

COOPERATION OF ARYLIMINODIMAGNESIUM MOLECULES: DEOXYGENATION OF AZOXYARENES BY MONO- AND BIFUNCTIONAL REAGENTS IN COMPARISON WITH THAT BY PHOSPHORUS(III) REAGENTS*

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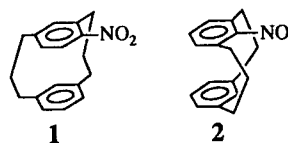
Reaction of aryliminodimagnesium [$\text{ArN}(\text{MgBr})_2$, IDMg] with nitrobenzene (Ar^1NO_2) in tetrahydrofuran (THF) gives unsymmetrical (unsym) azoxybenzene, which is deoxygenated to give unsym-azobenzene. The reaction is utilized for the independent preparation of ONN and NNO isomers of unsym-azoxy compounds. The effects of the relative value of the difference between oxidation and reduction potentials of *para*-substituted reactants, special effects of *ortho*-substituents of the substrate and also effects of structure and concentration of mono- and bis-IDMg reagents were studied previously, and 'cooperation of their aggregate excess needed for product formation' was proposed. This unfamiliar concept for reactions of magnesium reagents was studied further. Supporting evidence was obtained from the retarding effect of trimethylene chains of nitro [3.3]metacyclophanes and the derived azoxy [3.3]metacyclophanes and also from the effect of the length of bis-IDMg's central α,ω -polymethylenedioxy chain appropriate for azoxy deoxygenation. By comparison with deoxygenation by X_3P reagents ($\text{X} = \text{EtO}, \text{Me}_2\text{N}$), the general needs of cooperation of excess magnesium reagents were confirmed and its role in their reactions is discussed.

INTRODUCTION

Reactions of C-Mg (Grignard) and N-Mg [aryliminodimagnesium [$\text{ArN}(\text{MgBr})_2$, IDMg]] reagents are classified on the basis of relative efficiency of single-electron transfer (SET): the efficiency is evaluated by the difference between the oxidation and reduction potentials of reactants¹ ($\Delta E = E_{\text{ox}} - E_{\text{red}}$). According to the classification of reactions in terms of ΔE , the medium value of reactions of IDMg with Ar^1NO_2 [equation (1)] and of C-Mg with Ar^2CO [equation (2)] is responsible for the common features (1) in relative yields of normal (addition and condensation) and abnormal (radical) products, (2) in substituent effects on radical generation and/or product formation and (3) in the need for excess of C-Mg and N-Mg reagents.² Feature (3) implies that an aggregate of reagent and radical intermediates form an assembly in which a radical migrates to generate the final products.

As similar role of aggregate reagent molecules has

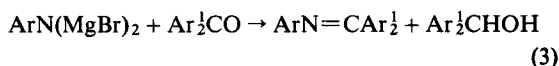
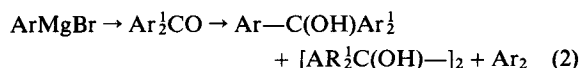
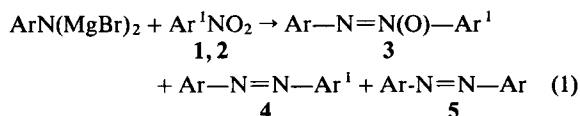
also been postulated in high- ΔE reactions of IDMg [equation (3) and (4)].³ This feature in reactions of magnesium reagents is not widely accepted and, therefore, further evidence has been explored. From the relative yields of the main products (3, 4 and 5) in IDMg reactions of outer- and inner-nitro isomers of [3.3]metacyclophane ([3.3]MCP; 1 and 2), steric hindrance by trimethylene chains of azoxybenzenes (3) retarding its deoxygenation [second stage of reaction (1)] was revealed. Deoxygenation of isolated ordinary azoxybenzene by bis-IDMg having an α,ω -polymethylenedioxy central chain is affected by its chain length. The observed effects originating from the



* Aryliminodimagnesium Reagents: Part XXV. For Part XXIV, see K. Matsuo, Y. Shichida, H. Nishida, S. Nakata and M. Okubo, *J. Phys. Org. Chem.*, 7, 9–17.

