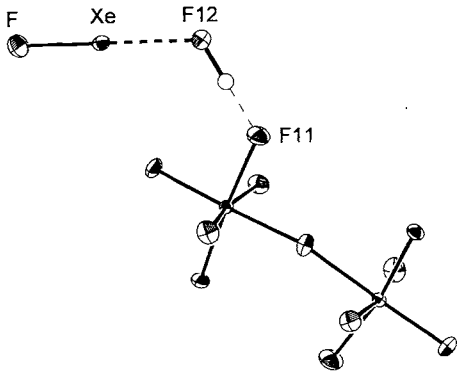

Figure 2. The structure of $XeF(HF)^+Sb_2F_{11}^-$ in the crystal (ORTEP, ellipsoids with 50% probability). One formula unit is shown with the characteristic bridge F–Xe···F–H···F–Sb. The position of the proton could not be determined and is therefore assumed; selected bond lengths [pm]: Xe–F 193.8(4), Xe–F12 235.9(4), F11–F12 253.4(5).

device [20], colorless, yellow, and dark green crystals were separated. A dark green crystal of approximate dimensions $0.2 \times 0.2 \times 0.1$ mm was mounted on an Enraf-Nonius CAD 4 four-circle diffractometer and measured at $-143\,^{\circ}C$: $a = 1041.6(2)$, $b = 821.8(2)$, $c = 1140.4(2)$ pm, $\beta = 94.14(2)^{\circ}$, $V = 973.6(3) \times 10^6$ pm^3; space group $P2_1/n$, no. 14, $Z = 2$, $2\theta_{max} = 60^{\circ}$, $Mo_{K\alpha}$, $\lambda = 71.069$ pm, ω scan; 2966 measured reflections, 2826 independent reflections, 2810 of which are used for the calculation, Lorentz polarization correction, Ψ scan absorption correction, max absorption 59%, $\mu = 9.1$ mm^{-1}. Structure solution was carried out with the program SHELXS 86 [21], refinement with the program SHELXS 93 [22], 120 parameters, $R = 0.038$, $wR_2 = 0.091$ [23]. $XeF(HF)^+Sb_2F_{11}^-$: From a reaction similar to that described above, however, without addition of elemental xenon, a $0.2 \times 0.2 \times 0.2$ mm yellow crystal was isolated, mounted, and measured at $-143\,^{\circ}C$: $a = 775.9(1)$, $b = 866.1(1)$, $c = 890.2(2)$ pm, $\alpha = 104.9(1)$, $\beta = 104.85(1)$, $\gamma = 105.34(1)^{\circ}$, $V = 522.6(1) \times 10^6$ pm^3, space group $P\bar{1}$, no. 2, $Z = 2$, $2\theta_{max} = 70^{\circ}$, 2156 measured, 2033 independent, 2033 used reflections, DIFABS absorption correction [24], $\mu = 8.5$ mm^{-1}, min/max correction 1.061/1.416, 145 parameters. $R_1 = 0.025$, $wR_2 = 0.078$ [23].

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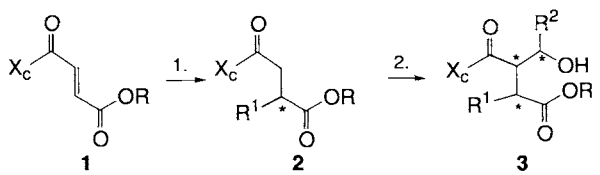
Regio- and Stereocontrolled Conjugate Radical Addition to a Desymmetrized Fumarate Derivative: An Efficient Synthesis of (−)-Nephrosteranic Acid and (−)-Roccellaric Acid**

Mukund P. Sibi* and Jianguo Ji

The readily available, simple four-carbon dicarboxylic acids, succinic, fumaric, and maleic acids, serve as important building blocks in organic chemistry. Succinates with dissimilar substituents on the carbon backbone have received attention because of their potential use as components in the development of metalloproteinase inhibitors.[1] We have recently reported highly selective radical conjugate reactions.[2] We surmised that regio- and stereocontrolled radical additions to differentially protected fumarates[3] could be used to prepare functionalized succinates (Scheme 1). In step 1, the remote chiral center is established through a regio- and stereoselective radical addition to the fumarate **1** (X_c = chiral auxiliary). In step 2, the chiral auxiliary controls the regio- and stereochemistry in the introduction of the second substituent by an aldol process. Thus, a single chiral center



1 2 3

Scheme 1. X_c = chiral auxiliary.

