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Oxidative Carbonylation as a Powerful Tool for the Direct Synthesis of Carbonylated Heterocycles

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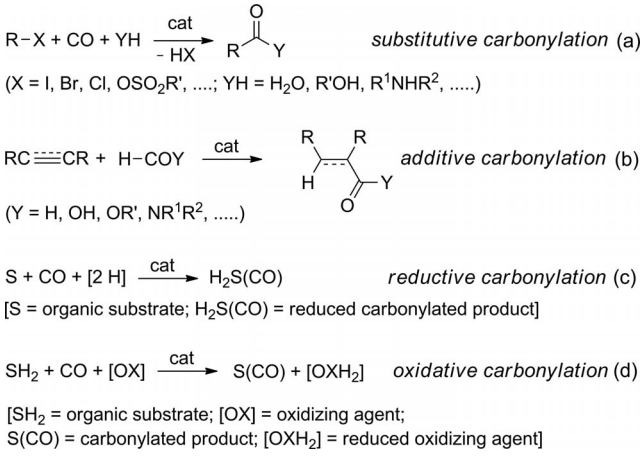
Keywords: Synthetic methods / Carbonylation / Cyclization / Heterocycles

Recent advances in the field of oxidative carbonylation reactions leading to carbonylated heterocyclic derivatives are presented (coverage: 2006 to the beginning of 2012).

Introduction

Carbonylation, the incorporation of carbon monoxide into an organic substrate, is now widely recognized as a very important tool in industrial and organic chemistry.[1,2] It allows the direct synthesis of carbonyl compounds starting from the simplest C-1 unit, which also meets the requirements of "atom economy",[3] step economy[4] and "green chemistry"[5] in general. The growing importance of carbonylation methods in organic synthesis is attested to by the increasing number of publications dealing with this topic, including reviews.[1,2]

Carbon monoxide is a relatively inert molecule, so carbonylations usually need to be carried out in the presence of a suitable metal catalyst. Different kinds of carbonylation reactions can be defined, depending on the particular type of process under consideration. A "substitutive carbonylation" is a process in which a certain functional group, such as a C–X bond (X = I, Br, Cl, or another possible leaving group) is formally substituted with a COY moiety [Y usually corresponding to an OH, OR, NHR, or NR_2 group, Scheme 1 (a)]. On the other hand, an "additive carbonylation" is a reaction in which a W–COY moiety (W usually corresponding to H; Y = H, OH, OR, NHR, NR_2, or some other nucleophilic group) formally adds to an unsaturated bond, as shown in Scheme 1 (b). In some cases the carbonylation process takes place with simultaneous reduction or oxidation of the starting material(s), as exem-



Scheme 1. Schematic representation of substitutive, additive, reductive and oxidative carbonylations.

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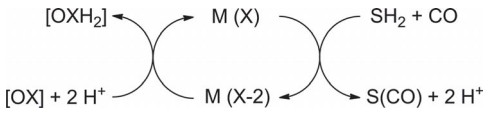
Bartolo Gabriele was born in Cosenza (Southern Italy) in 1966. He received his laurea in Chemistry (with honors) in 1990 from the University of Calabria (Italy). In 1991 he joined Professor Gian Paolo Chiusoli's group at the University of Parma, where he worked for seven months on the development of novel carbonylation reactions. He then returned to the University of Calabria, where he completed his PhD in 1994 with Professor Giuseppe Salerno. In 1995 he became a Researcher at the same University. From 1997–1998 he was a NATO-CNR fellow at the Department of Chemistry, Columbia University, New York, NY (USA) with Professor Ronald Breslow, where he worked on the development of new artificial enzymes for the selective hydroxylation of steroids. He then returned to the University of Calabria, where he was promoted to Associate Professor in 2002 and to Full Professor in 2006. Since 2005 he has been an Associate Editor of Current Organic Chemistry and he is (since 2012) the Editor-in-Chief of The Open Organic Chemistry Journal and Member of the Editorial Board of the E-Journal of Chemistry. His research interests include the development of novel methods for the synthesis of heterocycles by metal-catalysed heterocyclization reactions and the application of carbonylation chemistry to the one-step synthesis of fine chemicals.

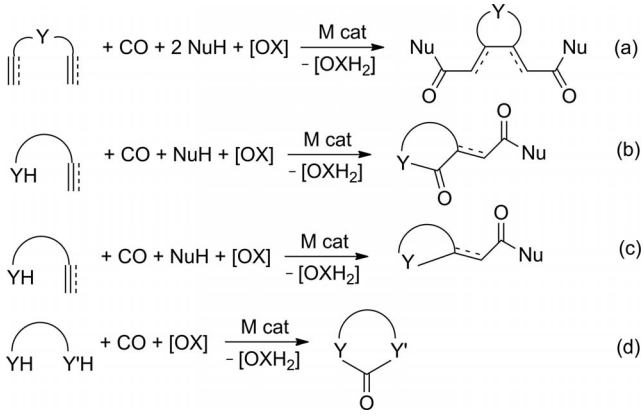
plified in parts c and d of Scheme 1. The terms "reductive carbonylation" and "oxidative carbonylation", respectively, are used to refer to processes of these kinds.

An oxidative carbonylation process is usually promoted by a metal in a relatively high oxidation state, most commonly Pd^{II}, in the presence of an external oxidant. Operatively, an oxidative carbonylation process can be defined as a process in which carbon monoxide is inserted into an organic substrate through the action of a metal species undergoing a reduction of its oxidation state [M(X) to M(X–2), the reduction $Pd^{II} \rightarrow Pd^0$ being the most common case].[1w] Clearly, in order to achieve a catalytic process, the reduced metal must be reoxidized to its original oxidation state through the action of a suitable external oxidant (Scheme 2).



Scheme 2. The principle of oxidative carbonylation. M (X) = metal catalyst promoting the process; [SH_2] = organic substrate; [OX] = oxidant; [S(CO)] = carbonylated product; [OXH_2] = reduced oxidant.

In the case of a suitable bifunctional organic substrate, it is possible that the oxidative carbonylation process is accompanied by cyclization. In particular, an oxidative carbonylation reaction leads to the formation of a carbonylated heterocycle either when the substrate contains a heteroatom on the main chain undergoing cyclization, as depicted in Scheme 3 (a), or when a heteroatom is directly involved in the cyclization process [Scheme 3 (b–d)].



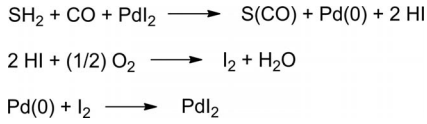
Scheme 3. Representative examples of oxidative carbonylations leading to carbonylated heterocycles. Y, Y′ = O, NR, S; NuH = external nucleophile (H_2O, ROH, RR′NH, R′SH); [OX] = oxidant; [OXH_2] = reduced oxidant.

We previously reviewed the basic principles of oxidative carbonylation, together with its synthetic applications (including those leading to carbonylated heterocycles) in 2006,[1w] so in this microreview we illustrate the most important recent advances in this research area from 2006 to the beginning of 2012.

Oxidative Carbonylation of Acetylenic Substrates Leading to Carbonylated Heterocycles

PdI_2/KI-Catalysed Oxidative Carbonylation of Acetylenic Substrates Leading to Carbonylated Heterocycles

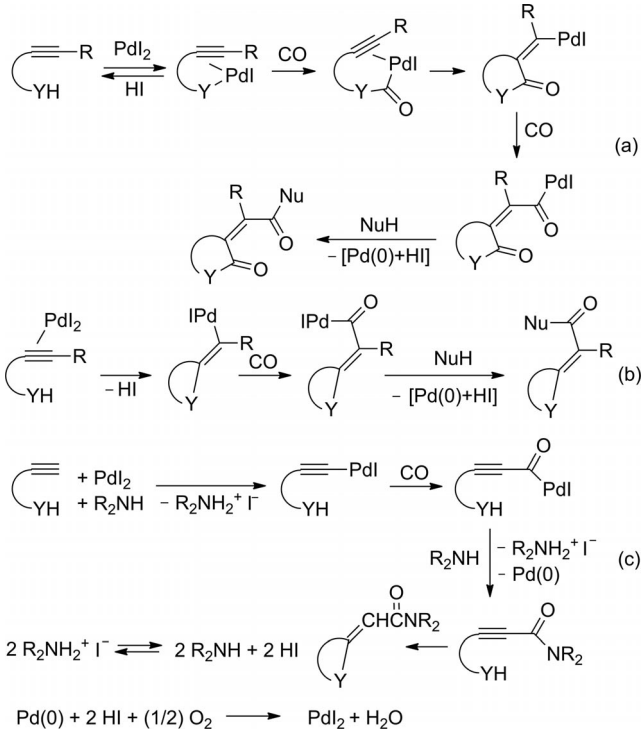
The PdI_2/KI catalytic system, introduced by our research group about 20 years ago,[6] is now established as one of the most versatile and efficient catalysts for the oxidative carbonylation of simple and functionalized alkynes.[1w,1y–1aa,7] The main characteristics of this system are its simplicity (the only ligands for Pd^{II} being iodide anions) coupled with its potential for the use of oxygen directly as the external oxidant, with production only of water as coproduct {[OX] = (1/2)O_2 and [OXH_2] = H_2O in Scheme 1 (d)}. In fact, with this system a very efficient mechanism for the reoxidation of the Pd^0 species resulting from the oxidative carbonylation process takes place: Pd^0 reoxidation occurs through oxidative addition of I_2, formed in its turn by oxidation of the hydrogen iodide also arising from the process (Scheme 4; in this and in the following schemes anionic iodide ligands are omitted for clarity).



Scheme 4. Mechanism of Pd^0 reoxidation in PdI_2/KI-catalysed oxidative carbonylation reactions. Anionic iodide ligands are omitted for clarity. SH_2 = organic substrate; S(CO) = carbonylated product.