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substrate side and the reagent side will be discussed in terms of efficiency in inter- and intramolecular cooperation of IDMg groups.



RESULTS AND DISCUSSION

IDMg reactions with outer- and inner-nitro [3.3] MCP

In reaction (1) with ordinary *para*-substituted nitrobenzenes, a four molar amount of IDMg is needed for sufficient overall yields of 3–5 without recovery.⁴ For reaction with 1 and 2, an 8.0 molar amount of IDMg was used in order to diminish unchanged substrate.^{4c} Considering the barrier effect caused by the trimethylene chains of 1 and 2 on the access of reagent molecules to the nitro group, 2,4,6-Me₃C₆H₂NO₂ (MesNO₂, 6) was also used for comparison. The yields of 3–5 in the reactions with 1, 2 and 6 are summarized in Table 1. The combined yield of 3 plus 4 implies 'total condensation efficiency', and the ratio of 4/(3 + 4), indicating 'deoxygenation efficiency,' is included in the table.

Prior to discussion, the effect of transannular π -donation (from unsubstituted benzene rings) in **1** and **2** on their E_{red} values [i.e. on ΔE of reaction (1)] is estimated by comparison with those of 2,4,6-Me₃-(**6**),

2,4-Me₂- (**7**) and 2,6-Me₂- nitrobenzenes (**8**): **1**, -1.538 V; **2**, -1.619 V; **6**, -1.651 V; **7**, -1.484 V; **8**, -1.567 V. The larger E_{red} of **1** and **2** than those of **7** and **8**, respectively, indicate a transannular effect. However, the larger E_{red} of **6** than that of **2** is not related to the respective patterns of product distributions from **2** and **6**. From Table 1, there are two anomalies due to the especially crowded structure of **2**, as follows.

(i) An anomaly in deoxygenation efficiency is noted. In runs 1–3 and 4–6 using **6** and **1**, respectively, the efficiency decreases as E_{ox} increases. In runs 7–9 using **2**, in contrast, the efficiency is low and unaltered by the E_{ox} values. The relative yield of **3** and **4** in run 7 shows that product **3** is hardly deoxygenated even in the low- ΔE reaction using a strong reagent (compare with the higher efficiency in runs 1 and 4).

(ii) An anomaly in the yield of sym-azobenzene **5** is noted. It arises from oxidative coupling of IDMg molecules⁴ in reaction (1) caused by their aggregation, induced by pre-interaction with Ar'NO₂ of smaller E_{red} and accompanying SET;² its low yield is due to (a) large ΔE and (b) hindered aggregation of IDMg around NO₂. Reason (a) is responsible for the low yields of **5** in runs 3, 6 and 9 due to the large E_{ox} of IDMg. A good overall yield in run 6, in comparison with the low yield in run 3, is allowed by the strong positive charge on the Mg atom of weak IDMg, favouring σ -complexation. Reason (b) is thus responsible for low yield of **5** in run 8 in spite of the medium E_{ox} .

Anomaly (i) indicates steric hindrance against the second deoxygenation stage of reaction (1). According to the molecular model of the most probable 'chair-chair' conformation⁵ of MCP, the nitro group of **2** is surrounded by two or four benzyl protons of trimethylene chains and the 'inner proton' of unsubstituted benzene ring; the resultant azoxy group of **3** is more hindered by ArN= group (if the original conformation holds a after the first condensation stage), and

Table 1. Yields of azoxy (3) and azo (4 and 5) products in reaction (1) of *p*-RC₆H₄-IDMg with MesNO₂ (6) and nitro[3.3]MCPs (1 and 2)^a

