Phytochemistry, 1979, Vol. 18, pp. 617–620. © Pergamon Press Ltd. Printed in England. 0031-9422/79/0401-0617 $02.00/0

HALOGENATED ACETIC AND ACRYLIC ACIDS FROM THE RED ALGA *ASPARAGOPSIS TAXIFORMIS*

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(*Revised received* 9 *October* 1978)

Key Word Index—*Asparagopsis taxiformis*; Bonnemaisoniaceae; red alga; haloacetic acids; haloacrylic acids.

Abstract—Nine halogenated acetic acids and nine halogenated acrylic acids have been identified in the aqueous extract of Hawaiian *Asparagopsis taxiformis*.

INTRODUCTION

The favorite edible seaweed in Hawaii is the red alga *Asparagopsis taxiformis* [1]. The pungent aroma of this alga is due to an essential oil that is composed mainly of bromoform with smaller amounts of other bromine, chlorine, and iodine-containing methanes, ethanes, ethanols, acetaldehydes, acetones, 2-acetoxypropanes, propenes, epoxypropanes, acroleins and butenones [2]. The methylene chloride extract from the vacuum-dried alga contains a variety of halogenated isopropanols, but-3-en-2-ols and acetamides [3]. We have examined the aqueous extract of Hawaiian *A. taxiformis* and report here the identification of a number of halogenated acetic and acrylic acids (Table 1).

Table 1. Halogenated acids from Hawaiian *A. taxiformis*

Type of Compound		Structure	GLC Retention time (min) Acid*	Methyl ester†
Haloacetic acids	1	$ClCH_2CO_2H$		4.5
	2	$BrCH_2CO_2H$		8.4
	3	ICH_2CO_2H		12.6
Dihaloacetic acids	4	Cl_2CHCO_2H		
	5	$BrClCHCO_2H$		12.3
	6	$ClICHCO_2H$		15.7
	7	Br_2CHCO_2H		14.6
	8	$BrICHCO_2H$		17.6
	9	I_2CHCO_2H		21.2
Haloacrylic acids	10	$ClCH{=}CHCO_2H$ or $CH_2{=}CClCO_2H$		9.5
	11	$BrCH{=}CHCO_2H$	9.2	12.6
	12	$ICH{=}CHCO_2H$ or $CH_2{=}CICO_2H$	11.5	14.3
Dihaloacrylic acids	13	$Cl_2C{=}CHCO_2H$ or $CHCl{=}CClCO_2H$		11.8
	14	Br_2CHCO_2H	12.7	17.0
	15	$BrIC{=}CHCO_2H$, $CHBr{=}ClCO_2H$, or $CHI{=}CBrCO_2H$	15.6	19.1
	16	$I_2C{=}CHCO_2H$ or $CHI{=}ClCO_2H$		22.5
Trihaloacrylic acids	17	$Br_2C{=}CBrCO_2H$		20.8
	18	$BrIC{=}CBrCO_2H$ or $Br_2C{=}ClCO_2H$		23.7

* Determined on a 2 m × 2 mm stainless steel column of 3% OV-17 on Supelcoport heated isothermally at 60° for 4 min after injection, then temperature programmed from 60 to 200° at 8°/min, and finally heated isothermally at 200° using a flow rate (He) of 30 ml/min.

† Same column and flow rate as above. Heated isothermally at 40° for 8 min after injection, then temperature programmed from 40 to 200° at 8°/min, and finally heated isothermally at 200°.

RESULTS AND DISCUSSION

The aqueous extract was obtained by partitioning the combined methanol and methylene chloride extracts of the vacuum-dried plants between methylene chloride and water. The aqueous phase was separated, acidified with phosphoric acid and subjected to continuous ether extraction. Upon evaporation of the ether, an oily mixture of halogenated acids was obtained in 2.8% yield. Analysis of the mixture by GC–MS showed several sharp peaks for halogenated acrylic acids atop broad, poorly resolved bands for halogenated acetic acids. Esterification of the mixture with diazomethane or methanolic hydrochloric acid improved the resolution of the mixture considerably and 9 halogenated Me acetates (**1–9**) and 9 halogenated Me acrylates (**10–18**) were found.

