1-(1-Piperidino)cyclopropanol-*cis*-2,3-d_2 was prepared from **11d**-d_2 (from ACC-d_2) and PIFA in the same amounts and by the same procedure as described above. The yield was approximately 20%. MS m/z calcd for $C_8D_2H_{13}NO$, 143.127 84, found 143.1307.

Registry No. **3**, 119326-93-1; **5**, 119326-90-8; **7**, 485-47-2; **8**, 119326-91-9; **9**, 119326-92-0; **11a**, 22059-21-8; **11b**, 119111-65-8; **11c**, 119111-63-6; **11c** (benzyl ester), 119326-95-3; **11d**, 119111-64-7; **11d**-d_2, 119111-71-6; **11d** (ester), 119326-96-4; **11e**, 72784-43-1; **11e**·HCl, 72784-42-0; **12b**, 37520-26-6; **12c**, 119326-94-2; **12d**, 27161-21-3; **13**, 119111-76-1; PIFA, 2712-78-9; methyl *N*-acetylmethioninate, 7451-74-3; ethylene-*1,2*-d_2, 2382-91-4; *meso*-1,2-dibromoethane-*1,2*-d_2, 86860-52-8; benzyl bromide, 100-39-0; diiodopentane, 628-77-3; 1,2,3-indantrione, 938-24-9; *N*-phenylmaleimide, 941-69-5; diethyl azodicarboxylate, 1972-28-7; cyclopropylamine, 765-30-0; phenanthrenequinone, 84-11-7.

Reaction of Cyclopropanamines with Hypochlorite

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Ethylene was formed in 65% yield when 1-(1-piperidino)cyclopropanol, **6**, was treated with hypochlorite. This observation raised the possibility that 1-aminocyclopropanecarboxylic acids (ACCs) could yield ethylene by a mechanism that involves (1) decarboxylation to a 1-aminocyclopropanol, followed by (2) a fragmentation of the carbinolamine to ethylene induced by a hypochlorite equivalent. Although this mechanism could be ruled out only for **1e**, no evidence could be found for it in the reactions of other ACCs, **1a–f**, with hypochlorite. The fact that **1b**-*cis*-2,3-d_2 yielded only ethylene-*cis*-1,2-d_2 is consistent with either the mechanism described above or a nitrenium ion mechanism. In the reaction of cyclopropanamines with neutral hypochlorite, ethylene is not the major product. From the primary and secondary amino acids **1a–c**, a 3-hydroxypropanenitrile or propanamide, **2a–c**, probably the product of a nucleophilic ring-opening step followed by decarboxylation, is formed. Similar products are formed from other cyclopropanamines: **2a** from **1g**, **2d** from **1h**, **2e** and **2f** from **1i**, and lactone **5** from **1j**.

Decarboxylation to an imine is the normal course of the reaction of amino acids with hypochlorite.[1] In the case of 1-aminocyclopropanecarboxylic acid (ACC), the product expected from such a reaction is an imine of cyclopropanone. However, it has been known for some time that when ACC is treated with basic hypochlorite and mercuric ion, *ethylene* is formed in good yield.

In this paper we report on the reactions of hypochlorite with ACC and related cyclopropanamines. Our initial aim was to investigate the possibility that some of the ethylene produced by the reaction of hypochlorite with N-substituted ACCs begins with a decarboxylation, i.e., that there is a connection between the two types of reactions mentioned in the first paragraph. In the process of that investigation, we uncovered several new reactions and recorded observations relevant to the mechanism by which ethylene is formed.

Results

The products of the reaction of hypochlorite with a series of cyclopropanamines—primary, secondary, and tertiary amines, with and without carboxyl groups (**1a–j**)—are summarized in Table I. Ethylene was not the major product in any of these reactions. From most of the primary and secondary amines, the chief isolable organic product was a 1,2-substituted ethane, **2**, a product of cyclopropane ring-opening. From ACC, for example, 3-hydroxypropanenitrile, **2a**, was the major product. In D_2O the same product, without deuterium incorporation, was isolated.

No ethylene was produced from the tertiary amines. In two cases, **1e** and **1f**, intractable mixtures were formed. Repeated attempts at reaction under a variety of conditions (including the use of *tert*-butyl hypochlorite in chloroform) gave mixtures that exhibited many spots by thin-layer chromatography and could not be separated by that technique. An indication of what might be happening with **1e** and **1f** was provided by the reaction of 1-(*N,N*-dibenzylamino)cyclopropanecarboxylic acid, **1d**, with *tert*-butyl hypochlorite in chloroform. The secondary amino acid **1c** was isolated as its hydrochloride in 63% yield along with a quantitative yield of benzaldehyde, **3**. Its formation is rationalized as a β-elimination of HCl from the *N*-chloroammonium salt followed by hydrolysis to the aldehyde with adventitious water.[2] (From the treatment of **1d** with aqueous hypochlorite, only benzaldehyde and benzylamine, in varying yields, were isolated in a state pure enough for identification.) A similar process applied to **1e** would introduce a double bond in the piperidine ring, from which point a variety of reactions would occur.

When the decarboxylation product of **1e**, 1-(1-piperidino)cyclopropanol (**6**), was treated with hypochlorite, ethylene was formed in 65% yield. *N*-Chloropiperidine and CO_2 were identified as other products. (With alkaline hydrogen peroxide and **1e**, in addition to ethylene and CO_2, two products of ring-opening reactions, described in the Experimental Section, were observed.) Labeled **6**, 1-(1-piperidino)cyclopropanol-*cis*-2,3-d_2, yielded only ethylene-*cis*-1,2-d_2, according to infrared spectroscopy.

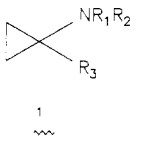
In the case of the secondary amine **1j**, it was possible to isolate an *N*-chloroamine. The product of the treatment of **1j** with *tert*-butyl hypochlorite in chloroform was an oil, which was characterized by proton NMR. The principal change from the spectrum of **1j** was a downfield shift of the *N*-methyl protons from 2.40 ppm in the original ester **1j** to 3.15 ppm in the *N*-chloro ester, shifts consistent with

(1) Schonberg, A.; Moubacher, R. *Chem. Rev.* **1952**, *50*, 261.

(2) See, for example: (a) Lee, G. A.; Freedman, H. H. *Tetrahedron Lett.* **1976**, 1641. (b) Cho, B. R.; Yoon, J. C.; Bartsch, R. A. *J. Org. Chem.* **1985**, *50*, 4943. (c) Ellis, A. J.; Soper, F. G. *J. Chem. Soc.* **1954**, 1750. (d) Friedman, A. H.; Morgulis, S. *J. Am. Chem. Soc.* **1936**, *58*, 909.

