and C-10 Me), 2.83 (br s, H-14), 7.12 (br s, H-12), 9.45 (s, H-16), 9.54 (d, J = 4 Hz, H-15); mass spectrum, m/e (relative intensity) 302 (M^+, 2), 274 (29), 259 (23), 177 (8), 135 (10), 121 (100), 107 (18), 95 (21), 69 (28), 55 (15); ^{13}C NMR δ 39.6 (t, C-1), 18.1[a] (t, C-2), 41.6[b] (t, C-3), 32.9 (s, C-4), 56.2 (d, C-5), 17.9[a] (t, C-6), 41.0[b] (t, C-7), 36.9 (s, C-8), 56.7 (d, C-9), 37.4 (s, C-10), 24.1 (t, C-11), 153.7 (d, C-12), 138.6 (s, C-13), 60.7 (d, C-14), 198.1 (d, C-15), 192.5 (d, C-16), 15.5[c] (q, C-17), 33.0 (q, C-18), 21.4 (q, C-19), 15.9[c] (q, C-20). (Assignments with superscripts a–c may be reversed.)

(±)-14-Epiisocopal-12-ene-15,16-dial (2). Basic alumina (500 mg) was added to a stirred solution of 1 (100 mg) in CH_2Cl_2 (40 mL). After 8 h of heating at reflux, the mixture was filtered and the solvent evaporated. Chromatography of the crude product over silica gel with hexane and with mixtures of hexane and increasing amounts of EtOAc resulted in the recovery of starting material 1 (25 mg, 25%) and the isolation of the crystalline dialdehyde **2**: 58 mg, 58%; mp 105–110 °C [lit.[4] mp 115–118 °C]; IR (KBr) 2945–2890, 1735, 1695, 1475, 1400, 1225, 1115, 1000 cm^{-1}; ^1H NMR δ 0.83, 0.85, 0.93 (s, C-4, C-8 and C-10 Me), 3.26 (m, H-14), 7.08 (m, H-12), 9.40 (s, H-16), 9.83 (d, J = 2.4 Hz, H-15); ^{13}C NMR δ 39.3 (t, C-1), 18.1 (t, C-2), 41.3 (t, C-3), 32.9 (s, C-4), 56.1 (d, C-5), 18.1 (t, C-6), 37.9 (t, C-7), 37.0 (s, C-8), 48.8 (d, C-9), 37.6 (s, C-10), 24.5 (t, C-11), 153.5 (d, C-12), 136.7 (s, C-13), 58.3 (d, C-14), 202.0 (d, C-15), 192.5 (d, C-16), 22.4 (q, C-17), 33.0 (q, C-18), 21.5 (q, C-19), 15.1 (q, C-20).

(±)-15-Acetoxyisocopal-12-en-16-al (3). To a stirred solution of **7a** (100 mg, 0.3 mmol) and imidazole (155 mg, 2.2 mmol) in DMF (3 mL) at 0 °C and under N_2 was added *tert*-butyldimethylsilyl chloride (120 mg, 0.6 mmol). After 5 min of stirring at 0 °C and 20 min at room temperature, the mixture was poured into Et_2O (50 mL) and washed with H_2O (50 mL). The organic extract was then dried (Na_2SO_4) and evaporated. Chromatography of the residue (150 mg) over silica gel with hexane and with mixtures of hexane and increasing amounts of EtOAc afforded pure **7c**: [65 mg, 38%; ^1H NMR δ 0.046 (s, 6 H, SiMe), 0.063 (s, 6 H, SiMe), 0.78 and 0.82 (s, C-4, C-8, and C-10 Me), 0.89 (s, $SiCMe_3$), 0.92 (s, $SiCMe_3$), 3.44–3.88 (m, 2 H, $-CH_2OSi-$), 4.20 (br s, 2 H, $-CH_2OSi-$), 5.79 (br s, H-12)] and **7b** [54 mg, 40%; ^1H NMR δ 0.097 (s, 6 H, SiMe), 0.76, 0.82, and 0.88 (s, C-4, C-8, and C-10 Me), 0.90 (s, $SiCMe_3$), 3.77 (br s, 2 H, $-CH_2OH$), 4.07 (d, J = 12 Hz, H-15), 4.36 (d, J = 12 Hz, H-15), 5.69 (br s, H-12).

