37 °C) and the mixture was filtered in a UltraFree MC 30000 MWCO centrifugal filtration unit (Millipore) at 3500 g for 7 min at 37 °C. The concentration of free substrate in the filtrate was quantified by ICP-MS and the bound fraction was calculated as % bound = ([total]-[free])/[total].

The proton T_1 (longitudinal NMR relaxation time) value of water was measured at 20 MHz at 24 and 37 °C by inversion recovery on a Brucker Minispec; the data were obtained in PBS or with 4.5 % HSA by using 0–40 μM of the Gd^{3+} complex. The relaxivity (r_1) was determined from the slope of the plot of $1/T_1$ versus the sample concentration.

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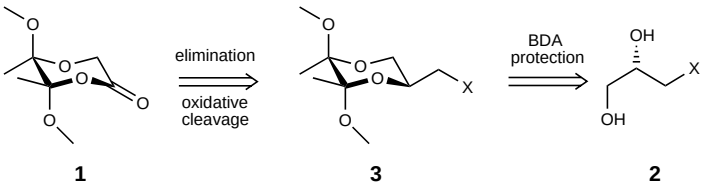
Butane-2,3-Diacetal-Desymmetrized Glycolic Acid—A New Building Block for the Stereoselective Synthesis of Enantiopure α-Hydroxy Acids**

Elena Díez, Darren J. Dixon, and Steven V. Ley*

Of the many classes of functional groups and motifs present in biologically and pharmacologically important compounds, mono- or dialkylated α-hydroxy acids occur commonly.[1–3] As a result of this feature, a range of synthesis methods has appeared over the years.[4–11] A commonly adopted strategy is the α-alkylation of chiral glycolic acid equivalents.[12, 13] Following our earlier reports using dispiroketal desymmetrization for this purpose, we here report the design, preparation, and alkylation reactions of a new chiral glycolic acid equivalent—the butane-2,3-diacetal-desymmetrized glycolate **1**.[14]

Our synthetic plan relied on a chiral memory procedure[15] whereby the chirality of a readily available 3-halopropane-1,2-diol **2** would be used to fix the chirality of the butane diacetal group in the stereoselective protection step.[16] It was envisaged that the alkyl halide product **3** would undergo ready elimination of hydrogen halide to form the *exo*-methylene enol ether,[17] which, after oxidative cleavage, would yield the facially desymmetrized glycolate **1** (Scheme 1).



1 **3** **2**

Scheme 1. Synthetic strategy for the development of a BDA-desymmetrized glycolate equivalent (BDA = butane diacetal).

The initial route employed (*S*)-3-bromopropane-1,2-diol **4** (available by the Jacobsen dynamic hydrolytic resolution of epibromohydrin[18]) as starting material. Treatment with butane-2,3-dione (1.1 equiv) in methanol in the presence of trimethyl orthoformate (2.1 equiv) and camphorsulfonic acid (CSA; 0.1 equiv) at reflux for two hours lead to the BDA-protected alkyl bromide **5** as a single diastereomer in 84 % yield (Scheme 2). To a solution of this material in THF at 0 °C was added an excess (1.2 equiv) of potassium hexamethyldisilazide (KHMDS), which on warming to room temperature overnight, effected a smooth elimination to the desired *exo*-methylene enol ether **6** in 85 % yield. Ozonolysis under standard conditions, followed by triphenyl phosphaine workup, gave the desired building block **1** in 69 % yield as a colorless solid. Recrystallization of this material from diethyl ether/hexanes afforded **1** in > 99 % *ee* as determined by chiral GC.

This route was readily modified to allow synthesis on a multigram scale. Thus, the commercially available and relatively cheap (*S*)-3-chloropropane-1,2-diol[19] **7** was used as the starting material. Standard BDA protection of this compound under the identical conditions described for **5** gave the crude BDA adduct **8** which was treated with an excess of potassium *tert*-butoxide in THF at reflux for 30 minutes. Ozonolysis with a dimethyl sulfide (DMS) workup afforded the crude glycolate product as a colorless solid, which on recrystallization from diethyl ether/hexanes gave enantiomerically pure **1** in 56 % yield over the three steps (Scheme 2).

