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CROSS-COUPLING OF ALKENYL, ARYL OR ALLYLIC SELENIDES AND GRIGNARD REAGENTS CATALYZED BY NICKEL-PHOSPHINE COMPLEXES

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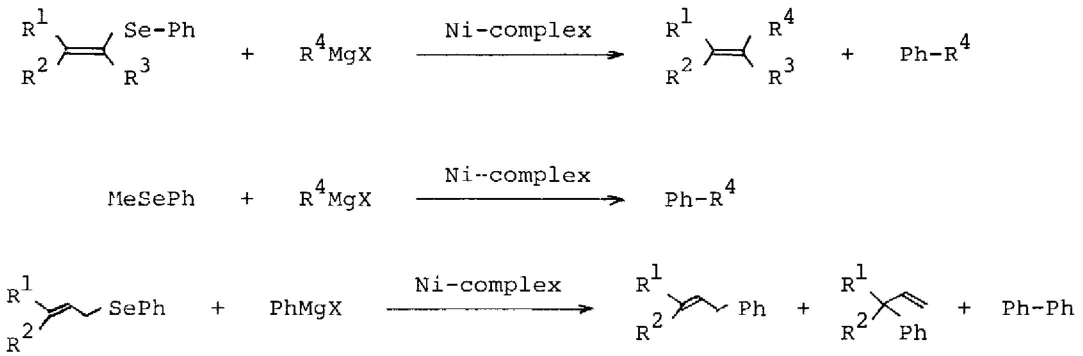
Summary: Alkenyl, aryl or allylic selenides smoothly couple with Grignard reagents in the presence of Ni(II)-phosphine complexes as catalysts to afford the corresponding unsaturated compounds in good yields. The reactivity order of coupling reaction with BuMgBr catalyzed by $NiCl_2[Ph_2PCH_2CH_2CH_2PPh_2]$ was found to be PhSeMe >> PhCl > PhSMe by the competitive reactions.

Organo-selenium compounds have attracted much attention in recent years, mainly as important intermediates in various synthetic transformations.[1] However, direct replacement reaction of selenium-containing groups by alkyl or aryl groups has not been described.[2]

Recently it was found that alkenyl,[3] aryl,[3] heterocyclic,[4] or allylic[5] sulfides couple with Grignard reagents in the presence of catalytic amounts of nickel-phosphine complexes to afford the corresponding unsaturated hydrocarbons or heterocycles with loss of sufur containing groups. In this connection, we examined the cross-coupling reaction of alkenyl phenyl selenides, or methyl phenyl selenide with Grignard reagents. Expectedly, coupling products were obtained in good yields by $NiCl_2(PPh_3)_2$ or $NiCl_2(dpp)$ ($dpp=Ph_2PCH_2CH_2CH_2PPh_2$)[6] catalyzed reaction as shown in the following scheme.



For example, phenylmagnesium bromide reacted with phenyl (Z)-styryl selenide[7] in the presence of NiCl$_2$(PPh$_3$)$_2$ to give (Z)-stilbene and biphenyl in good yields. The formation of hydrogen selenide was confirmed after quenching the reaction with dilute acid. Allylic selenides also coupled with phenylmagnesium bromide, though the S$_N'$-type products were formed together with the S$_N$-type products.[8] The results of the nickel complexes promoted coupling reaction between some selenides and Grignard reagents are shown in Table 1.

Table 1. Cross-Coupling of Alkenyl, Aryl, and Allylic Selenides with Grignard Reagents Catalyzed by Nickel-Phosphine Complexes[a]