The monosilyl ether **7b** (54 mg) was treated with Ac_2O (0.6 mL), TEA (3 mL), and DMAP (10 mg) overnight at room temperature. The mixture was then poured into H_2O (30 mL) and extracted. The Et_2O extracts were washed with aqueous 10% Na_2CO_3 and H_2O, dried (Na_2SO_4), and evaporated. The crude product, purified by a short column chromatography, afforded pure **7d**: 50 mg, 85%; ^1H NMR δ 0.097 (s, 6 H, SiMe), 0.76 and 0.88 (s, C-4, C-8, and C-10 Me), 0.90 (s, $SiCMe_3$), 2.04 (s, OCMe), 3.85 (br s, CH_2OAc), 3.91 (d, H-15), 4.14 (d, H-15), 5.80 (br s, H-12).

Without further purification **7d** (50 mg) was hydrolyzed with a mixture of THF:HOAc:H_2O (1:3:1) (10 mL) for 9 h at room temperature. The mixture was then poured into H_2O (20 mL) and extracted with Et_2O. The combined organic extracts were washed with aqueous 10% $NaHCO_3$ and H_2O, dried (Na_2SO_4), and evaporated. The crude product was purified by a short column chromatography, yielding **7e** (30 mg, 81%); ^1H NMR δ 0.79, 0.82, 0.88, and 0.89 (s, C-4, C-8, and C-10 Me), 2.06 (s, OCMe), 3.78–4.69 (complex m, 4 H, H-15 and H-16), 5.83 (br s, H-12).

A mixture of **7e** (30 mg, 0.08 mmol) and active MnO_2 (900 mg), dried as prescribed by Goldman,[14] in benzene (40 mL) was stirred for 18 h. After filtration of the mixture through a Celite pad, the filtrate and washings were concentrated to dryness. Chromatography of the residue on silica gel with EtOAc–hexane afforded **3** (20 mg, 69%) as an oily product: IR ($CHCl_3$) 3940, 2860, 1740, 1695, 1470, 1380, 1100 cm^{-1}; ^1H NMR δ 0.83, 0.87, and 0.97 (s, C-4, C-8, and C-10 Me), 1.94 (s, OCMe), 4.30–4.75 (AB part of an ABX system, 2 H, H-15), 6.90 (br s, H-12), 9.42 (s, H-16); mass spectrum, m/e (relative intensity) 347 ($(M + 1)^+$, 15), 303 (30), 287 (28), 286 (28), 271 (35), 192 (90), 177 (95), 105 (60), 95 (70), 91 (99), 81 (100); ^{13}C NMR δ 39.7 (t, C-1), 18.3 (t, C-2), 41.6 (t, C-3), 33.2 (s, C-4), 56.1 (d, C-5), 18.4 (t, C-6), 41.2 (t, C-7), 36.0 (s, C-8), 53.7 (d, C-9), 36.0 (s, C-10), 23.8 (t, C-11), 153.0 (d, C-12), 139.8 (s, C-13), 49.1 (d, C-14), 59.9 (t, C-15), 193.9 (d, C-16), 15.8 (q, C-17), 33.0 (q, C-18), 21.5 (q, C-19), 15.3 (q, C-20), 170.7 and 21.5 (OCMe).

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Registry No. (±)-**1**, 89772-24-7; (±)-**2**, 89772-25-8; (±)-**3**, 89772-26-9; (±)-**4**, 82570-42-1; (±)-**5**, 89772-27-0; (±)-**6**, 82570-43-2; (±)-**7a**, 82570-48-7; (±)-**7b**, 89710-56-5; (±)-**7c**, 89710-57-6; (±)-**7d**, 89710-58-7; (±)-**7e**, 89710-59-8.

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A Practical Synthesis of Racemic Vinylglycine from (*Z*)-2-Butene-1,4-diol

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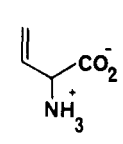
β,γ[1] and γ,δ-Unsaturated[2,3] amino acids belong to a growing class of natural products that possess biological activity both as irreversible enzyme inhibitors[4,5] and as antibiotics.[6,7] This class of compounds has held long-standing interest[8–11] among chemists. In particular, the total synthesis of vinylglycine 1 has received the most



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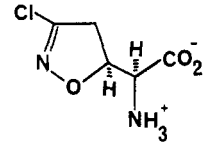

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attention.[8,10] During our efforts toward a total synthesis[12] of acivicin (**2**),[13] an antitumor, antimetabolite from fermentation broth of *Streptomyces sviceus*, we developed a practical synthesis of racemic vinylglycine using a synthetic route that holds considerable promise for a commercial synthesis of this amino acid.

