Pergamon

Tetrahedron Letters 39 (1998) 6159–6162

TETRAHEDRON
LETTERS

Cobalt-Catalyzed Alkenylation of Organomagnesium Reagents

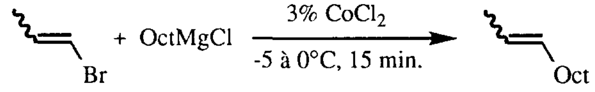
Gérard Cahiez* and Hovsep Avedissian

Ecole Supérieure de Chimie Organique et Minérale, Département de Chimie
13, Boulevard de l'Hautil, F-95092 Cergy-Pontoise, France

Received 4 May 1998; accepted 2 June 1998

Abstract: Alkenyl iodides, bromides and chlorides react with organomagnesium reagents in THF, in the presence of $Co(acac)_2$ and NMP (9 to 4 equiv.), to give the cross-coupling products in good yields. The reaction is chemoselective (aryl or alkyl bromides, esters and ketones) and stereoselective (≥ 99.5%). © 1998 Elsevier Science Ltd. All rights reserved.

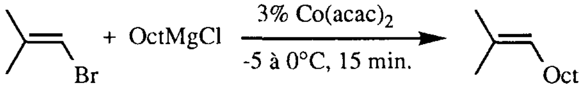
Recently, we have shown that the use of NMP as cosolvent has a remarkable beneficial influence on various cross-coupling reactions (Cu-catalyzed alkylation of RMnX[1,2] and Fe-catalyzed alkenylation of RMnX[2,3] and RMgX[4]). In this letter, we report a similar improvement in the case of the cobalt-catalyzed alkenylation of Grignard reagents previously studied by Kharasch[5]. Thus, in the presence of 3% $CoCl_2$, 1-bromo-1-propene reacted with octylmagnesium chloride to give 45% of 2-undecene in THF alone whereas in a mixture THF-NMP (9 equiv. of NMP based on OctMgCl) a 88% yield was obtained.



THF: 45%
THF-NMP (9 equiv.): 88%

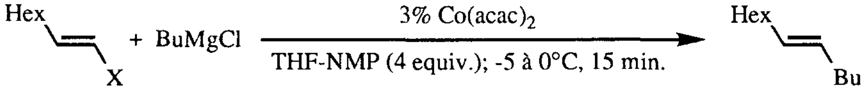
Some polar cosolvents also allow to increase the yield but only DMPU gave a similar result (*i. e.* DMF: 58%, $(EtO)_2CO_2$: 63%, Sulfolane: 53, DMPU[6]: 88%). In the case of the reactive 1-bromo-1-propene only a small amount of NMP is enough (4 equiv. NMP: 86%). Various cobalt salts can be used as catalyst in place of $CoCl_2$ (*i. e.* 3% $CoCl_2•2LiCl$: 87%, 3% $Co(acac)_2$: 87%, 3% $Co(OAc)_2$: 83%, $Co(acac)_3$: 74%). However, by using only 1% of catalyst the best result was obtained with $Co(acac)_2$ (1% $CoCl_2$: 80%, 1% $Co(acac)_2$: 87%).

The effect of NMP is more noticeable with the less reactive 2-methyl-1-bromo-1-propene.



THF: 23%
THF-NMP (9 equiv.): 63%

Interestingly, alkenyl iodides, bromides and chlorides furnish all good yields of cross-coupling products.

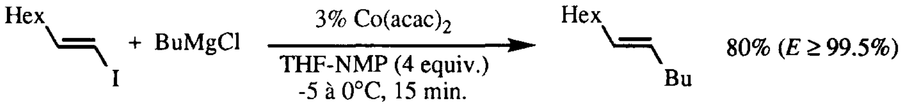


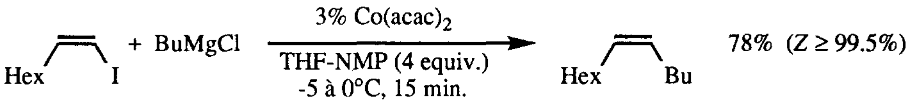
X= I: 80%; X= Br: 80%; X= Cl: 73%

Fax: (33) 01 30 75 60 21

0040-4039/98/$ - see front matter
PII: S0040-4039(98)01266-0

It should be noted that the reaction is highly stereoselective (≥ 99.5%)