0022-3263/89/1954-1815$01.50/0

Table I. Products from the Reaction of Hypochlorite with Cyclopropanamines 1

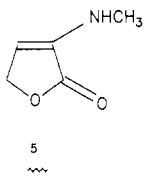


1

XCH_2CH_2Y

2a: X = OH, Y = CN
b: X = OH, Y = $CONHCH_3$
c: X = OH, Y = $CONHCH_2Ph$
d: X = OH, Y = $COCH_3$
e,f: unknown

PhCHO **3** $PhCH_2NH_2$ **4**

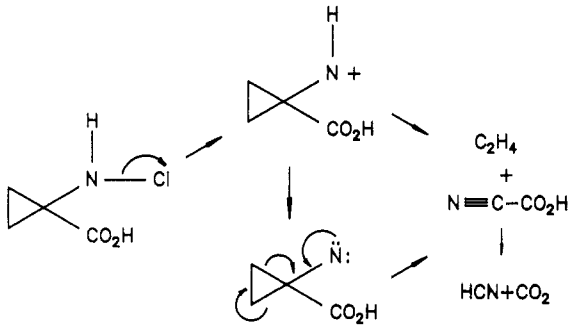


5

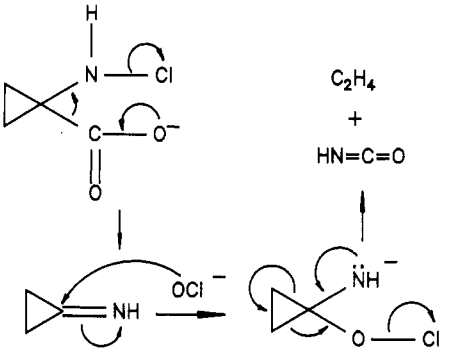
compound	R_1	R_2	R_3	% C_2H_4	% CO_2	other products[a]
1a	H	H	CO_2H	10	85	**2a** (60)
1b	H	CH_3	CO_2H	23	93	**2b** (48)
1c	H	$PhCH_2$	CO_2H	10		**2c** (8)
1d	$PhCH_2$	$PhCH_2$	CO_2H	0	35	**1c**, **3**, **4**
1e	$-(CH_2)_5-$		CO_2H	0	80	mixture
1f	CH_3	CH_3	CO_2H	0		mixture
1g	H	H	H	15	–	**2a** (75)
1h	H	H	CH_3	36	–	**2d** (ca. 30)
1i	H	H	CO_2CH_3	20		**2e**, **2f**
1j	H	CH_3	CO_2CH_3	10		**5** (ca. 10)

[a] Percent yield of the product is in parentheses.

Scheme I



Scheme II



the literature.[3] When this product was treated with sodium methoxide in methanol, the original ester was regenerated. When the corresponding acid labeled with deuterium (1-(*N*-methylamino)cyclopropanecarboxylic acid-*cis*-2,3-d_2) was treated with hypochlorite, only ethylene-*cis*-1,2-d_2 was formed.

Discussion

A mechanism for the formation of ethylene from ACC and hypochlorite is shown in Scheme I. It is supported by several observations. (1) In the presence of basic hypochlorite and mercuric ion, the fate of C-1 of the cyclopropane ring is cyanide.[4] (2) Ethylene is formed in a concerted step because when *cis*-2,3-dideuterio-ACC is treated with hypochlorite, with or without mercuric ion, only the cis-labeled ethylene is produced.[5] (3) Ethylene is produced when the nitrene is formed from other sources, as for example from 1-azidocyclopropanecarboxylic acid (**7**).[6,7] A nitrenium ion is also a competent intermediate, for when **7** is decomposed in trifluoroacetic acid, ethylene (15%) is still produced.[6]

Other mechanisms have been considered.[4] A mechanism that begins with transfer of an electron from nitrogen to hypochlorite or with homolytic cleavage of an N–Cl bond is not compatible with the observed stereospecificity of ethylene production by hypochlorite, for it has been shown that single electron transfer from ACC results in nonstereospecific ethylene production.[7] A mechanism that begins with decarboxylation to a cyclopropanimine followed directly by concerted loss of ethylene has been characterized as symmetry-disallowed.[6] A mechanism that begins with decarboxylation and is followed by hypochlorite attack on the imine has not been considered previously.

Such a mechanism is outlined in Scheme II. Recent results have demonstrated the feasibility of the decarboxylation step.[8] The report of a peroxide-induced fragmentation of 2,3-di-*tert*-butylcyclopropanone to di-*tert*-butylethylene serves as a precedent for the fragmentation step.[9] The fate of C-1 in such a mechanism is isocyanate. This mechanism cannot apply to the mercuric ion induced formation of ethylene, for under those conditions the yield of cyanide is 88%.[4] The nitrene mechanism of Scheme I is the most likely mechanism in that case. For reactions with hypochlorite in the absence of heavy metal ions or for reactions of N-substituted ACCs, the mechanism of Scheme II remained a possibility.

1-(1-Piperidino)cyclopropanecarboxylic acid (**1e**)[8] was chosen for the first experiments, for the hydrate of its decarboxylation product is an isolable solid, 1-(1-piperidino)cyclopropanol (**6**).[10] When we tested the stability of **6** to hypochlorite, we found that ethylene was formed from it in 65% yield, a result consistent with the

(3) A similar downfield shift of about 0.7 ppm is observed for the pair dimethylamine and *N*-chlorodimethylamine. Vahrenkamp, H.; Noth, H. *J. Organomet. Chem.* **1968**, *12*, 281.
(4) Leete, E.; Morris, G. J.; Rao, H. S. P. *Rev. Latinoam. Quim.* **1986**, *17*, 24.
(5) Adlington, R. M.; Baldwin, J. G.; Rawlings, B. J. *J. Chem. Soc., Chem. Commun.* **1983**, 290.
(6) Pirrung, M. C.; McGeehan, G. M. *J. Org. Chem.* **1983**, *48*, 5143.
(7) Baldwin, J. E.; Jackson, D. A.; Adlington, R. M.; Rawlings, B. J. *J. Chem. Soc., Chem. Commun.* **1985**, 206.
(8) Vaidyanathan, G.; Wilson, J. W. *J. Org. Chem.*, preceding paper in this issue.
(9) Greene, F. D., quoted in: Baldwin, J. E.; Cardellia, J. H. I. *Chem. Commun.* **1968**, 558.
(10) Wasserman, H. H.; Dion, R. P. *Tetrahedron Lett.* **1982**, *23*, 785.

