3: ^{1}H NMR 0.9–1.8 (m, 7 H, C_3H_7), 1.38 (d, 3 H, CH_3), 1.91 (dt, 1 H, $J_{3,3'}$ = 14.5, $J_{2,3}$ + $J_{3,4}$ = 12.5 Hz, H-3), 2.22 (dt, 1 H, $J_{2,3'}$ + $J_{3',4}$ = 8.7 Hz, H-3'), 2.98 (m, 2 H, H-4,5), 4.30 (t, 2 H, OCH_2), 4.45 (dd, 1 H, $J_{2,3}$ + $J_{2,3'}$ = 10.7 Hz, H-2) ppm.

4: ^{1}H NMR 0.9–1.8 (m, 7 H, C_3H_7), 1.39 (d, 3 H, H-3,3'), 2.99 (m, 2 H, H-4,5), 4.26 (t, 2 H, OCH_2), 4.46 (t, 1 H, $J_{2,3}$ + $J_{2,3'}$ = 12.7 Hz, H-2) ppm.

Anal. Calcd for (the mixture of epoxides) $C_{10}H_{18}O_4$: C, 59.38; H, 8.97. Found: C, 59.1; H, 8.90.

Butyl 2,5-Anhydro-3,6-dideoxy-DL-*arabino*-hexaldonate (5). A solution of the mixture of epoxides 3 and 4 (0.5 g, 2.47 mmol) in dry CH_2Cl_2 (15 mL) was cooled to −40 °C and treated under dry argon with SnCl, in CH_2Cl_2 (2 mL). After 1 h Et_3N (0.5 mL) was added to neutralize the solution. The mixture was diluted with 20 mL of CH_2Cl_2, washed with saturated $NaHCO_3$ and water, and dried and the solvent evaporated. The oily residue was separated on a silica gel column with hexane–Et_2O–MeOH (10:5:0.5 v/v) as eluent (flash chromatography). Two fractions were obtained: a less polar one, the mixture of 6 and 7 (0.025 g, 5%), and a more polar one, 5 (0.20 g, 40%).

The mixture of 6 and 7: colorless crystals; IR (Nujol) 3500 cm^{-1}, no carbonyl absorption was observed; ^{1}H NMR (signals of the major isomer[7]) 0.9–1.7 (m, 7 H, C_3H_7), 1.31 (d, 3 H, CH_3), 1.84 (ddd, 1 H, J = 11.1, 3.3, and 13.6 Hz, H-3), 2.08 (ddd, 1 H, J = 4.8, 3.0 and 13.6 Hz, H-3'), 3.4–3.8 (m, 4 H, OCH_2, H-2,5), 4.02 (t, 1 H, $\sum|J|$ = 6.1 Hz, H-4) ppm; ^{13}C NMR (the assignments of lines to diastereomers are based on ^{13}C line intensities and should be considered as tentative) [major component] 13.86, 19.40, 31.70, 59.78 (butyl), 17.62 (CH_3), 34.60 (CH_2), 67.37, 70.51, 73.30 (C-2,4,5), 106.20 (C-1), [minor component] 13.81, 19.40, 31.60, 59.84 (butyl), 17.92 (CH_3), 34.60 (CH_2), 67.14, 70.40, 73.42 (C-2,4,5), 105.44 (C-1) ppm.

Anal. Calcd for (the mixture) $C_{10}H_{18}O_4$: C, 59.38; H, 8.97. Found: C, 59.5; H, 9.2.

Acetate of the mixture of 6 and 7: ^{1}H NMR (signals of the major component[7]) 0.9–1.7 (m, 7 H, C_3H_7), 1.21 (d, 3 H, CH_3), 1.91 (ddd, 1 H, J = 11.4, 3.0, and 13.4 Hz, H-3), 2.04 (s, 3 H, OAc), 2.15 (ddd, 1 H, J = 3.2, 6.1, and 13.4 Hz, H-3'), 3.4–3.8 (m, 3 H, OCH_2, H-5), 3.95 (t, 1 H, $\sum|J|$ = 5.8 Hz, H-4), 4.87 (m, 1 H, H-2) ppm.

Anal. Calcd for (a mixture) $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 58.8; H, 8.4.

5: colorless oil; bp 120 °C [0.2 torr (air bath)]; IR (film) 3500, 1735 cm^{-1}; ^{1}H NMR 0.9–1.7 (m, 7 H, C_3H_7), 1.20 (d, 3 H, J = 6.5 Hz, CH_3), 2.09 (dt, 1 H, $J_{2,3}$ = 3.6 Hz, $J_{3,4}$ = 3.2 Hz, $J_{3,3'}$ = 13.7 Hz, H-3), 2.49 (ddd, 1 H, $J_{2,3'}$ = 9.0 Hz, $J_{3',4}$ = 6.1 Hz, H-3'), 3.97 (m, 1 H, $J_{4,5}$ = 2.9 Hz, H-4), 4.16 (t, 2 H, OCH_2), 4.19 (dq, 1 H, H-5) ppm; ^{13}C NMR 13.66, 19.04, 30.54, 65.27 (butyl), 19.25 (C-6), 37.82 (C-3), 75.77 (C-4), 76.73 (C-5), 83.88 (C-2), 174 (C-1) ppm.

Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97. Found: C, 59.3; H, 9.1.

