

REACTIONS OF IMINODIMAGNESIUM REAGENTS WITH 1,4-QUINONES: THEIR STRUCTURAL FACTORS GOVERNING THE MODES OF REACTIONS*

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Reactions of benzo-, naphtho- and anthraquinone derivatives (unsubstituted and substituted) with arylimino-dimagnesium $[\text{ArN}(\text{MgBr})_2]$ and aryloxymagnesium of a weak electron-donating ability were studied. In addition to the reduction products (quinhydrones and hydroquinones), nuclear substitution and condensation

(with >C=O)

products were formed. The efficiency of single electron transfer (SET) from $\text{ArN}(\text{MgBr})_2$, evaluated by the relative values of the difference between the oxidation and reduction potentials of the reactants ($\Delta E = E_{\text{ox}} - E_{\text{red}}$), varies with the electron-accepting power of quinones. ΔE governs the modes of semiquinone appearance (ESR signals) and the relative amounts of the heat of reactions, reflecting the types and yields of the products. It is concluded that condensation products of both components are produced in the reactions of quinones with the lower SET efficiency by the presence of a fused benzene ring or MeO substituent. The structure–reactivity relationship proposed previously for reactions of various magnesium reagents is extended in the reactions with a variety of quinones even in cases of higher SET efficiency.

INTRODUCTION

Some quinones have strong electron-accepting ability (EAA; small negative E_{red} value); some acting as oxidizing agents. Because of this nature, the reaction with Grignard reagents often leads to their quinhydrones and hydroquinones, recognized as typical ‘abnormal’ products via single electron transfer (SET) from Grignard reagents (RMgBr) depending on the individual electron-donating ability (EDA) of RMgBr . The weak EDA (large positive E_{ox} value) of aryliminodimagnesium $[\text{ArN}(\text{MgBr})_2]$, IDMg, would be profitable for investigating the factors governing of IDMg reactions with various substrates. Thus, a structure–reactivity relationship for reactions of all types of magnesium reagents could be proposed by using the difference (ΔE) between E_{ox} and E_{red} of the respective reactants.^{1–4} The types and relative yields of products are systematically related to ΔE values.

RESULTS AND DISCUSSION

The abbreviations of the quinones and IDMg-type reagents and the E_{red} and E_{ox} values, including those previously determined,^{5a} are given in Scheme 1: smaller negative and positive values indicate stronger EAA and EDA, respectively. A smaller ΔE leads to the hydroquinones (Hq) and/or decomposition product (Dc) whereas a larger ΔE leads to the products of nuclear substitution, replacement and condensation

with >C=O .

Smaller ΔE values of all the present reactions are in a narrower range (1.67–2.56 V; see Scheme 1 and Figure 1) in comparison with that (2.17–3.14 V) of IDMg reactions with nitrobenzenes,^{5a} but are related to structural features of individual reactants.

* Aryliminodimagnesium Reagents. Part XXVI. For Part XXV, see M. Okubo, Y. Inatomi, I. Eguchi, H. Nishida, S. Gotoh and K. Matsuo, *J. Phys. Org. Chem.* 7, 18 (1994).

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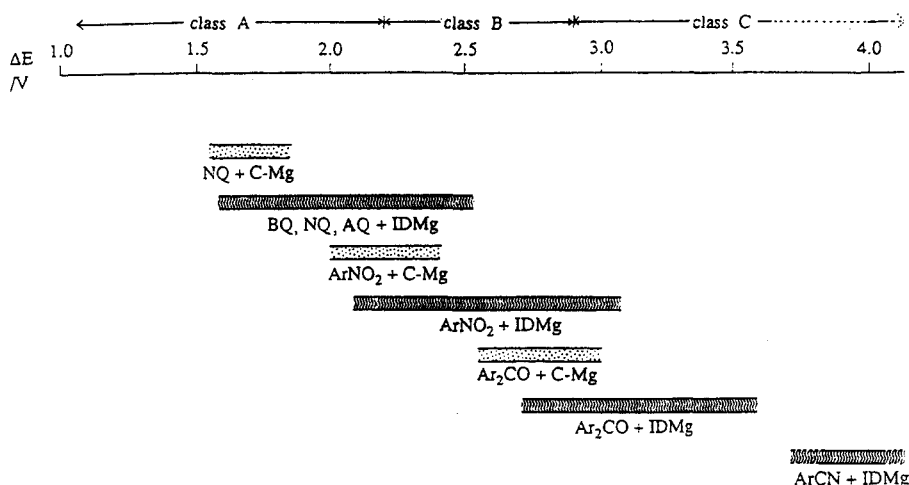
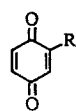


