<sup>10</sup>: C, 53.01; H, 4.77; N, 4.47.

**1-Hydroxy-7-methylphenanthridizinium Bromide (XVIII).**—A solution of 1.125 g. of 1-acetyl-3-hydroxy-2-phenylpyridinium bromide (XVII) in 15 ml. of 48% hydrobromic acid was refluxed for 50 hours. Isolated in the usual way, 0.875 g. (85%) of light tan product, m.p. 306–313° dec. (cor.), was obtained. The analytical sample crystallized from ethanol as a cream-colored powder, m.p. 310–313° dec. (cor.);  $\lambda_{max}$  230, 283, 309, 342, 357 and 375  $m\mu$ ;  $\lambda_{min}$  256, 304, 331, 345 and 365  $m\mu$ .

*Anal.* Calcd. for  $C_{14}H_{12}NOBr$ : C, 57.94; H, 4.17; N, 4.83. Found<sup>10</sup>: C, 57.58; H, 4.12; N, 4.52.

The picrate was obtained as yellow crystals from ethanol, m.p. 244–247.5°, which appeared to be solvated.

*Anal.* Calcd. for  $C_{20}H_{14}N_4O_8 \cdot C_2H_5O$ : C, 54.54; H, 4.16. Found<sup>10</sup>: C, 54.77; H, 3.99.

**10-Methoxy-7-methylphenanthridizinium Picrate (XV).**<sup>12</sup>—The quaternization of 2-(3-methoxyphenyl)pyridine<sup>13</sup> with iodoacetone (III) was carried out at room temperature over a period of 10 days. The iodide XIV was converted to the chloride in the usual way and cyclization was effected by refluxing the salt for 3 minutes with 48% hydrobromic acid. The product which was recrystallized from alcohol and obtained in an over-all yield of 50% is believed to be 10-methoxy-7-methylphenanthridizinium bromide, m.p. 283° dec. The bromide was converted to the picrate XV which crystallized from acetone as very fine yellow needles, m.p. 232–234° dec.<sup>14</sup>

*Anal.* Calcd. for  $C_{21}H_{16}N_4O_8$ : C, 55.75; H, 3.57. Found: C, 55.58; H, 3.52.

**1-Acetyl-2-(3-methoxyphenyl)pyridinium Picrate (XV).**—A sample of the crude 1-acetyl-2-(3-methoxyphenyl)pyridinium iodide obtained in the previous experiment was converted to the picrate XV which formed feathery yellow needles, m.p. 150–150.5°<sup>14</sup> (with previous softening).

*Anal.* Calcd. for  $C_{21}H_{18}N_4O_8$ : C, 53.62; H, 3.85. Found: C, 53.84; H, 3.79.

(12) This preparation as well as that following was carried out by Dr. Leo E. Beavers.

(13) J. W. Haworth, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, 358 (1940).

(14) Capillary melting point (uncorrected).

DURHAM, N. C.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS COMPANY]

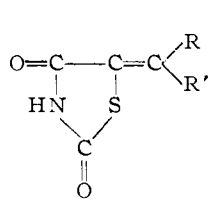
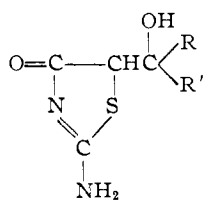
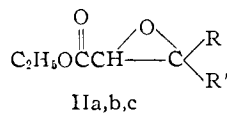
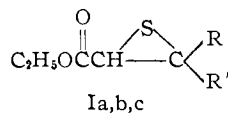
## The Reaction of Glycidic Esters with Thiourea in Aqueous Sulfuric Acid Solution

BY JOHN A. DURDEN, JR., HARRY A. STANSBURY, JR., AND WILLIAM H. CATLETTE

RECEIVED SEPTEMBER 27, 1958

The reaction of glycidic esters with thiourea has been studied in the presence of aqueous sulfuric acid. With ethyl 2,3-epoxy-3-methylvalerate the reaction proceeded to form ethyl 2,3-epithio-3-methylvalerate in low yield. This is apparently the first reported synthesis of an  $\alpha,\beta$ -epithioester. The reaction proceeded with less substituted glycidic esters to produce either 2-amino-2-thiazolin-4-ones or the dihydroxyesters resulting from hydration of the epoxide. The probable mechanisms involved in the formation of these products are discussed.

