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Allylation Of Aryl Grignard Reagents in the Presence of Transition Metal Catalysis and Organic Catalysis

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Abstract: The allylation yield and regioselectivity of phenyl Grignard reagent in THF was investigated in the presence of complexed transition metals and also uncomplexed or complexed transition metal salts. Additionally, the effect of Lewis acids and Lewis bases on the yield and the regioselectivity of the allylic arylation was also observed. Neither P-containing ligands for transition metal complexes, nor transition metal salts did make a difference on the yield and α:γ product ratio and gave the is α-product as the main product. However, donor cosolvents resulted in decrease in the yield and change of the regioselectivity.

Keywords: Regioselectivity, Allylic arylation, Transition metal salts/complexes, Organic catalyst.

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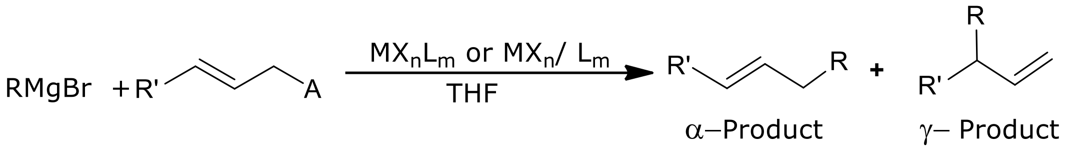
INTRODUCTION

Allylation of organometallic compounds in the presence of transition metal catalysis provides one of the most valuable methodologies for the formation of C-C bonds (1-7).

Allylic coupling reactions are employed to prepare double bond containing compounds which attract much attention because of their various synthetic, biological and industrial applications (8,9). In allylic coupling reactions, Grignard reagents are commonly used as partners since they are easier to use and they have advantages of high reactivity, easy preparation and functional group tolerance (10-15). So far, numerous reports have been reported on the regioselective allylation and stereoselective allylation of Grignard reagents (16-23).

In allylic coupling, the regioselectivity depends on the reaction parameters, *i.e.* type of Grignard reagent, allylic partner transition metal catalyst and organic catalyst as well as reaction conditions (24) (Scheme 1).



M = Cu, Ni, Pd, Co, Fe
A = Halogen, OCOR, $OPO(OR)_2$, OSO_2R
X = Halogen, OAc, CN
L = Achiral or chiral ligand

Scheme 1

Our group already worked on Cu(I) catalyzed allylic coupling of Grignard reagents in Barbier type reactions, i.e. magnesium is allowed to react with organyl halide and electrophile in one pot and then electrophile is reacted with *in situ* prepared Grignard reagent (25). We demonstrated that CuCN catalyzed alkyl-allyl coupling can be carried out under Barbier conditions with comparable yields and γ-selectivity to CuCN catalyzed allylation of clasically prepared alkyl Grignard reagents. Recently, we also reported succesful α-selective nano CuO catalyzed allylation of *in situ* formed aryl Grignard reagents (26).

According to the best of our knowledge, the number of reports on the allylic coupling of aryl Grignard reagents are not as high as those of alkyl Grignard reagents. Mostly, enantioselective allylation reactions have been investigated. For regioselective allylation, a number of transition metal catalysts, such as Cu (27-30), Ni (31,32), Pd (33,34), Co (35,36) and Fe (37) have been used. However, much research has been directed to the use of different ligands for catalysts to see their effect on the outcome of the reaction. However, there are not reports on allylic coupling of clasically prepared Grignard reagents to compare the regioselectivity of transition metal catalysts. For this purpose, investigation of the effect of transition metal catalysis on the regioselectivity of allylation of arylmagnesium reagents was planned. Herein, details of the work to find out the optimum conditions for aryl-allyl coupling with transition metal catalysts and also organic catalysts is reported.

MATERIALS AND METHODS

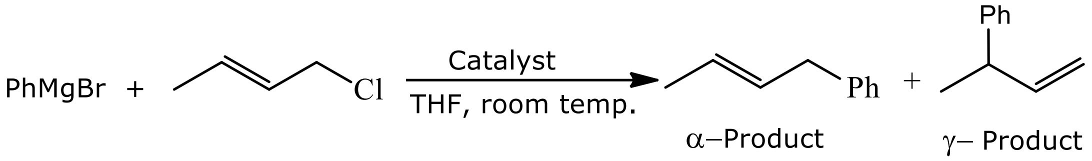
All reactions were carried out in oven-dried glassware under a positive pressure of nitrogen using standard syringe-septum cap techniques (38). GC analyses were performed on a Thermo Finnigan gas chromatograph equipped with a ZB-5 capillary column packed with phenylpolysiloxane at 70-200 ^{o}C using the internal standard technique. THF was distilled from sodium benzophenonedianion. Bromobenzene and *E*-crotyl chloride were obtained commercially and used without purification. Magnesium turnings for Grignard reactions were used without purification. CuI, CuSCN (38), CuBr, CuCl, $CuCl_2$ (39) and CuCN (40) were purified according to the published procedures, dried under reduced pressure and kept under nitrogen. Both Cu and Ni, Pd, Co, Ag, Fe catalysts were obtained commercially and kept under nitrogen.HMPA, NMP, DMF, DMPU, diglyme and TMEDA were distilled under reduced pressure and kept over molecular sieves under nitrogen. $MgCl_2$, $ZnCl_2$ and LiCl were dried under reduced pressure. Other Lewis acids and Lewis bases were obtained commercially and kept under nitrogen.

