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Synthesis of Heterocycles via Radical Carbonylation

Ilhyong Ryu and Takahide Fukuyama

Abstract Alkyl, aryl, and alkenyl radicals react with CO to form the corresponding acyl radicals, which serve as key intermediates for the synthesis of a wide variety of carbonyl compounds. This chapter focuses on the applications of radical carbonylation for the synthesis of heterocyclic compounds. Radical carbonylation process is reliable for alkyl substrates, since alkyl radicals are sufficiently stable to isomerization unlike rather instable alkyl Pd species. Acyl radicals, key intermediates in the radical carbonylation, have both nucleophilic and electrophilic characters, depending on the attacking reagents and the electrophilic nature is particularly useful to achieve synthesis of nitrogen-containing heterocycles by the reactions with imines, amines, azides, and amidines.

Keywords Acyl radical · Atom transfer carbonylation · Intramolecular homolytic substitution · Radical cyclization · α-Ketenyl radical

Contents

Carbon monoxide is a potentially abundant feedstock, which is produced from naphtha and coal as the resources in industry, and has an important role in C1 chemistry. A wide variety of transition metal-catalyzed carbonylation reactions have been developed to date [1–3], and some of which have already found industrial applications. Spending a long period of hibernation, radical carbonylations had

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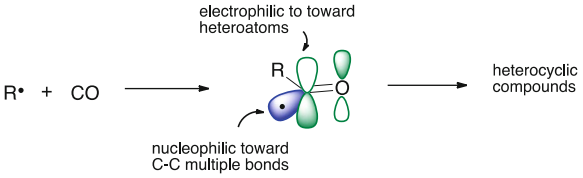
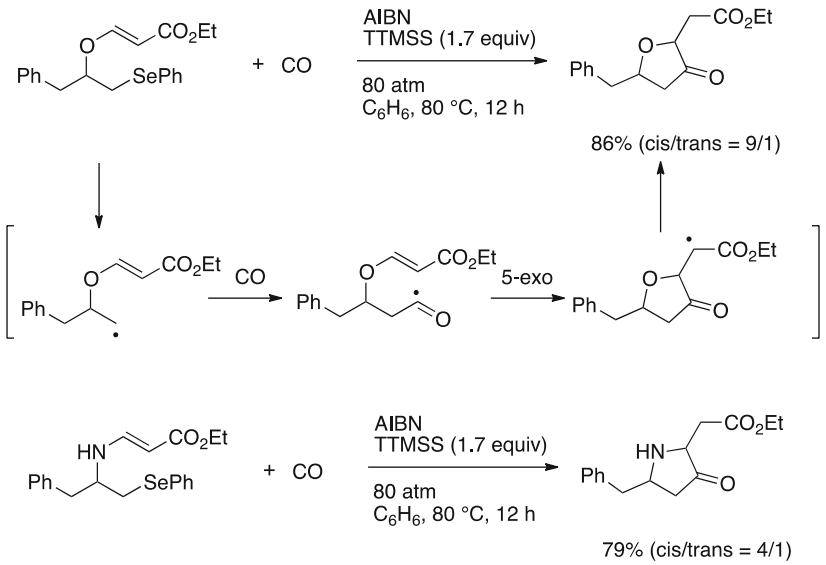
restarted in the 1990s, having the opportunity of the discovery of the first efficient radical carbonylation leading to aldehydes [4]. Nowadays radical carbonylation chemistry has been recognized as a promising repertoire in carbonylation chemistry. (For reviews on radical carbonylations, see [5–9]). One important issue in radical carbonylation distinguished from transition metal-catalyzed carbonylation is what the process is reliable for *alkyl* substrates, since the resulting alkyl radical species do not isomerize unlike the case of somewhat labile metal alkyl species. Key species arising from carbonylation of radicals are acyl radicals. Acyl radicals have nucleophilic nature toward carbon–carbon multiple bonds and also exhibit electrophilic nature toward heteroatoms such as nitrogen and oxygen (Scheme 1). The nucleophilic nature is considered to be due to the interaction between acyl radical SOMO and olefin LUMO and the electrophilic nature to be the interaction between LUMO of acyl radical carbonyl and lone pair of heteroatoms. In designing the synthesis of heterocycles by acyl radical cyclization, these double-face characters can be a direction to be considered. This chapter focuses on the synthesis of heterocyclic compounds, in which radical carbonylation serves as the basis.

Acyl radical cyclization onto C–C multiple bonds provides cyclic ketones [10]. If the alkenyl tether has a heteroatom, the corresponding heterocyclic compounds can be obtained. 5-Exo acyl radical cyclizations can be applied to the formation of five-membered ring heterocycles by way of radical carbonylation. Engman and coworkers reported synthesis of 2,5-disubstituted tetrahydrofuran-3-ones by radical carbonylation and the 5-exo subsequent cyclization of the resultant acyl radicals (Scheme 2) [11, 12]. The reaction of vinyloxy ethyl selenides with CO in the presence of AIBN (2,2′-azobisisobutyronitrile) as a radical initiator and TTMSS (tris(trimethylsilyl)silane) as a radical mediator gives tetrahydrofuran-3-ones in good yields. Tributylgermanium hydride can also be employed as a radical mediator. The same strategy is applicable to the synthesis of pyrrolidin-3-ones starting from vinylated aminoalkyl phenyl selenides [12]

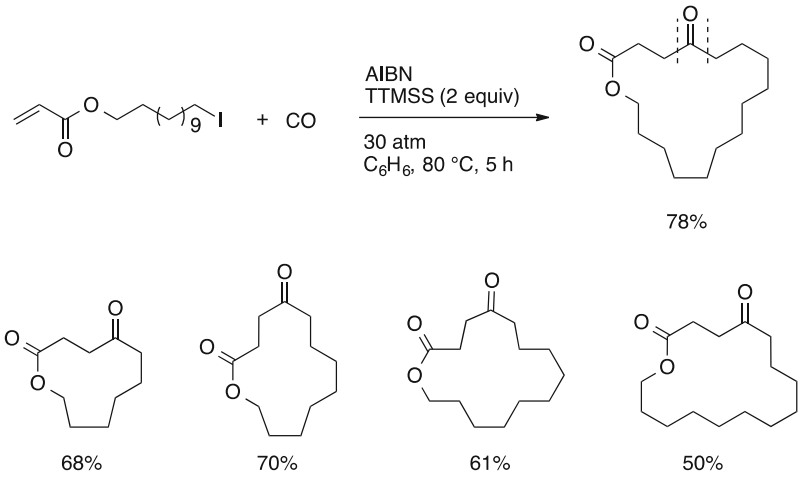
Three-component coupling reaction comprised of alkyl iodides, carbon monoxide, and acrylic acid esters under radical conditions provides a useful means for the synthesis of 4-keto esters [13, 14], and the scheme is applied to synthesis of macrocyclic keto esters [15, 16]. The reaction of ω-iodoalkyl acrylates with CO in the presence of AIBN as a radical initiator and TTMSS as a radical mediator gives 10–17-membered keto lactones in good yields (Scheme 3). Highly diluted conditions are employed to encourage carbonylative macrocyclization over premature quenching of the alkyl radicals by TTMSS. Later on Kishimoto and Ikariya



Scheme 1 Structure and natures of acyl radicals



Scheme 2 Synthesis of tetrahydrofran-3-ones and pyrolidin-3-ones via acyl radical cyclization onto a C=C bond