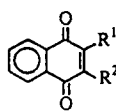
Figure 1. Ranges of ΔE values for combinations of C-Mg and N-Mg reagents with typical substrates

Quinones (E_{red} / V)

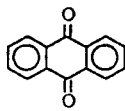
strong $\xleftarrow{\text{EAA}}$ weak



BQ: R=H
(-0.753)



MeNQ: R¹=Me, R²=H
(-0.935)



AQ
(-1.074)

MeBQ: R=Me
(-0.787)

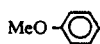
MeONQ: R¹=MeO, R²=H
(-0.957)

MeOBQ: R=MeO
(-0.784)

DMeONQ: R¹=R²=MeO
(-0.940)

Ar-IDMg (E_{ox} / V)

strong $\xleftarrow{\text{EDA}}$ weak



MeO
(0.912)



Me
(0.941)



F
(1.056)



Py
(1.295)



Cl
(1.485)

Scheme 1

Semiquinone radicals: modes of appearance related to ΔE

The SET from IDMg to quinones was confirmed. ESR spectra of the navy-blue semiquinone radicals of NQ and MeONQ, observed just after mixing with IDMg,

are shown in Figure 2(a) and (b), respectively, the spectra being simulated using the reported splitting constants.⁶ The hyperfine structures deteriorate in 10–60 min with an accompanying colour change to dark green, and the signals are weakened. In the case of AQ, the colour change was similar but with a weaker and poorly resolved ESR signal. In the case of BQ, neither the colour change nor an ESR signal was observable.

By assigning the navy-blue radical to the paramagnetic monomer and the green radical to the diamagnetic dimer,⁷ the ESR results are related to ΔE . No semiquinone radical of BQ was observable because the Mg salt of Hq was rapidly formed. The semiquinone monomer of NQ is generated at a higher rate than in succeeding processes. The monomeric semiquinone of AQ is slowly generated and rapidly aggregates with neutral AQ. The arylaminyl radical expected to be generated from IDMg is not observed, probably owing to transformation into a diamagnetic dimer similar to the reactions of Ar₂CO with ArMgBr⁷ (partly giving Ar₂) and Ar¹NO₂ with IDMg (partly giving ArN=NAr)^{5b} in cases of medium ΔE .

Types and yields of products in IDMg reactions

The types of products in reaction with excess IDMg are given in Scheme 2. A simple condensation product (1) is obtained in low yield in the cases of BQs and NQs and in fair yield in the case of AQ. A nuclear substitution product (2) is formed from BQs and NQs, and a replacement product (4) is formed from MeONQ. Replacement condensation products (5 and 6) from MeONQ and substitution-condensation products (3 and 7) from MeNQ are obtained. A phenazine (7) (see

