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Competitive kinetic study of the amination of organomagnesium and -zinc reagents with acetone *O*-sulfonyloxime

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Kinetic studies are reported for the electrophilic amination of substituted phenylmagnesium bromides and CuCN-catalyzed phenylzinc chlorides with acetone *O*-(2,4,6-trimethylphenylsulfonyl)oxime in tetrahydrofuran at reflux temperature and at room temperature respectively. Substituent effects were determined by competition experiments. Rate data are analyzed via Hammett relationships to support the proposed mechanisms for the substitution of these organometallics with an electrophilic amino transfer reagent. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: Grignard reagents; zinc cyanocuprates; electrophilic amination; competitive kinetics; *O*-(arenesulfonyl)ketoximes; Hammett plots

INTRODUCTION

The importance of primary amines as synthetic intermediates creates an increasing need for reagents capable of direct delivery of the amino group to electrophilic or nucleophilic carbon.[1] Arylamines have special importance as entries into nitrogen-containing heterocyclic systems, which are found in many natural and pharmaceutical products. Transition-metal-catalyzed nucleophilic amination of aryl halides, i.e. Buchwald–Hartwig coupling,[2–4] has received special attention for the synthesis of arylamines, whereas electrophilic amination of main group organometallics has found increasing application for synthesis of all types of amine (Scheme 1).[5–9]

A variety of synthetic equivalents of the $NH_2^{\oplus}$ synthon have been developed over the years, and efficient nonsymmetric and symmetric methodologies for the synthesis of amines **7**[5–10] and α-aminocarbonyl compounds **8**[8,11–13] have been published. Electrophilic amino transfer reagents **1**–**6** (Scheme 2) contain either sp^3N, such as *O*-substituted hydroxylamines **1a**–**d** (*O*-methyl- (**1a**), *O*-2,4-dinitrophenyl- (**1b**), *O*-(diaryl)(phosphinyl- (**1c**), *O*-(arenesulfonyl) (**1d**)), *N*,*O*-bis(trimethylsilyl)hydroxylamine (**1e**), *N*-(t-butoxycarbonyl)-*O*-tosylhydroxylamine (**1f**) and oxaziridines (**2**) or sp^2N, such as azides (**3**), diazene dicarboxylates (**4**), ketone *O*-(arenesulphonyl)oximes (**5**) and arenediazonium salts (**6**).

So far, amination of organo-lithium, -magnesium, -copper and -zinc reagents has found numerous applications in the synthesis of primary amines. However, a few reports dealt with the mechanistic investigation and (according to the best of our knowledge) no report has appeared about the kinetic investigation of amination of carbanions and α-metallocarbonyl compounds.

Beak's group, in a series of detailed papers, reported on the mechanistic investigation of amination of organolithiums[14,15] and α-lithionitriles[16] with *O*-methylhydroxylamine (**1a**)[14,15] and *O*-(diarylphosphinyl) hydroxylamine (**1c**)[16] and provided evidence for a polar S_N2-like mechanism. Ricci and coworkers, in their work on the amination of higher order lithium cuprates with **1e**, offered a mechanism[17] that closely follows Beak's approach.

Ketone *O*-(arenesulfonyl)oximes (**5**) have recently been developed as amino transfer reagents (Scheme 3). For amination of aryllithiums, **5a** has been used.[18] Amination of alkyl Grignard reagents with **5b** in the presence of CuCN catalysis,[19] and also of alkyl and aryl Grignard reagents with **5c**[20] and **5d**[21], and very recently with **5e**,[22] without catalysis have been developed in Narasaka's laboratories.