Interpretation of the MS of the Me acetates and acrylates was straightforward; M^+ was observed for all compounds. Generally the *m/e* 59 ion ($CH_3O—C\equiv O^+$) was the base peak in the MS of the halogenated acetates whereas the M^+-OCH_3 ion was the most intense peak in that of the halogenated acrylates. The halogen positions in the mono- and dihaloacrylic acids could not be established unambiguously from the MS data. The structure and stereochemistry of the bromoacrylic acid (**11**) was concluded to be *Z* by comparing the GLC R_t of its Me ester with those of synthetic Me 2-bromoacrylate and Me *E*- and *Z*-3-bromoacrylates. The GLC R_t of Me *Z*-3-bromoacrylate was considerably longer than those of the two other isomers. Similarly the dibromoacrylic acid (**14**) was identified as the 3,3-isomer by comparing the GLC R_t of its Me ester with those of synthetic Me *E*- and *Z*-2,3-dibromoacrylates and Me 3,3-dibromoacrylate. The structures of the other mono- and dihaloacrylic acids, however, were not rigorously determined as direct comparisons with synthetic compounds were not made.

Partial separation of the aqueous extract of the alga was achieved by chromatography on DEAE-Sephadex. Elution with 0.01 N hydrochloric acid removed the acrylic acids first followed by the acetic acids. The acids were converted to the ammonium salts and a few compounds were further identified from ^1H NMR data.

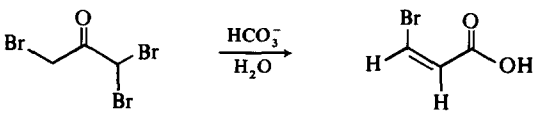
The ^1H NMR spectrum of the acrylate fraction, for example, exhibited a singlet at δ 7.52 in D_2O, assigned to the olefinic proton of ammonium 3,3-dibromoacrylate. The synthetic compound had an identical proton chemical shift whereas ammonium 2,3-dibromoacrylate showed the olefinic signal at δ 7.04 for the *Z* isomer or at 8.3 for the *E* isomer. The ^1H NMR spectrum of the acetate fraction in D_2O showed a 6:41:48:2 set of singlet signals δ 6.83, 6.28, 6.38 and 6.46, assigned to ammonium diiodo-, bromoiodo-, dibromo-, and dichloroacetate, respectively. The ammonium salts of commercial dichloro- and dibromoacetic acids exhibited the same chemical shifts.

Biomimetic synthesis

In the absence of labeling studies, the biogenesis of the many compounds in *A. taxiformis* is largely speculative. It appears, however, that the halogenated acetic acids may be at least partially derived from the haloform reaction of polyhaloacetones. The degradation may not not be enzymatically controlled since 1,1,1-trihaloacetones decompose to haloforms and acetic acids upon standing in aqueous solution. 1,1,1,3,3-Pentabromoacetone, formed when 1,1,3,3-tetrabromoacetone is brominated in aqueous sodium bicarbonate solution, readily decomposes to bromoform and dibromoacetic acid [2, 4].

Enzymatic halogenation of malonic acid in the seaweed is another possible route to the dihaloacetic acids. Under non-enzymatic conditions, malonic acid readily adds two equivalents of bromine and decarboxylates in aqueous medium to form **7**.

Biogenetically, the halogenated acrylic acids may be formed either by the haloform reaction of halogenated butenones [2] or via the Favorski rearrangement of tri- and tetrahaloacetones. 1,1,3-Tribromoacetone, a minor constituent of the seaweed, rearranges readily and exclusively to *Z*-3-bromoacrylic acid (**11**) in aqueous



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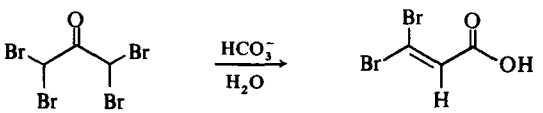
sodium bicarbonate at room temperature [6, 7]. Similarly, 1,1,3,3-tetrabromoacetone, also a minor constituent of the alga, is converted to 3,3-dibromoacrylic acid (**14**) in aqueous bicarbonate [8, 9].