When applied to suitably functionalized acetylenic derivatives, the PdI_2/KI catalytic system has proved valuable for the direct synthesis of a variety of carbonylated heterocycles.[1w,1y–1aa,7] With an alkyne bearing a suitably placed nucleophilic group, under appropriate conditions, this system is able to promote three different kinds of reactivity: the oxidative cyclocarbonylation/alkoxycarbonylation (or ~/aminocarbonylation) mechanism [Scheme 5, path (a)], the oxidative heterocyclization/alkoxycarbonylation (or ~/aminocarbonylation) mechanism [Scheme 5, path (b)], or the oxidative monoaminocarbonylation of the terminal triple bond followed by intramolecular conjugate addition [Scheme 5, path (c)].

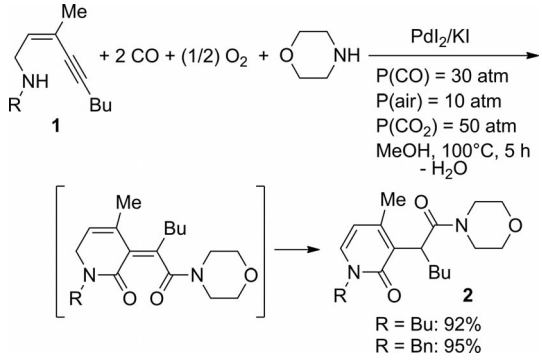
In pathway (a), the formation of an alkoxycarbonylpalladium (or carbamoylpalladium) intermediate takes place [through the reaction between the nucleophilic function of the substrate –YH (Y = O, NR), CO and PdI_2], followed by intramolecular *syn* insertion of the triple bond, CO insertion and nucleophilic displacement by an external nucleophile (NuH). In pathway (b), *anti* intramolecular nucleophilic attack by the –YH group on the triple bond coordinated to PdI_2 occurs (the cyclization mode being either *exo* or *endo*; only the *exo* mode is shown in Scheme 5), followed by CO insertion and nucleophilic displacement by an external nucleophile (NuH). In pathway (c), the formation of an alkynylpalladium species (from the reaction between the substrate, PdI_2 and a secondary amine) is followed by CO



Scheme 5. Different pathways in PdI_2/KI-catalysed oxidative carbonylations of functionalized acetylenic derivatives leading to carbonylated heterocycles (Y = O, NR; NuH = external nucleophile).

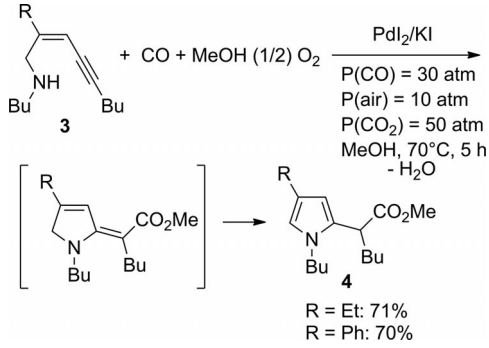
insertion, nucleophilic displacement by the amine and intramolecular conjugate addition to the ensuing ynamide intermediate. In all cases, the Pd^0 species ensuing from the oxidative process is reoxidized to PdI_2 through the action of oxygen.

Both mechanisms (a) and (b) in Scheme 5 were operative in the PdI_2/KI-catalysed oxidative carbonylations of (*Z*)-(alk-2-en-4-ynyl)amines, depending on the substitution patterns of the substrates and the reaction conditions.[8] (*Z*)-(Alk-2-en-4-ynyl)amines bearing a substituent at C-3 (**1**) were selectively converted into (2-oxopyridin-3-yl)acetamides **2** (Scheme 6) in the presence of a secondary amine as external nucleophile, through the cyclocarbonylation/aminocarbonylation pathway [Scheme 5 (a), Y = NR, NuH = R_2NH] followed by isomerization, as illustrated in Scheme 6. In this case, path (b), leading to pyridone formation, prevails because the substituent at C-3 hinders coordination of the triple bond to Pd^{II} on the opposite site with respect to the amino group, so amino group activation becomes more competitive.



Scheme 6. Synthesis of (2-oxopyridin-3-yl)acetamides **2** by PdI_2/KI-catalysed oxidative cyclocarbonylation/aminocarbonylation of 3-alkyl-substituted (*Z*)-(alk-2-en-4-ynyl)amines **1**.[8]

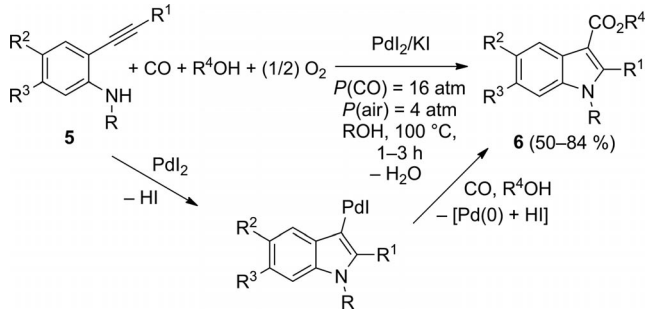
On the other hand, (*Z*)-(alk-2-en-4-ynyl)amines bearing a substituent at C-2 and unsubstituted at C-3 (**3**) selectively afforded pyrrol-2-acetic acid esters **4** (Scheme 7) in the presence of MeOH as external nucleophile, through the heterocyclization/alkoxycarbonylation pathway shown in Scheme 5 (b) (Y = O, NuH = MeOH) followed by aromatization, as illustrated in Scheme 7.



Scheme 7. Synthesis of pyrrol-2-acetic acid esters **4** by PdI_2/KI-catalysed oxidative 5-*exo-dig* heterocyclization/alkoxycarbonylation of 2-substituted (*Z*)-(alk-2-en-4-ynyl)amines **3**.[8]

In this case, path (b) prevails because the steric effect exerted by the substituent at C-2 tends to increase the population of the rotamer in which the amino group and the triple bond are closer to each other. In both cases, working in the presence of an excess of carbon dioxide had a beneficial effect on the carbonylation process.[8]

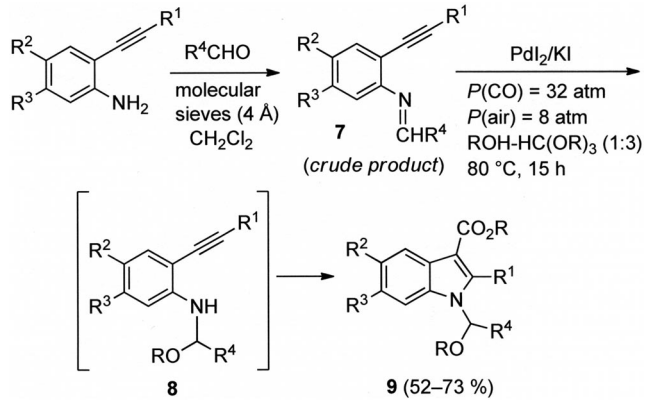
The heterocyclization/alkoxycarbonylation pathway was also followed by 2-alkynyl anilines **5** (Scheme 8), each containing an internal triple bond and a secondary amino group. With these substrates, a 5-*endo-dig* cyclization mode was operative, with selective formation of indole-3-carboxylic acid esters **6**, as shown in Scheme 8.[9] The presence of a secondary amino group and of an internal triple bond in the starting material was essential for the selectivity of the



Scheme 8. Synthesis of indole-3-carboxylates **6** by PdI_2/KI-catalysed oxidative 5-*endo-dig* heterocyclization/alkoxycarbonylation of 2-alkynyl anilines **5**, each containing an internal triple bond and a secondary amino group.[9]

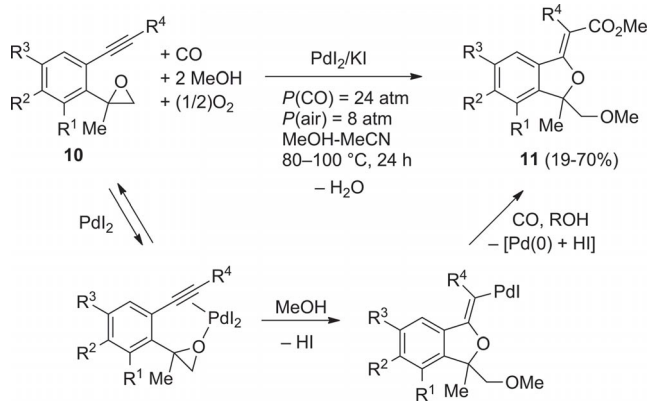
process. In fact, 2-ethynylanilines possessing a terminal triple bond and a primary or a secondary amino group are known to lead to dihydroindol-2-one derivatives,[10] whereas 2-alkynylanilines with an internal triple bond and a primary amino group afforded acyclic carbamates[10] through the intermediate formation of isocyanates.[11]

Interestingly, the formation of particular 2-alkynyl aniline intermediates – [(alkoxycarbonyl)(2-alkynylaryl)]-amines **8** (Scheme 9) – could be achieved in situ from 2-alkynylaniline-imines **7**. PdI_2/KI-catalysed oxidative carbonylation of these, carried out in the presence of an alcohol as external nucleophile and of trialkyl orthoformate as dehydration agent (to avoid substrate hydrolysis), directly afforded 1-(alkoxyarylmethyl)indole-3-carboxylates **9** through a multicomponent cascade process (Scheme 9).[12]



Scheme 9. PdI_2/KI-catalysed multicomponent cascade reaction leading to 1-(alkoxyarylmethyl)indole-3-carboxylates **9** from 2-alkynylaniline-imines **7** through the intermediate formation of [(alkoxymethyl)(2-alkynylaryl)]amines **8**.[12]

Another interesting cascade process, involving nucleophilic ring opening followed by oxidative heterocyclization/alkoxycarbonylation, was recently reported. Functionalized 1,3-dihydroisobenzofurans **11** (Scheme 10) were obtained from the starting 2-(2-alkynyl)oxiranes **10** in the presence of PdI_2/KI in MeOH as the solvent and external nucleophile.[13]