Acetate of 5: IR (film) 1740 cm^{-1}; ^{1}H NMR 0.9–1.9 (m, 7 H, C_3H_7), 1.28 (d, 1 H, J = 6.7 Hz, CH_3), 2.08 (s, 3 H, OAc), 2.26 (dt, 1 H, $J_{2,3}$ = 3.6 Hz, $J_{3,4}$ = 2.7 Hz, $J_{3,3'}$ = 14.1 Hz, H-3), 2.60 (ddd, 1 H, $J_{2,3'}$ = 9.2 Hz, $J_{3',4}$ = 6.6 Hz, H-3'), 4.18 (t, 2 H, OCH_2), 4.30 (dq, 1 H, $J_{4,5}$ = 3.2 Hz, H-5), 4.61 (dd, 1 H, H-2), 4.85 (m, 1 H, H-4) ppm.

Anal. Calcd for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 58.9; H, 8.1.

The experiment performed in a NMR test tube was as follows: A solution of the epoxide 3 or 4 (30 mg) in $CDCl_3$ (0.5 mL) at −40 °C was treated with $SnCl_4$ in the same solvent to make the substrate:catalyst ratio equal to 4:1. The spectra were recorded 10, 30, and 60 min after mixing the substrate with $SnCl_4$.

2,5-Di-*O*-acetyl-3,6-dideoxy-DL-*arabino*- and -DL-*ribo*-aldonolactones (11 and 12). A solution of a mixture of 6 and 7 (0.1 g, 0.5 mmol) in 50% aqueous AcOH (2 mL) was refluxed for 6 h and then the solvent evaporated to dryness under reduced pressure. The oily residue was acetylated with Ac_2O and pyridine. Solvents were removed under diminished pressure, and the residue was purified on a silica gel column to give a mixture of lactones 11 and 12 (0.5 g, 87%) in proportion of about 5.5:4.5, respectively.

2,5-Anhydro-3,6-dideoxy-*N*,*N*-dimethyl-DL-*arabino*-hexaldonamide (13). A solution of 5 (0.20 g, 1 mmol) in 20% methanolic dimethylamine (5 mL) was heated at 80 °C in a steel bomb for 24 h. The solution was evaporated and purified by chromatography to give 13 (0.12 g, 69%); mp 74–75 °C; IR (KBr) 3350, 1640 cm^{-1}; ^{1}H NMR 1.17 (d, 1 H, J = 6.5 Hz, CH_3), 2.22 (d, 1 H, $J_{3,3'}$ = 14.0 Hz, H-3), 2.32 (ddd, 1 H, $J_{2,3'}$ = 8.6 Hz, $J_{3',4}$ = 6.2 Hz, H-3'), 3.97 (dd, 1 H, $J_{4,OH}$ = 10.6 Hz, H-4), 4.22 (dq, $J_{4,5}$ = 1.6 Hz, H-5), 4.96 (dd, 1 H, $J_{2,3}$ = 1.8 Hz, H-2) ppm.

Anal. Calcd for $C_8H_{15}NO_3$: C, 55.47; H, 8.73; N, 8.09. Found: C, 55.3; H, 9.0; N, 8.0.

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Synthesis of 4-Methyl- and 4,4-Dimethyl-1,3-dioxin-2(4*H*)-one and Related Enol Carboxylates

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Recently we had occasion to examine the synthesis of derivatives of 1,3-dioxin-2(4*H*)-one (**1a**). Although numerous alkenyl carboxylates and acyclic alkenyl carbonate esters[1] are well documented, **1a** and simple derivatives are unknown. Indeed we were concerned that the paucity of information on **1** may well have resulted from instability as a result of facile decomposition via a retro–Diels–Alder reaction. Recently, Trost reported the synthesis of **2** using the reflux of the selenoxide derived from **3a** in 1,2-dichloroethane and norbornadiene as a key step.[2] Herein we report a method for the facile synthesis of **1b**, **1c**, and three related acyclic analogues **10a**, **10b**, and **10c** (Chart I).

Results and Discussion

2-Methyl-3-buten-2-ol was converted into **4a** (58%) by sequential reaction with diphenyl diselenide–benzeneselininic acid[3] and carbonyl diimidazole[4] in toluene solution. It was essential that **4a** was purified by rapid chromatography on silica to prevent partial isomerization on the column to give **3b**. On ozonolysis[5] in dichloromethane solution at −78 °C, **4a** was converted into the corresponding selenoxide which on warming up to 0 °C in the presence of pyridine smoothly underwent syn elimination[4] to produce the cyclic enol carbonate **1b**. In contrast to the slow

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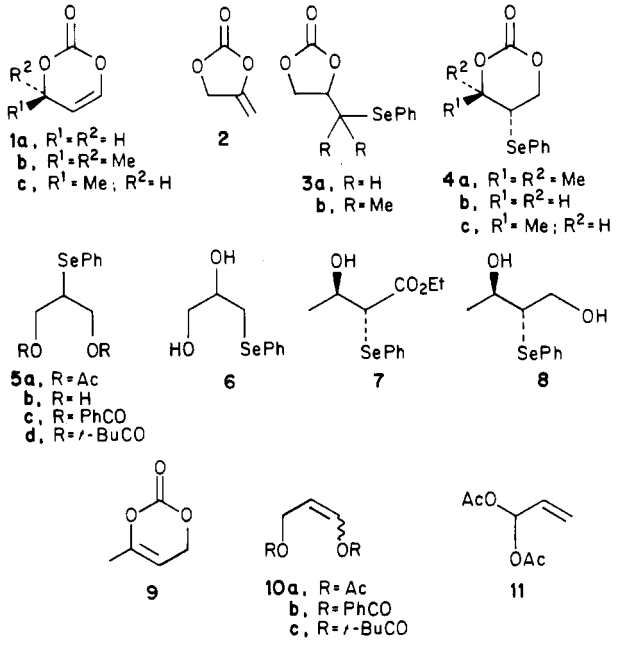
(5) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22. Liotta, D. *Ibid.* **1984**, *17*, 28.