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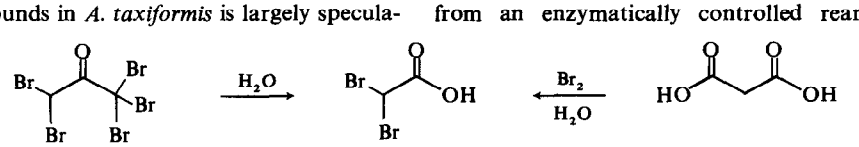
Comparison of Hawaiian, Mexican and Spanish Asparagopsis

Halogenated acetic and acrylic acids (isolated and characterized as Et esters) have also been found in Mexican *A. taxiformis* and Spanish *A. armata* [5]. The halogenated acetic acids identified were **7**, **8** and tribromoacetic acid. A monobromo-, a monoiodo-, a chlorobromo, a dibromo-, a bromoiodo- and a diiodoacrylic acid were also detected in the seaweeds, but only the structure of the dibromoacrylic acid was rigorously established as the *E*-2,3 isomer by $LiAlH_4$ reduction to *E*-2,3-dibromoallyl alcohol.

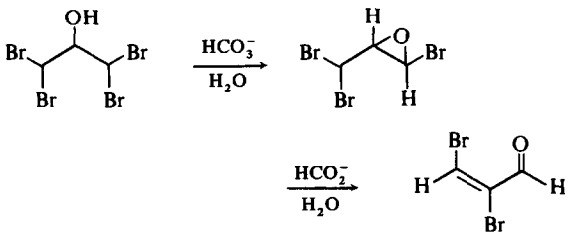
The isolation of *E*-2,3-dibromoacrylic acid from Mexican *A. taxiformis* and Spanish *A. armata* is an interesting contrast to the isolation of 3,3-dibromoacrylic acid from Hawaiian *A. taxiformis*. This difference suggests that the other halogenated acrylic acids in the Mexican and Spanish seaweeds may also be structurally different from those in the Hawaiian alga.

Biogenetically *E*-2,3-dibromoacrylic acid could arise from an enzymatically controlled rearrangement of

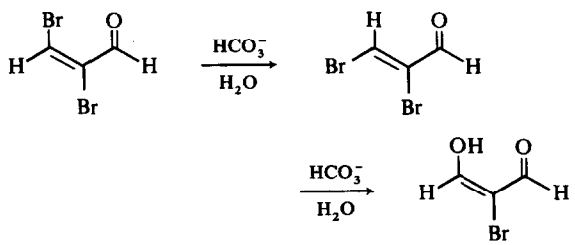


1,1,3,3-tetrabromoacetone. In our study of the non-enzymatic Favorski rearrangement of 1,1,3,3-tetrabromoacetone in aqueous bicarbonate solution, however, *E*- and *Z*-2,3-dibromoacrylic acid could not be detected in the reaction mixture. *E*-2,3-Dibromoacrylic acid could also be formed by the oxidation of *E*-2,3-dibromoacrolein. We find that *E*-2,3-dibromoacrolein is formed from 1,1,3,3-tetrabromo-2-propanol under non-enzymatic conditions.

When 1,1,3,3-tetrabromo-2-propanol is allowed to stand in aqueous bicarbonate solution at room temperature, it readily cyclizes to *trans*-1,3,3-tribromopropene oxide. On further standing the epoxide rearranges and eliminates hydrogen bromide to give *E*-2,3-dibromo-



acrolein. 1,1,3,3-Tetrabromo-2-propanol [3] and *trans*-1,3,3-tribromopropene oxide [2] are both constituents of *Asparagopsis*, but to date *E*-2,3-dibromoacrolein has not been detected. In our studies, we have further noted that *E*-2,3-dibromoacrolein isomerizes slowly to the more stable *Z* isomer in aqueous bicarbonate solution. On prolonged standing in this medium *Z*-2,3-dibromoacrolein is very slowly converted to 2-bromomalonodialdehyde.



