$cm^{-1}$. 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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**Registry No.** **5**, 6117-80-2; **6**, 89619-74-9; **7**, 89619-75-0; **8**, 89619-76-1; **9**, 89619-77-2; **10**, 89619-78-3; **11**, 89619-79-4; **12**, 89619-80-7; **13**, 89619-81-8; $CCl_3CN$, 545-06-2.

(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)

Josyane Gharbi-Benarous, Martha S. Morales-Rios, and Gilbert Dana*

*Laboratoire de Stéréochimie Réactionnelle, Université Pierre et Marie Curie, 75230 Paris Cedex 05, France*

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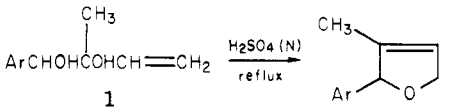
The main dehydration products of the diol **1** series by sulfuric acid are the 2,5-dihydrofuran derivatives **2**[1,2] (Scheme I).

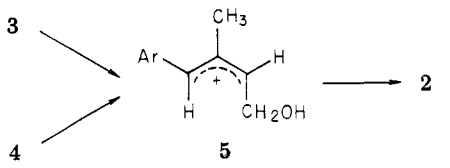
(1) Dana, G.; Le Thi Thuan, S.; Gharbi-Benarous, J. *Bull. Soc. Chim. Fr.* **1974**, 2089.
(2) Prevost, C. *Bull. Soc. Chim. Fr.* **1944**, 218. Prevost, C.; Robert, H. *Ibid.* **1944** 225.

0022-3263/84/1949-2039$01.50/0 

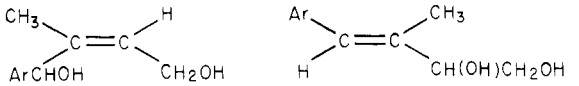
Scheme I



Scheme II



Under mild experimental conditions we detected an intermediate that we assumed to be the *Z* olefinic 1,4-diol **3**, precursor of **2**.[3,4] However, the compound that we



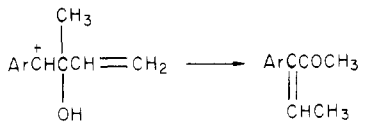
obtained and synthesized with good yield was an isomeric diol (**4**) in which the hydroxyl groups were shifted from the 1,2-positions to the 3,4-positions with an exchange of the olefinic function. Starting from erythro or threo isomers of diol **1**, we obtained the diols **4** in pure *E* configuration.

These new diols **4** are also possible precursors of **2**[3] since like compounds **3** their ionization gives the mesomeric carbocation **5** that can yield the cyclic form **2** (Scheme II).

In the present note we first examine the best yield of **1** → **4** transformation; since the synthesis of the diol **1** series is easy to perform[5] this isomerization appears to be a good approach to the synthesis of the diol **4** series, with *E* configuration.

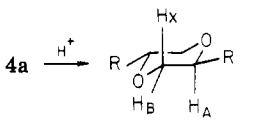
The yields have been optimized in three different cases (Table I, supplementary material): **4a**, Ar = $C_6H_5$, 68%; **4b**, Ar = *p*-$CH_3C_6H_4$, 35%; **4c**, Ar = *p*-$ClC_6H_4$: 66%. These best yields, measured by NMR on the crude material, have been obtained with 0.5 M $H_2SO_4$ solutions, during 1 day at 70 °C for **4a**, 1 day at 60 °C for **4b**, and 2 days at 70 °C for **4c**.

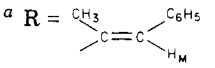
When an electron-attracting aromatic group (**1c**) is used instead of a phenyl group (**1a**), the isomerization is slowed down but the yield is identical (65–70%). In contrast, the tolyl group enhances the dehydration rate of diol (**4b**) but decreases the yield to about 35%. There is probably, in the first ionization step, more benzylic carbocation leading to the classical dehydration, with migration of the ethylenic group.[1]



Under the conditions used to prepare them, diols **4** dehydrate slowly but apparently they do not return to the starting diol **1**.

Scheme III[a]



[a] R = 

While studying the isomerization with equimolar mixtures of erythro and threo diols **1**, we constantly observed an increase in the threo/erythro molecular ratio. The two isomeric **1a** diols or **1c** diols were separated by silica TLC in petroleum ether/ether (50:50). They both give the same diol (**4a** or **4c**), but we observed that the erythro isomer reacts two to three times faster than the threo isomer[6] (Table II, supplementary material). There does not appear to exist an equilibrium between erythro and threo (Table II).

