

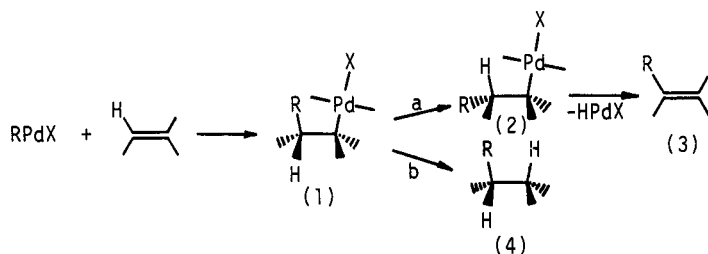
## The palladium-catalyzed hydroarylation and hydrovinylation of carbon-carbon multiple bonds: new perspectives in organic synthesis

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### GENERAL CONSIDERATIONS

It is well known that  $\sigma$ -aryl and  $\sigma$ -vinylpalladium complexes can react with carbon-carbon double bonds to produce vinylic substitution products (3) through a syn-addition/syn- $\beta$ -elimination path, (a):

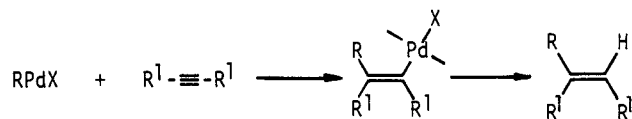


This reaction, the Heck's reaction, has been the subject of several mechanistic and synthetic studies and has a wide field of application in organic synthesis.<sup>1</sup>

$\sigma$ -Alkylpalladium complexes (1), however, under suitable reaction conditions, are able to undergo a carbon-palladium bond fission substituting the carbon-hydrogen bond for the carbon-palladium bond (pathway b). The net result is the formation of the addition product (4).

Depending on the nature of the added carbon unit, hydroarylation (R = aryl) and hydrovinylation (R = alkenyl) reactions can be performed.

A related addition reaction can occur by reacting  $\sigma$ -aryl and  $\sigma$ -vinylpalladium intermediates with acetylenic systems.



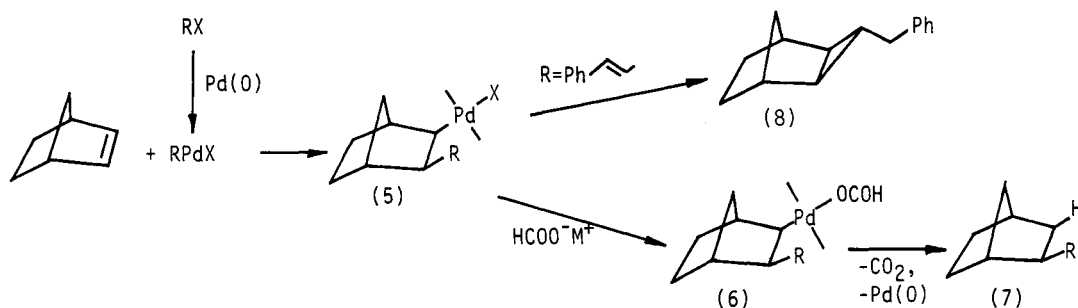
R = aryl, alkenyl

The aim of the present review is to report an account on these palladium-catalyzed addition reactions with olefinic and acetylenic systems.

#### a) Olefins

Usually mono- and disubstituted olefinic systems do not undergo hydroarylation and hydrovinylation reactions. The syn- $\beta$ -elimination of HPdX is by far the preferred decomposition pathway of intermediates (1).

Olefins containing particular structural features, however, can produce addition products (4). For example cyclic, strained olefins, like norbornenes, are almost ideal substrates for such a reaction. In fact,  $\sigma$ -alkylpalladium intermediates (5), derived from the addition of RPdX species to the carbon-carbon double bond, are unable to undergo rotation to reach the conformation required for the syn- $\beta$ -elimination of HPdX and can wait for reacting with the hydrogen donor. Some bicyclic olefinic systems have been reported to react with aryl and vinyl halides in the presence of Pd(OAc)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, formic acid as the hydrogen donor, and n-Bu<sub>3</sub>N as the base<sup>2</sup> or Pd(OAc)<sub>2</sub>, n-Bu<sub>4</sub>NCl, and HCOOK (HCOONa, HCOOLi and HCOOCs were also tested)<sup>3</sup> to give the corresponding hydroarylated and hydrovinylated derivatives (7) usually in good yield.

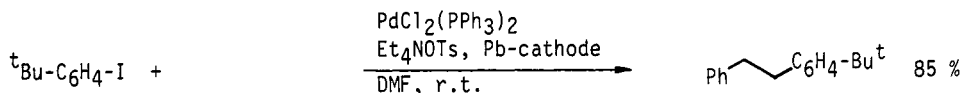


$\text{M}^+ = n\text{-Bu}_3\text{NH}^+, \text{Na}^+, \text{K}^+, \text{Cs}^+$ ;  $\text{R} = \text{aryl, alkenyl}$

According to the above scheme, the formate anion reacts with the intermediate (5) producing the norbornyl palladium formate (6) from which (7) is generated through decarboxylation and Pd(0) deinsertion. With vinyl halides competing cyclopropanation to (8) can be observed.<sup>2,4</sup>

Addition products can also be obtained when  $\sigma$ -alkylpalladium intermediates (1) do not contain  $\beta$ -hydrogens.<sup>5</sup>

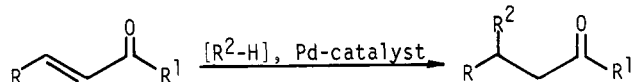
The hydroarylation of styrene has been performed through an electroreductive reaction.<sup>6</sup>



The reaction fails to produce hydroarylated products in the presence of non-conjugated olefins, e.g., ethylvinyl ether, allyl alcohol, and allyl bromide.

