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Electrochemical Allylation of Carbonyl Compounds Using Nickel Catalyst and Zinc(II) Species

Sylvie Durandetti,* Soline Sibille, and Jacques Pêrichon

Laboratoire d'Electrochimie, Catalyse et Synthêse Organique (U.M. No. 28), CNRS, 2, rue Henri Dunant, 94320 Thiais, France

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An efficient electrosynthesis of homoallylic alcohols from allylic chlorides or acetates and carbonyl compounds in the presence of catalytic amounts of $NiBr_2$(bpy) complex (bpy = 2,2′-bipyridine) is achieved in a one-compartment cell fitted with a sacrificial zinc anode. The role of both Zn(II) and Ni(II) species in the coupling reaction is pointed out. An exchange between allylnickel and zinc species is suggested, on the basis of the stereochemistry and kinetics of the allyl addition.

Introduction

The addition of an allylic unit to carbonyl compounds is an important synthetic process, homoallylic alcohols being useful intermediates in the synthesis of natural products. Different methods have been developed based essentially on the nucleophilic character of the allylmetal obtained from allyl bromides and metallic species (M = Li, Mg, Al, Zn, Ni, ...).[1–6]

The use of reducing salts such as $CrCl_2$,[7] SmI_2,[8] $SnCl_2$,[9] and $CeCl_3$[10] (used in stoichiometric amounts) has recently been developed, and particular attention has been given to the stereochemical aspects of the reaction.

A different access to allylic anions is their electrochemical generation. Electroreduction of allylic halides in the presence of carbonyl compounds in HMPT has been reported[11] to give the expected homoallylic alcohol only in the case of acetone in excess.

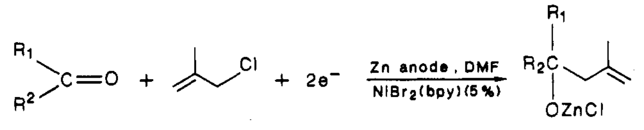
An electrochemical activation of allyl bromide using catalytic amounts of tin has also been reported[12] to yield homoallylic alcohols.

We recently described[13] an electrosynthetic process using a sacrificial zinc anode and catalytic amounts of $NiBr_2$(bpy) complex (bpy = 2,2′-bipyridine) that affords homoallylic alcohols with good to high yields, from methallyl chloride and a variety of carbonyl compounds.

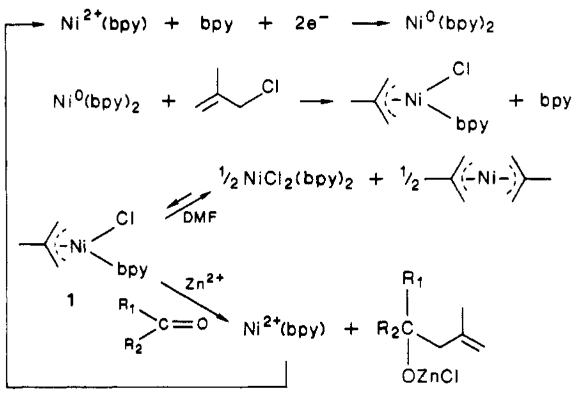
Further investigations were undertaken in order to determine the role of the zinc anode and that of the nickel catalyst, both of which proved essential in the coupling reaction. Due to the synthetic potential of the process, its scope of application has been explored and the selectivity of the addition has been examined.

The coupling reaction of methallyl chloride with a wide variety of carbonyl compounds has been studied as well as the influence of several reaction parameters (part A). A stereochemical study concerning axial/equatorial addition of methallyl chloride to 4-*tert*-butylcyclohexanone is presented in part B and a regiochemical approach to the addition of isomeric chlorobutenes on various substrates in part C.

Scheme I



Scheme II



Results and Discussion

A. General Addition of Allyl Compounds to Ketones and Aldehydes. The results of the addition reaction of methallyl chloride to various aldehydes and ketones (Scheme I) are presented in Table I. Aromatic as well as aliphatic compounds give good yields of the corresponding homoallylic alcohols. Limitations are encountered only with hindered ketones. In these cases, the coupling becomes difficult (for example, with diisopropyl ketone), and only traces of alcohol are detected with fenchone.

An allylic acetate can be used instead of the chloride derivative (Table II). The coupling of the allyl acetate with benzaldehyde or cyclohexanone has the same efficiency as that from the corresponding chloride.

We also studied the addition of methallyl chloride to α,β-unsaturated carbonyl compounds (Table III). The yields of alcohols are in the range of 50%, the rest being nonrecovered polymers. Exclusive 1,2-addition is observed in all cases. Several ligands were tested in order to change the regioselectivity of the addition, but no changes were observed and alcohols were obtained in lower yields. This point was unexpected since Luche et al.[14] reported that

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[13] Sibille, S.; d'Incan, E.; Leport, L.; Massebieau, M. C.; Perichon, J. *Tetrahedron Lett.* **1987**, *28*, 55.

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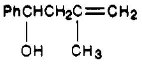
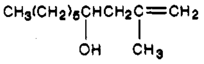
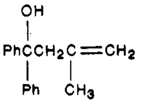
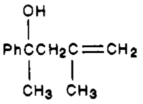
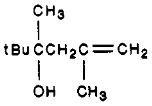
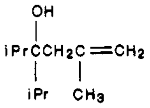
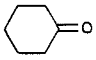
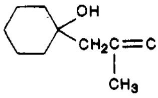
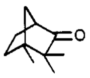
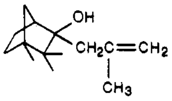
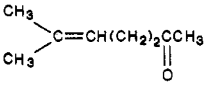
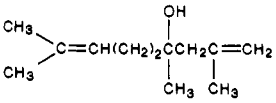
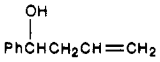
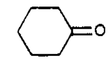
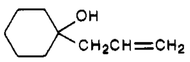
Table I. Nickel-Catalyzed Electrochemical Reaction of Methallyl Chloride with Various Carbonyl Compounds[a]