Phenylmagnesium bromide was prepared in THF according to standard procedure and its concentration was found by titration prior to use (41). For authentic samples, 1-phenyl-2-butene was purchased and 3-phenyl-1-butene was synthesized (42). Yields and product ratios are given as average of at least two experiments.

To PhMgBr reagent (1.1 mmol), catalyst (2 % mol, 0.02 mmol) and/or Lewis base or Lewis acid (necessary equiv.) was added at 25^{o}C and then E-crotyl chloride (1 mmol) was added dropwise. The mixture was stirred at 25^{o}C for 1 h. After addition of internal standard (nonane), the mixture was hydrolyzed with saturated NH_4Cl solution. The aqueous phase was extracted with ether and aliquots were analyzed with GC to determine the coupling yield and α-product: γ-product ratio of aryl coupling product.

RESULTS AND DISCUSSION

As a model reaction, allylation of phenylmagnesium bromide with *E*-crotyl chloride was chosen (Scheme 2).

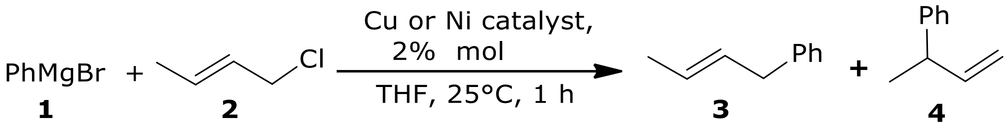


Catalyst = MX_n, MX_nL_m, MX_n+L, ML_m
M= Cu(I) and Cu(II), Ni(0) and Ni(II), Pd(0) and Pd(II), Co(II), Ag(I), Fe(II) and Fe(III)
L= dppf, dppen, (c-Hex)$_3$P, Ph$_3$P, t-Bu-P$_4$, PEPPSI-IPr, dba, COD
Organic catalyst= Lewis base and donor solvent, Lewis acid

Scheme 2

For comparison, uncatalyzed reaction in THF was also carried out and 98% total yield and 92:8 α:γ ratio was obtained. Due to the different mechanisms of the catalysts, Cu(I), Cu(II), Ni(II) salts and Cu(II) and Ni(II) nano oxides were investigated firstly to find out the dependence of regioselectivity on the anion of the metal salt. However, α:γ ratio did not show any dependence on the metal and reactions, Cu and Ni salts were tried as catalyst to see the effect of the counter ion of the transition metal salt on the regioselectivity (Table 1). As seen, the coupling yield is medium to high and α:γ ratio is higher than 89:19 in Cu(I), Cu(II) and Ni(II) catalyzed aryl-allyl coupling.

Table 1. Regioselectivity in the allylation of PhMgBr **1** with E-crotyl chloride **2** in THF in the presence of Cu(I), Cu(II) and Ni(II) catalysts [a,b]



Entry	Catalyst	Coupling yield,%[c]	Regioselectivity[d]
1	-	98	92:8
2	CuI	83	90:10
3	CuCl	74	91:9
4	CuBr	77	91:9
5	CuCN	73	91:9
6	CuSCN	73	91:9
7	Cu(OAc)	71	90:10
8	Cu(acac)$_2$	91	89:11
9	CuCl$_2$	76	93:7
10	Cu(II)O nano[e]	81	88:12
11	Cu(CF$_3$SO$_3$)$_2$	70	90:10
12	Cu(OAc)$_2$	74	89:11
13	NiCl$_2$	53	81:19
14	Ni(II)O nano[e]	78	91:9
15	Ni(acac)$_2$	49	80:20

aThe data are averages of at least two independent experiments.

b Molar ratio of **1**: **2** was optimized to be 2 : 1.

c The sum of GC yields of α-coupling product **3** and γ-coupling product **4**. The stereomer ratio E:Z in **3** is not lower than 9:1.

d The ratio of GC yield of **3** and **4**.