Recently, Bartlett and Barstow[14] elegantly demonstrated the application of the ester–enolate Claisen rearrangement of α-amino acid derivatives to the synthesis of natural γ,δ-unsaturated amino acids. In contrast, our synthetic strategy toward the β,γ-unsaturated amino acid 1 is centered upon the well-documented[15] [3,3] sigmatropic rear-

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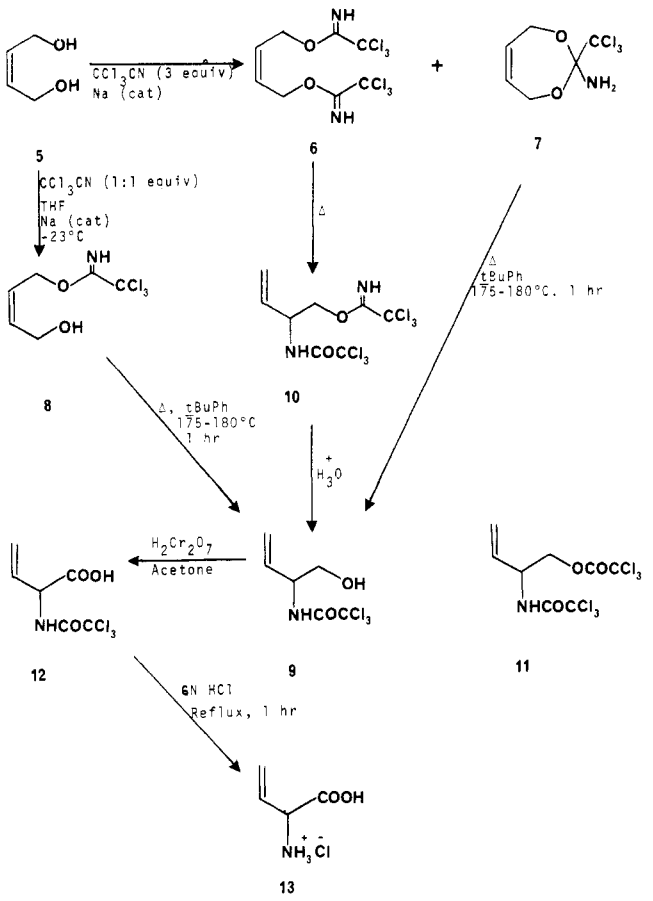
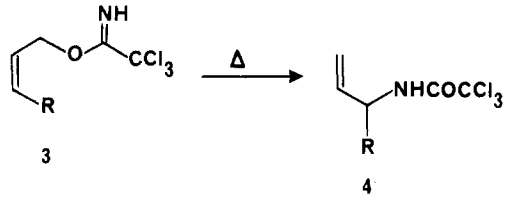
Scheme I



rangement (e.g., 3 → 4) of an allylic trichloroimidate to an allylic transposed trichloroacetamide.



As our starting material, we elected to use the readily available (*Z*)-2-butene-1,4-diol (**5**). The sequence was initiated by studying the imidation reaction (Scheme I) of compound **5** with trichloroacetonitrile (CCl_3CN) using the published procedure of Cramer and co-workers.[16] Thus, when 3 equiv of CCl_3CN were used, **5** afforded a mixture of bis(imidate) **6** (62.7%) and the dioxepine **7** (8.3%). Interestingly, by contrast, when modified imidation conditions (1.1 equiv of CCl_3CN, catalytic Na, 70 °C) were used, **5** afforded the dioxepin **7** in 84% yield. With 1.1 equiv of CCl_3CN (THF, catalytic Na, −23 °C), monoimidation of **5** was achieved to give **8** (58%) as the major isolable product (fractional distillation). Comparison of the ^1H NMR spectra of pure **6**, **7**, and **8** with that of the monoimidation reaction mixture led to the realization that all three compounds coexist in the reaction mixture in an approximate ratio of 5:20:75, respectively.

