Organic Process Research & Development **2006**, *10,* 733–738

Minimization of Side Reactions in Bromine Magnesium Exchanges with *i*-PrMgCl/LiCl and *s*-BuMgCl/LiCl Mixtures

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Abstract:

The efficiency of halogen−magnesium exchange reactions can dramatically be increased by the addition of LiCl. However, also the organic substituents at the magnesium center of the Grignard reagent play an important role. In a competitive reaction gaseous side products are formed. In the presence of LiCl this interfering reaction is suppressed. Thus, carrying out bromine−magnesium exchanges with RMgCl/LiCl TurboGrignard solutions instead of RMgCl gives better results (R = *i*-Pr, *s*-Bu). The application either of *i*-PrMgCl/LiCl or of *s*-BuMgCl/LiCl in halogen−magnesium exchange reactions results in higher conversions and also in less gaseous side products, facts that should be considered for scale-up processes.

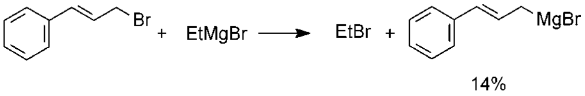
Introduction

Halogen−magnesium exchange reactions are the method of choice for preparing functionalized organometallic compounds.[1] These exchange reactions show much higher functional group tolerance than, for example, corresponding exchanges with alkyl lithium reagents.[2] In 1931, Prévost reported the first example of a bromine−magnesium exchange, however, only in moderate yield (Scheme 1).[3]

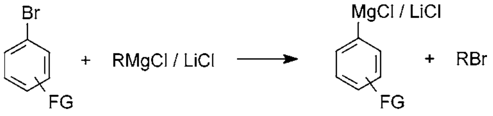
Good conversions could only be obtained when aromatic iodides or highly activated aromatic bromides, for example, 1-bromo-3,5-ditrifluoromethylbenzene, were employed.[4] With less activated bromides, long reaction times were needed, and even then, only moderate conversions could be obtained.[1,5]

The restrictions of halogen−magnesium exchange reactions were overcome after the recent discovery of P. Knochel and A. Krasovskiy that lithium chloride accelerates these exchanges dramatically. Additionally, they showed that the presence of lithium chloride results in higher yields of the desired products (Scheme 2).[6]

Scheme 1. **First synthesis of a Grignard reagent via bromine−magnesium exchange reaction**



Scheme 2. **LiCl accelerated halogen−magnesium exchange reactions**



R = *i*-Pr, *s*-Bu
FG = Alkyl, Alkenyl, OR', CO_2R', CN, NH_2, ...

Meanwhile, several examples illustrating the superiority of mixtures of Grignard solutions with LiCl (hereafter referred to as TurboGrignard) in halogen−magnesium exchange reactions have been published.[7] These reactions, using commercially attractive organic halides are becoming more and more relevant for industrial applications.

Halogen−magnesium exchanges are equilibrium processes, favoring the formation of the most stable Grignard reagent (sp > sp^2(vinyl) > sp^2(aryl) > sp^3(primary) > sp^3(secondary)). However, the mechanism of halogen−magnesium exchange reactions is not fully understood, but a halogenate complex is believed to be an intermediate.[5] For TurboGrignard reagents, it has been proposed that LiCl breaks the polymeric aggregates of the Grignard, forming a magnesiumate complex, in which the magnesium fragment is more negatively charged and hence displays a higher reactivity towards organic halides.[5a,6] However, relatively little is known about the influence of different *s*-alkyl substituents at the magnesium center.

To develop commercially attractive mixtures of LiCl and Grignard reagents for halogen−magnesium exchange reactions, we decided to prepare THF solutions of *i*-PrMgCl/LiCl and *s*-BuMgCl/LiCl. During this development work, we obtained some interesting results on the difference between *i*-PrMgCl/LiCl and *s*-BuMgCl/LiCl mixtures and on the influence of LiCl in halogen−magnesium exchange reactions, which are topics of the present report.

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(1) Knochel, P.; Dohle, W.; Gommermann, N.; Kneisel, F. F.; Kopp, F.; Korn, T.; Sapountzis, I.; Vu, V. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 4302.

