

New Synthetic Reactions of Allyl Alkyl Carbonates, Allyl β -Keto Carboxylates, and Allyl Vinylic Carbonates Catalyzed by Palladium Complexes

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In 1965 we reported that (π -allyl)palladium chloride reacts with carbonucleophiles such as malonates, acetoacetates, and enamines, thereby offering a new method for carbon-carbon bond formation^{1,2} (see Scheme I). Later synthetic applications of this reaction have been explored mainly by Trost.³

Certain allylic compounds, such as allylic acetates, react with Pd(0) complexes to form (π -allyl)palladium complexes in situ; these, without being isolated, react with carbonucleophiles. On the basis of these reactions, a catalytic allylation of carbonucleophiles with allylic esters has been developed,^{4,5} and this catalytic process is now widely used for carbon-carbon bond formation in organic synthesis^{3,6} (see Scheme II). In addition to allylic esters, many other allylic compounds such as allylic ethers, phosphates, amines, nitro compounds, sulfones, and halides can also be used for catalytic allylation in the presence of bases.

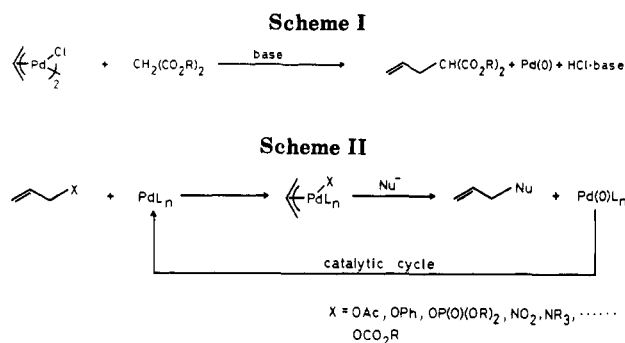
Thus far, the main synthetic application of (π -allyl)palladium chemistry has been the catalytic allylation of carbonucleophiles using allylic acetates. Recently, however, we have broadened the scope and usefulness of (π -allyl)palladium chemistry by discovering several new reactions using allyl carbonates and allyl β -keto carboxylates. We have found that allyl alkyl carbonates 1, allyl β -keto carboxylates 2, and allyl vinylic carbonates 3 are very reactive substrates and undergo a number of reactions that are difficult to achieve with allylic acetates under mild conditions. These substrates, which react with Pd(0) complexes to form (π -allyl)palladium alkoxides 5 or enolates 12a and 12b after facile decarboxylation, undergo various transformations depending on reaction conditions. The major reactions paths can be summarized in Scheme III. All these reactions proceed with facile decarboxylation. Mechanistically, they are closely related to each other and are discussed from common viewpoints in this Account.

Reactions of Allyl Alkyl Carbonates

Allylation reaction of carbonucleophiles with various allylic compounds has now seen widespread use in organic synthesis.^{3,6} Allylic acetates are mainly used in the presence of bases. Several years ago we and Trost

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found independently that diene monoepoxides are very reactive allylating agents for carbonucleophiles^{7,8} to yield a regioselective 1,4-addition. More importantly, the palladium-catalyzed reaction of diene monooxides 15 with carbonucleophiles proceeds under neutral conditions. When a (π -allyl)palladium complex is formed as an intermediate, alkoxide anion 16 is formed, which behaves as a base and picks up a proton from carbonucleophiles (Scheme IV). This is the reason why the reaction proceeds under neutral conditions.

The reaction of diene monooxides under neutral conditions led us to expect in situ formation of alkoxide anion from allyl carbonates. We found that allylic carbonates are extremely reactive and that allylation of carbonucleophiles proceeds under mild neutral conditions.^{9,10} Allyl carbamates react similarly.¹¹ These reactions can be easily understood by the mechanism

