

EFFECTS OF STRUCTURES AND CONCENTRATIONS OF MONO- AND BIS-ARYLIMINODIMAGNESIUM ON THE REACTIONS WITH NITROBENZENES.*

FORMATION OF AZOXY AND AZO PRODUCTS ASSISTED BY AGGREGATED EXCESS OF MAGNESIUM REAGENT

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The relative yields of azoxy- and azo-type products in the reactions of aryliminodimagnesium [$\text{ArN}(\text{MgBr})_2$ (IDMg)] with nitrobenzene were greatly affected by changes in the molar concentration in tetrahydrofuran, addition of hexamethylphosphoramide to the reagent solution and the structures of mono- and bis-IDMg reagents. All the modes of variation of the product distribution, including extreme cases, were roughly but systematically related to a series of qualitative degrees of aggregation of IDMg. The role of aggregation is ascribed to the assistance of excess reagent molecules in the product formation process in the reaction. From the present and previous results and discussion on the reactions of IDMg and RMgBr , the IDMg aggregation is concluded to be an essential modification factor for useful reactions of the N-Mg (and also C-Mg) reagents having a suitable efficiency of single electron transfer.

INTRODUCTION

Aryliminodimagnesium [$\text{ArN}(\text{MgBr})_2$ (IDMg)], derived from anilines, is a useful nitrogenation agent. Its ability to condense with aromatic carbonyl and nitro compounds was established for the formation of

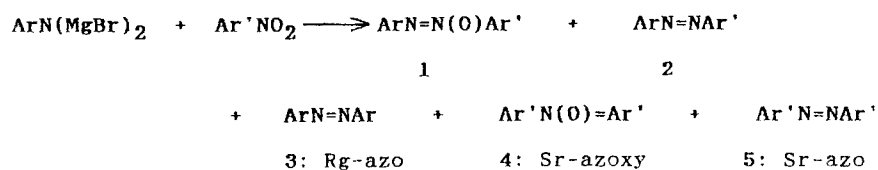
$\text{C}=\text{N}-\text{Ar}$ and $-\text{N}(\text{O})=\text{N}-\text{Ar}$ type products in the reaction in tetrahydrofuran (THF).^{1,2} The latter reaction [Scheme 1(a)] provides a method for the independent preparation of NNO and ONN isomers of unsymmetrical azoxybenzenes.³ Reaction (1a) proceeds in a stepwise manner: process I is condensation with $\text{Ar}'\text{NO}_2$ to give **1** and process II is a sluggish deoxygenation of **1** by excess of IDMg to give **2**.^{2,3} Concurrent coupling processes take place; oxidative coupling of IDMg leads to major by-product **3**⁴ whereas reductive coupling of $\text{Ar}'\text{NO}_2$ leads to minor by-products **4** and **5**.

Single electron transfer (SET) involved in the reaction in THF [1(a)] is suggested by formation of **3** and **4** and confirmed by ESR (the broad triplet ESR signal observed on the treatment of $\text{C}_6\text{H}_5\text{NO}_2$ with p -

$\text{MeOC}_6\text{H}_4-\text{IDMg}$ was assigned to nitrobenzene anion radical). The relative yields of **1**–**5** under fixed reaction conditions are governed principally by the respective value of the difference (ΔE) between the oxidation potential of IDMg (E_{ox}) and the reduction potential of $\text{Ar}'\text{NO}_2$ (E_{red}), depending on the substituents of the reactants:^{2,6b} a large ΔE due to the p -Cl group of IDMg and the p -MeO group of $\text{Ar}'\text{NO}_2$ favours the formation of **1** whereas a small ΔE due to reversed substituents favours the formation of **2** and also **3**–**5**.

At least *ca* 4 mol equiv. of IDMg are needed to obtain a sufficient combined yield of **1** + **2** in reaction 1(a),² and IDMg having a long p -alkoxy group leads exclusively to **2** in reaction 1(b).^{7a} This suggests an assistant role of excess IDMg molecules arising from interaction with strongly electron-accepting $\text{Ar}'\text{NO}_2$ (small and/or medium E_{red}). Hence the effects of reagent concentration on the reaction of mono- and bis-IDMgs (Schemes 1 and 2) were studied. The product distribution varies greatly depending on the structure and concentration of the IDMgs, and also on the addition of hexamethylphosphoramide (HMPA).