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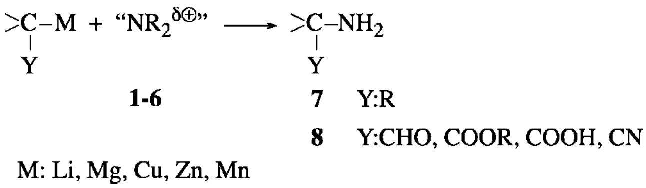
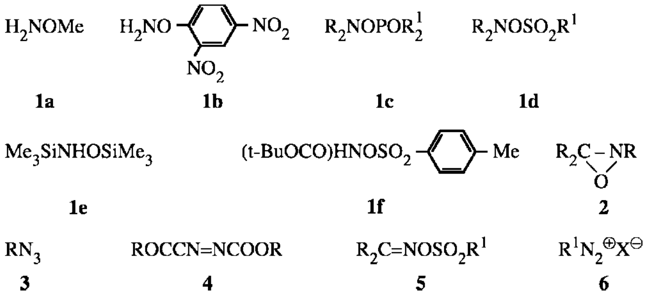
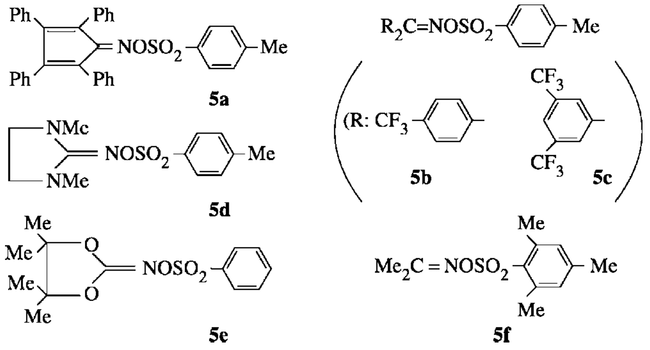


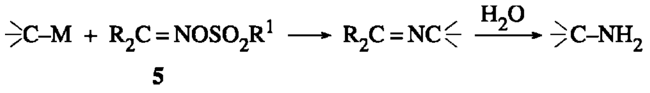
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

We developed **5f** for amination of alkyl and benzyl Grignard reagents in the presence of CuI catalysis in ether–toluene[23] or without catalysis in tetrahydrofuran (THF),[24] both at reflux temperature. Recently, successful amination of Grignard reagents under Barbier conditions was reported.[25] We also used **5f** for amination of organozincs in the presence of CuCN catalysis at room temperature.[26,27] Ketone *O*-(arenesulfonyl)oximes (**5**) aminate carbanions, giving *N*-organylimines as isolable intermediates, which then hydrolyzed to imines (Scheme 4).[18,20,21]

We are currently trying to provide kinetic supports for the possible mechanisms of electrophilic aminations of carbanions in a program of research. Stimulated by recent progress on the use of competitive kinetics for mechanistic investigation, we first carried out competition experiments for the amination of aryl-magnesium, -copper and -zinc reagents with *O*-methylhydroxylamine (**1**) and acetone *O*-(2,4,6-trimethylphenylsulfonyl)oxime (**5f**) as model reactions for amination of aryl carbanions on sp^3N and sp^2N respectively. It seemed reasonable to us to expect that the rate would be dependent on the structural effects in the amination of carbanions with a polar mechanism and then rate data would give Hammett relationships. Nakamura and coworkers have already shown that substitution on sp^2N is an energetically feasible process in their theoretical studies on intramolecular nucleophilic displacement of the protonated oxime oxygen with an aryl ring.[28]

In this study, we report on a competitive kinetics study and on structure–reactivity relationships in the amination of substituted phenyl magnesium and zinc cyanocuprates with acetone *O*-(2,4,6-trimethylphenyl)sulfonyloxime (**5f**). Mechanisms of these reactions are also discussed on the basis of the experimental results.

EXPERIMENTAL

General

All reactions were carried out under dry nitrogen atmosphere using oven-dried glassware. Reagents and solvents were handled by using standard syringe–septum cap techniques.[29] Quantitative gas–liquid partition chromatography (GLPC) analyses were performed on a Unicam 610 gas chromatograph equipped with a DB-1 glass capillary column packed with dimethylpolysiloxane using the internal standard technique.

Bromobenzene, all substituted bromobenzenes and authentic samples of aniline and substituted anilines were obtained commercially and, except for reagent-grade chemicals, were purified using literature procedures. THF was distilled from sodium benzophenone dianion under nitrogen immediately before use. Magnesium turnings for Grignard reactions (Fischer) were used without purification. Zinc chloride (Aldrich) was dried under reduced pressure (2 mmHg) at 100 °C for 2 h and dissolved in THF prior to use. Copper(I) cyanide (Aldrich) was purified according to the published procedure[30] dried at 60–90 °C under reduced pressure for 1 h, and kept under dry nitrogen for at least 2 months without any noticeable change.