carbonyl compound	ratio allyl/carbonyl	product	isolated yield,[b] %
PhCHO	1.5	 $\underset{\mathrm{OH}}{\mathrm{PhCH}}\mathrm{CH_2}\underset{\mathrm{CH_3}}{\mathrm{C}}{=}\mathrm{CH_2}$	85
$CH_3(CH_2)_5CHO$	1.5	 $\mathrm{CH_3(CH_2)_5}\underset{\mathrm{OH}}{\mathrm{CH}}\mathrm{CH_2}\underset{\mathrm{CH_3}}{\mathrm{C}}{=}\mathrm{CH_2}$	70
PhCOPh	2	 $\mathrm{Ph}\overset{\mathrm{OH}}{\underset{\mathrm{Ph}}{\mathrm{C}}}\mathrm{CH_2}\underset{\mathrm{CH_3}}{\mathrm{C}}{=}\mathrm{CH_2}$	86
$PhCOCH_3$	1.5	 $\mathrm{Ph}\overset{\mathrm{OH}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_2}\underset{\mathrm{CH_3}}{\mathrm{C}}{=}\mathrm{CH_2}$	92
$tBuCOCH_3$	3	 $\mathrm{tBu}\overset{\mathrm{CH_3}}{\underset{\mathrm{OH}}{\mathrm{C}}}\mathrm{CH_2}\underset{\mathrm{CH_3}}{\mathrm{C}}{=}\mathrm{CH_2}$	60
iPrCOiPr	4	 $\mathrm{iPr}\overset{\mathrm{OH}}{\underset{\mathrm{iPr}}{\mathrm{C}}}\mathrm{CH_2}\underset{\mathrm{CH_3}}{\mathrm{C}}{=}\mathrm{CH_2}$	9[c]
	2		85
	8		trace[c]
 $(\mathrm{CH_3})_2\mathrm{C{=}CH(CH_2)_2}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{CH_3}$	2	 $(\mathrm{CH_3})_2\mathrm{C{=}CH(CH_2)_2}\overset{\mathrm{OH}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_2}\underset{\mathrm{CH_3}}{\mathrm{C}}{=}\mathrm{CH_2}$	85

[a] Catalytic procedure; DMF, NBu_4Br (4×10^{-2} M), $NiBr_2(bpy)$ (2×10^{-2} M) + 2bpy, carbonyl compound (4×10^{-1} M), room temperature, I = 100 mA, Q = 2 F/mol of methallyl chloride, under argon, zinc anode and carbon cathode. [b] Yields are relative to initial carbonyl. [c] Unreacted ketone is recovered.

Table II. Nickel-Catalyzed Electrochemical Reaction of Allyl Acetate with Carbonyl Compounds[a]

carbonyl compound	product	isolated yield,[b] %
PhCHO	 $\mathrm{Ph}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCH_2CH{=}CH_2}$	80
		83

[a] Catalytic procedure: DMF, NBu_4Br (4×10^{-2} M), $NiBr_2(bpy)$ (2×10^{-2} M) + 2bpy, carbonyl compound (4×10^{-1} M), room temperature, I = 100 mA, Q = 2 F/mol of allyl acetate under argon, zinc anode and carbon cathode. [b] Yields are relative to initial carbonyl.

catalytic amounts of nickel acetylacetonate ($Ni(acac)_2$) induced conjugate addition of organozinc reagents to such substrates. However, in this study, the behavior of allyl compounds was not reported.

Voltametric experiments have been performed on the nickel bipyridine–methallyl chloride system to give insight into the mechanism of the electrocatalytic process. Of all the species present, the nickel bipyridine complex is the most readily reducible one (−1.2 V/SCE). The zero-valent nickel species reacts very rapidly with an allylic chloride ($k > 200$ M^{-1} s^{-1}), affording (π-allyl)nickel chloride.[15] In dimethylformamide (DMF), in contrast to acetonitrile, disproportionation of the complex is observed[16] and the catalytic Scheme II can be proposed.

The complexity of the process prompted us to investigate some of its significant parameters: electrodes, solvent, and catalyst (Table IV). The main side reactions, when the yield is low, are the protonation or the dimerization of the allyl moiety and the base-catalyzed dimerization of the ketone.

The optimized conditions (entry 1, Table IV) involve the use of a carbon fiber cathode, a zinc anode, and $NiBr_2(bpy)$ complex with a slight excess of ligand in DMF solution. As expected from the proposed Scheme II, the nickel ligand is an important factor, and replacing phosphine for bipyridine (entries 6 and 7, Table IV) lowers significantly the yield of alcohol. While the nature of the cathode and the solvent are of little importance (entries 4 and 5, Table IV), the nature of the anodic material is a crucial factor (entries 8–12, Table IV).

Concerning the role of the anode, two explanations can be proposed: the cations generated in the anodic process can participate in the cathodic coupling reaction. Comparison of entries 9 and 13 (Table IV) shows the positive effect on the addition reaction of added Zn(II) salt. On the other hand, the presence in the reaction medium of the metal itself can induce some of the observed side reactions. The use of a magnesium anode (entry 13, Table IV), even if a zinc salt is added, leads to yields lower than those obtained with a zinc anode (entry 1, Table IV).

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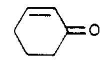
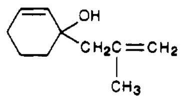
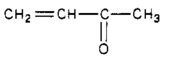
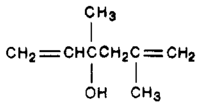
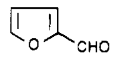
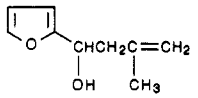
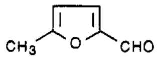
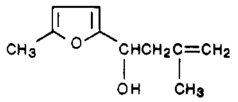
[15] Bontempelli, G.; Daniele, S.; Fiorani, M. *Ann. Chim. (Rome)* **1985**, *75*, 19.

[16] Hegedus, L. S.; Thompson, D. H. P. *J. Am. Chem. Soc.* **1985**, *107*, 5663.