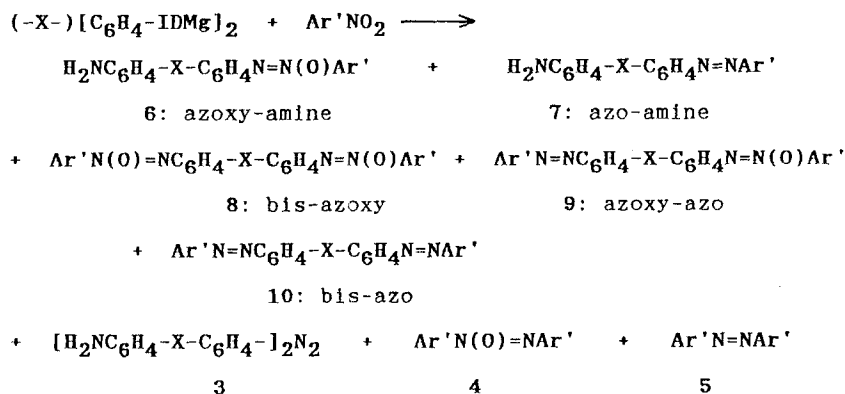
* Aryliminodimagnesium Reagents. Part XXI. For Part XX, see M. Ōkubo, M. Tanaka, Y. Murata, N. Tsurusaki, Y. Omote, Y. Ikubo and K. Matsuo, *Chem. Lett.* 1965 (1991).



a) Ar = Ar' = p-Cl-, Me-, and MeO-C₆H₄.

b) Ar = p-H(CH₂)_nOC₆H₄; n = 8, 10, 11, 12, 18; Ar' = p-MeC₆H₄

Scheme 1



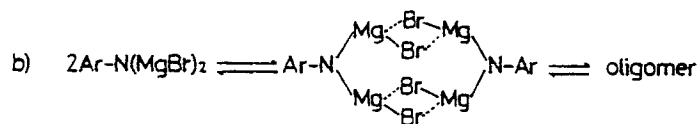
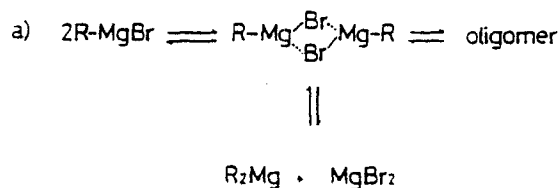
a) X = O, S, CH₂, OCH₂O, and SCH₂S.

Ar' = p-MeC₆H₄, p-MeOC₆H₄, p-ClC₆H₄.

b) X = O(CH₂)_nO; n = 4, 6, 8, 12.

Ar' = p-MeC₆H₄.

Scheme 2



Scheme 3

All the modes of variation, including extreme cases, of the product distribution in 1 and 2 are qualitatively but systematically related to the visibly observed degree of 'static and intermolecular' aggregation of IDMg [Scheme 3(b) evoking the Schlenk equilibrium of RMgBr shown in Scheme 3(a)].⁸ 'Dynamic aggregation' of IDMg molecules caused by interaction with substrates having small E_{red} and 'intramolecular' aggregation of bis-IDMg will also be described, and the role of reagent aggregation will be discussed from the unified viewpoint of the relative SET efficiency in typical reactions not only of N-Mg but also of C-Mg reagents.^{5,6}

RESULTS AND DISCUSSION

Effects of concentration and added HMPA on product distribution

Reactions of mono-IDMg (Scheme 1)

The effect of the concentration of mono-IDMg in THF

on the relative yields of 1–5 in reaction 1(a)_T, at a fixed molar ratio ($[\text{IDMg}]/[\text{Ar}'\text{NO}_2] = 4.2$) and reaction time and temperature, is shown in Figures 1(A) ($\text{Ar} = p\text{-MeOC}_6\text{H}_4$, $\text{Ar}' = p\text{-MeC}_6\text{H}_4$) and 1(B) ($\text{Ar} = p\text{-MeC}_6\text{H}_4$, $\text{Ar}' = p\text{-MeOC}_6\text{H}_4$), which represent typical cases of higher and lower SET efficiencies, respectively.² Higher concentrations, in both cases, favour an increase in 2 accompanied by a decrease in 1. This indicates that sluggish process II⁷ is more sensitive than I to the degree of aggregation.

