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HIGHLY STEREOSPECIFIC PALLADIUM-CATALYSED VINYLATION OF VINYLIC HALIDES UNDER SOLID-LIQUID PHASE TRANSFER CONDITIONS.

Tuyêt JEFFERY

ER 12 du CNRS - Laboratoire de Chimie de l'Ecole Normale Supérieure -
24, rue Lhomond - 75231 Paris Cedex 05 - France.

Summary : (E,E) and (E,Z) conjugated dienoates, dienones and dienals are obtained with high stereospecificity (>95%) and in high yields from the corresponding (E) and (Z) vinylic halides and vinylic substrates (methyl acrylate, methyl vinyl ketone or acrolein), in the presence of potassium carbonate, tetrabutylammonium chloride and a catalytic amount of palladium acetate, in N,N-dimethylformamide at room temperature.

The Pd-catalysed vinylation of vinylic halides has been well described [1], in particular the reaction being highly chemo and regiocontrolled with respect to the vinylic halide. However, from a synthetic standpoint, stereospecificity remains a challenge for this type of reaction, even under milder reaction conditions [2].

We wish to report herein that the Pd-catalysed vinylation of vinylic halides can be performed at room temperature with high stereospecificity (>95%) under solid-liquid phase transfer conditions.

We recently reported [3] that Heck type reactions from organic halides can successfully proceed in the presence of sodium hydrogen carbonate, tetrabutylammonium chloride and a catalytic amount of palladium acetate, in DMF, at or near room temperature. The mild conditions allowed this type of reaction to be generalised to thermally unstable vinylic substrates such as methyl vinyl ketone or acrolein. Lowering the reaction temperature would be expected to improve the stereospecificity of the vinylation of

Table 1 : Pd-catalysed vinylation of vinylic halides under phase transfer conditions using $NaHCO_3$ as base and NBu_4Cl as the phase transfer agent [a].

Run n°	RX	Vinylic Substrate	Reaction Temp. (°C)	Time (days)	Products	Total Yield[b] (E,E)+(E,Z) (%)	(E,E)/(E,Z) Ratio [c]
1	(E)$C_4H_9CH{=}CHI$	$CH_2{=}CHCOOCH_3$	30	2.5	(E,E)$C_4H_9CH{=}CHCH{=}CHCOOCH_3$ (E,Z)$C_4H_9CH{=}CHCH{=}CHCOOCH_3$	90	94/6
2	(Z)$C_4H_9CH{=}CHI$	"	25	4	" "	93	77/23
3	(E)$C_4H_9CH{=}CHI$	$CH_2{=}CHCOCH_3$	"	3	(E,E)$C_4H_9CH{=}CHCH{=}CHCOCH_3$ (E,Z)$C_4H_9CH{=}CHCH{=}CHCOCH_3$	97	93/7
4	(Z)$C_4H_9CH{=}CHI$	"	"	3	" "	90	78/22
5	(Z)$C_4H_9CH{=}CHI$ [d]	"	"	1.5	" "	3 [c]	6/94
6	"	"	"	3.5	" "	14 [c]	57/43

a) RX (1 equiv.), vinylic substrate (2 equiv.), $Pd(OAc)_2$(0.02 equiv.), $NaHCO_3$(3.5 equiv.), NBu_4Cl (1 equiv.) in DMF under nitrogen.

b) The mixture of products are isolated by rapid filtration through a short silica gel column unless otherwise stated.

c) Determined by GLC analysis on capillary UCON 75H column.

d) The reaction is performed in the presence of 5 mole % of triphenylphosphine.

vinylic halides. However, under the conditions described above, the (E,E) stereoisomer is predominantly obtained from the treatment of vinylic substrates with either (E) or (Z) vinylic halide (Table 1, Runs n° 1,2,3,4). The stereochemistry about the RX double bond is thus partly lost when RX is a (Z) stereoisomer. Addition of triphenylphosphine improved the stereospecificity but greatly lowered the rate of the reaction (Run n°5) ; and the proportion of the more stable (E,E) stereoisomer increased with a longer reaction time (Run n°6). It thus seemed that not only a low reaction temperature but also a short reaction time would be necessary to achieve a high stereospecificity of the vinylation of vinylic halides.