Table III. Reaction of Methallyl Chloride with Conjugated Carbonyl Compounds Using Nickel Catalyst[a]

carbonyl compound	complex	product	isolated yield,[b] %
	$NiBr_2(bpy) + 2bpy$		55
 $CH_2{=}CH{-}C({=}O){-}CH_3$	$NiBr_2(cyclam)$[c] $Ni(acac)_2 + ZnBr_2$[d] $NiBr_2(bpy) + 2bpy$	 $CH_2{=}CHC(OH)(CH_3)CH_2C(CH_3){=}CH_2$	26 37 43
	$NiBr_2(bpy) + 2bpy$		40
	$NiBr_2(bpy) + 2bpy$		48

[a] Catalytic procedure: DMF, NBu_4Br (4×10^{-2} M), Ni catalyst (2×10^{-2} M), carbonyl compound (4×10^{-1} M), RX/ketone = 2, room temperature, $I = 100$ mA, $Q = 2$ F/mol of methallyl chloride, under argon, zinc anode and carbon cathode, neutral hydrolysis. [b] Yields are relative to initial carbonyl. [c] Cyclam = 1,4,8,11-tetraazacyclotetradecane. [d] $ZnBr_2$ (2×10^{-2} M).

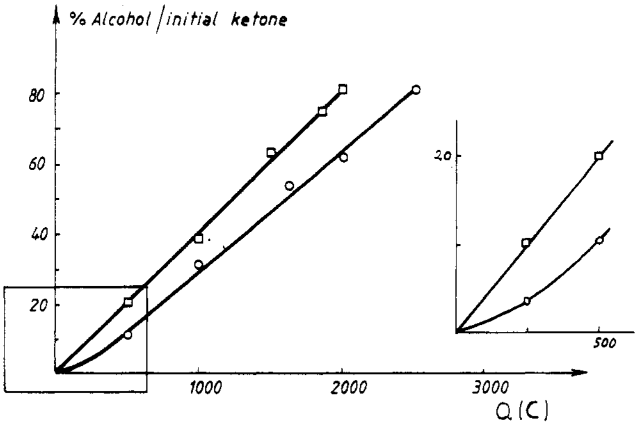


Figure 1. Variation of the alcohol/initial ketone ratio during the electrolysis. Zinc anode, carbon cathode, solvent DMF (25 mL), $NiBr_2(bpy)$ (0.5 mmol) + bpy (1 mmol), cyclohexanone (10 mmol), and methallyl chloride (20 mmol); ○, without $ZnBr_2$; □, with $ZnBr_2$ (5 mmol).

Magnesium is too powerful a reducing metal, and enolization of the ketone is enhanced. Using a zinc anode is doubly advantageous: it produces Zn(II) species and avoids side reactions involving the carbonyl compounds.

The role of the zinc(II) ions was further demonstrated by following the evolution of the coupling reaction during the electrolysis (Figure 1). An "induction period" preceding the formation of the alcohol is suppressed by adding anhydrous $ZnBr_2$ before the electrolysis. During this induction period, the only reduction products of the methallyl chloride are 2-methylpropene and 2,5-dimethyl-1,5-hexadiene. These side reactions are minimized in the presence of zinc salts, allowing the faradic yield to increase. The ratio of methallyl chloride to the carbonyl compound is lowered, but the chemical yield (relative to carbonyl compound) remains unchanged (entries 1 and 14, Table IV).

(π-Allyl)nickel complexes are known to be less reactive toward carbonyl compounds than the other classical allylmetal species (Li, Mg, Zn).[17] According to Hegedus et al.,[17] the coupling of (π-methallyl)nickel bromide and cyclohexanone in DMF requires severe conditions (24 h at 50 °C). The presence of zinc salts in our catalytic process may explain its efficiency, which cannot be due only to the nickel complex.

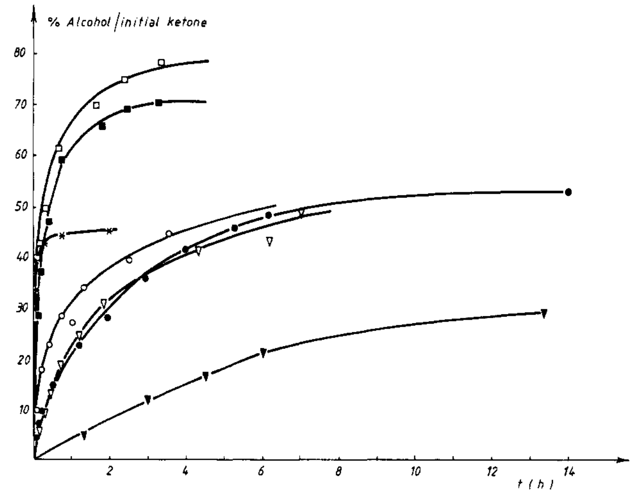
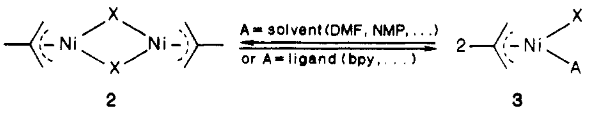


Figure 2. Kinetics of alcohol formation from methallyl chloride and 4-*tert*-butylcyclohexanone (stoichiometric procedure). In DMF: [Ni(II)] = 0.1 M; RX/ketone = 1.5. In acetonitrile: [Ni(II)] = 0.04 M; RX/ketone = 1. [RX] = [Ni(II)]. (1) (▼) without any salt in CH_3CN. (2) (▽) without any salt in DMF. (3) (●) with $MgBr_2$ in DMF; Ni/Mg, 1/1; Mg/Br, 1/2.4. (4) (○) with $ZnBr_2$ in DMF; Ni/Zn, 1/1; Zn/Br, 1/3.9. (5) (■) with $ZnBr_2$ in DMF; Ni/Zn, 1/2; Zn/Br, 1/3.2. (6) (□) with $ZnBr_2$ in DMF; Ni/Zn, 1/4; Zn/Br, 1/2.6. (7) (*) with $ZnBr_2$ in CH_3CN; Ni/Zn, 1/4; Zn/Br, 1/2.2.