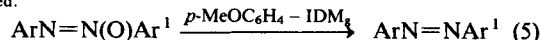
Run No.	R	Substrate	ΔE (V)	Yield (%)			Recovery (%)	4/3 + 4
				3	4	5		
1	MeO	6	2.56	6	80	28	0	0.93
2	Me	6	2.59	20	41	21	0	0.67
3	Cl	6	3.14	21	16	4	29	0.48
4	MeO	1	2.45	14	51	29	0	0.78
5	Me	1	2.48	55	23	24	0	0.29
6	Cl	1	3.02	69	18	8	0	0.21
7	MeO	2	2.53	46	13	21	0	0.22
8	Me	2	2.56	60	17	7	0	0.22
9	Cl	2	3.10	49	12	3	28	0.20

^a [IDMg]/[substrate] = 8·0: reaction temperatures = 55 °C for 3 h.

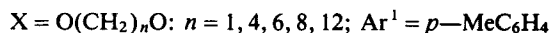
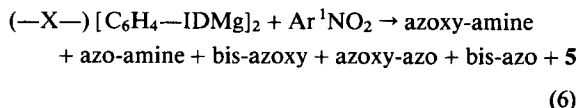
allows IDMg attack only from a limited direction. The requirement of closer cooperation of IDMg molecules, suggested for the second deoxygenation stages of reaction (1),^{2b,4b} is verified by the reactions with nitro-MCP.

Deoxygenation of isolated azoxybenzene: intramolecular cooperation of terminal IDMg sites of bis-IDMg

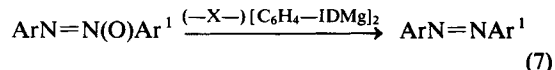
Previously, sym- and unsym- (ONN and NNO isomers of) azoxybenzenes were independently prepared for the first time by the IDMg reaction (1), and their deoxygenation was studied^{4b} using stronger *p*-MeO-mono-IDMg [equation (5)]. The logarithmic percentage deoxygenation, inversely proportional to $\lambda_{\max}$ of the $\pi-\pi^*$ band of azoxybenzenes, indicates attack of anionic nitrogen (N^-) of IDMg on cationic azoxy nitrogen (N^+); this was supported by the formation of a by-product due to binding of the ArN group with a fragment of 'strong' azoxybenzenes having a small E_{red} .^{4b}



As previously reported, the reaction of bis-IDMg with Ar^1NO_2 affords all the expected products via condensation, deoxygenation and oxidative coupling [equation (5)]. When bis-IDMg having a central chain of eight atoms ($n=6$) is used, the overall yield suffers no retardation by dilution with tetrahydrofuran (THF) (200 ml). This led to the proposal of 'cooperation' of terminal IDMg sites intramolecularly aggregating via an $\text{Mg}-\text{Br} \rightarrow \text{Mg}$ bridge to assist the condensation.²



Thus, bis-IDMg's having a central chain of $n=5$, 6 and 7 are used for deoxygenation of isolated azoxybenzene under ordinary (THF 50 ml) and diluted (THF 200 ml) conditions [equation (7)]. The percentage deoxygenation, together with those with the use of *p*-MeO-mono-IDMg for comparison, is given in Table 2.



A similar cooperation appears in run 5 using bis-IDMg having a central chain X of seven atoms ($n=5$): the deoxygenation efficiency is highest at ordinary and lower concentrations, and the ratio of the yields obtained at lower versus ordinary concentrations is also highest when $n=5$. As supported by the molecular model, N^- of one IDMg site and Mg^+ of the other site cooperate in an intramolecular manner via concurrent access to N^+ and O^- , respectively. The favour of the electron-attracting substituent of azoxybenzenes (runs 3 and 4) for deoxygenation is consistent with the results of reaction (5) using *p*-MeO-mono-IDMg.^{4b}

The yield of 4 in reaction (1) with the use of *p*-MeO-mono-IDMg is notably higher^{4b} than that of 4 in reaction (5) with isolated azoxybenzene. This is reasonable because the precursor of 4 formed via the first stage of reaction (1) has '+MgBr bound with azoxy O^- ', acting as the centre to gather excess IDMg molecules,⁶ and favours the second stage. Also in reaction (5), O^- must be bound with Mg^+ of IDMg.

