Radical Reactions Hot Paper

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Decarbonylative Radical Coupling of α-Aminoacyl Tellurides: Single-Step Preparation of γ-Amino and α,β-Diamino Acids and Rapid Synthesis of Gabapentin and Manzacidin A**

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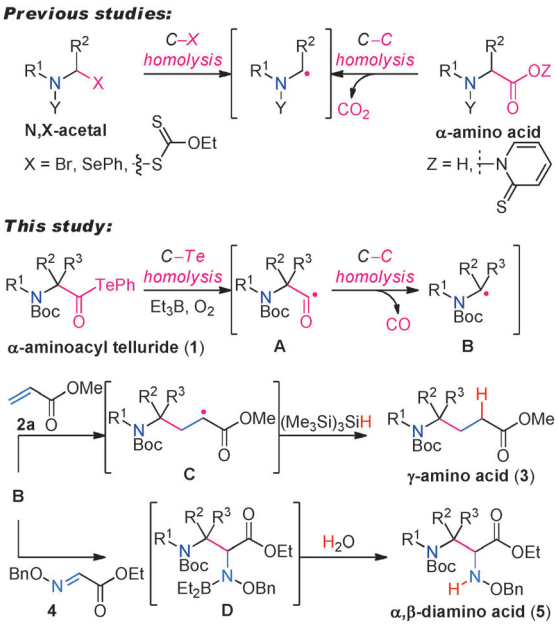
Abstract: *A new radical-based coupling method has been developed for the single-step generation of various γ-amino acids and α,β-diamino acids from α-aminoacyl tellurides. Upon activation by Et_3B and O_2 at ambient temperature, α-aminoacyl tellurides were readily converted into α-amino carbon radicals through facile decarbonylation, which then reacted intermolecularly with acrylates or glyoxylic oxime ethers. This mild and powerful method was effectively incorporated into expeditious synthetic routes to the pharmaceutical agent gabapentin and the natural product (−)-manzacidin A.*

Alkyl amines and their derivatives are key substructures in biologically important molecules, including alkaloids, peptides, and pharmaceuticals. Accordingly, the development of novel and efficient methods for their synthesis is an intensively investigated field of utmost importance. Coupling processes are particularly desirable, as a variety of complex nitrogen-containing compounds can be readily produced by assembly of simple fragments. Radical reactions are generally powerful, yet highly chemoselective, and thus are potentially suitable for such processes.[1]

α-Amino carbon radicals have served as useful species for the intermolecular construction of C–C bonds (Scheme 1).[2] In the context of coupling methods, N,X-acetals and α-amino acids have been typically used for the generation of α-amino carbon radicals.[3] Namely, radical formation and subsequent coupling were realized by homolytic cleavage of the C–X bond of N,X-acetals (X = Br,[4] SePh,[5] SC(=S)OEt[6]) or the decarboxylation of α-amino acids (Z = H[7] or N(C=S)R[8]). Despite these important advances, most of these methods suffer from a narrow substrate scope, which is due to the chemical instability of the precursors or the employment of relatively harsh conditions (e.g., high temperature, irradiation). Therefore, the versatility of α-amino carbon radicals has not been fully explored thus far. Herein, we report a mild and generic method for the formation of primary, secondary, and tertiary α-amino carbon radicals from α-aminoacyl tellurides. The high utility of this coupling process was demonstrated by the single-step preparation of γ-amino acids and α,β-diamino acids and the syntheses of the anticonvulsant gabapentin and the alkaloid (−)-manzacidin A.



Scheme 1. Previous and present methods for the generation of α-amino carbon radicals, and possible reaction mechanism of the decarbonylative radical coupling.