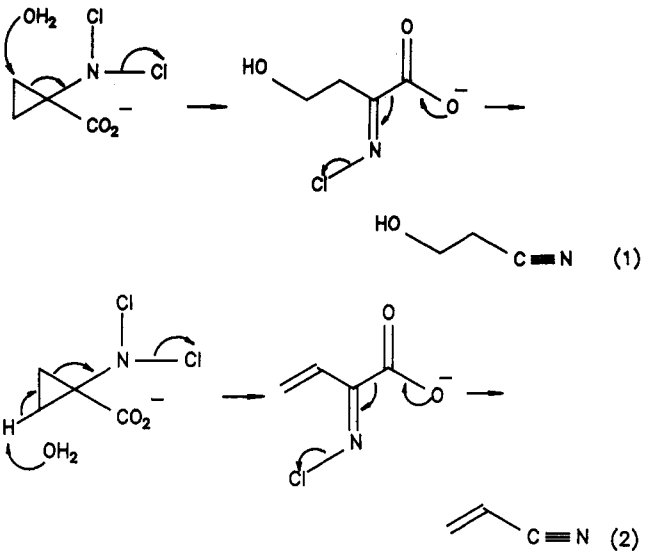
mechanism of Scheme II.[11] The equilibrium of **6** with an iminium salt in acidic solution has been observed directly by NMR spectroscopy.[12] Consistent with this concerted mechanism is the observation that the *cis*-2,3-d_2 analogue yielded only ethylene-*cis*-1,2-d_2. Isomerization of the type reported by Vilsmaier[13] for certain 1,1-diaminocyclopropanes does not, therefore, occur with carbinolamines under these reaction conditions.

However, the fact that no ethylene was formed from **1e** removes this mechanism from consideration in this case. A reaction did occur, for CO_2 was evolved in 80% yield (with excess acidic hypochlorite), but we were unable to identify any products.

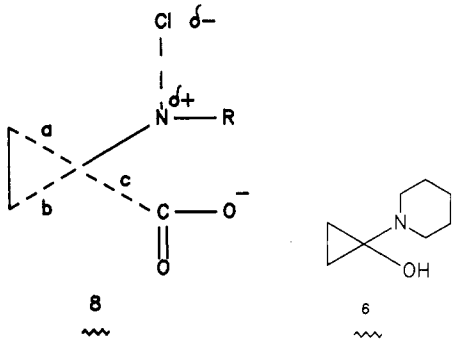
The possibility that the decarboxylation–fragmentation mechanism might apply to the case of the secondary amino acid **1b**, which cannot form a nitrene (though it can form a nitrenium ion), was raised by the observations that **1b** yielded ethylene in 23% yield, whereas its methyl ester, **1j**, gave much less ethylene, most of which probably came from hydrolysis of the ester to **1b** under the basic reaction conditions. However, the only other product that could be isolated from the reaction of **1b** with hypochlorite was **2b** in 40% yield. Without knowing the fate of C-1 in **1b**, it is impossible to know whether the mechanism of Scheme II applies here. The fact that the formation of ethylene from **1b** is stereospecific is consistent with either a nitrenium ion mechanism or Scheme II.[14]

We were surprised to find, given the emphasis in the literature on ethylene formation, that the major product of the reaction of ACC with lithium hypochlorite (without added base other than the lithium carbonate present in the reagent[15]) was not ethylene but 3-hydroxypropanenitrile, **2a**, a product not previously mentioned in this connection.[16] (Lizada and Yang found that in the absence of mercuric ion the yield of ethylene drops to 13%.[17]) In fact, ethylene is a minor product in the reactions of all the cyclopropylamines and **2** is the major product, formed, we presume, by mechanisms similar to the one by which **2a** is formed.

Such ring-opening reactions are typical of cyclopropylamines with a leaving group attached to the nitrogen.[18] A mechanistic rationale for the reaction is given in eq 1. (In excess hypochlorite, it is probable that the *N*,*N*-dichloroamine is the starting point for the reaction.[16a]) Alternative mechanisms that involve nitrenium ions or initial decarboxylation are not excluded. It was possible to exclude a mechanism that starts with an elimination reaction[19] (eq 2), because there was no deuterium incorporation when the reaction was conducted in D_2O. α-Ketobutyrolactone, presumably formed by a mechanism similar to that of eq 1, was the product when ACC was treated with *N*-chlorosuccinimide by Leete and co-workers.[4]



Still undefined are the structural features that determine which neighboring carbon–carbon bond (a, b, or c of **8**) will be broken following (or concerted with) loss of a leaving group from the nitrogen of cyclopropanamines. It is clear from the literature that when a nitrene is formed, fragmentation to ethylene is the major product. Whether ethylene is formed only by that mechanism is still unclear.



Experimental Section[20]

1-Methylcyclopropanamine (1h)[21] was prepared from 1-methylcyclopropanecarboxamide (prepared from the acid (Aldrich), $SOCl_2$, and NH_4OH; 40%, mp 143 °C) by treating 1.1 g (0.011 mol) of the amide with Br_2 (0.57 mL, 0.011 mol) followed by 800 mg of KOH in 7 mL of water in several portions. The *N*-bromoamide that was isolated (1.0 g, 50%, mp 98 °C) was added to a solution of 890 mg of NaOH in 7 mL of water and heated. Amine **1h** was collected by distillation (bp 58–60 °C): yield 250 mg (62%); NMR ($CDCl_3$) δ 0.38 (m, 2 H), 0.53 (m, 2 H), 1.27 (s, 3 H), 1.72 (br s, 2 H).

