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DOUBLE BOND FORMATION BY ONE POT PALLADIUM INDUCED REACTIONS BETWEEN ALDEHYDES, ALLYLIC ALCOHOLS AND TRIPHENYLPHOSPHINE[1]

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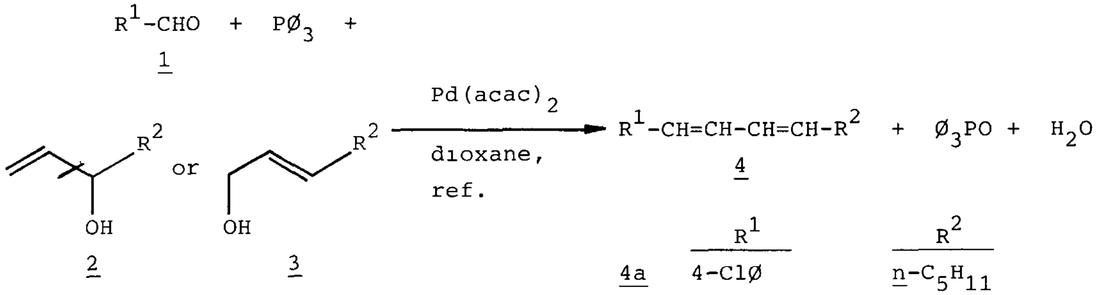
Abstract. The reactions between several aldehydes, two allylic alcohols and triphenylphosphine under palladium catalysis leads to double bond formation, synthetically parallelizing the Wittig reaction.

Transition metals promoted reactions have attracted a great deal of interest in the last few years. Now we want to report our initial results on the title reactions. These give the corresponding olefins, which would be also obtained by the classical Wittig reaction. Thus, when 4-chlorobenzaldehyde, 1-octen-3-ol and triphenylphosphine were refluxed together in dry dioxane, under N_2, in the presence of 5% molar $Pd(acac)_2$, and passing the refluxing solvent through molecular sieves(4Å), 1-(4-chlorophenyl)nona-1,3-diene, 4a was isolated as a mixture of stereoisomers (g.l.c.) in 49% yield. The diene 4a was hydrogenated (10% Pd-C, AcOEt) to 1-(4-chlorophenyl)nonane, 5a which was shown to be pure (>99%) by g.l.c. Unreacted aldehyde and phosphine were recovered but no 1-octen-3-ol could be detected. The reaction was also carried out with two equivalents of the alcohol (run 2), the diene yield being raised to 68%. Part of the refluxing dioxane was distilled off showing two additional peaks in g.l.c. The distillate was hydrogenated (10% Pd-C) and n-octane was then characterized by comparison with an authentical specimen. The two additional peaks detected before hydrogenation can be consequently assigned to Z and E-octa-1,3-diene. Indeed, eliminations in allylic alcohols and derivatives under palladium catalysis are well precedented[2-6].

The above described double bond formation seems to be quite general as indicated in the table. Examples with one primary and one secondary alcohol are collected as well as cases involving several aromatic and one aliphatic aldehydes. An allylic acetate (run 6) reacts also properly.

The studied reactions take place at the terminal allylic carbon regardless of the primary or secondary nature of the starting alcohol.



	R^1	R^2
4a	4-ClØ	n-C_5H_{11}
4b	4-O_2NØ	n-C_5H_{11}
4c	4-MeOØ	n-C_5H_{11}
4d	n-C_5H_{11}	n-C_5H_{11}
4e	4-O_2NØ	n-C_3H_7

Hydrogenations of olefins 4[7] (mixture of stereoisomers) gave the saturated compounds 5, with additional reduction of the nitro groups of 4b and 4e. Products 5[8] were >99% pure by g.l.c.

$$\underline{4} \xrightarrow[\text{AcOEt}]{H_2/Pd\text{-}C} R^3\text{-}(CH_2)_4\text{-}R^2$$

	R^3	R^2
5a	4-ClØ	n-C_5H_{11}
5b	4-H_2NØ	n-C_5H_{11}
5c	4-MeOØ	n-C_5H_{11}
5d	n-C_5H_{11}	n-C_5H_{11}
5e	4-H_2NØ	n-C_3H_7

Two mechanisms can account for these results. In both, cationic π-allylpalladium complexes are invoked, since they can be formed from allylic alcohols[2,9]. The inversion of reactivity at the carbonyl carbon required in mechanism A has been previously postulated[10] and the gradation of yields and required reaction times given in the table support such a mechanism.