Scheme 3 Synthesis of macrocyclic keto esters via acyl radical cyclization onto a C=C bond

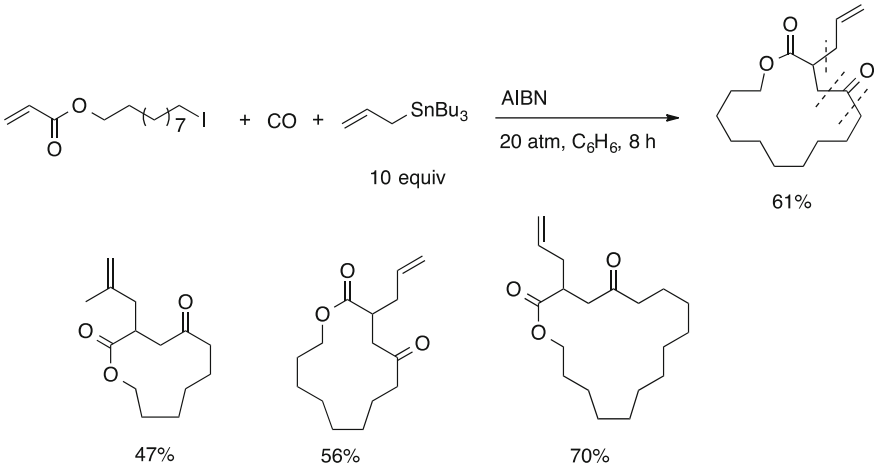
reported the TTMSS-mediated macrocyclic keto ester synthesis in supercritical carbon dioxide worked quite well. [17]

Allyltributyltin acts as an excellent unimolecular chain transfer reagent, which serves as a radical acceptor and at the same time a source of tributyltin radical [18]. The combination of the reagent with radical carbonylation is particularly useful to obtain allyl-functionalized products [19, 20]. The reaction of

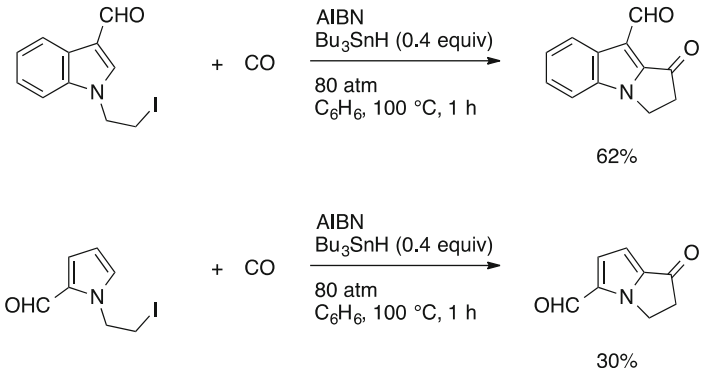
ω-iodoalkyl acrylates with CO mediated by allyltributyltin or methallyltributyltin affords allyl-substituted macrocyclic keto esters in good yields (Scheme 4) [16].

Miranda and coworkers applied tin hydride-mediated radical carbonylation/cyclization sequence [10] to the synthesis of cyclopentanones fused by nitrogen heterocycles, such as indole and pyrrole (Scheme 5) [21]. In the reaction of *N*-iodoethyl indole with CO in the presence of Bu_3SnH as a radical mediator, acyl radical undergoes intramolecular addition to C-2 position of the indole ring to give the envisaged tricyclic compound via aromatization by an in situ oxidation process.

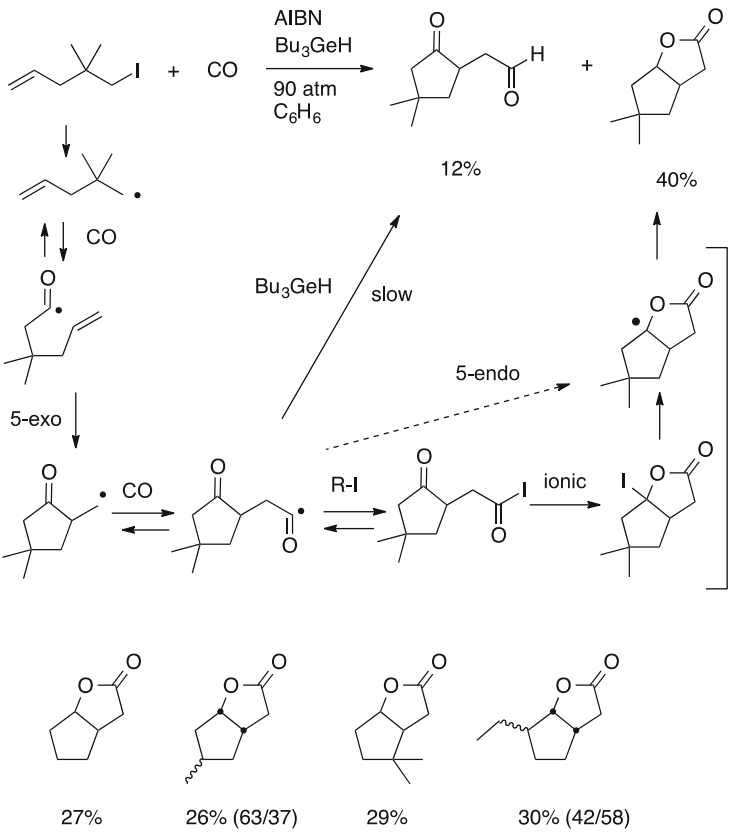
In the study aiming at cyclizative double carbonylation of 4-pentenyl iodides [22], unusual bicyclic lactone ring formation is observed when slow radical



Scheme 4 Synthesis of allyl-functionalized macrocyclic keto esters via acyl radical cyclization onto a C=C bond



Scheme 5 Synthesis of indole- and pyrrole-fused cyclopentanones via acyl radical cyclization onto a C=C Bond

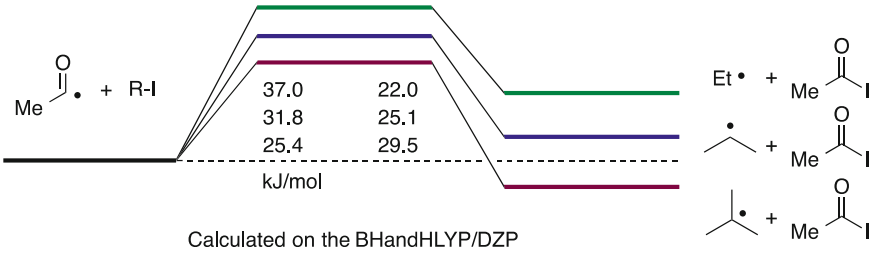


Scheme 6 Bicyclic lactone ring formation via Bu_3GeH-mediated cyclizative double carbonylation of 4-pentenyl iodides