Recent work in this Laboratory has made the preparation of  $\alpha,\beta$ -epithioesters (I) from the corresponding glycidic esters (II) of interest. Apparently no  $\alpha,\beta$ -epithioester has been described, but



a, R = CH<sub>3</sub>, R' = H; b, R = R' = CH<sub>3</sub>; c, R = CH<sub>3</sub>, R' = C<sub>2</sub>H<sub>5</sub>

several syntheses of episulfides from epoxides have been reported in the literature.<sup>1–4</sup>

Culvenor, *et al.*,<sup>2</sup> have reported the synthesis of episulfides by the reaction of epoxides with thiourea

(1) E. E. van Tamelen, *THIS JOURNAL*, **73**, 3444 (1951).

(2) C. C. J. Culvenor, W. Davies and W. E. Savidge, *J. Chem. Soc.*, 4480 (1952).

(3) F. G. Bordwell and H. M. Anderson, *THIS JOURNAL*, **75**, 4959 (1953).

(4) C. C. J. Culvenor, W. Davies and K. H. Pausacker, *J. Chem. Soc.*, 1050 (1946).

in either anhydrous or aqueous methanol. A group led by Culvenor<sup>5</sup> has also reported an attempted synthesis of Ib by action of thiourea on ethyl 2,3-epoxy-3-methylbutyrate (IIb). The product obtained in the reaction was shown by them to be 2-amino-5-(1-hydroxy-1-methylethyl)-2-thiazolin-4-one (IIIb).

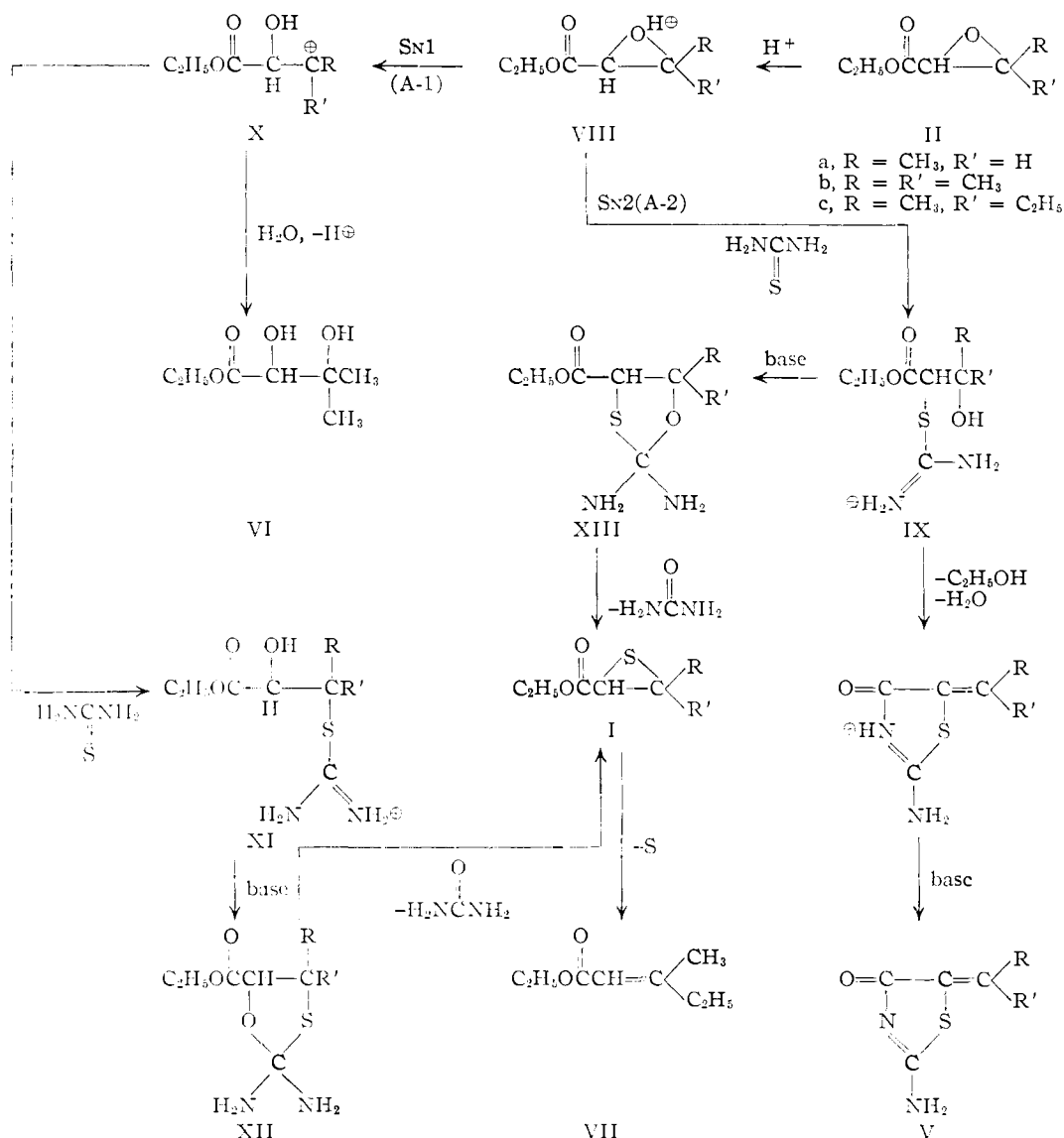
Bordwell and Anderson<sup>3</sup> have shown that the use of mineral acid in the reaction of thiourea with epoxides followed by neutralization of the reaction mixture with base resulted in enhanced yields of episulfides.