Thermal [3,3] sigmatropic rearrangement of compounds **6**–**8** was investigated next under varying conditions.[17] The bis(imidate) **6**, heating neat at 180–185 °C for 1 h, underwent the rearrangement smoothly to the trichloroacetamide **10** (83%). Under similar conditions, the mono(imidate) **8** underwent extensive decomposition; however, a solution of **8** in *tert*-butylbenzene,[18] after refluxing for ~1 h, afforded alcohol **9** (68%). Interestingly, the same alcohol **9** was obtained in 80% yield after heating the dioxepine **7** under similar conditions. This is suggestive of an equilibrium between the open-chain imidate **8** and its cyclic form **7**. Furthermore, alcohol **9** was also obtained as a major product from the acid hydrolysis (1 N HCl, acetone, ~0 °C) of **10**; the minor product was the trichloroacetate **11** (~17%). The above sequence of reactions provide an easy access to derivatives (e.g., **9** and **10**) of the parent amino alcohol, namely, 2-amino-3-buten-1-ol. The reported synthesis of 2-amino-3-buten-1-ol from butadiene monoepoxide is inefficient and hazardous.[19]

Finally, the synthesis of racemic vinylglycine hydrochloride **13** was accomplished by Jones oxidation ($H_2Cr_2O_7$, acetone, room temperature)[20] of alcohol **9** to acid **12** (87%) and subsequent acid hydrolysis (6 N HCl, reflux, 1 h) to **13** (44%). Base hydrolysis of **12** was avoided due to the tendency of the double bond to migrate to the α,β-position.[8] The ^1H NMR spectrum of **13** was in agreement with the published data.[8]

This paper describes a four-step synthesis of racemic vinylglycine hydrochloride, in an overall yield of 26% from the readily available diol **5**. The synthetic route described here requires inexpensive chemicals and avoids elaborate purification procedures. Although the results reported here are based on optically inactive starting material, the suprafacial nature[21] of the [3,3] sigmatropic rearrangement may provide a synthesis of optically active vinylglycine starting from a chiral precursor.

Experimental Section

General Methods. Melting points were recorded on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^1H NMR spectra were recorded either on a Varian XL100 or on a JOEL FX-90Q (90 MHz) spectrometer in $CDCl_3$. Chemical shifts are reported in δ units and coupling constants in Hertz. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. Infrared spectra were determined on a Beckman Model 4240 spectrophotometer and are reported in reciprocal centimeters. Thin-layer chromatography (TLC) was carried out on 0.25-mm E. Merck precoated silica gel plates (60F-254) by using UV light and/or iodine vapors as visualizing agents. Flash chromatography was run with Woelm silica gel (32–63 μm) in the indicated solvent. All evaporations of solvents were performed under reduced pressure and below 50 °C.

(*Z*)-2-Butene-1,4-diol Bis(2,2,2-trichloroethanimidate) (6) and 2-Amino-2-(trichloromethyl)-4,7-dihydro-1,3-dioxepine (7). To the stirred, commercial diol **5** (Aldrich, 22.28 g, 252.9 mmol) was added a catalytic amount of sodium (~40 mg) followed by a slow addition of trichloroacetonitrile (110 g, 726.4 mmol) at 0–4 °C (ice bath). On completion of the addition of trichloroacetonitrile, the solution was stirred for 16 h at room temperature. The solution was acidified with glacial acetic acid (1 mL) and stirred for 14 min. The resulting solution was subjected to fractional distillation under reduced pressure (~0.25 mmHg). The major fraction, distilling at ~120–138 °C, was characterized as the bis(imidate) **6** (60 g, 62.7%): ^1H NMR (100 MHz) δ 5.00 (m, 2 H), 5.98 (m, 2 H), 8.40 (b, 1 H); IR ($CDCl_3$) 3350, 1675, 805, 835

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cm^{-1}. Anal. Calcd for $C_8H_8N_2O_2Cl_6$: C, 25.50; H, 2.14; N, 7.43; Cl, 56.44; Found: C, 25.31; H, 2.17; N, 7.43; Cl, 58.96.

The minor fraction, distilling at 98–100 °C, was identified as the dioxepine **7** (9.17 g, 8.3%): ^1H NMR (100 MHz) δ 2.50 (b, 2 H), 4.00–5.10 (m, 4 H), 5.70 (m, 2 H); IR (KBr) 3430, 3350, 3040, 2940, 2920, 1607, 1110, 825 cm^{-1}. Anal. Calcd for $C_6H_8NO_2Cl_3$: C, 31.00; H, 3.47; N, 6.02, Cl, 45.75. Found: C, 30.90; H, 3.38; N, 6.24; Cl, 46.95.