1-(*N*-Methylamino)cyclopropanecarboxylic Acid (1b). To a stirred solution of ACC (505 mg, 5 mmol) and triethylamine (1 mL) in 6 mL of 50% aqueous dioxane was added 1.36 g (5.5 mmol) of BOC-ON (Aldrich). The mixture was stirred for 2 h and then partitioned between EtOAc (10 mL) and water (7 mL). The aqueous layer was washed with 10 mL of EtOAc and cooled. Its pH was adjusted to 3 by addition of solid citric acid. The precipitated *N*-Boc-ACC was taken up in EtOAc, and the solution was dried and evaporated to yield 800 mg (80%) of white solid: mp 175 °C; NMR ($CDCl_3$) δ 1.47 (s, 9 H), 1.23 (m, 2 H), 1.6 (m,

(11) (*N*-Chloro-*N*-alkylamino)cyclopropanols undergo ring expansion to β-lactams on treatment with silver ion: Wasserman, H. H.; Adickes, H. W.; de Ochoa, O. E. *J. Am. Chem. Soc.* **1971**, *93*, 5586.
(12) Wasserman, H. H.; Baird, M. S. *Tetrahedron Lett.* **1970**, 1729.
(13) Vilsmaier, E.; Schwaben, B.; Joerg, K. *Chem. Ber.* **1984**, *117*, 1900.
(14) It should be noted that the presence of a free carboxyl group is not a requirement for ethylene production, as entries **1g**, **1h**, and **1i** show.
(15) Lithium hypochlorite from Fluka contains 30% LiOCl, 34% NaCl, 20% Na_2SO_4 + K_2SO_4, 9% Li salts, 7% H_2O. The presence of carbonate was detected when the gas evolved on acidification gave a precipitate with $Ba(OH)_2$. Weights of LiOCl given in the Experimental Section are weights of this mixture, whereas molar equivalents of LiOCl are calculated at 30% of the measured weights.
(16) Examples of the formation of nitriles from chloroamines and chloroamino acids can be found in the following: (a) Kovacic, P.; Lowery, M. K.; Field, K. W. *Chem. Rev.* **1970**, *70*, 639. (b) Dakin, H. D. *Biochem. J.* **1916**, *10*, 319. (c) Pereira, W. E.; Hoyano, Y.; Summons, R. E.; Bacon, V. A. *Biochim. Biophys. Acta* **1973**, *313*, 170.
(17) Lizada, M. C. C.; Yang, S. F. *Anal. Biochem.* **1979**, *100*, 140.
(18) Gassman, P. G. *Acc. Chem. Res.* **1970**, *3*, 26.
(19) Deyrup, J. A.; Greenwald, R. B. *Tetrahedron Lett.* **1973**, 4771.
(20) For general information on experimental methods, see the Experimental Section of the previous paper.[8] Unless otherwise noted, reactions were conducted at room temperature.
(21) For a similar preparation using hypochlorite, see: Neighbors, R. P.; Phillips, L. V. U.S. Patent 3 451 802, 1969; *Chem. Abstr.* **1969**, *71*, 61426f.

2 H). To 201 mg (1 mmol) of *N*-Boc-ACC in 3 mL of dry THF was added 0.5 mL (8 mmol) of iodomethane. The solution was cooled, NaH (132 mg, 5.5 mmol) was added, and the mixture was stirred at room temperature for 24 h. The reaction was quenched by adding a few drops of water and 5 mL of EtOAc. Most of the organic solvent was evaporated, and 10 mL of water and 3 mL of ether were added. The ether layer was washed with a 5% sodium bicarbonate solution. The pH of the combined aqueous layers was adjusted to 3 with solid citric acid. The precipitated *N*-Boc-*N*-methyl-ACC was taken up in EtOAc, and the solution was dried and evaporated to yield 185 mg (86%) of white solid: mp 125 °C; NMR ($CDCl_3$) δ 1.27 (m, 2 H), 1.43 (s, 9 H), 1.6 (m, 2 H), 2.53 (s, 3 H), 11.57 (s, COOH). A solution of trifluoroacetic acid (1.0 mL) and *N*-Boc-**1b** (185 mg) was stirred at room temperature for 1 h. Trifluoroacetic acid was evaporated, and 1 mL of 1 N HCl was added and evaporated. The residue, **1b**·HCl, was dried overnight in a desiccator containing NaOH and then stirred with propylene oxide for several hours. The product was collected, washed with acetone, and recrystallized from acetone–water to yield 70 mg of **1b** (60%): mp 237 °C; IR (KBr) 3440, 3060, 2860, 1615 cm^{-1}; NMR (D_2O) δ 4.73 (HOD) 1.30 (m, 2 H), 1.37 (m, 2 H), 2.73 (s, 3 H); ^{13}C NMR (D_2O) δ 12.11, 31.84, 42.55, 66.50 (dioxane reference), 173.71; MS, *m/z* 115, 100, 69 (base peak). Anal. Calcd for $C_5H_9NO_2$: 115.063 27. Found: 115.0634.

***cis*-1-(*N*-Methylamino)cyclopropanecarboxylic Acid-2,3-d_2 (1b-d_2).** Except for the use of ACC-d_2 and di-*tert*-butyl dicarbonate (instead of BOC-ON), this compound was prepared in the manner of its undeuterated analogue, **1b**. From 206 mg (2 mmol) of ACC-d_2 was obtained 85 mg (36%) of **1b**-d_2: mp 200–232 °C sublimes; NMR (D_2O) δ 4.3 (HOD), 1.10 (s, 1 H), 1.2 (s, 1 H), 2.5 (s, 3 H); IR (KBr) 3400, 3040, 2840, 2420, 1600, 1380 cm^{-1}; MS, *m/z* 117, 102, 71 (base peak). Anal. Calcd for $C_5H_7D_2NO_2$: 117.075 83. Found: 117.0789.

Methyl 1-(*N*-Methylamino)cyclopropanecarboxylate (1j). From 1.15 g (10 mmol) of **1b** was obtained (in the manner by which **1i** was prepared[8]) 1 g (78%) of an oil (**1j**): NMR ($CDCl_3$) δ 1.0 (m, 2 H), 1.23 (m, 2 H), 2.07 (br s, 1 H), 2.40 (s, 3 H), 3.67 (s, 3 H); IR (thin film) 3330, 3020, 2940 (s), 2850, 1720 (s), 1430, 1290; MS, *m/z* 129, 114, 83, 70 (base peak, M^+ – COOMe). Anal. Calcd for $C_6H_{11}NO_2$: 129.0790. Found: 129.0791.