### Discussion and Results

The application of the method of Bordwell and Anderson<sup>3</sup> to the preparation of  $\alpha,\beta$ -epithioesters from glycidic esters has now been studied. Using the alkyl-substituted glycidic esters, ethyl 2,3-epoxybutyrate (IIa), ethyl 2,3-epoxy-3-methylbutyrate (IIb) and ethyl 2,3-epoxy-3-methylvalerate (IIc), three different types of products were formed.

When ethyl 2,3-epoxybutyrate (IIa) was treated with thiourea-sulfuric acid mixture there was obtained, as the only isolable product, a white solid which was shown to be 2-amino-5-ethylidene-2-thiazolin-4-one (Va). This compound was synthe-

(5) C. C. J. Culvenor, W. Davies, J. A. MacLaven, P. F. Nelson and W. E. Savidge, *ibid.*, 2573 (1949).



sized alternatively by the action of thiourea in methanol on ethyl 2,3-epoxybutyrate to yield 2-amino-5-(1-hydroxyethyl)-2-thiazolin-4-one (IIIa), which was then dehydrated in acetic acid to form Va. Compound IIIa was very similar to the well characterized compound (IIIb) in infrared and ultraviolet spectra (see Tables I and II). Refluxing Va with aqueous hydrochloric acid gave rise to 5-ethylidene-2-thiazolidine-2,4-dione (IVa).

When the method of van Tamelen,<sup>1</sup> involving the action of potassium thiocyanate on epoxides, was applied to alkyl 2,3-epoxybutyrate (IIa), there was obtained a dark red oil which decomposed upon attempted distillation.

Reaction of ethyl 2,3-epoxy-3-methylbutyrate (IIb) with thiourea-acid mixture under similar conditions produced, instead of the desired episulfide Ib, a colorless liquid which was shown to be ethyl 2,3-dihydroxy-3-methylbutyrate (VI).<sup>6</sup> Also isolated was a small amount of crystalline product identified as 2-amino-5-isopropylidene-2-thiazolin-

4-one (Vb) by analysis and by comparison with an authentic sample (prepared by dehydration of IIIb in acetic acid).<sup>5</sup>

Finally, the reaction of ethyl 2,3-epoxy-3-methylvalerate (IIc) with thiourea-acid mixture produced the desired ethyl 2,3-epithio-3-methylbutyrate (Ic) along with some ethyl 3-methyl-2-pentenoate (VII). The unsaturated ester was probably formed by desulfurization of the epithioester.<sup>5</sup>

The products obtained in these three cases are explained by the equations in the diagram.