2-Amino-2-(trichloromethyl)-4,7-dihydro-1,3-dioxepine (7). A catalytic amount of sodium was added to the stirred commercial diol **5** (2 g, 2.92 mmol) at 70 °C. Trichloroacetonitrile (4.7 g, 1.1 equiv) was added dropwise over a period of 35 min and the solultion was stirred at 70 °C for 2 h. The solution was cooled to room temperature, and to it was added 4 drops of glacial acetic acid. After being stirred at room temperature for 48 h, the mixture was fractionally distilled at reduced pressure (0.3 mmHg). The major fraction (5.72 g, 84%), distilling between 80 and 118 °C, was characterized as the title compound **7**, whose ^1H NMR spectrum was identical with the minor compound obtained from the imidation reaction described above.

(*Z*)-2-Butene-1,4-diol Mono(2,2,2-trichloroethanimidate) (8). To a solution of tetrahydrofuran (5 mL) containing diol **5** (3.2 g, 35 mmol) was added sodium (~5 mg) with stirring. The solution was cooled to −23 °C (CCl_4–dry ice) and to it was slowly added trichloroacetonitrile (5.3 g, 35 mmol) over a 15-min period. After continued stirring at −23 °C for 3 h, the solution was stored at ~4 °C (cold room) for 16 h. Tetrahydrofuran was removed under reduced pressure and the resulting solution was subjected to fractional distillation at ~0.3 mmHg pressure. The major fraction, distilling at ~88–102 °C, was identified as the mono-(imidate) **8** (4.77 g, 58%): ^1H NMR (100 MHz) δ 3.15 (b, 1 H), 4.30 (b, 2 H), 5.05 (d, 2 H), 5.90 (m, 2 H), 8.30 (m, 1 H); IR ($CDCl_3$) 3610, 3340, 1667, 1100, 810 cm^{-1}. Anal. Calcd for $C_6H_8NO_2Cl_3$: C, 31.00; H, 3.45; N, 6.02; Cl, 45.75. Found: C, 31.60; H, 3.66; N, 6.05; Cl, 45.06.

(*R,S*)-2-[(2,2,2-Trichloro-1-oxoethyl)amino]-3-buten-1-ol (9). A solution of imidate **8** (32 g, 137.6 mmol) in *tert*-butylbenzene (55 mL) was refluxed at 175–180 °C for 50 min. The progress of the rearrangement was followed by TLC (3% CH_3OH in CH_2Cl_2). The solution was cooled to room temperature and then loaded on a silica gel (45 g) column. The column was initially eluted with Skellysolve B until all of the *tert*-butylbenzene was removed. Elution with methylene chloride then afforded, after evaporation of the pooled fractions, the desired product **9** as a semicrystalline solid (21.1 g, 68%): ^1H NMR (100 MHz) δ 1.95 (b, 1 H), 3.83 (d, 2 H), 4.60 (m, 1 H), 5.26 (m, 2 H), 5.90 (m, 1 H), 7.15 (b, 1 H); IR (KBr) 3420, 1700, 1520, 820 cm^{-1}. Anal. Calcd for $C_6H_8NO_2Cl_3$: C, 31.00; H, 3.47; N, 6.02; Cl, 45.75. Found: C, 30.50; H, 3.06; N, 6.56; Cl, 46.64.

[3,3] Sigmatropic Rearrangement of Bis(imidate) 6. A neat sample of bis(imidate) **6** (8.47 g, 22.45 mmol) was heated in an oil bath at 180–185 °C for 1 h, with constant stirring. The resulting dark syrup was dissolved in diethyl ether (50 mL) and decolorized with charcoal to a light orange solution, which upon concentration afforded an orange syrup (7.1 g, 83.8%). ^1H NMR of this syrup indicated it to be the desired vinyl compound **10** (>90% purity). The analytical sample was obtained as a white solid by column chromatography using Skellysolve B/methylene chloride (1:3, v/v) as the eluting solvent: mp 71.5–73 °C (Skellysolve B/ether); ^1H NMR (100 MHz) δ 5.00 (m, 4 H), 5.98 (m, 2 H), 8.40 (b, 2 H); IR (KBr) 3450, 3420, 1685, 1670, 1535, 800, 835 cm^{-1}. Anal. Calcd for $C_8H_8N_2O_2Cl_6$: C, 25.50; H, 2.14; N, 7.43; Cl, 56.44. Found: C, 25.48; H, 1.93; N, 7.48; Cl, 56.53.

[3,3] Sigmatropic Rearrangement of 7. A solution of dioxepine **7** (362 mg, 1.56 mmol) in *tert*-butylbenzene (2 mL) was refluxed at 175–180 °C for 1.5 h. The reaction mixture was cooled to room temperature and worked up as in the case of **8** to afford vinyl compound **9** in 80% yield.