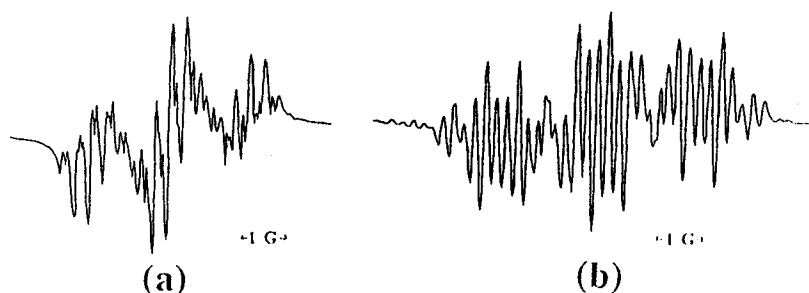


Figure 2. ESR spectra observed in IDMg reacts with (a) NQ and (b) MeONQ

Table 1. Yields of products

Run no. ^a	Quinones	IDMg	Molar ratio	Yield (%)						Hq + Dc (%) ^k	Recovery (%)
				1	2	3 + 7(7)	4	5 + 6(6)	9		
1	MeBQ	Py	4:0	—	10	—	—	—	— ⁱ	+++	—
2	MeBQ	Cl	4:0	—	9	—	—	—	6	67	—
3	MeOBQ	Cl	4:0	5	10	—	—	—	24	68	—
4 ^c	MeOBQ	Cl	2:0	3	19	—	—	—	15	32	—
5 ^d	MeOBQ	Cl	2:0	—	28	—	—	—	20	47	—
6	MeNQ	MeO	4:0	—	21	6	—	—	10	+++	42
7	MeNQ	Me	4:0	—	16	25(13)	—	—	9	+	36
8	MeNQ	F	4:0	—	13	11	—	—	4	++	24
9	MeNQ	Py	4:0	2	25	—	—	—	— ⁱ	+	39
10 ^b	MeNQ	Py	4:0	2	20	—	—	—	— ⁱ	+	26
11	MeNQ	Py	8:0	3	23	—	—	—	— ⁱ	+	22
12 ^c	MeNQ	Py	8:0	6	19	—	—	—	— ⁱ	++	15
13	MeNQ	Cl	4:0	5	9	24(10)	—	—	11	+	51
14	MeONQ	MeO	4:0	—	6	—	14	21	18	+++	42
15 ^b	MeONQ	MeO	1:4	2	10	—	27	—	23	+	51
16	MeONQ	F	4:0	—	4	—	51	26(6)	18	+	Trace
17	MeONQ	F	4:0	—	12	7	20	18	20	+	25
18	MeONQ	Py	4:0	—	—	—	31	30	— ⁱ	+	12
19 ^f	MeONQ	Py	4:0	—	—	—	44	2	— ⁱ	+	46
20	MeONQ	Py	8:0	—	2	—	28	50	— ⁱ	+	11
21	MeONQ	Cl	4:0	—	8	—	50	34	12	—	—
22 ^f	MeONQ	Cl	4:0	—	21	—	25	1	31	—	47
23	AQ	MeO	4:0	22	—	—	—	—	12	—	57
24 ^{s,h}	AQ	MeO	8:0	41 ^j	—	—	—	—	— ⁱ	—	23
25	AQ	Me	4:0	23	—	—	—	—	4	—	66
26 ^{s,h}	AQ	Me	8:0	68	—	—	—	—	— ⁱ	—	Yes
27	AQ	F	4:0	Trace	—	—	—	—	Trace	—	91
28	AQ	Py	4:0	—	—	—	No SET	—	—	—	—

Reaction conditions are tabulated below: ^atypical (omitted from the table); ^{b-s}modified. N indicates normal addition of quinones to IDMg solution and R indicates reverse addition of IDMg to quinone solution.

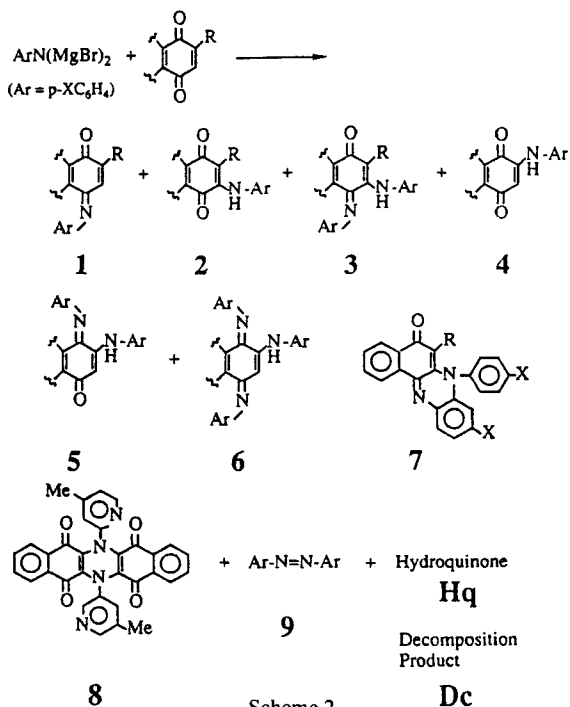
	-40 °C	-20 °C	0 °C	Room temp.	55 °C
^a	—	—	N, and 1 h	1 h	0.5 h
^b	—	—	R for 1 h, and 1 h	1 h	0.5 h
^c	—	N, and 1 h	1 h	1 h	—
^d	N, and 2 h	—	—	—	—
^e	—	—	—	—	3 h
^f	—	—	N, and 1 h	1 h	—
^g	—	—	N	—	6 h

^h Previously reported.