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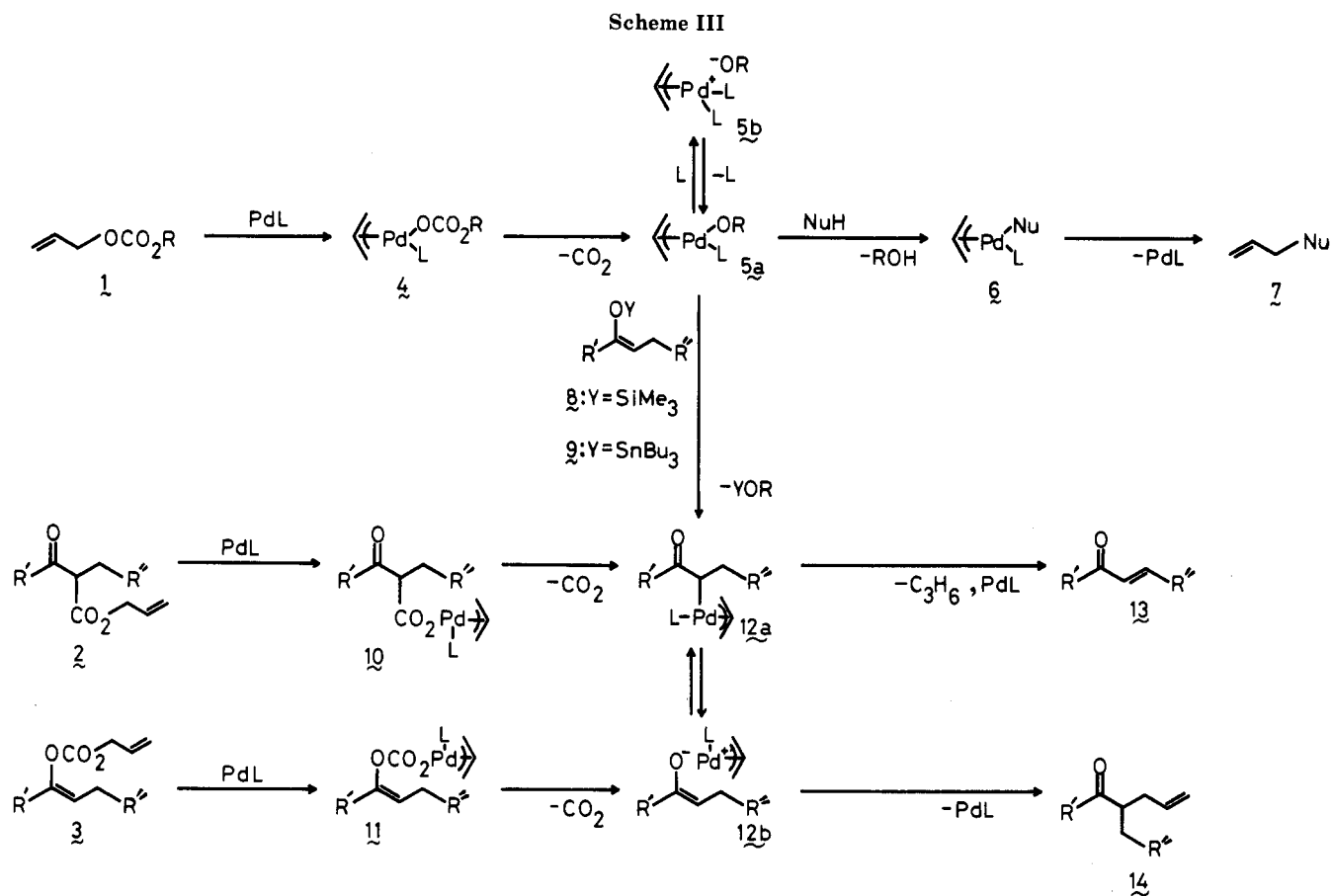
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shown in Scheme III. Oxidative addition of an allyl carbonate 1 to a Pd(0) complex forms the (π -allyl)-palladium carbonate complex 4, which undergoes smooth decarboxylation to give palladium alkoxide complex 5. This alkoxide formed in situ behaves as a base and abstracts a proton from carbonucleophiles. It is known that alkyl allyl carbonates undergo palladium-catalyzed intramolecular decarboxylation-allylation in the absence of carbonucleophiles to afford alkyl allyl ethers,¹² but allylation of carbonucleophiles with allyl carbonates takes place much faster than ether formation.

Various carbonucleophiles, such as β -keto esters, β -diketones, and malonates, are allylated with allyl carbonates by using $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3 \cdot \text{PPh}_3$ as the catalyst. A bidentate ligand, dppe (1,2-bis(diphenylphosphino)ethane), is effective for less reactive nucleophiles having one electron-withdrawing group. The bidentate ligand may activate the alkoxide anion of 5a to afford the cationic complex 5b.¹³ The higher reactivity of allyl carbonates than acetates was shown by the chemoselective reaction of 4-acetoxy-2-butenyl methyl carbonate (17) with the β -keto ester 18. The reaction takes place only with the allylic carbonate group to give 19 without attacking the allylic acetate

group under neutral conditions (Scheme V).