Four features arise from different SET efficiencies. First, at the lowest concentration in Figure 1(B), a large amount of recovered $\text{Ar}'\text{NO}_2$ accompanies a low yield of 1 even with the use of excess of IDMg. Second, as shown by the crossing of the yield curve of 1 with that of 2 in Figure 1(A) appearing at a lower concentration region than the crossing in Figure 1(B), the decrease in 1 and increase in 2 in Figure 1(A) are greater than those in Figure 1(B). Third, the yield of 3 in Figure 1(A) is higher than that in Figure 1(B). Fourth, small amounts of 4 and 5 are present only in Figure 1(A). The first,

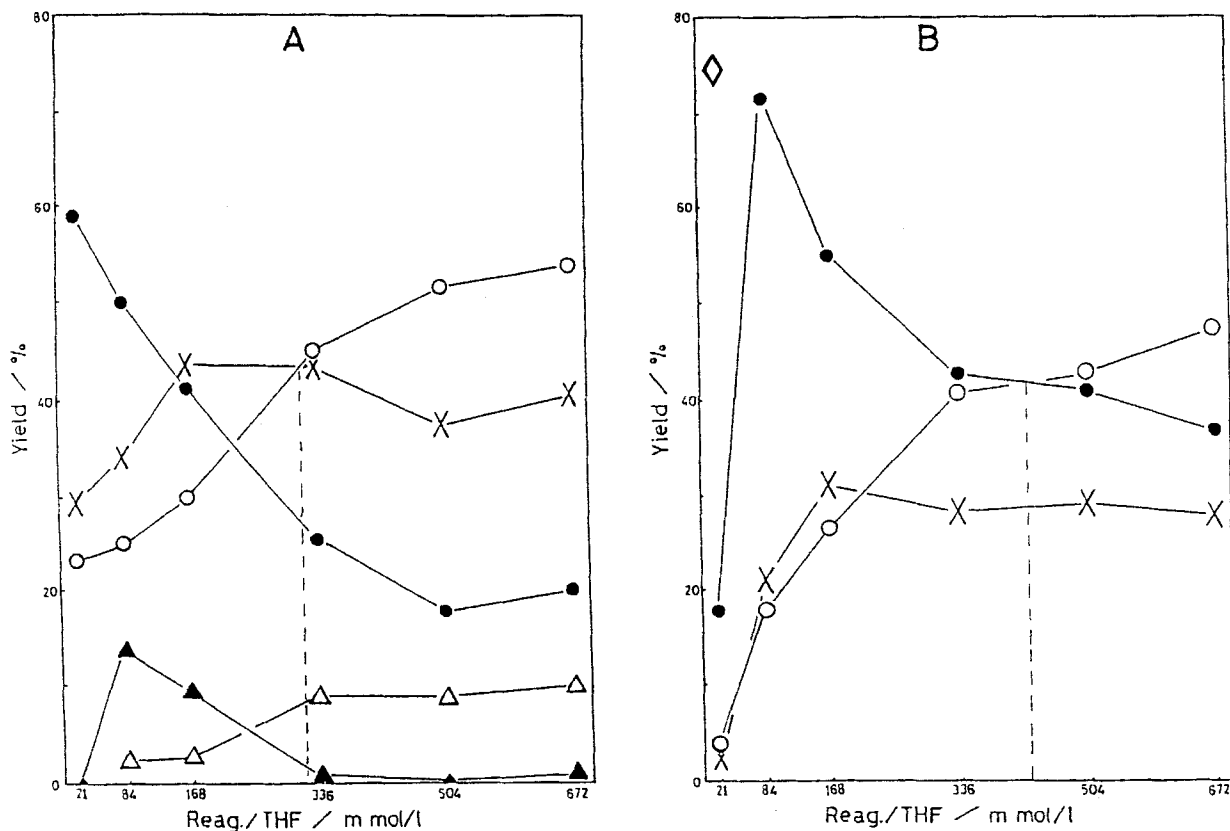


Figure 1. Effect of IDMg concentration on the relative yields of products 1–5 in reaction 1(a)_T. (A) $\text{Ar} = p\text{-MeOC}_6\text{H}_4$, $\text{Ar}' = p\text{-MeC}_6\text{H}_4$ ($\Delta E = 2.33$ V); (B) $\text{Ar} = p\text{-MeC}_6\text{H}_4$, $\text{Ar}' = p\text{-MeOC}_6\text{H}_4$ ($\Delta E = 2.56$ V). $[\text{IDMg}]:[\text{Ar}'\text{NO}_2] = 4.2:1.0$; THF, 50 ml; temperature 55°C ; time 3 h. Products: (●) 1; (○) 2; (×) 3; (▲) 4; (△) 5; (◇) recovered $\text{Ar}'\text{NO}_2$

second, third and fourth features suggest that IDMg aggregate is formed owing to a smaller ΔE and participates for processes I and II and also abnormal processes, respectively (see below). A pair of reactants having a small ΔE will 'pre-interact' with each other to cause 'dynamic aggregation' prior to SET, which will take place from IDMg aggregate⁶ (see final section).