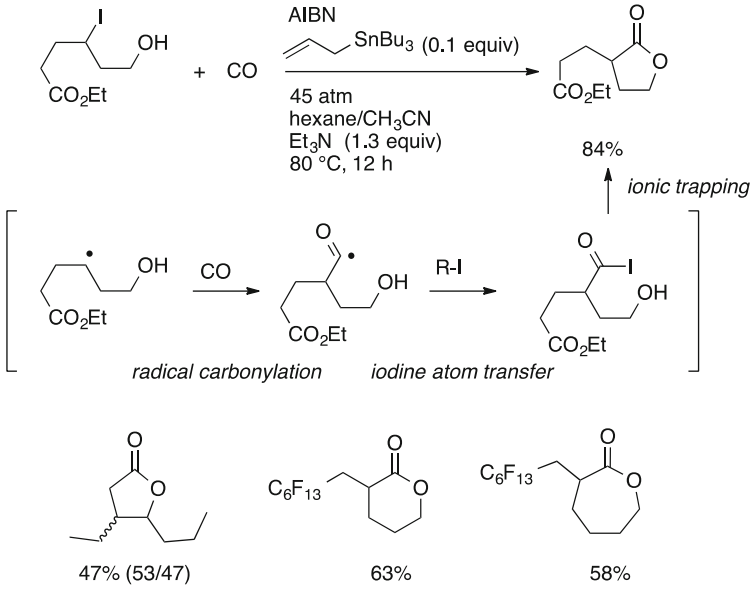
mediator such as Bu_3GeH is employed (Scheme 6), whereas the use of tin hydride only gives the expected double Carbonylation products, 4-keto aldehydes. The lactone ring formation is not because of 5-endo radical cyclization of acyl radical onto carbonyl oxygen but because of iodine atom transfer reaction to give acyl iodide, which is allowed by slow hydrogen transfer from Bu_3GeH. Spontaneous ionic cyclization of the resulting acyl iodide then takes place, and ultimately the cyclized lactone iodide is reduced by Bu_3GeH/AIBN.

Iodine atom transfer to acyl radicals is not necessarily a smooth process except for the case which gives stable alkyl radicals such as *tert*-butyl radical (Scheme 7) [23]. However, even sluggish iodine atom transfer to acyl radicals, the subsequent ionic capture of the resulting acyl iodides by electrophiles, can shift the equilibrium to forward, which makes atom transfer carbonylation possible to carry out even for primary and secondary alkyl iodides [24, 25].

Indeed, coupled with an appropriate radical initiation process (photo-irradiation or thermal initiation with AIBN/TTMSS or allyltin), alkyl iodides undergo atom



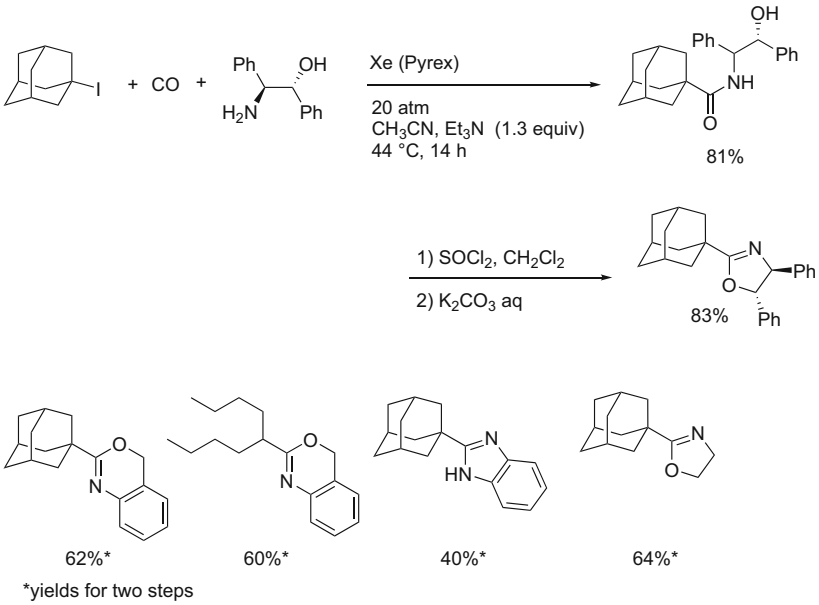
Scheme 7 Energy diagram on iodine atom transfer from iodoalkanes to acyl radicals



Scheme 8 Lactone synthesis via iodine atom transfer carbonylation of iodoalcohols

transfer carbonylation in the presence of alcohols and a base to give good yields of carboxylic acid esters [24, 25]. This reaction can be successfully applied to the synthesis of lactones [26]. The reaction of ω-hydroxyalkyl iodides with CO in the presence of a catalytic amount of AIBN and allyltributyltin and Et_3N takes place smoothly to give five- to seven-membered ring lactones in moderate to good yields (Scheme 8).

Atom transfer carbonylation of alkyl iodides with diamines and ω-hydroxylamines leads to the formation of functionalized amides that could easily cyclize to afford nitrogen-containing heterocycles via the subsequent dehydrative cyclization reaction (Scheme 9). According to the two-step process, nitrogen-containing heterocycles, such as benzoxazines, benzimidazoles, and oxazolines, are prepared in good yields [27].

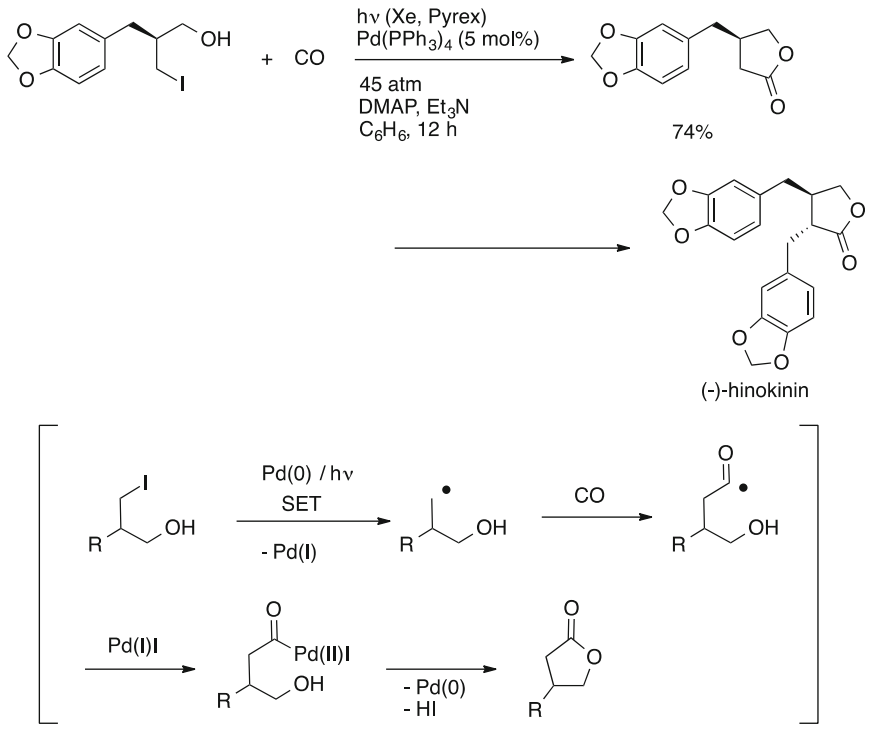


Scheme 9 Synthesis of heterocyclic compounds via atom transfer carbonylation/dehydrative cyclization sequence