Although allyl carbonates 1 are reactive, they cannot allylate simple ketones directly.¹⁴ Thus, we attempted the allylation of ketone enolate equivalents with alkyl allyl carbonates. Enol silyl ethers 8 are useful ketone enolate equivalents in organic synthesis; usually their reactions are carried out in the presence of promoters such as fluoride anion or Lewis acids.¹⁵ Although a poor result was reported for the palladium-catalyzed allylation of enol silyl ethers with allylic acetates,¹⁶ we found that palladium-catalyzed reactions of enol silyl ethers 8 with allyl carbonates 1 in boiling THF gave α -allyl ketones 14 in high yield.¹⁷ Neither fluoride anion nor Lewis acids are required in this reaction, indicating that the (π -allyl)palladium alkoxide complex 5 has activity high enough for smooth transmetalation of palladium with silicon as a key step ($5 + 8 \rightarrow 12 + \text{Me}_3\text{SiOR}$; see Scheme III). (π -Allyl)palladium enolate complexes 12, formed by the transmetalation, undergo reductive elimination to afford α -allyl ketones and regenerate the Pd(0) complex, which starts the catalytic cycle again. In this reaction, the bidentate ligand, dppe, is effective rather than the monodentate ligand, PPh_3 .

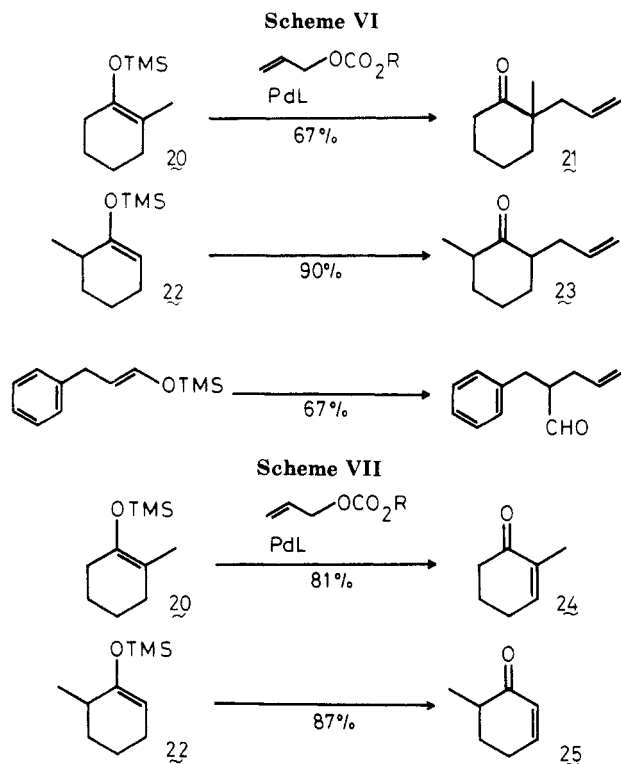
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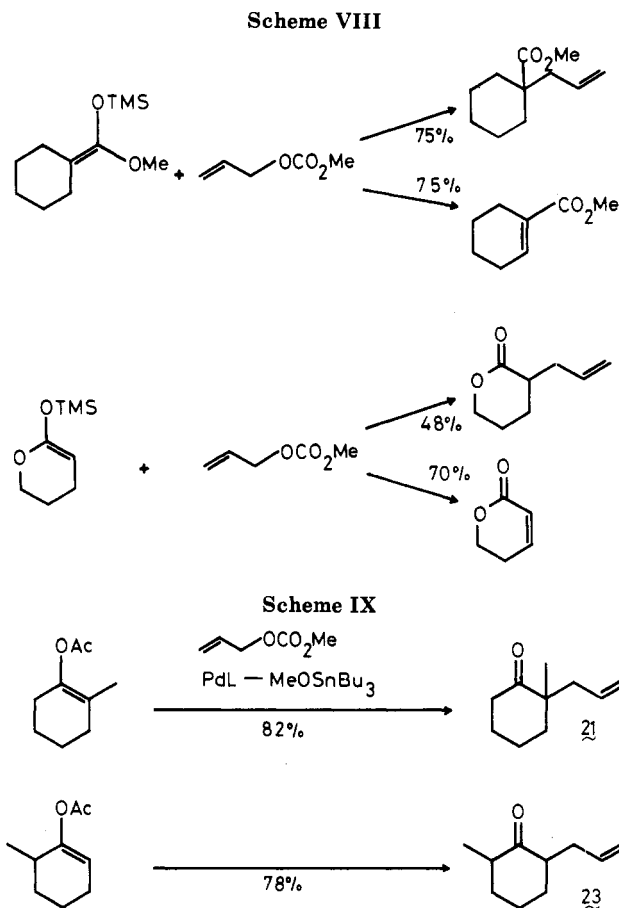
The cationic complex **5b** must be the active species for the transmetalation.