Grignard reagents, RMgBr (**9a**–**g**) were prepared in THF by conventional, standard methods found elsewhere, and their concentrations were found prior to use by titration with *sec*-butyl alcohol using *O*-phenanthroline as an indicator.[31] Organozinc chlorides, RZnCl (**10a**–**g**) were prepared by addition of 1 mol equivalent of Grignard reagent to a solution of 1 mol equivalent of $ZnCl_2$ in THF at −15 to 0 °C and stirring at this temperature for 15–30 min.[32,33]

Acetone *O*-(2,4,6-trimethylphenylsulfonyl)oxime (**5a**) was prepared and purified according to the published procedure.[34]

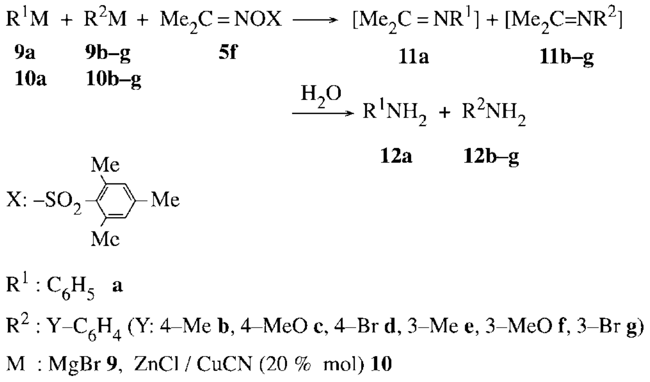
Competitive amination of pairs of Grignard reagents

To a flame-dried, two-necked and round-bottom flask equipped with a septum cap, a stirring bar and a septum-capped reflux condenser, a substituted phenylmagnesium bromide (**9b**–**g**; 2 mmol) and phenylmagnesium bromide (**9a**; 2 mmol) were placed by syringes and (**5f**; 0.1275 g; 0.5 mmol in 5 cm^3 THF) was added rapidly by means of a cannula. The flask was then immersed in a previously heated water bath on a magnetic stirrer and the brown reaction mixture was refluxed at 72–75 °C for an appropriate time (60 and 120 min for optimum conditions). For hydrolytic work-up, concentrated HCl (5 cm^3) was added and the reaction mixture was stirred at room temperature for 3–4 h. The brown solution was washed with diethyl ether to remove ether-soluble products. The aqueous phase was made basic with concentrated NaOH solution and the free amines were extracted with diethyl ether. After evaporation of the solution to a convenient volume, internal standard was added and the solution was subjected to GLPC analysis.

The same procedure was applied for the competitive amination of a pair of CuCN-catalyzed organozinc chlorides, except that the reaction was carried out at 25 °C. Transmetallation of **10b**–**g** (2 mmol) and **10a** (2 mmol) using $ZnCl_2$ (0.5453 g; 4 mmol) was carried out in the same reaction flask. 20 mol% CuCN (0.117 g; 0.8 mmol) was added, the temperature was allowed to rise to 25 °C and, after stirring for 15 min, **5f** (0.5 mmol) was added.

RESULTS AND DISCUSSION

In order to find the structural effects on the azaphilic reactivity of carbanions in their amination with acetone *O*-(2,4,6-trimethylphenylsulfonyl)oxime (**5f**), we have been interested in the relative rates of amination of a series substituted phenylmagnesium and zinc–copper reagents. For this purpose, we used the competitive kinetics method, in which a pair of phenylmetals, R^1M and R^2M reacted with a limited amount of **5f** (Scheme 5). As model reactions, we chose amination of phenylmagnesium bromides in THF at reflux temperature and phenylzinc chlorides in the presence of CuCN catalysis in THF at room temperature. These conditions were already optimized in the synthetic investigation of the amination of arylmetals with **5f** (metal: MgBr,[23–25] ZnCl/'CuCN'[26,27]). The effect of substituents were studied by collecting competitive rate data in the amination of phenylmetals and six of their 3- and 4- substituted derivatives, and looking for a Hammett correlation for the competitive rate ratios of phenylmetal-substituted phenylmetal pairs.



Scheme 5.