0022-3263/85/1950-5362$01.50/0

Chart I



elimination of β-alkoxy selenoxides[6] the production of **1b** was rapid at 0 °C. It was possible to produce **1b** in acceptable yields (84–89%), providing that the elimination was carried out at 0 °C; at room temperature considerable quantities of 3-methyl-2-butenol were produced in addition to **1b**.

Allyl acetate was converted into **4b** via **5a** and **5b**. Although the intermediate **5b** was pure, the subsequent reaction with carbonyl diimidazole gave both **4b** and **3a**. The direct preparation of **5b** from allyl alcohol, by reaction with diphenyl diselenide and benzeneseleninic acid,[3] was also investigated: this procedure however gave **6**[2] predominantly. When **4b** was reacted with ozone as for **4a** none of the parent heterocycle **1a** could be isolated; only carbon dioxide and an intractable polymer were obtained. Although we were unsuccessful in the preparation of **1a**, the racemic monomethyl derivative **1c** was readily obtained. When ethyl (*E*)-2,3-epoxybutyrate was treated with sodium phenyl selenide at 0 °C, hydroxy ester **7** could be isolated in 74% yield. Reduction by dibal and cyclization with carbonyl diimidazole produced the carbonate **4c**. The proton α to selenium appears as a doublet of doublet of doublets with J = 11.5, 10.5, and 5.1 Hz, thus verifying the trans stereochemistry of methyl- and phenylselenyl moieties. Treatment of **4c** with hydrogen peroxide in the presence of pyridine produced the enol carbonate **1c** in 46% yield. The ^{1}H NMR of the purified material showed contamination with approximately 5% of the isomeric enol carbonate **9**. While this high degree of regioselectivity is interesting, the modest yield and the appearance of effervescence during the reaction suggests that this result might be complicated by retro-Diels–Alder reaction of one or both enol carbonates.

The selenoxide elimination reaction was extended to the diester-selenides **5a**, **5c**, and **5d** to produce **10a**, **10b**, and **10c** in excellent yields. Previously **10a** was obtained as an equilibrium mixture with **11** by the Lewis acid or transition metal complex catalyzed isomerization[7,8] of the latter. In addition, the purification of **10a** prepared by this method requires careful fractional distillation. In our hands preparation of this synthetically useful[8] vinyl ester **10a** and related systems from **5** via the selenoxide elimination is the method of choice.

Experimental Section

General Procedures. Reactions were carried out under dry N_2 unless stated to the contrary. Chromatography was carried out on Merck Kieselgel H or 60; eluants are given in parentheses. Samples for combustion analysis were purified via rechromatography with rotary evaporation (<40 °C) of the appropriate fractions and further evaporation (0.1 mm) overnight.

3-Methyl-2-(phenylselenyl)-1,3-butanediol. 2-Methyl-3-buten-2-ol (2.58 g), diphenyl diselenide (3.12 g), benezeneseleninic acid (1.89 g), and H_2O (0.90 g) were heated to reflux for 72 h. After being cooled to room temperature, the solution was diluted with CH_2Cl_2 and was washed with H_2O (20 mL), and the aqueous layer was back-extracted with CH_2Cl_2 (3×). The combined organic phase was dried ($MgSO_4$) and concentrated by rotary evaporation. Chromatography of the residue on silica (CH_2Cl–hexane gradient) gave 3-methyl-2-(phenylselenyl)-1,3-butanediol (4.97 g, 64%), as a colorless oil: IR (neat) 3320, 2960, 1580, 1480, 1440, 1380, 1170, 1075, 1030, 1010, 950, 870 cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.7 (m, 5 H), 3.96 (d, 2 H, J = 8 Hz), 3.30 (t, 1 H, J = 8Hz), 2.95 (s, 2 H, exchangeable with D_2O), 1.42 (s, 6H); mass spectrum, m/e 260, 258 ($M^{+\cdot}$), 184, 182, 180, 157, 104, 78, 77, 59, 43. Anal. Calcd for $C_{11}H_{16}O_2Se$: C, 50.97; H, 6.22. Found: C, 51.13; H, 6.43.