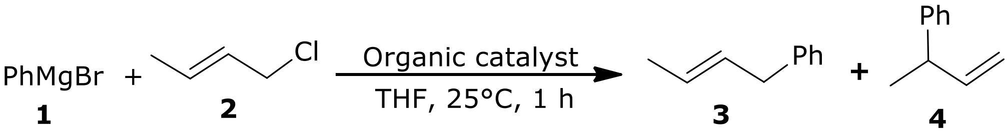
e nanopowder, <50 nm particle size, Aldrich

In the allylation, Lewis acids, P-containing Lewis bases and N-, P-, or O- containing Lewis bases as donor solvents were also tried to see if a change could be obtained on the yield and regioselectivity has been summarized in Table 2. As P-containing Lewis bases, Ph_3P (triphenylphosphine), dppf (diphenylphosphinoferrocene) and P4-t-Bu (phosphazene base) were used. As donor solvents, HMPA (hexamethylphosphoramide) and urotropine (Hexamethylenetetramine) were chosen. The main product is α-product again in the presence of Lewis acids (entries 1-6). P-Containing Lewis bases, which are mostly used as ligands for transition metal complexes (entries 7-11) did not make a difference in the yield and α:γ product ratio. However, donor cosolvents (entries 12-13) resulted in decrease of yield and change of the regioselectivity.

In THF:HMPA (4:1), the yield did not change appreciably (entry 12) however as HMPA increases (i.e. THF:HMPA= 2:1 and 1:1), α:γ ratio decreases and mainly γ-selective allylation takes place (entries 13 and 14). Similarly, in THF:DMPU (2:1), the yield and also α:γ ratio decrease and the increase of cosolvent (THF:DMPU=1:1) results in a new decrease and almost 1:1 α:γ product ratio (entries 15 and 16). Unfortunately, in the presence of TMEDA, NMP, diglyme and DMF (entries 17-20) the reaction did not take place. The use of Et_3N, 2,2'-bipyridyl and urotropine did not change the yield and α:γ ratio.

It was already reported that the use phosphine ligands together with transition metal catalysts caused change in the regioselectivity of the allylation. So monodentate phosphine ligands (Ph_3P, $(c\text{-}Hex)_3P$) and bidentate diphosphine ligands (dppf, dppen) and transition metals and transition metal salts complexed with these ligands were also tried in the allylic coupling of phenylmagnesium bromide (Table 3).

Table 2. Regioselectivity in the allylation of PhMgBr **1** with *E*-crotyl chloride **2** in THF in the presence of Lewis acids and Lewis bases[a,b]



Organic catalyst= Lewis base and donor solvent, Lewis acid

Entry	Lewis acid or Lewis base, mol%	Coupling yield, %[c]	Regioselectivity[d]
1	LiCl, 5	86	91:9
2	LiBr, 5	88	91:9
3	$MgCl_2$, 10	94	91:9
4	$MgCl_2$, 10	99	92:8
5	$ZnCl_2$, 5	94	91:9
6	$ZnCl_2$.TMEDA	67	90:10
7	Ph_3P, 2	79	91:9
8	Dppf, 2	49	90:10
9	Dppen, 2	76	91:9
10	$(n\text{-}Bu)_3P$, 4	73	93:7
11	P4-t-Bu, 4	75	88:12
12	HMPA[e]	81	80:20
13	HMPA[f]	87	37:63
14	HMPA[g]	86	40:60
15	TMEDA[g]	3	100:0
16	NMP[g]	3	0:100
18	DMPU[f]	60	75:25
17	DMPU[g]	38	47:53
19	Diglyme[f]	-	-
20	DMF[f]	-	-
21	Et_3N[f]	61	90:10
22	2,2'-Bipyridyl, 5	88	92:8
23	Urotropine, 5	84	90:10

[a] The data are averages of at least two independent experiments.

[b] Molar ratio of **1**: **2** was optimized to be 2 : 1.

[c] The sum of GC yields of α-coupling product **3** and γ-coupling product **4**. The stereomer ratio E:Z in **3** is not lower than 9:1.

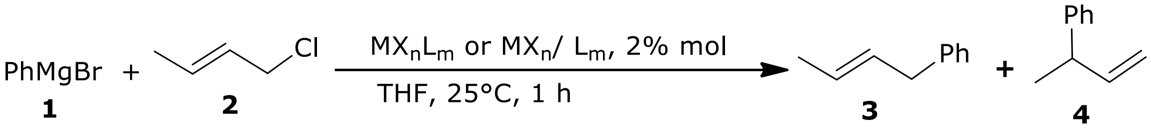
[d] The ratio of GC yield of **3** and **4**.

[e] THF: cosolvent (v/v) = 4/1.

[f] THF: cosolvent (v/v) = 2/1.

[g] THF: cosolvent (v/v) = 1/1.