## b) $\alpha,\beta$ -Enones and -Enals

When  $\alpha,\beta$ -enones and -enals are concerned, the reaction is usually referred to as a conjugate addition-type reaction



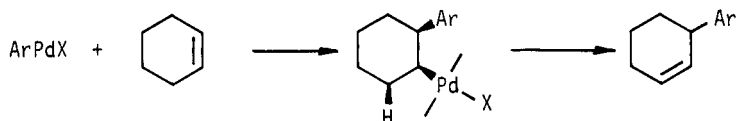
The formation of C-C bond between the  $\beta$ -carbon atom of an  $\alpha,\beta$ -unsaturated carbonyl system and an unstabilized carbanion is generally achieved through conjugate addition of organocopper reagents<sup>7</sup> or organomagnesium reagents in the presence of catalytic amounts of copper.<sup>7</sup> In addition to these largely applied methods, even organoaluminium compounds with<sup>8</sup> and without<sup>9</sup> the presence of nickel as catalyst, organozirconium species in the presence of nickel,<sup>10</sup> and organoboron compounds<sup>11</sup> have been reported to undergo conjugate addition to  $\alpha,\beta$ -unsaturated carbonyl compounds.

All these methods allow placement of a variety of hydrocarbons  $\beta$  to a carbonyl function. Regarding ease of preparation of starting materials, stability of reagents, efficiency, and selectivity of the reaction, each procedure has its relative advantages and disadvantages. However, an essentially common limitation can be recognized in what concerns the nature of functional groups tolerated in the carbon framework to be transferred to the  $\beta$ -carbon atom.

In this respect, the use of organopalladium complexes as carbon donors, known to tolerate a wide variety of functionalities, allows widening the scope of the conjugate addition in organic synthesis. Clearly, the realization of such addition reactions with palladium complexes has to face diverse difficulties depending on whether acyclic or cyclic systems are concerned. With acyclic  $\alpha,\beta$ -unsaturated carbonyl compounds a more arduous task is to be reached since the corresponding intermediate (1) should be forced to undergo substitution of the  $\text{C}_\alpha\text{-H}$  bond for the  $\text{C}_\alpha\text{-Pd}$  bond faster than rotation around the  $\text{C}_\alpha\text{-C}_\beta$  bond and syn- $\beta$ -elimination of  $\text{HPdX}$ . With cyclic systems the rigidity of the ring should prevent the  $\sigma$ -alkylpalladium adduct from achieving the syn-relationship between the  $\beta$ -hydrogen and the palladium atom which is normally required for the syn- $\beta$ -elimination.

Thus, in the presence of a suitable hydrogen donor, the formation of the C<sub>α</sub>-H bond should be favoured.

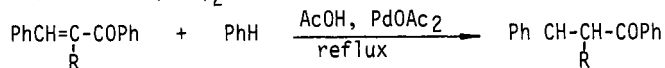
For example, because of the ring rigidity,  $\sigma$ -alkylpalladium adducts derived from the reaction of  $\sigma$ -arylpalladium complexes with cycloalkenes produce allylic derivatives instead of vinylic substitution products.<sup>12</sup>



Significant results have been obtained by using benzene, arylmercury compounds, aryltin compounds, and aryl halides as precursors of  $\sigma$ -arylpalladium intermediates under a variety of reaction conditions.

### Reaction with benzene

The first example of a palladium-catalyzed conjugate addition deals with the reaction of chalcones containing bulky electron-withdrawing groups on the  $\alpha$ -carbon with benzene in the presence of AcOH and Pd(OAc)<sub>2</sub>.<sup>13</sup>



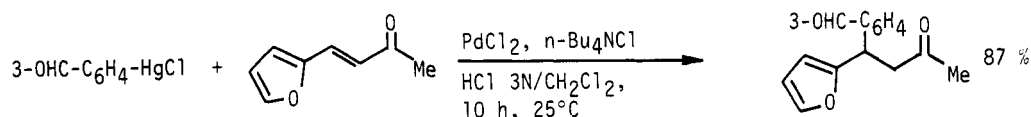
R = CPh, NO<sub>2</sub>, COOEt, COOH

15-52 % yield

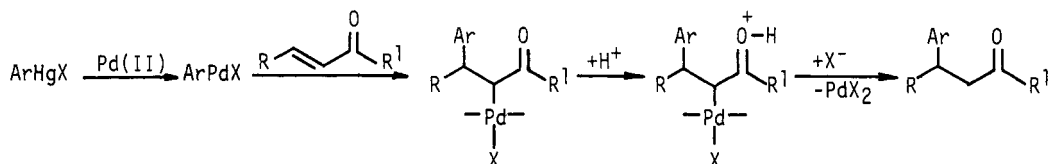
Although interesting, this addition reaction appears to be of limited synthetic value because of the strict requirements in the structure of the substrate. Furthermore, arenes produce  $\sigma$ -arylpalladium intermediates through an electrophilic substitution reaction.<sup>14</sup> A lack of selectivity in the formation of the carbon-palladium bond when substituted benzenes are concerned is to be expected, thus giving rise to a variety of  $\sigma$ -arylpalladium intermediates and consequently to a mixture of conjugate addition-type products.

### Reaction with arylmercury and aryltin compounds

The scope and usefulness of the palladium-catalyzed conjugate addition-type reaction was significantly broadened by the discovery that arylmercury compounds could be used as aryl donors to the  $\beta$ -carbon.<sup>15,16</sup> The reaction is carried out in the presence of catalytic amounts of PdCl<sub>2</sub> and *n*-Bu<sub>4</sub>NCl in an acidic two-phase system at room temperature.