With multigram quantities of enantiopure **1** available, alkylation reactions were investigated. Initial methylation studies with lithium hexamethyldisilazide (LHMDS) and methyl iodide revealed a strong dependence of the crude

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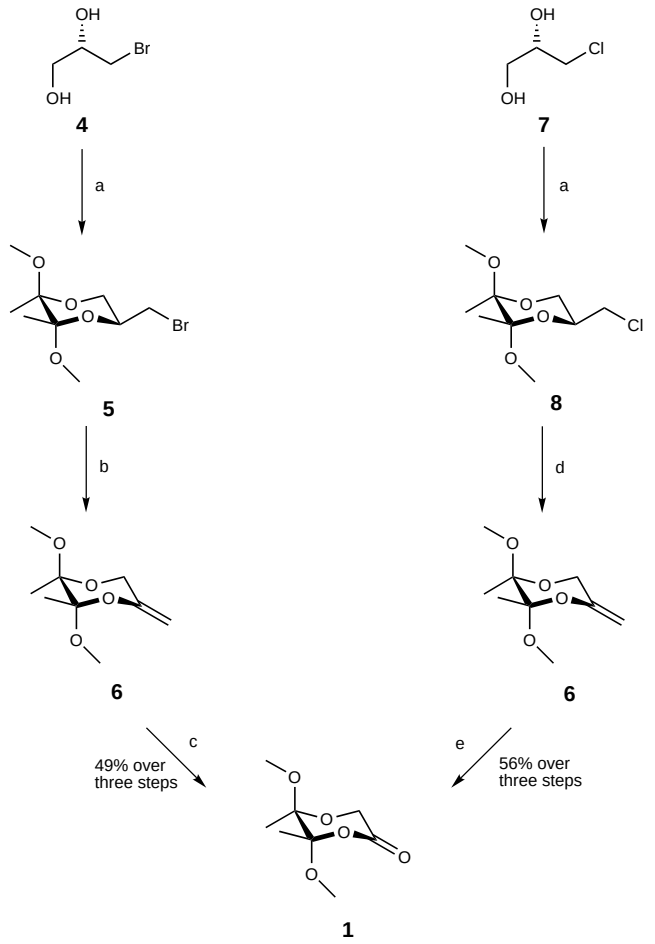
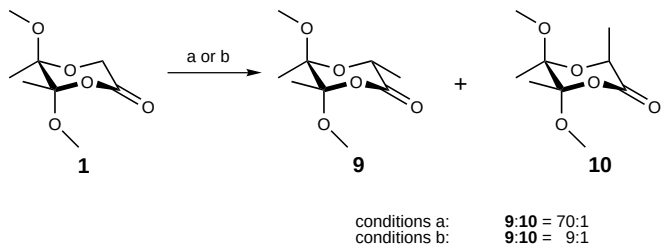


Scheme 2. Synthesis of BDA-desymmetrized glycolic acid from 1-halopropane-2,3-diols. a) MeCOCOMe (1.1 equiv), CSA (0.1 equiv), $CH(OMe)_3$ (2.1 equiv), MeOH, reflux, 2 h; b) KHMDS (1.2 equiv), THF, 0 °C→RT; c) O_3, CH_2Cl_2, −78 °C, then PPh_3 (1.1 equiv), −78 °C→RT; d) *t*BuOK (2.0 equiv), THF, reflux, 2 h; e) O_3, CH_2Cl_2/MeOH (1:1), −78 °C, then DMS (2.0 equiv), −78 °C→RT.

diastereomeric ratio (d.r.) on the equivalents of base used. Thus, with 1.05 equivalents of LHMDS, **9** and **10** were afforded in an excellent 70:1 ratio, alongside a small amount (≤10%) of dimethylated material. However, with 0.90 equivalents of LHMDS, the same products **9** and **10** were formed in the ratio of 9:1 with a yield of 84% at 93% conversion (Scheme 3).

