

calculations were carried out with the X-ray 76 system<sup>8</sup> on a UNIVAC 1100/82 computer. The least-squares structure refinement minimized  $\sum w(F_o - F_c)^2$ ,  $w = 1/\sigma^2(F_o)$ . Anisotropic temperature factors were used for carbon, nitrogen, and oxygen. The framework hydrogen atoms were placed in calculated positions at distances of C-H = 1.03 Å and N-H = 1.00 Å. Only the hydrogen temperature factors were refined. The methyl group hydrogens were not included in the calculations. The final  $R$  ( $\sum [F_o - F_c]/\sum F_o$ ) and weighted  $R$  ( $\sum (F_o L - F_c)^2 / \sum (F_o)^2$ )<sup>1/2</sup> are 0.074 and 0.087. Tables of atomic coordinates and temperature factors are included with the supplementary material.

(8) Stewart, J. M.; Machin, P. A.; Dickinson, C.; Ammon, H. L. "The XRAY System-Version of 1976", Tech. Rep. 446, Computer Science Center; University of Maryland, 1976.

**Acknowledgment.** Support for these studies by grants from NIH (GM-29016) and the University of Maryland Computer Science Center is acknowledged. The 200-MHz NMR spectrometer used in this research was purchased in part by funds derived in part from an NSF grant. The kind assistance provided by Dr. Kenneth B. Seaman in recording 400-MHz NMR spectra is gratefully appreciated.

**Registry No.** 1, 90693-43-9; 6, 90623-26-0; 8, 90693-44-0; 9, 90605-67-7; *tert*-butyl propiolate, 13831-03-3.

**Supplementary Material Available:** Tables of atomic coordinates and temperature factors (2 pages). Ordering information is given on any current masthead page.

## 1,1-Dichloroethyl Hydroperoxide and 1,1-Dichloroethyl Peroxide Ion as Intermediates in the Ozonolysis of 2,3-Dichloro-2-butene<sup>†</sup>

Siegmar Gäb\* and Walter V. Turner

*Institut für Ökologische Chemie der Gesellschaft für Strahlen- und Umweltforschung mbH München, D-8050 Freising-Weihenstephan, Federal Republic of Germany*

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On the basis of its spectroscopic and chemical properties, an unstable intermediate previously detected in the ozonolysis of *trans*-2,3-dichloro-2-butene (1) in inert solvents is reformulated as 1,1-dichloroethyl hydroperoxide (5). Ozonolysis of 1 in ethyl formate saturated with anhydrous HCl leads to high yields of this intermediate. 1,1-Dichloroethyl peroxide ion (10), rather than 5, is believed to be the precursor of acetyl 1,1-dichloroethyl peroxide (8), which is produced in higher yield on ozonolysis of 1 in the presence of tetraalkylammonium chloride.

### Introduction

In a very thorough study of the ozonolysis of *trans*-2,3-dichloro-2-butene (1) in nonparticipating solvents, Griesbaum and Hofmann<sup>1</sup> have identified most of the products of the reaction, examined the influence of various solvents, and proposed a reaction scheme. An unstable species was observed in the <sup>1</sup>H NMR spectra of the fresh ozonolysis mixture as a singlet at  $\delta$  2.33; 3,5-dichloro-3,5-dimethyl-1,2,4-trioxolane (4), considered to arise by addition of the carbonyl oxide 2 to acetyl chloride (3) in analogy with the Criegee mechanism,<sup>2</sup> was suggested as a likely structure for this intermediate.

We have found that a number of 3,5-dichlorinated 1,2,4-trioxolanes derived from bi- or tricyclic olefins are stable enough to be isolated by column chromatography and be characterized by the usual analytical methods (NMR, IR, elemental analyses).<sup>3</sup> Although the trioxolane from 1,2-dichloroacene decomposes at temperatures as low as 0 °C with loss of chlorine to naphthalic anhydride, the decomposition of the other trioxolanes, which also yield the corresponding anhydrides, begins only in the region of their melting points ( $T > 100$  °C). Decomposition of the unstable species with  $\delta$  2.33 from 1 to acetic anhydride is not observed.