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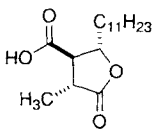
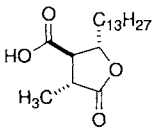
in the auxiliary facilitates the sequential introduction of multiple stereocenters with both regio- and stereocontrol.

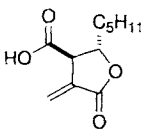
Trisubstituted butyrolactone natural products have kindled much interest recently because of their wide range of biological activity.[4] Nephrosteranic acid (**4**), roccellaric acid (**5**), and methylenolactocin (**6**), differentially functionalized succinates, are three examples of such butyrolactones. We describe here the selective functionalization outlined in Scheme 1 and apply it in the highly efficient synthesis of **4** and **5**.



4
(–)-nephrosteranic acid



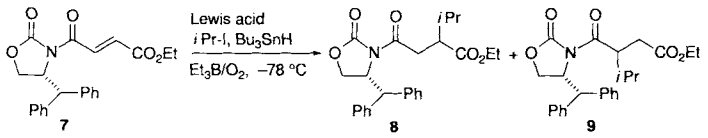
5
(–)-roccellaric acid



6
(–)-methylenolactocin

Lewis acid mediated addition[5] of isopropyl radical to the desymmetrized fumarate **7**[6] was initially evaluated to establish optimal reaction conditions (Table 1). The auxiliary of choice was the oxazolidinone derived from diphenylalanine[7] since it had shown the best characteristics in our earlier work. Several

Table 1. Lewis acid mediated isopropyl radical addition to **7**.



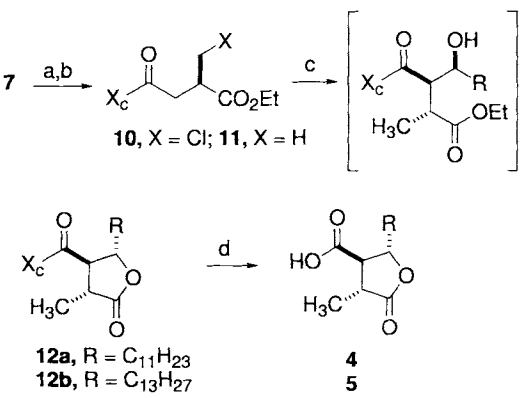
Entry	Lewis acid (equiv) [a]	Solvent	Yield. [%] [b]	*ds* (**8**) [c]	**8**:**9** [c]
1	–	CH_2Cl_2	92	1.6:1.0	11:1
2	$BF_3 \cdot Et_2O$ (1)	CH_2Cl_2	86	1.2:1.0	9:1
3	$Mg(OTf)_2$ (1)	CH_2Cl_2	87	1.0:1.0	7:1
4	$Zn(OTf)_2$ (1)	CH_2Cl_2	88	1.6:1.0	33:1
5	$Sc(OTf)_3$ (1)	CH_2Cl_2/THF, 4/1	95	2.1:1.0	6:1
6	$Y(OTf)_3$ (1)	CH_2Cl_2/THF, 4/1	90	21:1	>100:1
7	$Sm(OTf)_3$ (1)	CH_2Cl_2/THF, 4/1	95	29:1	>100:1
8	$Sm(OTf)_3$ (2)	CH_2Cl_2/THF, 4/1	95	5.0:1.0	24:1
9	$Ho(OTf)_3$ (1)	CH_2Cl_2/THF, 4/1	88	13:1	>100:1
10	$Tm(OTf)_3$ (1)	CH_2Cl_2/THF, 4/1	92	47:1	>100:1
11	$Yb(OTf)_3$ (1)	CH_2Cl_2/THF, 4/1	91	10:1	80:1
12	$Lu(OTf)_3$ (1)	CH_2Cl_2/THF, 4/1	95	31:1	87:1
13	$Er(OTf)_3$ (1)	CH_2Cl_2/THF, 4/1	90	33:1	>100:1
14	$Er(OTf)_3$ (3)	CH_2Cl_2/THF, 4/1	91	71:1	>100:1
15	$Er(OTf)_3$ (0.2)	CH_2Cl_2/THF, 4/1	88	3.0:1	11:1
16	$Er(OTf)_3$ (1)	THF	93	53:1	>100:1
17	$Er(OTf)_3$ (1)	Et_2O	90	34:1	>100:1