It has been observed [4] that the vinylation of aromatic halides under solid-liquid phase transfer conditions [3] can be greatly accelerated by using potassium carbonate instead of sodium hydrogen carbonate as inorganic base [5]. Its use was thus expected to improve the stereospecificity of the vinylation of vinylic halides by enhancing the reaction rate.

Indeed, as shown in Table 2, a total conversion of vinylic halides is observed after only a few hours at room temperature, from their treatment with vinylic substrates (methyl acrylate, methyl vinyl ketone, acrolein) in DMF, in the presence of a catalytic amount of palladium acetate, under phase transfer conditions using potassium carbonate as base and tetrabutylammonium chloride as the phase transfer agent. Moreover, (E,E) and (E,Z) stereoisomers (dienoate, dienone or dienal)[6] are obtained in high yields from the corresponding (E) and (Z) vinylic halides.

Table 2 : Highly regio and stereocontrolled Pd-catalysed synthesis of conjugated dienoates, dienones and dienals from vinylic halides and vinylic substrates [a].

RX	Vinylic Substrate	Reaction Temp.	Time	Products	(E,E)/(E,Z) Ratio [b]	Isolated product (yield [c])
(E)$C_4H_9CH=CHI$	$CH_2=CHCOOCH_3$	27°C	4h	(E,E)$C_4H_9CH=CHCH=CHCOOCH_3$ (E,Z)$C_4H_9CH=CHCH=CHCOOCH_3$	99/1	(E,E)$C_4H_9CH=CHCH=CHCOOCH_3$ (96%)
(Z)$C_4H_9CH=CHI$ [d]	"	25°C	1h	" "	5/95	(E,Z)$C_4H_9CH=CHCH=CHCOOCH_3$ (90%)
(E)$C_4H_9CH=CHI$	$CH_2=CHCOCH_3$	"	4.5h	(E,E)$C_4H_9CH=CHCH=CHCOCH_3$ (E,Z)$C_4H_9CH=CHCH=CHCOCH_3$	97/3	(E,E)$C_4H_9CH=CHCH=CHCOCH_3$ (95%)
(Z)$C_4H_9CH=CHI$	"	"	4.5h	" "	2/98	(E,Z)$C_4H_9CH=CHCH=CHCOCH_3$ (93%)
(E)$C_4H_9CH=CHI$	$CH_2=CHCHO$	20°C	5h	(E,E)$C_4H_9CH=CHCH=CHCHO$ (E,Z)$C_4H_9CH=CHCH=CHCHO$	98/2	(E,E)$C_4H_9CH=CHCH=CHCHO$ (90%)
(Z)$C_4H_9CH=CHI$	"	18°C	5h	" "	2/98	(E,Z)$C_4H_9CH=CHCH=CHCHO$ (90%)

a) RX (1 equiv.), vinylic substrate (2-10 equiv.), $Pd(OAc)_2$(0.02 equiv.), K_2CO_3(2.5 equiv.), NBu_4Cl (1 equiv.) in DMF under nitrogen unless otherwise stated. Reaction conditions have not been optimized.

b) GLC analysis on capillary UCON 75H column of the crude product obtained by rapid filtration through a short silica gel column.

c) Yield of spectroscopically pure product, isolated by chromatography on silica gel.

d) 6 mole % of $Pd(OAc)_2$ was used.

These results provide another example of the efficiency of phase transfer catalysis in organometallic chemistry [7]. From a synthetic standpoint, they should be useful providing a convenient, mild, efficient, regio and stereocontrolled approach to compounds involving a stereodefined conjugated dienic carbonyl moiety in their structure[8,9].

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