Before collection of the rate data, we first carried out preliminary experiments to see whether the model amination reaction would meet the requirements of the competitive kinetics method. As we observed that the differences between the reaction rates of R^1M and R^2M are not large and that experimental conditions could be arranged to keep the amounts of the products R^1NH_2 and R^2NH_2 much higher than the experimental error during the progress of the reaction, we decided that competition experiments in amination with **5f** would allow us to obtain reliable and reproducible results. Second, we surveyed the reported methods to be used for the competitive organometallic reactions. In the competitive reaction of A^1 and A^2 with subequimolar B to give products C^1 and C^2, assuming a first-order reaction in A, Eqn (1) is used[35,36] for the calculation of relative reactivities of A^1 and A^2:

$$A^1 + B \xrightarrow{k_1} C^1$$

$$A^2 + B \xrightarrow{k_2} C^2$$

$$\frac{k_2}{k_1} = \frac{\log([A^2]_t/[A^2]_0)}{\log([A^1]_t/[A^1]_0)} \qquad (1)$$

where $[A]_t$ and $[A]_0$ are the concentrations of the competitive reactants at the time *t* and 0 respectively.

In the reported methods for competitive kinetics,[35–47] competitive rate ratios k_1/k_2 are calculated by (i) finding $[A]_t$ and $[A]_0$ values at the end of the reaction[35,37–40] or after a definite amount of reaction time or (ii) finding the slope of the linear plot of $\log([A^2]_t/[A^2]_0)$ vs $\log([A^1]_t/[A^1]_0^0)$ in a reaction completed up to 90%.[36–42] Or rather than using Eqn (1), (iii) Eqn (2) was used:

$$\frac{k_2}{k_1} = \frac{\%\text{ yield of }C^2}{\%\text{ yield of }C^1} \qquad (2)$$

where the yields of products C^1 and C^2 are measured at the end of the reaction or at a suitable reaction time.[43–45] The method used most seems to be (iii), and some appropriate mathematics are also frequently reported to apply this method for chosen experimental conditions[46] or direct kinetic methods are also applied to find k_1 and k_2 in competition experiments.[47]

For calculating the rate ratios of the competitive amination reaction of R^1M and R^2M, we used Eqn (3) written in the same form as Eqn (1):

$$\frac{k_2}{k_1} = \frac{\log([R^2M]_t/[R^2M]_0)}{\log([R^1M]_t/[R^1M]_0)} \qquad (3)$$

where $[RM]_t$ and $[RM]_0$ are the amounts of competing reactants at time t and $t = 0$ respectively. However, being interested in the competitive formation rate of product amines, we expressed Eqn (3) in terms of amine amounts $[R^1NH_2]$ and $[R^2NH_2]$. Some simplifications from the assumptions of small perturbations of side reactions, and almost complete hydrolysis of imines to amines, resulted in Eqn (4) to calculate the competitive rate ratios:

$$\frac{k_2}{k_1} = \frac{\log\{([R^2M]_0 - [R^2NH_2]_t)/[R^2M]_0\}}{\log\{([R^1M]_0 - [R^1NH_2]_t)/[R^1M]_0\}} = \frac{\log\{1 - ([R^2NH_2]t/[R^2M]_0)\}}{\log\{1 - ([R^1NH_2]_t/[R^1M]_0)\}} \qquad (4)$$

where $[RNH_2]_t$ is the amount of product amines at a defined reaction time t.

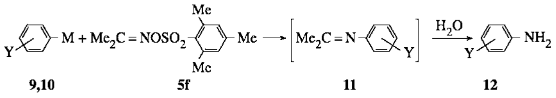
Third, we carried out initial experiments to find the best competitive kinetics method among (i)–(iii) for model amination kinetics. As model reactions, we chose the reaction of the C_6H_5MgBr (**9a**)–4-MeC_6H_4MgBr (**9b**) pair and also C_6H_5ZnCl/'CuCN' (**10a**)–4-MeC_6H_4ZnCl/'CuCN' (**10b**) pair with **5f**. We first optimized the scale for competition to be **9a**:**9b**:**5f** (and **10a** : **10b** : **5f**) = 4 : 4 : 1. Then, we tried to collect data for method (ii) by taking a definite number of samples (i.e. seven to nine) at suitable reaction times, leading to a reactivity profile. However, the important point is that quenching the reaction samples by acidic hydrolysis and isolation of amines as hydrochlorides restricted us from carrying out the reactions in the presence of an internal standard for an accurate GLPC analysis of the products. For this purpose, a definite number of reactions was carried out in different flasks and each reaction was quenched at appropriate time points with 15, 30 or 60 min intervals. This method, although time consuming, led to reproducible GLPC analyses. In the evaluation of reactivity profiles, taken in the competitive aminations of both Grignard reagents and catalytic zinc-cyanocuprates, we observed that the amounts of aniline (**12a**) and 4-toluidine (**12b**) did not change after 15 min during a reaction of 120 min. So we could not apply method (ii), and method (i) seemed reasonable. Duplicate analyses of amine amounts $[R^1NH_2]_t$ and $[R^2NH_2]_t$ at 60 and 120 min and using their average value in Eqn (4) gave reproducible values for competitive rate ratios k_2/k_1. The mean deviation of the average values of $[RNH_2]_t$ amounts was not found higher than 9%, which is within the error limit of GLPC analysis. It is interesting to note that applying method (iii) for calculation of k_2/k_1 values gave the same results as those found by method (i) within the 5% error.

