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Pd-PROMOTED VINYLIC HYDROGEN SUBSTITUTION OF ALKENE AND α CARBONYLATED ALKENE BY LITHIUM AND MAGNESIUM ORGANOCUPRATES .

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SUMMARY : In the presence of $PdCl_2$, LiCl and K_2CO_3 , vinylic hydrogen substitution of styrene and acrylic ester, in MeCN and MeCN - HMPA respectively , has been successfully performed using lithium and magnesium organocuprates .

We have recently described the arylation of styrene by Grignard reagents in the presence of $PdCl_2$[1] . We now wish to report the reactivity of lithium and magnesium organocuprates in the Pd-promoted vinylic hydrogen substitution of alkenes . This study has been undertaken as the well-known unreactivity of these reagents towards carbonyl functions would allow to consider their use in reactions involving carbonylated alkenes .

Results obtained with styrene and n-butyl acrylic ester are reported in this paper.

As shown in Table 1 , using acetonitrile as solvent , good yields of trans-stilbene were obtained by treatment of styrene with lithium or magnesium diphenylcuprate in the presence of palladium chloride , lithium chloride and potassium carbonate for 1h at room temperature under nitrogen atmosphere (Run no. 3 and 7) .
Unlike the corresponding Grignard reaction [1] , tri-n-butylamine proved ineffective as a base in these reactions even under stoichiometric conditions (Table 1 , Run no. 2) . This might be attributed to a competitive deactivating complexation of the organocuprate reagent by the amine .
With magnesium organocuprate , the phenylation of styrene could be performed under catalytic conditions , $CuCl_2$ being used as co-catalyst (Table 1 , Run no. 6) .

These reactions very probably proceed via a mechanism similar to that proposed for organomercury compounds [2] involving organopalladium formation from organocuprate and palladium salt [3] and alkene insertion followed by β elimination .

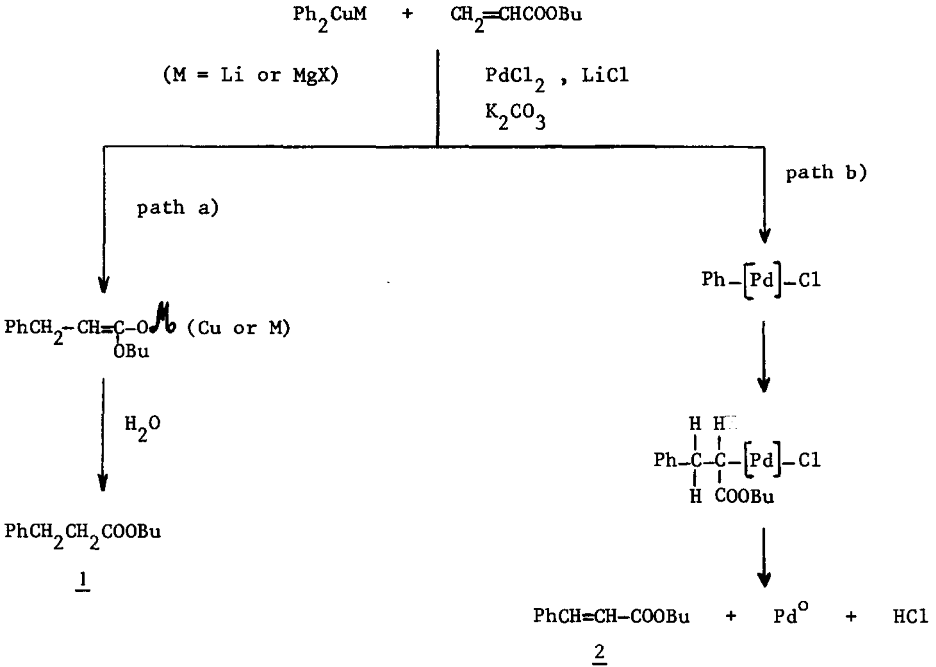
Table 1 : Phenylation of styrene by lithium and magnesium diphenylcuprate [a)]
(room temperature, 1h under N_2)