4,4-Dimethyl-5-(phenylselenyl)-1,3-dioxan-2-one (4a). Carbonyl diimidazole (0.53 g) was added to 3-methyl-2-(phenylselenyl)-1,3-butanediol (0.56 g) in dry PhMe (50 mL). After being stirred overnight at room temperature, the solution was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (2 × 50 mL), dried ($MgSO_4$), and rotary evaporated. The residue was *rapidly* chromatographed on silica (CH_2Cl_2) to give **4a** (0.557 g, 90%) as a colorless oil: IR ($CHCl_3$) 2940, 1770, 1480, 1400, 1280, 1255, 1120, 1085, 860 cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.7 (m, 5 H), 4.43 (d, 2 H, J = 10 Hz), 3.35 (t, 1 H, J = 10 Hz), 1.65 (s, 3 H), 1.50 (s, 3 H); mass spectrum, m/e 314 ($Ph_2Se_2^{+\cdot}$), 286 ($M^{+\cdot}$ ^{80}Se), 184, 158, 129, 77, 41. Anal. Calcd for $C_{12}H_{14}O_3Se$: C, 50.53; H, 4.95. Found, C, 50.39; H, 4.97. During the purification of **4a** it was essential that the chromatography was carried out rapidly to prevent partial decomposition of **4a** on the silica to produce **3b** (4–42%): mp 41–42 °C (from EtOAc–hexane); IR (CH_2Cl_2) 1800, 1370, 1350, 1150, 1120, 1075, 1045, 1025, 1000 cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.7 (m, 5 H), 4.45–4.55 (m, 3 H) 1.48 (s, 3 H), 1.37 (s, 3 H); mass spectrum, m/e 286 (M^+ · ^{80}Se), 158, 129, 78. Anal. Calcd for $C_{12}H_{14}O_3Se$: C, 50.53; H, 4.95. Found: C, 50.75; H, 4.86.

4,4-Dimethyl-1,3-dioxin-2(4*H*)-one (1b). Ozone was bubbled through **4a** (333 mg) in dry CH_2Cl_2 (25 mL) at −78 °C until all **4a** had been consumed (TLC). The solution was purged with nitrogen to remove ozone, dry pyridine (0.47 mL) was added, and the solution was allowed to warm up to 0 °C. After being stirred overnight at 0 °C, the mixture was rotary evaporated at 20 °C and the residue was chromatographed on silica (30 g) (CH_2Cl_2) to give **1b** (125 mg, 84%) as a colorless oil: IR (CH_2Cl_2) 1800, 1270, 1165, 1090 cm^{-1}; NMR ($CDCl_3$) δ 6.38 (d, 1 H, J = 6 Hz), 5.28 (d, 1 H, J = 6 Hz), 1.5 (s, 6 H); mass spectrum, m/e 129 (M − H$^+$), 113, 85. The material could not be obtained microanalytically pure. A repeat reaction using an identical protocol gave **1b** (65 mg, 89%) starting from **4a** (140 mg). The elimination of the intermediate selenoxide was most efficiently carried out at 0 °C. When the elimination was carried out at room temperature, considerable quantities of 3-methylpropenal were produced.

3-(Phenylselenyl)-1,2-propanediol (6). Allyl alcohol (3.48 g), PhSeSePh (3.12 g), benzeneseleninic acid (1.89 g), and H_2O (0.90 g) were heated to reflux for 60 h. After evaporation the residue was chromatographed on silica (hexane–diethyl ether gradient) to give **6** (1.61 g, 23%) as a colorless oil: IR (CH_2Cl_2) 3580, 1580, 1050, 1020, 870 cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.8 (m, 5 H, Ph), 3.5–4.0 (m, 3 H), 3.0–3.2 (m, 2 H); mass spectrum, m/e 232 ($M^{+\cdot}$ ^{80}Se), 183, 158. Anal. Calcd for $C_9H_{12}O_2Se$: C, 46.76; H, 5.23. Found: C, 46.78; H, 4.99.

1,3-Diacetoxy-2-(phenylselenyl)propane (5a). Br_2 (0.80 g) and PhSeSePh (1.56 g) were added sequentially to glacial AcOH (25 mL). After 20 min, allyl alcohol (1.00 g) followed by anhydrous

(6) For example, see: Petrzilka, M. *Helv. Chem. Acta* **1978**, *61*, 2286.
(7) Kurkov, V. P. U.S. Patent 4 044 050, 1977.
(8) Bristol-Myers Co. Ger. Offen. 2 950 898, 1981; U.S. Patent, 4 272 437, 1981.

KOAc[9] (1.96 g) were added. After 5 min a cloudy white precipitate formed and the mixture was allowed to stand overnight. The mixture was added to H_2O (100 mL) and extracted with EtOAc (4 × 50 mL). The organic phase was washed with H_2O (50 mL) and 10% aqueous Na_2CO_3 (2 × 50 mL), dried ($MgSO_4$), and rotary evaporated. Chromatography on silica (CH_2Cl_2–Et_2O gradient) gave **5a** (2.20 g, 70%) as a colorless oil: IR (film) 3060, 2950, 1735, 1580, 1480, 1440, 1370, 1240, 1025, 740, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.7 (m, 5 H), 4.30 (2 dd, 4 H, J = 11, 6.5, 5.5 Hz), 3.47 (overlapping tt, 1 H, J = 6.5, 5.5 Hz), 2.00 (s, 6 H); mass spectrum, m/e 316 ($M^{+\cdot}$ ^{80}Se), 256, 159, 99. Anal. Calcd for $C_{13}H_{16}O_4Se$: C, 49.53; H, 5.12. Found: C, 49.49; H, 5.11. A repeat reaction starting from PhSeSePh (7.8 g) gave **5a** (11.25 g, 72%).