Scheme 10. Synthesis of (*Z*)-1-methoxymethyl-1-methyl-3-(methoxycarbonyl)methylene-1,3-dihydroisobenzofurans **11** by PdI_2/KI-catalysed sequential oxidative nucleophilic ring opening/*syn*-5-*exo*-*dig*-heterocyclization/alkoxycarbonylation of 2-(2-alkynylaryl)-2-methyloxiranes **10**.[13]

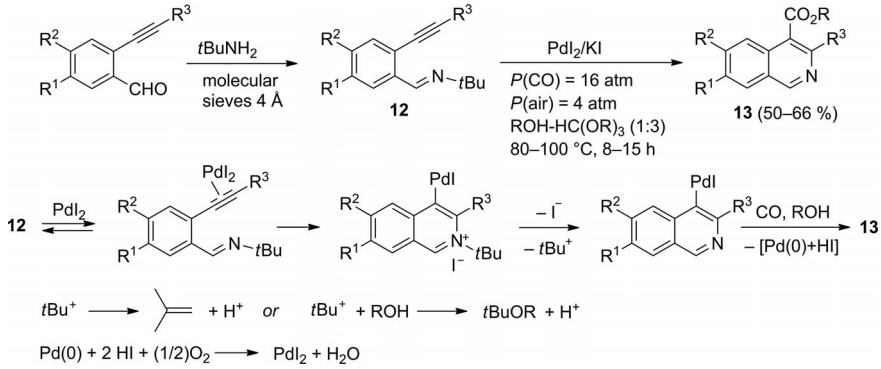
An imino nitrogen can also serve as nucleophile in an oxidative heterocyclization/alkoxycarbonylation process. We have recently found that isoquinoline-4-carboxylates **13** (Scheme 11) can be obtained in good yields from (2-alkynylbenzylidene)(*tert*-butyl)amines **12** through a sequential oxidative 6-*endo*-*dig*-heterocyclization/alkoxycarbonylation process with simultaneous loss of the *tert*-butyl carbocation.[14]

Interestingly, *N*-[(2-alkynyl)benzylidene]-*N*′-phenylhydrazines **14** (Scheme 12) underwent *O*-cyclization as a result of water attack on the imino groups of the substrates, with formation of isochromene-4-carboxylates **15**.[14]

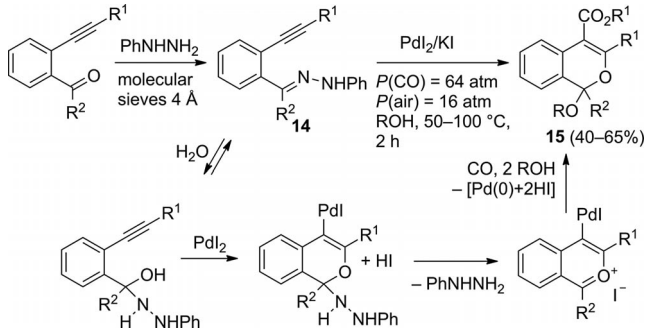
With particular substrates, the heterocyclization/alkoxycarbonylation process is accompanied by dehydration, triggered by aromatization. Quinoline-3-carboxylates **17** (Scheme 13) were obtained by PdI_2/KI-catalysed oxidative heterocyclodehydration/alkoxycarbonylation of 1-(2-aminoaryl)-2-yn-1-ols **16**.[15]

In a similar way, 3-yne-1,3-diols **18** (Scheme 14) were smoothly converted into furan-3-carboxylates **19**.[16]

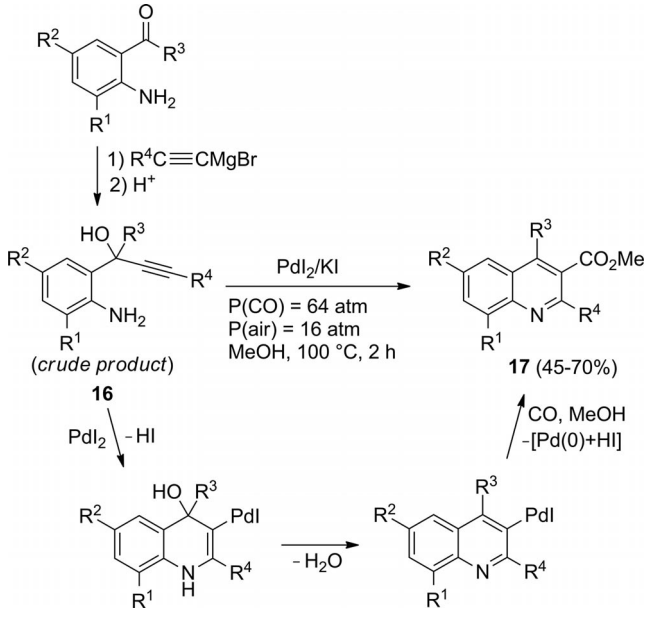
On the other hand, PdI_2/KI-catalysed oxidative heterocyclodehydration/alkoxycarbonylation of *N*-Boc-1-amino-3-yn-2-ols **20** (Scheme 15), followed by base-promoted de-



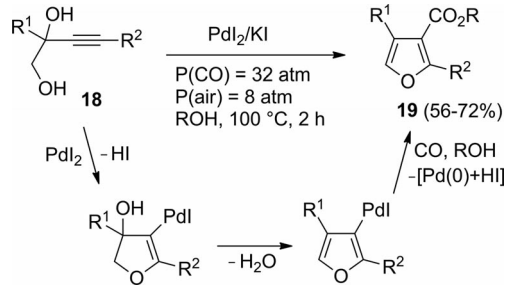
Scheme 11. Synthesis of isoquinoline-4-carboxylates **13** by PdI_2/KI-catalysed oxidative heterocyclization/alkoxycarbonylation of (2-alkynylbenzylidene)(*tert*-butyl)amines **12**.[14]



Scheme 12. Synthesis of isochromene-4-carboxylates **15** by PdI_2/KI-catalysed oxidative heterocyclization/alkoxycarbonylation of *N*-[(2-alkynyl)benzylidene]-*N*′-phenylhydrazines **14**.[14]

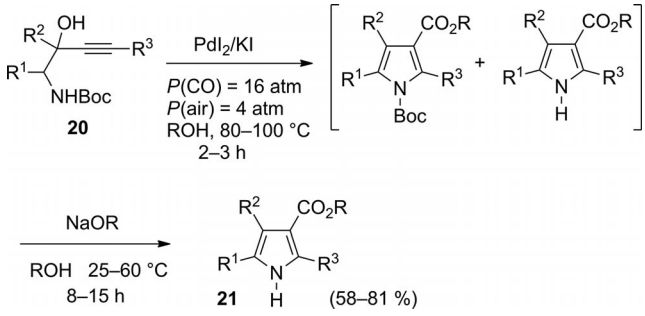


Scheme 13. Synthesis of quinoline-3-carboxylates **17** by PdI_2/KI-catalysed oxidative heterocyclodehydration/alkoxycarbonylation of 1-(2-aminoaryl)-2-yn-1-ols **16**.[15]

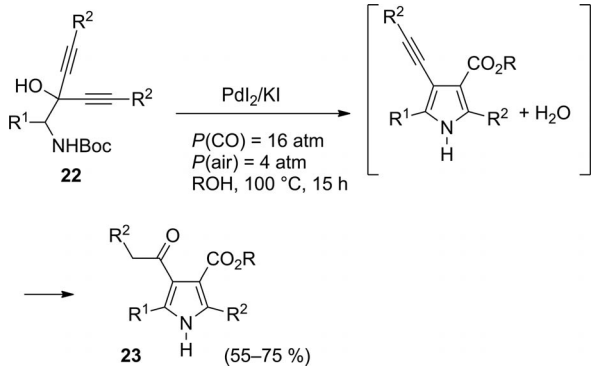


Scheme 14. Synthesis of furan-3-carboxylates **19** by PdI_2/KI-catalysed oxidative heterocyclodehydration/alkoxycarbonylation of 3-yne-1,2-diols **18**.[16]

protection, afforded the *N*-unsubstituted pyrrole-3-carboxylates **21**.[17] In the case of *N*-Boc-2-alkynyl-1-amino-3-yn-2-ols **22** (Scheme 16), each bearing an additional alkynyl substituent α to the hydroxy group, *N*-deprotection occurred spontaneously under the reaction conditions, together with regioselective addition of water to the triple bond of the alkynyl substituent, with direct formation of 4-acylpyrrole-3-carboxylates **23**.[17]

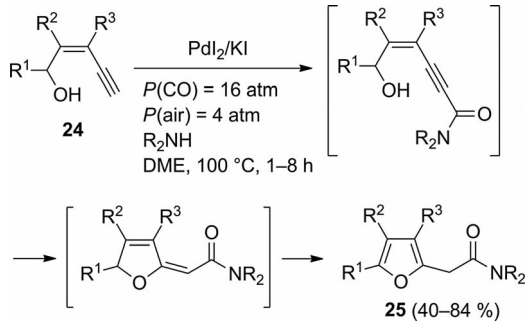


Scheme 15. Synthesis of pyrrole-3-carboxylates **21** by PdI_2/KI-catalysed oxidative heterocyclodehydration/alkoxycarbonylation of *N*-Boc-1-amino-3-yn-2-ols **20**.[17]



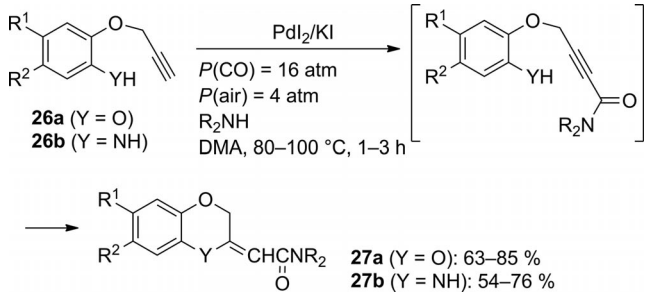
Scheme 16. Synthesis of 4-acylpyrrole-3-carboxylates **23** by PdI_2/KI-catalysed oxidative heterocyclodehydration/alkoxycarbonylation/hydration of *N*-Boc-2-alkynyl-1-amino-3-yn-2-ols **22**.[17]