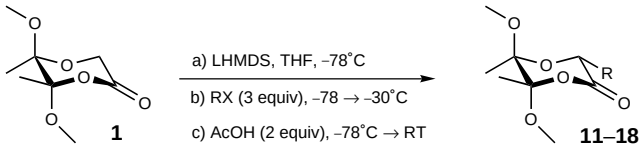
Encouraged by these initial results we examined the alkylation reactions of **1** further. However, care was taken to ensure that the observed selectivity in the reactions was due

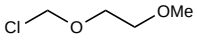
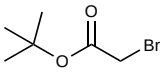
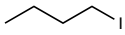
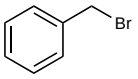
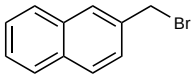


Scheme 3. Lithium enolate methylations of **1**. a) LHMDS (1.05 equiv), THF, −78 °C, 10 min, then MeI (3.0 equiv), −78→−30 °C over 2 h, then AcOH (2.0 equiv); b) LHMDS (0.9 equiv), THF, −78 °C, 10 min, then MeI (3.0 equiv), −78→−30 °C over 2 h, then AcOH (2.0 equiv).

to the principle attack of the lithium enolate of **1** on the alkyl halide and not through any secondary enhancement effect. This was implemented by using substoichiometric quantities of base. Table 1 shows the results for the alkylation of **1** with a range of alkyl halides using 0.95 equivalents of LHMDS and excess electrophile in THF at −78 to −30 °C.

Table 1. Monoalkylations of glycolate **1**.



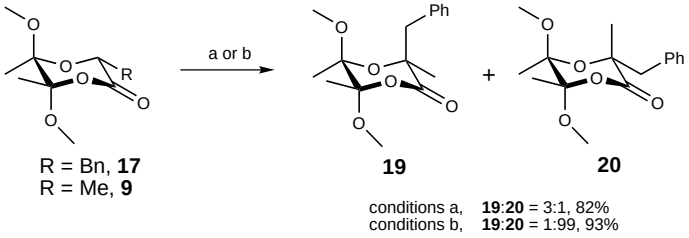
Entry	RX	d.r.	Product	Yield (conv.)
1		10:1[a]	**11**	64%
2		10:1[b]	**12**[c]	85% (97%)
3		15:1	**13**[d]	61% (87%)
4		18:1[a]	**14**[d,e]	92%
5		21:1	**15**	57%
6		60:1	**16**[c,d]	89% (96%)
7		>99:1	**17**[e]	96%
8		>99:1	**18**[d]	84% (91%)

[a] >99:1 after column chromatography. [b] >99:1 after recrystallization. [c] Configuration determined by single-crystal X-ray determination. [d] Configuration determined by NOE experiments. [e] Configuration determined by specific rotation comparison after deprotection.

In general, the selectivity of the alkylation improved with increasing size of the electrophile and the reactions gave good to excellent chemical yields of the alkylated products even with less reactive alkyl halides such as ethyl and butyl iodide. With bulky halides such as benzyl bromide and 2-(bromomethyl)naphthalene, no minor diastereomer could be detected within the crude reaction mixture. NOE experiments on the major diastereomeric products suggested the newly introduced alkyl group was located in an equatorial position and therefore the newly formed stereogenic center was of the (*R*)-configuration. Single-crystal X-ray determination of nitrile **12** and the allylated product **16** confirmed the stereochemical outcome. This suggested attack of the alkyl halide on the enolate carbon atom was occurring from the side opposing the 1,3-related axial methoxy group.

Further alkylation reactions of the monoalkylated products leading to the dialkylated products were also very effective. In the first case, successive treatment of the benzylated product **17** in THF at −78 °C with LHMDS (1.1 equiv) and methyl iodide (3.0 equiv) afforded the two diastereomers **19** and **20** in the ratio of 3:1 and in combined yield of 82% after separation

by column chromatography. In a complimentary study the methylated glycolate product **9** was treated with LHMDS and then benzyl bromide. These conditions afforded **20** as the only observable diastereomeric product by ^{1}H NMR spectroscopy. The diastereoselectivities in the dialkylation studies clearly depend on the relative sizes of the attached alkyl group and the attacking electrophile (Scheme 4).[20]



Scheme 4. Dialkylations of monoalkylated BDA-glycolates. a) R = Bn, LHMDS (1.1 equiv), THF, −78 °C, 10 min, then MeI (3.0 equiv), −78 → 0 °C over 2 h, then AcOH (2.0 equiv); b) R = Me, LHMDS (1.1 equiv), THF, −78 °C, 10 min, then BnBr (3.0 equiv), −78 → 0 °C over 2 h, then AcOH (2.0 equiv).

