

# On the mechanism of the *N,N*-dimethyl amination of Grignard reagents: a kinetic study

Ender Erdik\* and Selma Ateş Ülhü†

Science Faculty, Ankara University, Beşevler, Ankara 06100, Turkey

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**ABSTRACT:** A direct kinetic study is reported for the electrophilic amination of substituted phenylmagnesium bromides with *N,N*-dimethyl *O*-(mesitylenesulfonyl)hydroxylamine in THF. Rate data, Hammett relationship, and activation entropy are consistent with a S<sub>N</sub>2 displacement involving the attack of carbanions to sp<sup>3</sup>N in the amination reagent (AR). Copyright © 2007 John Wiley & Sons, Ltd.

**KEYWORDS:** Grignard reagents; aryl carbanions; electrophilic amination; C—N coupling; *N,N*-dimethyl *O*-(mesitylenesulfonyl)hydroxylamine; Hammett plot; activation parameter

## INTRODUCTION

Amines are one of the important class of compounds in organic synthesis and also substructures of many naturally occurring compounds and pharmaceuticals. For the amine synthesis,<sup>1</sup> nucleophilic amination strategy is commonly in use, however transition metal catalyzed C—N couplings between aryl halides and amines have received special attention.<sup>2–4</sup> Electrophilic amination strategy is also a potentially valuable method for nonsymmetric and symmetric synthesis of amines<sup>1,5–7</sup> and  $\alpha$ -amino carbonyl compounds (Scheme 1).<sup>8,9</sup> A number of electrophilic amination reagents (ARs), that is, synthetic equivalents of  $\oplus\text{NR}_2$  synthon (**1,2**) have been reported for C—N coupling with carbanions (Scheme 1). Notably among these are: (i) sp<sup>3</sup>N type ARs (**1**). *O*-Organyl hydroxylamines (**1a**),<sup>5–9</sup> *O*-acylhydroxylamines (**1b**),<sup>10–14</sup> *O*-silylhydroxylamines (**1c**),<sup>5–9</sup> *O*-sulfonylhydroxylamines (**1d**),<sup>5–9,15</sup> and *O*-phosphinylhydroxylamines (**1e**)<sup>5–9</sup> react with carbanions directly. (ii) sp<sup>2</sup>N type ARs (**2**). *O*-Sulfonyloximes (**2a**)<sup>16–18</sup> form imines, which are hydrolyzed to amines. Azides (**2b**),<sup>5–9</sup> diazene dicarboxylates (**2c**),<sup>5–9</sup> arene diazonium salts (**2d**),<sup>19–21</sup> and nitroarenes (**2e**)<sup>22</sup> form intermediates which require reductive work-up to produce amines.

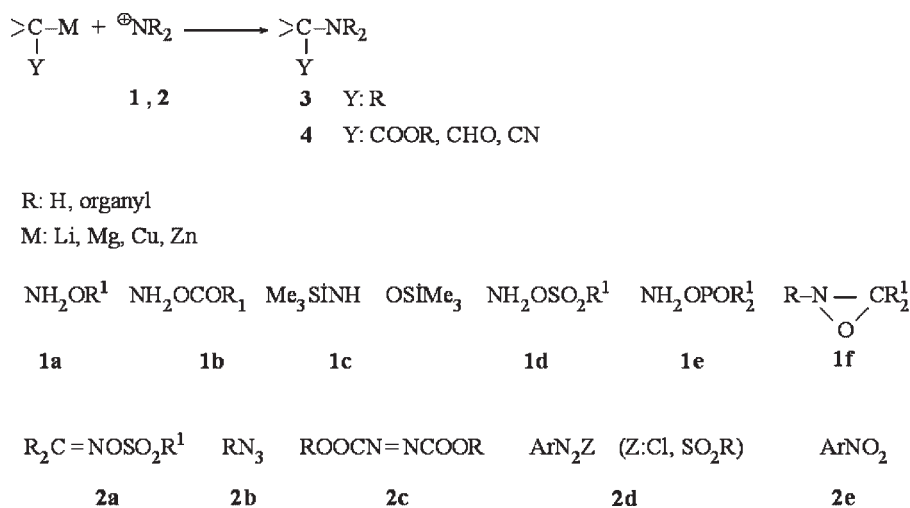
Although synthetic potential of electrophilic amination has been extensively studied, mechanistic investigations