Table 1 lists the competitive rate ratios, k_2/k_1 values, i.e. k_Y/k_H values, for amination kinetics of substituted phenylmagnesium bromides **9a–g** with **5f** in THF at 72 °C and CuCN-catalyzed substituted phenylzinc chlorides **10a–g** in THF at 25 °C. Figure 1A and B shows the Hammett plots of these reactions. The $\log(k_Y/k_H)$ values were plotted against σ_p and σ_m substituent constants, and reasonably good straight lines were obtained, except for the 4-MeO substituent in Fig. 1A. However, the downward deviations of 4-MeO-containing reagents or substrates in Hammett plots for organometallic reactions have frequently been observed and attributed to the inadequacy of applying the standard σ constants of the hydrogen-bond-accepting substituents for reactions carried out in aprotic solvents.[38–40]

Hammett plots for amination of Grignard reagents (Fig. 1A) and catalytic zinc cyanocuprates (Fig. 1B) give values of $\rho = -2.94$ ($r = 0.977$, excluding 4-MeO group) and $\rho = -0.84$($r = 0.936$) for reaction constants respectively. These correlations first support the assumption of first-order reaction in[35,36,42] organometallic reagent in the amination of Grignard reagents and zinc cyanocuprates. Second, the signs of the ρ values are negative, as expected,[49–51] i.e. the reactions are accelerated by electron-donating substituents which help transfer of negative charge on the substituted phenyl carbanion to electrophilic nitrogen. These results confirm, even at a supportive level, the mechanisms that we will propose for aminations of RMgBr and RCu(CN)ZnCl reagents with **5f** in the light of the reaction mechanisms of these organometallics.

The amination of RMgBr reagents seems to be a formal S_N2 displacement by donation of the electrons from carbanions of **9a–g** to sp^2N in the N–OX bond of **5f** (Scheme 6). In the

Table 1. Relative reactivities of substituted phenyl Grignard reagents **9a–g** and catalytic zinc cyanocuprates **10a–g** in their amination with **5f**



M: MgBr **9**, ZnCl / CuCN (20 mol%) **10**

Y	σ[a]	k_Y/k_H[b] M: MgBr[c]	k_Y/k_H[b] M: ZnCl/'CuCN'[d]
4-MeO	−0.27	1.16	1.31
4-Me	−0.17	1.38	1.02
3-Me	−0.07	1.45	1.12
H	0.00	1.00	1.00
3-Me	0.12	0.60	0.53
4-Br	0.23	0.12	0.56
3-Br	0.39	0.06	0.38

[a] Substituent constants are taken from Ref. 48.
[b] The values were calculated from the competition experiments using Eqn (4). The relative error on the values does not exceed 9%.
[c] Reactions were carried out in THF at reflux temperature, 72 °C.
[d] Reactions were carried out in THF at 25 °C.