To achieve facile radical generation at ambient temperature, we planned to incorporate a weak C–Te bond into the substrate (Scheme 1).[9–11] As we presumed that the C–Te bond of a N,Te-acetal would easily undergo heterolytic cleavage by electron donation from the nitrogen lone pair, the carbonyl group was inserted between the α-amino carbon atom and the PhTe group. C–Te homolysis of acyl telluride **1** would first lead to acyl radical **A**;[12] decarbonylation would then give rise to requisite α-amino carbon radical **B**. Intermediate **B** would react intermolecularly with acrylate **2a** or glyoxylic oxime ether **4** to provide protected γ-amino acid **3** and α,β-diamino acid **5**, respectively. A prerequisite to realize this scenario is that decarbonylation from **A** occurs prior to the intermolecular reaction of **A** with **2a** or **4**. Although the rate of decarbonylation is generally slower than that of decarboxylation, stabilization of the resulting radical **B** is known to accelerate C–C homolysis.[13] Therefore, we

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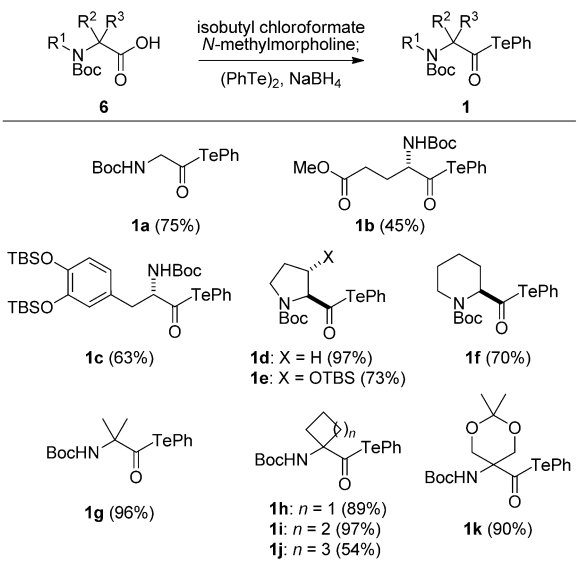
expected that the orbital interaction between the alkyl radical and the adjacent nitrogen lone pair in **B** would favorably affect the rapid formation of **B** from **A**.[14]

Eleven structurally distinct α-aminoacyl tellurides **1a–k** were prepared from readily available *N*-Boc-protected α-amino acids **6a–k** in a single step (Scheme 2). For instance,

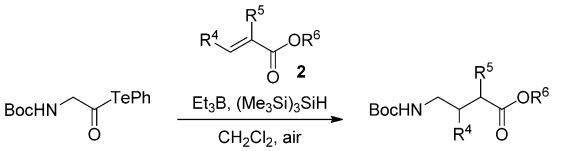


Scheme 2. Preparation of α-aminoacyl tellurides. Reagents and conditions: **6** (1 equiv), isobutyl chloroformate (1.2 equiv), *N*-methylmorpholine (1.2 equiv), THF (0.2 M), 0 °C, 30 min; $(PhTe)_2$ (1 equiv), $NaBH_4$ (3 equiv), THF (0.2 M), MeOH (2 M), 0 °C, 30 min; RT, 30 min. Boc = *tert*-butyloxycarbonyl, TBS = *tert*-butyldimethylsilyl.

N-Boc-protected glycine **6a** was transformed into its activated ester by condensation with isobutyl chloroformate, and was then treated in situ with PhTeNa, which had been prepared from $(PhTe)_2$ and $NaBH_4$, providing α-aminoacyl telluride **1a**. Tellurides **1b–k** were obtained in the same fashion, and all of the products were found to be stable to air, light, and silica gel. It is also noteworthy that Boc (**1a–k**), TBS (**1c**,**e**), and acetonide (**1k**) groups were all tolerated under these conditions.

Next, we explored the intermolecular radical 1,4-addition of glycine derivative **1a** to various acrylates (Table 1). Acyl tellurides had previously been converted into the acyl radicals either by thermolysis (> 100 °C) or UV photolysis.[15] We found that a combination of Et_3B and O_2[16] promoted C–Te bond homolysis under significantly milder conditions. Namely, when **1a** and methyl acrylate (**2a**; 2 equiv) were treated with Et_3B (3 equiv) and $(Me_3Si)_3SiH$ (3 equiv) in CH_2Cl_2 under air, γ-amino acid **3aa** was smoothly produced at ambient temperature within 15 minutes (entry 1). The potential side product between the acyl radical and **2a** was not detected, confirming that decarbonylation from the acyl radical proceeded even at room temperature. The primary radical prepared from **1a** underwent intermolecular reactions with acrylates **2b**, **2c**,[17] **2d**, and **2e** (entries 2–5) to produce the protected α-hydroxy (**3ab**), α-amino (**3ac**), α-fluoro (**3ad**), and α-trifluoromethyl (**3ae**) γ-amino acids, respectively. Moreover, the reaction of **1a** with dimethyl fumarate (**2f**) furnished β-methoxycarbonyl-γ-amino acid **3af** (entry 6). Remarkably, these reactions enabled the one-step construction of the neurotransmitter γ-aminobutyric acid (GABA) in a protected form (**3aa**) as well as of its α- or β-functionalized artificial analogues **3ab–af**.[18]