The oxidative aminocarbonylation/conjugate addition mechanism shown in Scheme 5(c), followed by aromatization, was operative in the case of the PdI_2/KI-catalysed formation of furan-2-ylacetamides **25** (Scheme 17) from (*Z*)-2-en-4-yn-1-ols **24** and secondary amines.[18]



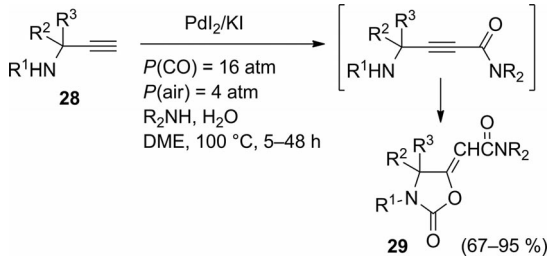
Scheme 17. Synthesis of furan-2-ylacetamides **25** by PdI_2/KI-catalysed oxidative aminocarbonylation of (*Z*)-2-en-4-yn-1-ols **24**/conjugate addition/aromatization.[18]

In a similar way, 2,3-dihydrobenzo[1,4]dioxine derivative **27a** (Scheme 18) and 3,4-dihydro-2*H*-benzo[1,4]oxazine derivative **27b** (Y = O or NH, respectively) were obtained from 2-prop-2-ynyloxyphenols **26a** and 2-prop-2-ynyloxyanilines **26b**, respectively.[19]



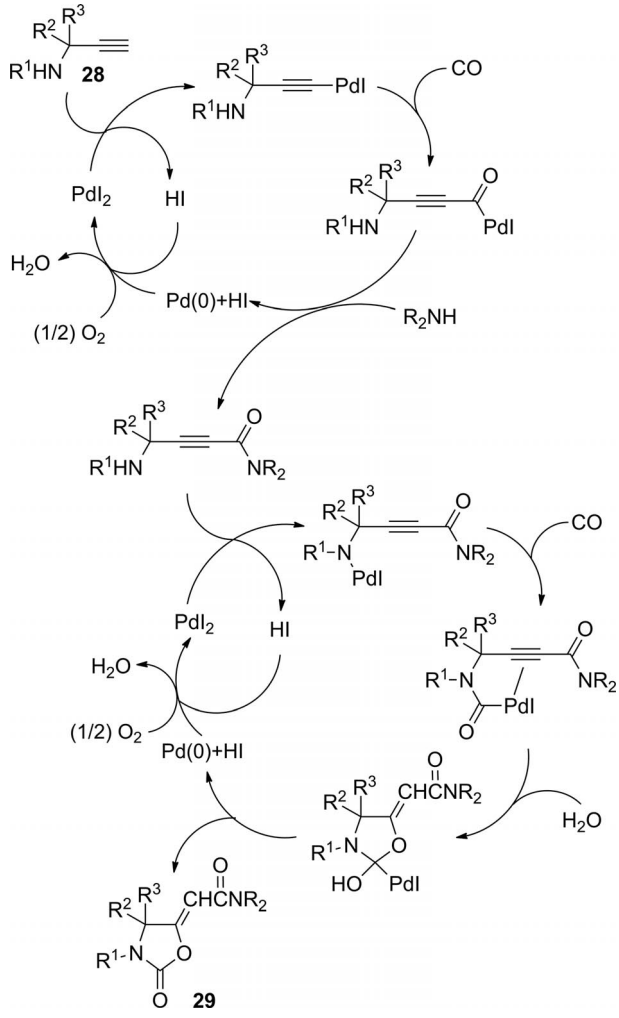
Scheme 18. Synthesis of 2,3-dihydrobenzo[1,4]dioxine and 3,4-dihydro-2*H*-benzo[1,4]oxazine derivatives **27a** and **27b**, respectively, by PdI_2/KI-catalysed oxidative aminocarbonylation of 2-prop-2-ynyloxyphenols **26a** and 2-prop-2-ynyloxyanilines **26b**, respectively, followed by intramolecular conjugate addition.[19]

Of particular interest were the reactions of α,α-disubstituted 2-ynylamines **28** (Scheme 19), carried out in the presence of water and a secondary amine, resulting in a sequential oxidative aminocarbonylation/cyclocarbonylation process leading to oxazolidin-2-ones **29**.[20]



Scheme 19. Synthesis of 5-(carbamoylmethylene)oxazolidinin-2-ones **29** by sequential PdI_2/KI-catalysed oxidative aminocarbonylation/cyclocarbonylation of 2-ynylamines **28**.[20]

Two sequential catalytic processes, both catalysed by PdI_2, were involved in these reactions (Scheme 20). The first corresponded to the oxidative aminocarbonylation of the triple bond of the substrate, with formation of the corresponding 2-ynamide derivative, and the second was a cyclocarbonylation, resulting from *N*-palladation, carbon monoxide insertion, water attack on the resulting carbamoylpalladium intermediate, intramolecular conjugate addition and [Pd^0 + HI] elimination.[20] According to the current terminology, this is an example of "auto-tandem catalysis".[21]



Scheme 20. "Auto-tandem catalysis" leading to 5-(carbamoylmethylene)oxazolidinin-2-ones **29**.[20]

Oxidative Carbonylation of Acetylenic Substrates Leading to Carbonylated Heterocycles Promoted by Other Catalytic Systems

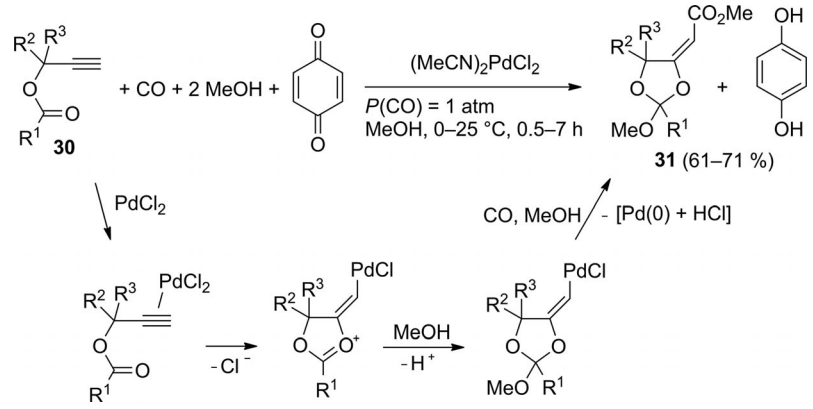
The group of Kato and co-workers has reported a useful strategy for the preparation of cyclic orthoesters **31** (Scheme 21), obtained in good yields by oxidative carbonylation of propargylates **30** in the presence of $(MeCN)_2$-$PdCl_2$ as the catalyst and *p*-benzoquinone as the external oxidant.[22]

Mechanistically, the reaction is believed to proceed through intramolecular nucleophilic attack of the carbonyl group at the triple bond coordinated to Pd^{II}, followed by MeOH attack at the corresponding oxonium intermediate and alkoxycarbonylation.[22]

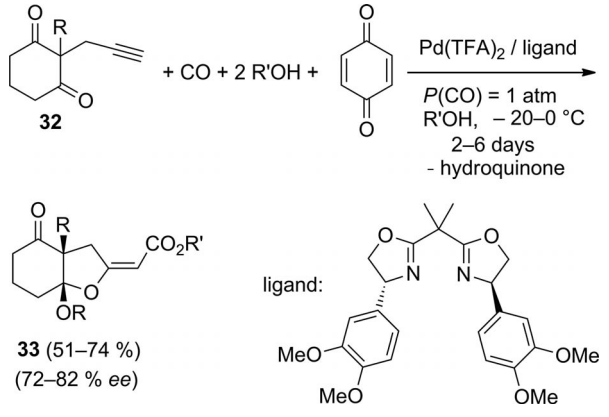
An enantioselective version of this kind of reactivity has been applied to the synthesis of nonracemic bicyclic β-alkoxyacrylates **33** (Scheme 22) starting from 2-alkyl-2-propargylcyclohexane-1,3-diones **32** in the presence of Pd(TFA)$_2$/2,2′-isopropylidene-bis[(4*R*)-4-(3,4-dimethoxyphenyl)-2-oxaxine].[23]

The same group has recently reported the one-pot synthesis of 4-methoxy-6-(3-phenylpropyl)-5,6-dihydropyran-2-one (**35**, dihydrokawain, an important natural product, Scheme 23) by oxidative alkoxy-cyclocarbonylation of 7-phenylhept-1-yn-4-ol (**34**).[24] Propargyl alcohols were converted into the corresponding five-membered lactones in a similar way.[24b]

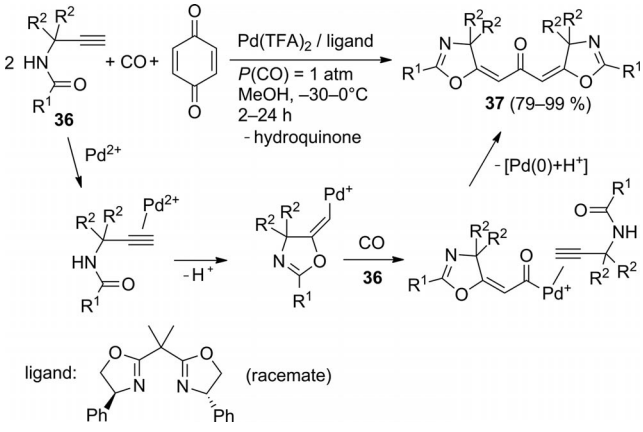
A novel oxidative cyclization/carbonylation/cyclization coupling reaction, leading to symmetrical ketones **37** (Scheme 24), each with two heterocyclic groups, from propargyl amides **36**, was also recently reported by Kato and