The aggregation of magnesium reagents involves the exchange of an ether ligand molecule flanking the Mg atom, and the degree of aggregation must be affected by the addition of solvents having different coordinating abilities: HMPA is far stronger than THF as evaluated by Gutmann's donor numbers (DN : HMPA = 38.8, THF = 20.0, Et₂O = 19.0),⁹ and is unchanged on treatment of diaryl ketones with Grignard reagents in this solvent.¹⁰ By considering that the Grignard Mg atom is coordinated by two ether molecules,¹¹ HMPA was added in a 4 mol equiv. amount based on that of prepared IDMg. Reflecting the difference in DN values, ligand exchange of THF with HMPA results in the evolution of about twice the amount of heat evolved in Scheme 1(a) in THF using the reactants in a 1:1 molar ratio (estimated according to the reported method).^{6b} Yields of 1–5 obtained in the absence and presence of HMPA [i.e. in 1(a)_T and 1(a)_P] are shown in Table 1 (runs 1–8).

Two features arise from the addition of HMPA [1(a)_P; runs 2, 4, 6 and 8]. First, resembling the dilution effect in 1(a)_T, the yield of 1 is improved at the expense of 2 and 3. The IDMg molecules, less mobilized by the tight binding of four HMPA molecules, do not aggregate around the azoxy oxygen of 1 to retard process II and also are unfavourable for dimerization, but are still able to aggregate around the strongly polar nitro group to produce 1.

Second, *N*-ethylanilines are formed in 1(a)_P and not in 1(a)_T. Their yields (15–20% based on IDMg) are comparable to the excess amount of ethyl bromide used for complete conversion of metallic Mg into EtMgBr,⁵ and an S_{RN} -like process involving the generation of

ethyl radical from [EtBr]⁻ is suggested.¹² For SET to EtBr (weak acceptor), a strengthened electron-donating ability for IDMg by coordination of HMPA having a high DN must be responsible. This is compatible with the heat evolution (see above) and the following two facts: large elevation of (free) Grignard HOMO level by coordination of two ether molecules (small DN) disclosed by *ab initio* SCF MO calculations,¹³ and efficient accumulation of diaryl ketone anion radical in high concentration due to efficient SET by the treatment with RMgX in HMPA.¹⁰

Exclusive formation of 2 in reaction 1(b) of IDMg having a long (such as C₁₈) *p*-alkoxy chain was reported.^{7a} This was ascribed to the tying effect of the chain to raise the population of aggregated IDMg molecules favouring processes I and II.

Reactions of bis-IDMg (Scheme 2)

Interesting cases arising from extreme degrees of aggregation of bis-IDMgs were disclosed. Those derived from bisanilines having 'one and/or three central atoms in X' [reaction 2(a)_T] form precipitates of tight aggregates undissolvable even by the use of a fourfold volume of THF. The good combined yield of 6–10 [corresponding to 1 and 2 in 1(a)_T] and 3–5 implies a favourable effect of tightness on the expected processes. Surprisingly constant yields of each product (Table 2), irrespective of not only the amount of THF but also the central X moiety of bis-IDMg and/or the substituents of Ar'NO₂, are observed, and are ascribed to the effect of the tightest aggregation overwhelming the electronic effects of the substituents (cf. runs 1, 3, 5 and 7 in Table 1).² In addition to the route in Scheme 3(b), these bis-IDMg molecules probably interact in a face-to-face π - π manner [but not for the loose aggregation in Scheme 2(b); see below].

The tightest aggregate of bis-IDMg (X = CH₂ or S) was solubilized by stirring with an eight-fold molar amount of HMPA to give a clear solution [reaction

Table 1. Comparison of product distribution in the absence [1(a)_T] and presence [1(b)_P] of HMPA

Run No.	Ar=	Ar' -	HMPA (- or +)	Yield ^a (%)				
	<i>p</i> -RC ₆ H ₄ : R	<i>p</i> -R'C ₆ H ₄ : R'		1	2	3	4	5
1	MeO	Cl	-	36	23	33	-	7
2	MeO	Cl	+	58	13	-	-	9
3	Cl	MeO	-	77	9	14	-	-
4	Cl	MeO	+	70	8	4	-	-
5	MeO	Me	-	30	25	19	2	7
6	MeO	Me	+	55	11	4	6	-
7	Me	MeO	-	51	29	25	-	-
8	Me	MeO	+	71	11	6	-	-

^a Molar ratio [IDMg]:[Ar'NO₂]:[HMPA] = 4.2:1.0:16.8; THF, 50 ml; temperature, 55°C for 3 h. Yields are based on the amount of Ar'NO₂ used.

