

Mechanistic Investigation of the Selective Reduction of Meldrum's Acids to β -Hydroxy Acids using SmI₂ and H₂O

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General Methods/List of Known Compounds

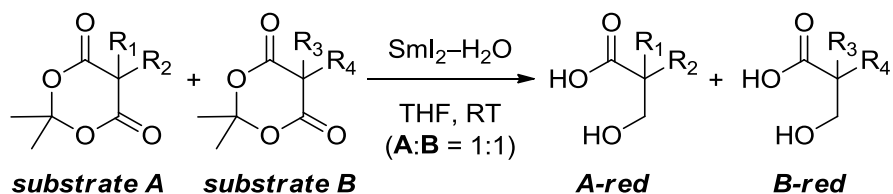
All compounds reported in the manuscript study have been previously reported or are commercially available. Meldrum's acids were purchased from commercial suppliers or prepared by standard methods.¹⁻⁴ All experiments involving SmI_2 were performed using standard Schlenk or glovebox techniques under argon or nitrogen atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). Samarium(II) iodide was prepared by standard methods and titrated prior to use.⁵⁻⁹ ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 on Bruker spectrometers at 300, 400 and 500 MHz (^1H NMR) and 75, 100 and 125 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual CHCl_3 peak (7.27 and 77.2 ppm, ^1H NMR and ^{13}C NMR, respectively). All coupling constants (J) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; br s, broad singlet. All flash chromatography was performed using silica gel, 60 Å, 230–400 mesh. TLC analysis was carried out on aluminium sheets coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions. ^1H NMR and ^{13}C NMR data are given for all compounds in the Supporting Experimental for characterization purposes. ^1H NMR, ^{13}C NMR, IR and HRMS data are reported for all new compounds.

Intermolecular Competition Experiments

General Procedure. An oven-dried vial containing a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, typically 0.20 mmol, 2.0 equiv, 0.10 M) was added followed by H_2O (0.72 mL, 400 equiv) with vigorous stirring, which resulted in the formation of a characteristic burgundy red color of the $\text{SmI}_2\text{-H}_2\text{O}$ complex. A preformed solution of two substrates (each 0.10 mmol, 1.0 equiv, stock solution in THF, 1.0 mL) was added and the reaction mixture was stirred until decolorization to white had occurred. The reaction mixture was diluted with CH_2Cl_2 (30 mL) and HCl (1 N, 30 mL). The aqueous layer was extracted

with CH_2Cl_2 (3 x 30 mL), the organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated. The sample was analyzed by ^1H NMR (CDCl_3 , 500 MHz) to obtain conversion and yield using internal standard and comparison with authentic samples.

Table SI-1. Steric and Electronic Influence on the Relative Rates in the Reduction of Meldrum's Acids.^a



entry	A	B	R ₁ , R ₂	R ₃ , R ₄	k_A/k_B^b
1	1a	1b	Ph, H	Bn, H	1.66
2	1b	1c	Bn, H	<i>i</i> -Bu, H	2.46
3	1a	1c	Ph, H	<i>i</i> -Bu, H	5.21
4	1d	1a	Ph, Me	Ph, H	>20:1
5	1e	1c	<i>i</i> -Bu, Me	<i>i</i> -Bu, H	>20:1
6	1d	1e	Ph, Me	<i>i</i> -Bu, Me	3.74
7 ^c	1f	1e	=CH <i>i</i> -Pr	<i>i</i> -Bu, Me	>20:1
8 ^c	1f	1d	=CH <i>i</i> -Pr	Ph, Me	>20:1
9	1h	1e	-(CH ₂) ₂ -	<i>i</i> -Bu, Me	>20:1
10	1h	1d	-(CH ₂) ₂ -	Ph, Me	5.13
11 ^c	1f	1h	=CH <i>i</i> -Pr	-(CH ₂) ₂ -	>20:1
12 ^c	1f	1g	=CH <i>i</i> -Pr	=CHPh	1.37

^aConditions: Meldrum's acid (1 equiv), SmI_2 (2 equiv, THF), H_2O (400 equiv), 23 °C. Reaction time 30-60 s.