The species at  $\delta$  2.33 is reported to react with 3 and trideuterioacetyl chloride to produce 1,1-dichloroethyl peresters.<sup>1</sup> Although such a reaction of trioxolanes would be unprecedented, it is typical of the reaction of acid chlorides with hydroperoxides. On the basis of these observations, we have re-examined the ozonolysis of 1, with

emphasis on the properties of the unstable intermediate. Considerable evidence has been adduced that this intermediate is not the trioxolane 4, but 1,1-dichloroethyl hydroperoxide (5).

### Results and Discussion

The unstable species was found in very low yield, except in methyl formate, where it amounted to 18–20% of the total <sup>1</sup>H NMR signal intensity.<sup>1</sup> We found similar yields in ethyl formate. Because the formation of 5 requires the addition of HCl to the carbonyl oxide 2 (eq 3), we ozonized 1 in ethyl formate saturated with anhydrous HCl and obtained a 1:1 ratio of 3 and the unstable species with  $\delta$  2.33.<sup>4</sup> No other products were detected by NMR. This fact in itself speaks strongly for structure 5, since it is difficult to understand how the presence of HCl could lead to increased yields of 4. Careful removal of the solvent and

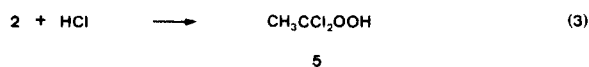
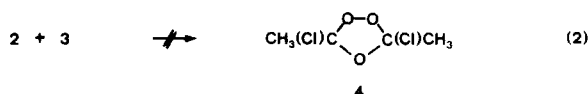
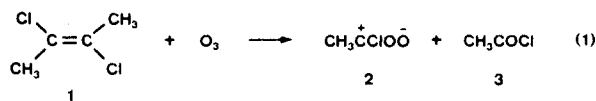
(1) Griesbaum, K.; Hofmann, P. *J. Am. Chem. Soc.* 1976, 98, 2877–2881.

(2) Criegee, R. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 745–752.

(3) Gäb, S.; Nitz, S.; Parlar, H.; Korte, F. *Angew. Chem., Int. Ed. Engl.* 1976, 15, 433. Gäb, S.; Nitz, S.; Parlar, H.; Korte, F. *Chem. Ber.* 1978, 111, 1440–1445. Seltzer, H.; Gäb, S.; Korte, F. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 474–475.

(4) Identical results were obtained with the *cis* isomer of 1. The <sup>1</sup>H resonance of the unstable intermediate appears at  $\delta$  2.32–2.33 in mixtures of ethyl formate and CDCl<sub>3</sub>, but at  $\delta$  2.34–2.35 in CDCl<sub>3</sub> alone. One of the referees questioned whether we could distinguish between direct attack by HCl on either a primary or a normal ozonide and attack on the carbonyl oxide to yield 5. We have not been able to detect any reaction of HCl with several chlorinated normal ozonides. Reaction of HCl with the primary ozonide cannot be excluded, but it should be pointed out that Bailey and Carter were able to show that in at least one case the reaction to form a methoxy hydroperoxide does not involve direct attack of methanol on the primary ozonide. (Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1982; Vol. I, p 111.)

<sup>†</sup> Dedicated to Professor F. Korte on the occasion of his sixtieth birthday.

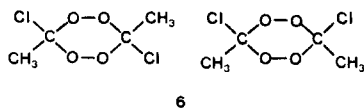


**3** from the mixture under vacuum at temperatures of  $-10$  to  $0^\circ\text{C}$  provided a convenient source of the species free from other reactive substances.

It remains unclear why higher yields of the unstable species are obtained in formate esters, even in the initial absence of HCl. Perhaps these solvents are themselves not truly inert toward **2** and react to produce some HCl by an as yet undiscovered route.

Ozonolysis mixtures rich in the unstable species were examined by low-temperature  $^{13}\text{C}$  NMR. Two resonances were present which could not be assigned to other components of the mixture:  $\delta$  34.66 and 114.01. For comparison with these resonances, we examined several other peroxidic products from the ozonolysis of **1** in  $\text{CH}_2\text{Cl}_2$ .

The tetroxane with a  $^1\text{H}$  resonance at  $\delta$  2.05 (**6a**), characterized by Griesbaum and Hofmann, has  $^{13}\text{C}$  resonances at  $\delta$  26.12 and 118.72. A second nonpolar substance was found to give a  $^1\text{H}$  singlet at  $\delta$  2.11 and  $^{13}\text{C}$  resonances at  $\delta$  25.50 and 121.50. Both compounds decompose



thermally to yield diacetyl peroxide (**7**).<sup>5</sup> On the basis of these similarities with each other, we believe the second compound is a stereoisomer of **6a**, but no specific assignment has been made. The fact that no second isomer of the species with  $\delta$  2.33 can be detected argues further that this species is not **4**, but **5**.