are limited. Beak's<sup>23–25</sup> group provided evidence for a polar S<sub>N</sub>2-like mechanism for the reactions of organolithiums and  $\alpha$ -lithionitriles with **1a** and **1e**. Ricci and coworkers<sup>26</sup> offered a similar mechanism for the amination of higher order lithium cuprates with **1c**. Theoretical calculations by Boche and Wagner,<sup>27</sup> Armstrong, *et al.*,<sup>28</sup> and McKee<sup>29</sup> support a transition state for this mechanism. We recently reported our work on the kinetic studies of the amination of carbanions with acetone *O*-(mesitylenesulfonyl)oxime (**2a**, R = CH<sub>3</sub>, R<sup>1</sup> = C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3-2,4,6</sub>)<sup>30</sup> and with *O*-methyl hydroxylamine (**1a**, R<sup>1</sup> = CH<sub>3</sub>).<sup>31</sup> We investigated substituent effects on the amination rate of phenylmagnesium bromides,<sup>30,31</sup> magnesium diphenylcuprates,<sup>31</sup> and also CuCN catalyzed phenylzinc chlorides<sup>30</sup> and diphenylzincs<sup>31</sup> by competitive kinetic studies. Analyses of rate data via Hammett treatment were explained by S<sub>N</sub>2 mechanism for Grignard reagents and by nucleophilic oxidative addition mechanism for catalytic and stoichiometric cuprates. Although linear Hammett plots supported the assumption of first-order reaction in organometallic reagent in the amination with these reagents, we have been exploring reaction conditions to carry out a direct kinetic study for the electrophilic amination.

In our recent work<sup>15</sup> on the successful use of Grignard–Barbier type amination with *N,N*-dimethyl derivative of *O*-(mesitylenesulfonyl)hydroxylamine (**1d**, R<sup>1</sup> = C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>3-2,4,6</sub>), we observed that amination takes place in a homogeneous solution. This finding and our continuing investigations into synthetic and mechanistic aspects of electrophilic amination encouraged us to perform an extensive kinetic investigation of the C—N

\*Correspondence to: E. Erdik, Science Faculty, Ankara University, Beşevler, Ankara 06100, Turkey.  
E-mail: erdik@science.ankara.edu.tr

† Present Address: College of Liberal Arts and Sciences, Wayne State University, Detroit, Michigan 48202, USA.



Scheme 1

coupling of aryl magnesium bromides with *N,N*-dimethylamino transfer reagent **1d** in the hope of finding additional support for the proposed S<sub>N</sub>2-like mechanism.

In the present paper, we report our successful results for the first direct rate measurements for the electrophilic amination of carbanions with a sp<sup>3</sup>N type reagent and we also discuss their relative reactivities.

## RESULTS AND DISCUSSION

For the kinetic study of amination of aryl Grignard reagents with *N,N*-dimethyl *O*-(mesitylenesulfonyl) hydroxylamine (**1g**), we planned (i) to determine the reaction order in both reactants, (ii) to find structural effects on the reactivity of carbanions, and also (iii) to find the activation parameters.

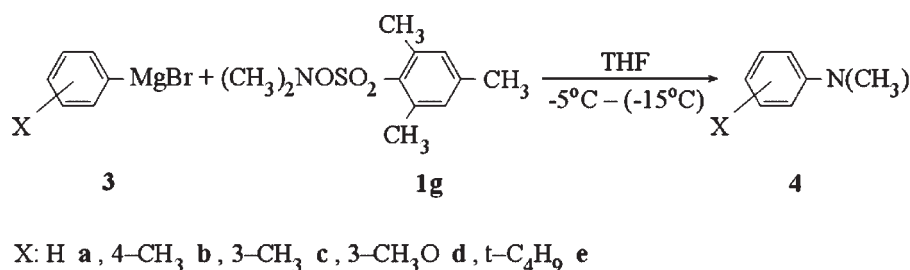
We have been interested in the amination of a series of substituted phenylmagnesium bromides and as a model reagent, we chose phenylmagnesium bromide (Scheme 2). Although the amination of phenylmagnesium bromides were carried out at room temperature for synthetic purposes,<sup>15</sup> we carried out kinetic experiments at 5 °C to –15 °C to follow the reaction easily.