Deoxygenation of azoxybenzene by X_3P reagent [equation (8)]

This reaction was reported previously,⁷ but no substituent effect of azoxybenzene was studied because no

Table 2. Yields of azo products in reaction (7) of bis-IDMg with isolated azoxybenzenes^a

Run No.	IDMg: n	Azoxy ^b		THF (ml)	Yield (%) (azo)	Recovery (%) (azoxy)	$\frac{[\text{Azo}]_{200 \text{ ml}}}{[\text{Azo}]_{50 \text{ ml}}}$
		R ¹	R ²				
1	(<i>p</i> -MeOC ₆ H ₄)	H	H	50	25	52	0.120
2	(<i>p</i> -MeOC ₆ H ₄)	H	H	200	3	97	
3	6	<i>p</i> -Me	<i>p</i> -MeO	50	34	54	—
4	6	<i>p</i> -Cl	<i>p</i> -Cl	50	68	23	
5	5	H	H	50	62	31	0.355
6	5	H	H	200	22	65	
7	6	H	H	50	48	46	0.292
8	6	H	H	200	14	85	
9	7	H	H	50	18	82	0.222
10	7	H	H	200	4	93	

^a IDMg, 4.2 mmol in THF; [IDMg]/[azoxy] = 4.2; reaction temperature = 55 °C for 3 h.

^b Substituents R¹ and R² indicate that close to and remote from azoxy nitrogen, respectively.

simple method for independent preparation of ONN and NNO isomers was known at that time. The deoxygenation of some azoxybenzenes by $(\text{EtO})_3\text{P}$ and $(\text{Me}_2\text{N})_3\text{P}$ was studied [reaction (8)], and the results were compared with previous results for reaction (5) using *p*-MeO-mono-IDMg.

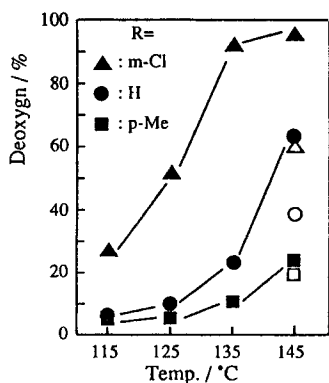
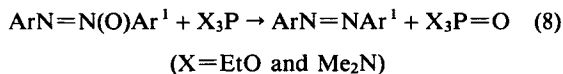


Figure 1. Temperature effect on azoxy deoxygenation of reaction 7 using X_3P . (R: remote from azoxy N^+); Δ , $\circ$, $\square$: by $(\text{EtO})_3\text{P}$; $\blacktriangle$, $\bullet$, $\blacksquare$: by $(\text{Me}_2\text{N})_3\text{P}$

Reaction (8) was carried out by heating a 4 : 1 molar mixture of X_3P and azoxybenzenes for 3 h. The deoxygenation of three substituted (R on Ar) azoxybenzenes by $(\text{Me}_2\text{N})_3\text{P}$ at different temperatures is shown in Figure 1: the weaker nucleophilicity of $(\text{EtO})_3\text{P}$ than that of $(\text{Me}_2\text{N})_3\text{P}^{7c}$ is indicated by three plots. With regard to the effect of azoxy substituent observed by refluxing with $(\text{EtO})_3\text{P}$ depicted in Figure 2, the results of reaction (8) resemble, in spite of the different reaction conditions, those of reaction (5) obtained by heating a 5 : 1 molar mixture of *p*-MeO-mono-IDMg at 55 °C in tetrahydrofuran (THF). Electron-rich azoxybenzenes are sluggishly and electron-deficient azoxybenzenes are easily deoxygenated (see also Figure 1), and the substituent remote from the azoxy nitrogen causes a major effect.