The perester **8** has  $^{13}\text{C}$  resonances at  $\delta$  166.28 (C=O), 111.24 ( $\text{CCl}_2$ ), 34.34 ( $\text{CH}_3\text{CCl}_2$ ), and 17.10 ( $\text{CH}_3\text{CO}$ ). A series of related acyl and aroyl peresters which we have prepared<sup>6</sup> have almost identical methyl resonances for the  $\text{CH}_3\text{CCl}_2\text{OO}$  group ( $\delta$  34.3–34.7). The  $\text{CH}_3$  resonance of the unstable species is obviously much more like those of the 1,1-dichloroethyl peresters than those of the tetroxanes at ca.  $\delta$  26.

In the presence of benzyltriethylammonium chloride, the resonances of acetic acid and of the unstable species are shifted upfield as much as 0.06–0.10 ppm. Similar results are observed for several other hydroxy compounds, but methyl formate, **3**, **6a**, **6b**, and **8** are not shifted more than 0.01 ppm. This is further evidence that the unstable species is hydroxylic.

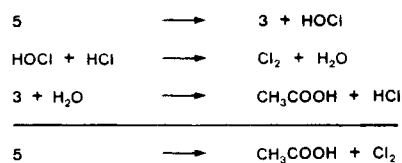
At temperatures near  $0^\circ\text{C}$ , the unstable intermediate reacts slowly with **3** to yield acetyl 1,1-dichloroethyl peroxide (**8**).<sup>7</sup> On standing in solution at room temperature, however, the unstable intermediate decomposes over sev-

(5) Both **6a** and **6b** are too stable to be the source of the small amount of **7** observed in most ozonolyses. Perhaps this **7** arises from reaction of peracetic acid and acetyl chloride.

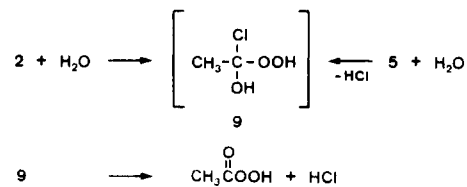
(6) Gáb, S.; Turner, W. V.; Hellpointner, E.; Korte, F., article in preparation.

(7) Nevertheless, the rate of this reaction is probably too low to account for the amount of **8** reported from ozonolyses at  $-30^\circ\text{C}$ .<sup>1</sup> Under those conditions, **8** may arise from the ion **10**, as described below.

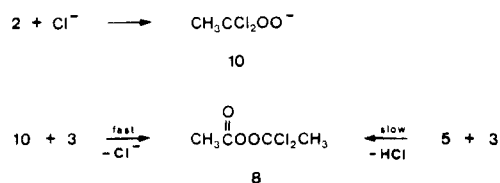
## Scheme I



## Scheme II



## Scheme III



eral hours to give acetic acid; even in the presence of a large excess of **3** only traces of **8** are formed. Griesbaum and Hofmann have shown that  $\text{Cl}_2$  is also produced in this decomposition. Huh et al.<sup>8</sup> proved that HOCl is formed in the ozonolysis of **1** in methanol, and it is reasonable to expect **5** to yield HOCl, which with catalytic amounts of HCl, as in Scheme I, would lead to acetic acid and  $\text{Cl}_2$  as end products.

When a drop of  $\text{H}_2\text{O}$  is shaken with a  $\text{CDCl}_3$  solution of the unstable species in the absence of **3**, the resonance at  $\delta$  2.34 disappears quickly, even at  $0^\circ\text{C}$ , with the formation of peracetic acid ( $\delta$  2.17); at room temperature the latter reacts further to give acetic acid ( $\delta$  2.09). Similar results were obtained on addition of  $\text{D}_2\text{O}$  to the unstable species in dioxane- $d_8$ , where the mixture remained homogeneous.