We collected the rate data by taking seven to nine samples at suitable reaction times keeping the concentration of AR (**1g**) constant and concentration of Grignard

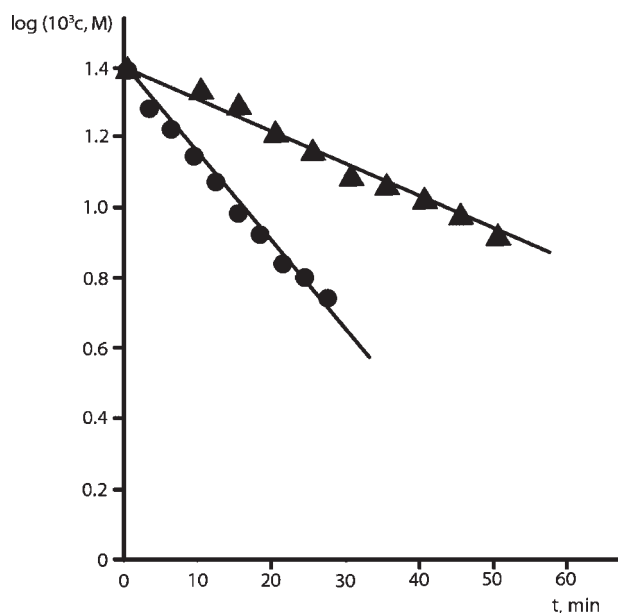
reagent (**3a–e**) in excess and varied to determine the reaction order in **1g** and in **3a–e**.

In the experiments, we found the concentration of formed amines (**4a–e**) by GLC analysis. Being interested in the formation rate of amines, we calculated the concentration of remaining AR (**1g**) at time *t* as [AR]<sub>*t*</sub> = [AR]<sub>0</sub> – [amine]<sub>*t*</sub>, where [AR]<sub>0</sub> is the initial concentration of aminating reagent and [amine]<sub>*t*</sub> is the concentration of formed *N,N*-dimethylanilines (**4a–e**) at time *t*.

The rate data were evaluated as pseudo-first-order and plots of log[AR]<sub>*t*</sub> values versus time proved linear up to 60–80% completion of the reaction. Pseudo-first-order plots for the amination of phenylmagnesium bromide at 5.0 ± 0.1 °C and 3-methoxyphenylmagnesium bromide at –10.0 ± 0.1 °C are given in Fig. 1. Pseudo-first-order rate constants *k*<sub>1</sub> were calculated by linear regression analysis (*r* ≥ 0.99). In order to test the effect of varying concentration of Grignard reagents (**3a–a**) on *k*<sub>1</sub> values, we chose phenylmagnesium bromide (**3a**) as a model reagent. The concentration of **3a** was varied between 10 and 30 times that of AR (**1g**). The results taken at two different temperatures, that is, 5.0 ± 0.1 °C and –10.0 ± 0.1 °C are given in Table 1 and the data are plotted in Fig. 2. Linear regression analysis of the log*k*<sub>1</sub> values versus log[C<sub>6</sub>H<sub>5</sub>MgBr] yielded a slope of 1.00 (*r* = 0.9971) for the reaction at 5.0 ± 0.1 °C and a slope of 1.04 (*r* = 0.9842) for the reaction at –10.0 ± 0.1 °C,



Scheme 2



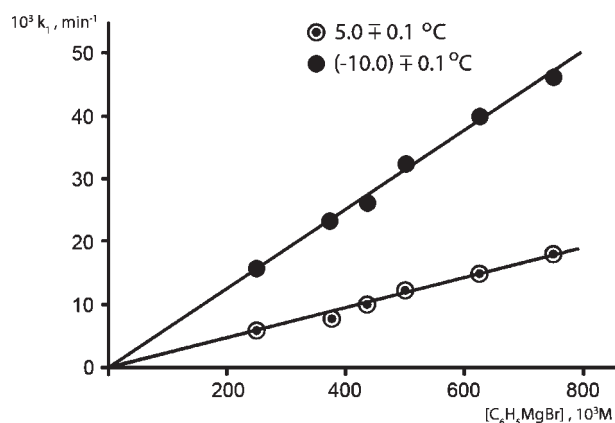
**Figure 1.** Typical first-order plots for the reaction of (a) phenylmagnesium bromide (**3a**) (●) and (b) 3-methoxyphenylmagnesium bromide (**3e**) (▲) with *N,N*-dimethyl *O*-(mesitylenesulfonyl)hydroxylamine (AR) (**1g**) in THF. Experimental conditions: (a)  $[C_6H_5MgBr] = 0.750$  M,  $c = [AR] = 0.025$  M,  $t = 5.0 \pm 0.1$  °C. (b)  $[3-CH_3OC_6H_4MgBr] = 0.500$  M,  $c = [AR] = 0.025$  M,  $t = 0.0 \pm 0.1$  °C