(2) (a) Wittig, G. *Chem. Ber.* **1938**, *71*, 1903. (b) Jones, R. *Org. React.* **1951**, *6*, 339. (c) Gilman, H. *J. Am. Chem. Soc.* **1939**, *61*, 106. (d) Parham, W. *J. Org. Chem.* **1976**, *41*, 1187. (e) Parham, W. *J. Org. Chem.* **1975**, *40*, 2394. (f) Parham, W. *J. Org. Chem.* **1976**, *41*, 2704. (g) Parham, W. *J. Org. Chem.* **1977**, *42*, 260. (h) Parham, W. *J. Org. Chem.* **1977**, *42*, 257. (i) Tucker, C. *J. Am. Chem. Soc.* **1992**, *114*, 3983.

(3) Prévost, C. *Bull. Soc. Chim. Fr.* **1931**, *49*, 1372.

(4) Leazer, J. L., Jr.; Cvetochiv, R.; Tsay, F.-R.; Dolling, U.; Vickery, T.; Bachert, D. *J. Org. Chem.* **2003**, *68*, 3695.

(5) (a) Knochel, P. *Handbook of Functionalized Organometallics*; Wiley-VCH: Weinheim: 2005. (b) Bailey, W. F.; Patricia, J. J. *J. Organomet. Chem.* **1988**, 352. (c) Farnham, W. B.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2449. (d) Reich, H. J.; Philipps, N. H.; Reich, I. L. *J. Am. Chem. Soc.* **1985**, *107*, 4101.

(6) (a) Knochel, P.; Krasovskiy, A. EP 1 582 523 A1, 2005. (b) Knochel, P.; Krasovskiy, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 3333.

(7) (a) Kopp, F.; Krasovskiy, A.; Knochel, P. *Chem. Commun.* **2004**, 2288. (b) Ren, H.; Krasovskiy, A.; Knochel, P. *Org. Lett.* **2004**, *6*, 4215. (c) Ren, H.; Krasovskiy, A.; Knochel, P. *Chem. Commun.* **2005**, 543. (d) Sapountzis, I.; Lin, W.; Kofink, C.; Despotopoulou, C.; Knochel, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 1654. (e) Baron, O.; Knochel, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 3133.

10.1021/op0600153 CCC: $33.50

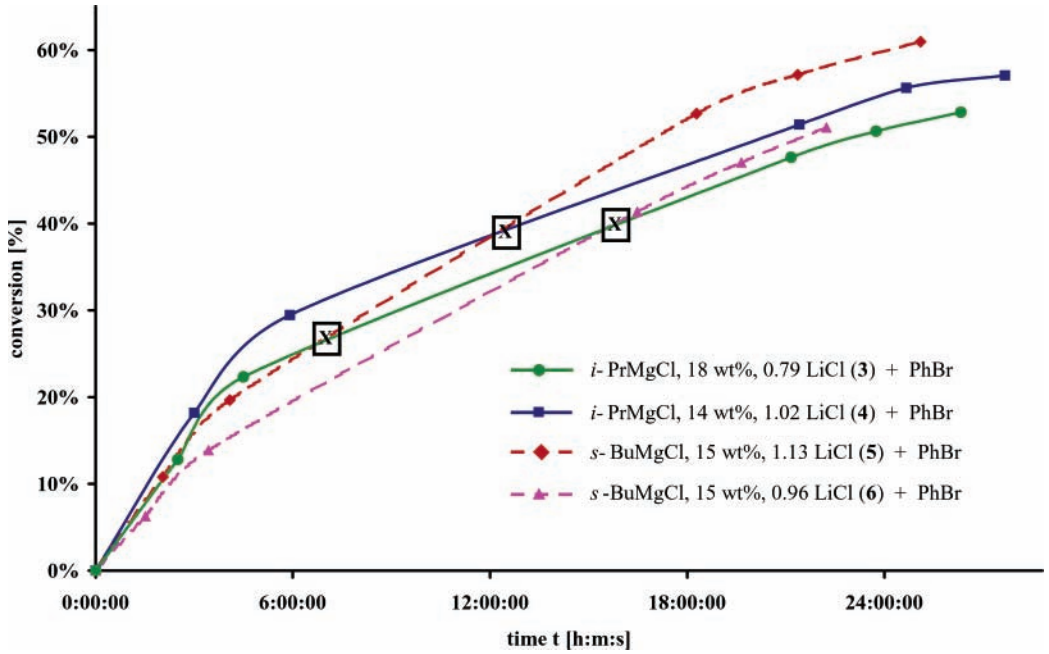


Figure 1. **Comparison of *i*-PrMgCl/LiCl mixtures (3, 4; solid lines) with *s*-BuMgCl/LiCl solutions (5, 6; dashed lines) in the benchmark exchange reaction with bromobenzene.**