[a] See *Experimental Section* for reaction conditions. [b] Yields of isolated products. [c] Determined from the 400 MHz ^1H NMR spectrum of the crude reaction mixture.

trends are evident (Table 1). The conjugate addition reaction proceeds in excellent yields. High regio- and diastereoselectivity is observed with lanthanide and other selected Lewis acids (entries 6, 7, 9, 10, 12, and 13), but the reaction is essentially nonselective in the absence of a Lewis acid (entry 1).[8] Of the Lewis acids examined,[9] yttrium, samarium, thulium, lutetium, and erbium triflates gave the best selectivity (entries 6, 7, 10, 12, and 13). The high regio- and stereoselectivity observed in the radical reactions are of significance because addition of copper reagents to **7** leads to olefin reduction products or cleavage of the auxiliary.[10] Stoichiometric amounts of Lewis acid were required for high selectivity (entries 13, 15). Whereas excess erbium triflate led to a small enhancement in diastereoselectivity (entries 13, 14), excess samarium triflate greatly lowered both regio- and diastereoselectivity (entries 7, 8).

These results indicate that a chelating Lewis acid is required for high selectivity (entries 10, 13, 2). The Lewis acid selectively coordinates to the imide group and activates the substrate for conjugate addition β to the imide carbonyl, resulting in high regioselectivity. Chelation to the Lewis acid also locks the substrate in an *s-cis* conformation and the isopropyl radical approaches from the face opposite to the bulky diphenylmethyl substituent, providing high diastereoselectivity. We have previously established that radical addition to crotonates and cinnamates can be accomplished with substoichiometric amounts of Lewis acid with minimal change in yield and selectivity.[2a] However, with the more reactive fumarate **7**, radical addition to the uncomplexed substrate presumably competes effectively (entry 1) with that to the Lewis acid/substrate complex (entry 15), leading to lower selectivity. The dependence of regio- and diastereoselectivity with variation in chelating Lewis acids remains unexplained.

Having established that regio- and stereocontrolled radical addition to **7** was feasible, we turned our attention to the synthesis of the nephrosteranic and roccellaric acids. This required the addition of methyl radical to **7** followed by *syn*-selective aldol reaction at the methylene group α to the carbonyl of the chiral auxiliary. Addition of methyl radical to **7** using methyl iodide and tributyltin hydride gave mostly the starting material.[11] The successful installation of the methyl group was achieved in two steps (Scheme 2). Addition of chloromethyl radical to **7**



Scheme 2. a) $Sm(OTf)_3$, $ClCH_2I$, Bu_3SnH, Et_3B/O_2, CH_2Cl_2/THF, 1 h, –78 °C, 91% (>100:1); b) Bu_3SnH, AIBN, toluene, reflux, 12 h, 76%; c) Bu_2BOTf, CH_2Cl_2, Et_3N, –78 → 0 °C, RCHO, 12 h, **12a**: 84%, **12b**: 65%; d) LiOH, H_2O_2, THF/H_2O, room temperature, **4**: 92%, **5**: 94%. X_c = chiral auxiliary, AIBN = α,α'-azobisisobutyronitrile, Tf = trifluoromethanesulfonate.