confirming the first-order reaction in Grignard reagent, which we assumed in the competitive kinetic study of the amination reaction of phenylmagnesium bromides (**3a–e**) with *O*-methyl hydroxylamine (**1a**,  $R^1 = CH_3$ ).<sup>30,31</sup>

Thus, the total rate law for the amination of phenylmagnesium bromide (**3g**) with AR (**1g**) in THF can be expressed by Eqn (1).

$$-\frac{d[AR]}{dt} = k[C_6H_5MgBr][AR] = k_1[AR]$$

The second-order rate constants  $k$  were calculated as  $k = k_1/[C_6H_5MgBr]$  and taking the average of  $k$  values gave  $62.4 \pm 1.3$  M<sup>-1</sup> min<sup>-1</sup> at  $5.0 \pm 0.1$  °C and  $23.1 \pm$



**Figure 2.** Effect of phenylmagnesium bromide (**3a**) concentration on the pseudo-first-order rate constants for the reaction of phenylmagnesium bromide (**3a**) with *N,N*-dimethyl *O*-(mesitylenesulfonyl)hydroxylamine (AR) (**1g**) in THF at  $5.0 \pm 0.1$  °C and at  $-10.0 \pm 0.1$  °C. Data are from Table 1

$0.8$  M<sup>-1</sup> min<sup>-1</sup> at  $-10.0 \pm 0.1$  °C with the uncertainty of 4–7%, which is in the error limit of GLC analysis. The kinetic reactions of all substituted phenylmagnesium bromides (**3b–e**) obeyed pseudo-first-order kinetics.

Electronic effects in the amination of Grignard reagents with *N,N*-dimethylamino transfer reagent (**1g**) were also investigated. Since deviations have been observed with 4-CH<sub>3</sub>O and also with 4-Br and 3-Br containing phenylmagnesium,<sup>30–32</sup> -copper,<sup>31</sup> and -zinc reagents<sup>31</sup> in the Hammett plots for their reactions, we investigated kinetics of only alkyl and 3-CH<sub>3</sub>O-substituted phenylmagnesium bromides at  $0.0 \pm 0.1$  °C for Hammett relationship. We calculated the second-order rate constants  $k$  of substituted phenylmagnesium bromides (**3b–e**) with **1g** under pseudo-first-order conditions and correlated with Hammett  $\sigma$  constants (Table 2). Hammett plot gave a reasonably straight line with a value of  $\rho = -1.02$  ( $r = 0.918$ ) for the reaction constant (Fig. 3). The sign of the reaction constant indicates that the reaction is decelerated with electron attracting substituents and this result is consistent with the electrophilic

**Table 1.** Effect of phenylmagnesium bromide concentration on the reaction rate of phenylmagnesium bromide (**3a**) with *N,N*-dimethyl *O*-(mesitylenesulfonyl)hydroxylamine (**1g**) in THF at two different temperatures<sup>a</sup>

$[C_6H_5MgBr]$ (M)	$t = 5.0 \pm 0.1$ °C		$t = -10.0 \pm 0.1$ °C	
	$k_1$ ( $\times 10^3$ ) (min <sup>-1</sup> )	$k$ ( $\times 10^3$ ) (M <sup>-1</sup> min <sup>-1</sup> ) <sup>b</sup>	$k_1$ ( $\times 10^3$ ) (min <sup>-1</sup> )	$k$ ( $\times 10^3$ ) (M <sup>-1</sup> min <sup>-1</sup> ) <sup>b</sup>
0.250	15.66	62.6	5.89	23.0
0.375	23.26	62.0	7.83	20.9
0.437	26.02	59.5	10.13	23.2
0.500	32.47	64.9	12.21	24.4
0.625	39.84	63.7	14.97	22.9
0.750	46.06	62.1	17.96	23.9

<sup>a</sup>  $[AR] = 0.025$  M.