2(a)p]. However, except for *N*-ethylation [see reaction 1(a)p], neither Ar'NO₂ recovery nor azoxy (or azo) formation was observed. Owing to tight binding with eight HMPA molecules, the bulky and heavy bis-IDMg molecules must be the least mobile and actually monomerized: they do not aggregate to any notable extent in either a 'static' or 'dynamic' manner. Accordingly, the transfer of single electrons to the LUMO of Ar'NO₂ takes place in a facile manner from the elevated HOMO level of IDMg while the generated anion radical of Ar'NO₂ is left to decompose by itself.¹⁴ A contrastingly extreme case of 'non-aggregation' is thus provided.

Bis-IDMg having more than six central atoms in X [reaction 2(b); *n* = 4, 6, 8, 12] form precipitates of aggregates at normal concentrations. All the aggregates are loose and are solubilized by the use of THF in a fourfold volume to vary the yields of 6–10 and 3–5 (Table 3, runs 1–9). The exceptional behaviour of bis-IDMg having eight central atoms on dilution is noted (*n* = 6; compare run 5 with runs 2, 7 and 9); the combined yield of 6–10 when *n* = 6 is still fairly good and no Ar'NO₂ was recovered. From comparison of molecular models, it is shown that 'intramolecular aggregation in a cyclic manner' [as in 3(b)] is possible with *n* = 6 but is impossible with *n* = 4, 8 and 12.

Table 2. Yields of products in the reaction of bis-IDMg having a short central chain [reaction (2a)_T]

Ar' = <i>p</i> -RC ₆ H ₄ : R	X	Yield ^a (%)					
		6	7	8	9	10	3
Me	O	38	21	11	6	0	5
Me	CH ₂	46	12	19	8	0	2
Me	S	46	17	10	7	0	13
MeO	O	37	19	13	12	0	—
MeO	CH ₂	33	11	18	19	Trace	—
MeO	S	61	17	11	9	0	—
MeO ^b	S	37	18	11	9	0	—
MeO	OCH ₂ O	38	11	12	15	0	—
MeO	SCH ₂ S	35	9	20	16	0	3
MeO ^b	SCH ₂ S	27	11	12	0	9	—
Cl	O	39	16	12	9	0	—
Cl	CH ₂	50	12	21	10	0	—
Cl	S	43	17	19	9	0	Trace

^a Yields are based on the amount of Ar'NO₂ used. Equivalent ratio: [IDMg]:[Ar'NO₂] = 4·21:1·0; THF, 50 ml.

^b THF, 200 ml; recovery of Ar'NO₂ was 21–23%.

Table 3. Product distribution in the reaction of bis-IDMg having a long central chain [reaction 2(b)]

Run No.	<i>n</i>	Yield ^a (%)								Recovery (%)
		6	7	8	9	10	3	4	5	
1 ^b	4	27	22	7	9	3	Trace	24	3	0
2 ^c	4	12	15	4	3	2	Trace	14	Trace	44
3 ^d	6	28	15	11	19	6	Trace	10	Trace	0
4 ^b	6	30	22	11	15	4	Trace	10	Trace	Trace
5 ^c	6	20	44	Trace	17	5	Trace	0	10	0
6 ^b	8	34	24	7	9	4	2	10	Trace	1
7 ^c	8	3	16	Trace	1	3	Trace	Trace	Trace	61
8 ^b	12	34	19	9	12	4	Trace	10	0	0
9 ^c	12	1	20	0	0	5	Trace	0	0	57

^a Equivalent ratio: [IDMg]:[Ar'NO₂] = 4·2:1·0. Yields are based on the amount of Ar'NO₂ used.

^b 55 °C for 0·5 h; THF, 50 ml.

^c 55 °C for 3 h; THF, 200 ml.

^d 55 °C for 3 h; THF, 50 ml.