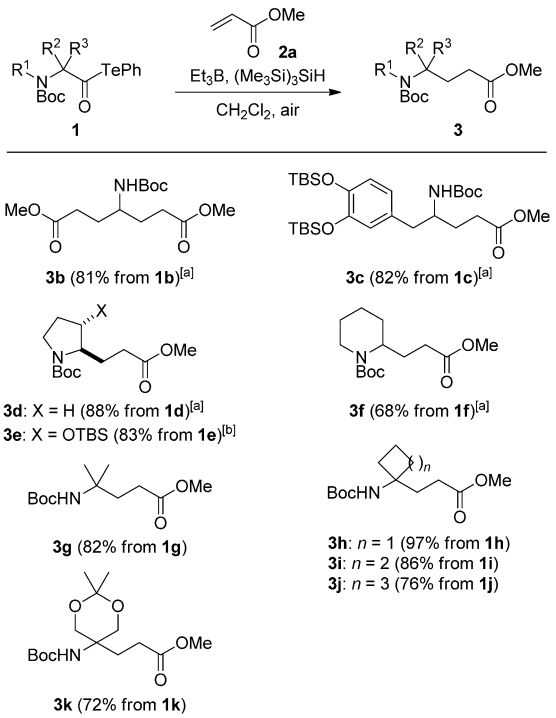
Table 1: Synthesis of γ-amino acid derivatives from **1a** and **2a–f**.[a]



Entry	2	R^4	R^5	R^6	3	Yield [%]
1	**2a**	H	H	Me	**3aa**	78
2	**2b**	H	OAc	Me	**3ab**	61
3	**2c**	H	NPhth	Me	**3ac**	71
4	**2d**	H	F	Bn	**3ad**	50
5	**2e**	H	CF_3	Bn	**3ae**	75
6	**2f**	CO_2Me	H	Me	**3af**	79

[a] Conditions: **1a** (1 equiv), **2** (2 equiv), Et_3B (3 equiv), $(Me_3Si)_3SiH$ (3 equiv), CH_2Cl_2 (0.02 M), air, RT. Phth = phthaloyl.

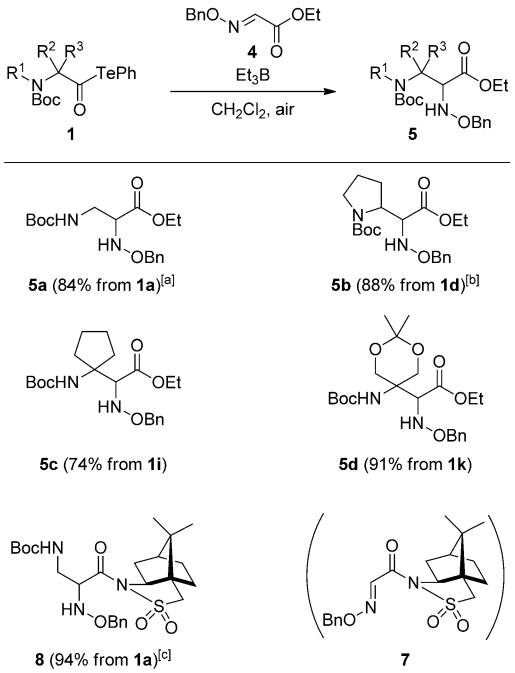
The synthetic generality of the decarbonylative C–C bond formation was further corroborated by applying **1b–k** as the radical donors and methyl acrylate **2a** as a radical acceptor (Scheme 3). The corresponding primary α-amino carbon radicals from glutamic acid derived **1b** and dihydroxyphenylalanine-derived **1c** were efficiently formed in the presence of



Scheme 3. Synthesis of γ-amino acid derivatives from **1b–k** and **2a**. Conditions: **1** (1 equiv), **2a** (2 equiv), Et_3B (3 equiv), $(Me_3Si)_3SiH$ (3 equiv), CH_2Cl_2 (0.02 M), air, RT. [a] racemate. [b] 15:1 d.r.