<sup>b</sup>  $k = k_1/[C_6H_5MgBr]$ .

**Table 2.** Rate constants for the amination of substituted phenylmagnesium bromides (**3a–e**) with *N,N*-dimethyl *O*-(mesitylenesulfonyl)hydroxylamine (**1g**) in THF at  $0.0 \pm 0.1$  °C.

Substituent	$\sigma^a$	$k$ ( $\times 10^3$ ) ( $M^{-1} \text{ min}^{-1}$ ) <sup>b</sup>
4-(CH <sub>3</sub> ) <sub>3</sub> C	-0.20	90.6
4-CH <sub>3</sub>	-0.17	90.3
3-CH <sub>3</sub>	-0.07	59.1
H	0.00	45.5
3-CH <sub>3</sub> O	0.12	47.4

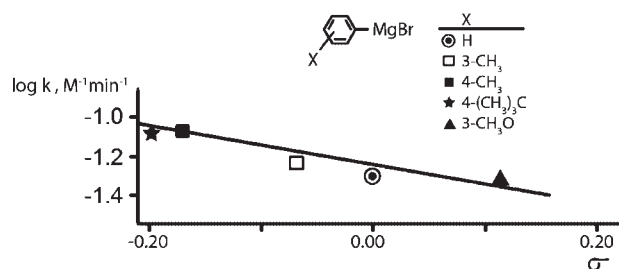
<sup>a</sup> Substituent constants are taken from Ref. 33.

<sup>b</sup> Second-order rate constants were calculated under pseudo-first-order conditions.

character of the AR in the rate determining step. It is quite impressive that we already obtained<sup>31</sup> a value of  $\rho = -0.95$  for the reaction of substituted phenylmagnesium bromides with *O*-methyl hydroxylamine (**1a**,  $R^1 = \text{CH}_3$ ) in THF at  $-15.0 \pm 0.1$  °C. The similarity of these two reaction constants shows<sup>33</sup> that there is almost no difference in the amount of carbanion character and thus no difference in the extent of C—N bond formation in the transition states of the reactions of substituted phenylmagnesium bromides with  $^{\oplus}\text{NH}_2$  transfer reagent (**1a**) and  $^{\oplus}\text{N}(\text{CH}_3)_2$  transfer reagent (**1g**).

The above kinetic data and Hammett relationship demonstrate that C—N coupling of aryl Grignard reagents with *N,N*-dimethylamine *O*-(mesitylenesulfonyl)hydroxylamine **1g** seems to take place by a formal S<sub>N</sub>2 displacement involving donation of the electrons of carbanions derived from Grignard reagents **3a–e** to sp<sup>3</sup>N in the N—OY bond of aminating reagent **1g** (Scheme 3). This study also supports the mechanism that we proposed in the competitive kinetic study of the aryl Grignard reagents with sp<sup>3</sup>N type<sup>31</sup> and also sp<sup>2</sup>N type<sup>30</sup> ARs.

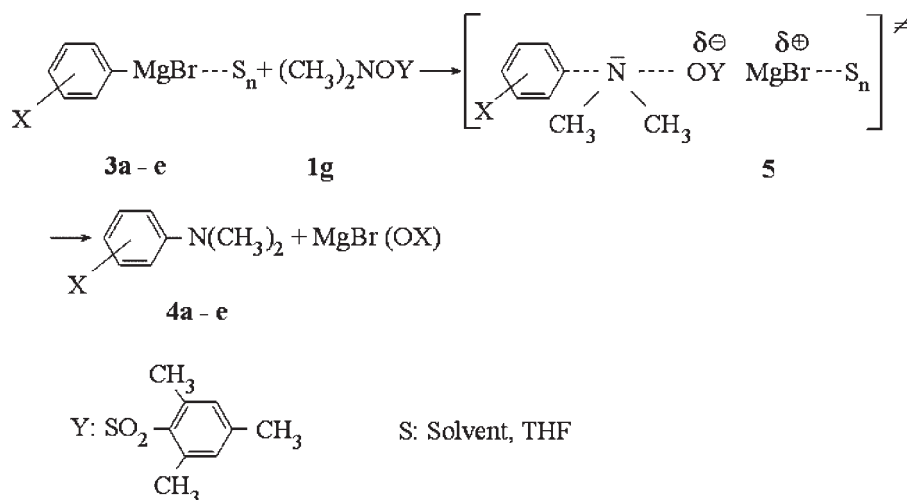
We also tried to find the activation enthalpy  $\Delta H^\ddagger$  and activation entropy  $\Delta S^\ddagger$  for the amination of phenylmag-