The initial step in the series of reactions leading to the various products was undoubtedly protonation of the epoxide oxygen in II to form the intermediate VIII. This oxonium ion could then react in one of two ways, by an  $S_N2(A-2)$  mechanism with thiourea to yield IX or by an  $S_N1(A-1)$  mechanism to yield products *via* the carbonium ion X. Long and Pritchard<sup>7</sup> have shown that the acid-catalyzed hydrolysis of epoxides probably proceeds by an A-1 mechanism. The results of the present work make

(6) I. N. Nazarov and A. A. Akhrem, *Zhur. Obshchei Khim.*, **26**, 1186 (1956).

(7) F. A. Long and J. G. Pritchard, *THIS JOURNAL*, **78**, 2665 (1956); J. G. Pritchard and F. A. Long, *ibid.*, **78**, 2667, 6008 (1956).

it apparent that glycidic esters react with thiourea in sulfuric acid either by an A-1 or an A-2 mechanism, depending on the structure of the glycidic ester. In the glycidic ester system, SN2(A-2) attack alpha to the carbonyl group will be enhanced and may become a competing reaction when the alternative SN1(A-1) mechanism involves a secondary carbonium ion. The formation of Va from VIIa indicates that the SN2(A-2) path is being followed.

Ethyl 2,3-epoxy-3-methylbutyrate (IIb) appeared to react primarily by an A-1 mechanism involving the tertiary carbonium ion Xb. Reaction of this ion with water, the most readily available but not the strongest nucleophile, would then yield the dihydroxyester VI. In our work the A-2 reaction competed to some extent with the A-1, since a small yield of 2-amino-5-isopropylidene-2-thiazolin-4-one (Vb) was also isolated in addition to the dihydroxyester (VI).

Finally, ethyl 2,3-epoxy-3-methylvalerate (IIc), under these reaction conditions yielded Xc, most probably by an A-1 mechanism. This carbonium ion apparently showed more discrimination than Xb and reacted at least partially with thiourea instead of water to form the isothiuronium salt (XI) which upon treatment with base cyclized to the 1,3-oxathiolane (XII). Formation of episulfide Ic could then occur by decomposition of XII.

The relative stability of the carbonium ion Xc arising from ethyl 2,3-epoxy-3-methylvalerate as compared with the ion Xb derived from ethyl 2,3-epoxy-3-methylbutyrate may be rationalized partially by analogy to certain investigations described in the literature.<sup>8-12</sup>

In Tables I and II there are listed the infrared and ultraviolet absorption maxima for the thiazol-

TABLE I  
ULTRAVIOLET ABSORPTION MAXIMA OF THIAZOLINES AND THIAZOLIDINES<sup>a</sup>

Compound	Absorption $\lambda_{\max}$ , m $\mu$	$\epsilon$
2-Amino-2-thiazolin-4-one <sup>13</sup> (XIV)	220	14,803
	250	6,579
2-Amino-5-(1-hydroxyethyl)-2-thiazolin-4-one (IIIa)	249	9,576
2-Amino-5-ethylidene-2-thiazolin-4-one (Va)	255	21,507
	295	7,553
5-Ethylidene-thiazolidine-2,4-one (IVa)	277	4,826
2-Amino-5-(1-hydroxy-1-methylethyl)-2-thiazolin-4-one (IIIb)	250	9,500
	295	1,966
2-Amino-5-isopropylidene-2-thiazolin-4-one <sup>5</sup> (Vb)	257	23,186
	295	11,686

<sup>a</sup> Determined on a Beckman DK-2 instrument.

linone derivatives prepared in this work. These are compared with the maxima for 2-amino-2-thiazolin-4-one, a known compound. The comparison supports the assigned structures.

(8) C. G. Swain, C. B. Smith and K. H. Lohman, *THIS JOURNAL*, **75**, 136 (1953).

(9) L. C. Bateman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 960 (1940).

(10) A. Streitwieser, *Chem. Revs.*, **56**, 614 (1956).