By reaction with alkyl allyl carbonates **1**, regiospecific monoallylation at the α -position of ketones and aldehydes is possible. For example, two isomeric enol silyl ethers **20** and **22**, prepared from 2-methylcyclohexanone via the thermodynamically stable and kinetically generated enolates, were allylated regiospecifically to give 2-allyl-2-methylcyclohexanone (**21**) and 2-allyl-6-methylcyclohexanone (**23**), respectively (Scheme VI). Allylation of aldehydes via enol silyl ethers is also possible.

The efficient conversion of a saturated ketone to an α,β -unsaturated ketone is an important synthetic method. This usually is done by introducing a heteroatom such as S, Se, or halogen at the α -position, followed by elimination. In the palladium-catalyzed reaction of enol silyl ethers **8** with alkyl allyl carbonates **1**, we found an interesting effect of solvents during the course of the reaction. We found that enol silyl ethers **8** can be converted in one step in good yields to α,β -unsaturated carbonyl compounds **13** by reaction with allyl carbonates in boiling CH_3CN using palladium-dppe as the catalyst, via the complex **12**.^{18,19}

Enone and enal formation proceed satisfactorily only in nitrile solvents, with CH_3CN used most conveniently. The enol silyl ethers **20** and **22** were subjected to the palladium-catalyzed dehydrogenation to give 2-methyl-2-cyclohexenone (**24**) and 6-methyl-2-cyclohexenone (**25**) regioselectively (Scheme VII).

Ito and co-workers reported a useful method for enone formation by the reaction of enol silyl ethers with palladium acetate.²⁰ In their method, Pd(II) is the



oxidant that is reduced to Pd(0), and some reoxidant such as $\text{Cu}(\text{OAc})_2$ must be used for the catalytic process. In the present method, the allyl group in the complex **12** accepts a β -hydrogen intramolecularly and generates propene, and the catalytic reaction proceeds without using any oxidant.

Ketene silyl acetals, prepared by the silylation of ester enolates, were found to react with allyl carbonates by catalysis of palladium-phosphine complexes to give α -allyl esters in high yields. The reaction can be applied also to the allylation of lactones.²¹

The palladium-catalyzed decarboxylation-dehydrogenation of ketene silyl acetals derived from saturated esters and lactones can be carried out satisfactorily in boiling CH_3CN with $\text{Pd}(\text{OAc})_2$, without using a phosphine ligand.²¹ In the presence of a phosphine ligand, the allylation reaction proceeds to a considerable extent (see Scheme VIII).

Enol acetates **26** are stable enolate equivalents that are easily prepared from ketones and that can be allylated with allyl methyl carbonates by using palladium-phosphine and tributyltin methoxide as a bimetallic catalyst to give α -allyl ketones in high yields.²² For this reaction, dppe is the most suitable ligand. The allylation is regiospecific, as shown in Scheme IX.

When the reaction is carried out in CH_3CN , enol acetates are converted to enones selectively.^{19,24} From