Acid Hydrolysis of 10. The trichloroimidate **10** (4.0 g, 10.61 mmol) was dissolved in acetone (100 mL) and cooled to ~0 °C (ice bath); 1 N HCl (5 mL) was added and the solution was stirred at ~0 °C for 1 h. The progress of the reaction was monitored by TLC (methylene chloride). After 1 h, almost all of the starting material (R_f 0.6) was consumed and two new spots at R_f 0.7 and 0.15 were visible. Evaporation of acetone afforded a solid residue, which was chromatographed on silica gel (74 g) by using methylene chloride/Skellysolve B (2:1, 500 mL), methylene chloride (500 mL), 1% methanol in methylene chloride (500 mL), and 2% methanol in methylene chloride (300 mL) as eluting solvents.

The faster moving component (R_f 0.7) was characterized as the trichloroacetate **11** (706 mg, 17%): mp 105.5–107 °C; ^1H NMR (100 MHz) δ 4.70 (d, 2 H), 5.05 (m, 1 H), 5.57 (m, 2 H), 6.10 (m, 1 H), 7.10 (b, 1 H); IR (KBr) 3300, 1760, 1695, 1535 cm^{-1}. Anal. Calcd for $C_8H_7NO_3Cl_6$: C, 25.43; H, 1.87; N, 3.71; Cl, 56.29. Found: C, 25.84; H, 1.94; N, 3.92; Cl, 56.05.

The major, slower component (R_f 0.15) was characterized as the alcohol **9** (1.3 g, 53%), which was identical with the alcohol obtained from the thermal, [3,3] sigmatropic rearrangement of imidate **8**.

(*R,S*)-2-[(2,2,2-Trichloro-1-oxoethyl)amino]-3-butenoic Acid (12). The olefin **9** (5.1 g, 21.93 mmol) was dissolved in acetone (200 mL). Chromic acid (20 mL, prepared according to ref 20) was added in portions at room temperature with continuous stirring. After the addition was complete (~1 h) and further stirring for 2 h, the excess oxidant was destroyed by the addition of isopropyl alcohol (4 mL). The reaction mixture was filtered, and the filtrate was rendered alkaline by the careful addition of saturated aqueous $NaHCO_3$ solution. Acetone was evaporated under reduced pressure, and the remaining aqueous solution was extracted with methylene chloride (2 × 100 mL); this extraction afforded the unreacted starting material **9** (1.12 g). The aqueous solution was acidified to pH 2 with 2 N HCl and extracted with diethyl ether (5 × 120 mL). The combined ether extracts were dried (Na_2SO_4) and evaporated to afford the desired acid **12** (3.68 g, 87%) as an oil, which solidified on cooling. The analytical sample was obtained by flash chromatography using 5% methanol in methylene chloride as the eluant: mp 84–87 °C; ^1H NMR (100 MHz) δ 5.17 (t, 1 H), 5.50 (m, 2 H), 6.00 (m, 1 H), 6.32 (b, 1 H), 8.90 (b, 1 H); IR (KBr) 3320, 2800–3400, 1725, 1690, 1520, 830, 835 cm^{-1}. Anal. Calcd for $C_6H_6NO_3Cl_3$: C, 29.24; H, 2.45; N, 5.68; Cl, 43.15. Found: C, 29.43; H, 2.52; N, 5.75, Cl, 41.76.

Racemic Vinylglycine Hydrochloride (13). The acid **12** (800 mg, 3.24 mmol) was dissolved in 6 N HCl (15 mL) and the solution was refluxed for 1 h. Upon cooling the solution to room temperature, it was extracted with $CHCl_3$ (2 × 20 mL) and concentrated under high vacuum (~0.25 mmHg) to a pale yellow solid (200 mg, 44.7%). Crystallization from methanol–acetone afforded an analytical sample of **13**: mp 185–187 °C (lit.[8] mp for L enantiomer, 175–177 °C); ^1H NMR (90 MHz) δ 4.56 (d, 1 H), 5.40–6.25 (m, 3 H).[22]

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(22) 60-MHz ^1H NMR spectral data (ref 8): δ 4.6 (d, 1 H, J = 6 Hz), 5.35–6.1 (m, 3 H).

Rearrangement of Ethylenic α-Diols (3-Butene-1,2-diols) to Ethylenic α-Diols (1-Butene-3,4-diols)

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The main dehydration products of the diol **1** series by sulfuric acid are the 2,5-dihydrofuran derivatives **2**[1,2] (Scheme I).

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