EXPERIMENTAL

^{1}H NMR spectra were obtained on a 100 MHz instrument equipped with a Fourier transform system. Chemical shifts are reported in δ units (ppm) using TMS as an int. standard in $CDCl_3$ or Me_2CO-d_6 or using *p*-dioxane (δ 3.8 relative to Na, 2,2-diMe-2-silapentane-5-sulfonate, δ 0) as an int. standard in D_2O. GC–MS was carried out with a GLC coupled through a double stage jet separator to a double focusing mass spectrometer operating at 70 eV.

Isolation of acids. (a) *Extraction and identification as* Me *esters.* Vacuum-dried plants of *A. taxiformis* (Delile) Trev. (97 g) were soaked in MeOH (1 l.) for 84 hr. The solvent was decanted and the extraction was continued successively with MeOH (1 l.) and $CHCl_3$ (2 × 1 l.). The extracts were combined and the solvents removed *in vacuo* to give a dark oil which was then partitioned between H_2O and $CHCl_3$. The aq. layer (400 ml) was separated and filtered. A small portion (25 ml) of the aq. extract was acidified with conc H_3PO_4(3 ml) and extracted continuously for 48 hr with Et_2O. Removal of the Et_2O *in vacuo* afforded 170 mg of an orange oil. A sample of this oil was esterified with excess CH_2N_2 and another one was esterfied with MeOH–HCl. Analysis of the resulting two mixtures of esters by GC–MS (see Table 1, footnote †, for conditions) indicated the presence of the following Me esters: Me chloroacetate, R_t 4.5 min, 1%, *m/e* (rel. intensity) 108 (12), 110 (5), 77 (35), 79 (14), 73 (19), 59 (100), 49 (48), 51 (16); Me bromoacetate, 8.4 min, 2%, 152 (20), 154 (20), 121 (30), 123 (30), 93 (45), 95 (45), 59 (100); Me chloroacrylate, 9.5 min, <1%, 120 (14), 122 (6), 89 (100), 91 (39), 85 (25), 61 (31), 59 (31); Me dichloroacrylate, 11.8 min, 2%, 154 (15), 156 (9), 158 (2), 123 (100), 125 (65), 127 (15), 95 (21), 97 (10), 99 (6), 59 (40); Me bromochloroacetate, 12.3 min, 4%, 186 (2), 188 (1), 190 (0.5), 155 (3), 157 (4), 159 (1), 127 (69), 129 (58), 131 (15), 59 (100); Me iodoacetate 12.6 min, 8%, 200 (34), 169 (18), 141 (35), 73 (78), 59 (100); Me *Z*-3-bromoacrylate, 12.6 min, <1%, 164 (12), 166 (11), 133 (100), 135 (99), 105 (35), 107 (34), 85 (47), 59 (22); Me dibromoacetate, 14.6 min, 22%, 230 (3), 232 (5), 234 (3), 199 (2), 201 (4), 203 (2), 171 (36), 173 (66), 175 (32), 120 (18), 122 (17), 79 (10), 81 (10), 59 (100); Me iodoacrylate, 15.5 min, <1%, 212 (83), 181 (100), 153 (39), 127 (39), 59 (89); Me chloroiodoacetate, 15.7 min, 2%, 234 (30), 236 (15), 175 (40), 177 (20), 127 (50), 107 (90), 109 (40), 59 (100); Me 3,3-dibromoacrylate, 17 min, 10%, 242 (9), 244 (16), 246 (8), 211 (53), 213 (100), 215 (49), 183 (13), 185 (23), 187 (11), 163 (13), 165 (12), 135 (22), 137 (18), 104 (57), 106 (56), 79 (9), 81 (9), 59 (32); Me bromoiodoacetate, 17.6 min, 15%, 278 (55), 280 (55), 247 (9), 249 (9), 219 (50), 221 (50), 168 (28), 151 (100), 153 (100), 140 (31), 127 (62), 120 (23), 122 (24), 59 (42); Me bromoiodoacrylate, 19.1 min, 25%, 290 (72), 292 (70), 259 (60), 261 (58), 231 (20), 233 (19), 211 (10), 163 (50), 165 (49), 127 (40), 59 (100); Me tribromoacrylate, 20.8 min, <1%, 320 (4), 322 (9), 324 (8), 326 (3), 289 (6), 291 (15), 293 (15), 295 (7), 241 (15), 243 (25), 245 (15), 59 (100); Me diiodoacetate, 21.2 min, 8%, 326 (69), 295 (10), 267 (21), 254 (16), 199 (100), 127 (84), 59 (63); Me diiodoacrylate, 22.5 min, 7%, 338 (30), 307 (10), 279 (5), 254 (3), 211 (78), 152 (56), 127 (45), 59 (100); Me dibromoiodoacrylate, 23.7 min, <1%, 368 (1), 370 (2), 337 (1), 339 (2), 341 (1), 127 (15), 59 (100).