Experimental evidences are consistent with the following reaction mechanism.



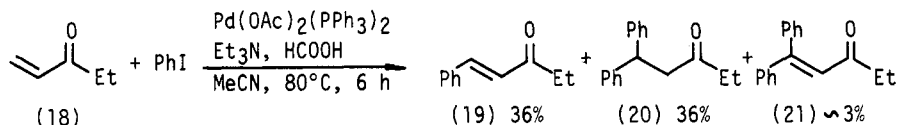
Since arylmercury compounds are readily available, stable compounds, able to accommodate essentially all of the important organic functional groups and no particular steric and/or electronic constraints in the  $\alpha,\beta$ -unsaturated carbonyl compounds are required, this reaction provides a very efficient route for introducing functionalized aryl unit B to  $\alpha,\beta$ -enones and enals. Only hindered  $\alpha,\beta$ -unsaturated carbonyl compounds fail to give conjugate addition-type products.

Tetraphenyltin, the only tin compound examined, afforded results very close to those obtained with phenylmercury chloride.<sup>15</sup>

An interesting consequence of the introduction of functionalized aryl units is that addition products containing an aromatic ring with a nucleophilic site in the ortho position have potential as convenient reagents for annulation reactions.

Annulation reactions have been indeed realized and 2-chromanols (9),<sup>17</sup> 2-chromenes (10),<sup>17</sup> quinolines (11-13),<sup>18</sup> and indanols (14)<sup>19</sup> have been prepared in good to high yields.

changes: more hindered groups tend to favour the conjugate addition path presumably through restriction in rotation around the  $C_{\alpha}$ - $C_{\beta}$  bond necessary to attain the conformation required for syn- $\beta$ -elimination of HPdX. A convincing evidence of how the substituent on the  $\beta$ -carbon can affect the reaction pathway is given by the reaction of pent-1-en-3-one with phenyl iodide.



This result can be accounted for by assuming that the  $\beta$ -unsubstituted- $\alpha,\beta$ -enonic system (18) reacts initially through the known vinylic substitution path; then, the in situ formed  $\beta$ -substituted- $\alpha,\beta$ -enonic derivative (19) reacts further to produce selectively the conjugate addition derivative (20). Compound (21) was detected only in traces.

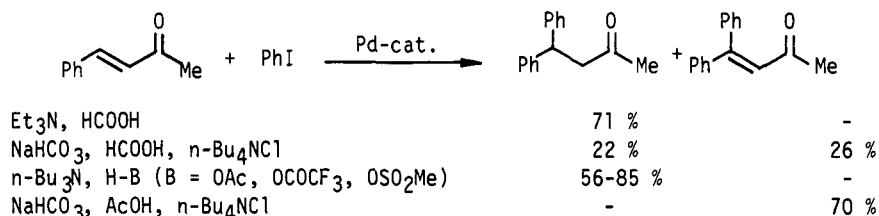
Based on this observation, a variety of aryl iodides have been reacted with butenone, 1-penten-3-one, and propenal to give saturated  $\beta,\beta$ -diaryl ketones and  $\beta,\beta$ -diaryl aldehydes.<sup>22</sup>

Electronic effects related to the group attached to the olefinic double bond affect the conjugate addition/vinylic substitution ratio. An increase in the electron withdrawing power tends to favour the formation of the conjugate addition product (see Table).

Table - Relative percentages of Conjugate Addition and Vinylic Substitution Product

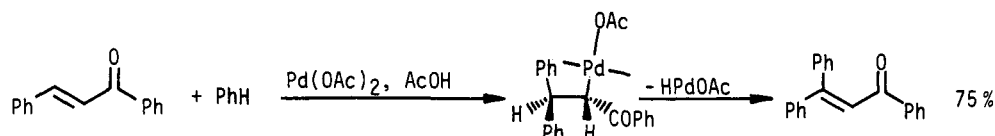
Entry	$\alpha,\beta$ -unsaturated carbonyl system	Conjugate addition product (%)	Vinylic substitution product (%)
a	PhCH=CHCOMe	94	6
b	PhCH=CHCHO	92	8
c	PhCH=CHCOOMe	19	81
d	PhCH=CHCONH <sub>2</sub>	23	77

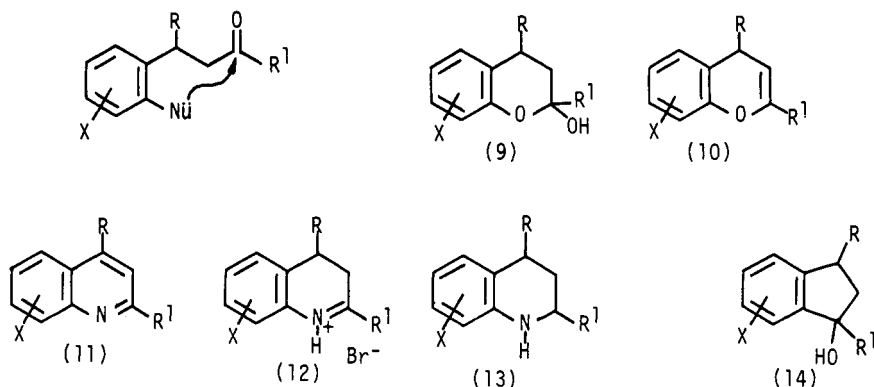
Even the added base plays a not negligible role in the competition between conjugate addition and vinylic substitution.<sup>20,23</sup> The results obtained for the reaction of benzalacetone with phenyl iodide show that tertiary amines tend to favour the decomposition of  $\sigma$ -alkylpalladium intermediates (15) to give conjugate addition-type products, most likely through coordination of palladium.<sup>24</sup> Protonation\* could occur on this  $\sigma$ -alkylpalladium species containing a nitrogen-palladium bond favouring the  $C_{\alpha}$ -Pd bond breaking.<sup>23</sup>



The behaviour of acyclic  $\beta$ -substituted- $\alpha,\beta$ -enones and -enals in the presence of tertiary amines omitting formic acid or any other acid supports the view that formation of a nitrogen-Pd bond should be involved along the conjugate addition pathway. In fact, under these conditions,  $\beta$ -substituted- $\alpha,\beta$ -enones and -enals show a tendency to give conjugate addition-type products.