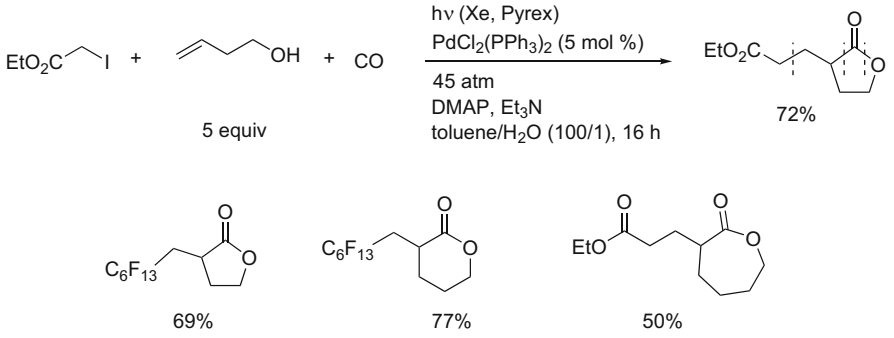
The addition of a catalytic amount of palladium complex turned out to accelerate the atom transfer carbonylation under irradiation conditions (for a review, see [28]). Since atom transfer carbonylation of primary alkyl iodides is quite sluggish, the employment of Pd/light system is especially useful. The Pd/light-induced atom transfer reaction is applied to lactone synthesis [29]. For example, the synthesis of a precursor of (−)-hinokinin is achieved based on the species hybrid concept (Scheme 10). Under photo-irradiation, single-electron transfer from Pd(0) to alkyl iodides takes place to lead to alkyl radical and Pd(I)I species, the latter of which is regarded as persistent radical. The alkyl radical adds to CO to form an acyl radical, which couples with PdI radical to give acylpalladium species, and the intramolecular alcoholysis gives the desired lactone and regenerates Pd(0) species.

The Pd/light-induced atom transfer reaction is successfully applied to three-component type lactone synthesis comprising RI, alkenyl alcohols, and CO. For example, the reaction α-iodo ethyl acetate with 3-butenol and CO proceeds well to give α-substituted lactone in a 72% yield (Scheme 11) [30, 31]. Similar reaction using perfluorohexyl iodide also works well. A series of five- to seven-membered lactones are obtained according to this procedure.

C–H functionalization is among the most important topics in organic synthesis. Unique synthesis of six-membered lactones is attained based on direct carbonylation at δ-C–H bonds of saturated alcohols, in which Barton-type 1,5-radical translocation reaction from O to δ-C operates (Scheme 12) [32, 33]. Thus, using a combination of

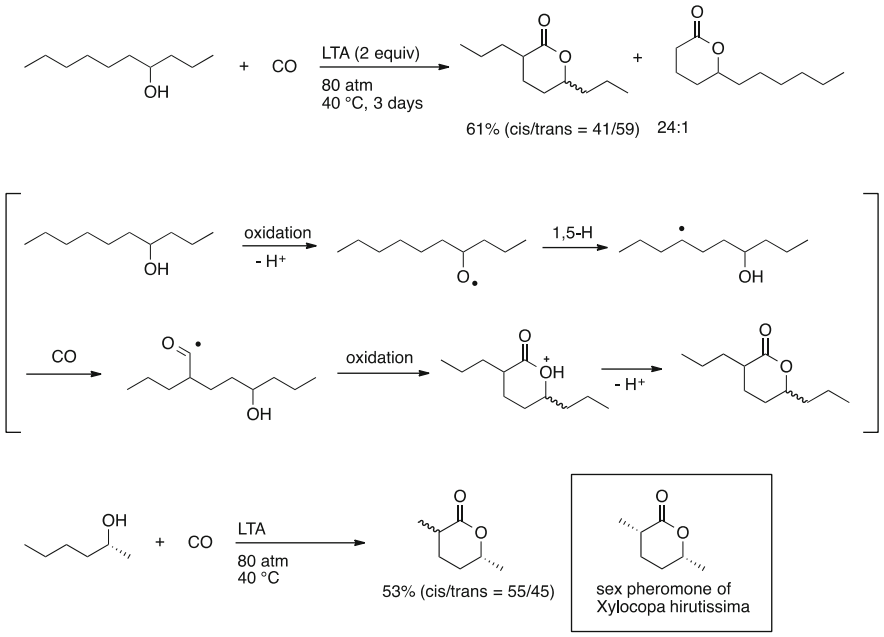


Scheme 10 Formal synthesis of (−)-hinokinin via Pd/light induced atom transfer carbonylation



Scheme 11 Three-component lactone synthesis via Pd/light induced atom transfer carbonylation

lead tetraacetate (LTA) as one-electron oxidant and CO, one-electron oxidation of saturated alcohols takes place to generate oxygen-centered radicals, which undergo 1,5-H transfer to create δ-alkyl radicals. Radical carbonylation followed by the oxidation and the deprotonative cyclization affords δ-lactones in good yields. In the



Scheme 12 δ-Lactone synthesis via oxidative C–H carbonylation of saturated alcohols

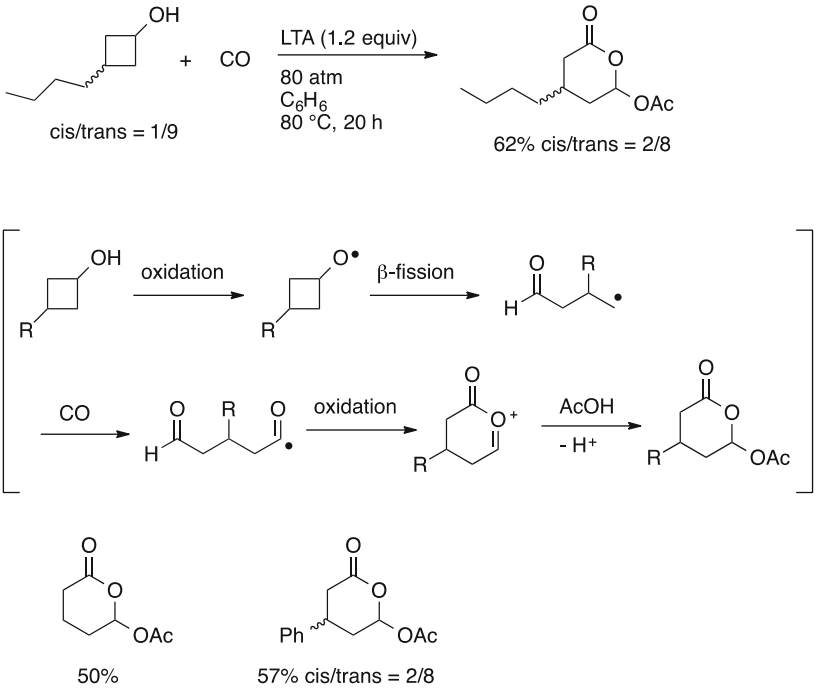
first example given in Scheme 12, high regioselectivity in favor of methylene group is observed, and this is a reflection of the weaker bond strength of methylene C–H compared to methyl C–H (95 vs. 98 kcal/mol). The oxidative C–H carbonylation is successfully applied to the one-step synthesis of carpenter bee sex pheromone starting from chiral 2-hexanol.

It is also possible to prepare six-membered ring lactones using carbonylative oxidative ring cleavage of cyclobutanols (Scheme 13) [34].