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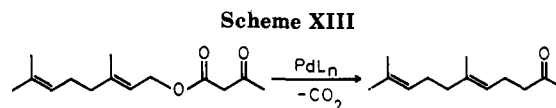
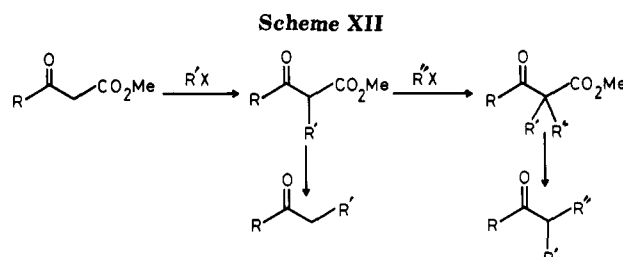
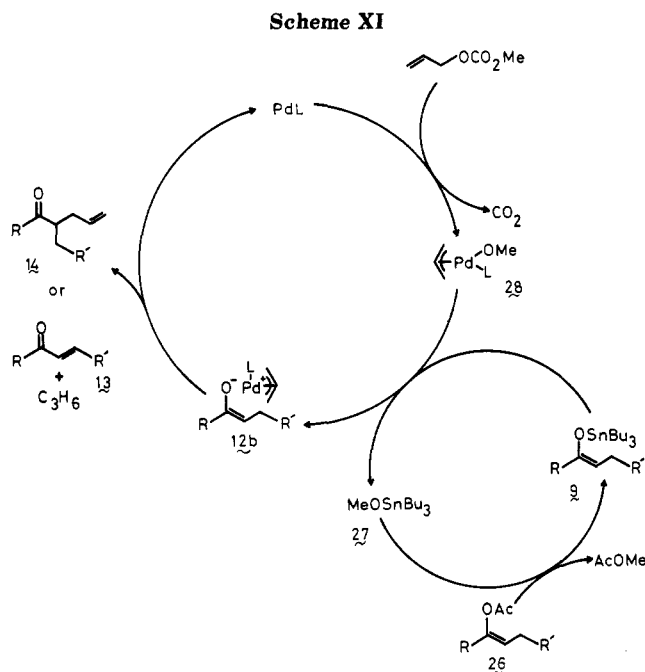
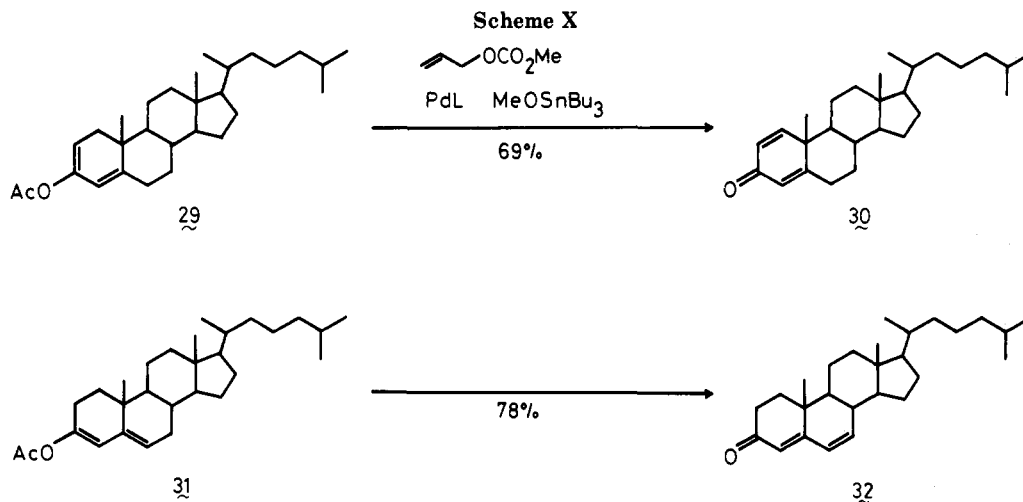
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4-cholesten-3-one, two enol acetates **29** and **31** were prepared, and the dehydrogenation took place at the direction of the enolization regioselectively to give different dienones **30** and **32** cleanly^{19,25} (Scheme X).

This unique bimetallic catalysis can be explained by the following mechanism (see Scheme XI). The in situ formation of tin enolates **9** by the reaction of enol acetates with tin methoxide **27** is known.²³ Transmetalation of tin enolates **9** with (π -allyl)palladium methoxide complex **28**, formed by the oxidative addition of allyl carbonates to Pd(0) complex and subsequent decarboxylation, gives (π -allyl)palladium enolates **12b**, which undergo reductive elimination to give α -allyl ketones **14**. Regeneration of the tin methoxide **27** and Pd(0) species makes the reaction catalytic. In CH_3CN , the complex **12** undergoes β -hydrogen elimination to afford α,β -unsaturated ketones. Allylation of tin enolates with allylic acetates has been reported.¹⁶

Reactions of Allyl β -Keto Carboxylates

In classical organic synthesis, β -keto esters are useful for regioselective alkylation. After regioselective mono-

or dialkylation, β -keto esters are hydrolyzed and then decarboxylated by heating to afford alkylated ketones, as shown in Scheme XII.²⁶