Table 3. Regioselectivity in the allylation of PhMgBr **1** with *E*-crotyl chloride **2** in THF in the presence of transition metal catalyst and/or phosphine ligand[a,b]



M = Cu(I) and Cu(II), Ni(0) and Ni(II), Pd(0) and Pd(II), Co(II), Ag(I), Fe(II) and Fe(III)
L= dppf, dppen, (c-Hex)$_3$P, Ph$_3$P, t-Bu-P$_4$, PEPPSI-IPr, dba, COD

Entry	Catalyst	Coupling yield, %[c]	Regioselectivity[d]
1	CuCl+Ph$_3$P	68	90:10
2	CuCl+(c-Hex)$_3$P	75	89:11
3	CuCl+dppf	79	90:10
4	CuCl+dppen	71	90:10
5	CuCl+P4-t-Bu	77	90:10
6	CuCl$_2$+ Ph$_3$P	69	90:10
7	CuCl$_2$+dppf	75	91:9
8	NiCl$_2$(Ph$_3$P)$_2$	71	68:32
9	NiCl$_2$(c-Hex)$_3$P	68	71:29
10	NiCl$_2$+n-Bu$_3$P	44	86:14
11	NiCl$_2$(dppf)	78	56:44
12	NiCl$_2$+dppen	49	67:33
13	Ni(COD)$_2$	74	88:12
14	PdCl$_2$+ Ph$_3$P	63	62:38
15	PdCl$_2$(dppf)	68	82:18
16	PEPPSI-IPr	20	100:0
17	Pd(Ph$_3$P)$_4$	73	86:14
18	Pd(OAc)$_2$+2Ph$_3$P	52	83:17
19	Pd(OAc)$_2$+dppf	45	84:16
20	Pd(dba)$_2$	60	95:5
21	CoCl$_2$+2 Ph$_3$P	64	91:9
22	CoCl$_2$+2(c-Hex$_3$P)	65	89:11
23	CoCl$_2$+dppf	57	79:21
24	CoCl$_2$+dppen	60	87:13
25	AgI+2 Ph$_3$P	88	93:7
26	AgI+2(c-Hex$_3$P)	81	93:7
27	AgI+dppf	75	92:8
28	AgI+dppen	73	92:8
29	Ag(CF$_3$SO$_3$)+2Ph$_3$P	79	91:9
30	FeCl$_2$+2Ph$_3$P	59	76:24
31	Fe(acac)$_2$+2Ph$_3$P	23	57:43
32	Fe(acac)$_2$+dppf	18	50:50
33	FeCl$_3$+2 Ph$_3$P	22	59:41
34	FeCl$_3$+dppf	20	55:45

[a] The data are averages of at least two independent experiments.

[b] Molar ratio of **1**: **2** was optimized to be 2 : 1.

[c] The sum of GC yields of α-coupling product **3** and γ-coupling product **4**. The stereomer ratio E:Z in **3** is not lower than 9:1.

[d] The ratio of GC yield of **3** and **4**.

As seen, the use of these ligands as organic catalysts in the presence of CuCl and CuCl$_2$ did not make a change in the outcome of the reaction (entries 1-7). However NiCl$_2$ complexed with a phosphine (entries 8,9 and 11) caused a decrease in α:γ ratio. Use of phosphines in the presence of NiCl$_2$ (entries 10 and 12) led to a much decrease in the yield. Ni(COD)$_2$ was also tried as a catalyst (COD=1,5-cyclooctadiene), but did not give a difference in the outcome of the reaction (entry 13).

No remarkable change in the regioselectivity was observed in the allylation catalyzed with Pd complexes and $PdCl_2$ complexes (entries 14,15,17 and 20). However the use of Ph_3P or dppf in the presence of $Pd(OAc)_2$ (entries 18 and 19) decreased the yield and catalytic activity of PEPPSI-IPr resulted in a quite low yield (entry 16). $Pd(dba)_2$ was also tried as a catalyst (dba=dibenzylideneacetone) (entry 20). Allylation in the presence of $CoCl_2$ and a phosphine ligand gave somewhat lower yield, but did not change the regioselectivity (entries 21-24). Ag-catalyzed allylation in the presence of phosphines gave quite similar results to those obtained by Cu and phosphine catalyzed allylation (entries 25-29). The presence of phosphine in the allylation catalyzed $FeCl_2$ did not result in much change of yield and regioselectivity (entry 30). However, the catalytic activity of $Fe(acac)_2$ in the presence of a phosphine decreased the yield remarkably and gave an α:γ ratio of ~1:1.

CONCLUSIONS

In this study, the catalytic activities of Cu(I), Cu(II), Ni(0), Ni(II), Pd(0), Pd(II), Co(II), Ag(I) and Fe(II), either complexed or in the presence of phosphines and the catalytic activities of Lewis acids and Lewis bases as organic catalyst in the allylation of aryl Grignard reagents was investigated in detail. It was observed that Lewis bases and transition metal salt/phosphine complexes or phosphine complexed transition metal salts resulted in change in the yield and regioselectivity.

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