ⁱ Undetermined.

^j Quinone diimine.

^k Definite number indicates yield of Hq, and the number of plus signs indicates relative amount of Dc.



Experimental), an abnormal dimeric product (8) and a symmetrical azobenzene (9) are also obtained.

From the yields of 1–7, 9 and Hq together with unidentified decomposition product (Dc) and the recovered amount of quinones (Table 1 and Figure 3), seven features (see below) are derived.

(1) MeONQ gave better overall yields (runs 6–13, Figure 3) than those from MeNQ (runs 14–22), regardless of the EDA of IDMgs.

(2) Instead of 1, 2 (and 3 + 7) was formed from MeNQ (runs 6–13) and 2 and 4 (and 5 + 6) were formed from MeONQ in fair yields (runs 14–22), formation of 4 being more favoured.

(3) From MeONQ with use of Py and Cl, the combined yield of 5 + 6 in runs 19 and 22 is lower than that in runs 18 and 21, respectively. Without heating, the condensation was depressed.

(4) The overall and individual yields were better from Me than those from MeO, and from Cl than those from F (Figure 3).

(5) BQs led mainly to Hq formation without recovery (runs 1–5). Condensation and replacement were negligible, while substitution from MeOBQ was appreciable.

(6) AQ gave 1 (runs 23–28; without Hq, Dc or other product) sluggishly by use of 4.0 mol of MeO and Me. The yield was improved by longer heating with large excess (8.0 mol) of reagent.^{2c}

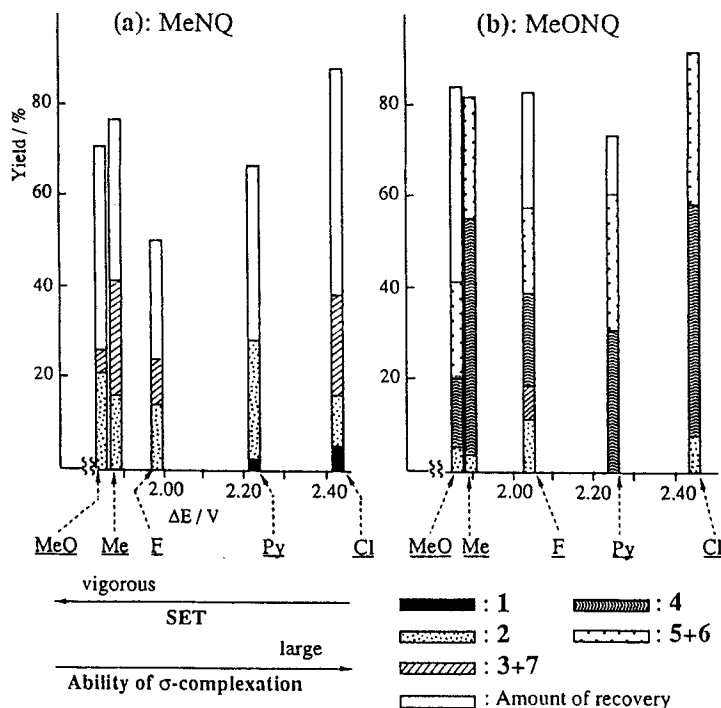
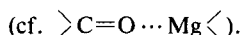


Figure 3. Structural effects of IDMg reagents on relative yields of 1–7 in the reaction with NQs under fixed conditions: (a) with MeNQ (Table 1, runs 6, 7, 8, 9 and 13); (b) with MeONQ (Table 1, runs 14, 16, 17, 18 and 21).

(7) Formation of **9** was notable in reactions of MeOBQ and MeONQ, and was negligible in that of AQ.