Table 1. **Grignard solutions and Grignard/LiCl mixtures used for the experiments**

	RMgCl	LiCl:RMgCl[a]	$[OH]^{-}$ [b]	[wt%][c]
1	*i*-PrMgCl	–	1.99	20
2	*s*-BuMgCl	–	2.15	25
3	*i*-PrMgCl	0.79	1.78	18
4	*i*-PrMgCl	1.02	1.35	14
5	*s*-BuMgCl	1.13	1.26	15
6	*s*-BuMgCl	0.96	1.25	15

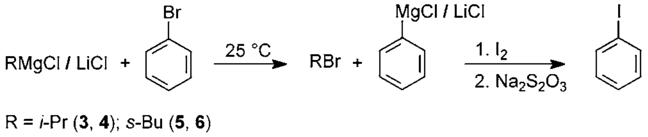
[a] LiCl as $[Li]^{+}$. [b] In [mmol/g]. [c] RMgCl as total base $[OH]^{-}$.

Synthesis

Concentrated THF solutions of *i*-PrMgCl **1** (20 wt %) and *s*-BuMgCl **2** (25 wt %) were prepared by standard oxidative addition of the corresponding chlorides to magnesium turnings. An excess of dry LiCl was added, and the dissolved amount was determined by wet analyses. Stepwise dilution with THF gave higher concentrations of dissolved LiCl. The prepared *i*-PrMgCl and *s*-BuMgCl solutions and their mixtures with LiCl are listed in Table 1.[8]

To obtain a reliable comparison of the abovementioned Grignard/LiCl mixtures **3**−**6** in halogen−magnesium exchange reactions, we chose deliberately the very slow exchange with unactivated, electron-poor bromobenzene as a benchmark reaction, to be able to detect even small differences in the behavior of the TurboGrignard reagents. Stoichiometric amounts of bromobenzene were reacted with Grignard/LiCl mixtures **3**−**6**, and reaction aliquots were taken after defined reaction times and subjected to quantitative GC analyses after derivatization of the aliquots with iodine (Scheme 3).

Scheme 3. **Benchmark reaction of *i*-PrMgCl/LiCl (3, 4) and *s*-BuMgCl/LiCl solutions (5, 6) with bromobenzene**



Results and Discussion

A plot of the conversion versus reaction time illustrates the progress of the reactions (Figure 1). For both *i*-PrMgCl/LiCl mixtures (**3**, **4**) as well as for *s*-BuMgCl/LiCl solutions (**5**, **6**), it is obvious that in each system the conversion improves with higher LiCl content. For all four curves, the shape is almost identical, and after a certain time the high rate of conversion observed at the beginning of the reactions decreases.

The reduction in rate is similar for both *s*-BuMgCl TurboGrignard solutions (**5**, **6**) and for both *i*-PrMgCl TurboGrignard reagents (**3**, **4**). This property seems to be insensitive to the LiCl content. However, the apparent rate decrease is greater when using *i*-PrMgCl/LiCl mixtures (**3**, **4**), than when carrying out the exchanges with *s*-BuMgCl/LiCl solutions (**5**, **6**). Hence, at a given point (marked X in Figure 1), *s*-BuMgCl/LiCl solutions (**5**, **6**) display a higher rate of conversion than *i*-Pr TurboGrignard reagents (**3**, **4**), finally resulting in higher conversions. From these experiments, one can conclude that, not only the content of LiCl present in solution during the exchange reaction is important for a fast halogen−magnesium exchange, but also the nature of the organic fragment attached to the magnesium center. Just one methyl group more results in indeed small, but obvious, changes.[8]

The reason for this different behavior of *i*-PrMgCl and *s*-BuMgCl TurboGrignard solutions in bromine−magnesium exchange reactions was unclear. During the exchange reac-

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[8] More detailed information, figures and tables are given in the Supporting Information.