(11) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 316.

(12) K. A. Cooper, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1280 (1937); E. D. Hughes and B. J. MacNulty, 1283 (1937).

(13) C. F. H. Allen and J. A. Van Allan, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 751.

TABLE II

INFRARED ABSORPTION OF THIAZOLINES AND THIAZOLIDINES<sup>a</sup>

Compound	Band maxima in microns				
	-OH	-NH	C=O	$\overset{\ominus}{\text{S}}-\overset{\oplus}{\text{N}}$	C=C
2-Amino-2-thiazolin-4-one <sup>13</sup> (XIV)	..	3.1	6.04	6.6	..
2-Amino-5-(1-hydroxyethyl)-2-thiazolin-4-one (IIIa)	3.15 8.9	3.15	6.03	6.6	..
2-Amino-5-ethylidene-2-thiazolin-4-one (Va)	..	3.13	5.97	6.60	6.10
5-Ethylidene-thiazolidine-2,4-dione (IVa)	..	3.19	5.90 <sup>b</sup> 5.74	..	6.13
2-Amino-5-(1-hydroxy-1-methylethyl)-2-thiazolin-4-one (IIIb)	2.72 8.37	3.13	6.04	6.65	..
2-Amino-5-isopropylidene-2-thiazolin-4-one <sup>5</sup> (Vb)	..	3.10	6.00	6.6	6.17

<sup>a</sup> Determined on a Baird atomic 4-55 instrument with NaCl optics. <sup>b</sup> This is an hydantoin type of structure. The 4-carbonyl is assigned the shorter wave length, while the 2-carbonyl is assigned the longer.<sup>14</sup>

Ethyl 2,3-epithio-3-methylvalerate prepared in this work is apparently the first reported example of an  $\alpha,\beta$ -epithioester.

### Experimental

**2-Amino-5-ethylidene-2-thiazolin-4-one (Va).**—To a cooled mixture of 40 g. (0.5 mole) of thiourea and 15 ml. (0.25 mole) of sulfuric acid was added dropwise with stirring 65 g. (0.15 mole) of ethyl 2,3-epoxybutyrate at such a rate that the temperature remained between 0 and 10°. After the addition was complete, the reaction mixture was stirred for 10 minutes and allowed to stand at room temperature overnight. Then 53 g. (0.5 mole) of sodium carbonate in 250 ml. of water was added with stirring. After 30 minutes, the solid which separated during addition of the base was collected on a filter, washed with water, and air-dried to give 34 g. (48%) of crude product, m.p. 230–234° dec. Recrystallization from alcohol gave 16.5 g. (23%) of white crystalline product, m.p. 234–235°. It was subsequently found that water is a better recrystallization solvent giving a product of m.p. 240–241° dec.

*Anal.* Calcd. for C<sub>5</sub>H<sub>9</sub>N<sub>2</sub>OS: C, 42.24; H, 4.25; N, 19.71; S, 22.56. Found: C, 41.53; H, 3.98; N, 19.41; S, 22.56.

**5-Ethylidene-thiazolidine-2,4-dione (IVa).**—A solution of 4 g. (0.03 mole) of Va in 20 ml. of water containing 10 ml. of 37% hydrochloric acid was heated at reflux for about two hours. Cooling in an ice-bath gave 3.8 g. (95%) of white shiny plates. This material was dissolved in a small amount of 10% sodium hydroxide solution, reprecipitated by addition of acetic acid, chilled, and the solid collected on the filter. Recrystallization from water gave 2.5 g. (63%) of shiny white plates, m.p. 115–119°.

*Anal.* Calcd. for C<sub>5</sub>H<sub>7</sub>NO<sub>2</sub>S: C, 41.95; H, 3.53; N, 9.78; S, 22.40. Found: C, 41.74; H, 3.64; N, 10.09; S, 22.37.

**2-Amino-5-(1-hydroxyethyl)-2-thiazolin-4-one (IIIa).**—A mixture of 65 g. (0.5 mole) of ethyl 2,3-epoxybutyrate and 39 g. (0.5 mole) of thiourea in 200 ml. of methanol was allowed to stand at room temperature for two weeks. The mixture was then chilled and the solid which had formed on standing was collected on the filter to give 32 g. (49%) of product, m.p. 162–163°. A small amount of this material was recrystallized from ethanol and air-dried, m.p. 157–158°.

