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Et₃B-mediated two- and three-component coupling reactions *via* radical decarbonylation of α -alkoxyacyl tellurides: single-step construction of densely oxygenated carboskeletons†

Masanori Nagatomo, Daigo Kamimura, Yuki Matsui, Keisuke Masuda and Masayuki Inoue*

The single-step construction of various densely oxygenated carboskeletons was achieved by radical-based two- and three-component coupling reactions of sugar derivatives, without the need for light or heat. Et₃B/O₂-mediated decarbonylation readily converted α -alkoxyacyl tellurides to α -alkoxy carbon radicals, which intermolecularly added to glyoxylic oxime ether or enones to provide the two-component adducts. Furthermore, the three-component adducts were produced by an intermolecular aldol reaction between the aldehyde and the boron enolates generated by capture of the two-component radical intermediates by Et₃B. This powerful coupling method serves as a novel strategy for the convergent synthesis of polyol natural products.

Received 6th February 2015

Accepted 5th March 2015

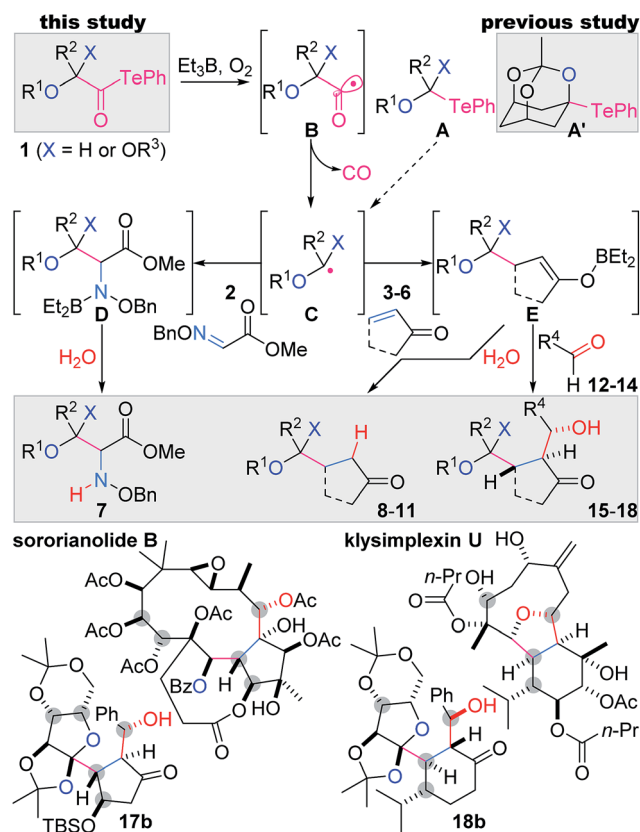
DOI: 10.1039/c5sc00457h

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Introduction

Contiguously substituted polyol structures are found not only in numerous saccharides, but also in diverse secondary metabolites. For example, highly oxygenated terpenoids often accommodate such substructures (*e.g.*, sororianolide B,¹ klysimplixin U,² Scheme 1). As the oxygen-based functional groups potentially form hydrogen bonds with biological polymers, polyol natural products often exhibit potent bioactivities. Therefore, these complex terpenoids are expected to function as selective cellular probes and pharmacologically useful compounds.

The presence of a greater number of oxygen-attached stereocenters with increased density in bioactive polyol natural products heightens the challenge of their chemical synthesis.³ In designing shorter and simpler synthetic routes to these complex targets, the convergent assembly of oxygenated fragments is most desirable, as this would minimize post-coupling manipulations of the functional groups. Radical-based reactions enable the highly chemoselective formation of carbon-carbon (C-C) bonds without affecting most oxygen-based functional groups and thus are particularly suitable as powerful convergent methodologies.⁴ Here we report mild and robust two- and three-component radical coupling reactions using multiply oxygenated α -alkoxyacyl tellurides **1** and Et₃B as the key reagents. The versatility of this process was demonstrated



Scheme 1 The present two- and three-component coupling reactions *via* radical decarbonylation of α -alkoxyacyl tellurides, and representative polyol natural products.