Table 2. **Results from inline IR and gas flow measurements**

Inline IR Results

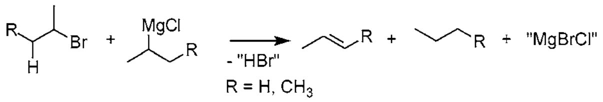
Grignard	concentrated[a] [wt %]	LiCl:RMgCl	alkyl bromide	IR mode at [cm^{-1}]	period of analyses [min]	gradient (Figure 3)	relative rate[c]
i-PrMgCl (**1**)	20	–	*i*-PrBr	1227	150–210	-4.20×10^{-4}	11.40
s-BuMgCl (**2**)	25	–	*s*-BuBr	1208	150–210	-7.46×10^{-5}	2.03
i-PrMgCl/LiCl (**4**)	14	1.02	*i*-PrBr	1227	150–210	-8.01×10^{-5}	2.18
s-BuMgCl/LiCl (**6**)	15	0.96	*s*-BuBr	1208	150–210	-3.67×10^{-5}	1.00

Gas Flow Results

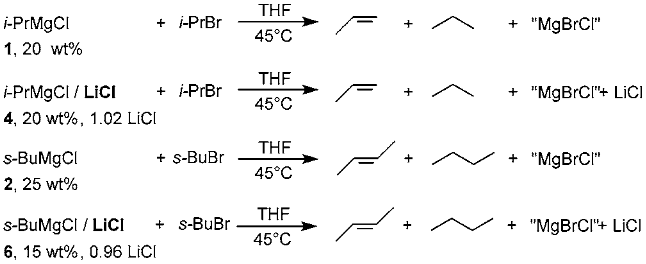
Grignard	concentrated[a] [wt %]	LiCl:RMgCl	alkyl bromide	gas volume [L][b]	period of analyses [min]	gradient (Figure 4)	relative rate[c]
i-PrMgCl (**1**)	20	–	*i*-PrBr	3.48	221–321	2.73×10^{-2}	13.65
s-BuMgCl (**2**)	25	–	*s*-BuBr	1.16	137–291	5.20×10^{-3}	2.60
i-PrMgCl/LiCl (**4**)	14	1.02	*i*-PrBr	1.78	146–335	6.80×10^{-3}	3.40
s-BuMgCl/LiCl (**6**)	15	0.96	*s*-BuBr	0.50	130–316	2.00×10^{-3}	1.00

[a] As total base $[OH]^-$. [b] From start until end of the reaction. [c] Via division of the gradients by the gradient of the slowest reaction with TurboGrignard **6**.

Scheme 4. **Competitive formal HBr elimination in halogen–magnesium exchange reactions**



Scheme 5. **Reactions to study the kinetics of the HBr elimination observed in halogen–magnesium exchange reactions**



tions, the formation of gaseous products was observed, and GC/MS identified propane in solutions from exchange reactions with *i*-PrMgCl/LiCl, and butane for the transformations with the *s*-BuMgCl TurboGrignard. These gases are formed by reaction of TurboGrignard solutions with the *i*-PrBr or the *s*-BuBr byproduct which results from the respective halogen–magnesium exchange. Formally, a HBr elimination takes place (Scheme 4).[5,6]

We think that this competitive HBr elimination is faster for *i*-PrMgCl TurboGrignard (**3**, **4**) than for *s*-BuMgCl/LiCl mixtures (**5**, **6**) and that this is the reason for the observed differences in both the slope of the curves and extent of conversions in the benchmark reaction of the different TurboGrignard solutions with bromobenzene. To verify this thesis, *i*-PrMgCl was reacted with *i*-PrBr, and *s*-BuMgCl was reacted with *s*-BuBr both in the presence and absence of lithium chloride (Scheme 5).

To quantify the kinetics of the HBr elimination reaction in these experiments, they were monitored by inline IR and gas flow measurements. Details are given in Table 2 in the Experimental Section and in the Supporting Information.

Results from Inline IR Measurements. The specific IR active modes of *i*-PrBr at 1227 cm^{-1} and *s*-BuBr at 1208 cm^{-1} could easily be identified in the waterfall diagrams.[8] To determine the kinetics of each reaction, the period at constant reaction conditions, i.e., after the end of the addition of the alkyl bromide and at a constant temperature of 45 °C, were taken. The wetting of the surface of the diamond IR dipper can be considered to be equal in all experiments. This, together with the assumption of almost equal molar coefficients of the extinction for both alkyl bromides (ϵ = constant, d = constant), the law of Lambert–Beer can be taken to determine the decrease of the concentration of the alkyl bromides ($\log(I/I_0) \propto$ concentration).