*Anal.* Calcd. for C<sub>5</sub>H<sub>9</sub>N<sub>2</sub>O<sub>2</sub>S: C, 37.49; H, 5.03; N, 17.49; S, 20.02. Found: C, 37.62; H, 5.14; N, 16.47; S, 20.50.

(14) H. M. Randall, R. G. Fowler, N. Fuson and J. R. Douglass, "Infrared Determination of Organic Structures," Van Nostrand Co., Inc., Princeton, N. J., 1949, p. 11.

A solution of 17 g. (0.106 mole) of IIIa was heated on the steam-bath in 40 ml. of acetic acid until a solid began to separate. This suspension was allowed to stand at room temperature overnight and the product was then collected on the filter and air-dried to give 16.5 g. (100%) of colorless crystals. The latter was recrystallized from two liters of ethanol to give 11 g. (67%) of a white solid, m.p. 231–233° dec. Comparison of the infrared and ultraviolet spectra showed this product to be identical with 2-amino-5-ethylidene-2-thiazoline-4-one (Va).

A solution of 4 g. of product Va was heated at reflux for 3 hours in 30 ml. of water containing 7 ml. of concentrated hydrochloric acid. The mixture was chilled and filtered to obtain 3.2 g. (80%) of white crystalline product of m.p. 115–117°. The mixed m.p. with an authentic sample of 5-ethylidene-2-thiazolidin-2,4-dione (IVa) showed no depression.

**Reaction between Ethyl 2,3-Epoxy-3-methylbutyrate (IIb), Thiourea and Sulfuric Acid.**—Ethyl 2,3-epoxy-3-methylbutyrate (72 g., 0.5 mole) was treated with 40 g. (0.5 mole) of thiourea and 15 ml. (0.25 mole) of sulfuric acid following a procedure analogous to that used in the synthesis of Va. Neutralization gave a solid and an oil. The solid was collected on the filter, and recrystallized from water to give 2 g. (2%) of 2-amino-5-isopropylidene-2-thiazolin-4-one (Vb), m.p. 262–270° dec. Direct comparison of the infrared and ultraviolet spectra showed it was identical with the compound first prepared by Culvenor, *et al.*<sup>5</sup>

*Anal.* Calcd. for C<sub>8</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S: C, 46.13; H, 5.16; N, 17.79; S, 20.52. Found: C, 46.87; H, 5.23; N, 18.30; S, 20.24.

The oil from the above filtrate was extracted with methylene chloride, the solution dried over sodium sulfate and distilled twice to give ethyl 2,3-dihydroxy-3-methylbutyrate (VI), b.p. 70–71° (1.2 mm.), *n*<sub>D</sub><sup>20</sup> 1.4391 (reported<sup>6</sup> b.p. 70–71° (2 mm.), *n*<sub>D</sub><sup>20</sup> 1.4415).

*Anal.* Calcd. for C<sub>7</sub>H<sub>14</sub>O<sub>4</sub>: C, 51.84; H, 8.70. Found: C, 52.04; H, 8.87.

The infrared spectrum supported the assigned structure. The yield of dihydroxy ester was 28 g. (35%).

A sample of Vb was refluxed in 10% hydrochloric acid solution to form 5-isopropylidene-2-thiazolidin-2,4-dione (IVb).<sup>5</sup>