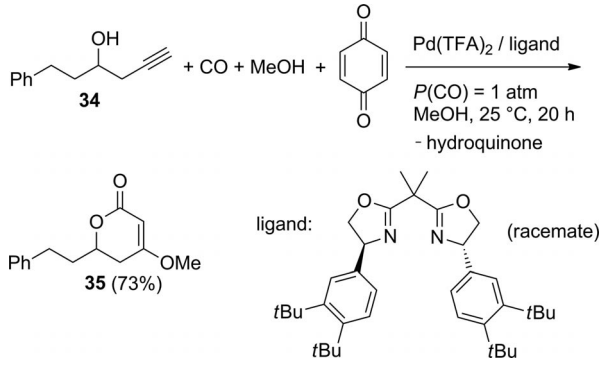
Scheme 21. Synthesis of cyclic orthoesters **31** by $(MeCN)_2PdCl_2$-catalysed oxidative heterocyclization/alkoxycarbonylation of propargylates **30**.[22]



Scheme 22. Enantioselective synthesis of nonracemic bicyclic β-alkoxyacrylates **33** by $Pd(TFA)_2$-catalysed oxidative heterocyclization/alkoxycarbonylation of 2-alkyl-2-propargylcyclohexane-1,3-diones **32** in the presence of a suitable nonracemic ligand.[23]



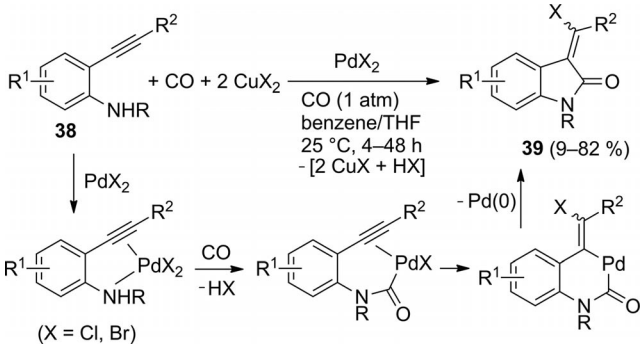
Scheme 24. Synthesis of symmetrical ketones **37**, each bearing two oxazoline moieties, by $Pd(TFA)_2$-catalysed oxidative cyclization/carbonylation/cyclization of propargylic amides **36**.[25]



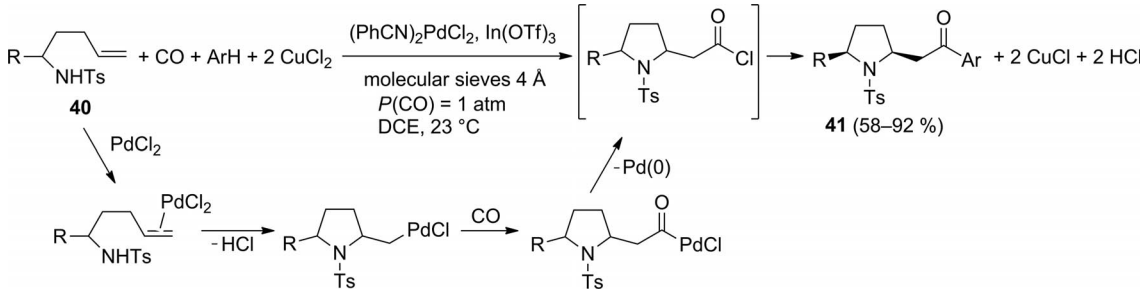
Scheme 23. Synthesis of racemic dihydrokawain [4-methoxy-6-(3-phenylpropyl)-5,6-dihydropyran-2-one, **35**] by $Pd(TFA)_2$-catalysed oxidative alkoxy-cyclocarbonylation of 7-phenylhept-1-yn-4-ol (**34**).[24]

co-workers.[25] The process begins with an intramolecular nucleophilic attack at the triple bond coordinated to Pd^{II} followed by insertion of CO, coordination of a second molecule of substrate, heterocyclization and coupling.[25]

The direct formation of 3-(halomethylene)indolin-2-ones **39** (Scheme 25, X = Cl or Br) by PdX_2-catalysed oxidative carbonylation of 2-(1-alkynyl)anilines **38** in the presence of CuX_2 was recently achieved.[26] The process is similar to the previously reported alkoxycarbonylation of the same substrates to afford 3-(alkoxycarbonyl)methylene-1,3-dihydroindol-2-ones.[27]



Scheme 25. Synthesis of 3-(halomethylene)indolin-2-ones **39** by PdX_2-catalysed oxidative halocyclocarbonylation of 2-(1-alkynyl)-anilines **38**.[26]



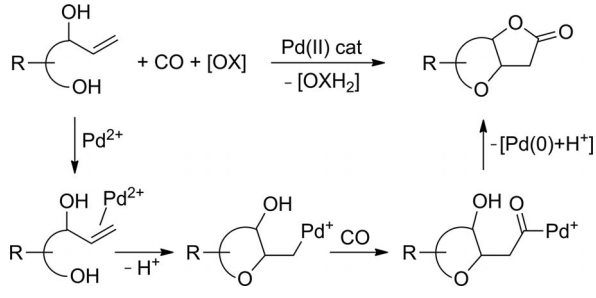
Scheme 26. Multicatalytic synthesis of α-pyrrolidinyl ketones **41** by sequential Pd^{II}-catalysed oxidative aminochlorocarbonylation/In^{III}-catalysed Friedel–Crafts acylation of *N*-tosylpentenamines **40**.[28]

Oxidative Carbonylation of Miscellaneous Substrates Leading to Carbonylated Heterocycles

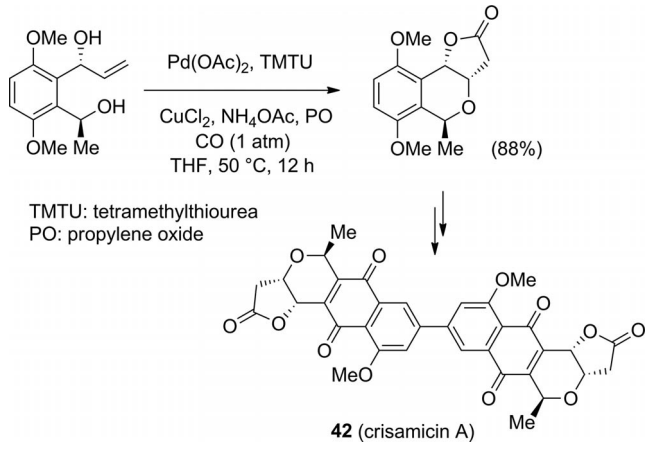
Oxidative Carbonylation of Olefinic and Related Substrates Leading to Carbonylated Heterocycles

Cernak and Lambert have recently reported an interesting multicatalytic and diastereoselective synthesis of α-pyrrolidinyl ketones **41** (Scheme 26) by sequential Pd^{II}-catalysed oxidative aminochlorocarbonylation/In^{III}-catalysed Friedel–Crafts acylation of *N*-tosylpentenamines **40**, carried out in the presence of $CuCl_2$ and molecular sieves (4 Å, to trap the HCl ensuing from the process).[28] The carbonylation reaction proceeds through intramolecular nucleophilic attack at the double bond coordinated to Pd^{II}, followed by CO insertion and reductive elimination, to give the corresponding pyrrolidinyl acid chlorides.[28]

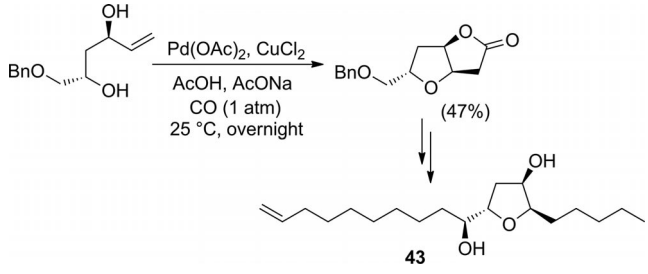
Palladium-catalysed oxidative heterocyclization/intramolecular alkoxycarbonylation of alk-4-ene-1,2-diols, alk-5-ene-1,2-diols and related substrates represents a useful approach to bis-heterocyclic lactones (Scheme 27).[1] Reactivity of this kind has recently been exploited in the total synthesis of biologically relevant compounds such as crisamicin A (**42**, Scheme 28)[29] and C_{19} lipid diols containing 2,5-disubstituted 3-oxygenated tetrahydrofuran moieties, such as **43** (Scheme 29).[30] The enantioselective version of the oxidative oxycarbonylation of 4-ene-1,2-diols has also recently been achieved by kinetic resolution in the presence of nonracemic bis-oxazoline ligands.[31]



Scheme 27. Pd^{II}-catalysed oxidative heterocyclization/intramolecular alkoxycarbonylation of alk-4-ene-1,2-diols or alk-5-ene-1,2-diols to afford bis-heterocyclic lactones.