run	Selenide	RMgX(eq.)	Cat.[b]	Product[c] (Yield[d] %)	
1	PhSe  Ph[7]	PhMgBr(2.5)	A	Ph  Ph[e] (88)	Ph-Ph[i] (114)
2	(Z)	PhMgBr(2.5)	B	Ph  Ph[f] (89)	Ph-Ph[i] (118)
3		BuMgBr(2.5)	A	Ph  Bu[g] (28)	Ph-Bu (47)
4		BuMgBr(2.5)	B	Ph  Bu[h] (76)	Ph-Bu (30)
5	PhSe  Bu[9]	PhMgBr(2.5)	A	Bu  Ph(70)	Ph-Ph[i] (100)
6		PhMgBr(2.5)	B	Bu  Ph(83)	Ph-Ph[i] (100)
7		BuMgBr(2.5)	A	Bu  Bu(45)	Ph-Bu (46)
8		BuMgBr(2.5)	B	Bu  Bu(86)	Ph-Bu (49)
9	MeSePh	BuMgBr(1.2)	A	Ph-Bu(40)	
10		BuMgBr(1.2)	B	Ph-Bu(95)	
11	PhSe 	PhMgBr(2.5)	A	Ph  (89)	Ph-Ph[i] (109)
12		PhMgBr(1.2)	A	Ph  (81)	Ph-Ph[i] (41)
13		PhMgBr(1.2)	B	Ph  (83)	Ph-Ph[i] (49)
14	PhSe 	PhMgBr(2.5)	A	Ph  (47) Ph  (30)	Ph-Ph[i] (128)
15		PhMgBr(2.5)	B	Ph  (8) Ph  (6)	Ph-Ph[i] (36) [j]

a) All of the reactions were carried out in refluxing ether for 8 h in the presence of catalyst (3 mole %). b) A: NiCl$_2$(PPh$_3$)$_2$, B: NiCl$_2$(dpp). c) The structures of the products were confirmed by comparison with authentic samples. d) The yields were determined by glpc, and calculated based on the starting selenides. e,f,g, and h) The ratio of isomers was Z/E=98/2, 93/7, 98/2, and 99/1 respectively. i) Biphenyl was produced by homo-coupling of PhMgBr as well as cross-coupling. j) Phenyl prenyl selenide was recoverd in 73% yield.

The results summarized in Table 1 contain several features worthy of note. (1) When phenylmagnesium bromide was used, both catalysts, NiCl$_2$(PPh$_3$)$_2$ and NiCl$_2$(dpp) were highly effective for simple selenides and the products were obtained in high yields (runs 1, 2, 5, 6, 11, 12, and 13). However, NiCl$_2$(dpp) showed low catalytic activity in the reaction of sterically hindered phenyl prenyl selenide (run 15), while NiCl$_2$(PPh$_3$)$_2$ was fairly effective (run 14).[8] On the other hand, when butylmagnesium bromide was used, the yields of coupling products catalyzed by NiCl$_2$(PPh$_3$)$_2$ were relatively low (runs 3, 7, and 9), probably

due to the dehydrometalation from the intermediates[10] [R(Bu)NiL$_2$ $\rightleftarrows$ R(H)NiL$_2$ + Et-CH=CH$_2$], while NiCl$_2$(dpp) exhibited high catalytic activity (runs 4, 8, and 10).
(2) This Ni-catalyzed reaction of alkenyl selenides is highly stereospecific ($\geq$ 93%), supporting an assumption that all steps proceed with retention of configuration similar to the cases of alkenyl halides[11] and sulfides[3] (runs 1-4).
(3) In the reaction of alkenyl aryl selenides, the cleavage of C-Se bonds occurs at the both sides of the selenium atom. So alkenyl aryl selenides require 2 equiv. of Grignard reagents (runs 1-10), while methyl phenyl selenide requires 1 equiv. (runs 9 and 10).[3]
(4) Cleavage of the Se-allyl bond took place much faster than that of the Se-Ph bond. Thus the phenyl group of phenylmagnesium bromide coupled predominantly with the allyl residue of allyl phenyl selenide even when 1.2 equiv. of the Grignard reagent was used (runs 11-13).[8]

In order to compare the reactivity of selenide, sulfide and halide, the competitive reactions with butylmagnesium bromide were carried out using PhSeMe, PhSMe and PhCl in the presence of NiCl$_2$(dpp) as a catalyst. The results are summarized in Table 2. As shown in Table 2, the reactivity order was PhSeMe >> PhCl > PhSMe. This order is not unexpected since the C-Se bond is weaker than the others.