**Ethyl 2,3-Epithio-3-methylvalerate (Ic).**—A mixture of thiourea (23.4 g., 0.3 mole) and sulfuric acid (9 g., 0.3 equiv.) in 70 ml. of water was cooled at 0–10° and 47.4 g. (0.3 mole) of ethyl 2,3-epoxy-3-methylvalerate was added dropwise with stirring at such a rate that the temperature remained under 20° (about one hour). The mixture was stirred at room temperature for 20 hours and then treated with 0.3 mole of sodium carbonate in 70 ml. of water. The oil was separated and the aqueous layer extracted exhaustively with methylene chloride and ethyl ether. The organic layers were combined and fractionated to yield 6 g. (16%) of ethyl 3-methyl-2-pentenoate (VII), b.p. 51–71° (7 mm.), *n*<sub>D</sub><sup>23</sup> 1.4323. Identification was made by both infrared and mass spectrometric studies; mol. wt. calcd., 142; found by mass spectrograph, 142. Nine grams (17%) of ethyl 2,3-epithio-3-methylvalerate (Ic), b.p. 77–79° (7 mm.), *n*<sub>D</sub><sup>23</sup> 1.4683 was isolated. *Anal.* Calcd. for C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>S: C, 55.14; H, 8.10; S, 18.84; mol. wt., 174. Found: C, 55.18; H, 8.04; S, 17.59; mol. wt., by ebullioscopy (acetone), 169 ± 5%; by mass spectrograph 174. The infrared spectrum supported the assigned structure.

**Acknowledgments.**—The authors gratefully acknowledge the mass spectrometric analyses performed by Mr. H. R. Harless and the infrared and ultraviolet absorption studies conducted by Dr. H. F. White and Mr. C. M. Lovell. They also wish to thank Dr. Harry Wasserman of Yale University for his helpful advice in the preparation of this paper.

SOUTH CHARLESTON, W. VA.

[CONTRIBUTION FROM THE SECTION ON ENZYMES, LABORATORY OF CELLULAR PHYSIOLOGY, NATIONAL HEART INSTITUTE, NATIONAL INSTITUTES OF HEALTH]

## Bacterial Degradation Products of Riboflavin. III. Isolation, Structure Determination and Biological Transformations of 1-Ribityl-2,3-diketo-1,2,3,4-tetrahydro-6,7-dimethylquinoxaline

By H. TODD MILES, P. Z. SMYRNIOTIS AND E. R. STADTMAN

RECEIVED SEPTEMBER 25, 1958

A new compound, C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>, has been isolated as a bacterial degradation product of riboflavin and shown to be 1-ribityl-2,3-diketo-1,2,3,4-tetrahydro-6,7-dimethylquinoxaline. This compound is in turn converted to the 3,4-dimethyl-6-carboxy- $\alpha$ -pyrone isolated previously.

Previous work in this study of the bacterial degradation of riboflavin showed that riboflavin is converted by anaerobic bacteria to 6,7-dimethyl-9-(2'-hydroxyethyl)-isoalloxazine and to free radical, quinhydrone-like complexes of the same compound.<sup>1a,2</sup>

During the oxidation of riboflavin to carbon dioxide and ammonia by an aerobic organism isolated from soil, a number of compounds accumulate in the culture medium as transitory degradation products. Absorption spectroscopy and paper chromatography of aliquots of the culture medium at various stages of growth reveal the appearance in early

(1) (a) Preceding papers, H. T. Miles and E. R. Stadtman, *THIS JOURNAL*, **77**, 6747 (1955); (b) P. Z. Smyrniotis, H. T. Miles and E. R. Stadtman, *ibid.*, **80**, 2541 (1958).

(2) The authors are indebted to Dr. Edwin Becker for electron spin resonance measurements which confirm the free radical nature of the solid complexes isolated earlier.<sup>1a</sup>

phases of growth of numerous substances which later disappear after the riboflavin has all been consumed. Among the substances that appear in the early phases are two strongly blue fluorescent compounds and a "quenching" compound that can be detected on paper chromatograms when viewed under ultraviolet light. With paper chromatography in a solvent system composed of butanol-acetic acid-water (160:40:75) the blue fluorescent compounds have *R<sub>f</sub>* values of 0.58 (compound I) and 0.78 (compound II), and the "quenching" (compound III) has an *R<sub>f</sub>* of 0.92. The isolation of III and its identification as 3,4-dimethyl-6-carboxy- $\alpha$ -pyrone was previously reported.<sup>1b</sup> Compounds I and II have been isolated as pure substances and are found to have identical absorption spectra<sup>4</sup>; the elemental composition of II (C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>) was reported in a preliminary communi-