(*b*) *Ion exchange chromatography of aqueous fraction.* A small portion of the aq. soln [^{1}H NMR spectrum between 5 and 9 ppm (D_2O): singlets at δ (intensity relative to peak at 5.55 ppm) 5.55 (100), 5.58 (93), 5.85 (13), 5.87 (17), 6.30 (58), 6.40 (80), 6.47 (3), 6.52 (5), 6.59 (5), 6.64 (12), 6.98 (12), 7.12 (12), 7.52 (46), 7.65 (25), 8.26 (7), and 8.86 (10)] was introduced onto a 15 cm × 3 cm column of DEAE-Sphadex A-25 (Cl^- form). After washing the column with 400 ml of H_2O, elution with 0.01 N aq. HCl gave 3 fractions (monitored by UV) which were neutralized with dil. NH_4OH soln and lyophilized. Fraction 1 contained ammonium 3,3-dibromoacrylate (^{1}H NMR D_2O δ 7.52). None of the compounds in fraction 2 were identified. Fraction 3 contained ammonium diiodoacetate (^{1}H NMR D_2O δ 5.83), bromoiodoacetate (δ 6.28), dibromoacetate (δ 6.38), and dichloroacetate (δ 6.46) in a 19: 87:100:4 ratio.

Z-3-Bromoacrylic acid. The acid was prepared as described in ref. [6] and had mp 57–58.5°; ^{1}H NMR ($CDCl_3$) δ 6.62 (*d*, J = 8 Hz, 1H), 7.12 (*d*, J = 8 Hz, 1H), 9.92 (*bs*, 1H).

E-3-*Bromoacrylic acid. Z*-3-Bromoacrylic acid (690 mg) was dissolved in 6 ml of 6 N HBr and stirred at 105° for 5 hr. The mixture was cooled, 5 ml of H_2O added and the mixture extracted with CH_2Cl_2 (3 × 10 ml). The extracts were combined, dried ($MgSO_4$) and the solvent removed *in vacuo* to give a light tan solid. Recrystallization from hexane gave 310 mg (45%) of *E*-3-bromoacrylic acid as colorless needles; mp 115–116.2°; ^{1}H NMR ($CDCl_3$) δ 6.48 (*d*, J = 14 Hz, 1H), 7.7 (*d*, J = 14 Hz, 1H), 10.7 (*bs*, 1H).