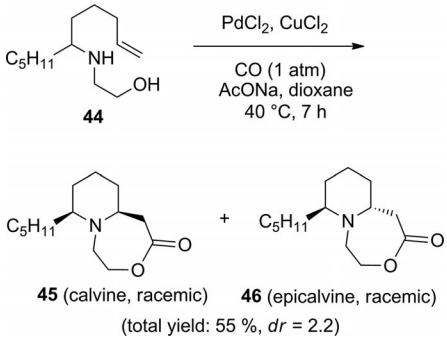


Scheme 28. Pd^{II}-catalysed oxidative heterocyclization/intramolecular alkoxycarbonylation of (*R*)-1-{2-[(*S*)-1-hydroxyethyl]-3,6-dimethoxyphenyl}prop-2-en-1-ol as the key step in the total synthesis of crisamicin A (**42**).[29]

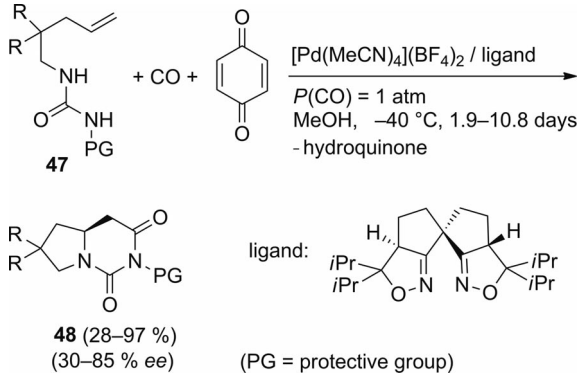


Scheme 29. Pd^{II}-catalysed oxidative heterocyclization/intramolecular alkoxycarbonylation of (2*S*,4*R*)-1-(benzyloxy)hex-5-ene-2,4-diol as the key step in the synthesis of C_{19} lipid diols containing 2,5-disubstituted 3-oxygenated tetrahydrofuran moieties, such as **43**.[30]

Oxidative aminocyclization/cyclocarbonylation has also been reported. 2-(Undec-1-en-6-ylamino)ethanol (**44**, Scheme 30) has been converted into a mixture of racemic alkaloids calvine (**45**) and epicalvine (**46**),[32] whereas nonracemic tetrahydropyrrolo[1,2-*c*]pyrimidine-1,3-diones **48** (Scheme 31) were obtained from alkenylurea substrates **47** in the presence of a Pd^{II} catalyst and a nonracemic spiro bis(isoxazoline) ligand.[33]



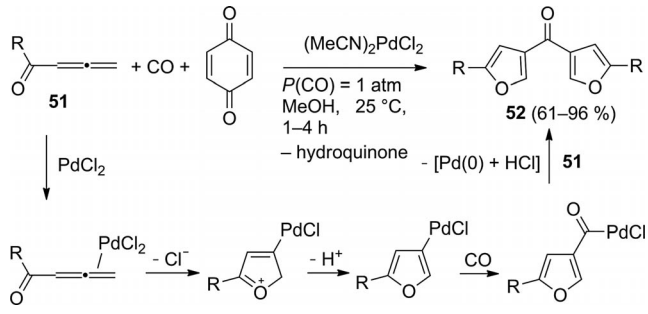
Scheme 30. Pd^{II}-catalysed oxidative heterocyclization/intramolecular alkoxycarbonylation of 2-(undec-1-en-6-ylamino)ethanol (**44**) leading to a mixture of racemic calvine (**45**) and epicalvine (**46**).[32]



Scheme 31. Pd^{II}-catalysed oxidative enantioselective synthesis of tetrahydropyrrolo[1,2-*c*]pyrimidine-1,3-diones **48** by oxidative aminocyclization/cyclocarbonylation of alkenylurea substrates **47** in the presence of a nonracemic spiro-bis(isoxazoline) ligand.[33]

Functionalized allenes can also be useful substrates for oxidative carbonylation to afford heterocyclic derivatives. 3-Chloromethyl-2-(5*H*)-furanones and 3-chloromethyl-5,6-dihydropyran-2-ones **50** (Scheme 32) have recently been obtained by Pd^{II}-catalysed oxidative chlorocyclocarbonylation of 2,3- or 3,4-allenols **49**, respectively.[34]

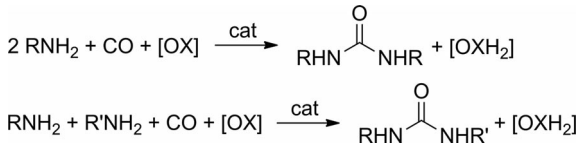
A convenient synthesis of difuranyl ketones **52** (Scheme 33) has been achieved through Pd^{II}-catalysed oxidative carbonylative dimerization of allenyl ketones **51**.[35] The products are formed by heterocyclization followed by CO insertion to give acylpalladium intermediates, which then undergo second heterocyclization processes (Scheme 33).[35]



Scheme 33. Pd^{II}-catalysed oxidative carbonylative dimerization of allenyl ketones **51** leading to difuranylketones **52**.[35]

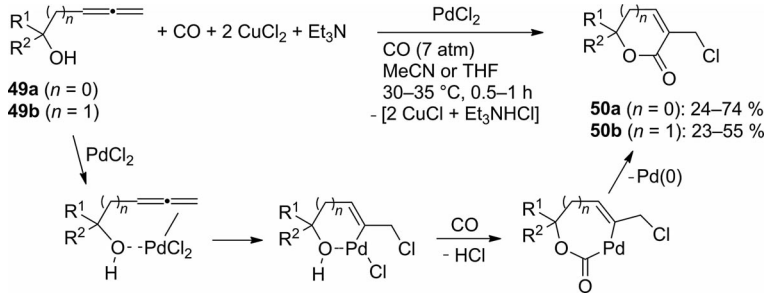
Oxidative Carbonylation of Diamines, Amino Alcohols, Diols and Related Compounds Leading to Carbonylated Heterocycles

Oxidative carbonylation of amines is a very attractive approach to the phosgene-free synthesis of ureas (Scheme 34), and several methods to achieve this important synthetic goal have been reported in the recent literature.[36] Two important reviews on this topic have recently been published.[37]

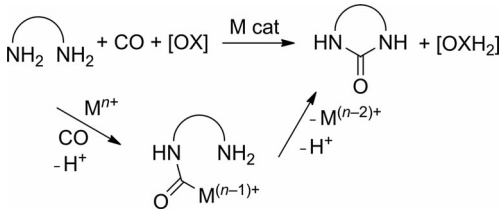


Scheme 34. Catalytic oxidative carbonylation of amines to afford ureas. [OX] = oxidizing agent; [OXH_2] = reduced oxidant.

When applied to suitable diamines, the reaction can lead to cyclic ureas, a particularly important subclass of urea derivatives (Scheme 35). Mechanistically, the process starts with the formation of a carbamoylmetal complex, followed by intramolecular nucleophilic displacement (Scheme 35).

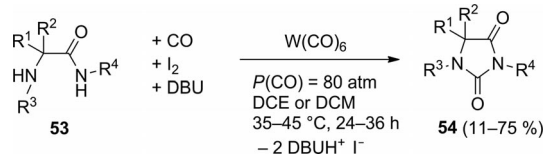


Scheme 32. Pd^{II}-catalysed oxidative chlorocyclocarbonylation of 2,3- or 3,4-allenols (**49a** and **49b**, respectively) leading to 3-chloromethyl-2-(5*H*)-furanones **50a** and 3-chloromethyl-5,6-dihydropyran-2-ones **50b**, respectively.[34]

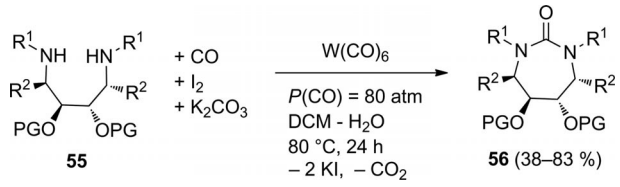


Scheme 35. Catalytic oxidative carbonylation of diamines to afford cyclic ureas. [OX] = oxidizing agent; $[OXH_2]$ = reduced oxidant.

Recently, the use of $W(CO)_6$ as the catalyst in the presence of I_2 as oxidant has been reported to promote the synthesis of hydantoins **54** from α-amino amides **53** (Scheme 36),[38] as well as the synthesis of the cyclic urea core structure of the HIV protease inhibitor DMP 450 (cf. compound **56**, Scheme 37) from bis(amino)hexanediol derivatives **55**.[39]

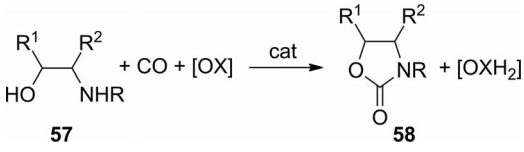


Scheme 36. Synthesis of hydantoins **54** by tungsten-catalysed oxidative carbonylation of α-amino amides **53**.[38]



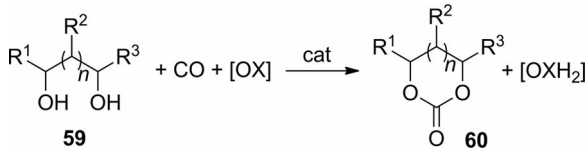
Scheme 37. Synthesis of **56**, containing the core structure of DMP 450, by tungsten-catalysed oxidative carbonylation of bis(amino)hexanediol derivatives **55** (PG = protective group).[39]

Just as diamines can be oxidatively carbonylated to afford ureas, oxazolidin-2-ones **58** (Scheme 38) can be directly obtained by oxidative carbonylation of β-amino alcohols **57**.[40] Several catalytic systems and oxidizing agents designed to achieve this have been proposed recently; they include sulfur/$NaNO_2$,[41] (NHC)Cu^{I}/O_2 (NHC = *N*-heterocyclic carbene),[42] selenium/O_2,[43] (chitosan-Schiff base) Co^{II}/O_2,[44] (salen)Co^{II} or (salen)Co^{III}/O_2,[45] (phen)$PdCl_2$-BmimI/O_2,[46] $Pd(OAc)_2$-mmimI/O_2,[47] and cross-linked polymer-supported Pd/O_2.[48] It has to be noted, however, that most of these procedures[42–48] make use of CO/O_2 mixtures in volume ratios very close to, or even within, the flammability range for this kind of mixture.[49]



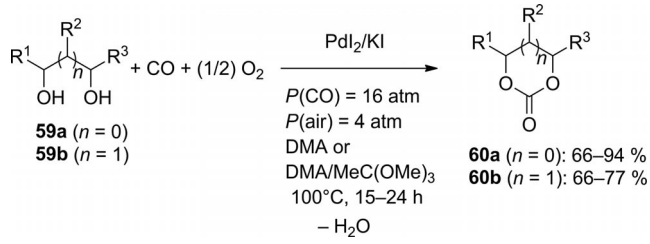
Scheme 38. Catalytic oxidative carbonylation of β-amino alcohols **57** to oxazolidin-2-ones **58**. [OX] = oxidizing agent; $[OXH_2]$ = reduced oxidant.