Graduate School of Pharmaceutical Sciences, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. E-mail: inoue@mol.f.u-tokyo.ac.jp

† Electronic supplementary information (ESI) available: Experimental protocols, characterization data, and NMR spectra of all new compounds. See DOI: 10.1039/c5sc00457h

Table 1 Preparation of α -alkoxyacyl tellurides and their reactions with glyoxylic oxime ether and enones

<div><div><div><div><div>R^1O</div><div>R^2</div><div>X</div></div><div><div>$HO-C(=O)-$</div><div>19</div></div></div><div><div>$\xrightarrow[\text{conditions}^a]{\text{i-butyl chloroformate, } N\text{-methylmorpholine; } (PhTe)_2, NaBH_4}$</div></div><div><div><div>R^1O</div><div>R^2</div><div>X</div></div><div><div>$-C(=O)-TePh$</div><div>1</div></div></div><div><div>$\xrightarrow[\text{conditions}^b]{\text{radical acceptor (2-4), } Et_3B, \text{ air, } CH_2Cl_2}$</div></div><div><div><div><div><div>R^1O</div><div>R^2</div><div>X</div></div><div><div>$-C(=O)-OMe$</div><div>7</div></div><div>$NH-OBn$</div></div></div><div>or</div><div><div><div><div>R^1O</div><div>R^2</div><div>X</div></div><div><div>$-C(=O)-$</div><div>$8,9$</div></div></div><div><div>cyclopentenone</div></div></div></div></div></div>				
<div>second component first component</div>	<div><div><div>$BnON=CH-C(=O)OMe$</div><div>2</div></div></div>	<div><div><div>$CH_2=CH-C(=O)Me$</div><div>3</div></div></div>	<div><div><div>cyclopentenone</div><div>4</div></div></div>	<div>plausible conformation of radical C</div>
<div><div><div><div><div>MeO</div><div>cyclic acetal</div></div><div><div>$-C(=O)-TePh$</div><div>$1a$</div></div><div>(90%, from 19a)</div></div></div></div>	<div><div><div><div><div>MeO</div><div>cyclic acetal</div></div><div><div>$-C(=O)OMe$</div><div>$NH-OBn$</div></div><div>$7a$</div></div><div>(75%)^c</div></div></div>	<div><div><div><div><div>MeO</div><div>cyclic acetal</div></div><div><div>$-CH_2CH_2C(=O)Me$</div><div>$8a$</div></div><div>(92%)</div></div></div></div>	<div><div><div><div><div>MeO</div><div>cyclic acetal</div></div><div><div>$-C(=O)-$</div><div>cyclopentenone</div></div><div>$9a$</div></div><div>(82%)^d</div></div></div>	<div><div><div>cyclic acetal</div><div>Ca</div></div></div>
<div><div><div><div><div>cyclic acetal</div></div><div><div>$-C(=O)-TePh$</div><div>$1b$</div></div><div>(83%, from 19b)</div></div></div></div>	<div><div><div><div><div>cyclic acetal</div></div><div><div>$-C(=O)OMe$</div><div>$NH-OBn$</div></div><div>$7b$</div></div><div>(88%)^{e,f}</div></div></div>	<div><div><div><div><div>cyclic acetal</div></div><div><div>$-CH_2CH_2C(=O)Me$</div><div>$8b$</div></div><div>(82%)</div></div></div></div>	<div><div><div><div><div>cyclic acetal</div></div><div><div>$-C(=O)-$</div><div>cyclopentenone</div></div><div>$9b$</div></div><div>(64%)^g</div></div></div>	<div><div><div>cyclic acetal</div><div>Cb</div></div></div>
<div><div><div><div><div>cyclic acetal</div></div><div><div>$-C(=O)-TePh$</div><div>$1c$</div></div><div>(81%, from 19c)</div></div></div></div>	<div><div><div><div><div>cyclic acetal</div></div><div><div>$-C(=O)OMe$</div><div>$NH-OBn$</div></div><div>$7c$</div></div><div>(66%)^{e,h}</div></div></div>	<div><div><div><div><div>cyclic acetal</div></div><div><div>$-CH_2CH_2C(=O)Me$</div><div>$8c$</div></div><div>(70%)</div></div></div></div>	<div><div><div><div><div>cyclic acetal</div></div><div><div>$-C(=O)-$</div><div>cyclopentenone</div></div><div>$9c$</div></div><div>(60%)ⁱ</div></div></div>	<div><div><div>cyclic acetal</div><div>Cc</div></div></div>