It is important for the reproducibility of the ozonolysis that the ethyl formate be quite dry. If only small amounts of water are present, the yield of the unstable species is greatly reduced. Ozonolysis of **1** in ethyl formate nearly saturated with water produced almost equal amounts of acetic acid and peracetic acid ( $\delta$  2.16–2.18) as the only products. The latter was distinguished from diacetyl peroxide (**7**), which appears at  $\delta$  2.17–2.19, by its ready extraction from the  $\text{CDCl}_3$  solution into  $\text{D}_2\text{O}$ ; **7** is mostly retained in the  $\text{CDCl}_3$  phase. Because the resonances of these compounds may overlap, it is necessary to exercise care in making assignments in this region.

This effect of water on the ozonolysis is readily explained by hydrolysis of **3** and addition of water to **2** (Scheme II). The species **9** would lose HCl to yield peracetic acid. Niki et al.<sup>9</sup> have suggested the same reaction sequence to explain the formation of performic acid in the gas-phase ozonolysis of chloroethylenes. Hydrolysis of **5** may also proceed through **9**.

In  $\text{CH}_2\text{Cl}_2$  the yield of **8**, as Griesbaum and Hofmann determined it by NMR, is only 4%. We find that addition of a tetraalkylammonium chloride to the solution before

(8) Huh, T.-S.; Neumeister, J.; Griesbaum, K. *Can. J. Chem.* **1981**, *59*, 3188–3191.

(9) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1982**, *86*, 1858–1861.

ozonolysis leads to an isolated yield of chromatographically pure 8 of 35%. This striking effect may be due to attack of chloride ion on 2 to produce the peroxide ion 10 (Scheme III), which would be expected to be much more reactive toward 3 than the hydroperoxide 5. While we have not been able to obtain any direct evidence for the intermediacy of 10, we note that the previous workers<sup>1</sup> obtained their highest yields of 8 in the presence of pyridine, where the formation of 5 may be suppressed in favor of 10.

Attempts to trap 5 in a form other than a perester have thus far had little success. Some <sup>1</sup>H NMR evidence was obtained for the formation of an adduct with chloral, viz., new singlets at  $\delta$  2.38 and 5.72 in a ratio of 3:1. However, there were other unknown resonances, and no hemiacetal could be isolated. The instability of 5 has prevented us from obtaining elemental analyses, a molecular weight, or a mass spectrum.

### Conclusion

Strong evidence has been presented that the unstable intermediate in the ozonolysis of 1 in nonparticipating solvents is 1,1-dichloroethyl hydroperoxide (5), not the trioxolane 4, as previously believed. This intermediate is the only product from the carbonyl oxide in the presence of added HCl; in addition, its esterification with acetyl chloride (and other acid chlorides<sup>6</sup>), its decomposition to acetic acid, and its hydrolysis to peracetic acid are all more in harmony with structure 5 than with 4. Furthermore, the <sup>13</sup>C NMR spectrum and the effect of salt on the <sup>1</sup>H chemical shift are more appropriate for 5.

So far as we have been able to determine, no 1-chloro hydroperoxides have previously been isolated. Huh et al.<sup>8</sup> proposed 1-chloro-1-methoxyethyl hydroperoxide as an intermediate in the ozonolysis of 1 in methanol, but could not detect it. Analogous 1-bromo-1-alkoxyethyl hydroperoxides were suggested as intermediates in the ozonolysis of 2,3-dibromo-2-butene<sup>10</sup> in alcohols, but again the only evidence was reaction products. The isolation of 5 supports the existence of these similar species and raises the question whether 1-halo hydroperoxides or 1,1-dihalo hydroperoxides may be involved in ozonolyses of other halogenated olefins or of nonhalogenated olefins in the presence of hydrogen chloride or hydrogen bromide.