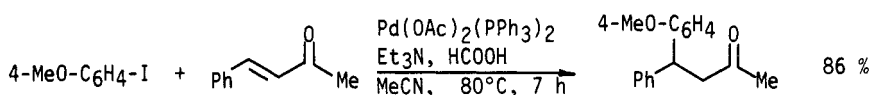
\* It is worth noting that the protonation by itself does not seem to play a dominant role. Decomposition of the  $\sigma$ -alkylpalladium intermediate derived from chalcone and phenylpalladium acetate in acetic acid has been reported to occur through syn- $\beta$ -elimination of HPdOAc.<sup>13</sup>





### Reaction with aryl halides

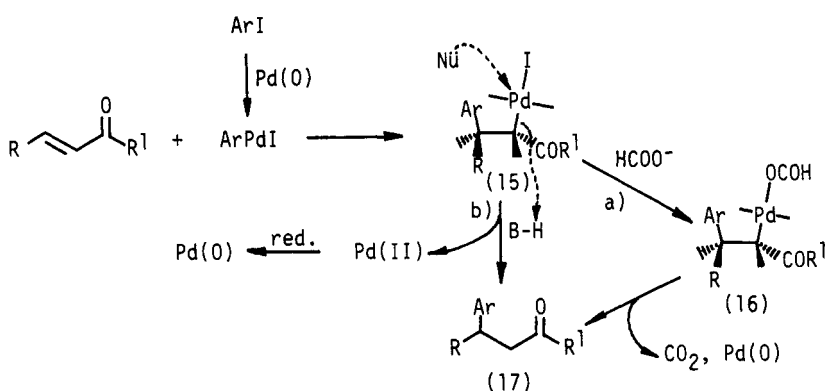
A further advance in the palladium-catalyzed conjugate addition-type reactions was brought about by the reaction of aryl iodides with  $\beta$ -substituted- $\alpha,\beta$ -enones and -enals in the presence of formic acid, tertiary amines, and catalytic amounts of palladium(II).<sup>19-21</sup>



Aryl iodides are clearly the most attractive starting materials since they are easily available and give rise to less problems (handling, waste processing, etc.) than mercurials.

Aryl bromides appear to be less effective than aryl iodides in participating in the conjugate addition path.<sup>20</sup>

Conjugate addition-type products (17) could arise from the addition of the in situ formed  $\text{ArPdI}$  species to the olefinic double bond to give (15), followed by its reaction with formate producing (16), deinsertion of carbon dioxide, and reductive elimination of palladium species (pathway a). Alternatively, compounds (17) could arise from the intermediate (15) through the  $\text{C}_\alpha$ -Pd heterolytic bond cleavage and protonation of the organic moiety (pathway b). According to this scheme, formic acid would be necessary to keep up the catalytic cycle by acting as the proton source for the protonation of the anionic moiety of  $\sigma$ -alkylpalladium species and as an efficient reducing agent for the conversion of  $\text{Pd(II)}$  species to  $\text{Pd(0)}$  species.



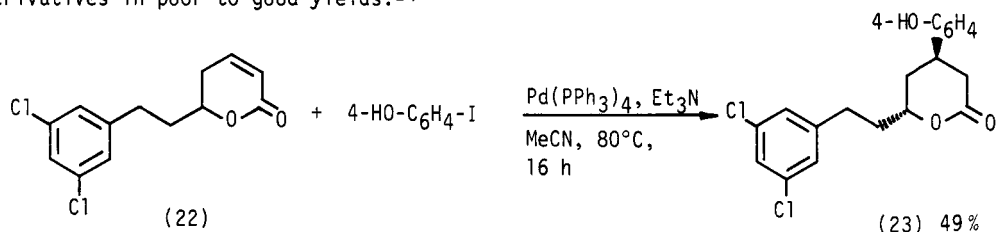
Competition between conjugate addition and vinylic substitution depends on a variety of steric, electronic, and medium effects affecting the reactivity of the intermediate (15).

No exhaustive studies on the role of steric effects have been reported. However, it was found that variations in the steric demand of the substituents bonded to the carbonyl group (from -H to  $-\text{C}_6\text{H}_4\text{-o-NO}_2$ ) or in the nature of the ligands of palladium [ $\text{Pd(OAc)}_2$ ,  $\text{Pd/C}$ ,  $\text{Pd(OAc)}_2(\text{PPh}_3)_2$ ] do not alter significantly the trend of the reaction.<sup>20</sup>

On the contrary, the nature of the substituent on the  $\beta$ -carbon can produce remarkable