^a Reagents and conditions: **19** (1 equiv.), *i*-butyl chloroformate (1.2 equiv.), *N*-methylmorpholine (1.2 equiv.), THF (0.2 M), 0 °C, 30 min; (PhTe)₂ (1 equiv.), NaBH₄ (3 equiv.), THF/MeOH (10 : 1, 0.2 M), 0 °C, 30 min; rt, 30 min. ^b **1** (1 equiv.), **2–4** (2 equiv.), Et₃B (3 equiv.), CH₂Cl₂ (0.02 M), rt, under air. ^c dr = 2 : 1. ^d dr = 3 : 1. ^e The reaction was carried out in CH₂Cl₂ (0.1 M). ^f dr = 1 : 1. ^g dr = 1.3 : 1. ^h dr = 1.5 : 1. ⁱ dr = 1.4 : 1.

by the single-step preparation of variously adorned structures (**7–11**, **15–18**), including the polyol fragments of sororianolide B (**17b**) and klysimplexin U (**18b**).

Results and discussion

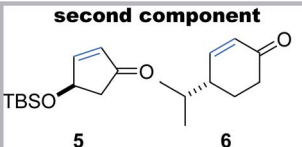
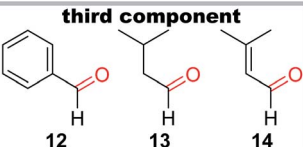
We recently demonstrated facile bridgehead radical formation from a mono-telluro acetal **A'** by the action of Et₃B and O₂ (Scheme 1).^{5,6} However, expansion of the substrate scope of this reaction was unsuccessful because of the chemical instability of the mono-telluro acetal (X = H) and the orthoester **A** (X = OR³).⁷ Thus, the C–Te bond of **A** typically undergoes heterolytic cleavage by electron donation from the oxygen lone pair, while such electron donation is uniquely impeded in **A'** due to the anti-Bredt character of the resultant oxocarbenium ion. In this context, we alternatively designed more stable α -alkoxyacyl tellurides **1** as precursors to α -alkoxy radical intermediates **C**.⁸ An Et radical generated from Et₃B/O₂⁹ would induce the C–Te homolysis of **1**, leading to the acyl radical **B**, the decarboxylation of which would give rise to the requisite radical **C**.^{10,11} According to our presumed scenario, the nucleophilic radical **C**

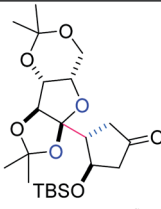
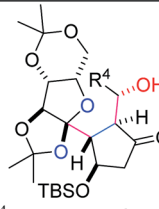
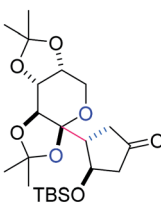
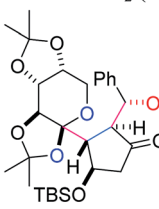
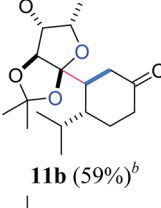
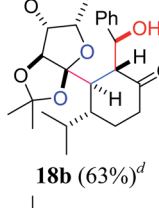
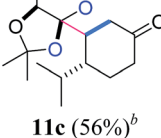
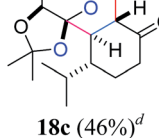
would then react intermolecularly with the electrophilic C=N bond of **2** and the C=C bond of **3–6** to generate the corresponding N- and C-radicals, respectively. Et₃B in turn would transform these radicals into the polar intermediates **D** and **E** through ejection of an Et radical,¹² and subsequent protonation would afford the two-component adducts **7** and **8–11**, respectively. The boron enolate **E** would further react with aldehydes **12–14** via the aldol reaction, resulting in the formation of the three-component products **15–18**. Most importantly, this intricate yet attractive plan would be realized only when all of the reactants properly follow the series of depicted radical and polar reactions in a single flask.