($ClCH_2I/Bu_3SnH$) in the presence of samarium triflate gave **10** as a single regio- and diastereomer in 91% yield. Surprisingly, when erbium triflate was employed lower diastereoselectivity (10:1) resulted. Reductive elimination of the chlorine substituent in **10** using freshly distilled Bu_3SnH gave **11**.[12] We have recently shown that differentially protected succinates undergo aldol reactions in a highly regio- and stereoselective manner.[13] Treatment of **11** with dibutylboron triflate and triethylamine[14] followed by quenching of the boron enolate with lauraldehyde and myristylaldehyde gave the lactones **12a** and **12b**, respectively. Both aldol reactions were >98% *syn*-selective as evidenced by the NMR spectra of the crude products. Selective removal of the chiral auxiliary from **12a** gave nephrosteranic acid (**4**) in 92% yield, and a similar sequence starting with **12b** gave roccellaric acid (**5**) in 94% yield.[15] The overall yields for

nephrosteranic[16] and roccellaric acids[17] were 53 and 42%, respectively, over four synthetic steps from **7**.

In conclusion, we have described a highly regio- and stereoselective method for the addition of radicals to a desymmetrized fumarate. The application of this method in the efficient total synthesis of the butyrolactone natural products nephrosteranic and roccellaric acids has also been demonstrated. The present methodology alleviates some of the problems encountered in our alternate approach to these natural products.[18] Extension to enantioselective radical additions, the synthesis of more complex natural products, and development of tandem addition protocols are underway in our laboratory.

Experimental Section

Typical procedure: To a solution of **7** (37.9 mg, 0.1 mmol) and $Sm(OTf)_3$ (59.7 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) and THF (0.5 mL) in a flame-dried flask under N_2, was added *i*PrI (85 mg, 0.5 mmol) and Bu_3SnH (58 μL, 0.2 mmol) at $-78\,^{\circ}C$. Triethylborane (1 M in hexane; 0.2 mL, 0.2 mmol) was then added. Oxygen (5 mL) was finally added by syringe over 10 min. The reaction mixture was stirred at $-78\,^{\circ}C$ for 1 h. After the reaction was complete the mixture was diluted with Et_2O (15 mL), washed with 10% HCl (2 × 2 mL), and brine (3 × 2 mL), and the organic layer was dried over $MgSO_4$. The residue was purified by chromatography on silica gel (hexane/ethyl acetate 4/1) to give the pure product **8** (40 mg, 95%). M.p. 134–135 °C; $R_f = 0.55$ (hexane/ethyl acetate 7/3); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.35$–7.20 (m, 6H), 7.12–7.06 (m, 4H), 5.27 (ddd, $J = 8.0$, 5.6, 2.7 Hz, 1H), 4.68 (d, $J = 5.6$ Hz, 1H), 4.43 (t, $J = 9.4$ Hz, 1H), 4.37 (dd, $J = 9.1$, 2.7 Hz, 1H), 4.18–4.08 (m, 2H), 3.34 (dd, $J = 18.5$, 11.6 Hz, 1H), 2.74 (dd, $J = 18.3$, 3.0 Hz, 1H), 2.67 (ddd, $J = 11.6$, 5.4, 3.2 Hz, 1H), 1.98 (m, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 0.95 (d, $J = 5.1$ Hz, 3H), 0.93 (d, $J = 5.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 174.8$, 172.7, 153.1, 140.2, 138.2, 129.8, 128.8, 128.7, 128.3, 127.7, 127.0, 64.1, 60.7, 56.7, 49.8, 44.7, 31.0, 29.6, 20.9, 17.8, 14.4; $[\alpha]_D^{26} = -106.58$ ($c = 0.380$ in CH_2Cl_2); Analysis calcd for $C_{25}H_{29}NO_5$: C 70.90, H 6.90, N 3.31; found: C 71.10, H 6.59, N 3.51.

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[7] For the preparation of the oxazolidinone derived from diphenylalanine see: M. P. Sibi, P. K. Deshpande, A. J. La Loggia, J. W. Christensen, *Tetrahedron Lett.* **1995**, *36*, 8961.

[8] The regioselectivity in the radical addition experiments was determined by NMR analysis of the reaction mixture. Authentic samples of the racemic regio- and diastereomeric (1:1) monoethyl succinic acids were prepared by independent synthesis (ref. [3b]) and the chiral auxiliary introduced by standard techniques. The 400 MHz NMR spectra of the four regio- and diastereomeric products show well-separated signals for the methylene protons, which allowed unambiguous determination of product ratios.