^bDetermined by ^1H NMR. ^c SmI_2 (1 equiv), H_2O (200 equiv). In all entries >95% yield based on reacted starting material. Entries 7-12, selective exo-cyclic reduction of olefin/cyclopropane was observed.

2,2-Dimethyl-5-phenyl-1,3-dioxane-4,6-dione (1a, Table 1, entry 1). ^1H NMR (400 MHz, CDCl_3) δ 1.77 (s, 3 H), 1.89 (s, 3 H), 4.78 (s, 1 H), 7.29-7.33 (m, 2 H), 7.39-7.47 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.4, 28.5, 52.7, 105.7, 128.8, 129.1, 129.1, 130.5, 164.7.

5-Benzyl-2,2-dimethyl-1,3-dioxane-4,6-dione (1b, Table 1, entry 2). ^1H NMR (500 MHz, CDCl_3) δ 1.50 (s, 3 H), 1.74 (s, 3 H), 3.51 (d, $J = 5.0$ Hz, 2 H), 3.77 (t, $J = 5.0$ Hz, 1 H), 7.23-7.26 (m, 1 H), 7.28-7.35 (m, 4 H); ^{13}C NMR (125 MHz, CDCl_3) δ 27.2, 28.4, 32.1, 48.2, 105.2, 127.2, 128.7, 129.7, 137.2, 165.3.

5-Isobutyl-2,2-dimethyl-1,3-dioxane-4,6-dione (1c, Table 1, entry 3). ^1H NMR (400 MHz, CDCl_3) δ 0.96 (d, $J = 6.3$ Hz, 6 H), 1.79 (s, 3 H), 1.83 (s, 3 H), 1.96-2.10 (m, 3 H), 3.45 (t, $J = 5.6$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.1, 25.9, 26.8, 28.6, 35.3, 44.2, 104.9, 166.0.

2,2,5-Trimethyl-5-phenyl-1,3-dioxane-4,6-dione (1d, Table 1, entry 4). ^1H NMR (400 MHz, CDCl_3) δ 1.26 (s, 3 H), 1.73 (s, 3 H), 1.87 (s, 3 H), 7.32-7.44 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 26.3, 27.2, 29.4, 55.4, 105.5, 125.6, 128.8, 129.7, 137.0, 167.4.

2,2,5-Trimethyl-5-phenyl-1,3-dioxane-4,6-dione (1e, Table 1, entry 5). ^1H NMR (500 MHz, CDCl_3) δ 0.91 (d, $J = 6.6$ Hz, 6 H), 1.64 (s, 3 H), 1.61-1.69 (m, 1 H), 1.77 (s, 3 H), 1.79 (s, 3 H), 2.04 (d, $J = 6.9$ Hz, 2 H); ^{13}C NMR (125 MHz, CDCl_3) δ 22.9, 25.6, 25.8, 28.3, 30.0, 48.1, 49.9, 104.9, 170.5.

2,2-Dimethyl-5-(2-methylpropylidene)-1,3-dioxane-4,6-dione (1f, Table 1, entry 7). ^1H NMR (400 MHz, CDCl_3) δ 1.16 (d, $J = 6.6$ Hz, 6 H), 1.75 (s, 6 H), 3.72-3.86 (m, 1 H), 7.70 (d, $J = 10.6$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.3, 27.6, 29.5, 104.8, 116.2, 159.6, 162.1, 173.6.

6,6-Dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (1h, Table 1, entry 8). ^1H NMR (500 MHz, CDCl_3) δ 1.82 (s, 6 H), 1.98 (s, 4 H); ^{13}C NMR (125 MHz, CDCl_3) δ 23.9, 24.1, 27.6, 105.2, 168.1.