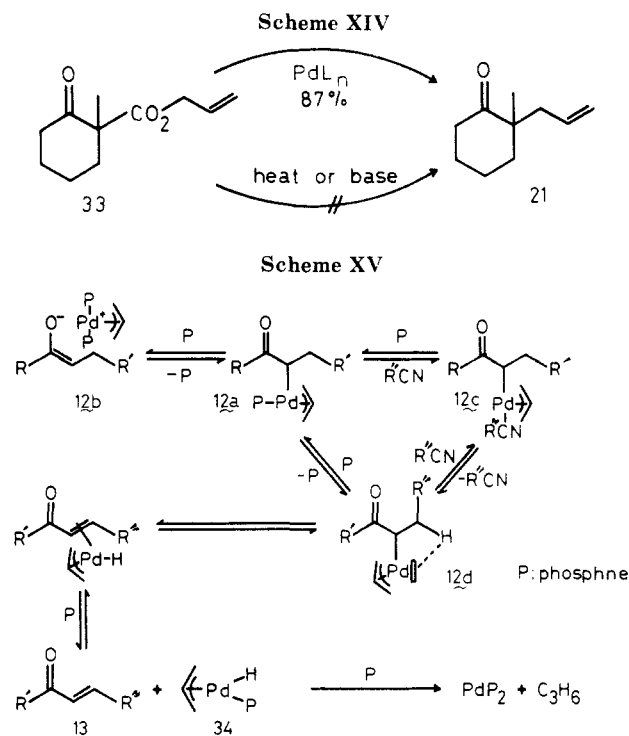
We have found four different transformations of allyl β -keto carboxylates catalyzed by palladium complexes under mild conditions, which greatly expand the synthetic usefulness of β -keto esters.

1. Decarboxylation-Allylation: Synthesis of α -Allyl Ketones 14. Decarboxylation-allylation of allyl β -keto carboxylates **2** to give α -allyl ketones **14** is known as the Carroll rearrangement. The reaction proceeds by heating,²⁷ addition of a base,²⁸ or catalysis by a transition-metal complex.²⁹⁻³¹ The thermal reaction proceeds at 170–200 °C, whereas in the presence of a base as a promotor, the reaction proceeds at lower temperatures. In sharp contrast, we found that the reaction proceeds under mild neutral conditions with a transition-metal catalyst such as palladium, molybdenum, nickel, and rhodium complexes. In particular, smooth rearrangement proceeds in boiling THF or even at a room temperature by using palladium-phosphine catalyst.^{29,30} Geranylacetone was obtained from geranyl acetoacetate with retention of the configuration of the double bond in boiling THF (Scheme XIII).

As shown in Scheme III, the palladium-catalyzed reactions can be explained by the following mechanism.

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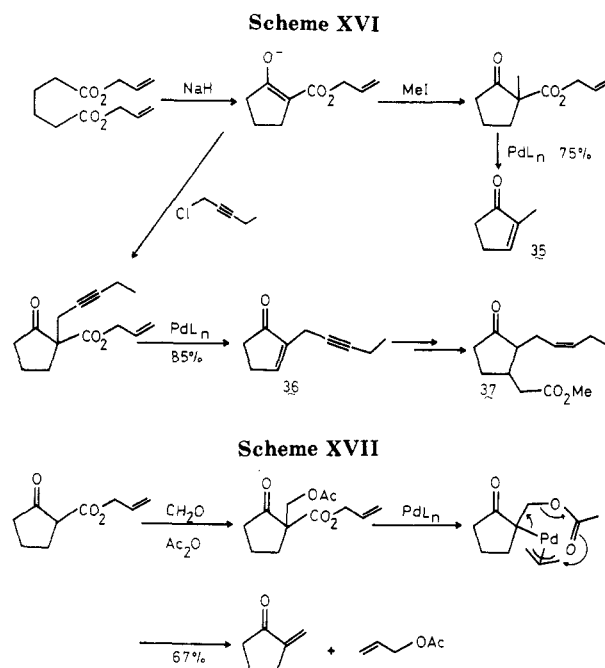
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Oxidative addition of allyl β -keto carboxylates **2** to the Pd(0) complex affords (π -allyl)palladium β -keto carboxylate complex **10**. Facile decarboxylation takes place to give (π -allyl)palladium enolate complex **12b**, which is in equilibrium with (π -allyl)palladium complex bonded to carbon **12a**. Finally, intramolecular nucleophilic substitution (or reductive elimination) of **12b** gives α -allyl ketone **14** and regenerates the Pd(0) complex. A quite different mechanism involving [3,3] sigmatropic rearrangement is proposed for the thermal or base-induced reaction, which requires generation of a dianion and enolization of a β -keto ester.^{27,28} The difference in mechanisms is clear by the following reaction (Scheme XIV). No thermal reactions proceed with allyl β -keto carboxylates **33**, which have no active protons, but the palladium-catalyzed reaction proceeds smoothly. Generally, the allylation reaction proceeds nearly quantitatively in THF at 20–60 °C with palladium–phosphine catalyst.