However, a plot of the logarithm of relative reactivity in reaction (8) versus the reciprocal of λ_{max} deviates considerably from the correlation line obtained in reaction 5^{4b} (Figure 3). To explain the deviation, the same trend of substituent effects on π -electron densities on the azoxy nitrogen and oxygen (revealed from the ^{15}N and ^{17}O NMR chemical shifts⁸) and also effects of donation and back-donation of the P(III) atom must be considered, although no UV shift of azoxybenzene on mixing with X_3P was detected at room temperature. In contrast to a clear push-pull cooperation of N^- and Mg^+ proposed for reactions (5) and (7), the fluctuating strength of P—O and P—N bonds (formed in an intermediate with two X_3P molecules) by the azoxy substituents may be reflected in the deviation in reaction (8).

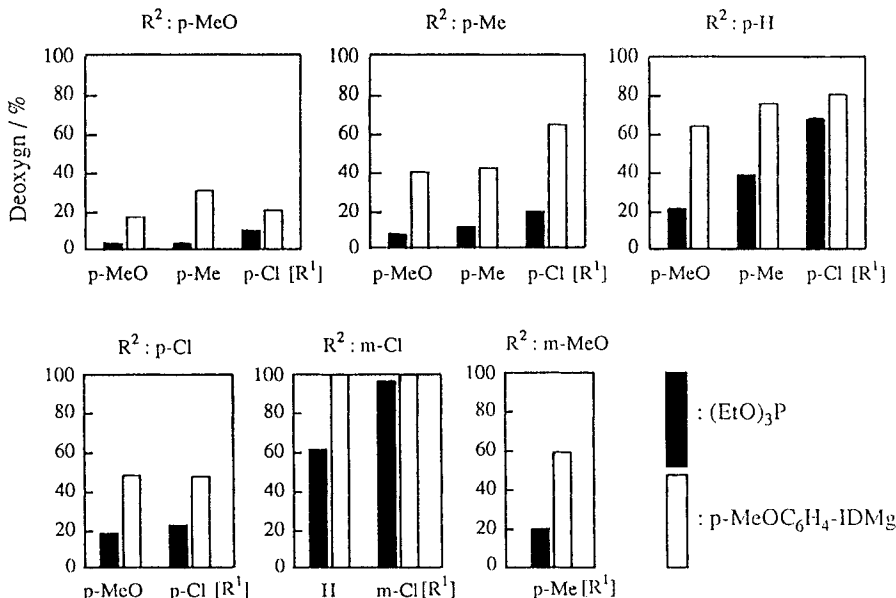


Figure 2. Percentage deoxygenation in reaction 7 using $(\text{EtO})_3\text{P}$ in comparison with that in reaction 5 using IDMg. R^2 indicates substituent remote from azoxy nitrogen

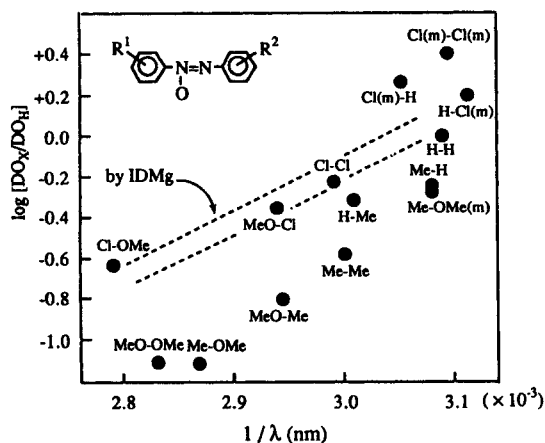


Figure 3. Relative reactivity in deoxygenation by $(\text{EtO})_3\text{P}$ (reaction 8) and $\pi-\pi^*$ transition energy. Dotted lines indicate correlation in reaction 5, and DO_x/DO_H indicates relative values of percentage deoxygenation based on that of unsubstituted azoxybenzene

CONCLUSION

The cooperation of an aggregate excess of IDMg molecules in the condensation reaction (1) was recently proposed,² and a similar cooperation was established in its later deoxygenation stage and also in IDMg treatment of isolated azoxybenzenes. The manifestation of this effect is due to the mildness of IDMg , having a larger E_{ox} implying a 'less reactive, more selective' principle.