Scheme III



The interaction between the (π-allyl)nickel halide and zinc(II) has been clearly demonstrated by a kinetic study of the last step of the catalytic cycle (Scheme II). The $Ni^0(bpy)_2$ complex was stoichiometrically prepared by potentiostatic reduction of $NiBr_2(bpy)$ in a divided cell in DMF. After addition of 1 equiv of methallyl chloride, the allylic complex 1 was obtained. 1 reacted with the 4-

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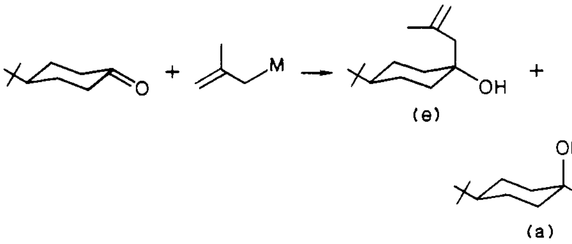
(17) Hegedus, L. S.; Wagner, S. D.; Waterman, E. L.; Siirala-Hansen, K. *J. Org. Chem.* **1975**, *40*, 593.

Table IV. Influence of Anode, Cathode, Ligand, and Solvent over the Electrochemical Coupling of Methallyl Chloride and Cyclohexanone[a]

entry	anode	cathode	complex	solvent	ratio allyl/carbonyl	isolated yield,[b] %
1	Zn	carbon	$NiBr_2(bpy) + 2bpy$	DMF	2	85
2	Zn	carbon	$NiBr_2(bpy)$	DMF	2	80
3	Zn	carbon	–	DMF	1.7	61[c]
4	Zn	foamy nickel	$NiBr_2(bpy) + 2bpy$	DMF	2	63
5	Zn	carbon	$NiBr_2(bpy) + 4bpy$	CH_3CN	2	62
6	Zn	carbon	$NiBr_2(PPh_3)_2 + 4PPh_3$	DMF	2.5	62
7	Zn	carbon	$NiCl_2$(diphos)[d]	DMF	2.5	48
8	Mn	carbon	$NiBr_2(bpy) + 2bpy$	DMF	2.5	38
9	Mg	carbon	$NiBr_2(bpy) + 2bpy$	DMF	0.3	20
10	Al	carbon	$NiBr_2(bpy) + 2bpy$	DMF	0.3	20
11	Mg	stainless steel	–	DMF	0.3	20
12	Al	stainless steel	–	DMF	0.3	20
13	Mg	carbon	$NiBr_2(bpy) + 2bpy + ZnBr_2$[e]	DMF	1.2	43
14	Zn	carbon	$NiBr_2(bpy) + 2bpy + ZnBr_2$[e]	DMF	1.2	85

[a] Catalytic procedure: NBr_4Br (4×10^{-2} M), NiX_2Ln (2×10^{-2} M), cyclohexanone (4×10^{-1} M), room temperature, under argon, $I = 100$ mA, $Q = 2$ F/mol of methallyl chloride. [b] Yields are relative to initial cyclohexanone. [c] Extensive zinc deposition occurs. [d] Diphos = 1,2-Bis(diphenylphosphino)ethane. [e] Ni/Zn, 1/10.

Scheme IV



tert-butylcyclohexanone. The formation of the addition product of the nickel complex 1 to the ketone was continuously followed by GC (Figure 2, curve 2). Similar kinetic experiments were done in the presence of $ZnBr_2$ (Figure 2, curves 4–6) or $MgBr_2$ (Figure 2, curve 3). A tremendous increase of the reaction rate was observed with the former but not with the latter (Figure 2, curves 2, 3, and 6). However, when the major form for Zn(II) is $ZnBr_3^-$, obtained by increasing the ratio Br^-/Zn(II), no significant increase can be evidenced (Figure 2, curves 2 and 4).

The same experiment was performed in acetonitrile as solvent, where the allylic complex is known to be in the dimeric form **2** (Scheme III), which is not reactive toward ketones.[1] In our conditions (without $ZnBr_2$), the coupling reaction in acetonitrile is less efficient than in DMF (Figure 2, curve 1), affording, however, a 30% yield of alcohol. This unexpected result could be due to the presence of bipyridine, which enables the complex to be in a monomeric active form **3**.

A similar accelerating effect of $ZnBr_2$ was observed in acetonitrile (Figure 2, curve 7) and correlates with the results of a catalytic experiment (entry 5, Table IV).

The important effect of $ZnBr_2$ salt on the kinetics of the coupling reaction prompted us to examine its influence on the selectivity of the reaction.

B. Stereochemistry of the Addition of Methallyl Chloride to 4-*tert*-Butylcyclohexanone. The stereochemistry of the addition of organometallics to 4-*tert*-butylcyclohexanone is very dependent on the nucleophile's hardness.[18] Two attacks are possible: equatorial attack gives the axial alcohol (a), and the other gives the equatorial alcohol (e) (Scheme IV).

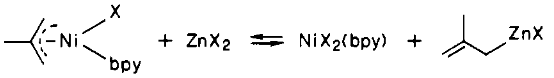
Important differences in e/a ratios were observed for the coupling of 4-*tert*-butylcyclohexanone and methallyl chloride, depending on the experimental conditions. The results of the stoichiometric experiments above described are compared to the catalytic ones in Table V.

Table V. Catalytic and Stoichiometric Reaction of Methallyl Chloride with 4-*tert*-Butylcyclohexanone

run	conditions	isolated yield,[a] %	e/a
	Stoichiometric Process[b]		
1	DMF; without $ZnBr_2$	49	40/60
2	DMF; Ni/Zn, 1/4	76	24/76
3	CH_3CN; without $ZnBr_2$	30	39/61
4	CH_3CN; Ni/Zn, 1/4	45	22/78
	Catalytic Process[c]		
5	DMF, $I = 20$ mA	82	25/75
6	DMF, $I = 330$ mA	82	25/75
7	CH_3CN, $I = 100$ mA	72	28/72

[a] Yields of both isomers are relative to initial ketone. [b] Stoichiometric procedure: NBu_4Br (2×10^{-2} M), NBu_4BF_4 (10^{-1} M), room temperature, under argon, $Q = 2$ F/mol of Ni(II). In DMF, $NiBr_2(bpy)$ (10^{-1} M) + 2bpy, methallyl chloride (10^{-1} M), RX/ketone = 1.5. In acetonitrile, $NiBr_2(bpy)$ (4×10^{-2} M) + 10bpy, methallyl chloride (4×10^{-2} M), RX/ketone = 1. [c] Catalytic procedure: $ZnBr_2$ (2×10^{-2} M), NBu_4Br (4×10^{-2} M), $NiBr_2(bpy)$ (2×10^{-2} M) + 2bpy in DMF and 10bpy in CH_3CN, carbonyl compound (4×10^{-1} M), room temperature, $Q = 2$ F/mol of RX, under argon, zinc anode and carbon cathode, RX/ketone = 2.