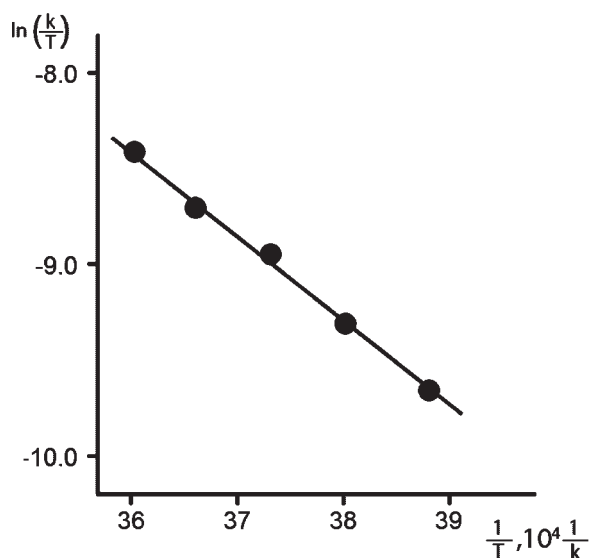
**Figure 3.** Variation of rate constants with Hammett substituent constants for the amination of substituted phenylmagnesium bromides (**3a–e**) with *N,N*-dimethyl *O*-(mesitylenesulfonyl)hydroxylamine (**1g**) in THF at  $0.0 \pm 0.1$  °C. Data are from Table 2

nesium bromide (**3a**) with *N,N*-dimethylamino transfer reagent (**1g**) hoping that the value of  $\Delta S^\ddagger$  will be negative due to the decreased disorder in the transition state. On the electrophilic amination, coupling of aryl magnesium bromides with the aminating reagent is expected to lead to the formation of transition state (**5**). Beak's<sup>23,24</sup> group also gave experimental information supporting the structure of a similar transition state in the electrophilic amination of organolithiums with a sp<sup>3</sup>N type AR.

The second-order rate constants  $k$  of the reaction of **3a** with **1g** were calculated at different temperatures and  $k$  were obtained to be  $62.1 \text{ M}^{-1} \text{ min}^{-1}$  (from the data in Table 1),  $45.5 \text{ M}^{-1} \text{ min}^{-1}$ ,  $23.1 \text{ M}^{-1} \text{ min}^{-1}$  (from the data in Table 1), and  $16.7 \text{ M}^{-1} \text{ min}^{-1}$  at 5.0, 0.0, -5.0, -10.0, and -15.0 °C, respectively. Eyring plot of  $\ln(k/T)$  versus  $1/T$  was found linear ( $r = 0.9985$ ) (Fig. 4) and activation parameters  $\Delta H^\ddagger = 36.7 \pm 3.0 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -135.3 \pm 9.0 \text{ J mol}^{-1} \text{ K}^{-1}$  were determined from the slope and intercept of the line, respectively.<sup>34,35</sup> The uncertainties in  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were determined from the mean deviations in the slope and intercept of this line, respectively. The value of  $\Delta S^\ddagger$  is consistent with an associative process in the formation of transition state as expected.