2-(Phenylselenyl)-1,3-propanediol (5b). Na (20 mg) in dry MeOH (30 mL) was added to **5a** (567 mg) in dry MeOH (5 mL) and the solution was stirred at room temperature for 1 h. After further stirring with Amberlyst IR120H$^+$ resin (14 g), filtration, and evaporation, the residue was dissolved in CH_2Cl_2–EtO_2 (3:1, 50 mL) and dried (Na_2SO_4). Evaporation and chromatography on silica (CH_2Cl_2–Et_2O gradient) gave **5b** (384 mg, 92%), as a colorless oil: IR (film) 3360 br, 3060, 2940, 2870, 1575, 1475, 1340, 1170, 1120, 980, 740, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.4–7.7 (m, 2 H), 7.2–7.4 (m, 3 H), 3.88 (d, 4 H, J = 6 Hz), 3.43 (quintet, 1 H, J = 6 Hz), 2.45 (br s, 2 H); mass spectrum, m/e 232 ($M^{+\cdot}$ ^{80}Se), 183, 158, 91, 78. Anal. Calcd for $C_9H_{12}O_2Se$: C, 46.76; H, 5.23. Found: C, 46.87; H, 5.07.

Reaction of 5b with *N,N'*-Carbonyldiimidazole. *N,N'*-carbonyldiimidazole (166 mg) in CH_2Cl_2 (20 mL) was added over 15 min to **5b** (215 mg) in CH_2Cl_2 (50 mL) at room temperature. After being stirred overnight the solution was added to H_2O (3 × 20 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was dried ($MgSO_4$) and rotary evaporated, and the residue was chromatographed on silica (CH_2Cl_2–Et_2O gradient) to give **4b** (98.5 mg, 41%), as a colorless oil: IR (film) 1750, 1575, 1465, 1440, 1405, 1280, 1230, 1170, 1130, 1080, 1020, 740, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.7 (m, 5 H), 4.55 (dd, 2 H, J = 11, 5 Hz), 4.20 (dd, 2 H, J = 11, 11 Hz), 3.4–3.7 (m, 1 H); mass spectrum, m/e 260, 258, 256, ($M^{+\cdot}$), 171, 158, 91, 78. Anal. Calcd for $C_{10}H_{10}O_3Se$: C, 46.71; H, 3.92. Found: C, 46.68; H, 3.87. Further elution of the column gave **3a**[2] (24.7 mg, 10%) as a colorless oil: (film) 1800, 1575, 1475, 1440, 1390, 1355, 1160, 1060, 1020, 770, 740, 710, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.7 (m, 5 H), 4.55–4.9 (m, 1 H), 4.50 (dd, 1 H, J = 9, 8.5 Hz), 4.10 (dd, 1 H, J = 8.5, 6 Hz), 3.26 (dd, 1 H, J = 13, 4 Hz), 3.00 (dd, 1 H, J = 13, 8.5 Hz); mass spectrum, m/e 258, 256 ($M^{+\cdot}$), 171, 158, 91, 77. Anal. Calcd for $C_{10}H_{10}O_3Se$: C, 46.71; H, 3.92. Found: C, 46.40; H, 3.85.

***dl-erythro*-Ethyl 3-Hydroxy-2-(phenylselenyl)butyrate (7).** $NaBH_4$ (9.46 g) was added slowly to a solution of diphenyl diselenide (39.0 g) in absolute ethanol (70 mL). After the solution became colorless, the flask was flushed with argon and chilled to 0 °C, and ethyl 2,3-epoxybutyrate (31 g) was added in one portion. The ice bath was removed, and the reaction was allowed to stir for 25 min (longer reaction times resulted in significantly decreased yields) and poured into H_2O (1000 mL). This solution was extracted (3×) with CH_2Cl_2 and the combined organics were washed (4×) with water. Drying ($MgSO_4$) and concentration in vacuo yielded a yellow oil which was further purified by flash chromatography (SiO_2, 10% EtOAc/CH_2Cl_2) to yield **7** (50.6 g, 74%) as a slightly yellow oil: IR (film) 3450, 3060, 2980, 2930, 1710, 1575, 1440, 1370, 1300, 1260, 1180, 1120, 1020, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (t, 3 H, J = 7 Hz), 1.36 (d, 3 H, J = 6 Hz), 1.95 (s, 1 H), 3.53 (d, 1 H, J = 8 Hz), 4.06 (q, 2 H, J = 7 Hz), 4.0–4.17 (m, 1 H), 7.24–7.30 (m, 3 H), 7.55–7.60 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 20.8, 50.4, 61.0, 68.0, 127.6, 128.4, 128.9, 135.3, 172.4. Exact mass calcd for $C_{12}H_{16}O_3Se$ 288.02612, found 288.02612. Anal. Calcd for $C_{12}H_{16}O_3Se$: C, 50.18; H, 5.62. Found: C, 50.26; H, 5.74.