Conclusion

A summary of the results in Tables 1–3 is depicted in Figure 2. An increase of concentration and tightness, if these are of medium extent, enhances processes I and

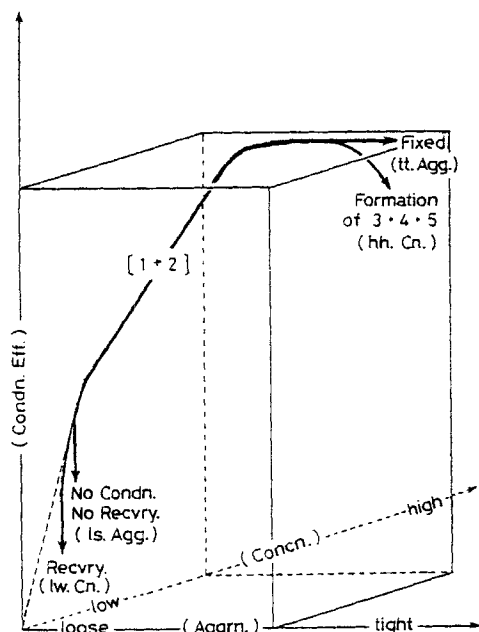


Figure 2. Illustration of different effects of concentration and degree of aggregation on the efficiencies of condensation and deoxygenation. Abbreviations: tt = tight; ls = loose; hh = high; lw = low

II; an increase in the combined yield of 1+2 is accompanied by an increase in the [2]:[1] ratio. A decrease in and/or fixation of the yields (or the ratio) are caused in apparently different manners by extreme concentration and tightness (or looseness). Nevertheless, as shown in Table 4 covering all the results for Schemes 1 and 2, the serial order of 'tight→loose→non' aggregation is roughly but systematically related to the variation of the product distribution: fixed [2(a)_T]→affected by concentration and length and/or electronic effect of substituents [1(a), 1(b), 2(b)]→solely process I favoured [1(a)_p]→neither progress of process I nor recovery of Ar'NO₂ [2(a)_p]. It should be stressed that the initial state of aggregation, represented in Scheme 4 by the equilibrium prior to addition of Ar'NO₂, has a definitive effect on the reaction.

GENERAL DISCUSSION

The role of 'dynamic aggregation' will be discussed in connection with the Grignard reaction from a unified viewpoint.

1. The role of SET attracts attention in a variety of fields of organic chemistry. As much evidence for SET has been accumulated in the field of Grignard chemistry, the diversity in the precise mechanism of the reaction depending on the structures of the respective reactants has recently been elucidated.¹⁵ The approach based on 'relative SET efficiency and modification factors' will contribute to providing a unified structure–reactivity relationship covering the reactions of magnesium reagents.

The ΔE approach (see above) is extended to the classification and characterization of SET-initiated

Table 4. Relative azoxy/azo yields in IDMg reactions related to visible and invisible IDMg aggregation in THF

Reaction No.	Azoxy and Azo yields	IDMg aggregate ^a (from tight to loose)
2(a) _T	Comparable, but not varied by dilution	Visible, and not solubilized by THF addition ^b
2(b) (<i>n</i> = 4, 6, 8 and 12)	Comparable, but varied by dilution except for <i>n</i> = 6	Visible, but solubilized by dilution ^c
1(b)	Exclusive azo formation from <i>p</i> -C ₁₈ -alkoxy of IDMg	Visible, but very easily solubilized by dilution ^d
1(a) _T	Relative yield of azoxy/azo depends on substituents	Invisible; sufficient aggregation for processes I and II ^e
1(a) _p	Yield of azoxy improved	Invisible; weak and insufficient aggregation for process II ^f
2(a) _p	No condensation, no recovery	Invisible; probably monomeric ^g

^a 'Visible and invisible' based on the observations under a concentration of 8.0 mmol IDMg in 50 ml of THF. 'Dilution' means observation under a concentration of 8.0 mmol IDMg in 200 ml of THF.

^b The exceptionally tight aggregation and depressed substituent effect (see text).

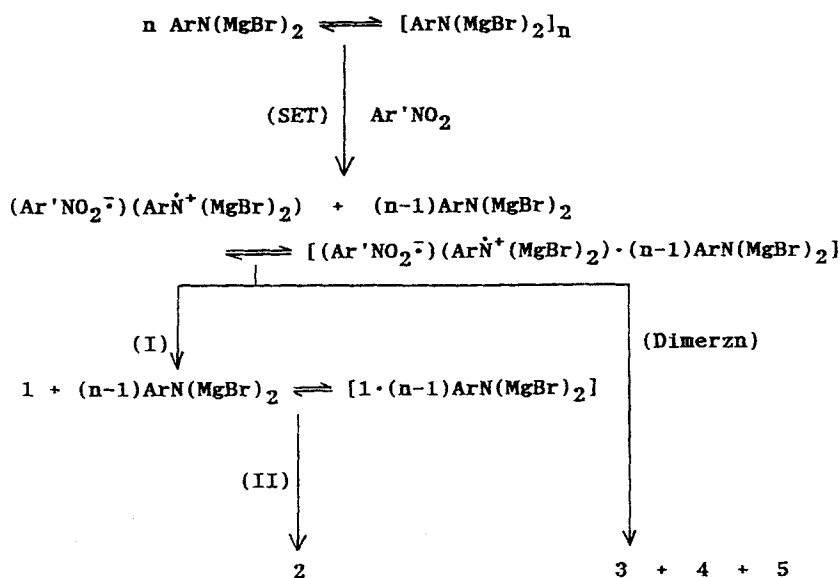
^c Intramolecular aggregation for *n* = 6 (see text).