1-(*N*-Benzylamino)cyclopropanecarboxylic Acid (1c). To a suspension of the hydrochloride of **1i** (prepared[8] from 505 mg, 5 mmol, of ACC) in 5 mL of $CHCl_3$ were added benzaldehyde (530 mg, 5 mmol) and triethylamine (505 mg, 5 mmol), and the mixture was stirred overnight at room temperature. Water was added, and the $CHCl_3$ layer was dried and evaporated to yield 711 mg (70%) of a yellow oil (the Schiff base): NMR ($CDCl_3$) δ 1.27 (m, 2 H), 1.58 (m, 2 H), 3.63 (s, 3 H), 7.2–7.53 (m, 3 H), 7.6–7.83 (m, 2 H), 8.92 (s, 1 H). This oil, which contained a little benzaldehyde, was taken up in 5 mL of methanol and cooled in ice. Sodium borohydride (140 mg, 4 mmol) was added, and the solution was stirred overnight. Methanol was evaporated, and the residue was partitioned between $CHCl_3$ and water. The $CHCl_3$ layer was dried and evaporated to yield 400 mg (56%) of an oil (the methyl ester of **1c**): NMR ($CDCl_3$) δ 0.97 (m, 2 H), 1.17 (m, 2 H), 2.33 (br s, NH), 3.5 (s, 3 H), 3.77 (s, 2 H), 7.2 (m, 5 H). This ester was hydrolyzed by being refluxed overnight in 40 mL of 5% NaOH solution. The reaction mixture was extracted with $CHCl_3$, and the aqueous layer was neutralized with glacial HOAc. The precipitated *N*-benzyl-ACC was filtered, washed with water, and dried. Recrystallization from hot methanol gave 240 mg of a white solid (**1c**) (25% from ACC): mp 180–192 °C dec; NMR (DMSO-d_6) δ 0.9 (m, 2 H), 1.07 (m, 2 H), 3.77 (s, 2 H), 7.23 (br s, 5 H); IR (KBr) 3020, 2840, 2780, 2280, 1630, 1550 cm^{-1}; MS, *m/z* 191, 176, 145, 100, 91, 77. Anal. Calcd for $C_{11}H_{13}NO_2$: 191.0946. Found: 191.0949.

***cis*-1-(1-Piperidino)cyclopropanecarboxylic Acid-2,3-d_2 (1e-d_2).** The procedure used to prepare deuterated **1e** was similar to that used for the undeuterated analogue.[8] From 1 g of ACC-d_2 was obtained 870 mg (77%) of its methyl ester: NMR ($CDCl_3$) δ 0.92 (s, 1 H), 1.2 (s, 1 H), 2.05 (br s, NH_2), 3.62 (s, 3 H). Treatment of the ester with diiodopentane gave, after chromatography, 1.34 g (97%) of methyl *cis*-2,3-dideuterio-1-(1-piperidino)cyclopropanecarboxylate as an oil: NMR ($CDCl_3$) δ 0.85 (s, 1 H), 1.18 (s, 1 H), 1.38 (br s, 6 H), 2.83 (br t, 4 H), 3.58 (s, 3 H). It was hydrolyzed by being refluxed overnight in 10% sodium hydroxide (60 mL). The yellow homogeneous solution was boiled with activated charcoal (0.5 g) and filtered. Water was evaporated, and the white solid residue was redissolved in a minimum amount of water and passed through a column of activated ion-exchange resin (Dowex 50-W-X8, H^+ form, 50 g). The resin bed was washed with distilled water until the eluate was neutral. The amino acid was eluted with 2 M NH_4OH (200 mL). Water was removed from the eluate to yield an off-white solid. It was recrystallized from methanol–acetone to yield 700 mg (42% from ACC-d_2; a second crop of 100 mg was obtained) of transparent crystals (**1e**-d_2): mp 208–210 °C; NMR (D_2O) δ 0.00 (TSP), 1.35 (m, 2 H), 1.83 (m, 6 H), 3.37 (t, 4 H), 4.7 (HOD); IR (KBr) 3420, 3000, 2940, 2860, 2350, 1610 cm^{-1}; MS, *m/z* 171, 155, 126. Anal. Calcd for $C_9H_{13}D_2NO_2$: 171.122 75. Found: 171.1179.

Reaction of ACC with Hypochlorite. To 51 mg (0.5 mmol) of ACC in 1 mL of water was added dropwise a solution of 483 mg (2.5 mmol) of LiOCl in 4 mL of water. There was an immediate evolution of gas (9.5 mL), which was, according to GC, mainly CO_2 and a little ethylene. When the experiment was repeated with $Ba(OH)_2$ traps attached, 74 mg (75%) of $BaCO_3$ was collected. The calculated amounts of CO_2 and ethylene in the mixture were 8.4 mL and 1.1 mL (9.8%), respectively. At the end of gas evolution, the reaction mixture was acidified with 1.5 mL of concentrated HCl in 2.5 mL of water. More $BaCO_3$, 9 mg (10% yield), was collected, and the total yield of CO_2, after correcting for carbonate present in the LiOCl, was 85%.

The aqueous reaction mixture (at neutral pH) was exhaustively extracted with EtOAc to get 20 mg (60%) of a colorless oil, which was identical (NMR, IR, MS, and TLC) with a commercial sample of 3-hydroxypropanenitrile (**2a**): NMR ($CDCl_3$) δ 2.67 (t, 2 H), 3.89 (t, 2 H), and concentration-dependent OH peak; NMR (D_2O) δ 0.00 (TSP), 2.70 (t, J = 5.4 Hz, 2 H), 3.82 (t, J = 5.4 Hz, 2 H), 4.7 (HOD); IR (neat) 3360, 2940, 2870, 2220 cm^{-1}; MS, *m/z* 54, 41, 31; TLC (EtOAc) R_f = 0.43. When the proportion of LiOCl was reduced, lower yields of products were formed; unreacted ACC was detected by NMR in the residual aqueous solution. An unidentified minor component, with an A_2B_2 pattern in the NMR, was produced in some experiments.

When the reaction was repeated in the presence of 1 equiv of $HgCl_2$, the yield of ethylene increased to 32%. According to NMR spectroscopy and GC, **2a** was still the major product. When the reaction was repeated with 1 equiv of 1 N HCl or acetic acid present before adding LiOCl, **2a** was isolated in ca. 50% yield.

Reaction of ACC with Hypochlorite in D_2O. To 20 mg (0.2 mmol) of ACC in 0.5 mL of D_2O in an NMR tube was added a solution of 76 mg (0.4 mmol) of LiOCl in 0.2–0.3 mL of D_2O. The tube was shaken, the gas that formed was released, and the NMR spectrum was recorded. A pair of triplets caused by **2a** and the multiplets of unreacted ACC were the main peaks. Another unassigned pair of triplets, very small in area, also appeared.

Reaction of Acrylonitrile with Hypochlorite in D_2O. To 10 mg (0.2 mmol) of acrylonitrile in 0.5 mL of D_2O in an NMR tube was added 75 mg (0.44 mmol) of LiOCl. No NMR peaks corresponding to deuterated **2a** were observed in spectra recorded at intervals over a half-hour.