***dl-erythro*-2-(Phenylselenyl)butane-1,3-diol (8).** A solution of **7** (24.0 g) in anhydrous Et_2O (200 mL) was chilled to 0 °C and treated with diisobutylaluminum hydride (266 mL of 1.0 M solution in hexane). The reaction was again cooled to 0 °C and carefully treated with MeOH (100 mL) and H_2O (100 mL). The ether layer was separated and the precipitated salts washed several times with ether. The combined ether layers were then washed with water and brine and dried over Na_2SO_4. Concentration in vacuo yielded a yellow oil which was further purified by flash chromatography (SiO_2, 20% EtOAc/CH_2Cl_2) to yield **8** (14.8 g, 72%) as a white solid: mp 43–45 °C; IR ($CHCl_3$) 3400, 3050, 2980, 2890, 1570, 1440, 1375, 1045, 1000, 935, 890 cm^{-1}: ^1H NMR ($CDCl_3$, 200 MHz) δ 1.39 (d, 3 H, J = 6.3 Hz), 3.15 (s, 2 H), 3.26 (dt, 1 H, J = 4.8, 6.0 Hz), 3.86 (dd, 1H, J = 11.7, 6.0 Hz), 4.0–4.15 (m, 2 H), 7.29–7.32 (m, 3 H), 7.57–7.61 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.7, 54.4, 63.5, 69.6, 127.6, 128.0, 129.0, 134.4; exact mass calcd for $C_{10}H_{14}O_2Se$ 246.0158, found 246.0136. Anal. Calcd for $C_{10}H_{14}O_2Se$: C, 48.99; H, 5.76, Found: C, 48.89; H, 5.69.

(4β,5α)-(±)-4-Methyl-5-(phenylselenyl)-1,3-dioxan-2-one (4c). Carbonyldiimidazole (4.86g) was added to a solution of **8** (4.9 g) in dry PhMe (140 mL). The solution was heated to reflux for 30 min and then cooled and concentrated in vacuo. Purification of the resulting material by flash chromatography (SiO_2, CH_2Cl_2) gave **4c** (3.17 g, 58%) as a colorless oil: IR (film) 3050, 2980, 2930, 1750, 1575, 1475, 1440, 1400, 1215, 1140, 1100, 1075, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.60 (d, 3 H, J = 6.25), 3.17 (ddd, 1H, J = 11.5, 10.5, 5.1 Hz), 4.19 (t, 1H, J = 11.5 Hz), 4.44 (m, 2 H), 7.28–7.44 (m, 3 H), 7.56–7.60 (m, 2 H); exact mass calcd for $C_{11}H_{12}O_3Se$ 271.9951, found 271.9975. Anal. Calcd for $C_{11}H_{12}O_3Se$: C, 48.72, H, 4.46; Found: C, 48.61; H, 4.55.

(±)-4-Methyl-1,3-dioxin-2(4*H*)-one (1c). A solution of **4c** (4.12 g) and pyridine (2.41 g) in CH_2Cl_2 (83 mL) was chilled to 0 °C and treated with 30% H_2O_2 (13.1 mL). The solution was then stirred at room temperature for 3 h. The reaction mixture was washed with water (2 × 20 mL), dried (Na_2SO_4), and concentrated to a volume of approximately 5 mL. This material was immediately purified by flash chromatography (SiO_2, CH_2Cl_2) to produce **1c** (0.8 g, 46%) as a slightly volatile colorless oil: IR (film) 3100, 2990, 2940, 1775, 1680, 1375, 1220, 1170, 1145, 1070, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.50 (d, 3 H, J = 6.5 Hz), 5.10–5.22 (m, 1 H), 5.39 (dd, 1 H, J = 5.9, 2.7 Hz), 6.48 (dd, 1 H, J = 5.9, 1.6 Hz). Signals ascribed to **1l**: 1.90 (br s, 3 H), 4.87 (m, 2 H), olefinic H obscured **1c**. Exact mass calcd for $C_5H_6O_3$ 114.03169, found 114.03157.

1,3-Diacetoxypropene (10a). O_3 was bubbled through a solution of **5a** (3.60 g) in dry CH_2Cl_2 (100 mL) at −78 °C to a blue end point. The solution was purged with nitrogen, Et_3N (7.9 mL) was added, and the mixture was allowed to warm up to room temperature. After being stirred overnight, the mixture was rotary evaporated, and the residue was dissolved in PhMe (50 mL) and rotary evaporated. The resultant yellow oil was chromatographed on silica (60 g) (hexane–CH_2Cl_2–Et_2O gradient) to give *E*:*Z* (1:1) **10a** (1.67 g, 93%) as a colorless oil: (film) 1750, 1735, 1670, 1370, 1195, 1120, 1025 cm^{-1}; NMR ($CDCl_3$) δ 7.40 (dt, 0.5 H, J = 12.3, 1.0 Hz, *E* isomer), 7.22 (dt, 0.5 H, J = 7.0, 1.0 Hz, *Z* isomer), 5.55 (dt, 0.5 H, J = 12.3, 7.3 Hz, *E* isomer), 5.08 (dt, 0.5 Hz, J = 7.0, 6.3 Hz, *Z* isomer), 4.71 (dd, 1 H, J = 6.3, 1.0 Hz, *Z* isomer), 4.55 (dd, 1 H, J = 7.2, 1.0 Hz, *E* isomer), 2.16 (s, 3 H), 2.06 (s, 3 H).