The Schlenk equilibrium of Grignard reagents involving aggregation is well known.⁹ However, the role of aggregation in reaction (2) (supposed many years ago¹⁰) has attracted little attention, and was only recently established¹¹ by a precise study of the behaviour of radical intermediates. An aggregate excess of reagent also cooperates in reactions (1)–(4) irrespective of the medium and large ΔE values. This means a 'closed environment' in later stages of the reactions of magnesium reagents distinct from that in the initial stage, and provides an important clue to the validity of the 'simple relationship of ΔE (representing initial conditions) with the final distribution of products.^{1d} In the

Table 3. Melting points and ^1H NMR data for 1–4

Compound No. ^a	M.P., θ_m ($^\circ\text{C}$)	^1H NMR data in CDCl_3 : δ (ppm)
1	147.5–149.5	7.48(2H, d), 6.93(2H, d), 6.84–6.60(3H, m), 3.11(2H, m), 2.77(6H, m), 2.07(4H, m)
2	123.5–125.0	7.30(1H, s), 6.83–6.58(6H, m), 2.78(8H, m), 2.31(2H, m), 1.91(2H, m)
¹³ MeO	120.0–121.0	8.22 and 6.99(4H, ABq, $J = 9.3$ Hz), 7.16(1H, d), 6.86(2H, s), 6.92–6.63(4H, m), 3.86(3H, s), 2.98(2H, m), 2.74 (6H, m), 2.08(2H, m), 1.97(2H, m)
¹³ Me	176.0–178.0	8.03 and 7.30(4H, ABq, $J = 8.3$ Hz), 7.17(1H, d), 6.88(2H, d), 6.78–6.64(4H, m), 2.99(2H, m), 2.75(6H, m), 2.42 (3H, s), 2.10(2H, m), 1.98(2H, m)
¹³ Cl	106.5–107.0	8.06 and 7.46(4H, ABq, $J = 8.8$ Hz), 7.15(1H, d), 6.89(2H, d), 6.91–6.64(4H, m), 2.99(2H, m), 2.78(6H, m), 2.10(2H, m), 1.98(2H, m)
²³ MeO	116.0–117.0	8.33 and 7.04(4H, ABq, $J = 9.3$ Hz), 7.82(1H, s), 6.80(1H, t), 6.67(3H, s), 6.60(2H, d), 3.89(3H, s), 2.85(4H, m), 2.74(4H, m), 2.36(2H, m), 1.92(2H, m)
²³ Me	112.5–113.5	8.14 and 7.35(4H, ABq, $J = 8.3$ Hz), 7.80(1H, s), 6.78(1H, t), 6.68(3H, s), 6.61(2H, d), 2.90–2.71(8H, m), 2.45 (3H, s), 2.42–2.31(2H, m), 1.97–1.82(2H, m)
²³ Cl	128.0–134.0 ^c	8.17 and 7.15(4H, ABq, $J = 9.3$ Hz), 7.72(1H, s), 6.78(1H, t), 6.69(3H, s), 6.61(2H, d), 2.75(8H, m), 2.36(2H, m), 1.94(2H, m)
¹⁴ MeO	87.5–88.5	7.58 and 6.99 (4H, ABq, $J = 9.3$ Hz), 7.18(1H, d), 6.91(2H, d), 6.78–6.54(4H, m), 3.83(3H, s), 3.18(2H, m), 2.74(6H, m), 2.14(2H, m), 2.05(2H, m)
¹⁴ Me	105.0–108.0	7.77 and 7.32(4H, ABq, $J = 8.3$ Hz), 7.18(1H, d), 6.95(2H, d), 6.79–6.55(4H, m), 3.21(2H, m), 2.78(6H, m), 2.44(3H, s), 2.16(4H, m)
¹⁴ Cl	88.0–89.0	7.80 and 7.48(4H, ABq, $J = 8.8$ Hz), 7.19(1H, d), 6.96(2H, s), 6.79–6.54(4H, m), 3.22(2H, m), 2.78(6H, m), 2.15(4H, m)
²⁴ MeO	Oil	8.00 and 7.11(4H, ABq, $J = 8.8$ Hz), 7.15(1H, s), 6.87(1H, m), 6.69(5H, m), 3.93(3H, s), 3.18(2H, m), 2.72(4H, m), 2.54(2H, m), 2.21(2H, m), 1.85(2H, m)
²⁴ Me	Oil	7.91 and 7.41(4H, ABq, $J = 8.3$ Hz), 7.14(1H, s), 6.84(1H, t), 6.69(3H, s), 6.68(2H, s), 3.20(2H, m), 2.72(4H, m), 2.54(2H, m), 2.49(3H, s), 2.21(2H, m), 1.86(2H, m)
²⁴ Cl	— ^b	7.93 and 7.58(4H, ABq, $J = 8.8$ Hz), 7.06–6.46(7H, m), 3.22(2H, m), 2.89(4H, m), 2.55(2H, m), 2.31(2H, m), 1.90(2H, m)