As shown in Table 1, the cobalt-catalyzed alkenylation of organomagnesium reagents described above has a large scope of application and various alkenyl halides were used sucessfully.[7]

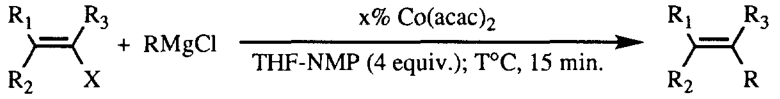
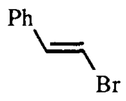
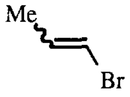
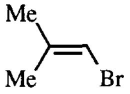
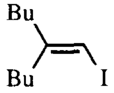
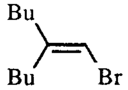
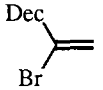


Table 1. Cobalt-Catalyzed Alkenylation of Organomagnesium Reagents.

Entry	Alkenyl Halide	R	Reaction Conditions	Yield (%)[a]
1		Bu	1.1 RMgCl, -5°C to 0°C, 3% $Co(acac)_2$	88
2		*s*-Bu	"	71
3		*c*-Hex	"	87
4		*t*-Bu	"	36
5		Me	1.1 RMgCl, 15°C to 20°C, 3% $Co(acac)_2$	82
6		Ph	"	90
7		$Me_2C{=}CH$	1.1 RMgBr[b], 60°C to 65°C, 5% $Co(acac)_2$	60
8		Ph	1.1 RMgCl, 15°C to 20°C, 3% $Co(acac)_2$	83
9		p-MeO-C_6H_4	"	80
10		p-Cl-C_6H_4	"	55
11		p-MeO-C_6H_4	1.5 RMgCl, 15°C to 20°C, 8% $Co(acac)_2$	71
12		Bu	1.2 RMgCl, -5°C to 0°C, 3% $Co(acac)_2$	75
13		Bu	"	67
14		Hex	1.3 RMgCl, -5°C to 0°C, 3% $Co(acac)_2$	73

a/ Yield of isolated product. For a typical procedure see note 7. **b**/ $Me_2C{=}CHMgBr$ was used.

Primary and secondary alkylmagnesium reagents gave good yields of substituted olefins (entries 1-3 and 12-14). It should be noted that no isomerization occurs in the case of a secondary alkyl groups.[8] However, the cobalt-catalysis is less efficient for introducing a tertiary alkyl group since the β-elimination process is then a competitive reaction. Thus, treatment of 2-bromostyrene with *t*-butylmagnesium chloride resulted in only 36% cross-coupling product (entry 4). From methyl and arylmagnesium halides which are less reactive, it is necessary to perform the reaction at room temperature (entries 5 and 6) and sometimes to add more catalyst and an excess of the Grignard reagent to improve the results (entry 11). In the case of the 2-methyl-1-propenylmagnesium bromide it is even necessary to heat the reaction mixture at 60-65°C (entry 7).

We have also tried to react 1,1,2-trichloro-, 1,1-dichloro- and (*Z*)-1,2-dichloroethylene but, in spite of various attempts we have never obtained the substitution product. However, contrary, to its (*Z*) isomer, the (*E*)-1,2-dichloroethylene reacted with octylmagnesium chloride to afford stereoselectively 57% of (*E*)-1-chloro-1-decene (Table 2, entry 15). Curiously, the formation of the product resulting from a double substitution of the 1,2-dichloroethylene (9-octadecene) was never observed.[9]