2. Decarboxylation–Dehydrogenation: Synthesis of α,β -Unsaturated Ketones. In the palladium-catalyzed reaction of allyl β -keto carboxylates, we found a crucial effect of solvents on the reaction path. Selective enone formation occurs by carrying out the reaction in boiling CH_3CN .³² At lower temperatures, allylation takes place even in CH_3CN . In addition to the solvent effect, the molar ratio of palladium to phosphine is crucial in affecting the equilibrium between **12a** and **12b**. The presence of excess phosphine favors the cationic complex **12b**, which undergoes facile allylation. When the molar ratio (Pd/P) is higher than 1, or even in the absence of the phosphine ligand, the C-bonded complex **12a** or **12c** is much favored and clean dehydrogenation takes place.²⁵ Dissociation of ligand from the complex **12a** or **12c** generates the complex **12d**, which has a vacant coordination site to interact with the β -hydrogen. Elimination of the β -hydrogen then gives α,β -unsaturated ketones **13** and (π -

(32) Shimizu, I.; Tsuji, J. *J. Am. Chem. Soc.* **1982**, *104*, 5844–5846.



allyl)palladium hydride complex **34**. Finally, reductive elimination of propene from **34** regenerates the Pd(0) catalyst. In this reaction, the π -allyl moiety acts as a hydrogen acceptor and is converted to propene.

Nitriles as the solvent are essential, probably because they coordinate weakly to the palladium to give the C-bonded complex **12c**, but easily dissociate to form the complex **12d** creating a vacant coordination site for β -elimination (Scheme XV).

Enone formation from allyl β -keto carboxylates is very useful for organic synthesis. One example is the facile synthesis of 2-methyl-2-cyclopentenone (**35**),³³ a useful intermediate for various cyclopentanoids, by the reaction sequence shown in Scheme XVI. Another application is the synthesis of 2-(2-pentynyl)-2-cyclopentenone (**36**), an important intermediate for the syntheses of *cis*-jasnone and methyl jasmonate (**37**). This enone formation can be carried out smoothly even on an industrial scale.

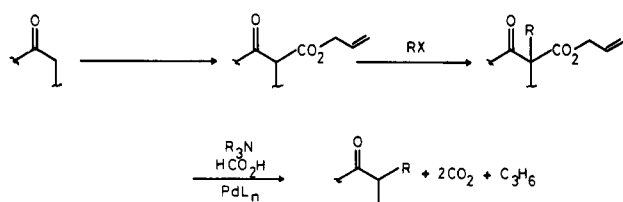
3. Decarboxylation–Deacetoxylation: Synthesis of α -Methylene Ketones. Allyl β -keto carboxylates react easily with aqueous formaldehyde to give α -hydroxymethyl- β -keto carboxylates, which are acetylated with acetic anhydride. We found that rapid decarboxylation of allyl α -acetoxymethyl- β -keto carboxylates, followed by elimination of acetoxy groups, gives α -methylene ketones in high yields when the compounds are treated with palladium catalyst in CH_3CN at room temperature.³⁴ In this reaction, a π -allyl ligand is converted to an allyl acetate. α -Methylene carbonyl groups are present in naturally occurring cyclic terpenoids and are important due to their antitumor activity.³⁵ Thus, an efficient synthesis of this functional group is an important problem. α -Methylene ketones are very reactive and must be synthesized under mild conditions. The palladium-catalyzed reaction is useful because it proceeds under neutral conditions at room

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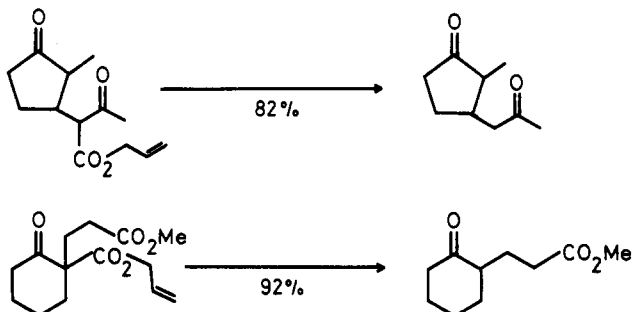
(34) Tsuji, J.; Nisar, M.; Minami, I. *Tetrahedron Lett.* **1986**, *27*, 2483–2486. Tsuji, J.; Nisar, M.; Minami, I. *Chem. Lett.*, **1987**, 23–24.