β -D-Ribofuranosiduronic acid derivative **19a**, 2-keto-L-gulonic acid derivative **19b**, and β -D-arabino-2-hexulopyranosonic acid derivative **19c** were selected as readily available carboxylic acids with four contiguous oxygen-attached stereocenters (Table 1). α -Alkoxyacyl tellurides **1a–c** were then obtained from the sugar-derived acids **19a–c** in one pot. Namely, **19** was first transformed into the activated ester via condensation with *i*-butyl chloroformate, and was then treated *in situ* with PhTeNa, prepared from (PhTe)₂ and NaBH₄, providing **1**. The structurally distinct



Table 2 Stereoselective two and three-component coupling reactions

		second component	third component
			
		5	12
		6	13
			14

	third component	
	none	R ⁴ CHO (12-14)
1b+5	 10b (65%) ^a	 15b: R ⁴ = Ph (88%) ^c 16b: R ⁴ = <i>i</i> -Bu (85%) ^c 17b: R ⁴ = CH=CHMe ₂ (79%) ^c
	 10c (57%) ^a	 15c (73%) ^c
1b+6	 11b (59%) ^b	 18b (63%) ^d
	 11c (56%) ^b	 18c (46%) ^d

^a Reagents and conditions: 1b,c (1 equiv.), 5 (2 equiv.), Et₃B (3 equiv.), CH₂Cl₂ (0.02 M), rt, under air. ^b 1b,c (1 equiv.), 6 (5 equiv.), Et₃B (3 equiv.), CH₂Cl₂ (0.1 M), rt, under air. ^c 1b,c (1 equiv.), 5 (2 equiv.), 12-14 (3 equiv.), Et₃B (3 equiv.), CH₂Cl₂ (0.1 M), rt, under air. ^d 1b,c (1 equiv.), 6 (3 equiv.), 12 (5 equiv.), Et₃B (3 equiv.), CH₂Cl₂ (0.1 M), rt, under air.

alkoxyacyl tellurides 1a-c were found to be stable to air, light and silica gel.

Significantly, the two-component radical reactions between the three radical donors 1a-c and three radical acceptors 2-4 all efficiently proceeded to generate nine complex adducts (Table 1).^{13,14} In these reactions, α -alkoxyacyl telluride (1a, b or c) was

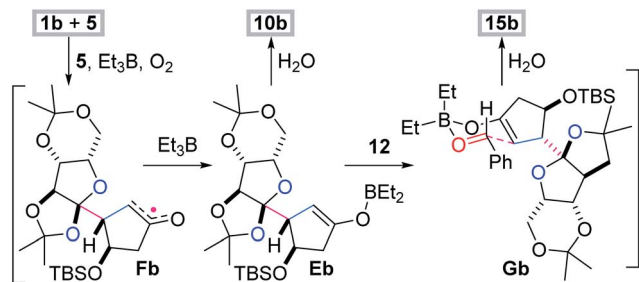
simply treated with 2 equiv. of the acceptor (2, 3 or 4) and 3 equiv. of Et₃B under air in CH₂Cl₂ at room temperature.¹⁵ As a result, three highly oxygenated α -amino acid derivatives 7a-c were directly constructed using the *O*-benzyl-protected methyl glyoxylate oxime 2 as the acceptor.¹⁶ An alternative application for α,β -unsaturated ketones 3 and 4 permitted the attachment to the linear carboskeleton of 8a-c and the branched carboskeleton of 9a-c, respectively. The absence of the formation of any potential by-products derived from the addition of the acyl radicals proved that radical decarbonylation consistently occurred prior to the intermolecular addition to the C=N or C=C bond. C-C homolysis of the acyl radicals is likely facilitated by the stabilizing orbital interaction between the alkyl radical and the adjacent oxygen lone pair in Ca-c.¹⁷

The resultant compounds Ca-c exhibited potent reactivity as nucleophilic radicals, and stereoselectively constructed the trisubstituted (7a-9a) and tetrasubstituted carbons (7b-9b, 7c-9c) on the ether rings (Table 1). The observed stereochemical outcome could be explained by a combination of stereo-electronic and steric effects. The three-dimensional structures of Ca-c represent their assumed conformations, where the interaction of the σ -radical orbital and the non-bonding O-electron pair increase both the stability and nucleophilicity of the axial σ -radical.^{18,19} The approach of the acceptor only occurs from the α -face of the molecule because of the concave nature of the β -face.²⁰ In the case of 7b-9b and 7c-9c, the favorable formation of the *cis*-fused bicycle in comparison to the strained *trans*-fused counterpart contributes to the excellent stereoselectivity at the ring junction.²¹ Overall, the results in Table 1 proved the high utility of the contiguously substituted polyol radical donors 1a-c.