Scheme V



The low yield obtained in the stoichiometric process without $ZnBr_2$ was expected, due to the slowness of the reaction. The observed e/a ratio (40/60) in DMF (run 1, Table V) as well as in acetonitrile (run 3, Table V) should be characteristic of the allylnickel complex, although literature data are lacking.

When $ZnBr_2$ is added (runs 2 and 4, Table V), an important modification in the stereochemistry is observed, together with the above-mentioned accelerating effect. The e/a ratios (24/76) are very close to the published results of the addition of allylzinc to the same substrate in HMPT.[18] The same e/a ratio is observed in the catalytic process and is independent of the current density (runs 5 and 6, Table V).

We are convinced that this change in stereoselectivity can be attributed to an exchange reaction between the allylnickel complex and the zinc(II) species, leading to an allylzinc complex (Scheme V). This assumption is also supported by the result of part A, since it is well-known

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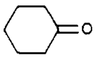
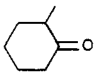
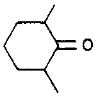
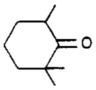
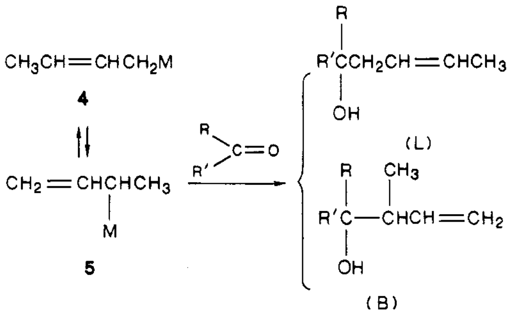
Table VI. Catalytic and Stoichiometric Reaction of Crotyl Chloride with Various Ketones

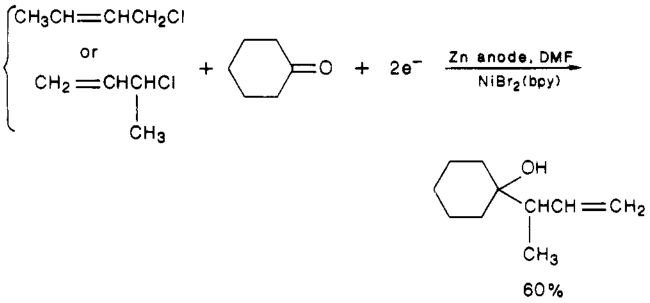
		run 1[a]		run 2[b]		run 3[c]	
entry	ketone	yield,[d] %	L/B	yield,[d] %	L/B	yield,[d] %	L/B
1		26	0/100	60	0/100	60	0/100
2		8	15/85	57	13/87	63	10/90
3[e]		0		10	50/50	67	35/65
4						0	

[a] Run 1: stoichiometric procedure without ZnBr$_2$. [b] Run 2: stoichiometric procedure with ZnBr$_2$ (Ni/Zn, 1/4). [c] Run 3: Catalytic procedure. [d] Yields of all isomers are relative to initial ketone. [e] Mixture of two isomers.

Scheme VI



Scheme VII



that the allylzinc complex is more reactive than the corresponding (π-allyl)nickel halide. This exchange seems to be very rapid since an increase in the current density from 10 to 165 A/m^2 was ineffective in changing the stereoselectivity of the addition.

C. Regioselectivity of the Addition of Chlorobutenes to Various Ketones. In order to ensure the proposed exchange between allylnickel and Zn(II) species, the products obtained in the coupling of the butenyl reagents (**4** and **5**) with sterically hindered ketones were examined. The ratio of linear to branched alcohol (L/B) is known to depend mainly on the nature of the metal in the organometallic reagent (Scheme VI).

Reactions of allylmagnesium and allylzinc are fully described in the literature,[19-23] but data are lacking about (π-allyl)nickel complexes.

We verified that the coupling of cyclohexanone and 1-chloro-2-butene (crotyl chloride) or 3-chloro-1-butene led to similar yields and L/B ratios, as shown in Scheme VII (same yield of 60% and B > 95%).

We then used crotyl chloride during the rest of the study. Three procedures were compared: a stoichiometric one without ZnBr$_2$ (run 1), a stoichiometric one with ZnBr$_2$ (run 2), and a catalytic one (run 3) reported in Table VI.

As expected, the L/B ratio increased from cyclohexanone to α-methylated cyclohexanones. A decrease in the yield of alcohol was also observed, according to the results of part A for the more hindered ketone (Table I).

The expected role of ZnBr$_2$ on the regiochemistry cannot be shown unequivocally due to the lack of reactivity of the allylnickel complex alone. The main conclusion concerns the different efficiencies of the three procedures. (π-Allyl)nickel halide is rather unreactive toward moderately hindered ketones (entry 2, Table VI). In the presence of Zn(II), an increase of reactivity is observed due to the formation of allylzinc species. But the presence of zinc is not the only determining factor, and the catalytic procedure alone enables the coupling with moderately hindered ketones such as 2,6-dimethylcyclohexanone (entry 3, Table VI); this may be due to a continuous electrochemical regeneration of the active species, allowing longer reaction times. However, the catalytic effect fails with 2,2,6-trimethylcyclohexanone (entry 4, Table VI).

Conclusion

The electrochemical procedure combining a nickel catalyst and a sacrificial zinc anode confers to the system the properties of both organometallic species. One of the main advantages lies in continuous regeneration of the active species.

Our catalytic process to synthesize homoallylic alcohols is efficient and gives high yields of alcohols from either aldehydes or ketones, except for the most hindered ones; exclusive 1,2-addition is observed with α,β-unsaturated carbonyl compounds. It compares favorably with chemical procedures involving organometallics: the starting materials are allylic chlorides or acetates instead of bromides, and the solvent is DMF instead of an ether. A rough metal is used and does not need any other activation than the electrolysis itself. The nickel complex is easily accessible and is used in catalytic amounts.