5-Benzylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (1g, Table 3, entry 12). ^1H NMR (400 MHz, CDCl_3) δ 1.82 (s, 6 H), 7.46-7.53 (m, 2 H), 7.54-7.60 (m, 1 H), 8.04-8.09 (m, 2 H), 8.44 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.6, 104.6, 114.8, 128.7, 131.7, 133.6, 133.7, 158.1, 159.7, 163.3.

3-Hydroxy-2-phenylpropanoic acid (2a, Table 1, entry 1). ^1H NMR (400 MHz, CDCl_3) δ 3.76-3.83 (m, 2 H), 4.80 (m, 1 H), 7.21-7.30 (m, 5 H); ^{13}C NMR (100 MHz, CD_3OD) δ 55.9, 65.1, 128.5, 129.2, 129.7, 137.9, 176.1.

2-Benzyl-3-hydroxypropanoic acid (2b, Table 1, entry 2). ^1H NMR (400 MHz, CDCl_3) δ 2.84-2.94 (m, 2 H), 3.04-3.14 (m, 1 H), 3.70-3.84 (m, 2 H), 7.21-7.35 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 34.0, 48.7, 61.9, 126.7, 128.6, 129.0, 138.2, 179.3.

2-(Hydroxymethyl)-4-methylpentanoic acid (2c, Table 1, entry 3). ^1H NMR (300 MHz, CDCl_3) δ 0.85 (d, $J = 6.3$ Hz, 3 H), 0.87 (d, $J = 6.6$ Hz, 3 H), 1.37 (m, 1 H), 1.58-1.72 (m, 2 H), 2.68-2.75 (m, 1 H), 3.77-3.79 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.3, 22.5, 25.8, 37.2, 45.7, 63.4, 180.8.

3-Hydroxy-2-methyl-2-phenylpropanoic acid (2d, Table 1, entry 4). ^1H NMR (300 MHz, CDCl_3) δ 1.69 (s, 3 H), 3.67 (d, $J = 11.4$ Hz, 1 H), 4.11 (d, $J = 11.4$ Hz, 1 H), 7.28-7.41 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.1, 52.4, 69.1, 126.3, 127.7, 128.8, 139.6, 181.1.

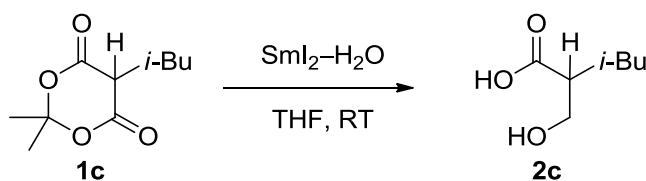
2-(Hydroxymethyl)-2,4-dimethylpentanoic acid (2e, Table 1, entry 5). ^1H NMR (500 MHz, CDCl_3) δ 0.83 (d, $J = 6.5$ Hz, 3 H), 0.85 (d, $J = 6.5$ Hz, 3 H), 1.17 (s, 3 H), 1.41 (dd, $J = 6.5, 14.0$ Hz, 1 H), 1.53 (dd, $J = 7.0, 14.0$ Hz, 1 H), 1.64-1.73 (m, 1 H), 3.40 (d, $J = 11.0$ Hz, 1 H), 3.73 (d, $J = 11.0$ Hz, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 19.9, 23.7, 24.1, 24.5, 44.7, 47.4, 68.8, 183.0.

5-Ethyl-2,2-dimethyl-1,3-dioxane-4,6-dione (2h, Table 1, entry 9). ^1H NMR (500 MHz, CDCl_3) δ 0.99 (t, $J = 7.5$ Hz, 3 H), 1.69 (s, 3 H), 1.72 (s, 3 H), 2.08-2.14 (qd, $J = 7.5, 5.0$ Hz, 2 H), 3.42 (t, $J = 5.0$ Hz, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 10.8, 20.1, 27.0, 28.4, 47.1, 104.8, 165.5.