Reaction of 1i with Hypochlorite. In a typical experiment, a solution of 2.0 g (10.4 mmol) of LiOCl in 10 mL of water was added dropwise to a stirred solution of **1i** (600 mg, 5.20 mmol) in the minimum amount of water at 5–10 °C. After 20 min, 25 mL of gas had evolved. This gas was a mixture of ethylene (major) and CO_2 (minor), the latter presumably formed by the hydrolysis of the ester to ACC. The aqueous reaction mixture was extracted with EtOAc to yield 150 mg of an oil. Chromatography of the oil (silica gel column, EtOAc:hexane = 3:2) yielded **2a** (50 mg) and two unidentified compounds, **2e** (45 mg) and **2f** (5 mg), each having, according to their proton NMR spectra, an A_2B_2 pattern with a carbomethoxy moiety. NMR ($CDCl_3$): **2e** δ 3.37 (t, 2 H), 3.80 (t, 2 H), 3.87 (s, 3 H); **2f** δ 2.70 (t, 2 H), 3.80 (s, 3 H), 4.3 (t, 2 H). IR ($CHCl_3$): **2e** 3030, 2970, 1740, 1610, 1440, 1315 cm^{-1}; **2f** 2970, 1760, 1450, 1275 cm^{-1}. Mass spectra were not useful in identifying **2e** and **2f**.

Reaction of 1g with Hypochlorite. A solution of 1.93 g (10 mmol) of LiOCl in 10 mL of water was injected dropwise into a cooled flask that held 285 mg (5 mmol) of cyclopropanamine in 1 mL of water and was attached to a gas buret. Ethylene, 16.5

mL (14.7%), was evolved. The reaction mixture was extracted with EtOAc (3 × 10 mL) to obtain 125 mg of colorless oil. Continuous extraction of the aqueous layer with EtOAc for 20 h yielded another 140 mg of brown oil. Both oils consisted mainly of **2a** according to their NMR spectra. Column chromatography (silica gel, EtOAc) of this mixture, however, yielded only 30 mg of **2a**, which was identified by NMR, IR, and mass spectrometry.

Reaction of 1h with Hypochlorite. To an ice-cold solution of 243 mg (3.42 mmol) of **1h** was added dropwise with stirring a solution of 1.33 g (6.84 mmol) of LiOCl in 7.5 mL of water over a few minutes. Ethylene (26.5 mL, 36%) was evolved. The aqueous reaction mixture was extracted with EtOAc to yield 100 mg of an oil, the major component of which was 4-hydroxy-2-butanone (**2d**), according to NMR. Repeated chromatography (preparative TLC, EtOAc:hexane = 1:1) of the crude product yielded 7 mg (3%) of a pure sample with IR, NMR, and mass spectral data identical with those of an authentic sample:[22] NMR ($CDCl_3$) δ 2.17 (s, 3 H), 2.66 (t, J = 5.1 Hz, 2 H), 3.15 (br s, OH), 3.8 (t, J = 5.1 Hz, 2 H); IR ($CHCl_3$) 3440, 2985, 2900, 1700 cm^{-1}; MS, m/z 88, 73.

Reaction of 1b with Hypochlorite. To 58 mg (0.5 mmol) of **1b** in 1 mL of water was added dropwise a solution of 483 mg (2.5 mmol) of LiOCl in 4 mL of water. By the end of the addition (2 min), 4.8 mL of gas had evolved; another 0.6 mL of gas was formed in the following 5 min. According to GC, the gas was a mixture of ethylene and CO_2. The aqueous reaction mixture was continuously extracted with EtOAc for 20 h to obtain 21 mg (40%) of a colorless oil, identical in all respects (NMR, IR, MS, and TLC) with an authentic sample of *N*-methyl-3-hydroxypropanamide (**2b**) prepared from β-propiolactone (vide infra): NMR ($CDCl_3$) δ 2.4 (t, J = 4.8 Hz, 2 H), 2.77 (d, J = 4.5 Hz, 3 H), 3.8 (t, J = 4.8 Hz, 2 H), 4.9 (br s, 1 H), 7.4 (m, 1 H); IR ($CHCl_3$) 3475, 3380, 3000, 2960, 1665, 1420 cm^{-1}; MS, m/z 103, 88, 86, 73 (base peak); TLC (EtOAc) R_f = 0.12. When the experiment was repeated with $Ba(OH)_2$ traps, 20 mg (0.1 mmol, 20% yield) of $BaCO_3$ was collected. Acidification of the reaction mixture raised the total yield of CO_2 to 93% (72 mg of $BaCO_3$, 72% after accounting for the blank). The calculated yield of ethylene was 28%.

Reaction of 1b-*cis*-d_2 with Hypochlorite. A solution of 390 mg (2 mmol) of LiOCl in 1.5 mL of water was injected into a small closed bottle that was fitted with a septum and contained 117 mg (1 mmol) of **1b**-d_2 in 1 mL of water. The IR spectrum of the head-space gas was recorded on a BOMEM DA.02 FTIR spectrometer using a CsI gas cell (25 mm i.d. × 10 cm long). The gaseous sample was transferred to an evacuated container, and the container was attached to a vacuum manifold. The container was cooled in a liquid nitrogen bath, and air was pumped out. Then the deuterated ethylene was transferred to the gas cell, which had its cold finger immersed in a liquid-nitrogen bath. Only the band of *cis*-ethylene-1,2-d_2 (841 cm^{-1}) was present.[23]

Reaction of 1j with Hypochlorite. Very little gas was evolved over 15 min when a solution of 270 mg (1.39 mmol) of LiOCl in 1.5 mL of water was added to a stirred solution of 160 mg (1.39 mmol) of **1j** in 1.5 mL of water in an ice bath. No ethylene could be detected by gas chromatographic analysis of the head space. The reaction mixture was extracted with 3 × 15 mL of EtOAc. The aqueous layer was treated with enough K_2CO_3 to absorb all the water, and the solid cake was extracted with EtOAc. The combined EtOAc extracts were dried and evaporated to obtain 50 mg of an oil, which was found by NMR to consist mainly of starting material and a new component. This mixture was chromatographed (preparative TLC, EtOAc) to obtain 10 mg of an oil, which was identified as lactone **5**: NMR ($CDCl_3$) δ 2.77 (s, 3 H), 4.77 (d, J = 2.7 Hz, 2 H), 5.57 (t, J = 2.7 Hz, 1 H); IR ($CHCl_3$) 3420, 1750, 1670 cm^{-1}. Anal. Calcd for $C_5H_7NO_2$: 113.047 63. Found: 113.0477.