The simplicity of the electrolysis procedure makes it an attractive alternative for the synthesis of homoallylic alcohols.

Work is in progress to obtain evidence by electrochemical analysis of the transmetalation reaction between (π-

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allyl)nickel complex and zinc(II).

Experimental Section

Nickel bromide, nickel chloride, zinc bromide, and 1,4,8,11-tetraazacyclotetradecane (cyclam) were obtained from Alfa. If necessary $ZnBr_2$ was dried by heating overnight at 150 °C in a vacuum oven. 2,2′-Bipyridine was purchased from Janssen; diphos, nickel acetylacetonate, and tetrabutyl ammonium bromide were purchased from Fluka. The anodes are zinc rod (Alfa), magnesium rod (Prolabo), aluminum rod (Alfa), and nickel wire (Alfa). The cathode is of carbon fiber. Other reagents were obtained from Aldrich or Janssen and generally used as received, except for the methallyl chloride and crotyl chloride, which were distilled before use. *N,N*-Dimethylformamide (Prolabo) was distilled from calcium hydride and copper sulfate under reduced pressure. Acetonitrile was used as received (Merck). Products were identified by the usual techniques: infrared spectra (Perkin-Elmer 577 spectrometer); NMR spectrometer (Varian EM 360L, Brücker (300 and 90 MHz), $\delta_{ppm}{}^{TMS}$); mass spectra (they were recorded on an ITD Finnigan spectrometer coupled with a capillary column gas chromatograph); microanalyses (they were monitored by the Service Central de Microanalyses (CNRS, Lyon)).

Preparation of NiX_2Ln. $NiBr_2(PPh_3)_2$,[24a] $NiCl_2$(diphos),[24b] $NiBr_2$(bpy),[25a] and $NiBr_2$(cyclam)[25b] were prepared according to literature methods.

General Procedure for the Catalytic Process. Reactions were carried out in a one-compartment cell containing a magnetic stirring bar, a carbon-fiber cathode (20-cm^2 area), and a zinc rod (2 cm^2) as anode at room temperature. The reaction flask was flushed with argon. To a solution of DMF (25 mL) containing 1 mmol of NBu_4Br, 0.5 mmol of $NiBr_2$(bpy), and 1 mmol of 2,2′-bipyridine were added the allylic (12–80 mmol) and the carbonyl (10 mmol) compounds. The electrolysis (I = 100–200 mA) was performed until completion. Then the reaction mixture was poured into a separatory funnel containing 100 mL of aqueous 3% HCl and 100 mL of ether and was thoroughly shaken. The aqueous phase was washed with three 50-mL portions of ether, and the combined ether extracts were washed with three 50-mL portions of water to ensure complete removal of DMF.

The organic phase was dried over anhydrous $MgSO_4$, and solvent was removed under vacuum. The crude product was purified by silica gel (60–200 μm) column chromatography with a pentane–ether mixture.

General Procedure for the Stoichiometric Process. Reactions were carried out in a two-compartment cell (sintered glass no. 4) equipped with a gold cathode and a nickel wire as anode. The electrolysis was performed at controlled potential (−1.4 V/SCE). The reaction flask was flushed with argon. The anodic compartment contained a DMF solution (30 mL) of NBu_4BF_4 (3 mmol) and NBu_4Br (0.5 mmol). The cathodic one contained the same solution to which 3 mmol of $NiBr_2$(bpy) and 6 mmol of 2,2′-bipyridine were added (for acetonitrile, as solvent, the amount of bpy was increased to a 1/10 Ni/bpy ratio). The electrolysis was stopped when the current had reached 5% of its initial value (2 F/mol of Ni), and then 3 mmol of RX was added. The dark-green solution changed to a red one, and then the carbonyl compound (1.5–2 mmol) was added and eventually the $ZnBr_2$ salt. The solution was stirred until the alcohol contents remained constant in the reaction mixture (followed by GC). Cathodic and anodic solutions were mixed in order to minimize the effect of diffusion through the separator. The workup was the same as that of the general procedure for the catalytic process.

A. Methallyl Chloride. The structures of the following products were confirmed by comparison with spectral data from the literature: 3-methyl-1-phenyl-3-buten-1-ol,[26] 2-methyl-1-decen-4-ol,[17] 4-methyl-2-phenyl-4-penten-2-ol,[27] 1-(2-methyl-2-propenyl)cyclohexanol,[17] 1-(2-methyl-2-propenyl)-2-cyclohexen-1-ol,[17] 2,4-dimethyl-1,5-hexadien-4-ol,[29] and 1,1-diphenyl-3-methyl-3-buten-1-ol.[27]

2,5-Dimethyl-3-(1-methylethyl)-5-hexen-3-ol:[28] NMR ($CDCl_3$, 60 MHz) δ 1.0 (d, J = 7 Hz, 12 H), 1.4 (s, OH), 1.6–2.2 (m, 2 H), 1.9 (s, 3 H), 2.3 (s, 2 H), 4.65–5.1 (m, 2 H); MS, 115 (M − 55), 97, 71, 55, 43 (base), 41, 39; IR (neat) 3450, 3070, 1640, 1375–1385 (doublet), 890 cm^{-1}.

2,4,8-Trimethyl-1,7-nonadien-4-ol: NMR ($CDCl_3$, 60 MHz) δ 1.2 (s, 3 H), 1.3–2.3 (m, 4 H), 1.65 (d, 6 H), 1.85 (s, 3 H), 2.2 (s, 2 H), 2.25 (s, OH), 4.7–5.3 (m, 3 H); MS, 164 (M − H_2O), 149, 127, 109 (base), 95, 83, 81, 69, 43; IR (neat) 3450, 3070, 3020, 1640, 890, 840 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.06; H, 12.19.

2,2,3,5-Tetramethyl-5-hexen-3-ol:[28] NMR ($CDCl_3$, 60 MHz) δ 0.95 (s, 9 H), 1.1 (s, 3 H), 1.5 (s, OH), 1.85 (s, 3 H), 2.2 (d, 2 H diastereotopic), 4.65–5 (m, 2 H).

1-(2-Furyl)-3-methyl-3-buten-1-ol:[30] NMR ($CDCl_3$, 60 MHz) δ 1.7 (s, 3 H), 2.5 (d, J = 7 Hz, 2 H), 3.1 (s, OH), 4.5–5 (m, 3 H), 6–6.4 (m, 2 H), 7.25 (s, 1 H).