Figure 2 depicts the decrease of the concentrations of the alkyl bromides, using the law of Lambert–Beer. The values for $\log(I/I_0) \propto$ concentration are relative to the intensity I_0 at 150 min.[8] It is obvious that the alkyl bromides are consumed in these reactions. The curves show almost linear behavior at constant reaction conditions; thus, the gradients of the curves, obtained by linear regression, illustrate the quantitative relationship between the four experiments. Consequently, one can deduce the relative kinetics of the four reactions. The results of these analyses are given in Table 2.

The observed loss of concentration is higher for the reactions of the Grignard solutions with the alkyl bromides in absence of LiCl (**1**, **2**) than for the respective experiments with the TurboGrignard solutions in the presence of LiCl (**4**, **6**). The formal HBr elimination from the reaction of *i*-PrMgCl (**1**) with *i*-PrBr is approximately 5 times faster than for the reaction carried out in the presence of LiCl, using the *i*-PrMgCl/LiCl TurboGrignard solution (**4**). For the reactions of *s*-BuBr with *s*-BuMgCl (**2**) and with *s*-BuMgCl/LiCl (**6**), respectively, this difference is indeed smaller, yet still a factor of ~2. From these data, it is obvious that the presence of LiCl in solution minimizes the side reaction of Grignard solutions with alkyl bromides. This is a hint for the low conversions observed for halogen–magnesium exchange reactions, carried out in the absence of LiCl, as it was state of the art before the discovery of Knochel: without LiCl, these kinds of transformations are slow. In rather slow halogen–magnesium exchanges, the reaction of formed alkyl

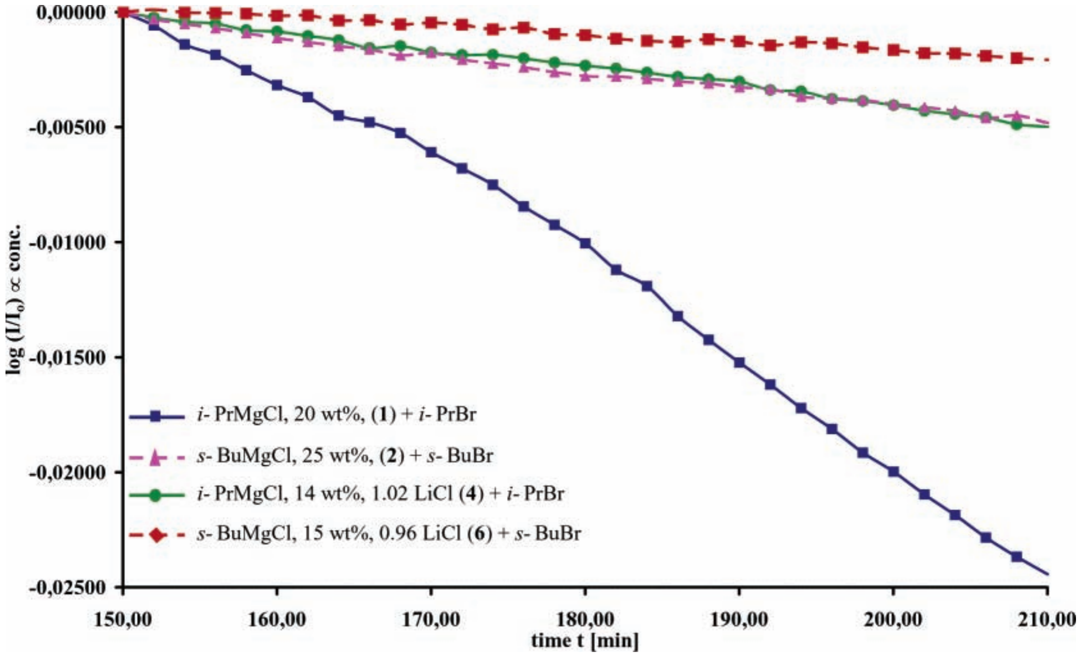


Figure 2. **Decrease of the concentrations of *i*-PrBr and *s*-BuBr, respectively, determined via inline IR measurements.**