Water Stoichiometry Study^{10,11}

General Procedure. An oven-dried vial containing a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, typically 0.60 mmol, 6.0 equiv, 0.085 M) was added followed by H₂O as indicated in Table 2 with vigorous stirring, which resulted in the formation of a characteristic burgundy red color of the SmI₂-H₂O complex. A solution of ester substrate (0.10 mmol, 1.0 equiv, stock solution in THF, 1.0 mL) was added and the reaction mixture was stirred for the indicated time. The excess of Sm(II) was oxidized by bubbling air through the reaction mixture, and the reaction mixture was diluted with CH₂Cl₂ (30 mL) and HCl (1 N, 30 mL). The aqueous layer was extracted with CH₂Cl₂ (3 x 30 mL), the organic layers were combined, dried over Na₂SO₄, filtered, and concentrated. The sample was analyzed by ¹H NMR (CDCl₃, 500 MHz) to obtain conversion and yield using internal standard and comparison with authentic samples.

Table SI-2. Reduction of Meldrum's Acids using SmI₂: the Role of Water Stoichiometry.^a



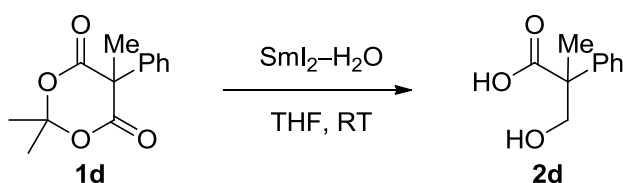
entry	SmI ₂ (equiv)	H ₂ O (equiv)	time ^b	conv. ^c (%)
1	6	-	3 h	<2.0
2	6	50	30 s	<2.0
3	6	100	30 s	1.0
4	6	200	30 s	6.4
5	6	400	30 s	13.2
6	6	800	30 s	10.2
7	6	1600	30 s	7.5
8	6	3200	30 s	4.1
9	6	6400	30 s	3.2
10	6	50	3 h	15.1
11	6	100	3 h	70.0
12	6	400	15 min	82.6

^aConditions: Meldrum's acid (1 equiv), SmI₂ (in THF), H₂O, 23 °C. In all entries, preformed solution of SmI₂-H₂O was used. ^bQuenched with air after the indicated time. ^cDetermined by ¹H NMR. In all entries >95% yield based on reacted starting material. When <2%, conversion to the hydroxy acid was not observed.

SmI₂ Stoichiometry Study

General Procedure. In an argon-filled glove box, samarium(II) iodide (AAPL, as indicated in Table 3) was weighed out into a vial equipped with a magnetic stir bar, transferred out of the glove box, and placed under a positive pressure of argon using standard Schenk techniques. Substrate (as a THF solution, to a final SmI₂ concentration of 0.10 M) was added, followed by a rapid injection of water, with vigorous stirring. After the specified time, the excess of SmI₂ was oxidized by bubbling air through the reaction mixture. The reaction mixture was diluted with CH₂Cl₂ (30 mL) and HCl (1.0 N, 30 mL). The aqueous layer was extracted with CH₂Cl₂ (3 x 30 mL), organic layers were combined, dried over Na₂SO₄, filtered and concentrated. The sample was analyzed by ¹H NMR (CDCl₃, 500 MHz) to obtain conversion and yield using internal standard and comparison with authentic samples.

Table SI-3. Reduction of Meldrum's Acids using SmI₂: the Role of SmI₂ Stoichiometry.^a



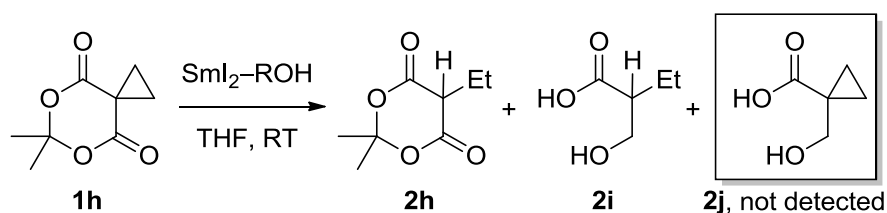
entry	SmI ₂ (equiv)	H ₂ O (equiv)	time ^b	conv. ^c (%)
1	0	200	3 h	<2.0
2	2	400	60 s	36.1
3	4	800	60 s	60.0
4	6	1200	60 s	84.7
5	8	1600	60 s	>98.0

^aConditions: Meldrum's acid (1 equiv), SmI₂ (powder, AAPL), H₂O, 23 °C. In all entries, preformed solution of SmI₂-H₂O was used. ^bQuenched with air after the indicated time. ^cDetermined by ¹H NMR. In all entries >85% yield based on reacted starting material.