Et_3B, $(Me_3Si)_3SiH$, and air, leading to **3b** and **3c**, respectively, after their addition to **2a**. Under the same conditions, proline derivatives **1d** and **1e** and pipecolinic acid derivative **1f** were converted into the adducts **3d**, **3e**, and **3f**, respectively, through the intermediacy of the secondary carbon radicals. In the case of **1e**, the preexisting α-oriented *tert*-butyldimethylsilyloxy group induced diastereoselectivity to provide **3e** as the major isomer (15:1 d.r.). Furthermore, the reactions of α,α-disubstituted aminoacyl tellurides **1g–k** resulted in **3g–k** by addition of the tertiary carbon radicals, and thus enabled the formation of tetrasubstituted carbon atoms in an intermolecular fashion. It is well-established that the decarbonylation rates of acyl radicals to form primary, secondary, and tertiary radicals differ by several orders of magnitude.[13] The decarbonylation of substrates **1a–k** was shown to be consistently faster than the intermolecular reaction of the acyl radicals, supporting the potent accelerating effect of the α-amino groups towards CO ejection. Taken together, the results in Table 1 and Scheme 3 confirmed that the present mild procedure is highly general for synthesizing primary, secondary, and tertiary amine analogues of GABA in the presence of a variety of polar functional groups.

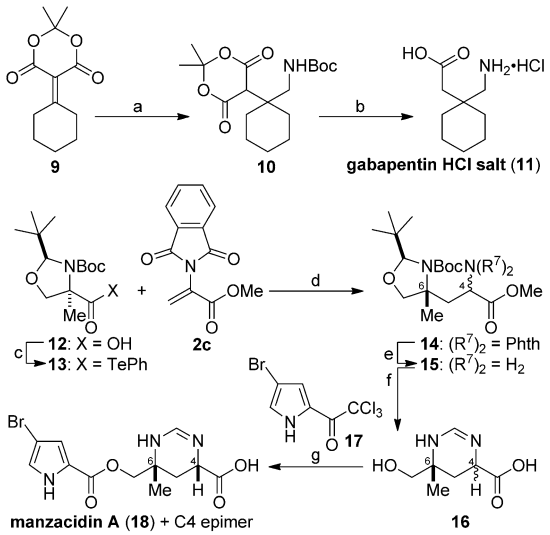
Not only γ-amino acid derivatives, but also α,β-diamino acid derivatives, which are key structural fragments of many biologically active compounds,[19] were prepared by using **4** as an alternative radical acceptor (Scheme 4). The α-amino carbon radical that was generated from **1a**, Et_3B (3 equiv), and air underwent 1,2-addition to the C=N bond of *O*-benzyl-protected ethyl glyoxylate oxime **4** (2 equiv), affording **5a** at ambient temperature.[20] Addition of a hydrogen source was not required in this reaction, suggesting that Et_3B functions as



Scheme 4. Synthesis of α,β-diamino acid derivatives. Conditions: **1** (1 equiv), **4** (2 equiv), Et_3B (3 equiv), CH_2Cl_2 (0.02 M), air, RT. [a] The formation of PhTeEt was observed. [b] 1:1 d.r. [c] **7** was used as a radical acceptor; 3.3:1 d.r.

both the radical initiating and terminating reagent. As proposed in Scheme 1, whereas hydrogen transfer from $(Me_3Si)_3SiH$ is necessary for the formation of **3** from α-carbonyl radical **C**, the aminyl radical is likely to be directly trapped by Et_3B with ejection of an ethyl radical,[16] and protonation of the resulting boron amide **D** by H_2O leads to **5**. This operationally simpler procedure was shown to be effective for the synthesis of **5b–d** from **1b–d**. Intermolecular formation of the sterically congested bonds between the nitrogen-substituted carbon atom and a tri- (**5b**) or tetrasubstituted carbon atom (**5c** and **5d**) showed the power of the present reaction in fragment assembly. Furthermore, the application of Oppolzer's camphorsultam derivative **7**[21] enabled the stereoselective addition of the glycyl radical, resulting in the formation of **8** in 3.3:1 d.r.