^d See Ref. 7a.

^e See Ref. 2 and Figure 1.

^f See text and Table 1.

^g Only *N*-ethylation (see text).



Scheme 4

reactions of Mg reagents. The IDMg has a larger positive E_{ox} than that of ArMgBr (i.e. the former is a weaker electron donor than the latter),⁵ while $\text{Ar}'_2\text{CO}$ has a larger negative E_{red} than that of $\text{Ar}'\text{NO}_2$ (i.e. the former is a weaker electron acceptor than the latter).⁶⁹ Thus, many reactions of C—Mg, N—Mg, S—Mg and O—Mg reagents were classified by ΔE irrespective of their different normal modes: IDMg condensation and RMgX addition.^{1,6} Reaction 1(a)_T and that of $\text{ArMgBr} + \text{Ar}'_2\text{CO}$ are classified in same class of medium ΔE and that of $\text{IDMg} + \text{Ar}'_2\text{CO}$ belongs to another class of large ΔE .

2. The fact that not only the rate of radical generation but also the final distribution of normal and abnormal products in reactions of ArMgBr ¹⁶ and in 1(a) are simply governed by ΔE irrespective of normal modes implies a definitive role of the initial conditions. The simplicity is rationalized from the specific circumstances of the later stage of the $\text{RMgBr} + \text{Ar}'_2\text{CO}$ reaction (after radical formation and leading to the final product) distinct from those of the initial stage: $[\text{Ar}'_2\text{CO}]^-$ and $[\text{RMgBr}]^+$ form a stable dimeric assembly, in which the R' radical migrates 'with assistance of another neutral RMgBr molecule'¹⁵ to give the normal product. The old problem of the considerable slowing of this reaction (1:1 molar ratio) after the carbinol yield has reached 50%¹⁷ is answered, and the simplicity is substantiated. Thus, 'excess neutral reagent molecules for assistance arising from dynamic pre-interaction' participate in common with the N—Mg and C—Mg reactions of medium ΔE .

3. ' ΔE -dependent aggregation' also concerns 'type of by-product', in common with C—Mg and N—Mg reactions:^{1,6} monomeric type in cases of large ΔE and dimeric type in cases of small and medium ΔE [3–5 in 1(a)_T and also biaryl and pinacol in the Grignard reaction]. 'Efficient accumulation of radical intermediates' due to smaller ΔE (reason i) is oversimplified. Alternatively, 'enhanced aggregation of reagent molecules around the substrate prior to SET' arising from 'dynamic pre-interaction' of reactants due to a smaller ΔE (reason ii)⁶ is more essential and compatible with the dimerization. The spectroscopic distinction of 'static' and 'dynamic' manners of IDMg aggregation is difficult because the reaction mixture instantly colours deep brown, and a precise mechanism based on direct evidence remains to be studied.

4. In so-called 'coordination controlled' cases of large ΔE ,^{1,5,6} the coordination of a special atom (oxygen) of the substrate to the Mg atom of the reagent (i.e. σ -complexation) assists SET and succeeding processes: the effect is called the 'modification factor'. In cases of very small ΔE , much more efficient SET takes places (even from a long distance) without the assistance of coordination and leads mainly to typical radical products. In so-called 'SET-efficiency controlled' cases of medium ΔE , SET takes places (from a medium distance) with a little assistance from coordination: the effect of reagent aggregation for sufficient 'assistance' is recognized as the common 'modification factor' for useful reactions of C—Mg and N—Mg reagents of suitable SET efficiency. Manifestation of the

modification factors owing to the mild reactivity of IDMg evokes the 'less reactive, more selective' principle.