Radical Clock Experiments¹²⁻¹⁴

General Procedure. An oven-dried vial containing a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, as indicated in Table 4) was added followed by H₂O with vigorous stirring, which resulted in the formation of a characteristic burgundy red color of the SmI₂-H₂O complex. A solution of ester substrate (0.10 mmol, 1.0 equiv, stock solution in THF, 1.0 mL) was added and the reaction mixture was stirred for the indicated time. The excess of Sm(II) was oxidized by bubbling air through the reaction mixture, and the reaction mixture was diluted with CH₂Cl₂ (30 mL) and HCl (1 N, 30 mL). The aqueous layer was extracted with CH₂Cl₂ (3 x 30 mL), the organic layers were combined, dried over Na₂SO₄, filtered, and concentrated. The sample was analyzed by ¹H NMR (CDCl₃, 500 MHz) to obtain conversion and yield using internal standard and comparison with authentic samples.

Table SI-4. Radical Clock Fragmentation Studies in the Reduction of Meldrum's Acids.^a



entry	SmI ₂ (equiv)	ROH	ROH (equiv)	time ^b	conv. ^c (%)	2h:2i ^c (%)
1	2	H ₂ O	200	< 1 min	87	>98:2
2 ^d	10	H ₂ O	1000	2 h	>95	<5:95
3	8	H ₂ O	1000	0.25 h	>95	21:79
4	8	H ₂ O	200	0.25 h	>95	42:58
5 ^e	3	MeOH	200	1 h	>95	>98:2
6	3	-	-	3 h	50	>98:2

^aConditions: Meldrum's acid (1 equiv), SmI₂ (in THF), ROH, 23 °C. ^bQuenched with air after the indicated time. ^cDetermined by ¹H NMR. Combined yield of **2h** and **2i**. Conversion = (100-SM). Entries 1-5, >85% yield based on reacted starting material. Entry 6, 23% yield. In all entries, **2j** <2.0%. ^dGuazzelli et al., *J. Am. Chem. Soc.* **2009**, *131*, 7214. ^eFragmentation product consists of 5-ethyl-2,2-dimethyl-1,3-dioxane-4,6-dione and its methanolysis product (15:85 ratio).

Deuterium Incorporation Studies

General Procedure. An oven-dried vial containing a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, typically 0.80 mmol, 8.0 equiv, 0.10 M) was added followed by D_2O (1000 equiv, 1.80 mL) with vigorous stirring, which resulted in the formation of a characteristic burgundy red color of the SmI_2 - D_2O complex. A solution of ester substrate (0.10 mmol, 1.0 equiv, stock solution in THF, 1.0 mL) was added and the reaction mixture was stirred for 2 h at room temperature. The excess of Sm(II) was oxidized by bubbling air through the reaction mixture, and the reaction mixture was diluted with CH_2Cl_2 (30 mL) and HCl (1 N, 30 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL), the organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated. The sample was analyzed by ^1H NMR (CDCl_3 , 500 MHz) to obtain conversion and yield using internal standard and comparison with authentic samples.

In addition, several control reactions were carried out to determine the origin of D^1 -incorporation at the α -position: the reaction of α -Ph- and Bn-substituted Meldrum's acids **1a** and **1b** with THF- D_2O (8.0 mL, 1000 equiv) for 2 h at rt resulted in a full recovery of the starting material with >98% D^1 incorporation at the alpha position; the reaction of 2-methyl-3-phenylpropanoic acid with THF- D_2O (8.0 mL, 1000 equiv) for 2 h at rt resulted in a full recovery of the starting material with <2% D^1 incorporation at the alpha position. These results suggest that in the case of α -monosubstituted precursors the D^1 -exchange takes place prior to the reduction of Meldrum's acids to the corresponding β -hydroxy acids.