The direct oxidative carbonylation of diols **59** (Scheme 39) is of particular interest, in view of the availabilities of the starting materials and the importance of the cyclic carbonates **60** obtained.[40g,50] Glycerol, in particular, is a highly abundant feedstock, and its efficient transformation into high-value-added glycerol carbonate is a very important synthetic goal.

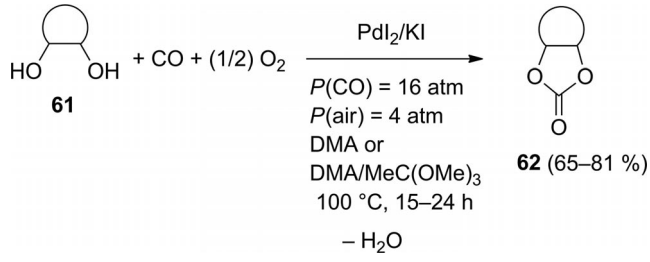


Scheme 39. Catalytic oxidative carbonylation of diols **59** to afford cyclic carbonates **60**. [OX] = oxidizing agent; $[OXH_2]$ = reduced oxidant.

Several catalytic systems have also been proposed in this case. The PdI_2/KI catalytic system, developed by our research group, was thus shown to be an excellent catalyst for the formation both of five- and of six-membered cyclic carbonates **60a** and **60b**, respectively (Scheme 40), from 1,2- and 1,3-diols **59a** and **59b**, respectively.[51] The method could be successfully applied both to acyclic diols **59** (Scheme 40) and to cyclic diols **61** (Scheme 41), as well as to polyols such as i) glycerol (**63**, Scheme 42), which was smoothly converted into glycerol carbonate (**64**), and ii) glucose (**65**), which led to the formation of α-D-glucofuranose 1,2:5,6-dicarbonate (**66**), resulting from a double carbonylation process.[51a]

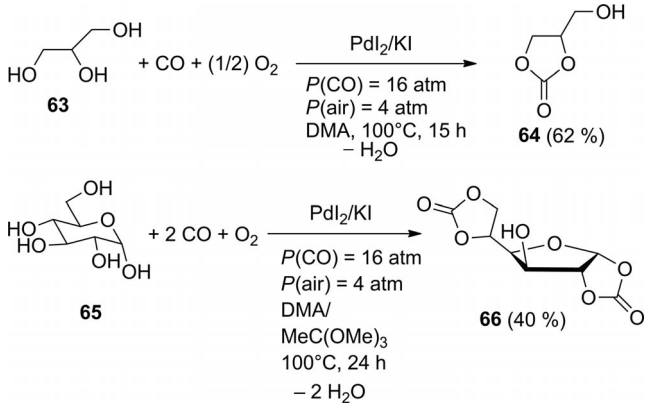


Scheme 40. Synthesis of five- and six-membered cyclic carbonates **60a** and **60b**, respectively, by PdI_2/KI-catalysed oxidative cyclocarbonylation of acyclic 1,2- and 1,3-diols **59a** and **59b**, respectively.[51]



Scheme 41. Synthesis of five-membered cyclic carbonates **62** by PdI_2/KI-catalysed oxidative cyclocarbonylation of cyclic 1,2-diols **61**.[51a]

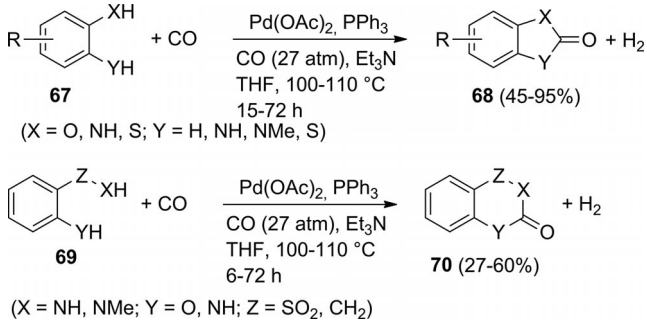
The oxidative carbonylation of 1,2- and 1,3-diols to afford the corresponding cyclic carbonates in moderate to good yields has also recently been achieved through the use



Scheme 42. Synthesis of glycerol carbonate (**64**) and α-D-glucofuranose 1,2:5,6-dicarbonate (**66**) by PdI_2/KI-catalysed oxidative cyclocarbonylation of glycerol (**63**) and glucose (**65**), respectively.[51a]

of (neocuproine)$Pd(OAc)_2$ or $Pd(OAc)_2$/(–)-sparteine as the catalytic system, in the presence of *N*-chlorosuccinimide or dichloroisocyanuric acid as the oxidant and under atmospheric pressure of CO.[52] A bimetallic system, based on $Pd(OAc)_2$/$Mn(acac)_3$, has also been employed for the oxidative carbonylation of some 1,2-diols, including glycerol, under 20 atm of a $CO/O_2/N_2$ mixture at 60 °C.[53] The conversion of glycerol into glycerol carbonate has also been achieved with (phen)$PdCl_2$ in the presence of KI[54] or CuI[55] as the catalysts – under 30 atm of a CO/O_2 mixture (2:1) at 140 °C[54] or 24 atm of a CO/O_2 mixture (2:1) at 120 °C,[55] respectively (these, it should be noted, are potentially explosive conditions)[49] or with selenium-based promotion.[56]

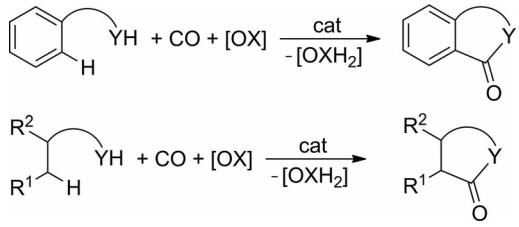
A direct synthesis of benzo-fused five- and six-membered heterocycles **68** and **70**, respectively (Scheme 43), by oxidative cyclocarbonylation of *ortho*-substituted phenol, thiophenol and aniline derivatives **67** and **69** with $Pd(OAc)_2$ as the catalyst in the presence of PPh_3 and Et_3N was recently reported.[57] Formation of molecular hydrogen accounted for the oxidative process (Scheme 43).[57]



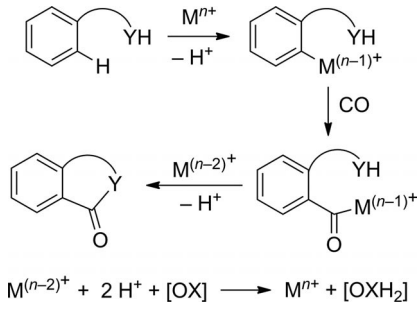
Scheme 43. Synthesis of benzo-fused five- and six-membered heterocycles **68** and **70**, respectively, by Pd-catalysed oxidative cyclocarbonylation of *ortho*-substituted phenol, thiophenol and aniline derivatives **67** and **69**.[57]

Oxidative Carbonylation with C–H Activation Leading to Carbonylated Heterocycles

Under suitable conditions and with appropriate substrates, oxidative carbonylation can take place with simultaneous C–H activation and heterocyclization, as shown in Scheme 44. Mechanistically, the process begins with metallation of a C–H bond (usually *ortho*-metallation), followed by CO insertion and intramolecular nucleophilic displacement, as illustrated in Scheme 45.

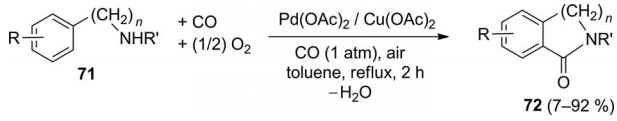


Scheme 44. Synthesis of carbonylated heterocycles by oxidative carbonylation with simultaneous C–H activation and heterocyclization.

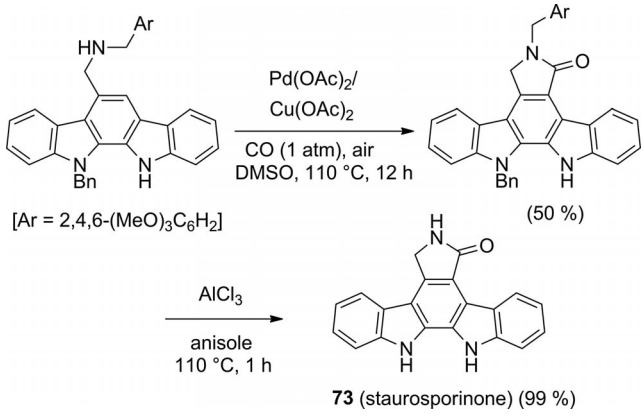


Scheme 45. Proposed mechanism for the oxidative carbonylation with simultaneous C–H activation and heterocyclization.