Removal of the BDA protecting group was easily accomplished for both the mono- and dialkylated products through acid-mediated hydrolysis or transesterification (Table 2). For entries 1, 2, and 5, the absolute configuration of the products was confirmed as (*R*) through comparison of the specific rotations of compounds **21**, **22**, and **25**, respectively, with those reported in the literature.[21]

Derivatization of **23** as the (*R*)- and (*S*)-Mosher's esters confirmed the enantiopurity as > 98 % *ee*, suggesting that no racemization was occurring in either the alkylation or the deprotection steps. In addition, this derivatization confirmed the stereochemistry as (*R*).[22]

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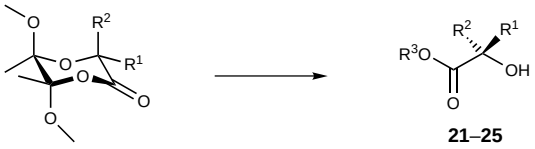
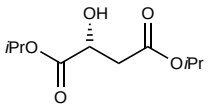
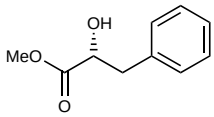
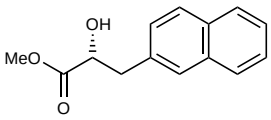
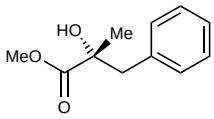
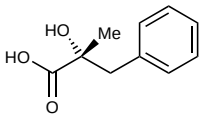
Table 2. Deprotection of mono- and dialkylated BDA-glycolates.



Entry	BDA glycolate	Conditions[a]	Product		Yield
1	**14**	A	**21**[b]		77 %
2	**17**	B	**22**[c]		quant.
3	**18**	B	**23**		95 %
4	**20**	C	**24**		87 %
5	**20**	D	**25**[d]		85 %

[a] Conditions: A) TMSCl in *i*PrOH (0.5 M), reflux; B) TMSCl in MeOH (0.5 M), 15 min, RT; C) TMSCl in MeOH (0.5 M), reflux; D) TFA/$H_2$0 (9:1), 10 min, RT. [b] **21**: $[\alpha]_D^{32} = +10.0$ ($c = 3.12$, $CHCl_3$) (ref. [21]: $[\alpha]_D^{20} = +11.0$, ($c = 3.21$, $CHCl_3$)). [c] **22**: $[\alpha]_D^{32} = +6.4$ ($c = 1.82$, $CHCl_3$) (ref. [21] for *S*-isomer: $[\alpha]_D^{20} = -7.6$, ($c = 2.0$, $CHCl_3$)). [d] **25**: $[\alpha]_D^{32} = +12.8$ ($c = 1.66$, dioxane) (ref. [21]: $[\alpha]_D^{20} = +13.2$ ($c = 1.51$, dioxane)).

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[21] Specific rotations: **21**: $[\alpha]_D^{32} = +10.0$ ($c = 3.12$, $CHCl_3$) (available from Aldrich, $[\alpha]_D^{20} = +11.0$, ($c = 3.21$, $CHCl_3$)); **22**: $[\alpha]_D^{32} = +6.4$ ($c = 1.82$, $CHCl_3$) (*S* isomer: $[\alpha]_D^{20} = -7.6$, ($c = 2.0$, $CHCl_3$), F. A. Davis, M. S. Haque, T. G. Ulatowski, J. C. Towson, *J. Org. Chem.* **1986**, *51*, 2402); **25**: $[\alpha]_D^{32} = +12.8$ ($c = 1.66$, dioxane) (*R*-isomer: $[\alpha]_D^{20} = +13.2$ ($c =$ 1.51, dioxane), S.-S. Jew, H.-A. Kim, J.-H. Kim, H.-G. Park, *Heterocycles* **1997**, *46*, 65).
[22] J. A. Dale, H. S. Mosher, *J. Am. Chem. Soc.* **1973**, *95*, 512.