The applicability of the new radical coupling method was further demonstrated by the syntheses of the pharmaceutical agent gabapentin and the natural product manzacidin A, both of which possess γ-amino acid substructures (Scheme 5). First, gabapentin, which has been widely used as a therapeutic



Scheme 5. Synthesis of gabapentin and total synthesis of (−)-manzacidin A. Reagents and conditions: a) **1a** (1 equiv), **9** (1.1 equiv), Et_3B (3 equiv), CH_2Cl_2 (0.02 M), air, RT; b) aqueous HCl (6 M), reflux, 52% (2 steps); c) isobutyl chloroformate, *N*-methylmorpholine, THF, 0°C; $(PhTe)_2$, $NaBH_4$, THF, MeOH, 0°C, 79%; d) **13** (1.1 equiv), **2c** (1 equiv), Et_3B (3 equiv), $(Me_3Si)_3SiH$ (3 equiv), $(CH_2Cl)_2$ (0.1 M), air, 50°C, 83% (1:1 d.r. at C4); e) $NH_2NH_2{\cdot}H_2O$, MeOH, reflux; f) CF_3CO_2H, $CH(OMe)_3$, RT; aqueous HCl (6 M), reflux; g) NaH, **17**, DMF, RT, 33% (over 3 steps, 1:1 d.r. at C4).

agent for epilepsy and neuropathic pain,[22] was synthesized in two steps. When glycine derivative **1a** was treated with Et_3B under air in the presence of **9** (1.1 equiv), adduct **10** was obtained through an efficient intermolecular coupling that installed the quaternary center.[23] Treatment of **10** with aqueous HCl (6 M) at reflux in turn induced simultaneous removal of the Boc and acetonide groups and, after decarboxylation, gave rise to gabapentin as its HCl salt (**11**).

Finally, an expeditious total synthesis of the natural bromopyrrole alkaloid (−)-manzacidin A (**18**) was accom-

plished (Scheme 5).[24,25] We specifically designed the enantiopure oxazolidine-acyl telluride **13** as the coupling partner of acrylate **2c** in this synthesis. By employing the conditions described in Scheme 2, the known carboxylic acid **12**[26] was first transformed into **13**. Then, **13** (1.1 equiv) was subjected to the radical coupling conditions with **2c** at 50 °C. Although the stereochemical information at the C6 position of **13** was lost upon radical generation, the remaining aminal stereocenter, with the β-oriented *t*Bu group, only permitted approach of **2c** at the α-face, resulting in the construction of **14** with the desired C6 stereochemistry in 83% yield (1:1 d.r. at C4).[27] Having realized the key coupling reaction, the *N*-phthaloyl group of **14** was removed using hydrazine to provide amine **15**. When the amine was subjected to CF_3CO_2H and $CH(OMe)_3$, removal of the Boc group and formation of the cyclic formadine took place. The crude mixture was next treated with aqueous HCl (6 M) to induce hydrolysis of the methyl ester and removal of the pivalaldehyde N,O-acetal, leading to tetrahydropyrimidine **16**. Lastly, the 4-bromopyrrole ester was constructed from **16** and **17** using NaH, delivering pure (−)-manzacidin A (**18**) and its C4 epimer after HPLC purification. The physical data of synthetic **18** (^{1}H and ^{13}C NMR, IR, and $[\alpha]_D$) are identical to those of **18** from the natural source.[24,25]

In summary, we have developed a new general radical-based method for the single-step construction of various γ-amino and α,β-diamino acids from α-aminoacyl tellurides. Primary, secondary, and tertiary α-amino carbon radicals were smoothly generated through facile decarbonylation by treatment with Et_3B/O_2 or $Et_3B/(Me_3Si)_3SiH/O_2$ at ambient temperature. The advantageous features of this procedure are operational simplicity, mild reaction conditions, high compatibility with diverse polar functional groups, and efficient intermolecular formation of hindered bonds. The synthetic robustness was further exemplified by the efficient assembly of gabapentin and (−)-manzacidin A from simple fragments. Consequently, this decarbonylative radical coupling will serve as a novel and valuable strategy for streamlining convergent syntheses of architecturally complex alkaloids, natural and artificial amino acids/peptides, and pharmaceuticals.

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