The reaction was repeated at room temperature. To 50 mg (0.4 mmol) of **1j** in 1 mL of water was added a solution of 86 mg (0.44 mmol) of LiOCl in 1 mL of water. This mixture was stirred for 30 min; 0.5 mL of gas (CO_2 and ethylene in the ratio of 2 parts to 1 part by GC) was evolved.

Reaction of 1j with *tert*-Butyl Hypochlorite. To 129 mg (1 mmol) of **1j** in 5 mL of $CHCl_3$ was added 108 mg (1 mmol) of Me_3COCl. The reaction mixture was stirred at room temperature for 2 h in the dark, and solvent was removed from the covered flask under vacuum at room temperature to yield 160 mg (98%) of an oil (*N*-chloro-**1j**): NMR ($CDCl_3$) δ 1.27 (m, 2 H), 1.5 (m, 2 H), 3.15 (s, 3 H), 3.75 (s, 3 H); NMR (CD_3OD) δ 1.2 (m, 2 H), 1.43 (m, 2 H), 3.13 (s, 3 H), 3.7 (s, 3 H).

Reaction of 1c with Hypochlorite. A solution of 243 mg of LiOCl (1.25 mmol) in 2.5 mL of water was added dropwise to a solution of **1c** (120 mg, 0.63 mmol) in 1 mL of 2% NaOH. The reaction mixture was stirred for 15 min. Ethylene (1.2 mL, 10%) was evolved. The aqueous reaction mixture was extracted with EtOAc (3 × 10 mL), which was dried and evaporated to yield 48 mg of an oil. It was chromatographed (preparative TLC, EtOAc) to yield 8 mg (8%) of a solid, which was identical, according to NMR, IR, and mass spectra, with *N*-benzyl-3-hydroxypropanamide (**2c**), prepared as described below:[24] NMR ($CDCl_3$) δ 2.43 (t, J = 5.7 Hz, 2 H), 3.87 (t, J = 5.7 Hz, 2 H), 4.43 (d, J = 6.0 Hz, 2 H), 7.27 (s, 5 H); IR ($CHCl_3$) 3430, 1660 cm^{-1}; MS, m/z 179, 161, 148, 106, 91.

Reaction of 1d with Aqueous Hypochlorite. In a typical reaction, a solution of 688 mg (3.5 mmol) of LiOCl in 5 mL of water was added to 200 mg (0.71 mmol) of **1d**. Then 5 mL of 3 N HCl was added, and the solution was stirred for 3 h. The yield of CO_2 was 35% (96 mg of $BaCO_3$, 40 mg of blank). The reaction mixture was neutralized with K_2CO_3 and extracted with EtOAc to obtain 126 mg of an oil. The NMR spectrum of this product indicated that it was a multicomponent mixture. Repeated preparative TLC ($CHCl_3$, EtOAc) yielded varying amounts of benzaldehyde, benzylamine, and other unidentified products having the A_2X_2 pattern in the proton NMR spectrum.

Reaction of 1d with *tert*-Butyl Hypochlorite. To 200 mg (0.71 mmol) of **1d** in 20 mL of $CHCl_3$ was added 0.2 mL of *tert*-butyl hypochlorite (ca. 2 mmol). The reaction mixture was stirred at room temperature overnight in the dark. The solid that separated was filtered and washed with $CHCl_3$: yield 85 mg (63%); NMR (DMSO-d_6) δ 1.36 (m, 2 H), 1.6 (m, 2 H), 4.23 (br s, 2 H), 7.5 (m, 5 H), which is identical with the NMR spectrum of **1c**·HCl. The mass spectrum is similar to that of **1c** (MS: m/z 191, 176, 145, 91). Evaporation of the filtrate gave an oil, which was chromatographed (preparative TLC, EtOAc) to yield 75 mg (100%) of benzaldehyde.

Reaction of 1e with Hypochlorite. To 85 mg (0.5 mmol) of **1e** was added a solution of 970 mg (5 mmol) of LiOCl in 5 mL of water, followed by 5 mL of 3 N HCl. $BaCO_3$ from the CO_2 traps weighed 130 mg (80%, after correction for blank). The aqueous reaction mixture was neutralized with K_2CO_3 and extracted with EtOAc to yield 60 mg of an oil, which was a mixture of many components, according to TLC and NMR. Repeated chromatography (preparative, TLC; several solvents) yielded 10 mg of an oil, which was still a mixture (NMR, TLC). The major peaks in its NMR spectrum were a multiplet assigned to the piperidine ring and a pair of triplets (A_2B_2). Further chromatography (preparative TLC) yielded 2 mg of an oil, with a strong peak at 1650 cm^{-1} in the infrared: NMR ($CDCl_3$) δ 1.60 (m, 6 H), 2.8 (t, 2 H), 3.6 (m, 4 H), 3.8 (t, 2 H) (plus minor impurity peaks); MS, m/z 174, 140, 112 (base peak: piperidine plus carbonyl), 84 (piperidine), 69, 55, 41.

Reaction of 1f with Hypochlorite. To 65 mg (0.5 mmol) of **1f** in 1 mL of water was added a solution of 485 mg (2.5 mmol) of LiOCl in 2.5 mL of water. Vigorous evolution of gas was noted. The gas (4.5 mL, 40%) was identified as CO_2. The aqueous reaction mixture was extracted with EtOAc to obtain 20 mg of an oil. The NMR spectrum showed a pair of triplets between 3.5 and 4.0 ppm (ring-opened products). No attempt was made to isolate these products.

Reaction of 6 with Hypochlorite. To 70 mg (0.5 mmol) of **6**[10] in a flask attached to a gas buret was added 2.2 mL (1.5 mmol) of NaOCl (Clorox) solution. Ethylene, 7.3 mL (65%), was evolved

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over several minutes. The aqueous reaction mixture was extracted with CH_2Cl_2 (3 × 15 mL). The organic layer was dried and evaporated to obtain 37 mg (62%) of an oil, which solidified in part on standing. *N*-Chloropiperidine, prepared by shaking piperidine with excess NaOCl or by the action of *N*-chlorosuccinimide on piperidine,[25] was also a liquid that solidified on standing. The NMR spectra, TLC, and mass spectra of all three samples were identical: NMR ($CDCl_3$) δ 1.18–1.82 (m, 6 H), 3.0 (distorted t, 4 H); MS, *m/z* 121 and 119, 120 and 118, 84, 55 and 42; TLC ($CHCl_3$) R_f = 0.59; unstained by I_2. The reaction was repeated and the reaction mixture acidified at the end with 3 mL of 1 N HCl. $BaCO_3$ from the CO_2 traps weighed 58 mg (59% after correcting for a blank). At times the NMR spectrum of the crude reaction product had an A_2B_2 pattern, presumably the result of a cyclopropane-ring-opening reaction.