Directed Assembly of Periodic Materials from Protein and Oligonucleotide-Modified Nanoparticle Building Blocks**

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In 1996 we reported a method for utilizing DNA and its synthetically programmable sequence recognition properties to assemble nanoparticles functionalized with oligonucleotides into preconceived architectures (Figure 1 B).[1] Since that initial report, our research group and many others have shown that this strategy[2–8] and off-shoots of it that rely on protein–receptor and antibody–antigen interactions[9–12] can be used to generate a wide range of architectures with many unusual and, in some cases, useful chemical and physical properties.

Since proteins and certain protein receptors can be functionalized with oligonucleotides, one, in principle, could immobilize such molecules onto oligonucleotide-modified nanoparticles and generate a new class of hybrid particles that exhibit the high stability of the oligonucleotide-modified particles but with molecular recognition properties that are dictated by the surface-immobilized protein or receptor rather than the DNA. Alternatively, one could functionalize a protein that has multiple receptor binding sites with receptor-modified oligonucleotides so that the protein receptor complex could be used as one of the building blocks, in place of one of the inorganic nanoparticles, in our original materials assembly scheme. Herein, we use 13-nm gold particles, streptavidin, and biotinylated DNA to explore these hypotheses (Figure 1 A) and some of the physical and chemical properties of the resulting new bioinorganic materials.

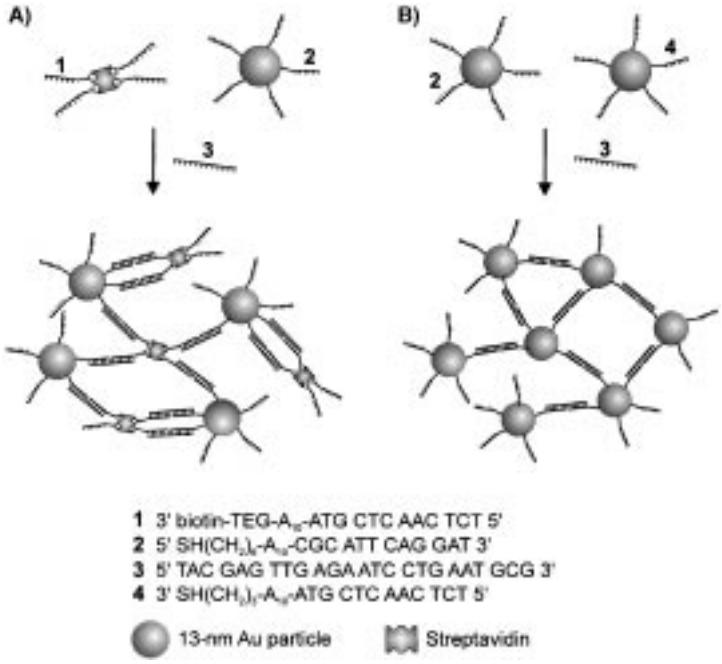

Figure 1. Schematic representation of DNA-directed assembly of Au nanoparticles and streptavidin. A) Assembly of oligonucleotide-functionalized streptavidin and Au nanoparticles (Au–STV assembly). B) Assembly of oligonucleotide-functionalized Au nanoparticles (Au–Au assembly). Note that **1** and **4** have the same DNA sequence.

The nanoparticle/protein assembly (Figure 1 A) reported herein relies on three building blocks: streptavidin complexed to four biotinylated oligonucleotides (**1**–STV), oligonucleotide-modified gold nanoparticles (**2**–Au), and a linker oligonucleotide (**3**) that has one half of its sequence complementary to **1** and the other half complementary to **2** (Figure 1). In a typical experiment, linker DNA (**3**; 10 μM, 21 μL) was introduced to a mixture of **2**–Au (9.7 nM, 260 μL) and **1**–STV (1.8 μM, 27 μL), or linker DNA **3** (10 μM, 21 μL) was premixed with **1**–STV (1.8 μM, 27 μL) and then the mixture was added to **2**–Au (9.7 nM, 260 μL) in 0.3 M phosphate-buffered saline (PBS) solution. Aggregates with similar properties could be formed by both methods, but premixing **3** and **1**–STV facilitates aggregate formation. Since a 13-nm gold particle is substantially larger than streptavidin ($4 \times 4 \times 5$ nm),[13, 14] a 1:20 molar ratio of Au nanoparticle to streptavidin was used to favor the formation of an extended polymeric structure rather than small aggregates comprised

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