EXPERIMENTAL

The mono- and bis-anilines used for the preparation of IDMg reagents were obtained as follows. Ordinary mono- and bis-anilines having central O, CH₂ and S moieties were commercially available. The bisanilines having OCH₂O and SCH₂S moieties were prepared by the reaction of dibromo- or diiodo-methane with potassium *p*-nitrophenolate or sodium *p*-nitrobenzenethiolate,¹⁸ followed by reduction with zinc powder.^{7a} The bisanilines having ω -alkylenedioxy groups were prepared by the reaction of the corresponding ω -dibromoalkanes and *p*-nitrophenolate followed by reduction.^{7a}

The mono- and bis-IDMg reagents were prepared in THF using the corresponding anilines and 2 mol equiv. of EtMgBr. At about 8.0 mmol of IDMg in 50 ml of THF were used under ordinary conditions. Hexamethylphosphoramide was added to the solution or suspension of IDMg at room temperature [reactions 1(a)_p and 2(a)_p], then the reagent solution (or suspension) was cooled to 0°C and 0.19 equiv. of nitrobenzene was added and the mixture was stirred at 55°C for 3 h.

After quenching with aqueous ammonium chloride and extraction with diethyl ether or dichloromethane, the product mixture was separated by column chromatography on silica gel (Wako Gel FC-40) and the structures and yields of the products were determined by ¹H NMR spectrometry. The signals appearing at δ 8.1–8.3 ppm were assigned to *ortho*-protons of azoxy products, whereas the signals at δ 7.7–7.9 ppm were assigned to those of azo products.^{2,3a}

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REFERENCES

1. M. Ōkubo, *Bull. Chem. Soc. Jpn.* **58**, 3108 (1985).
2. M. Ōkubo, T. Takahashi and K. Koga, *Bull. Chem. Soc. Jpn.* **56**, 199 (1983).
3. (a) M. Ōkubo and K. Koga, *Bull. Chem. Soc. Jpn.* **56**, 203 (1983); (b) M. Ōkubo, C. Sugimori, M. Tokisada and T. Tsutsumi, *Bull. Chem. Soc. Jpn.* **59**, 1644 (1986).
4. M. Ōkubo, S. Yoshida, Y. Egami and K. Matsuo, *Bull. Chem. Soc. Jpn.* **60**, 1741 (1987).
5. M. Ōkubo, T. Tsutsumi, A. Ichimura and T. Kitagawa, *Bull. Chem. Soc.* **57**, 2679 (1984).
6. (a) M. Ōkubo, T. Tsutsumi, and K. Matsuo, *Bull. Chem. Soc. Jpn.* **60**, 2085 (1987); (b) M. Ōkubo, Y. Fukuyama, M. Sato, K. Matsuo, T. Kitahara and M. Nakashima, *J. Phys. Org. Chem.* **3**, 379 (1990).
7. (a) M. Ōkubo, K. Matsuo and A. Yamauchi, *Bull. Chem. Soc. Jpn.* **62**, 915 (1989); (b) M. Ōkubo, T. Nakashima and H. Shiku, *Bull. Chem. Soc. Jpn.* **62**, 1621 (1989).
8. W. Schlenk and W. Schlenk, Jr, *Chem. Ber.*, **64**, 739 (1931).
9. V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Chapt. 2. Plenum Press, New York (1978).
10. J. F. Fauvarque and E. Rouget, *C. R. Acad. Sci. Ser. C* **287**, 1355 (1968).
11. L. J. Guggenberger and R. E. Rundle, *J. Am. Chem. Soc.* **90**, 5375 (1968).
12. (a) N. Kornblum, *Agnew, Chem. Int. Ed. Engl.* **734** (1975); (b) J. F. Bunnett, *Acc. Chem. Res.* **11**, 413 (1978).
13. S. Nagase and Y. Uchibori, *Tetrahedron Lett.* **23**, 2585 (1982); S. Nagase, paper presented at the 46th National Meeting of the Chemical Society of Japan, Niigata, October 1983.
14. G. A. Russell, E. G. Janzen and E. T. Strom, *J. Am. Chem. Soc.* **86**, 1807 (1964).
15. (a) K. Maruyama and T. Katagiri, *J. Am. Chem. Soc.* **108**, 6263 (1986); (b) K. Maruyama and T. Katagira, *Chem. Lett.* **735** (1987); (c) K. Maruyama, J. Hayami and T. Katagiri, *Chem. Lett.* **601** (1986); (d) K. Maruyama and T. Katagiri, *J. Phys. Org. Chem.* **1**, 21 (1989); **4**, 381 (1991).
16. M. Ōkubo, *Bull. Chem. Soc. Jpn.* **48**, 1327 (1975); **50**, 2379 (1977).
17. N. M. Bikales and E. I. Becker, *Chem. Ind. (London)* **1831** (1961).
18. W. R. Waldron and E. E. Reid, *J. Am. Chem. Soc.* **45**, 2408 (1923).