

METAL CATALYSIS IN ORGANIC REACTIONS. 17.

A NICKEL-PROMOTED ROUTE TO SUBSTITUTED ALLENES BY REACTION OF
1-BROMO-1,2-DIENES WITH ALKYL METALS.

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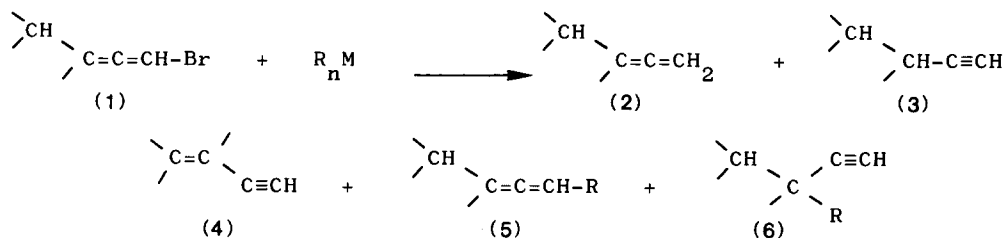
Summary : Nickel complexes are found to be catalytically active in the cross-coupling reactions of allenic bromides with alkyl metals to give substituted allenes in excellent yields. The catalytic process proceeds generally with inversion of configuration in the allenyl moiety.

Recently, interest in allenic chemistry has been noted from both mechanistic and synthetic aspects, and a number of papers¹ have reported new synthetic methods for substituted allenes via palladium-promoted cross-coupling reactions of allenic bromides with Grignard or organozinc reagents. In a very recent report,² it was also stated that such reactions may occur with inversion of configuration in the allenyl moiety affording optically active allenes starting from chiral bromoallenes.

In this context, as part of our continuing interest in transition-metal catalyzed reactions,³ we wish to report some preliminary results on the reaction of 3,3-dialkyl-1-bromoallenes (1) with alkyl compounds of main group metals (Al, Zn, Mg) in the presence of readily available nickel complexes as catalysts. In particular, we have investigated the synthetic utility and the stereochemical course of this reaction.

In the absence of any catalyst, organometallic reagents R_nM ($M = Al, MgX, Zn, ZnX$) react slowly (6-20 h at 25-35°C) with compounds (1) to provide a complex mixture of reduction, (2) and (3), elimination (4), and alkylation, (5) and (6), products (Scheme 1), with yields depending on the experimental conditions adopted and, prevalently, on the nature of the organometallic derivative itself.⁴ By contrast, when the starting compound (1) is allowed to react, under very mild conditions,⁵ with R_nM in the presence of few mole % of a nickel complex,

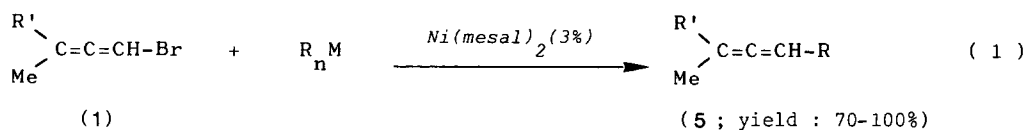
SCHEME 1



the trisubstituted allenic compound (5) is quickly obtained in a highly chemo- and regioselective fashion, together with little amounts of polymeric byproducts. However, to obtain the highest yields in (5), the proper nickel complex and suitable experimental conditions must be selected in relation to the different nature of the organometallic reagent employed.

The results obtained with 1-bromo-3-methyl-1,2-pentadiene (1a) and isobutylmetal compounds are representative (Table 1). Ni(dpe)Cl₂ and Ni(dppp)Cl₂ catalyze the reaction of (1a) with triisobutylaluminium giving the allene (5a) in high yields and >90% selectivity, while, under the same conditions, Ni(mesal)₂ gives considerable amounts of polymeric byproducts (entries 1-3). On the other hand, this last complex is found to be more efficient than the phosphine complexes in catalysing the reactions carried out with isobutylmagnesium chloride (entries 7 and 8) and diisobutylzinc (entries 10 and 11). Moreover, good results with the less expensive Ni(mesal)₂ catalyst can be generally obtained by using a higher nickel concentration (from 1 to 3 mol.%; entries 5 and 9) or an excess of the organometallic reagent (molar ratio R_nM/1a = 2; entries 4 and 13). The solvent also plays a definite and important role on the reactivity of the organometallic species. In fact, Grignard reagents and alkylzinc chlorides react readily in coordinating solvents, diethyl ether and diethyl ether/THF respectively, while trialkylaluminium and dialkylzinc compounds require hydrocarbon solvents (Table 1).