1,3-Bis(benzoyloxy)-2-(phenylselenyl)propane (5c). PhCOCl (0.375 mL) was added to **5b** (357 mg) in dry pyridine (10 mL) at 0 °C. The solution was subsequently stirred at room temperature for 2 h, added to citric acid (28.94 g) in H_2O (250 mL), and extracted with Et_2O (3 × 60 mL). The combined extracts were dried ($MgSO_4$) and rotary evaporated, and the residue was chromatographed on silica (hexane–CH_2Cl_2 gradient) to give **5c** (663 mg, 98%) as a colorless oil: IR (film) 1715, 1605, 1580, 1480, 1455, 1370, 1270, 1180, 1110, 1070, 1030, 740, 710, 690 cm^{-1}; NMR ($CDCl_3$) δ 8.3–7.9 (m, 4H), 7.75–7.25 (m, 11 H), 4.7 (2 dd, 4 H, J = 12, 6, 5 Hz), 3.82 (quintet, 1 H, J = 5 Hz); mass spectrum, m/e 440 ($M^{+\cdot}$ ^{80}Se), 161, 77. Anal. Calcd for $C_{23}H_{20}O_4Se$: C, 62.87; H, 4.59. Found: C, 63.05; H, 4.44. A repeat reaction on **5b** (4.388 g) gave **5c** (92%).

1,3-Bis(benzoyloxy)-1-propene (10b). O_3 was bubbled through **5c** (8.0 g) in dry CH_2Cl_2 (150 mL) at −78 °C until all **5c** was consumed (TLC). Et_3N (8 mL) was added and the reaction mixture was allowed to warm up to room temperature over 1 h. Rotary evaporation and chromatography on silica (hexane–CH_2Cl_2 gradient) gave **10b** (4.89 g, 95%) as a colorless oil: IR (film) 1730, 1675, 1480, 1400, 1370, 1280, 1130, 1035, 940, 920, 735 cm^{-1}; NMR ($CDCl_3$) δ 8.25–8.0 (m, 4 H), 7.8–7.2 (m, 7 H), 5.85 (dt, 0.4 H, J = 12, 7.5 Hz, *E* isomer), 5.3 (dt, 0.6 H, J = 7, 6 Hz, *Z* isomer),

(9) Sharpless, K. B., Lauer, R. F. *J Org. Chem.* **1974**, *39*, 429.

5.1 (dd, 1.2 H, J = 6, 1 Hz, Z isomer), 4.88 (dd, 0.8 H, J = 7, 1 Hz, E isomer); mass spectrum, m/e 282 ($M^{+\cdot}$), 105, 77. Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.31; H, 5.00. Found: C, 72.36; H, 5.27.

1,3-Bis[(2,2-dimethylpropanoyl)oxy]-2-(phenylselenyl)-propane (5d). t-BuCOCl (914 μL) was added to diol **5b** (817 mg) and a 4-(dimethylamino)pyridine (1 mg) in pyridine (15 mL) at 0 °C. After stirring at room temperature for 3 h, rotary evaporation and chromatography on silica (hexane–Et_2O gradient) gave **5d** (1.4 g, 92%) as a colorless oil: IR (film) 1730, 1580, 1480, 1460, 1395, 1365, 1280, 1150, 1030, 950, 770, 740, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.7–7.5 (m, 2 H), 7.4–7.2 (m, 3 H) 4.32 (d, 4 H, J = 6.5 Hz), 3.57 (quintet, 1 H, J = 6.5 Hz), 1.23 (s, 18 H); mass spectrum, m/e 400 ($M^{+\cdot}$ ^{80}Se), 298, 243, 141, 85, 57. Anal. Calcd for $C_{19}H_{28}O_4Se$: C, 57.14; H, 7.07. Found: C, 57.03; H, 6.88.

1,3-Bis[(2,2-dimethylpropanoyl)oxy]propene (10c). O_3 was bubbled through **5d** (0.800 g) in CH_2Cl_2 (15 mL) at −78 °C until blue. The solution was purged with N_2, Et_3N, (0.8 mL) was added, and the solution was allowed to warm up to room temperature over 1 h. Workup as for **10b** gave **10c** (442 mg, 91%) as a colorless oil: IR (film) 1730, 1670, 1480, 1460, 1400, 1365, 1280, 1130, 1035, 940 cm^{-1}: NMR ($CDCl_3$) δ 7.44 (d, 0.6 H, J = 12.5 Hz, E isomer), 7.23 (d, 0.4 H, J = 6 Hz, Z isomer), 5.6 (dt, 0.6 H, J = 12.5, 7 Hz, E isomer), 5.13 (dt, 0.4 H, J = 7, 6 Hz, Z isomer), 4.78 (d, 0.8 H, J = 7 Hz, Z isomer), 4.60 (d, 1.2 H, J = 7 Hz, E isomer); mass spectrum m/e 242 ($M^{+\cdot}$), 157, 85. Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.43; H, 9.15. Found: C, 64.44; H, 9.12.

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Registry No. **1b**, 99018-30-1; **1c**, 99018-31-2; **3a**, 86728-47-4; **3b**, 99033-17-7; **4a**, 99018-32-3; **4b**, 99018-33-4; **4c**, 99018-34-5; **5a**, 99018-35-6; **5b**, 99018-36-7; **5c**, 99018-37-8; **5d**, 99018-38-9; **6**, 65349-59-9; **7**, 99018-39-0; **8**, 99018-40-3; **9**, 99018-41-4; (*E*)-**10a**, 31447-25-3; (*Z*)-**10a**, 31447-24-2; (*E*)-**10b**, 99018-42-5; (*Z*)-**10b**, 99018-43-6; (*E*)-**10c**, 99018-44-7; (*Z*)-**10c**, 99018-45-8; **11**, 869-29-4; PhCOCl, 98-88-4; t-BuCOCl, 3282-30-2; 2-methyl-3-buten-2-ol, 115-18-4; 3-methyl-2-(phenylselenyl)-1,3-butanediol, 99018-46-9; allyl alcohol, 107-18-6; ethyl 2,3-epoxybutyrate, 19780-35-9.