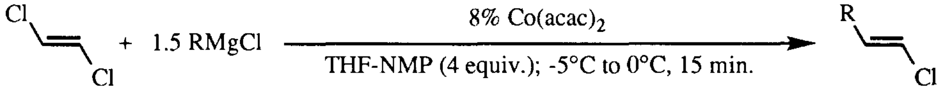
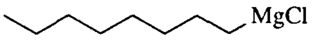
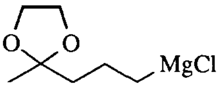
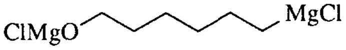


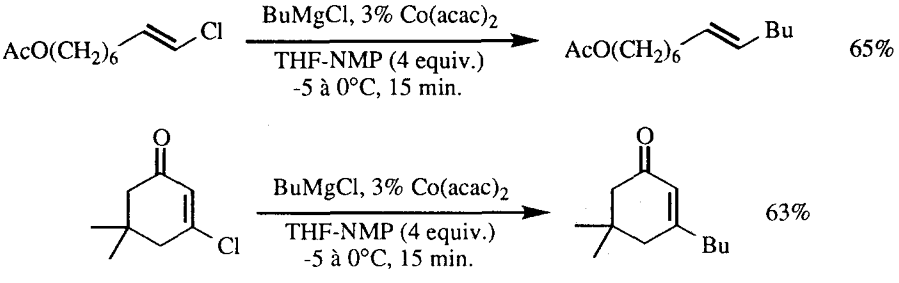
Table 2. Preparation of (*E*)1-Chloroalkenes from (*E*) 1,2-dichloroethylene.

Entry	RMgCl	Yield (%)[a]
15		57
16		52
17		56

[a] Yield of isolated RCH=CHCl.

The procedure has been applied to the synthesis of fonctionnalized alkenyl chlorides (entries 16 and 17). As a rule, 8% $Co(acac)_2$ and 1.5 equiv of Grignard reagent were used to obtain satisfactory results. The yields do not exceed 52 to 57% but it is a very easy and rapid route for the preparation of (*E*) functionnalized 1-chloroalkenes.

Preliminary competive experiments showed that the reaction is very chemoselective; thus, alkyl and aryl bromide as well as esters and ketones are tolerated. Two examples of selective cobalt-catalyzed alkylation of functionnalized alkenyl chlorides are depicted below.



In conclusion, we have shown that, in THF, organomagnesium reagents react with alkenyl iodides, bromides and chlorides, in the presence of both $Co(acac)_2$ and NMP, to give the cross-coupling products in satisfactory yields. The reaction is stereoselective ($\geq 99.5\%$) and chemoselective (alkyl or aryl bromides, esters and ketones are tolerated). As for the copper-, and iron-catalyzed cross-coupling reactions already studied[1-4], the presence of NMP is essential to improve the yields of the cobalt-catalyzed reaction which was not applicable for preparative chemistry up to now.

With the less reactive alkenyl halides (i. *e*. β-disubstituted alkenyl halides, alkenyl chlorides) the cobalt-catalyzed procedure described herein is less efficient than the iron-catalyzed reaction previously reported.[4] Nevertheless, it can be complementary. Thus, the substitution of 1,2-dichloroethylene cannot be performed in the presence of iron salts. An extension of this reaction to organozinc compounds is reported in the following communication.

Acknowledgements: G.C. belongs to the C.N.R.S. We thank the CNRS and the *Ecole Supérieure de Chimie Organique et Minérale (ESCOM)* for their financial support.

References and notes.