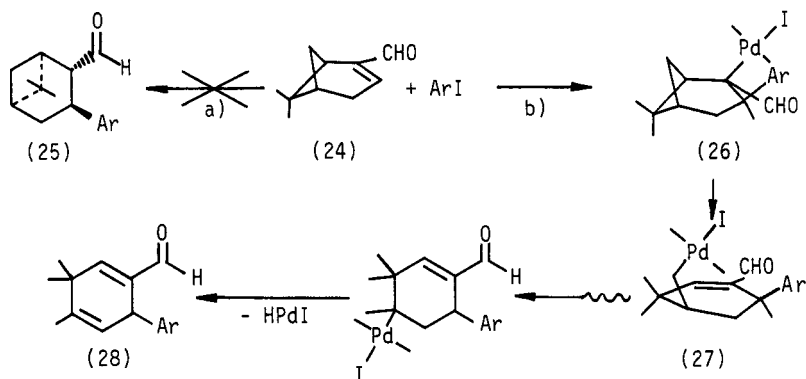
4,4-Diphenyl-butan-2-one was isolated in 14% yield treating benzalacetone with phenyl iodide in the presence of catalytic amounts of  $\text{Pd}(\text{OAc})_2(\text{PPh}_3)_2$  and  $n\text{-Bu}_3\text{N}$ .<sup>20</sup> Only traces, if any, of the corresponding vinylic substitution product were detected. With stoichiometric amounts of  $\text{Pd}(\text{OAc})_2(\text{PPh}_3)_2$  the yield of 4,4-diphenyl-butan-2-one increased up to 52%.<sup>20</sup> In practice, tertiary amines are able to behave as the hydrogen source in the conjugate addition pathway keeping up a catalytic cycle. Their efficiency, however, is not very high and the reaction stops quickly in the presence of catalytic amounts of palladium after producing variable amounts of conjugate addition-type derivatives (from traces to poor yields) and vinylic substitution derivatives (minor products).

Better yields of conjugate addition-type products with tertiary amines as the proton donors could be obtained with cyclic systems. Indeed, the reaction of aryl iodides with 6-alkyl-5,6-dihydro-2H-pyran-2-one (22) has been reported to give the reductively arylated derivatives in poor to good yields.<sup>24</sup>



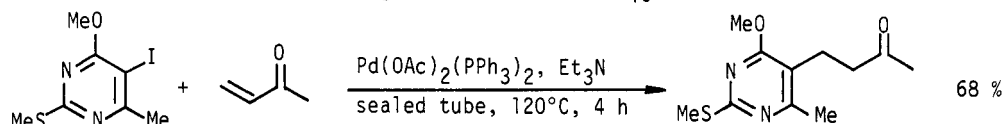
It is of interest to note that the cyclic structure allows the conjugate addition to occur preferentially in spite of the low electron withdrawing power of the carbonyl group.

Myrtenal (24), however, a strained bicyclic  $\alpha,\beta$ -enal reported to be a useful reagent for the preparation of pinane analogues of thromboxane  $\text{A}_2$ , does not give the conjugate addition product (25) in the presence of  $n\text{-Bu}_3\text{N}$  nor in the presence of the  $n\text{-Bu}_3\text{N}/\text{HCOOH}$  combination but the monocycle derivative (28), most likely according to the following scheme.<sup>2</sup>



Rearrangement of (26) to (27) is faster than trapping of (26) with formate or tertiary amine.

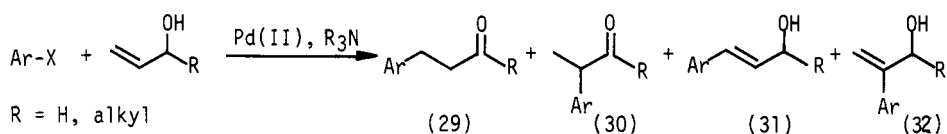
In the presence of  $\text{Et}_3\text{N}$  conjugate addition-type products were obtained at elevated temperatures from the palladium-catalyzed reaction of iodopyrimidines with butenone.<sup>25</sup>



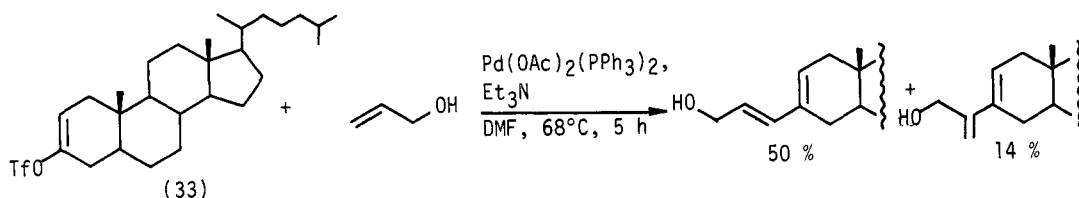
Bromopyrimidines give the usual vinylic substitution reaction. Steric and electronic effects have been invoked to account for the observed results.

### c) Allylic alcohols

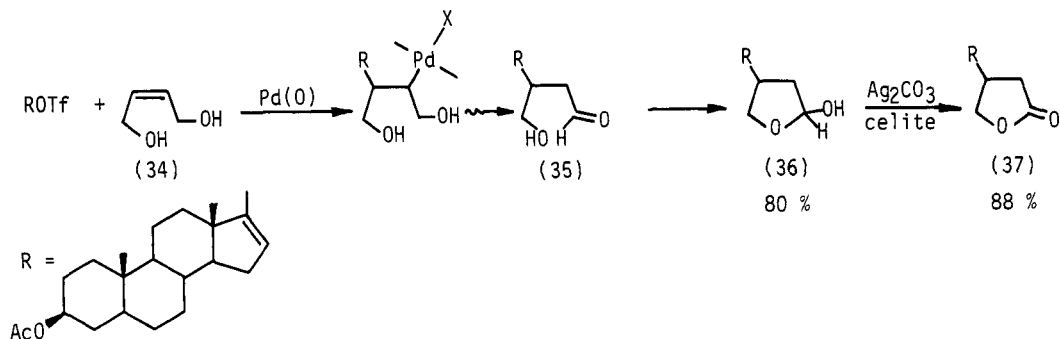
Allylic alcohols react with aryl and heteroaryl halides to give 3-arylated (hetero-arylated) aldehydes and ketones (29) as the main products through a reaction which formally corresponds to the conjugate addition-type reactions of  $\alpha,\beta$ -enones and -enals.<sup>26</sup>