## Experimental Section

The reaction was analyzed by $^1H$ NMR using the signals assignable to each methyl group: δ ($Me_4Si$, $CDCl_3$) 1.08 and 1.00, erythro and threo diol **1**; 1.8, diol **4**; and 1.54, 2,5-dihydrofurannic derivatives. Their yields were assigned on the basis of their Me/Ar integrated signal ratio.

Diols **4** were isolated either by silica TLC in petroleum ether/ether (50:50) or by crystallization in petroleum ether/benzene (90:10). These compounds are white crystals and appear as a single isomeric form. The structures of all isolated products were supported by an elemental analysis and exact mass determination (Table III, supplementary material).

**3-Methyl-4-phenyl-3-butene-1,2-diol (4a, mp 72 °C).** Its *E* geometrical structure was confirmed by nuclear Overhauser effect analysis on diol **4a** or on its dioxane derivative (**6a**). The UV spectrum of **4a** showed the following: $\lambda_{max}$ (EtOH) 247 nm (ε 15 000); IR (KBr) ν(C=C) 1600, ν(OH) 3360 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$) δ 7.24 (m, 5 H, Ph), 6.55 (s, 1 H, H-4), 4.29 (q, 1 H, H-2, $J_{2,1}$ = 1.3 and 10.4 Hz), 3.71 and 3.62 (centers of two multiplets, 2 H, H-1, $J_{1,1}$ = 10.6 Hz), 1.8 ( d, 3 H, $CH_3$, $J_{3,4}$ = 1.0 Hz); NOE H-4{Ph} 8%, H-4{H-2} 8%, H-4{$CH_3$} 0%; $^{13}C$ NMR (62.5 MHz, $CDCl_3$, 25 °C) δ 137.4 (s, C-3), 126.6 (d, C-4), 65.6 (t, C-1), 17.6 (d, C-2), 14.5 (q, C-Me).

The dioxane **6a** was obtained by mild dehydration and distillation of the benzenic solution with *p*-toluenesulfonic acid under a Dean–Stark trap (Scheme III): mp 162 °C; IR (KBr) ν(C=C) 1600 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$) δ 7.24 (m, 5 H, Ph), 6.56 (s, 1 H, H-M, $J_{M,A}$ = 1 and $J_{M,Me}$ = 1.3 Hz), 4.06 (m, 1 H, H-A, $J_{AX}$ = 10.3 and $J_{AB}$ = 2.5 Hz), 3.99 (m, 1 H, H-B, $J_{bx}$ = 11.5 Hz), 3.57 (dd, 1 H, H-X), 1.84 (d, 3 H, $CH_3$); NOE H-M{H-A} 16%, H-M{Ph} 14%, H-M{$CH_3$} 0%, H-M{H-X} 0%, $^{13}C$ NMR (62.5 MHz, $CDCl_3$) δ 136.9 (s), 124.8 (d), 80.2 (d), 70.7 (t), 15.0 (q); mass spectrometry gave ions at *m/z* 320 (28, $M^+$), 144 (40), 129 (100), 115 (14), 105 (5), 91 (19).

**3-Methyl-4-(*p*-chlorophenyl)-3-butene-1,2-diol (4b)**: mp 80 °C.

**3-Methyl-4-*p*-tolyl-3-butene-1,2-diol (4c)**: mp 74 °C.

Structure and *E* configuration of these two diols were supported by analogy with the spectroscopic properties of **2a** (IR, $^1H$ NMR, mass spectra) and analytical data (Table III).

**Registry No.** **1a**, 2082-50-0; **1b**, 56790-69-3; **1c**, 56790-68-2; **4a**, 55131-24-3; **4b**, 89726-38-5; **4c**, 89726-39-6; **6a**, 89726-40-9.

**Supplementary Material Available:** Table I (yields optimization), Table II (relative reactivities of erythro and threo isomers), and Table III (analytical data) are available (3 pages). Ordering information is given on any current masthead page.

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(6) Dana, G.; Chuche, J.; Monot, M. R. *Bull. Soc. Chim. Fr.* **1967**, 3308. Erythro is the 1*S*,2*R* and 1*R*,2*S* isomer.