Run no.	Reagent Ph_2CuM [b)]	Molar ratio x (Ph_2CuM / $PdCl_2$)	Solvent	Base	trans PhCH=CH-Ph yield (%) [c)]
1	Ph_2CuMgX	2	CH_2Cl_2 [d)]	NBu^n_3	10
2	"	2	MeCN [d)]	NBu^n_3	40
3	"	1.1	MeCN [d)]	K_2CO_3	100
4	"	10	CH_2Cl_2 [e)]	NBu^n_3	30
5	"	10	MeCN [e)]	NBu^n_3	45
6	"	10	MeCN [e)]	K_2CO_3	620
7	Ph_2CuLi	2	MeCN [d)]	K_2CO_3	100
8	"	10	MeCN [e)]	K_2CO_3	260

a) $Ph_2CuM/PdCl_2/LiCl/PhCH{=}CH_2$/base = x/1/excess/3/excess ; b) (2 PhM + CuI) ;
c) based on $PdCl_2$; d) $PdCl_2 \simeq 0.1N$; e) $PdCl_2 \simeq 0.01N$.

Lithium and magnesium organocuprates can thus be used as arylating agents in the Pd-promoted vinylic hydrogen substitution of alkenes . As they are unreactive towards carbonyl functions , these reagents should be more suitable than the corresponding organomagnesium compounds in reactions involving alkenes having such a function in their structure. The most complicated case is considered herein , i.e. when the carbonyl function is in α position of the double bond . Indeed , with such a substrate, the conjugate addition (path a) might be another competing reaction with the vinylic hydrogen substitution (path b) (Scheme).

Results obtained with n-butyl acrylic ester are shown in Table 2 . In acetonitrile, poor yields of the unsaturated ester 2 were obtained , the major product being the saturated ester 1 (Run no. 1 and 3) . This might suggest that under these conditions the conjugate addition is too fast to allow the vinylic hydrogen substitution to proceed .
An increased yield of the unsaturated ester 2 might be expected if path a) can be made less favourable . It has been reported that the conjugate addition of lithium organocuprate to α-enones can be inhibited by 12-crown-4 [5] or by HMPA [6] .



Scheme

Table 2 : Pd-promoted vinylic hydrogen substitution of CH_2=CHCOOBu by lithium or magnesium diphenylcuprate $^{a)}$. (0°C ,20h under N_2) .

Run nô.	Reagent Ph_2CuM	Solvent	trans PhCH=CHCOOBu yield (%) $^{b)}$
1	Ph_2CuMgX	MeCN	5
2	"	MeCN / HMPA $^{c)}$	55
3	Ph_2CuLi	MeCN	5
4	"	MeCN or THF /12-crown-4 $^{d)}$	20
5	"	THF / [2.1.1] $^{d)}$	35
6	"	MeCN / HMPA $^{c)}$	100

a) Ph_2CuM /$PdCl_2$/LiCl/CH_2=CHCOOBu/K_2CO_3 = 4/1/1/3/excess ; b) based on $PdCl_2$;
c) MeCN/HMPA = 2/1 ; d) Ph_2CuM /complexing agent = 1/5 .

Results showed that in the presence of 12-crown-4 or cryptand [2.1.1] , low yields of 1 and 2 were obtained , i.e. both routes a) and b) were inhibited . Hovewer when HMPA was added as co-solvent , good yields of 2 were obtained particularly when the reagent was lithium diphenylcuprate (Table 2 , Run no. 2 and 6) [7].

In conclusion , lithium and magnesium organocuprates can be good arylating agents for vinylic hydrogen substitution of alkenes . With α carbonylated alkene as substrate , i.e. when competition between conjugate addition and vinylic hydrogen substitution exists , the use of HMPA can selectively inhibit the former route and then allows the latter one to take place .

These results provide the first examples of direct reactions of organocuprates with alkenes promoted by palladium chloride .

References and notes

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