(35) Kupcahn, S. M.; Eakin, M. A.; Thomas, A. M. *J. Med. Chem.* **1971**, *14*, 1147–1152.

Scheme XVIII



Scheme XIX



temperature (see Scheme XVII).

4. Hydrogenolysis of Allyl β -Keto Carboxylates with Ammonium Formate. In the classical chemistry of β -keto esters, after regioselective mono- or dialkylation of β -keto esters, mono- or dialkyl ketones are derived by hydrolysis and subsequent decarboxylation. However, the usual alkaline hydrolysis is often complicated by a competing fission reaction to afford esters or acids, particularly when the α -position is disubstituted, and several improved methods for smooth dealkoxycarbonylation have been reported.²⁶ We have reported that allylic esters can be converted to free acids easily by palladium-catalyzed reaction with ammonium formate.³⁶ We have also found that decarboxylation of β -keto esters can be carried out under mild conditions by formate reduction. The deallyloxycarbonylation proceeds smoothly with tertiary amine salts (typically triethylamine) of formic acid in THF at room temperature to give ketones in high yields³⁷ (see Scheme XVIII).

The reaction conditions are mild and nearly neutral, and hence other functional groups present in the same molecule can be kept intact. For example, methyl esters are not hydrolyzed. No retro-Dieckmann or retro-Michael reactions, which are expected serious side reactions for β -keto esters, were observed, and the desired deallyloxycarbonylation proceeded selectively by the formate method (see Scheme XIX).

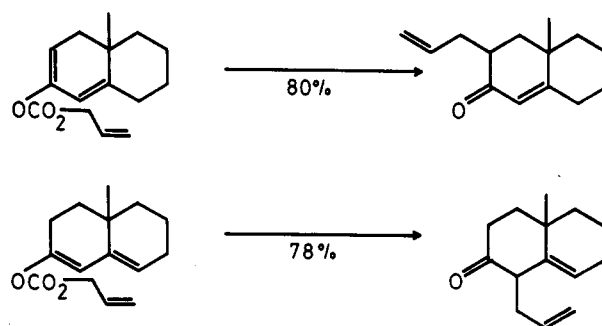
Decarboxylation-Allylation and Decarboxylation-Dehydrogenation of Allyl Vinylic Carbonates

Allyl vinylic carbonates **3** are isomeric with allyl β -keto carboxylates **2**, and we therefore expected similar

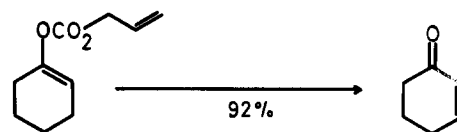
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Scheme XX



Scheme XXI



palladium-catalyzed reactions. Oxidative addition and decarboxylation of **3** with $Pd(0)$ complexes afford (π -allyl)palladium enolate complexes **12a** and **12b** (Scheme III). Since allyl carbonates are more reactive than allyl carboxylates,^{9,10,38} the decarboxylation-allylation of **3** takes place at lower temperatures, even at $-70^\circ C$.³⁹

In the reaction of allyl β -keto carboxylates bearing active hydrogen(s), proton transfer from **2** to the (π -allyl)palladium carboxylate complex **10** is possible, and diallylated ketones are obtained as minor products. Since no active hydrogens are present in the allyl vinylic carbonates **3**, clear monoallylation free from the proton transfer is achieved (Scheme XX).

Similar to allyl β -keto carboxylates **2**, allyl vinylic carbonates **3** can be converted to α,β -unsaturated ketones **13** in boiling CH_3CN ⁴⁰ (Scheme XXI).

Conclusion

A number of new palladium-catalyzed reactions of allyl β -keto carboxylates and carbonates based on facile decarboxylation and formation of (π -allyl)palladium complexes have been explored. These reactions are not only mechanistically interesting but are also useful in organic synthesis. Particularly, completely new synthetic methods for α,β -unsaturated carbonyl compounds would have wide application. The usefulness of β -keto esters in organic synthesis is greatly expanded by the introduction of four selective palladium-catalyzed reactions. It should be emphasized that all these reactions can be carried out efficiently with only a catalytic amount of palladium complexes under neutral conditions. The enone formation is now carried out on an industrial scale.

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(39) Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1983**, *24*, 1793-1796.

(40) Shimizu, I.; Minami, I.; Tsuji, J. *Tetrahedron Lett.* **1983**, *24*, 1797-1800.