Reaction of 6-*cis*-d_2 with Hypochlorite. To 20 mg (0.14 mmol) of 6-d_2[8] in a flask sealed with a septum was injected a solution of LiOCl (65 mg, 0.34 mmol) in 1 mL of water. The head-space gas was analyzed for ethylene-1,2-d_2 by infrared spectroscopy (see the section on 1-(*N*-methylamino)cyclopropanecarboxylic acid-2,3-d_2 above). Only ethylene-*cis*-1,2-d_2 (842 cm^{-1}) was observed.[23]

Reaction of 6 with Alkaline Peroxide. Into a solution of 70 mg (0.5 mmol) of **6** and 210 mg (2.5 mmol) of $NaHCO_3$ in 4 mL of water was injected 0.3 mL (3 mmol) of 30% H_2O_2. The solution was stirred for 2 h. The gas evolved (4.5 mL) was a mixture of ethylene and CO_2, according to GC. The reaction mixture was extracted with EtOAc (3 × 10 mL) to obtain 40 mg of an oil, which was, according to NMR, a mixture of *N*-acryloylpiperidine (**10**, prepared independently by the action of piperidine on acryloyl chloride) and *N*-(3-hydroxypropionyl)-piperidine (**2g**, prepared by the action of piperidine on β-propiolactone). NMR ($CDCl_3$): **10** δ 1.57 (br s, 6 H), 3.5 (distorted t, 4 H), 5.2–6.7 [ABX vinyl pattern 5.2–5.68 (dd, 1 H), 6.08–6.33 (distorted dd, 1 H), 6.4–6.7 (distorted dd, 1 H)]; **2g** δ 1.58 (br s, 6 H), 2.48 (t, *J* = 5.4 Hz, 2 H), 3.3 (distorted t, 2 H), 3.52 (distorted t, 2 H), 3.82 (t, *J* = 5.4 Hz, 2 H).

N-Substituted 3-Hydroxypropanamides 2b, 2c, and 2g.[24] A solution of 72 mg (1 mmol) of β-propiolactone in 2 mL of benzene was added dropwise to 1 mmol of amine, cooled in an ice bath. (In the case of methylamine, the vapors were trapped at −78 °C and excess amine was used.) The reaction mixture was stirred overnight at room temperature. Benzene was removed, and the residual oil was redissolved in EtOAc, washed with 1 N HCl and water, and dried. Solvent was removed to isolate the hydroxy amides in 70–80% yield.

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Registry No. **1b**, 99324-92-2; **1b**·HCl, 99324-91-1; **1b**-d_2, 119111-68-1; *N*-BOC-**1b**, 119145-87-8; **1c**, 119111-62-5; **1c**·HCl, 119111-75-0; **1c** (methyl ester), 119111-70-5; **1d**, 119111-63-6; **1e**, 119111-64-7; **1e**-d_2, 119111-71-6; **1f**, 119111-65-8; **1g**, 765-30-0; **1h**, 22936-83-0; **1i**, 72784-43-1; **1i**·HCl, 72784-42-0; **1i** (Schiff base), 119111-69-2; **1j**, 119111-66-9; *N*-chloro-**1j**, 119111-74-9; **2a**, 109-78-4; **2b**, 6830-81-5; **2c**, 19340-82-0; **2d**, 590-90-9; **2g**, 86452-58-6; **3**, 100-52-7; **4**, 100-46-9; **5**, 119111-61-4; **6**, 27161-21-3; **6**-*cis*-d_2, 119111-76-1; **10**, 10043-37-5; ACC, 22059-21-8; *N*-BOC-ACC, 88950-64-5; ACC-d_2, 119238-02-7; ACC-d_2 (methyl ester), 119111-72-7; 1-methylcyclopropanecarboxylic acid, 6914-76-7; 1-methylcyclopropanecarboxamide, 15910-91-5; *N*-bromo-1-methylcyclopropanecarboxamide, 119111-67-0; diiodopentane, 628-77-3; methyl *cis*-2,3-dideuterio-1-(1-piperidino)cyclopropanecarboxylate, 119111-73-8; ethylene, 74-85-1; acrylonitrile, 107-13-1; β-propiolactone, 57-57-8; *cis*-ethylene-1,2-d_2, 2813-62-9; *N*-chloropiperidine, 2156-71-0; piperidine, 110-89-4; acryloyl chloride, 814-68-6; methylamine, 74-89-5.

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Synthesis, Absolute Stereochemistry, and Circular Dichroism of Chiral 1,8a-Dihydroazulene Derivatives

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A model compound, (8a*S*)-(+)-1,8a-dihydro-8a-methylazulene (**6**), was synthesized from *trans*-ketone (1*S*,3a*R*,8a*S*)-(**9a**) in order to determine the absolute stereostructure of the liverwort sesquiterpene (+)-1,8a-dihydro-3,8-dimethylazulene (**1**) by CD spectroscopy. The CD Cotton effects of compound **6** were stronger and closer, in intensity, to those of the natural product **1** than those of the previous model compounds **4** and **5**. Another model compound **7** also showed similar CD Cotton effects to those of **1**. Therefore, the present CD data experimentally establish the absolute configuration of (+)-**1** previously predicted to be 8a*S* on the basis of theoretical CD spectra. The absolute configuration was also corroborated by an X-ray crystallographic analysis of compound (+)-**10**. The present CD and X-ray studies have thus experimentally validated the methodology for determining absolute stereostructures of twisted π-electron systems on the basis of the theoretical CD spectra calculated by the π-electron SCF-CI-DV MO method.

Theoretical calculation of CD spectra of twisted and conjugated π-electron systems by the π-electron SCF-CI-dipole velocity molecular orbital method[2-5] enables one to predict the absolute stereostructures of various natural and synthetic chiral organic compounds[6-11] in a nonempirical manner. For example, we have determined the absolute stereochemistry of (+)-halenaquinol and (+)-halenaqui-

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