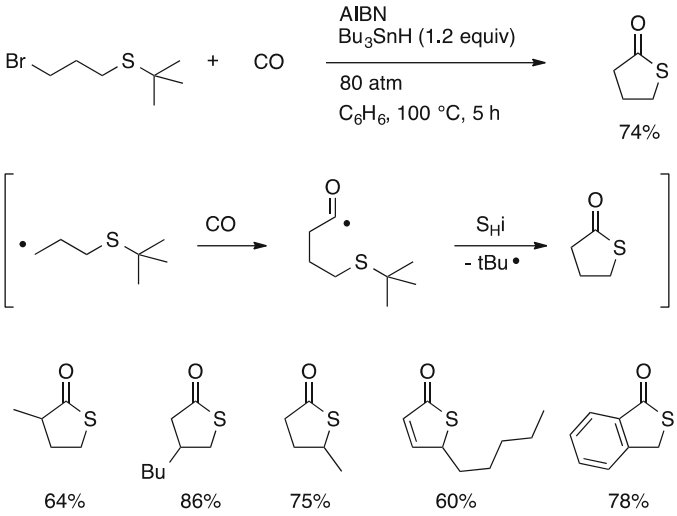
Radical substitution at heteroatoms is successfully combined with radical carbonylation. Thiolactones can be obtained by intramolecular homolytic substitution of acyl radical at sulfur [35]. For example, the reaction of *tert*-butyl bromopropyl thioether with CO in the presence of tributyltin hydride gives γ-thiolactone in a 74% yield (Scheme 14). α,β-Unsaturated thiolactone and benzothiolactone are also obtained from the corresponding vinyl iodide and aryl iodide, respectively.

The reaction of 3-[(trimethylstannyl)diphenylsilyl]propyl bromide with CO in the presence of TTMSS gives silacyclopentanone via intramolecular homolytic substitution of acyl radical at Si (Scheme 15) [36]. In this reaction, unusual 1,4-Sn shift from Si to C takes place and lowers the yield of silacyclopentanone.

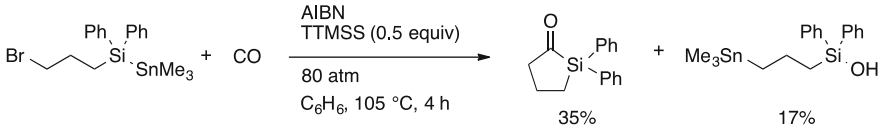
Combination of radical carbonylation with the subsequent cyclization onto N–C double bonds gives a promising tool for the synthesis of a variety of lactams. When the reaction of bromopropylimines under pressurized CO in the presence of tributyltin hydride is carried out, five-membered lactams are obtained in good yields



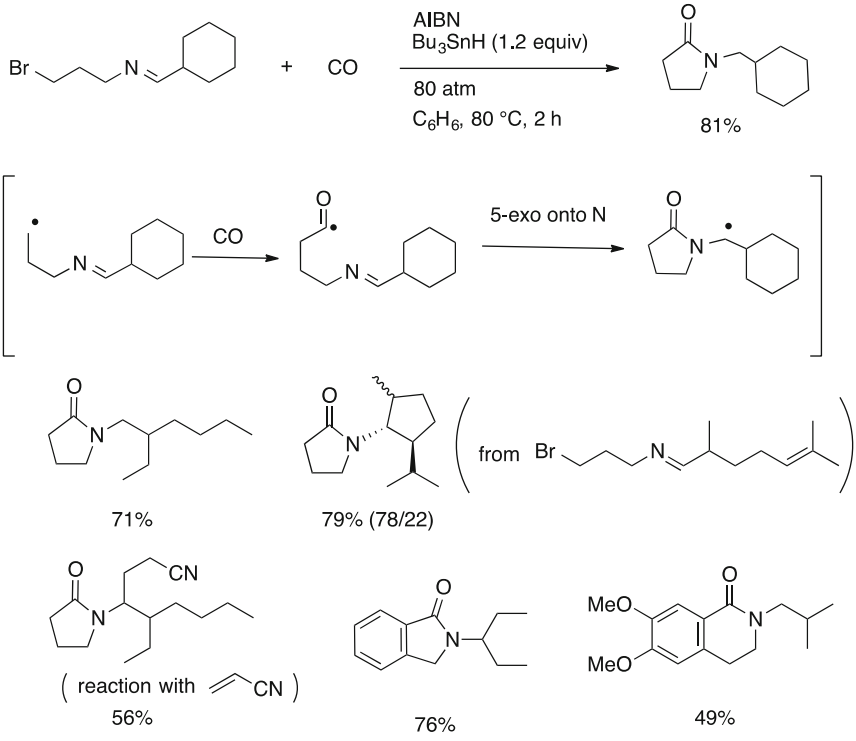
Scheme 13 δ-Lactone synthesis via carbonylative oxidative ring cleavage of cyclobutanols



Scheme 14 Synthesis of thiolactones via intramolecular homolytic substitution of acyl radical at sulfur



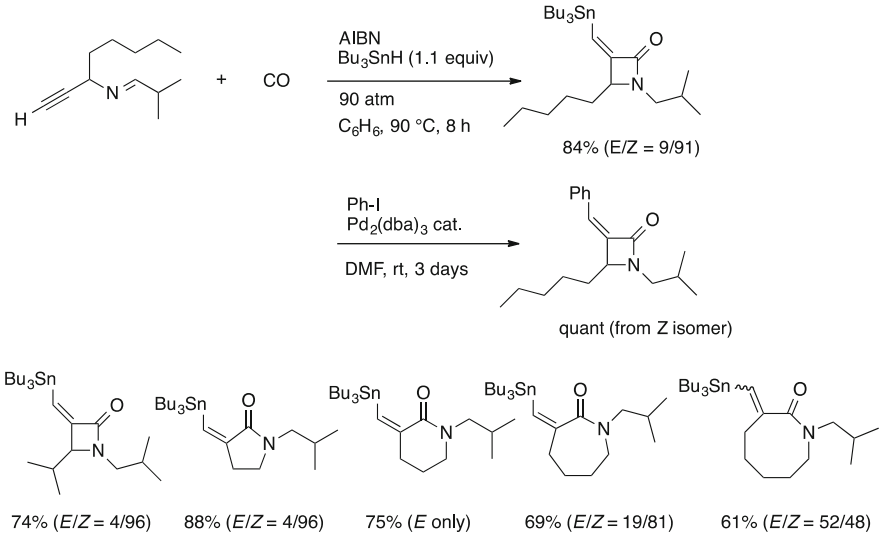
Scheme 15 Synthesis of a silacyclopentanone via intramolecular homolytic substitution of acyl radical at silicon



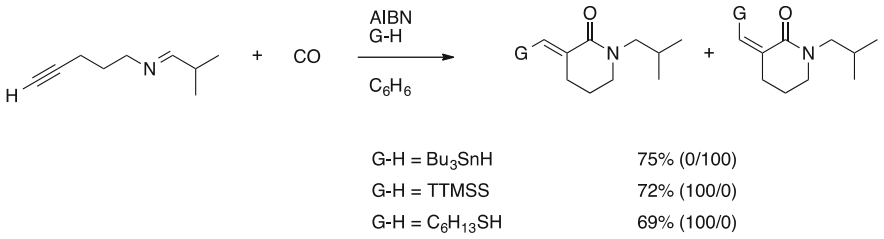
Scheme 16 Lactam synthesis via acyl radical cyclization of onto imine nitrogen

(Scheme 16) [37]. Cyclization of acyl radical takes place exclusively at imine nitrogen. The perfect selectivity for the 5-exo cyclization of acyl radical onto imine nitrogen is rationalized by dual orbital effect between nitrogen lone pair and acyl radical π* and acyl radical SOMO and imine π*, which is suggested by DFT calculation [38–41]. Benzolactams are also obtained from the corresponding aryl bromides.