[9] Other lanthanide Lewis acids ($La(OTf)_3$, $Gd(OTf)_3$, $Pr(OTf)_3$, $Tb(OTf)_3$, $Eu(OTf)_3$) were also evaluated but they showed inferior selectivity.

[10] Several reaction conditions were tested: *i*PrMgBr, $CuBr \cdot SMe_2$, $-78\,^{\circ}C$; MeMgBr, $CuBr \cdot SMe_2$; MeMgBr, CuCN; MeLi, CuCN.

[11] Minor amounts of ethyl radical addition (from triethylborane) were also observed.

[12] Older batches of tributyltin hydride led to some epimerization.

[13] M. P. Sibi, P. K. Deshpande, A. J. La Loggia, *Synlett* **1996**, 343.

[14] a) J. R. Gage, D. A. Evans, *Org. Synth.* **1989**, *68*, 83; b) D. L. Boger, S. L. Colletti, T. Honda, R. F. Menezes, *J. Am. Chem. Soc.* **1994**, *116*, 5607.

[15] The chiral auxiliary was recovered in 99% yield.

[16] Analytical data of **4** were similar to those reported in the literature: m.p. 105–107 °C; $[\alpha]_D^{26} = -28.14$ ($c = 1.020$ in $CHCl_3$); (+)-**4**: m.p. 96–98 °C; $[\alpha]_D^{26} = 27.2$ ($c = 1.45$ in $CHCl_3$); H. Takahata, Y. Uchida, T. Momose, *J. Org. Chem.* **1995**, *60*, 5628; *Tetrahedron Lett.* **1994**, *35*, 4123.

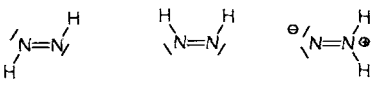
[17] Analytical data of **5** were identical to those reported in the literature: m.p. 110–111 °C [lit. 108 °C]; $[\alpha]_D^{26} = -26.29$ ($c = 1.240$ in $CHCl_3$) [lit. $[\alpha]_D^{26} = -26$ ($c = 1.93$ in $CHCl_3$)]; J. Mulzer, N. Salimi, H. Hartl, *Tetrahedron: Asymmetry* **1993**, *4*, 457; H. Takahata, Y. Uchida, T. Momose, *J. Org. Chem.* **1995**, *60*, 5628.

[18] The installation of the C-3 methyl group by enolate alkylation of the butyrolactone proceeds in low yields and is possible only with the carboxyl group as the C-4 substituent; M. P. Sibi, J. Ji et al., unpublished results.

Direct Proof of *trans*-Diazene in Solution by Trapping and Isolation of the Trapping Products**

Dieter Sellmann* and Andreas Hennige

More than a century after the existence of diazene (N_2H_2) was first postulated,[1] the structure and reactivity of this tetraatomic molecule is still controversial. Diazene, occasionally also still termed diimine or diimide, is the parent molecule of all azo compounds. It is extremely unstable in free state ($\Delta H_{f(298)}^0 = 212.3 \pm 8.4$ kJ mol^{-1}),[2] has been postulated as a metal-bound intermediate in enzymatic N_2 fixation,[3] and can be stabilized through coordination to metals in mono- and dinuclear complexes.[4] The existence of N_2H_2 in the gas phase under reduced pressure,[5] in the solid state at temperatures lower than $-165\,^{\circ}C$,[6] and in X-ray crystallographically characterized complexes[4] is irrefutable. In these complexes, N_2H_2 exhibits without exception the *trans* structure **A**. From spectroscopic investigations the same structure is concluded for uncomplexed diazene in the gaseous and solid states.[5, 6]



A **B** **C**

In contrast, diazene in solution still is an enigmatic species. Only indirect proof exists for its structure and strictly speaking even for its existence in solution. Mainly the characterization of reaction products serves as indirect evidence that, for example,

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[**] Transition metal complexes with sulfur Ligands, Part 121. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Part 120: D. Sellmann, T. Becker, F. Knoch, *Chem. Eur. J.* **1996**, *2*, 1092–1098.