3-Methyl-1-(2-(5-methylfuryl))-3-buten-1-ol: NMR ($CDCl_3$, 60 MHz) δ 1.75 (s, 3 H), 2.3 (s, 3 H), 2.55 (d, J = 7 Hz, 2 H), 4.6–5 (m, 3 H), 5.9 (dd, 1 H), 6.1 (d, J = 3 Hz, 1 H); IR (neat) 3400, 3075, 1645, 1565, 895, 785 cm^{-1}; MS, 149 (M − OH), 148, 133, 119, 111 (base), 105, 91, 83, 77, 65, 55. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.90; H, 8.72.

4-(1,1-Dimethylethyl)-1-(2-methyl-2-propenyl)cyclohexanol:[18] NMR ($CDCl_3$, 60 MHz) δ axial 0.85 (s, 9 H), 1–1.8 (m, 9 H + OH), 1.8 (s, 3 H), 2.15 (s, 2 H), 4.65–5.05 (m, 2 H), δ equatorial very similar except 2.25 (s, 2 H); IR (neat) 3450, 3080, 1645, 1075 (equatorial), 970 (axial), 895 cm^{-1}; MS, 193 (M − OH), 155, 137, 109, 95, 81 (base), 69, 67, 57.

B. Allyl Acetate. The structures of the following products were confirmed by comparison with spectral data from the literature: 1-phenyl-3-buten-1-ol[31] and 1-(2-propenyl)cyclohexanol.[2]

C. Crotyl Chloride. The structure of the 1-(1-methyl-2-propenyl)cyclohexanol[2] was confirmed by comparison with spectral data from the literature.

2-Methyl-1-(1-methyl-2-propenyl)cyclohexanol.[20,23] GC (capillary column DB1, 30 m, 60 °C + 2 deg/min) showed that all four possible diastereoisomers (a–d) were present. After two successive separations on column chromatography (pentane–ether, 98/2 v/v), two of these were obtained in pure form. The remaining two were difficult to separate and were collected as a mixture. The relative configurations of these isomers are unknown.

Diastereoisomer a: NMR ($CDCl_3$, 300 MHz) δ 0.87 (d, J = 6.6 Hz, 3 H), 0.98 (d, J = 7 Hz, 3 H), 1.1–1.7 (m, 9 H + OH), 2.46 (dq, 1 H), 5.05–5.15 (m, 2 H), 5.8–5.95 (m (8 lines), $^3J_1$ = 10.9 Hz, $^3J_2$ = 16.5 Hz, $^3J_3$ = 8.4 Hz, 1 H); NMR (DMSO, 60 MHz) δ 3.65 (s, OH); IR (neat) 3590, 3500, 3080, 1635, 995, 970, 920 cm^{-1}; MS, 151 (M − OH), 113, 95 (base), 83, 77, 69, 67, 55, 45, 43, 41, 39.

Diastereoisomer b: NMR ($CDCl_3$, 300 MHz) δ 0.86 (d, J = 6.6 Hz, 3 H), 1.02 (d, J = 7.2 Hz, 3 H), 1.1–1.7 (m, 9 H + OH), 2.52 (dq, 1 H), 5–5.1 (m, 2 H), 5.7–5.85 (m (8 lines), $^3J_1$ = 10.2 Hz, $^3J_2$ = 17.1 Hz, $^3J_3$ = 8.7 Hz, 1 H); NMR (DMSO, 60 MHz) δ 3.73 (s, OH); IR (neat) 3590, 3500, 3080, 1635, 1380, 1250, 1130, 1070, 1030, 980 cm^{-1}; MS is identical with that of diastereoisomer a.

Mixture of diastereoisomers c + d: NMR ($CDCl_3$, 300 MHz) δ 0.94–1.02 (m, 6 H), 1.1–1.7 (m, 9 H + OH), 2.27 (dq, 1 H), 4.95–5.15 (m, 2 H), 5.83–6.05 (m, 1 H); NMR (DMSO, 60 MHz) δ 3.68 (s, OH), 3.73 (s, OH); IR and MS are identical with those of diastereoisomers a and b.

2-Methyl-1-(2-butenyl)cyclohexanol.[20] GC (DB1, 30 m, 60 °C + 2 deg/min) showed two isomers, and these were collected as a mixture: NMR ($CDCl_3$, 300 MHz) δ 0.91 (d, J = 6.5 Hz, 3 H), 1.65 (dm, J = 6.3 Hz, 3 H), 1–1.7 (m, 9 H + OH), 2.35 (m,

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2 H diastereotopic), 5.35–5.9 (m, 2 H); NMR (DMSO, 60 MHz) δ 3.73 (s, OH), 3.78 (s, OH); IR (neat) 3500, 3020, 1650, 1005, 985, 975, 960, 915, 890 cm^{-1}; MS is identical with that of diastereoisomer a.

2,6-Dimethyl-1-(1-methyl-2-propenyl)cyclohexanol. GC (DB1, 30 m, 70 °C + 2 deg/min) showed that three isomers were present (a–c). Two of these were obtained in pure form; c was in too little quantity and was collected with 2,6-dimethyl-1-(2-butenyl)cyclohexanol. It was identified by NMR ($CDCl_3$, 300 MHz): δ 4.95–5.05 (m, 2 H), 5.15–6.1 (m (7 lines), 1 H). The eluant was a mixture of pentane–ether, 98/2 v/v. The relative configurations of these isomers are unknown.

Diastereoisomer a: NMR ($CDCl_3$, 300 MHz) δ 0.84 (d, J = 6.6 Hz, 3 H), 0.91 (d, J = 6.6 Hz, 3 H), 1.05 (d, J = 7 Hz, 3 H), 1.2–1.6 (m, 8 H + OH), 2.68 (dq, $J_1 = J_2$ = 7 Hz, 1 H), 5–5.1 (m, 2 H), 5.9–6.05 (m (7 lines), 1 H); IR (neat) 3570, 3075, 1630, 1000, 970, 945, 920 cm^{-1}; MS, 127 (M – 55), 109 (base), 83, 69, 55. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.11; H, 12.25.