Table 2. Relative Reactivity of PhSeMe, PhSMe and PhCl with BuMgBr Catalyzed by NiCl$_2$(dpp)[a]

Reactant (mmol)			BuMgBr (mmol)	Product (mmol)[b]	Recovery (mmol)[b]		
PhSeMe	PhSMe	PhCl		Ph-Bu	PhSeMe	PhSMe	PhCl
1.00	1.00	--	1.1	0.97	< 0.02	0.94	--
1.00	--	1.00	1.1	0.93	< 0.01	--	0.85
--	1.00	1.00	1.1	0.76	--	0.60	0.44
--	0.96	1.05	2.3	1.79	--	< 0.01	< 0.01

a) All of the reactions were carried out in refluxing ether (ca. 10 ml) for 8 h in the presence of NiCl$_2$(dpp) (0.03 mmol). b) The amounts of these compounds were determined by glpc using Ph-Pr as an internal standard.

A general procedure for the cross-coupling is as follows: Under an argon atmosphere, to a mixture of selenide (1 mmol) and nickel-phosphine complex (0.03 mmol) in ether (ca. 10 ml) was added a given amount of Grignard reagent (1.5-2.0 M ethereal solution) at room temperature with stirring. The resulting mixture was heated to reflux for a given period of time. After addition of 1 M CuSO$_4$ aq. solution, sat. NH$_4$Cl aq. solution and pentane, the mixture was filtered. The organic layer was separated, washed and dried. The amount of product was measured by glpc using a suitable internal standard.

References and Notes

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2) After the completion of this investigation, there appeared one example of the nickel-catalyzed reaction of phenyl vinyl selenide with p-tolylmagnesium bromide in benzene, in connection with a study of alkenyl and aryl sulfides: E. Wenkert, T. W. Ferreira, and E. L. Michelotti, J. Chem. Soc., Chem. Commun., 1979, 637.

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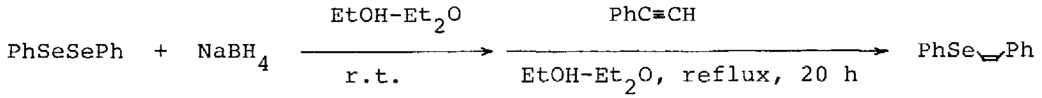
6) Generally, $NiCl_2(dpp)$ is a more effective catalyst than $NiCl_2(PPh_3)_2$ for cross-coupling of simple Grignard reagents with alkenyl of aryl halides.[11] In the cases of sulfides, a similar tendency was observed. Some of the results are shown below.

$$R^1SR^2 \quad + \quad R^3MgBr \xrightarrow{\text{Ni-complex}} R^1\text{-}R^3 \qquad \text{a)}$$

			Ni-complex (Catalyst)	
			$NiCl_2(PPh_3)_2$	$NiCl_2(dpp)$
R^1	R^2	R^3	Yield of R^1-R^3 (%)[b)]	
Ph	Me	Bu	14(ether 8 h)	96(ether 8 h)
1-cyclohexenyl	Et	Ph	38(THF 20 h)	98(ether 10 h)

a) All of the reactions were carried out at the refluxing temperature. A molar ratio of Ni-complex/R^1SR^2/R^3MgBr is 0.03/1.00/1.5. b) Determined by glpc.

7) Phenyl (Z)-styryl selenide was synthesized according to the following scheme in 97% (crude) or 76% (after recrystallization from EtOH) yield. Mp 45-46°C. NMR(CCl_4): δ=6.61 (1H, d, J=10Hz), 6.87 (1H, d, J=10Hz), and 7.05-7.60 (10H, m).



$$PhSeSePh \; + \; NaBH_4 \xrightarrow[\text{r.t.}]{\text{EtOH-Et}_2\text{O}} \xrightarrow[\text{EtOH-Et}_2\text{O, reflux, 20 h}]{\text{PhC≡CH}} PhSe\text{-}CH{=}CH\text{-}Ph$$

8) In the case of allylic sulfides, similar tendency was observed.[5)]

9) S. Raucher, J. Org. Chem., 42, 2950 (1977).

10) Although the mechanism of this reaction has not yet been fully clarified, the coupling may occur through the reaction sequence similar to that of halides[11)] and sulfides.[3,5)]

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