Stannylcarbonylation of aza-enynes using Bu_3SnH/CO in the presence of AIBN gives α-stannylmethylene lactams in good yields (Scheme 17) [42]. The obtained stannylmethylene lactam is subjected to Pd-catalyzed Stille coupling reaction with iodobenzene to give phenylmethylene lactam. The scope of the reaction is wide,



Scheme 17 Lactam synthesis via stannylcarbonylation of aza-enynes



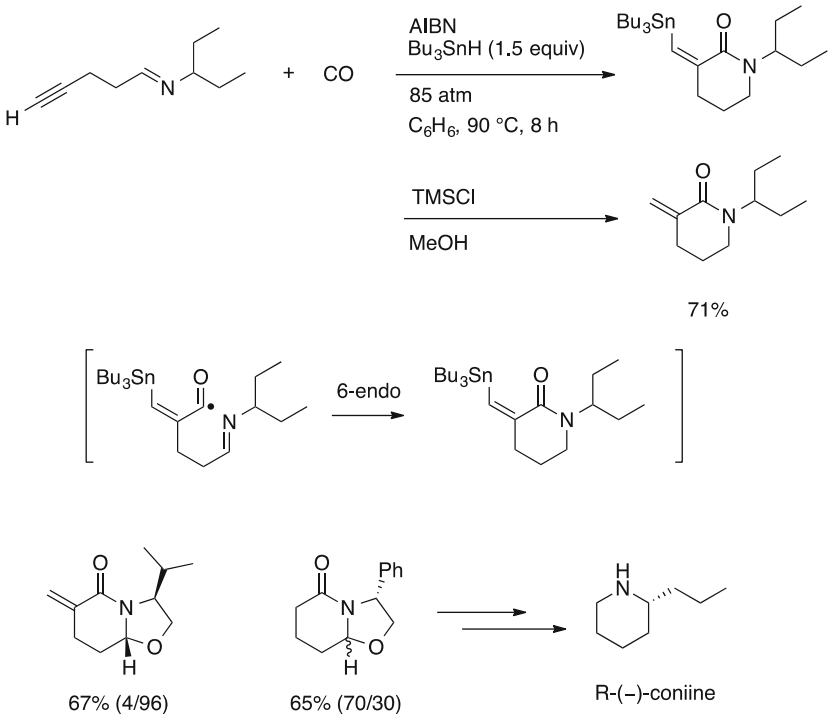
Scheme 18 Comparison of Bu_3SnH, TTMSS, and hexanethiol-mediated stannylcarbonylation of an aza-enyne

covering four- to eight-membered lactams. The subsequent treatment of the products with TMSCl/MeOH gives destannylated α-methylene lactams quantitatively.

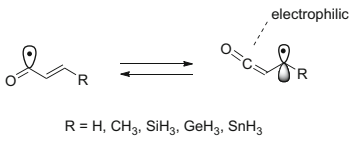
TTMSS and 1-hexanethiol can be used for the similar lactam synthesis by carbonylation of aza-enynes [43]. Interestingly, using these radical mediators, *E*-stereoselectivity is generally observed, while the reaction using tributyltin hydride exhibits *Z*-stereoselectivity (Scheme 18). DFT calculations suggest that coordination of carbonyl oxygen to tributylstannyl group renders the *Z*-form structure more stable.

Dual orbital effect between nitrogen and acyl radical allows for δ-lactam synthesis by selective 6-endo cyclization in preference to 5-exo cyclization onto N–C double bonds (Scheme 19) [40, 44]. N-Philic 6-endo cyclization is also attained for chiral oxazoline. The reaction is applicable to formal synthesis of (R)-(−)-coniine.

Vinyl radical carbonylation gives α,β-unsaturated acyl radicals as the first intermediate. Theoretical work suggests that α,β-unsaturated acyl radicals exist in



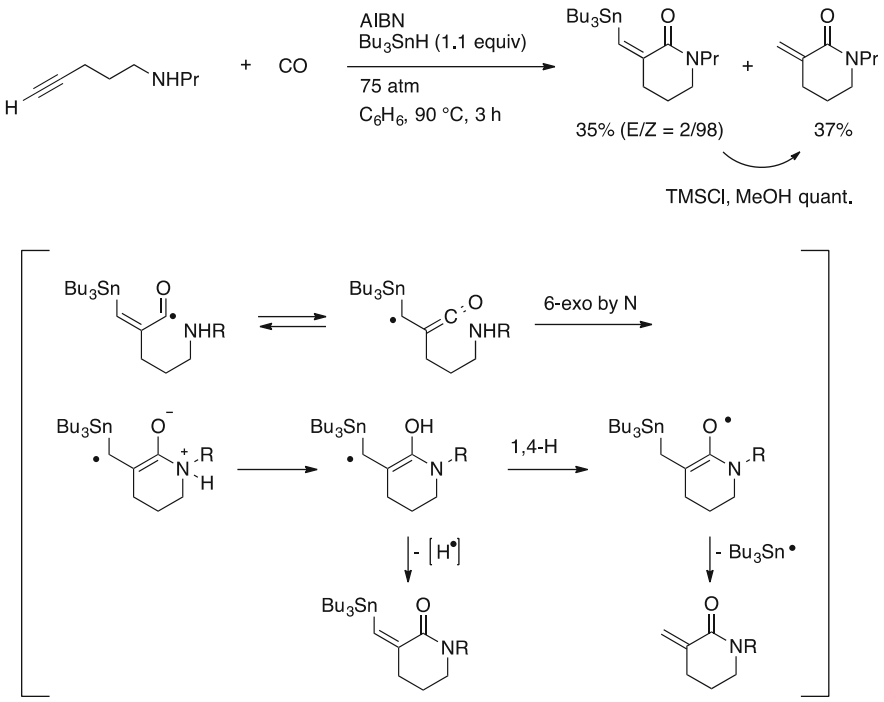
Scheme 19 Lactam synthesis via 6-endo acyl radical cyclization onto an N=C bond



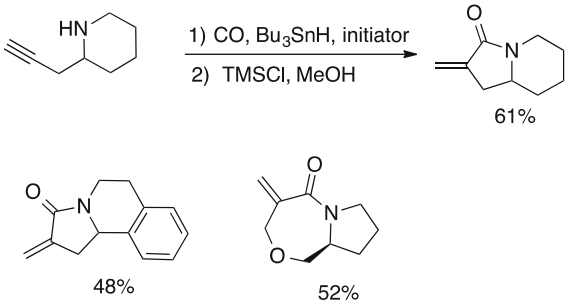
Scheme 20 Equilibrium between α,β-unsaturated acyl radicals and α-ketenyl radicals

an equilibrium with α-ketenyl radicals (Scheme 20) [45, 46]. We hypothesized that the carbonyl of α-ketenyl radicals can be electrophilic enough to react with a hydroxyl or amino group, and this serves as a resource of developing a useful method to give heterocycles.