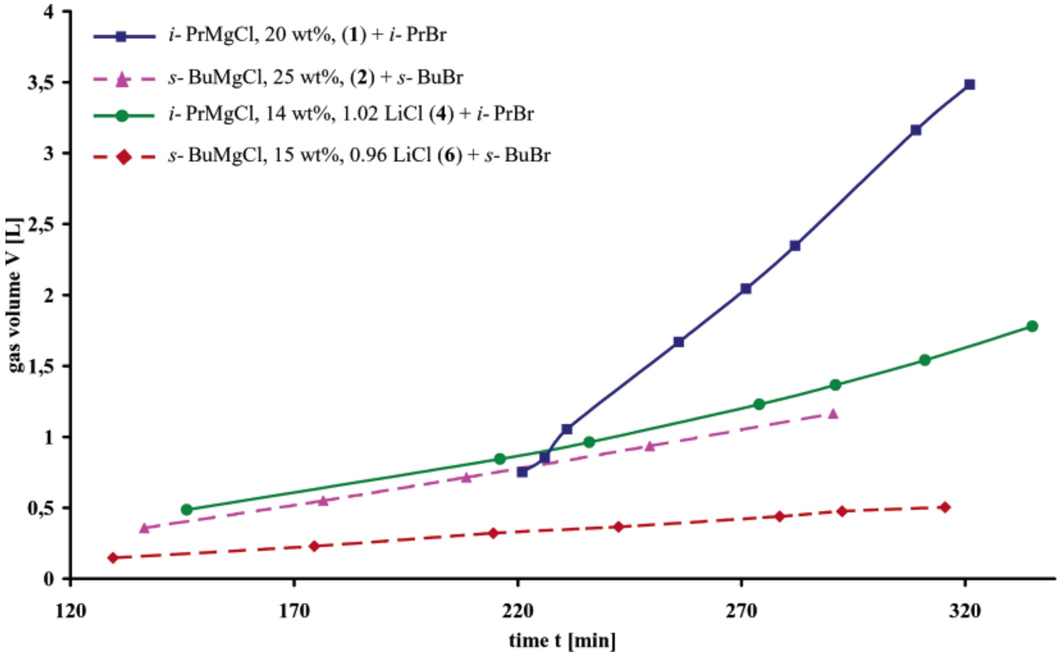


Figure 3. **Gas evolution at constant reaction conditions in reactions of *i*-PrMgCl and *s*-BuMgCl with *i*-PrBr and *s*-BuBr, in the presence and absence of LiCl, respectively.**

bromide with unreacted Grignard is an important (and rather fast) competitive reaction, consuming unreacted Grignard and therefore lowering conversions.

Figure 2 also clearly shows the difference between the two LiCl-containing TurboGrignard reagents (**4, 6**). In the reaction of *i*-PrBr with *i*-PrMgCl/LiCl (**4**), one observes a ~2 times faster decrease of the concentration of the alkyl bromide than that in the reaction of *s*-BuBr with *s*-BuMgCl/LiCl (**6**).

Results from Gas Flow Measurements. In addition to inline IR, the experiments were monitored with a gas meter to determine the evolution of the gaseous side products, propane and propene, and butane and butene, respectively. Figure 3 depicts the gas flow in the area of constant reaction conditions after addition of the alkyl bromides to the corresponding Grignard or TurboGrignard solutions. The determined relative rates are higher than those obtained from inline IR measurements, which is due to the minor accuracy of the method.[9] However, the obtained data are qualitatively in accordance with those discussed for the inline IR measurements and give the same trends (see Table 2).

Regarding the total gas evolved during the reactions of the Grignard and TurboGrignard reagents with the respective alkyl bromides (see Table 2), it is clear from the present

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(9) Possible reasons for the differences are different vapour pressures of the reaction mixtures or different solubilities of the gases in THF.

discussion that in the absence of LiCl a much higher total gas volume is observed than that in the presence of LiCl. Also, the total gas volume is less in the reaction of *s*-BuMgCl/LiCl with *s*-BuBr (**6**) than it is in the reaction of *i*-PrMgCl/LiCl with *i*-PrBr (**4**) during comparable reaction times. Hence, for scale up of halogen−magnesium exchange reactions, one has to consider that a much higher gas volume will be evolving when carrying out these transformations in the absence of LiCl. Also, applying *s*-BuMgCl/LiCl TurboGrignard solutions in halogen−magnesium exchange reactions gives less gas evolution than transformations with *i*-PrMgCl/LiCl TurboGrignard mixtures. Thus, regarding process safety, the use of *s*-BuMgCl/LiCl reagents may be better suited, at least for rather slow exchange reactions.