### Experimental Section

80-MHz <sup>1</sup>H and 20-MHz <sup>13</sup>C NMR spectra were obtained with Varian FT-80 and CFT-20 spectrometers. Unless otherwise specified, all NMR spectra were made in CDCl<sub>3</sub>. A Fischer-Labortechnik Model 502 ozone generator was used to produce a stream of ozone in O<sub>2</sub>. All reagents and solvents were from the Merck Company, Darmstadt, and were of p.A. quality. Ethyl formate for ozonolyses was dried over P<sub>2</sub>O<sub>5</sub> and distilled. *trans*-2,3-Dichloro-2-butene (1), prepared by the procedure of Scharf and Laux,<sup>11</sup> was obtained in ca. 95% purity by distillation over a 1-m column packed with Raschig rings; the remaining 5% was *cis*-2,3-dichloro-2-butene. Ozonolyses were carried out by bubbling ozone/oxygen mixtures through solutions of 1 (ca. 0.1–0.3 M) in gas washing bottles (10–150 mL) at –20 to 0 °C until the solutions remained blue. To characterize the reaction mixture, a portion, either before or after removal of solvent and volatile products such as acetyl chloride, was diluted with CDCl<sub>3</sub> and examined by <sup>1</sup>H or <sup>13</sup>C NMR and thin-layer chromatography on Merck silica gel 60 F-254 plates, with a 2:1 mixture of hexane:chloroform. Peroxidic substances were detected by the immediate grey or black spots they gave when the plates were sprayed with diphenylamine;<sup>3,12</sup> the peroxides were then separated by column

chromatography on Merck silica gel 60 (0.063–0.2 mm), with 3:1 mixtures of hexane:chloroform.

**1,1-Dichloroethyl Hydroperoxide (5).** A solution of 200 mg of 1 in 5 mL of dry ethyl formate was saturated at 0 °C with anhydrous HCl and then treated with ozone. A few drops of the product mixture were diluted about 3:1 with CDCl<sub>3</sub>. The <sup>1</sup>H NMR spectrum showed singlets at  $\delta$  2.67 (3) and 2.33 (5) in a ratio of 1:1; a broad resonance centered at about  $\delta$  9.5 was also present. The remainder of the mixture was stripped of solvent at –10 to 0 °C under vacuum and examined by <sup>13</sup>C NMR; resonances at  $\delta$  34.66 and 114.01 could be attributed to 5.

**Thermal Decomposition of 1,1-Dichloroethyl Hydroperoxide (5).** The intermediate 5 was prepared as above from 200 mg of 1. The oily residue after removal of solvent and 3 was taken into CDCl<sub>3</sub> and examined by <sup>1</sup>H NMR. Over 2 h at room temperature the resonance at  $\delta$  2.34 disappeared almost entirely as the resonance of acetic acid at  $\delta$  2.10 increased. The solution had the characteristic color and odor of Cl<sub>2</sub>.

**Hydrolysis of 1,1-Dichloroethyl Hydroperoxide (5).** (a) In CDCl<sub>3</sub>. To a CDCl<sub>3</sub> solution rich in 5 was added a drop of H<sub>2</sub>O. The two phases were shaken while being held at 0 °C. Over 10 min the resonance of 5 at  $\delta$  2.35 almost completely disappeared. Although some acetic acid and peracetic acid were extracted into the small H<sub>2</sub>O layer, there was a buildup of peracetic acid ( $\delta$  2.18). The peracetic acid was shown to react further at room temperature to give acetic acid.

(b) In Dioxane-*d*<sub>8</sub>. A few drops of 1 were ozonized in ethyl formate at –10 °C, stripped of acetyl chloride and most of the solvent, and dissolved in dioxane-*d*<sub>8</sub>. This was diluted 1:1 with D<sub>2</sub>O and examined by <sup>1</sup>H NMR, which revealed 73% peracetic acid ( $\delta$  2.07), 10% acetic acid ( $\delta$  2.02), and 16% of an unknown resonance ( $\delta$  2.18). These resonances were hardly changed after 0.5 h at –10 °C, but, held at room temperature, the peracetic acid resonance and that of the unknown disappeared rapidly, while the acetic acid resonance increased in intensity. After 1 h 20 min only acetic acid remained. During this time the ethyl formate was almost completely hydrolyzed. The chemical shifts of acetic acid and peracetic acids in a 1:1 mixture of dioxane-*d*<sub>8</sub> and D<sub>2</sub>O were confirmed in a separate measurement.

**Acetyl 1,1-Dichloroethyl Peroxide (8).** (a) A solution of 200 mg of 1 in 5 mL of HCl-saturated ethyl formate was ozonized at 0 °C. The oil remaining after removal of the solvent under vacuum was diluted with 5 mL of 3 and allowed to stand for 48 h at 0 °C. Excess 3 was removed under vacuum, and the residue was chromatographed on a column with 30-mL solvent volume with a 3:1 mixture of hexane:chloroform. The yield of 8 was 92 mg (33%), identical by <sup>1</sup>H NMR with 8 as described in the literature.<sup>1</sup> (b) A solution of 1 (1.0 g) and 100 mg of alkylbenzylidimethylammonium chloride in 100 mL of CH<sub>2</sub>Cl<sub>2</sub> was ozonized at –15 °C. After removal of the solvent, the oily residue was chromatographed. The yield of 8 was 482 mg (35%).