**Scheme 3**



**Figure 4.** Eyring plot for the reaction of phenylmagnesium bromide (**3a**) with *N,N*-dimethyl *O*-(mesitylenesulfonyl)hydroxylamine (**1g**) in THF

It is known that in  $S_N2$  reactions, activation parameters should be negative, but, as solvation plays an important role, the range of values will depend upon the charge type in the formation of transition state and also upon the solvent.<sup>36,37</sup> For charge separation, numerical values of activation entropies were reported to be  $-90$  to  $-120 \text{ J mol}^{-1} \text{ K}^{-1}$ , whereas lower numerical values of activation entropies, that is,  $-20$  to  $-40 \text{ J mol}^{-1} \text{ K}^{-1}$  were reported for charge delocalization. Activation entropy also assumes a larger negative value if transition state is solvated more extensively than the reactants. Then,  $AS^\ddagger$  value in the reaction of phenylmagnesium bromide (**3a**) with *N,N*-dimethylamino transfer reagent (**1g**) provides an explanation of almost total absence of  $^\oplus\text{N}(\text{CH}_3)_2$  species as well as the development of a partial charge in the formation of transition state.

In conclusion, our first direct kinetic study, Hammett relationship, and activation entropy for the homogeneous electrophilic amination of phenyl Grignard reagents with *N,N*-dimethylamino *O*-(mesitylenesulfonyl)hydroxylamine support the proposed  $S_N2$  type substitution mechanism for organolithium and Grignard reagent derived carbanions with  $sp^3\text{N}$  type amino transfer substrates. The results are also consistent with our previous competition experiments for electrophilic amination<sup>31</sup> of phenyl Grignard reagents with *O*-methyl hydroxylamine.

## EXPERIMENTAL

All experiments were carried out under dry nitrogen atmosphere using oven-dried glassware and standard syringe rubber septum techniques.<sup>38</sup> THF was distilled

from sodium benzophenone dianion. The magnesium generally used was more than 99.9% pure. Aryl bromides were purchased and purified according to the published procedures. Grignard reagents (**3a–e**) 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.<sup>39</sup> Authentic samples of *N,N*-dimethylanilines were prepared by our reported procedure<sup>15</sup> using amination of arylmagnesium bromides with *N,N*-dimethyl *O*-(mesitylenesulfonyl)hydroxylamine.

The kinetics were followed by measuring the concentration of formed amines by GLC analysis using internal standard technique on a ZB-5 capillary column (immobilized with phenylpolydimethylsiloxane) on a Thermo Finnigan gas chromatograph equipped with a flame ionization detector. In a jacketed reaction vessel of approximately 50 ml capacity capped with rubber septum and equipped with a magnetic stirrer, THF solution of *N,N*-dimethyl *O*-(mesitylenesulfonyl)hydroxylamine **1g** and internal standard was thermostated. Beginning at least 2 min after rapid injection of THF solution of arylmagnesium bromide, aliquots (8–12) were withdrawn at appropriate times by syringe and were added to a vial containing a saturated  $\text{NaHCO}_3$  solution for hydrolysis and ether. Extraction of amine and internal standard to the ethereal phase was found to be essentially quantitative. The ethereal phase was analyzed by GLC. Generally, self-consistent data could be obtained for two half lives. Observed pseudo-first-order rate constants were calculated from plots of  $\log c$  versus time  $t$ .  $c$  is the concentration of remaining aminating reagent (AR) (**1g**) at time  $t$  and is calculated as  $c = [\text{AR}]_t = [\text{AR}]_0 - [\text{amine}]_t$  where  $[\text{AR}]_0$  and  $[\text{amine}]_t$  are the initial concentration of **1g** and concentration of amine at time  $t$ , respectively. Reproducibility of the rate constants was generally  $\pm 4\%$ , which is in the error limit of GLC analysis.

## Acknowledgements

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## REFERENCES

- Ricci A (ed.). *Modern Amination Methods*. Wiley-VCH: Weinheim, 2000.
- (a) Kelkar AA, Patil NM, Chahudhuri CV. *Tetrahedron Lett.* 2002; **13**: 7143–7146; (b) Gujadhur RK, Bates CG, Venkataraman D. *Org. Lett.* 2001; **3**: 4135–4137; (c) Goudbrand HB, Hu N-X. *J. Org. Chem.* 1999; **64**: 670–674; (d) Kwong FY, Buchwald SL. *Org. Lett.* 2003; **5**: 793–796.
- Chen C, Yang LM. *Org. Lett.* 2005; **7**: 2209–2211.