Table SI-5. Deuterium Incorporation Studies in the Reduction of Meldrum's Acids using SmI_2 - H_2O .

entry	R_1, R_2	SmI_2 (equiv)	D_2O (equiv)	time ^a (h)	conv. ^b (%)	yield ^b (%)	D^2 ^b (%)	α - D^1 ^b (%)
1	Me, Ph	8	1000	18	>98	84	>98	-
2	H, Ph	8	1000	18	>98	82	>98	>98
3	H, <i>i</i> -Bu	8	1000	18	>98	97	>98	>98

All reactions carried out using standard Schlenk techniques. ^aQuenched with air after the indicated time.

^bDetermined by ^1H NMR. Conversion = (100-SM).

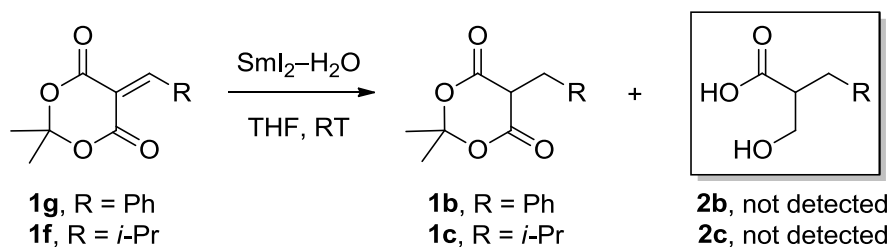
Kinetic Isotope Studies¹⁵⁻¹⁷

General Procedure. An oven-dried vial containing a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, 0.80 mmol, 8.0 equiv, 0.10 M) was added followed by $\text{H}_2\text{O}/\text{D}_2\text{O}$ (1000 equiv, 100 mmol) with vigorous stirring. A solution of ester substrate (0.10 mmol, 1.0 equiv, stock solution in THF, 1.0 mL) was added and the reaction mixture was stirred for 2 h at room temperature. The excess of Sm(II) was oxidized by bubbling air through the reaction mixture, and the reaction mixture was diluted with CH_2Cl_2 (30 mL) and HCl (1 N, 30 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL), the organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated. The sample was analyzed by ^1H NMR (CDCl_3 , 500 MHz) to obtain conversion and yield using internal standard and comparison with authentic samples. The amount of each species was determined by ^1H NMR (500 MHz, CDCl_3) and HRMS analysis. Kinetic isotope effect, $k_{\text{H}}/k_{\text{D}} = 1.5$, consistent with proton transfer to carbon not being involved in the rate determining step of the reaction.

1,4/1,2 Selectivity Studies¹⁸

General Procedure. An oven-dried vial containing a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution, 0.20 mmol, 2.0 equiv, 0.10 M) was added followed by H_2O (200 equiv, 20 mmol) with vigorous stirring. A solution of ester substrate (0.10 mmol, 1.0 equiv, stock solution in THF, 1.0 mL) was added and the reaction mixture was stirred for 5 min at room temperature. The excess of Sm(II) was oxidized by bubbling air through the reaction mixture, and the reaction mixture was diluted with CH_2Cl_2 (30 mL) and HCl (1 N, 30 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL), the organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated. The sample was analyzed by ^1H NMR (CDCl_3 , 500 MHz) to obtain conversion and yield using internal standard and comparison with authentic samples. **Run A:** reduction of **1g** afforded the corresponding product in 94% yield; **2b** was not detected. **Run B:** reduction of **1f** afforded the corresponding product in 97% yield; **2c** was not detected.

Table SI-6. Determination of 1,4/1,2-Selectivity in the Reduction of Meldrum's Acids using $\text{SmI}_2\text{-H}_2\text{O}$.