**Ozonolysis of 1 in Wet Ethyl Formate.** *trans*-2,3-Dichloro-2-butene (1) (200 mg) was ozonized in 5 mL of ethyl formate previously shaken with H<sub>2</sub>O at 0 °C. After removal of the solvent under vacuum, the residue was examined by <sup>1</sup>H NMR in CDCl<sub>3</sub>. The spectrum showed singlets at  $\delta$  2.17 and 2.10 in a ratio close to 1:1, which can be assigned to peracetic acid and acetic acid. On being shaken with an equal volume of D<sub>2</sub>O, both products were extracted almost quantitatively from the CDCl<sub>3</sub>.

To confirm the assignment of the resonance at  $\delta$  2.17 another portion of the ozonolysis mixture was diluted with CDCl<sub>3</sub> solution of authentic diacetyl peroxide.<sup>13</sup> <sup>1</sup>H NMR showed, in addition to the original two resonances, a new one at  $\delta$  2.18. On extraction with D<sub>2</sub>O, the resonances at  $\delta$  2.17 and 2.10 were greatly reduced in proportion to  $\delta$  2.18. In a similar extraction of a CDCl<sub>3</sub> solution of acetic acid and authentic peracetic acid,<sup>13</sup> both were almost completely removed from the CDCl<sub>3</sub> phase.

***cis*- and *trans*-1,4-Dichloro-1,4-dimethyl-2,3,5,6-tetroxanes (6a and 6b).** Olefin 1 (2.0 g) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was treated with ozone at –10 °C until the solution became blue (ca. 1 h). Excess ozone was driven out with a stream of N<sub>2</sub>, and the solvent was removed under vacuum. The residue was chromatographed on

(10) Griesbaum, K.; Brüggemann, J. In "Ozone Reactions with Organic Compounds"; Gould, R. F., Ed.; American Chemical Society: Washington, 1972, pp 50–64.

(11) Scharf, H. D.; Laux, F. *Synthesis* 1970, 11, 582.

(12) Gäb, S.; Turner, W. V.; Korte, F.; Born, L. *J. Org. Chem.* 1982, 47, 173–175.

(13) D'Ans, J.; Mattner, J. *Chem. Ztg.* 1950, 74, 435–436.

SiO<sub>2</sub> with a 3:1 mixture of hexane:chloroform. The tetroxanes **6a** and **6b** (63 mg, 2.1%) were obtained as a mixture. Further chromatography of this mixture with hexane gave nearly complete separation of the two isomers.

**Thermal Decomposition of 6a and 6b.** A solution of **6a** and **6b** in CDCl<sub>3</sub> was sealed in a <sup>1</sup>H NMR tube and held at 20 °C, with examination by NMR at intervals. There was a steady decrease in the intensity of the resonance for **6b** (δ 2.11) and a concomitant increase in that of **7** (δ 2.18). A half-life of ca. 60 h at 20 °C could be calculated for **6b**. After **6b** was almost gone, the sample was held at 47 °C till only **6a** and **7** remained (ca. 5 h). The decomposition of **6a** was followed at 65 °C by observing the decrease in intensity of its resonance at δ 2.05. A half-life of ca. 4 h at 65 °C was calculated for **6a**. Admixture of authentic diacetyl peroxide gave only an increase in the intensity of the resonance at δ 2.18.

Extraction of the CDCl<sub>3</sub> solution with D<sub>2</sub>O had a negligible effect on the intensity of this resonance.

**Caution!** Compounds **6a** and **8** are reported to have exploded when exposed to heat or shock.<sup>1</sup> We experienced no explosions with **5**, but on several occasions, either neat or in concentrated solutions, it decomposed rapidly on being warmed to room temperature, with evolution of a gas and considerable heat. Great caution in working with these substances is urged.

**Acknowledgment.** We thank Dr. B. Wrackmeyer, Department of Inorganic Chemistry, Munich University, for a 50-MHz <sup>13</sup>C spectrum of **6b**.