Although the stereoselectivity at the radical accepting position in 7a-c and 9a-c was not high (dr = 3 : 1-1 : 1), the pre-existing stereocenters of acceptors 5 and 6 perfectly governed the stereochemical outcome of the two-component reactions (Table 2). Specifically, the β -oriented TBS-oxy group of 5 induced the selective α -face addition of the radical that was generated from 1b or 1c in the presence of Et₃B/O₂, giving rise to 10b or 10c as the sole stereoisomer. On the other hand, the radical addition to 6 occurred *trans* to its α -configured isopropyl group, predominantly leading to 11b or 11c.

Furthermore, the three-component coupling reactions were realized with complete control of the four stereocenters (Table 2). When a mixture of acyl telluride 1b, 5 (2 equiv.) and benzaldehyde 12 (3 equiv.) was treated with Et₃B/O₂ at room temperature, only 15b was obtained in a high yield. The aliphatic aldehyde 13 and the even α,β -unsaturated aldehyde 14 also served as the third components without decreasing the yields to afford 16b and 17b, respectively. Application of the different radical donor 1c with 5 and 12 also resulted in the smooth formation of the adduct 15c. The 6-membered enone 6 participated in the three-component reactions upon use of 1b and 1c in the presence of 12, delivering 18b and 18c, respectively. It is noteworthy that the one-step construction of the complex products with eight contiguous stereocenters was achieved under neutral conditions, and the five stereocenters of 15b-17b and the four stereocenters of 18b directly matched





Scheme 2 Rationale of the stereochemical outcome.

those of sororianolide B and klysimplexin U, respectively (highlighted as gray circles in Scheme 1). These data together proved the power of the present convergent methodology for the synthesis of densely oxidized carboskeletons.

The radical-polar crossover mechanism of the two- and three-component reactions was exemplified by the synthesis of **10b** and **15b** (Scheme 2).²² The Et₃B-mediated radical reaction between **1b** and **5** stereoselectively generates the radical intermediate **Fb**,²³ which is transformed to the boron enolate **Eb** by capture with Et₃B. Protonation of the polar intermediate **Eb** affords the two-component adduct **10b**. Alternatively, aldehyde **12** approaches **Eb** from the face opposite to the bulky fused tricycle and forms the chair-like six-membered transition state **Gb**,²⁴ subsequently establishing the stereocenters of the α - and β -positions of the ketone of **15b**. Three of the four newly introduced stereocenters of **15–17** and **18** are opposite because the configuration of the isopropyl group of **6** is the inverse of the TBS-oxy group of **5** (Table 2). Hence the stereochemical consistency in both the radical and aldol reactions is one of the most remarkable features of the present methodology.

Conclusions

In summary, we devised new radical-based two- and three-component coupling reactions, and realized the one-step construction of contiguously substituted polyol structures, which are significantly difficult to access by other methods. Upon activation with Et₃B/O₂, α -alkoxyacyl tellurides were rapidly converted to α -alkoxy radicals through expulsion of CO, thereby serving as the surrogate of the unstable mono-telluro acetals or orthoesters. Despite the sterically hindered nature, the resultant secondary or tertiary radical possessed potent reactivity toward the oxime and enone to stereoselectively furnish a variety of two-component adducts. Furthermore, the boron enolate, the intermediate in the two-component reaction, effectively participated in the aldol reaction with the third component, leading to another series of products. The three component coupling reactions simultaneously installed four contiguous stereocenters, and thus are particularly useful in increasing the complexity of the molecule in a single step. Because of the simplicity of the reagent system and the mildness of the conditions, this powerful radical technology introduces a novel convergent strategy for the expedited total synthesis of densely oxidized natural products.

Acknowledgements

This research was financially supported by the Funding Program for a Grant-in-Aid for Scientific Research (A) to M. I., and a Grant-in-Aid for Young Scientists (B) (JSPS) to M. N.

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