2-Bromoacrylic acid. Acrylic acid (5 g, 69 mmol) and $NaHCO_3$ (17.4 g, 207 mmol) were dissolved with stirring in 100 ml

of H_2O, Br_2 (11 g, 69 mmol) was added dropwise over 5 min and the soln stirred overnight at room temp. The soln was then acidified with HCl and extracted with CH_2Cl_2. Removal of CH_2Cl_2 *in vacuo* gave a colorless oil which was dissolved in 25 ml of 5% aq. NaOH and the mixture stirred at room temp. for 1 hr. Acidification with HCl followed by extraction with CH_2Cl_2 afforded 4.1 g of a pale yellow oil which consisted of *ca* 30% 2-bromoacrylic acid and 70% 2,3-dibromopropionic acid (GC–MS). 2-Bromoacrylic acid: ^{1}H NMR ($CDCl_3$) δ 6.93 (*d*, J = 2 Hz, 1H), 7.06 (*d*, J = 2 Hz, 1H), 11.46 (*bs*, 1H).

Comparison of Me *esters of synthetic bromoacrylic acids with* Me *ester of natural Z-3-bromoacrylic acid.* Synthetic 2-, *E*-3-, and *Z*-3-bromoacrylic acid were converted to the Me esters with CH_2N_2. The esters were examined by GC–MS on a 3 m × 2 mm column of 10% SP-1000 heated isothermally at 80° for 2 min after injection, then temp. programmed from 80 to 200° at 8°/min using a gas flow rate of 40 ml/min. Me *E*-3-bromoacrylate: R_t 6.7 min; MS *m/e* (rel. intensity) 164 (24), 166 (24), 133 (100), 135 (100), 119 (2), 121 (2), 105 (56), 107 (56), 85 (100), 59 (29). Me 2-bromoacrylate: 7.2 min: 164 (59), 166 (58), 133 (88), 135 (92), 119 (2), 121 (2), 105 (100), 107 (94), 85 (80), 59 (47). Me *Z*-3-bromoacrylate: 10 min; 164 (12), 166 (11), 133 (100), 135 (99), 105 (35), 107 (24), 85 (47), 59 (22).

3,3-Dibromoacrylic acid (**14**). (*a*) *From* 3,3-*dibromacrolein.* The aldehyde [10] (250 mg) was ozidized by procedure B of ref. [11]. The dark reaction mixture was stored in the freezer overnight and **14** crystallized from the reaction mixture as white plates; mp 82–84°; ^{1}H NMR (Me_2CO-d_6) δ 7.08 (*s*, 1H), 10.22 (*bs*, 1H). (*b*) *From* 1,1,3,3-*tetrabromoacetone.* The acid was prepared as described in refs. [8, 9].

E- and Z-2,3-Dibromoacrylic acids. Propiolic acid (500 mg) was brominated using the procedure of ref. [12] to give 1.27 g (78%) of a mixture of *E* and *Z*-2,3-dibromoacrylic acids; ^{1}H NMR (D_2O) δ 7.04 (*s*, 1H, Z, 68% by integration), 8.3 (*s*, H, *E*, 32% by integration).

Comparison of Me *esters of synthetic dibromoacrylic acids with* Me *ester of natural* 3,3-*dibromoacrylic acid.* Small amounts of 3,3-dibromoacrylic acid and a mixture of *E*- and *Z*-2,3-dibromoacrylic acid were converted to the Me esters with CH_2N_2. The esters were examined by GC–MS using the conditions in Table 1, footnote †. Me *E*-2,3-dibromoacrylate: R_t 11.7 min; MS *m/e* (rel. intensity) 242 (19), 244 (32), 246 (19), 211 (32), 213 (64), 215 (32), 183 (20), 185 (40), 187 (20), 163 (100), 165 (100), 104 (34), 106 (34), 59 (61). Me *Z*-2,3-dibromoacrylate: 12.4 min; 242 (19), 244 (32), 246 (19), 211 (32), 213 (64), 215 (32), 183 (20), 185 (40), 187 (20), 163 (100), 165 (100), 104 (34), 106 (34), 59 (61). Me 3,3-dibromoacrylate: 17 min; 242 (9), 244 (16), 246 (8), 211 (53), 213 (100), 215 (49), 183 (13), 185 (23), 187 (11), 163 (13), 165 (12), 135 (22), 137 (18), 104 (57), 106 (57), 59 (32).