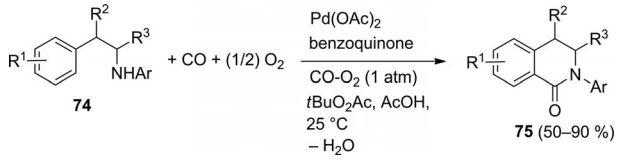
Several examples of reactivity of this kind, leading to a variety of carbonylated heterocycles, have been reported. Dialkylamines **71** (Scheme 46), with suitably placed phenyl groups on their alkyl chains, were converted into benzolactams **72** when allowed to react with CO (1 atm) in the presence of $Pd(OAc)_2$/$Cu(OAc)_2$ as the catalytic system and O_2 as the oxidant.[36o] This reaction has recently been applied to the synthesis of the natural product staurosporinone (**73**, Scheme 47).[58] More recently, conditions for the conversion of β-arylalkylamines **74** (Scheme 48) into the corresponding benzolactams **75** at room temperature have been developed,[59] and *N*-unsubstituted benzolactams **77** (Scheme 49) have also been obtained from β-arylalkylamines **76** with use of $Pd(OAc)_2$ as catalyst and benzoquinone as oxidant.[60]



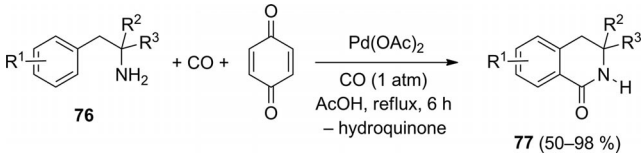
Scheme 46. Synthesis of benzolactam derivatives **72** by $Pd(OAc)_2$/$Cu(OAc)_2$-catalysed oxidative cyclocarbonylation of ω-arylalkylamines **71**.[36o]



Scheme 47. Pd^{II}-catalysed oxidative cyclocarbonylation as the key step in the synthesis of staurosporinone (**73**).[58]

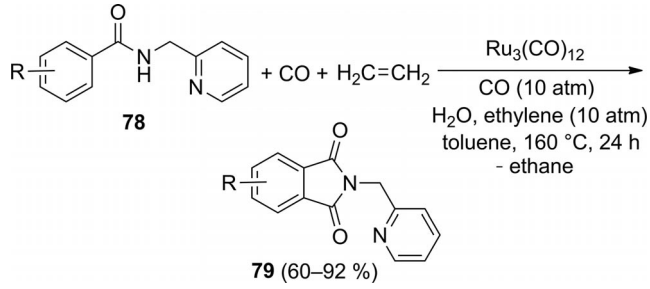


Scheme 48. Synthesis of benzolactam derivatives **75** by $Pd(OAc)_2$/benzoquinone-catalysed oxidative cyclocarbonylation of β-arylalkylamines **74**.[59]

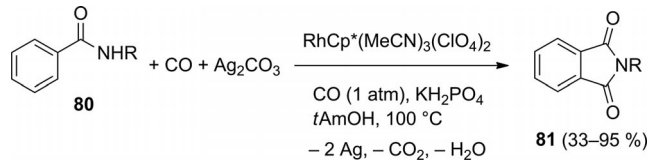


Scheme 49. Synthesis of *N*-unsubstituted benzolactam derivatives **77** by $Pd(OAc)_2$-catalysed oxidative cyclocarbonylation of β-arylalkylamines **76**.[60]

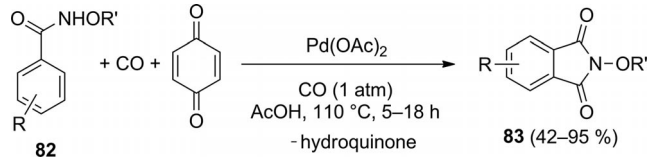
Phthalimides can be obtained from aromatic amides in a similar way. Different reaction conditions to achieve this kind of transformation have also been developed in this case. Chatani and co-workers used $Ru_3(CO)_{12}$ as catalyst, in the presence of water as promoter and ethylene as hydrogen acceptor, to convert *N*-(pyridin-2-ylmethyl)benzamides **78** (Scheme 50) into the corresponding phthalimide derivatives **79**.[61] The presence of the coordinating pyridyl substituent was essential for the success of the reaction,[61] but this limitation was recently overcome by Rovis and co-workers, who employed $RhCp^*(MeCN)_3(ClO_4)_2$ as catalyst in the presence of Ag_2CO_3 as oxidant and KH_2PO_4 under CO (1 atm) at 100 °C (Scheme 51).[62] In related works, *N*-alkoxybenzamides **82**[63] (Scheme 52) and electron-deficient amides **84**[64] (Scheme 53) were reported to afford phthalimides **83** and succinimides **85**, respectively, under Pd-catalysed oxidative carbonylation conditions.



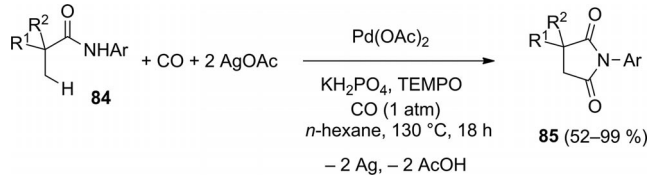
Scheme 50. Synthesis of *N*-(pyridin-2-ylmethyl)phthalimide derivatives **79** by $Pd(OAc)_2$-catalysed oxidative cyclocarbonylation of *N*-(pyridin-2-ylmethyl)benzamides **78**.[61]



Scheme 51. Synthesis of phthalimides derivatives **81** by Rh^{III}-catalysed oxidative cyclocarbonylation of benzamides **80**.[62]

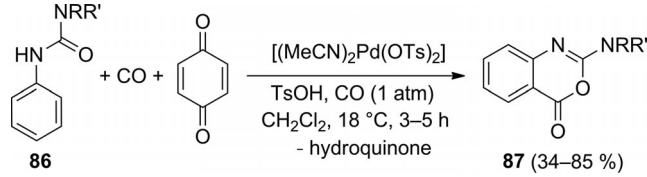


Scheme 52. Synthesis of *N*-alkoxyphthalimides derivatives **82** by Rh^{III}-catalysed oxidative cyclocarbonylation of *N*-alkoxybenzamides **81**.[63]

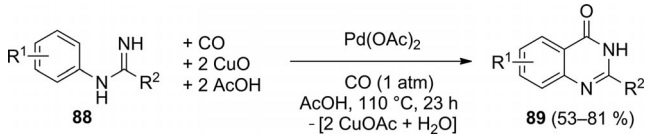


Scheme 53. Synthesis of succinimide derivatives by Pd^{II}-catalysed oxidative cyclocarbonylation of *N*-arylamides.[64]

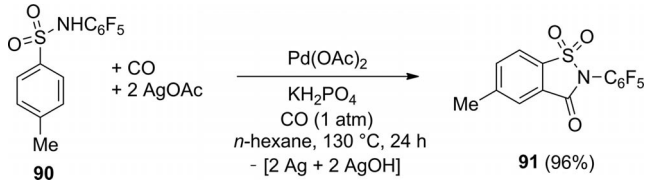
Palladium catalysis has also been employed for the synthesis of benzoxazinones **87** (Scheme 54),[65] quinazolinones **89** (Scheme 55),[66] benzosulfonimides **91** (Scheme 56),[67] 4*H*-isochromene-1,3-diones **93** (Scheme 57)[68] and 1-isochromanones **95** (Scheme 58).[69]



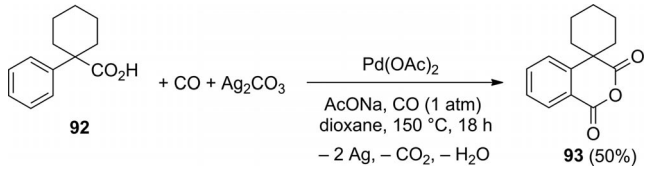
Scheme 54. Synthesis of benzoxazinones **87** by Pd^{II}-catalysed oxidative cyclocarbonylation of aryl urea derivatives **86**.[65]



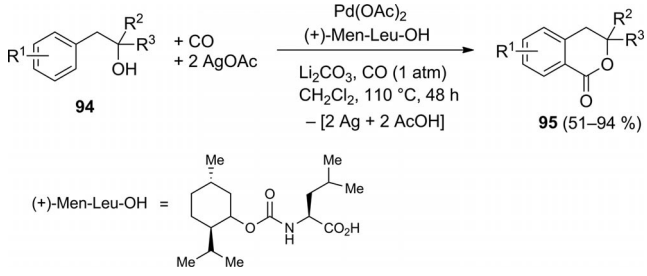
Scheme 55. Synthesis of quinazolinone derivatives **89** by Pd^{II}-catalysed oxidative cyclocarbonylation of *N*-arylamidines **88**.[66]



Scheme 56. An example of the synthesis of benzosulfonimides by Pd^{II}-catalysed oxidative cyclocarbonylation of sulfonamide derivatives.[67]



Scheme 57. An example of the synthesis of 4*H*-isochromene-1,3-diones by Pd^{II}-catalysed oxidative cyclocarbonylation of phenylacetic acid derivatives.[68]



Scheme 58. Synthesis of 1-isochromanone derivatives **95** by Pd^{II}-catalysed oxidative cyclocarbonylation of phenethyl alcohols **94**.[69]

Conclusions

Oxidative carbonylation is an excellent methodology for the direct synthesis of carbonyl compounds starting from simple building blocks. When applied to suitably functionalized substrates, the process can occur with concomitant heterocyclization, thus leading to carbonylated heterocycles in one-step fashion. Different catalytic systems and reaction conditions have been employed to achieve the synthesis of a variety of carbonylated heterocycles by the oxidative carbonylation approach. The PdI_2/KI catalytic system, developed in our laboratories, has proved particularly efficient for oxidative carbonylation of acetylenic substrates bearing nucleophile groups in suitable positions for cyclization. A key characteristic of this system is the efficiency of the metal reoxidation process, which occurs with use only of oxygen as the oxidant and with production of water as coproduct, making the PdI_2/KI-catalysed oxidative carbonylation reactions very attractive from the points of view of atom economy and sustainability. Another very important facet of this catalyst relates to its versatility, because it is able not only to promote different mechanistic pathways in the case of acetylenic substrates, but also to catalyse the oxidative carbonylation of different kinds of organic substrates, such as alkynes, amines, β-amino alcohols and diols. Other catalytic systems have been employed for the oxidative carbonylation of acetylenic, olefinic and allenic substrates, as well as of amines, β-amino alcohols and diols, mainly based on Pd^{II} complexes, in the presence of different oxidants, usually $CuCl_2$ or benzoquinone. Tungsten has also been successfully employed for the synthesis of cyclic ureas from diamines, whereas sulfur and selenium have been shown to catalyse the oxidative carbonylation of β-amino alcohols to oxazolidinones. Finally, C–H activation with simultaneous heterocyclization can also take place under oxidative carbonylation conditions, leading to carbonylated heterocycles. Different catalytic systems based on palladium, ruthenium or rhodium complexes have been developed to achieve processes of this kind.

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