Carbonylation of ω-alkynylamines in the presence of tributyltin hydride gives a mixture of α-stannylmethylene lactams and α-methylene lactams (Scheme 21) [47, 48]. Since the α-stannylmethylene group can be converted to α-methylene group by simple acid treatment (TMSCl/MeOH), the two-step procedure (stannylcarbonylation plus protodestannylation) provides a useful method for the synthesis of α-methylene lactams. Five- to eight-membered lactams can be synthesized by this method. In this reaction, nucleophilic addition of an amine moiety to the ketene carbonyl of α-ketenyl radical followed by proton transfer gives



Scheme 21 Synthesis of α-methylene lactams via carbonylation of ω-alkynylamines

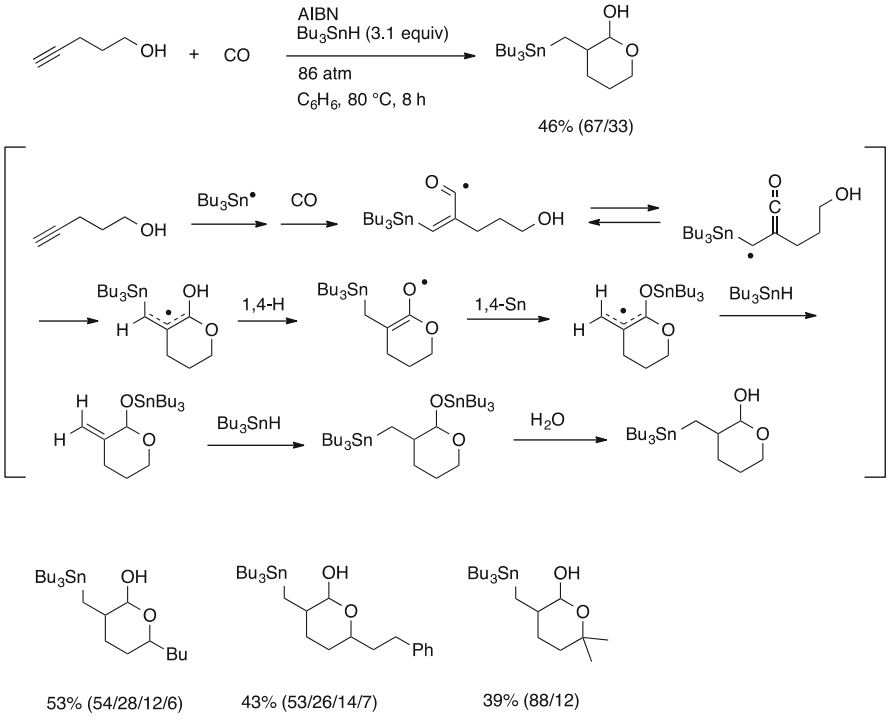


Scheme 22 Synthesis of bicyclic and tricyclic α-methylene lactams by two-step procedure

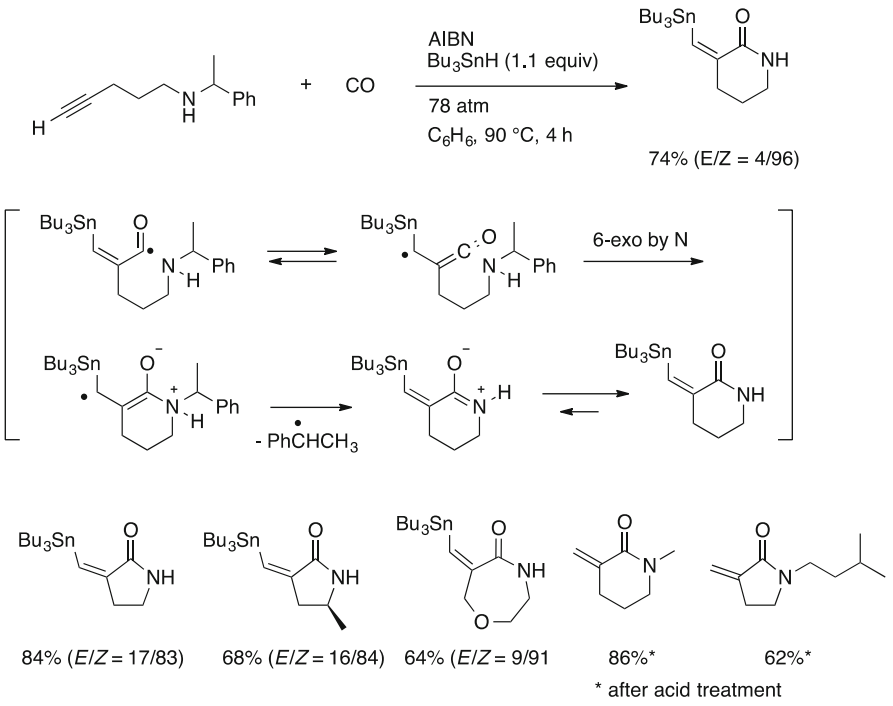
1-hydroxyallyl radical. The subsequent 1,4-H shifts leads to oxoallyl radical, which then liberates tributyltin radical to give α-methylene lactam. The DFT calculations suggest that 1,4-H shift of five- to eight-membered model lactams is highly exothermic (−71.2 to −105.7 kJ/mol) [48]. On the other hand, α-stannylmethylene lactams may be formed via oxidation from 1-hydroxyallyl radical and/or oxoallyl radical. Bicyclic and tricyclic α-methylene lactams are obtained from the corresponding alkynyl-substituted cyclic amines (Scheme 22).

Stannylcarbonylation of ω-alkynyl alcohols using tributyltin hydride and AIBN under CO pressures gives stannyl-substituted lactols (Scheme 23) [49]. The reaction pathway leading to the lactols is puzzling but a possible mechanism is illustrated in Scheme 23. Addition of tributyltin radical to alkyne terminus followed by CO trapping generates α,β-unsaturated acyl radical, which is in an equilibrium with α-ketenyl radical. Intramolecular trapping of the α-ketenyl radical by an internal hydroxy group then takes place to lead to a hydroxyallyl radical, which undergoes consecutive 1,4-hydrogen and 1,4-Sn shift to give a stannyloxy allyl radical. Hydrogen abstraction from tributyltin hydride followed by hydrostannylation gives bisstanylated lactol as a precursor for stannyl lactol.

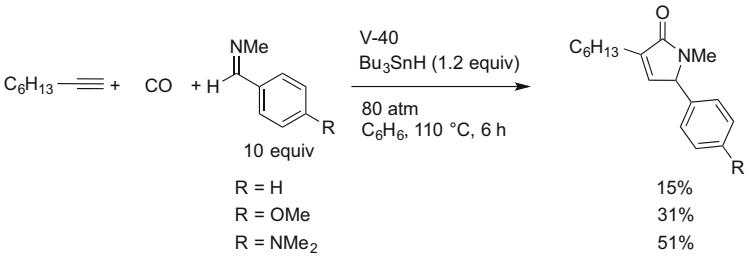
The high nitrogen philicity of acyl radicals can lead to the synthesis of lactams via intramolecular homolytic substitution reaction (S_Hi) of acyl radicals at nitrogen atom, in which phenethyl or *tert*-butyl substituent works as a radical leaving group. For example, stannylcarbonylation of an alkynyl phenethylamine followed by the elimination of a phenethyl radical takes place to give δ-lactam in good yield (Scheme 24) [48, 50]. Unlike the case of thiolactones, the S_Hi-type reaction probably proceeds in two-step mechanism comprising (i) nucleophilic trapping of the α-ketenyl radical by amine to give zwitter ionic radical intermediate, and (ii) β-fission to leave α-phenethyl radical out. DFT calculation supports this indirect S_Hi mechanism [48].