TABLE

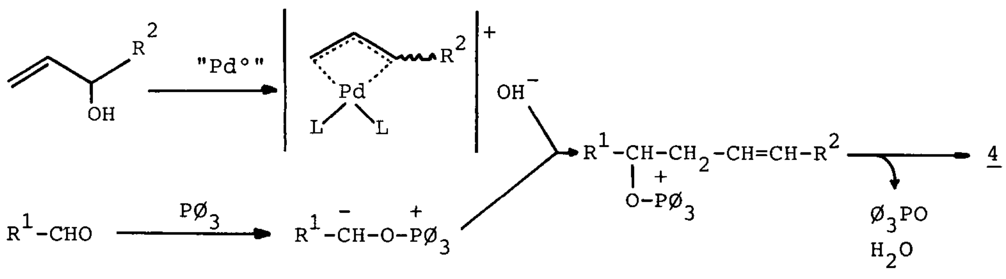
Run	R^1	alcohol, R^2	ratio 1/2 or 3/PØ$_3$	hours	4(%)[7]	Other isolated products
1	4-ClØ	2, n-C_5H_{11}	1.0/1.1/1.0	70	4a(49)	Ø$_3$P; 4-ClØCHO
2	4-ClØ	2, n-C_5H_{11}	1.0/2.2/1.0	70	4a(68)	Ø$_3$P; 4-ClØCHO; CH_2=CH-CH=CH-$(CH_2)_3$-CH_3
3[a]	4-O_2NØ	2, n-C_5H_{11}	1.0/1.1/1.0	5	4b(48)	Ac_2CHCH_2CH=CH-$(CH_2)_3$-CH_3[b] $Ac_2C(CH_2CH$=CH-$(CH_2)_3$-$CH_3)_2$[b]
4	4-MeOØ	2, n-C_5H_{11}	1.0/1.1/1.0	65	4c(20)	Ø$_3$P; 4-MeO-Ø-CHO
5	n-C_5H_{11}	2, n-C_5H_{11}	1.0/1.1/1.0	70	4d(32)	Ø$_3$P; n-C_5H_{11}-CHO
6[c]	n-C_5H_{11}	2-OAc, n-C_5H_{11}	1.0/1.1/1.0	65	4d(30)	Ø$_3$P; n-C_5H_{11}-CHO
7[a]	4-O_2NØ	3, n-C_3H_7	1.0/1.1/1.0	5	4e(45)	

[a] Side reactions, probably reductions of the nitro group are responsible of the relatively low yield of 4. PØ$_3$ and 4-O_2N-Ø-CHO were not recovered.

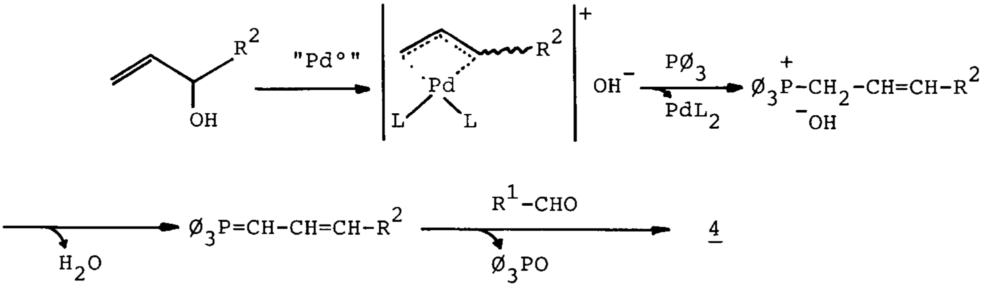
[b] Compared with authentical samples[2].

[c] A few drops of hydrazine hydrate were added to reduce Pd(II) to Pd(0).

Mechanism A



Mechanism B



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[7] All these compounds showed correct spectroscopic behaviour.

[8] All these compounds showed correct spectroscopic behaviour and, when not previously described, correct elemental analysis.

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