Diastereoisomer b: NMR ($CDCl_3$, 300 MHz) δ 0.9 (d, J = 6.6 Hz, 3 H), 1.06 (d, J = 6.6 Hz, 3 H), 1.09 (d, J = 7 Hz, 3 H), 1.2–1.8 (m, 8 H + OH), 2.43 (dq, $J_1 = J_2$ = 7 Hz, 1 H), 5.05–5.15 (m, 2 H), 5.95–6.1 (m (7 lines), 1 H); MS is identical with that of diastereoisomer a.

2,6-Dimethyl-1-(2-butenyl)cyclohexanol. GC (DB1, 30 m, 70 °C + 2 deg/min) showed four isomers (d–g), and these were collected as mixtures. The relative configurations of these isomers are unknown.

Mixture of diastereoisomers d + e: NMR ($CDCl_3$, 300 MHz) δ 0.93 (d, J = 7 Hz, 6 H), 1.66 (dm, 3 H), 1.2–1.8 (m, 8 H + OH), 2–2.5 (m, 2 H diastereotopic), 5.45–5.75 (m, 2 H); IR (neat) 3500, 3020, 1650, 1035, 990, 970, 945, 735 cm^{-1}; MS, 127 (M – 55), 109 (base), 83, 69, 67, 55.

Mixture of diastereoisomers f + g: NMR ($CDCl_3$, 300 MHz) δ 0.89 (d, J = 6.6 Hz, 6 H), 1.2–1.7 (m, 8 H + OH), 1.66 (dm, 3 H), 2.2–2.35 (m, 2 H diastereotopic), 5.2–5.6 (m, 2 H); IR very similar to that of d + e; MS, identical with that of d + e.

Mixture of diastereoisomers d–g. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.94; H, 12.32.

Acknowledgment. We thank the Société Nationale des Poudres et Explosifs and the CNRS for financial support of the work.

Azophilic Addition of Alkyllithium Reagents to Fluorenimines. The Synthesis of Secondary Amines

Wei Dai, Rajgopal Srinivasan, and John A. Katzenellenbogen*

Department of Chemistry, University of Illinois, 1209 W. California St., Urbana, Illinois 61801

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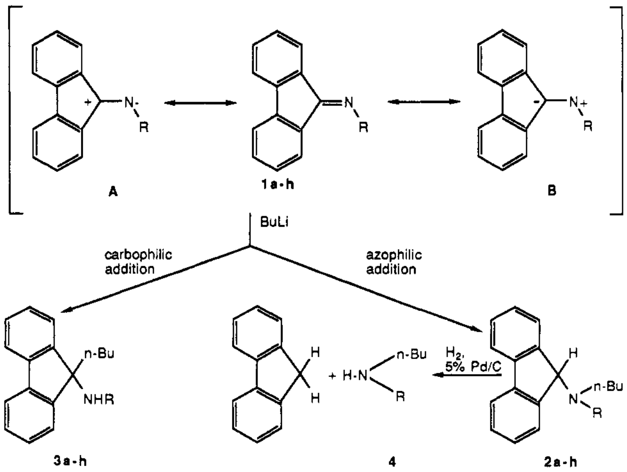
N-Alkyl- and *N*-arylfluorenimines undergo azophilic addition with *n*-BuLi to give *N*-butyl-*N*-alkyl- or *N*-butyl-*N*-aryl-9-aminofluorene systems. The fluorenyl group can then be hydrogenolyzed, furnishing the secondary amine. The selectivity for azophilic (vs carbophilic) addition ranges from 80 to 100% for the *N*-alkylfluorenimines to 24–29% for the *N*-arylfluorenimines. The decreased azophilic selectivity of the *N*-arylfluorenimines can be rationalized on the basis of frontier molecular orbital interactions as well as steric effects. Other related imines, that would appear to provide an inverse polarization similar to that of the fluorenimines, do not give satisfactory yields of azophilic addition products.

Introduction

It is well known that most organometallic addition reactions to carbon–nitrogen double bonds proceed with a nucleophile attacking on carbon (carbophilic addition). Even though there are a few reports of nucleophile attack on certain electrophilic nitrogen derivatives, such as oximes[1] or oxime tosylates,[2,3] nucleophilic addition to the nitrogen end of a carbon–nitrogen double bond (azophilic addition) has been mentioned only rarely.[3–5,6] For example, Metalova[5] reported that the reaction of *N*,*N*′-diphenyl-*p*-quinone (I) with MeLi or PhLi gave the product of azophilic 1,6-addition in 27–53% yield, and Murdoch[3] observed that *N*-alkyltetraphenylcyclopentadienimines (II) underwent reaction with aliphatic lithium and Grignard

Scheme I



a R = n-Bu-
b R = CH_3-
c R = Ph-$(CH_2)_4$-
d R = *i*-Bu-
e R = $PhCH_2CH_2$-
f R = 4-MeO-Ph-
g R = 4-Me-Ph-
h R = Ph-

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[3] Murdoch, J. R.; Hagopian, R. A.; Therien, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 5753.

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[6] There are, of course, many examples of organometallic additions on nitrogen in nitrogen–nitrogen multiply bonded systems. See, for example a–i. (a) Smith, P. A. S.; Rowe, C. D.; Bruner, L. B. *J. Org. Chem.* **1969**, *34*, 3430. (b) Trost, B. M.; Pearson, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 2483. (c) Hassner, A.; Munger, P.; Belinka, B. J., Jr. *Tetrahedron Lett.* **1982**, *23*, 669. (d) Reed, J. N.; Snieckus, V. *Tetrahedron Lett.* **1983**, *24*, 3795. (e) Trost, B. M.; Pearson, W. H. *J. Am. Chem. Soc.* **1983**, *105*, 1054. (f) Gennari, C.; Colombo, L.; Bertolini, G. *J. Am. Chem. Soc.* **1986**, *108*, 6394. (g) Evans, D. A.; Britton, T. C.; Dorow, R. L.; Dellaria, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6395. (h) Trimbie, L. A.; Vederas, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 6397. (i) Demers, J. P.; Klaubert, D. H. *Tetrahedron Lett.* **1987**, *28*, 4933.

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