Scheme 23 Synthesis of lactols via stannylcarbonylation of ω-alkynyl alcohols



Scheme 24 Lactam synthesis via S_Hi-type reaction of acyl radical at nitrogen



Scheme 25 Synthesis of α,β-unsaturated lactams via radical-mediated [2+2+1] cycloaddition of 1-octyne, imines, and CO

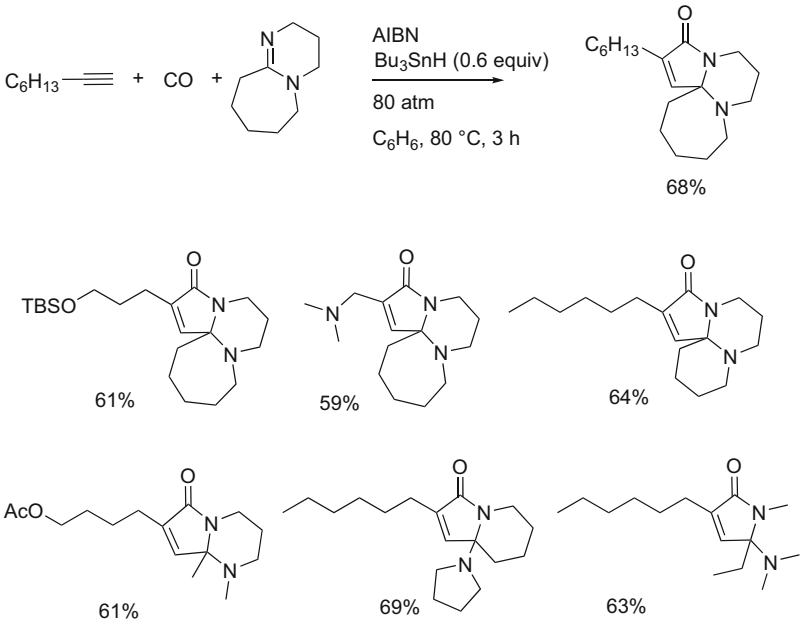
Three-component reaction of terminal alkynes, CO, and aromatic imines is achieved to give α,β-unsaturated lactams via rather unique [2 + 2 + 1] type cycloaddition reaction (Scheme 25) [51]. The reaction efficiency is affected by a substituent at *para*-position of the phenyl ring. Thus, aromatic imine having electron-donating dimethylamino substituent gives higher yield of the cycloaddition product. Interestingly, the annulation method represents a formal aza-Pauson–Khand reaction.

The [2 + 2 + 1] cycloaddition reaction of terminal alkynes, CO, and amidines, which has nitrogen atom directly at a C = N bond, proceeds smoothly to give α,β-unsaturated lactams in good yields [51]. For example, reaction of 1-octyne with CO and DBU gave tricyclic lactam in 68% yield. A variety of alkynes and amidines can be used in the radical-mediated [2 + 2 + 1] cycloaddition reaction (Scheme 26).

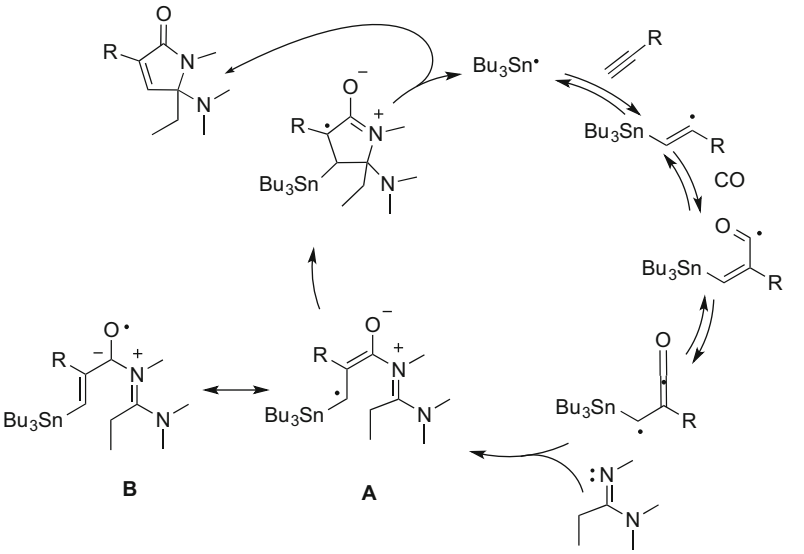
A possible mechanism for the [2 + 2 + 1] cycloaddition reaction is shown in Scheme 27. Intermolecular trapping of the α-ketenyl radical by amidine affords a highly conjugated, highly stabilized zwitter ionic radical intermediate **A**, which can be drawn in several canonical forms including **B**. Electrocyclization followed by β-fission leads to the formation of α,β-unsaturated lactam and regenerates the tributyltin radical.

4,4-Spirocyclic γ-lactams containing a quaternary carbon center can be synthesized by sequential aryl radical cyclization, radical carbonylation, and cyclization of acyl radical onto an azide group [52]. An example for the synthesis of 4,4-spirocyclic oxindole γ-lactam is shown in Scheme 28.

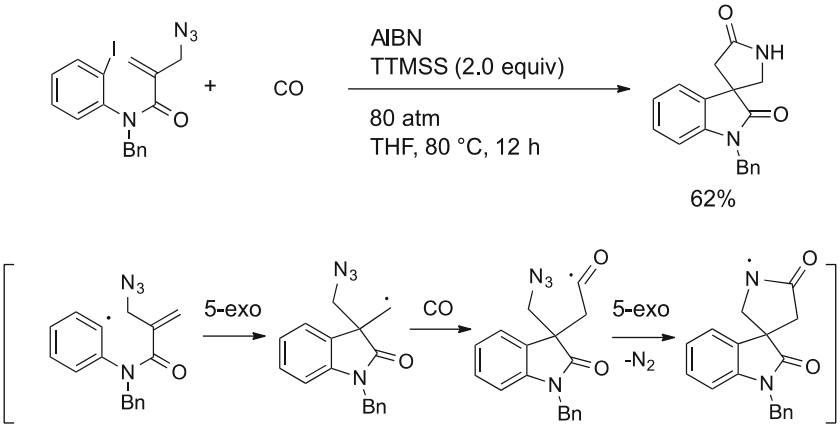
As we see in many examples illustrated in this chapter, radical carbonylation provides useful method for the synthesis of a variety of heterocyclic compounds, in which acyl radicals serve as the key species. Acyl radical cyclization onto C–C double bonds can have a heterocyclic variation when the cyclic chain has a heteroatom. Atom transfer carbonylation gives acyl iodides as the key



Scheme 26 Synthesis of α,β-unsaturated lactams via radical-mediated [2+2+1] cycloaddition of alkynes, amidines, and CO



Scheme 27 A possible mechanism for radical-mediated [2+2+1] cycloaddition reaction



Scheme 28 Synthesis of a 4,4-spirocyclic γ-lactam by cascade cyclization

intermediates, and therefore the reaction can be combined well with the subsequent ionic cyclization with an internal hydroxyl and amino group, which furnish lactones and lactams, respectively. In case of the slow iodine atom transfer reaction, Pd/light system is useful for the acceleration. Acyl radicals cyclize onto N–C double bonds selectively in N-philic manner. The carbonylative cyclization has a wide scope covering 4- to 8-exo cyclization for which dual orbital effect of acyl radicals and N–C double bonds account for the easiness. Nitrogen-philic cyclization is extended to include selective 6-endo cyclization onto C–N double bond. Carbonylation and the

subsequent intramolecular homolytic substitution of acyl radical at sulfur, silicon, and even nitrogen take place to give the corresponding thiolactone, silacyclopentanone, and lactams. Especially amino-functionalized alkynes are useful substrates for the synthesis of nitrogen-containing heterocycles, in which the alkyne portion can be converted to α-ketenyl radicals, serving as a target of nucleophilic attack of amines and amidines. Since the radical carbonylation chemistry is continuously growing, further exciting methods for the synthesis of heterocyclic compounds will be developed in the coming years.

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