Conclusion

The yields obtained in halogen−magnesium exchange reactions are dependent on the presence and amount of lithium chloride dissolved in the Grignard solutions and also on the organic substituents at the magnesium center of the Grignard. Changing the reagents from *i*-PrMgCl/LiCl to *s*-BuMgCl/LiCl gives obvious changes in conversions. Although slower at the beginning of exchange reactions, the rate of conversion using *s*-BuMgCl/LiCl mixtures for the transformation drops less as the reaction progresses than if carrying out the exchange with *i*-PrMgCl/LiCl solutions. Hence, with *s*-BuMgCl/LiCl TurboGrignard solutions, slightly better conversions are obtained.

As a competitive reaction a formal HBr elimination, accompanied by evolution of gaseous products, takes place: the Grignard reagent reacts with the respective alkyl halide, which is formed in equivalent stoichiometric amounts relative to the new Grignard product, giving magnesium salts, alkanes, and alkenes. The rate of this competitive formal HBr elimination, responsible for low conversions in exchange reactions, is strongly influenced by dissolved LiCl. In presence of LiCl, this elimination is slower, causing less of the Grignard reagent to be consumed in the side reaction, therefore giving higher conversions. Additionally, the competitive HBr elimination is slower for *s*-BuMgCl/LiCl solutions than for *i*-PrMgCl/LiCl TurboGrignard mixtures. Therefore, the application of *s*-BuMgCl/LiCl in halogen−magnesium exchange reactions results in higher conversions and also in less gaseous side products, facts that should be considered for scale-up of halogen−magnesium exchange reactions.

Experimental Section

All manipulations were performed in an atmosphere of dry argon using Schlenk techniques. Solvents and LiCl were dried prior to use. All other reagents were used as purchased. The Grignard reagents *i*-PrMgCl and *s*-BuMgCl were prepared by standard oxidative addition of the respective chlorides to Mg turnings in THF. TurboGrignard reagents, *i*-PrMgCl/LiCl and *s*-BuMgCl/LiCl, differing in the amount of dissolved LiCl were prepared by dilution of the previously prepared Grignard solutions with THF and addition of the appropriate amount of LiCl. The concentrations of $[Mg^{2+}]$ (complexometric), $[Cl^-]$ (argentometric), and $[OH^-]$ (acidimetric) were obtained via titrations, those of $[Li^+]$ via atomic absorption spectroscopy (AAS). GC/MS measurements were performed on a THERMO ELECTRON FINNIGAN Trace GC or a Trace-DSQ GC with the following parameters: column: DB1 (60 m × 0.25 mm; film: 0.25 μm); method: oven 90 °C for 10 min; heating rate 20 K/min until 280 min; injector/detector temperature 280 °C; split: He/FID; flow rate 1.5 mL/min (He).

Quantitative GC measurements were performed on a FOCUS GC from FINNIGAN with the following parameters: column: DB1 (60 m × 0.25 mm; film: 0.25 μm); method: oven 90 °C for 10 min; heating rate 20 K/min until 280 min; injector/detector temperature 280 °C; split: He/FID; flow rate 1.2 mL/min (He). Calibrations were performed with exact amounts of bromo- and iodobenzene as external standards. All measurements were repeated four times, and the average values of the integrals were taken to calculate the mass percents.