2-Arylated (heteroarylated) aldehydes and ketones (30) as well as allylic alcohols (31) and (32) are the observed by-products. Relative percentages were found to depend on the structure of the allylic alcohol, the steric hinderance of the added aryl (heteroaryl) unit, and the presence of a phosphine ligand. The reaction of allylic alcohols with vinyl halides proceeds through the formation of  $\pi$ -allylpalladium complexes. The use of piperidine instead of triethylamine as the acid acceptor has been reported to be necessary for keeping up a catalytic cycle. Depending on the nature of the allylic alcohol, the usual carbonyl derivatives and/or amino alcohols were obtained.<sup>27</sup> The reaction of allylic alcohols with vinyl triflates, recently introduced as efficient vinyl donors in palladium-catalyzed reactions,<sup>28</sup> has so far attracted only cursory examination and the reaction of cholest-2-en-3-yl triflate (33) with allyl alcohol in the presence of Et<sub>3</sub>N is the only example described. Two isomeric allylic alcohols were in this case isolated.



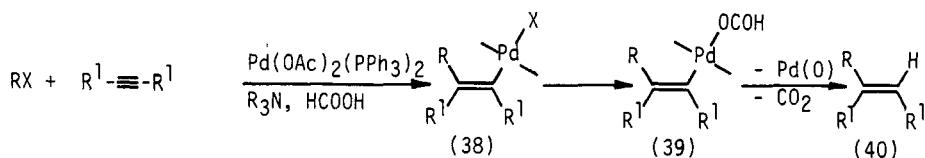
In the presence of the diallylic alcohol Z-1,4-butendiol (34), NaHCO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub>, and n-Bu<sub>4</sub>NCl, vinyl triflates afford hemiacetals (36) in good to high yield.<sup>29</sup>



In this reaction (34) behaves like a synthetic equivalent of 4-hydroxy-2-butenal and the aldol (35) formally corresponds to its conjugate addition derivative. Hemiacetals (36) can be smoothly converted into  $\beta$ -substituted- $\gamma$ -butyrolactones (37) by oxidation with Ag<sub>2</sub>CO<sub>3</sub> on celite so that the overall process allows an easy and efficient introduction of the butyrolactone ring into widely diffused ketonic compounds. The reaction has been successfully extended to a variety of aryl halides containing several functional groups.

#### d) Alkynes

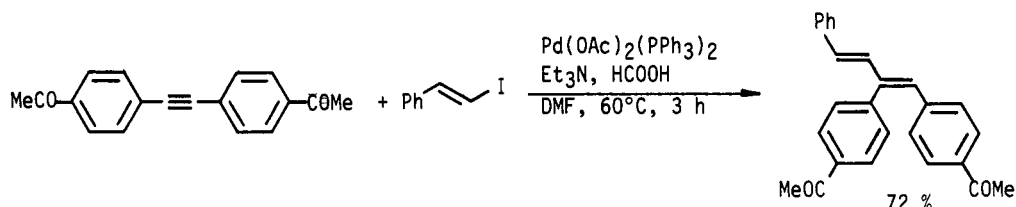
Symmetrically disubstituted alkynes react with aryl and vinyl halides in the presence of the formate-palladium system to give stereoselectively<sup>30,31</sup> hydroarylated and hydrovinylated products (40) according to the following reaction path.



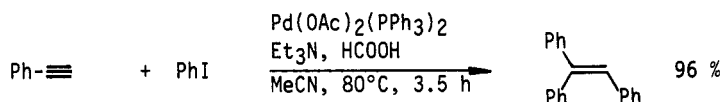
Very likely the reaction proceeds through the syn-addition of the in situ formed aryl or vinylpalladium intermediate to the carbon-carbon triple bond, followed by the reaction of (38) with formate to give (39). Subsequent decarboxylation and reductive elimination of palladium gives rise to the olefinic derivative (40).

The isolation of the deuterated olefinic derivative when the reaction is carried out with monodeuterated formic acid, DCOOH, is consistent with the above mechanism.

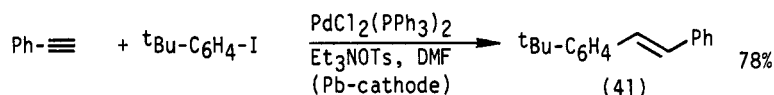
With vinyl halides the reaction allows a convenient entry into functionalized stereodefined 1,3,4-trisubstituted dienes not easily available by known procedures.<sup>32</sup>



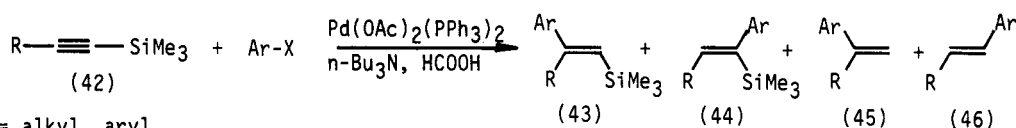
An interesting feature of the reaction is the possibility to carry out a one-pot synthesis of trisubstituted alkenes from monosubstituted alkynes.<sup>30</sup>