**Registry No.** 1, 1587-29-7; 5, 90584-32-0; **6a**, 90584-33-1; **6b**, 90584-34-2; 8, 90584-35-3; 10, 90584-36-4.

## Funebrine, a Structurally Novel Pyrrole Alkaloid, and Other γ-Hydroxyisoleucine-Related Metabolites of *Quararibea funebris* (Llave) Vischer (Bombacaceae)

Robert F. Raffauf,\*<sup>1a</sup> Thomas M. Zennie,<sup>1a</sup> Kay D. Onan,\*<sup>1b</sup> and Philip W. Le Quesne<sup>1b</sup>

*Section of Medicinal Chemistry and the Department of Chemistry, Northeastern University,  
Boston, Massachusetts 02115*

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The flowers of the Mexican tree *Quararibea funebris* (Llave) Vischer (Bombacaceae) have been shown to give rise to the enolic γ-lactone **1**, its amino analogue **3**, the saturated lactone **4**, and the parent amino acid (2*S*,3*S*,4*R*)-γ-hydroxyisoleucine (**5**), as well as the novel pyrrole alkaloid funebrine (**6**). The structure determination of funebrine by X-ray crystallography is discussed and a hypothesis for its biogenesis offered.

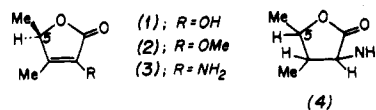
The plant family Bombacaceae comprises 31 genera and 225 species distributed among six tribes.<sup>2</sup> Despite the economic significance of *Ceiba* and *Ochroma* species as sources of kapok and balsa wood, respectively, the secondary metabolites of members of the family have been little investigated. Our attention was drawn to the genus *Quararibea* partly by its equivocal taxonomic position<sup>3</sup> but principally because of its ethnobotanical interest.

Early Spanish explorers observed the Zapotec Indians near Oaxaca, Mexico, conducting funerary rites beneath the branches of the tree *Q. funebris*. The strongly odorous flowers of the tree have also been used since pre-Columbian times as an additive to chocolate drinks, known locally as *ponzonque* or *tejate*. In local folk medicine the plant is known as *flor de cocoa* and is used to control psychopathic fears, to regulate the menses, and as a cough remedy.<sup>4</sup> We also noted a previous report<sup>5</sup> suggesting the presence of alkaloids in the flowers.

The dried, milled flowers were extracted with hexane and then with 95% ethanol. The hexane extract yielded waxy hydrocarbons, fatty acid esters of C<sub>29</sub> and C<sub>30</sub> triterpenoids, and related compounds which will be reported elsewhere.

The 95% ethanol extract was partitioned into alkaloidal, phenolic, neutral chloroform-soluble, and water-soluble

fractions. The phenolic fraction, in which the odor was concentrated, consisted of one major and many trace compounds. Flash chromatographic purification yielded the major component, a volatile, odorous compound of molecular formula C<sub>6</sub>H<sub>8</sub>O<sub>3</sub>. A positive ferric chloride test, an O-H stretching band (3300 cm<sup>-1</sup>) in the infrared spectrum, and other bands at 1750 and 1670 cm<sup>-1</sup> suggested an enolic lactone. The <sup>1</sup>H and <sup>13</sup>C NMR data, taken together with the ultraviolet spectrum (λ<sub>max</sub> 232 nm, ε 7250, bathochromic shift of 42 nm in the presence of NaOH) are best accommodated by structure **1**. The compound is optically active ([α]<sub>D</sub><sup>25</sup> -4.7°) and the absolute configuration shown in structure **1** (5*R*) is preferred on the basis of data given below. Compound **1** has not previously been obtained from a plant or animal source, but the racemate is known as the major flavoring constituent of aged sake.<sup>7</sup> Treatment of **1** with diazomethane yielded the methyl ether **2**.



Flash column chromatography of the basic fraction yielded two ninhydrin positive liquid compounds. The more abundant was assigned molecular formula C<sub>6</sub>H<sub>9</sub>NO<sub>2</sub> and structure **3**. In the electron-impact mass spectrum, fragments at *m/z* 99 (M - CO) and *m/z* 82 (M - COOH) indicate a lactone,<sup>8</sup> and the infrared carbonyl absorption

(1) (a) Section of Medicinal Chemistry, College of Pharmacy and Allied Health Professions. (b) Department of Chemistry, College of Arts and Sciences.

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