N-Protected α-Amino Ketones from Enamines and (Ethoxycarbonyl)nitrene[1]

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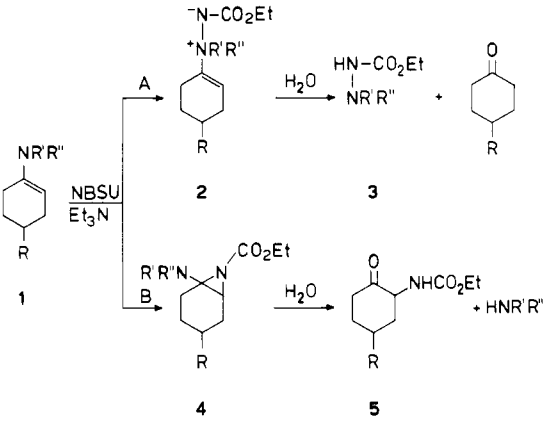
Recently, we reported a new synthesis of *N*-(ethoxycarbonyl)-α-amino ketones, via the thermolysis of ethyl azidoformate in enol trimethylsilyl ethers.[2]

Previously we studied[3] the reaction of (ethoxycarbonyl)nitrene (EtOCON), generated from *N*-[(4-nitrophenyl)sulfonoxy]urethane (NBSU) and enamines.[4]

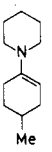
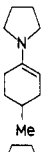
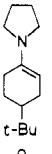
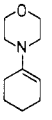
Scheme I



a, R′···R″ = -$(CH_2)_5$- (piperidine)
b, R′···R″ = -$(CH_2)_4$- (pyrrolidine)
c, R′···R″ = -$(CH_2CH_2)_2O$- (morpholine)
d, R′···R″ = -$(CHMeCH_2)_2$- (*cis*-2,5-dimethylpyrrolidine)
e, R′ = Me; R″ = Ph (*N*-methylaniline)

x, R = H
y, R = Me
z, R = t-Bu

Table I.[a] **Reaction of Enamines, NBSU, and Et_3N in Dichloromethane**

entry[b]	1	2	3	5
ay		42 (53)	30 (47)	
by		14 (31)	41 (36)	19 (33)
bz		9 (10)	25 (28)	24 (62)
cx		23 (80)	14 (16)	5 (4)

[a] Absolute yields in percent; GC percentages are given in parentheses. [b] See Scheme I.

For this reaction we showed that the reaction outcome could be partially shifted from aminimides (N–N ylides), as the main products, to α-amino ketone derivatives,[5] depending on the reaction conditions used in the generation of the nitrene.

In this paper we describe the results of our efforts directed toward a more selective preparation of α-amino ketones and toward the isolation of the α-amino ketone precursors. At this time the two routes can be illustrated

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(2) Lociuro, S.; Pellacani, L.; Tardella, P. A. *Tetrahedron Lett.* **1983**, *24*, 593.

(3) Pellacani, L.; Pulcini, P.; Tardella, P. A. *J. Org. Chem.* **1982**, *47*, 5023.

(4) For a very recent review on (ethoxycarbonyl)nitrene, see: Lwowski, W. In "Azides and Nitrenes"; Scriven, E. F. V., Ed.; Academic Press, Inc.: Orlando, FL, 1984. For recent reviews on enamines, see: (a) Hickmott, P. W. *Tetrahedron* **1982**, *38*, 1975, 3363. (b) Pitacco, G.; Valentin, E. In "The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives"; Patai, S., Ed.; John Wiley & Sons: New York, 1982; Supplement F, part 1, Chapter 15, p 623. (c) Granik, V. G. *Russ. Chem. Rev.* **1984**, *53*, 383.

(5) α-Amino ketones, besides the general methods of preparation (Mayer, D. In "Houben-Weyl, Methoden der Organischen Chemie", 4th ed.; Müller, E., Ed.; G. Thieme Verlag: Stuttgart, 1977; Vol. VII/2c, p 2253) have been obtained from azides and masked ketones such as enamines (Alder, K., Stein, G. *Liebigs Ann. Chem.* **1933**, 501, 1) or enol acetates (Keana, J. F. W.; Keana, S. B.; Beetham, D. *J. Org. Chem.* **1967**, *32*, 3057) as well as by chromous chloride promoted addition of *N*-chlorourethanes to enamines, enol ethers, or enol acetates (Driguez, H.; Paton, J. M.; Lessard, J. *Can. J. Chem.* **1977**, *55*, 700. Driguez, H.; Vermes, J. P.; Lessard, J. *Can. J. Chem.* **1978**, *56*, 119). An example of α-amino aldehydes from treatment of enamines with chloramine-T has been reported: Dyong, I. D.; Lam-Chi, Q. *Angew. Chem.* **1979**, *91*, 997.

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