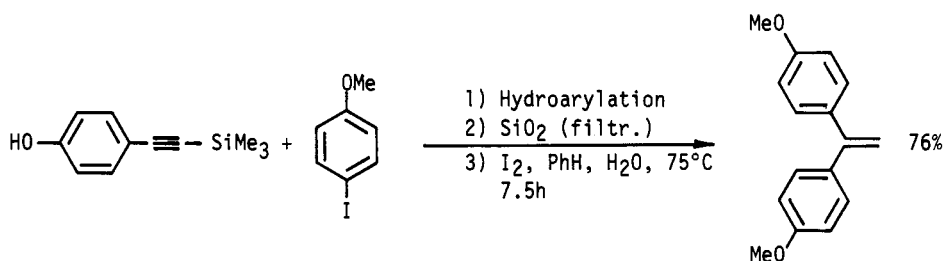
The reaction of phenylacetylene with 4-tert-butylphenyl iodide under electroreductive conditions, however, affords the olefinic derivative (41).<sup>6</sup>



In the presence of unsymmetrically disubstituted acetylenes a lack of regioselectivity is to be expected unless a bulky end is introduced on one side of the carbon-carbon triple bond. In fact, the reaction of aryl iodides with aryl and alkyl, ethynyltrimethylsilanes (42) shows that steric hindrance can control the regiochemical outcome of the reaction. The bulky trimethylsilyl group favours the regioselective formation of (43).<sup>33</sup>

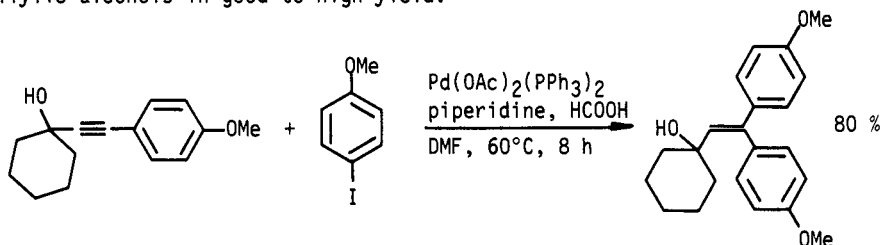


Depending on the nature of the functionalities in the starting ethynylsilane (42) and aryl iodide, variable amounts of the regioisomeric vinyl silanes (44) can be isolated as well as the desilylated olefins (45) and (46). The reaction is well suited also for direct conversion of (42) to 1,1-disubstituted ethylenes (45) without isolation of the silyl intermediates.



The addition of an hydroxy group on the bulky end of the acetylenic system can provide better regioselectivity very likely through the involvement of hydroxyl coordination to palladium in the addition step paralleling the dominant steric control.

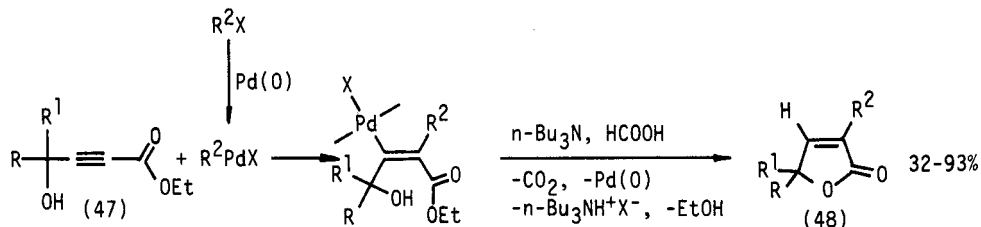
Several aryl, ethynyldialkylcarbinols have been regioselectively converted into  $\gamma,\gamma$ -diaryllallylic alcohols in good to high yield.<sup>34</sup>





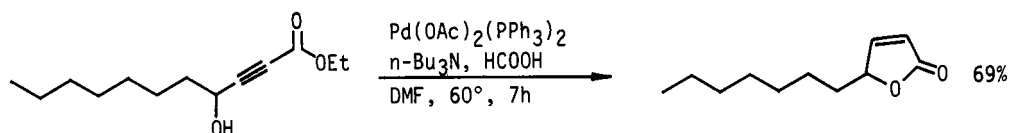
The reaction of propargyl alcohol derivatives with vinyl halides holds promise as a convenient entry into 1,3-dienes containing an oxygen atom and a center of chirality at the allylic position.<sup>32</sup> The nature of the base, the ligand, and the temperature affect the yield and the regiochemical outcome of the reaction.

Since the syn stereochemistry of addition of organopalladium species pushes the substituents of the acetylenic system on the same side of the carbon-carbon double bond, in the presence of suitable functionalities intramolecular cyclization can follow the addition step providing access to substituted cyclic derivatives. This addition/cyclization methodology has been successfully applied to the regioselective synthesis of 3-aryl and 3-alkenyl butenolides (48) from alkyl 4-hydroxy-2-alkynoates (47) and aryl and vinyl halides.<sup>35</sup>



Cyclization to the butenolide ring occurs under hydroarylation(vinylation) conditions.

It is of interest to report that in the presence of the palladium-tributylammonium formate reducing system, omitting aryl and vinyl halides, ethyl 4-hydroxy-2-alkynoates undergo a hydrogenation/cyclization reaction.



This reaction appears to be a useful alternative to established procedures using molecular hydrogen/Lindlar catalyst followed by acid catalyzed cyclization.<sup>36</sup>

### CONCLUDING REMARKS

A number of hydroarylation and hydrovinylation reactions on carbon-carbon double and triple bonds have been explored. These reactions, simple to carry out and not requiring any special techniques, are not only mechanistically interesting but also represent a useful tool in organic synthesis. The compatibility with many functional groups makes them of value for preparing polyfunctional derivatives without the necessity of employing protecting groups. Particularly, the conjugate addition-type reaction of  $\alpha,\beta$ -unsaturated carbonyl compounds widens further the usefulness and the scope of a well established methodology and the hydroarylation and hydrovinylation of acetylenic systems provide the organic chemist with completely new synthetic opportunities.