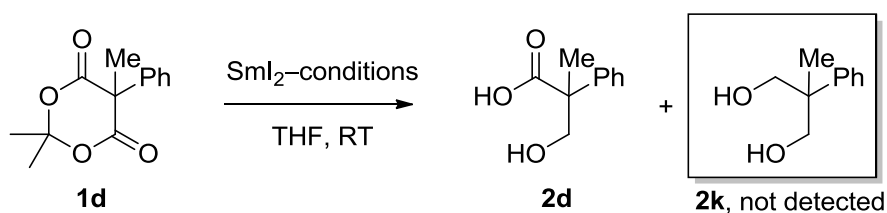
entry	R	SmI_2 (equiv)	H_2O (equiv)	time ^a (min)	conv. ^b (%)	yield ^b (%)	1,4/1,2- selectivity
1	Ph	2	200	5	>98	94	>95:5
2	<i>i</i> -Pr	2	200	5	>98	97	>95:5

All reactions carried out using standard Schlenk techniques. ^aQuenched with air after the indicated time.
^bDetermined by ^1H NMR. Conversion = (100-SM).

Evaluation of SmI_2 -ROH Systems^{19,20}

General Procedure. An oven-dried vial containing a stir bar was placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Samarium(II) iodide (THF solution) was added followed by amine and ROH or ROH with vigorous stirring. A solution of ester substrate (0.10 mmol, 1.0 equiv, stock solution in THF, 1.0 mL) was added and the reaction mixture was stirred for the indicated time. The excess of Sm(II) was oxidized by bubbling air through the reaction mixture, and the reaction mixture was diluted with CH_2Cl_2 (30 mL) and HCl (1 N, 30 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL), the organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated. The sample was analyzed by ^1H NMR (CDCl_3 , 500 MHz) to obtain conversion and yield using internal standard and comparison with authentic samples. In all entries, 2-methyl-2-phenylpropane-1,3-diol (see below) was not detected.

Table SI-7. Evaluation of Chemoselectivity in the Reduction of Meldrum's Acids.^a



entry	ROH	ROH (equiv)	time ^b	yield ^c (%)	selectivity ^c 2d:2k
1	MeOH	4/1 v/v	2 h	<5	-
2	ED	36	2 h	<5	-
3	DCH	36	2 h	<5	-
4	EG	36	2 h	84	>95:5
5	<i>n</i> -BuNH ₂ /H ₂ O	12/18	5 min	<5	-
6	pyrrolidine/H ₂ O	12/18	5 min	<5	-
7	Et ₃ N/H ₂ O	12/18	5 min	92	>95:5
8	Et ₃ N/EG	12/18	5 min	84	>95:5
9	Et ₃ N/MeOH	12/18	2 h	<5	-
10	TMEDA/H ₂ O	12/18	5 min	46	>95:5
11	<i>N</i> -Me-morpholine/H ₂ O	12/18	5 min	80	>95:5
12	(<i>i</i> -Pr) ₂ EtN/H ₂ O	12/18	5 min	48	>95:5

^aConditions: Meldrum's acid (1 equiv), SmI_2 (4-6 equiv, THF), 23 °C. In all entries, preformed solution of SmI_2 -ROH was used. ^bQuenched with air after the indicated time. ^cDetermined by ^1H NMR. In all entries, yield based on reacted starting material. In all entries, conversion to **2k** not observed. ED = Ethylenediamine; DCH = *trans*-*N,N'*-dimethyl-1,2-cyclohexyldiamine; EG = ethylene glycol; TMEDA = tetramethylethylenediamine.

2-Methyl-2-phenylpropane-1,3-diol (2k). ^1H NMR (400 MHz, CDCl_3) δ 1.32 (s, 3 H), 1.94 (br, 2 H), 3.87 (d, $J = 11.0$ Hz, 2 H), 4.00 (d, $J = 11.0$ Hz, 2 H), 7.25-7.30 (m, 1 H), 7.36-7.42 (m, 2 H), 7.42-7.47 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.8, 44.6, 70.2, 126.7, 126.8, 128.7, 142.8.

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