^a Superscripts indicate substrate number and IDMg substituent.

^b Not isolated.

^c Not purified.

high ΔE reaction (4) involving σ -complexation and mild SET, a higher than 3:1 molar ratio is needed; the excess of IDMG is assumed to form a σ -complex with nitrile in an $n:1$ (not 1:1) molar ration and assist SET in an inner-sphere manner.³

Transition metal reagents are frequently used in a catalytic manner owing to their variable valencies. The need for excess moles of magnesium reagents is a disadvantage, but factors revealed including the need for an excess are essential for small-sized Mg^{2+} having a strong polarizing ability and fixed valency. On this basis, the variety in the reaction modes of N -Mg reagents and the simple structure–reactivity relationship in terms of ΔE will contribute to the practical use of safe and inexpensive magnesium.

EXPERIMENTAL

Materials. [3.3]MCP was obtained by reported procedures,¹² and the nitro[3.3]MCPs were prepared by nitration with benzoyl nitrate.¹³ Treatment of MCP with a 1.2 molar amount of the nitrate in acetonitrile at room temperature for 40 min gave a mixture including **1** (26%), **2** (12%), unreacted MCP (55%) and no dinitro product. After chromatographic separation, the recovered MCP was used for repeated preparation. Isolated **1** and **2** were collected and purified by recrystallization.

Of the X_3P reagents, $(\text{EtO})_3\text{P}$ was obtained commercially and $(\text{Me}_2\text{N})_3\text{P}$ was prepared according to reported procedures.¹⁴ The bis-IDMGs were prepared by treatment of the corresponding bis-anilines with a four molar amount of EtMgBr in THF. Bis-anilines were obtained by the zinc dust reduction of the corresponding bis-nitrophenyl compounds, which were prepared from p -nitrophenolate and α,ω -dibromoalkanes.² Unsubstituted azoxybenzene was obtained commercially and the substituted azoxybenzenes were prepared according to the reported procedure of reaction (1).^{4b} The reduction potentials of nitro substrates were determined by cyclic voltammetry in $\text{THF}-\text{Bu}_4\text{NClO}_4$.^{1b}

Procedures and products. The IDMG reactions were carried out according to reported procedures,^{4a} and the azoxy and azo products were separated chromatographically and identified by of ^1H NMR spectrometry. Melting points and NMR data for the nitro[3.3]MCPs and the products derived from them are summarized in Table 3. Data for other azoxy and azo products have been reported.⁴

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