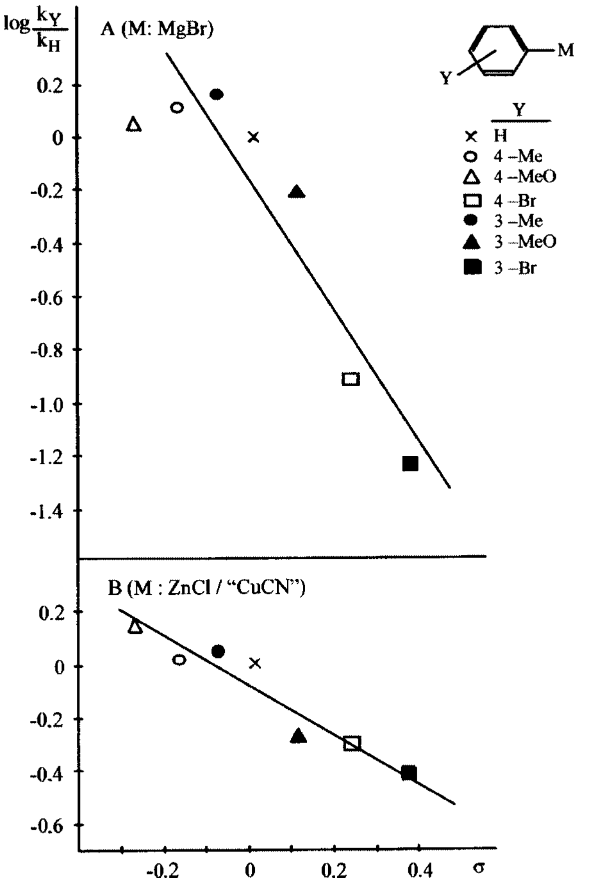
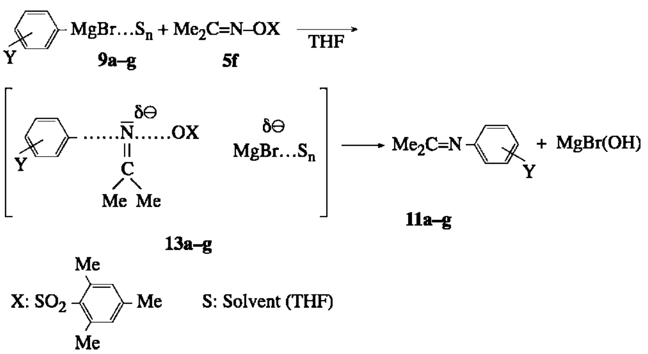
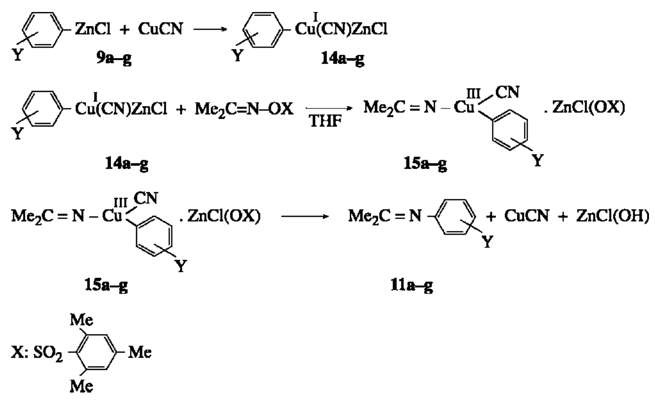


Figure 1. Hammett plots for the competitive amination kinetics of substituted phenylmetals with acetone *O*-(2,4,6-trimethylsulfonyl)oxime (**5f**) in THF. (A): Amination of substituted phenylmagnesium bromides **9a–g** at 72 °C. (B) Amination of substituted phenylzinc chlorides **10a–g** in the presence of 20 mol% CuCN in THF at 25 °C.

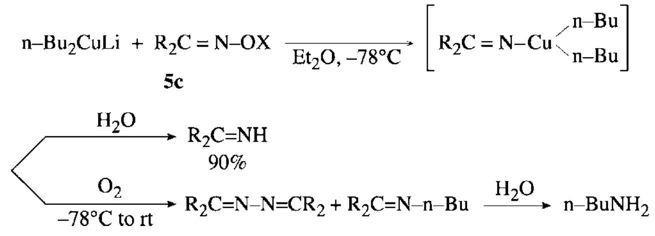


Scheme 6.

amination of RL_1 reagents with **1a** and **1c**; Beak and coworkers provided experimental information about the geometry of the transition state in **13a–g** analogous to that of a classic S_N2 displacement.[15,16]



Scheme 7.



Scheme 8.