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### REFERENCES

- 1) Heck, R.F., "Palladium Reagents in Organic Synthesis", Academic Press, Inc., 1985
- 2) Arcadi, A.; Marinelli, F.; Bernocchi, E.; Cacchi, S.; Ortar, G. J. Organomet. Chem. (1989) **368**, 249
- 3) Larock, R.C.; Johnson, P.L. J. Chem. Soc., Chem. Comm., in press
- 4) Catellani, M.; Chiusoli, G.P.; Giroladini, W.; Salerno, G. J. Organomet. Chem. (1980) **199**, C21
- 5) Larock, R.C.; Babu, S. Tetrahedron Lett. (1987) **28**, 5291
- 6) Torii, S.; Tanaka, H.; Morisaki, K. Chem. Lett. (1985) 1353

- 7) Posner, H.G. *Organic React.* (1972) 19, 1
- 8) Bagnell, L.; Jeffery, E.A.; Meister, A.; Mole, T. *Aust. J. Chem.* (1975) 28, 801; Ashby E.C.; Heinson, G. *J. Org. Chem.* (1974) 39, 3297
- 9) Bernaby, K.F.; Floyd, M.B.; Poletto, J.F.; Weiss, M.J. *J. Org. Chem.* (1979) 44, 1438; Collins, P.W.; Dajani, E.Z.; Bruhn, M.S.; Brown, H.C.; Palmer, J.R.; Rappo, R. *Tetrahedron Lett.* (1975) 4217; Kabalka, G.W.; Daley, R.F. (1973) 95, 4428
- 10) Schwartz, J.; Loots, M.J.; Kosugi, H. *J. Am. Chem. Soc.* (1980) 102, 1333
- 11) P. Jacob, Brown, H.C. *J. Am. Chem. Soc.* (1976) 98, 7832; Sinclair, J.A.; Molander, G.A.; Brown, H.C. *J. Am. Chem. Soc.* (1977) 99, 954; Molander, G.A.; Brown, H.C. *J. Org. Chem.* (1977) 42, 3106
- 12) Larock, R.C.; Baker, B.E. *Tetrahedron Lett.* (1988) 29, 905; Larock, R.C.; Gong, W.H. *J. Org. Chem.* (1989) 54, 2047
- 13) Yamamura, K. *J. Org. Chem.* (1978) 43, 724
- 14) Fujiwara, Y.; Asano, R.; Moritani, I.; Teranishi, S. *J. Org. Chem.* (1976) 41, 1681
- 15) Cacchi, S.; La Torre, F.; Misiti, D. *Tetrahedron Lett.* (1979) 4591
- 16) Cacchi, S.; Misiti, D.; Palmieri, G. *Tetrahedron* (1981) 37, 2941
- 17) Cacchi, S.; Misiti, D.; Palmieri, G. *J. Org. Chem.* (1982) 47, 2995
- 18) Cacchi, S.; Palmieri, G. *Tetrahedron* (1983) 39, 3373
- 19) Cacchi, S.; Palmieri, G. *J. Organomet. Chem.* (1985) 282, C3
- 20) Cacchi, S.; Arcadi, A. *J. Org. Chem.* (1983) 48, 4236
- 21) Cacchi, S.; La Torre, F.; Palmieri, G.; J. *Organomet. Chem.* (1984) 268, C48; Arcadi, A.; Cacchi, S.; Marinelli, F. *J. Organomet. Chem.* (1986) 312, C27
- 22) Cacchi, S.; Palmieri, G. *Synthesis* (1984) 575
- 23) Amorese, A.; Arcadi, A.; Bernocchi, E.; Cacchi, S.; Cerrini, S.; Fedeli, W.; Ortar, G. *Tetrahedron* (1989) 45, 813
- 24) Stokker, G.E.; *Tetrahedron Lett.* (1987) 28, 3179
- 25) Wada, A.; Yasuda, H.; Kanamoto, S. *Synthesis* (1988) 771
- 26) Melpoder, J.B.; Heck, R.F. *J. Org. Chem.* (1976) 41, 265; Chalk, A.J.; Magennis, S.A. *J. Org. Chem.* (1976) 41, 1206; Tamaru, Y.; Yamada, Y.; Yoshida, Z.-I. *Tetrahedron* (1979) 35, 329
- 27) Kao, L.-C.; Stakem, F.G.; Patel, B.A.; Heck, R.F. *J. Org. Chem.* (1982) 47, 1267
- 28) Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* (1984) 25, 2271
- 29) Arcadi, A.; Bernocchi, E.; Cacchi, S.; Marinelli, F. sent for publication
- 30) Cacchi, S.; Felici, M.; Pietroni, B. *Tetrahedron Lett.* (1984) 25, 3137
- 31) Arcadi, A.; Cacchi, S.; Ianelli, S.; Marinelli, F.; Nardelli, M. *Gazz. Chim. It.* (1986) 116, 725
- 32) Arcadi, A.; Bernocchi, E.; Burini, A.; Cacchi, S.; Marinelli, F.; Pietroni, B. *Tetrahedron Lett.* (1989) 30, 3465
- 33) Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron Lett.* (1986) 27, 6397
- 34) Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron* (1985) 41, 5121
- 35) Arcadi, A.; Bernocchi, E.; Burini, A.; Cacchi, S.; Marinelli, F.; Pietroni, B. *Tetrahedron* (1988) 44, 481; Arcadi, A.; Cacchi, S.; Marinelli, F.; Misiti, D. *Tetrahedron Lett.* (1988) 29, 1457
- 36) Barua, N.C.; Schmidt, R.R. *Synthesis* (1986) 891; Neumann, M.F.; Sedrati, M.; Vigneron, J.P.; Bloy, V. *Angew. Chem. Int. Ed. Engl.* (1985) 24, 996; Vigneron, J.P.; Blanchard, J.M. *Tetrahedron Lett.* (1980) 21, 1739