In the optimum conditions a variety of bromoallenes (1) was reacted with trialkylalanes and Grignard reagents (eq. 1). The method seems fairly general and gives access to a number of substituted allenes.⁵



M = Al, MgX

R' = Me, Et, Prⁱ, Bu^t; R = Et, Buⁱ, EtCH(Me), PrⁱCH(Me), Bu^tCH(Me), Ph, BuⁿC≡C

TABLE 1

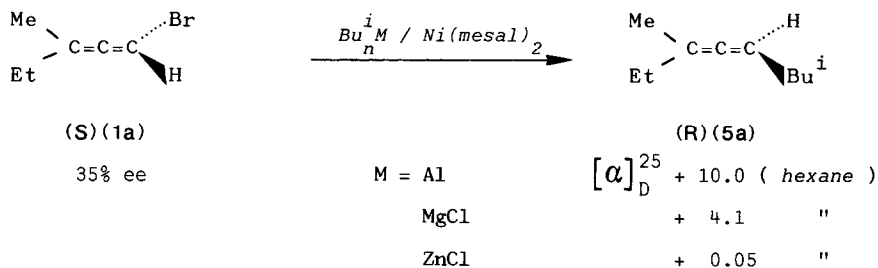


Entry ^a	Bu _n ⁱ M	Solvent	Catalyst(mol%) ^b	Conversion% ^c	Yield% ^c
1	Bu ₃ ⁱ Al	pentane	Ni(mesal) ₂ (1)	93	31
2			Ni(dpe)Cl ₂ (1)	78	95
3			Ni(dppp)Cl ₂ (1)	87	90
4 ^d			Ni(mesal) ₂ (1)	97	91
5			Ni(mesal) ₂ (3)	93	82
6 ^e		ether	Ni(mesal) ₂ (3)	0	-
7	Bu ⁱ MgCl	ether	Ni(mesal) ₂ (1)	76	85
8			Ni(dppp)Cl ₂ (1)	69	41
9			Ni(mesal) ₂ (3)	100	77
10	Bu ₂ ⁱ Zn	pentane	Ni(mesal) ₂ (1)	100	74
11			Ni(dppp)Cl ₂ (1)	5	90
12		ether	Ni(mesal) ₂ (1)	45	62
13 ^d		pentane	Ni(mesal) ₂ (1)	93	99
14	Bu ⁱ ZnCl	ether	Ni(mesal) ₂ (3)	56	27
15		ether/THF	Ni(mesal) ₂ (3)	97	72

^a All reactions were performed on a 10 mmol scale (molar ratio Bu_nⁱM/1a = 1, unless otherwise noted); for details see ref.5. ^b mesal = *N*-methylsilylaldimine; dpe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane. ^c Determined by g.l.c. using an internal standard. ^d Molar ratio Bu_nⁱM/1a = 2. ^e Reaction time 6 h at room temperature.

In order to determine the stereochemical behaviour of these nickel-promoted reactions we have employed as substrate (+)(*S*)-1-bromo-3-methyl-1,2-pentadiene, (*S*)(1a), prepared from (-)(*R*)-3-methyl-1-pentyn-3-ol following the procedure we have described elsewhere.⁵ The reactions of (*S*)(1a) ($[\alpha]_D^{25} +28.0$; 35% ee⁷) with isobutylmetal compounds, according to the experimental conditions of Table 1 (entries 5, 9, and 15), afford with excellent yields the dextro-rotatory 3,7-dimethyl-3,4-octadiene, (+)(5a), (Scheme 2).⁸ As the *R* configuration should be assigned to (+)(5a),⁹ the conversion of (*S*)(1a) into (5a) seems to proceed in each case with prevalent inversion in the allenyl moiety. It is noteworthy that the degree of stereoselectivity depends upon the nature of the organometallic reagent employed (Scheme 2).¹¹

SCHEME 2



REFERENCES AND NOTES

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2. C.J.Elsevier, H.H.Mooiweer, H.Kleijn, P.Vermeer, *Tetrahedron Lett.*, 25, 5571 (1984).
3. A.M.Caporusso, G.Giacomelli, L.Lardicci, *J.Org.Chem.*, 47, 4640 (1982), and references cited therein.
4. A.M.Caporusso, F.Da Settimo, L.Lardicci, *manuscript in preparation*.
5. In the typical procedure, to a stirred solution of the required organometallic reagent in the appropriate solvent were subsequently added, at -10°C , the nickel complex (1-3 mol %) and substrates (1), maintaining a nitrogen atmosphere. The resulting mixture was allowed to warm to room temperature for 30 min., then hydrolyzed with dilute sulphuric acid. All reactions were carried out in the presence of an internal standard (n-alkane); quantitative analyses were performed by g.l.c. All new compounds were isolated by distillation and showed satisfactory analytical and spectral data.
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7. A.M.Caporusso, *unpublished results*.
8. The $[\alpha]_D^{25}$ values refer to samples of (+)(5a) purified by g.l.c. (SE 301).
9. (+)(5a) was also obtained via $\text{Pd}(\text{PPh}_3)_4$ -catalyzed coupling of (S)(1a) with isobutylzinc chloride in diethyl ether/THF at -50°C .^{1c} According to Vermeer,² this palladium-promoted reaction should proceed with prevalent inversion in the allenyl moiety, in fact (S)(1a) with methylzinc chloride was converted into (-)-4-methyl-2,3-hexadiene of known R configuration.¹⁰
10. M.Bertrand, G.Gil, A.Kumar, *Nouv.J.Chim.*, 4, 69 (1980).
11. This research was assisted in part by a grant from Ministero della Pubblica Istruzione (Roma).

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