1,1,3-Tribromo-1,2-epoxypropane. A soln of 1,1,3,3-tetrabromoisopropanol (6.17 g) and $NaHCO_3$ (1.38 g) in 100 ml of Me_2CO–H_2O (1:1) was stirred at room temp. for 36 hr. The Me_2CO was removed *in vacuo* and the oily aq. mixture was extracted with CH_2Cl_2. Evaporation left a yellow oil which was chromatographed on a 25 × 3 cm column of Si gel with CH_2Cl_2–hexane (1:9). The forerun of the effluent afforded 1.02 g (21%) of the epoxide as a colorless oil; ^{1}H NMR ($CDCl_3$) δ 3.73 (*d*, J = 7 Hz, 1H), 5.14 (*s*, 1H), 5.28 (*d*, J = 7 Hz, 1H); IR (neat) ν_{max} 2990 (w), 1410 (m), 1264 (s), 1236 (m), 1140 (m), 1010 (w), 905 (s), 878 (w), 780 (s), 740 (s), 680 (s), 605 (s), 590 (s) cm^{-1}; MS *m/e* (rel. intensity) 292, 294, 296, 298 (0.6; 1; 1; 0.4, M^+ cluster <1%), 213 (28), 215 (49), 217 (22), 184 (7), 185 (23), 186 (15), 187 (37), 188 (8), 189 (19), 171 (6), 173 (12), 175 (7), 157 (1), 159 (3), 161 (1), 133 (7), 134 (4), 135 (6), 137 (4), 105 (99), 107 (100), 79 (16), 80 (7), 81 (17), 82 (7). An analytical sample was prepared by HPLC on a μ-Porasil column using $CHCl_2$–hexane (1:19). Calcd for $C_3H_3Br_3O$: C, 12.2: H, 1.0. Found: C, 12.4; H, 1.1%).

2-Bromomalondiadehyde. (*a*) *From* E-2,3-*dibromoacrolein. E*-2,3-dibromoacrolein was stirred in moist air for 48 hr. The resulting black semisolid was extracted with CH_2Cl_2. The brown solid was sublimed (100°, 0.1 torr) and crystallized from C_6H_6 to give 450 mg of bromomalonodialdehyde as white needles; mp 137–139° dec (lit. [13] 155° dec); ^{1}H NMR (Me_2CO-d_6) δ 8.68 (*s*); UV (EtOH) λ_{max} 262 nm (ε 14200) shifted to λ_{max} 215.5 nm (ε 17700), 278 (22600) in base, ^{13}C NMR (Me_2CO-d_6) δ 206.6 (*d*), 175.3 (*s*); MS *m/e* (rel. intensity) 150 (100), 152 (100), 149 (55), 151 (54), 132 (14), 134 (13), 122 (21), 124 (16), 121 (18), 123 (16), 104 (23), 106 (23), 93 (18), 95 (16), 79 (8), 81 (8), 71 (68), 53 (45), 42 (70). Anal. Calcd. for $C_3H_3BrO_2$: C, 23.9; H, 2.0. Found: C, 24.1; H, 2.1%. (*b*) *From* 1,1,3-*tribromo*-1,2-*epoxypropane.* A mixture of 588 mg of epoxide, 252 mg of $NaHCO_3$ and 20 ml of dioxane–H_2O (3:2) was stirred for 77 hr at room temp. Extraction of the mixture with VH_2Cl_2 and evaporation of the solvent afforded 181 mg of an oil which was a 6:3:1 mixture of starting material, *E*-2,3-dibromoacrolein [δ 9.28 (*s*, 1H), 8.28 (*s*, 1H)] and *Z*-2,3-dibromoacrolein [δ 9.29 (*s*, 1H), 7.96 (*s*, 1H)], respectively. The aq. portion above was acidified with conc HCl and extracted with CH_2Cl_2 to give 28 mg of crystalline 2-bromomalonodialdehyde.

Acknowledgements—Financial support by the National Science Foundation (Grant No. CHE74 01950) and the Dow Chemical Co. (in part) is gratefully acknowledged. The authors thank Mr. J. R. Miller for technical assistance.

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