4. (a) Hartwig JF. In *Handbook of Palladium Chemistry for Organic Synthesis* (vol. 1), Negishi E-i (ed.). Wiley: New York, 2002; (b) Mucci AR, Buchwald SL. *Top. Curr. Chem.* 2002; **219**: 131–209; (c) Hartwig JF. *Angew. Chem. Int. Edn.* 1998; **37**: 2046–2067.
5. Erdik E, Ay M. *Chem. Rev.* 1987; **29**: 1947–1980.
6. Mulzer J, Altenbach H, Brown M, Krohn K, Reissig HU. *Organic Synthesis Highlights*. VCH: Weinheim, 1991, 45–53.
7. Dembech B, Seconi G, Ricci A. *Chem. Eur. J.* 2000; **6**: 1281–1286.
8. Erdik E. *Tetrahedron* 2004; **60**: 8747–8782.
9. Greck C, Drouillat B, Thomassigny C. *Eur. J. Org. Chem.* 2004; **10**: 1377–1385.
10. Berman AM, Johnson JS. *J. Org. Chem.* 2006; **71**: 219–224.
11. Berman AM, Johnson JS. *Org. Synth.* 2005; **83**: 31–35.
12. Berman AM, Johnson JS. *J. Org. Chem.* 2005; **70**: 364–366.
13. Berman AM, Johnson JS. *Synlett* 2005; 1799–1801.
14. Berman AM, Johnson JS. *J. Am. Chem. Soc.* 2004; **126**: 5680–5681.
15. Erdik E, Ateş S. *Synth. Commun.* 2006; **36**: 2813–2818.
16. Erdik E, Daşkapan T. *Tetrahedron Lett.* 2002; **43**: 6237–6239.
17. Daşkapan T. *Tetrahedron Lett.* 2006; **47**: 2879–2881.
18. Kitanura M, Suga T, Shunsuka C, Narasaka K. *Org. Lett.* 2004; **6**: 4619–4621.
19. Erdik E, Koçoğlu M. *Main Group Metal Chem.* 2002; **25**: 621–627.
20. Sinha P, Kofink CC, Knochel P. *Org. Lett.* 2006; **8**: 3741–3744.
21. Sapountzis I, Knochel P. *Angew. Chem. Int. Edn.* 2004; **43**: 897–900.
22. Sapountzis I, Krachel P. *J. Am. Chem. Soc.* 2002; **124**: 9390–9391.
23. Beak P, Basha A, Rokko B, Loo DK. *J. Am. Chem. Soc.* 1986; **108**: 6016–6023.
24. Beak P, Selling GW. *J. Org. Chem.* 1989; **54**: 5574–5580.
25. Beak P, Li I. *J. Am. Chem. Soc.* 1991; **113**: 2796–2797.
26. Casarini A, Dembech P, Lazari D, Marini E, Reginato G, Ricci A, Seconi G. *J. Org. Chem.* 1993; **58**: 5620–5623.
27. Boche G, Wagner HU. *J. Chem. Soc. Chem. Commun.* 1984; 1591–1592.
28. Armstrong DR, Smith R, Walker GT. *J. Chem. Soc. Chem. Commun.* 1985; 789–791.
29. Mckee MI. *J. Am. Chem. Soc.* 1985; **107**: 859–864.
30. Erdik E, Ömür Ö. *Appl. Organometal. Chem.* 2005; **19**: 887–893.
31. Erdik E, Eroğlu F, Kâhya D. *J. Phys. Org. Chem.* 2005; **18**: 950–956.
32. Yanataka H, Miyano N, Hanafusa T. *J. Org. Chem.* 1991; 2573–2575, and references cited therein.
33. Zuman P, Patel RC. *Techniques in Organic Reaction Kinetics*. Wiley: New York, 1984.
34. Isaacs NS. *Physical Organic Chemistry*. Longman: Hartow, 1987.
35. Espenson JH. *Chemical Kinetics and Reaction Mechanisms*. Mc Graw-Hill: Toronto, 1995.
36. Ref. 33, Chap. 3.7.
37. Ref. 34, Chap. 10.1.
38. Leonard J, Lygo B, Procter G. *Advanced Practical Organic Chemistry*. Blackie: London, 1995.
39. Watson CH, Eastham JF. *J. Organomet. Chem.* 1967; **9**: 167–168.