1 Cahiez, G.; Marquais, S. *Synlett* **1993**, 45-47.

2. Cahiez, G.; Marquais, S. *Pure & Appl. Chem.* **1996**, *68*, 53-60.

3. Cahiez, G.; Marquais, S. *Tetrahedron Lett.* **1996**, *37*, 1773-1776.

4. Cahiez, G.; Avedissian, H. *Synthesis* **1998**, in press.

5. **a**/ Kharasch M. S.; Fields E. K. *J. Am. Chem. Soc.* **1941**, *63*, 2316-2320. **b**/ Kharasch M. S.; Fushs C. F. *J. Am. Chem. Soc.* **1943**, *65*, 504-507. **c**/ Kharasch M. S.; Urry W. H. *J. Org.Chem.* **1948**, *13*, 101-109. **d**/ Kharash M. S.; Fushs C. F. *J. Org.Chem.* **1945**, *10*, 292-297. **e**/ Smith W. B. *J.Org.Chem.* **1959**, *24*, 703-704. **f**/ Elsom L. F.; Hunt J. D.; Mckillop A. *Organomet. Chem. Rev. A* **1972**, *8*, 135-152.
The cross-coupling reaction between lithium organocobaltates and alkenyl halides has also been studied, see: **a**/ Corey E. J.; Posner G. H. *Tetrahedron Lett.* **1970**, 315-318. **b**/ Kauffmann T.; Stach D. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1684-1685. **c**/ Kauffman T.; Nienaber H.; Stach D. *Inorg. Chim. Acta.* **1994**, *220*, 85-92. **d**/ Kauffmann T. *Synthesis* **1995**, 745-755. **e**/ Kauffmann T.; Nienaber H *Synthesis* **1995**, 207-211. **f**/ Kauffmann T.; Laarmann B.; Menges D.; Voβ K.-U.; Wingbermühle D. *Tetrahedron Lett.*; **1990**, *31*, 507-510. **g**/ Kauffmann T.; Hopp G.; Laarmann B.; Stegemann D.; Wingbermühle D. *Tetrahedron Lett.* **1990**, *31*, 511-514.

6. DMPU= 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone

7. **Typical Procedure.**
To a solution of (*E*) 8-acetoxy-1-chloro-1-octene (25 mmoles, 5.11 g) and 3% $Co(acac)_2$ (0.19 g) in a mixture THF-NMP (50mL, 1:1) were added dropwise within 5 min, between -5° to 0°C, 27.5 mmoles of BuMgCl as a solution in THF. Stirring was continued for 15 min and the reaction mixture was hydrolyzed with 2N HCl. After standard workup, (*E*) 1-acetoxy-7-dodecene was isolated by distillation in 65% yield (Bp: 120-123°C/5 Torr, 3.68 g). IR (neat, cm^{-1}): 1742, 968, 729; ^1H-NMR ($CDCl_3$, TMS, δ in ppm, J in Hz): 0.95 (t, 3H, J= 5.6), 1.25 to 1.50 (m, 8H), 1.66 to 1.68 (m, 2H), 2.03 to 2.11 (m, 6H), 2.11 (s, 3H), 4.10 to 4.15 (m, 2H), 5.43 to 5.45 (m, 2H); ^{13}C-NMR ($CDCl_3$, TMS, δ in ppm): 13.53, 20.39, 21.83, 25.44, 28.26, 28.39, 29.13, 31.46, 31.93, 32.13, 64.06, 129.65, 130.08, 170.38

8. It is well established than the Ni- or Pd-catalyzed cross-coupling reactions between *s*-alkylmagnesium halides and alkenyl halides can lead to mixture of *n*- and *s*-alkylated products with variable amounts of reduced product. These drawbacks could be avoided by using $NiCl_2(dppf)$ or $PdCl_2(dppf)$. For instance, see: **a**/ Tamio H.; Konishi M.; Kumada M. *Tetrahedron Lett..* **1979**, *20*, 1871-1874. **b**/ Tamao H.; Konishi M.; Kobori Y.; Kumada M.; Higuchi T.; Hirotsu K. *J. Am. Chem. Soc.* **1984**, *106*, 158-163. **c**/ Tamio H.; Konishi M.; Yokata K. I.; Kumada M. *Chem. Lett*, **1980**, 767-768.

9. The synthesis of 1-chloro-1-alkenes from (*E*) 1,2-dichloroethylene can also be performed with a nickel catalysis. The yields are similar to those described in this letter, however, contrary to the cobalt-catalyzed procedure, the formation of the product resulting from the substitution of the two chlorine atoms is observed as side reaction and it is necessary to use an excess of 1,2 dichloroethylene (5 equiv.). Ratovelomanana V.; Linstrumelle G. *Tetrahedron Lett.* **1981**, *22*, 315-318.