Infrared spectra during the reactions of *i*-PrMgCl, *s*-BuMgCl, *i*-PrMgCl/LiCl, and *s*-BuMgCl/LiCl, with *i*-PrBr or *s*-BuBr, respectively, were recorded inline every 2 min on a REACTIR 1000 from ASI APPLIED SYSTEMS from 3000 to 700 cm^{-1} with a diamond IR dipper. The spectra are referenced against an Ar background spectrum. Characteristic modes of *i*-PrBr (1227 cm^{-1}) and *s*-BuBr (1208 cm^{-1}) were identified from waterfall diagrams obtained during the reactions. The reaction profiles (Figure 2) of the modes were obtained from the “quick profile function” of the software,[10] generating an absorption versus time plot for each mode. The kinetics of the reactions were evaluated at constant reaction conditions after 150 min. The calculated values $\log(I/I_0) \propto$ concentration are relative to the intensity I_0 after 150 min (see Supporting Information).

Bromo−Magnesium Exchanges of *i*-PrMgCl/LiCl and *s*-BuMgCl/LiCl Mixtures with Bromobenzene. To 50.0 mmol of TurboGrignard solutions (**3**−**6**) from Table 1 in 100-mL flasks was added 45.5 mmol of bromobenzene at 25 °C. After certain times, reaction aliquots were taken, derivatized with iodine, and subjected to quantitative GC. The conversion at a certain time was calculated as:

$$\text{conversion} = 1 - \frac{1}{\dfrac{\text{mass \% (PhI)/M(PhI)}}{\text{mass \% (PhBr)/M(PhBr)}} + 1}$$

The detailed time-dependent conversions are given in the Supporting Information.

Kinetics of the Formal HBr Elimination Reaction. In an 0.8-L double-jacketed reactor, equipped with a temperature-control device (internal and external), dosing pump, gas meter, condenser, and the inline IR dipper, each respective Grignard solution was added and heated to 45 °C. After a constant reaction temperature of 45 °C was reached, the respective alkyl bromide was added continuously over a period of 120 min, and the reaction temperature was maintained at 45 °C. After the complete addition, the solution

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[10] *ReactIR*, version 2.1; ASI Applied Systems, 1996.

was stirred at a temperature of 45 °C for the period, as indicated in Table 2.

***i*-PrMgCl (1) + *i*-PrBr.** To 270.4 g (538 mmol) of *i*-PrMgCl (20 wt % in THF) was added 66.2 g (538 mmol) of *i*-PrBr.

***i*-PrMgCl/LiCl (4) + *i*-PrBr.** To 266.7 g (360 mmol) of *i*-PrMgCl/LiCl (14 wt % in THF, with LiCl:*i*-PrMgCl = 1.02) was added 44.3 g (360 mmol) of *i*-PrBr.

***s*-BuMgCl (2) + *s*-BuBr.** To 285.6 g (614 mmol) of *s*-BuMgCl (25 wt % in THF) was added 84.1 g (614 mmol) of *s*-BuBr.

***s*-BuMgCl/LiCl (6) + *s*-BuBr.** To 288.8 g (361 mmol) of *s*-BuMgCl (15 wt % in THF, with LiCl:*s*-BuMgCl = 0.96) was added 49.5 g (361 mmol) of *s*-BuBr.

Supporting Information Available

Table 1: Analytical results of the Grignard and Turbo-Grignard reagents. Table 2: Time-dependent conversions in the reactions of *i*-PrMgCl/LiCl (**3**, **4**) and *s*-BuMgCl/LiCl (**5**, **6**) in the benchmark reaction with bromobenzene. Figures 1−4: Waterfall diagrams of the reactions of *i*-PrMgCl (**1**) and *i*-PrMgCl/LiCl (**4**) with *i*-PrBr and of *s*-BuMgCl (**2**) and *s*-BuCl/LiCl (**6**) with *s*-BuBr, respectively. Table 3: Time-dependent intensities of the characteristic IR modes of *i*-PrBr and of *s*-BuBr and lg(I/I_0) from Figures 1−4. Table 4: Time-dependent values for the gas flow measurements during the reactions of *i*-PrMgCl (**1**) and *i*-PrMgCl/LiCl (**4**) with *i*-PrBr and of *s*-BuMgCl (**2**) and *s*-BuCl/LiCl (**6**) with *s*-BuBr, respectively. Figure 5: Intensity versus time plot of the IR modes of *i*-PrBr and *s*-BuBr in the reactions with Turbo-Grignard reagents according to Scheme 5 in the paper, illustrating the loss of intensity of the IR modes and the procedure of data evaluation to determine reaction rates. This material is available free of charge via the Internet at http://pubs.acs.org.

Received for review January 16, 2006.

OP0600153