RCu(CN)ZnCl reagents (Knochel reagents) are obtained in the stoichiometric or catalytic transmetallation of RZnCl reagents with CuCN.[32,33,52] These reagents have a similar reactivity to RLi or RMgBr reagent derived cyanocuprates, and a Cu–CN bond is formed at some point during transmetallation.[32,52,53] For the substitution reactions of cuprates, an oxidative addition–reductive elimination mechanism proceeding via a copper(III) intermediate rather than a direct displacement is proposed.[52,54,55] A conceptual framework for the mechanism is given in Scheme 7, involving catalytic formation of copper(I) intermediate RCu(CN)ZnCl (**14a–g**), nucleophilic oxidative addition of **14a–g** to **5f** to give a dimethylmethaneimino-containing copper(III) intermediate **15a–g**, followed by reductive elimination of **15a–g** to the product and catalyst. In the catalytic turnover, the oxidative addition of the substrate to copper(I) intermediates is the rate-determining step, and reactions are usually first order in both cuprate and substrate.[54–56]

Formation of copper (III) intermediate was supported by the isolation of imine in the reaction of lithium di-*n*-butylcuprate with **5c** (Scheme 8).[20] The reductive elimination of the stable intermediate to *n*-butylamine could be carried out by bubbling oxygen instead of hydrolysis.

Nakamura and Yoshikai[57] recently indicated that standard lithium cuprates R_2CuLi (Gilman cuprates), cyanocuprates RCu(CN)Li (lower order), and $R_2Cu(CN)Li_2$ (higher order, Lipshutz reagents) involve similar reactive intermediates in their reactions. Studies have also shown that the cyanide anion is bonded to lithium atoms in the lithium cyanocuprates.[58–59]

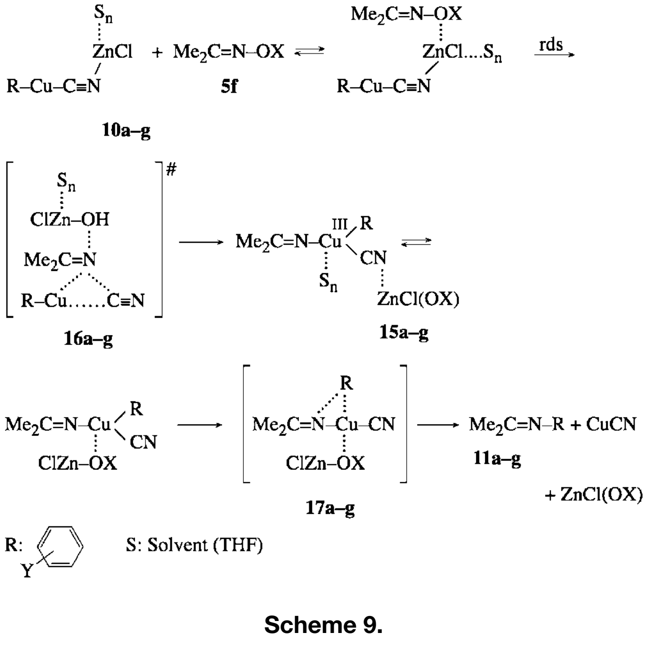
Assuming a similar structure for zinc cyanocuprates and taking the reaction pathway for the substitution of a lithium organocuprate cluster[57] into account, we suggest that the oxidative addition of zinc cyanocuprate to **10a–g** can take place through the formation of the transition state **16a–g** (Scheme 9).

The magnitudes of the ρ values in the aminations of RMgBr and RCu(CN)ZnCl reagents seem to be in accordance with the proposed mechanisms. As is known, ρ values can be used to characterize the interaction of the aromatic ring with the reaction center.[49] Al larger ρ value for the reaction of RMgBr reagents than that found for the reaction of RCu(CN)ZnCl reagents is consistent with the small interaction between the substituted phenyl ring and electrophilic nitrogen in the transition state **16a–g** leading to copper(III) complex **15a–g** (Scheme 9) compared with the interaction in the transition state **13a–g** (Scheme 6). However, we think that these results on the characteristics of the transition states for the substitution of RMgBr and RCu(CN)ZnCl on electrophilic nitrogen will apparently await further proof.

In conclusion, the competitive rate data and Hammett relationships obtained in this study support that electrophilic amination of substituted phenyl Grignard reagents and zinc cyanocuprates with an *O*-sulfonyloxime can be explained by S_N2 and nucleophilic oxidative addition mechanisms respectively.

These results also provide an example for the use of kinetics and quantitative structure–activity relationships in the investigation of C–N coupling mechanisms of Grignard reagents and organozinc cyanocuprates.

Another kinetic study on the electrophilic amination of Grignard reagents, magnesium organocuprates and zinc cyanocuprates with *O*-methylhydroxylamine will be published soon,[60] and our additional studies on the amination mechanisms of carbanions and enolates are also in progress.



Scheme 9.

Acknowledgements

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