Structural factors governing product distribution in the reactions with IDMg and O-Mg reagents

In IDMg reactions of nitro, carbonyl and cyano substrates, the correlation of ΔE with the final distribution of products (ΔE -approach) has been examined in detail, and two common characters A and B were given.^{3c,5b,7} Character A, indicating 'an environmental vicinity of reagents in later stage' irrespective of small or large ΔE , is deduced from the need for an excess amount of reagent which forms an assembly with intermediate radicals to assist the step of their migration-forming products (this character gives a clue to the validity of the ΔE -approach). Character B is that the σ -complexation



participating more strongly as the ΔE value increases (Figure 4), is responsible for addition and/or condensation reaction. As explained in the following, Characters A and B are also useful for understanding the above features (1)–(7).

IDMg and a variety of quinones

The role of σ -complexation (Character B) is indicated by feature (1). Since the EAAs of MeONQ and MeNQ are comparable, the better yield from the former is attributable to σ -complexation [Scheme 3(a)] favoured by the electron-repelling MeO group. Its replacement is

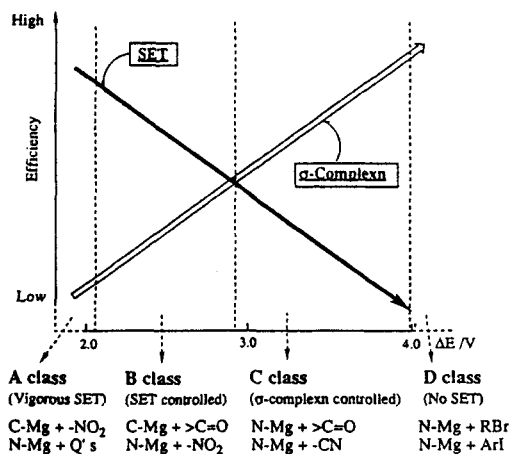
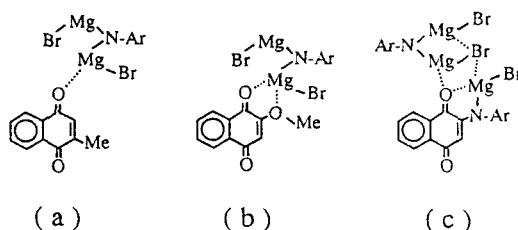


Figure 4. Illustration: relative degree in participation of SET efficiency and σ -complexation for the C-Mg and N-Mg reactions reported previously (reagents and substrates are abbreviated)



Scheme 3. σ -Complexation in IDMg reaction with 1,4-quinones: (a) simple quinone; (b) MeO-substituted quinone; (c) ArN(MgBr)-substituted quinone as the precursor of **2–7**

preferred by a chelate-like state [Scheme 3(b)], which is supported by the formation of an adduct with MgBr_2 (in Et_2O) from MeONQ (not formed from MeNQ).^{5b}

The precedence of substitution⁸ or MeO replacement^{1c} over the condensation of



with IDMg is indicated by features (2) and (3). Excess IDMg is gathered around the introduced ArN(MgBr) group [Scheme 3(c)] to assist condensation with the neighbouring



This evokes the role of the *o*-OMgBr group generated from *o*-hydroxynitrobenzene^{1c} to assist IDMg condensation with the neighbouring NO_2 , and implies the role of the aggregated excess IDMg (Character A). The E_{red} values of precursors [having ArN(MgBr)] of **2** and **4** are undetermined, but the difference from those of isolated **2** and **4** (Table 2) seems not great enough to give an appreciable effect on the combined yields of **3** + **7** and/or **5** + **6** (Table 1). Nuclear substitution, taking place on Grignard treatment of Ar¹NO₂ (small ΔE), has been reported.⁹

The structural effects of IDMs on the yields of **1–7** from NQs are indicated by feature (4), reflecting the relative EDA ($\text{MeO} > \text{Me}$ and $\text{F} > \text{Cl}$) accompanied by the relative strength of the positive charge on the Mg

Table 2. E_{red} values of **2** and **4** derived from NQs and difference in the values from those of parent quinones

Parent quinone	IDMg	Product	E_{red} (V)	Difference (V)
MeONQ	Me	4	–1.030	0.073
MeNQ	Me	2	–1.100	0.165
MeONQ	Py	4	–0.966	0.009
MeNQ	Py	2	–0.950	0.015
MeONQ	Cl	4	–0.890	–0.067
MeNQ	Cl	2	–0.928	–0.007

atom ($\text{MeO} < \text{Me}$ and $\text{F} < \text{Cl}$). The charge strength is related to the tightness in σ -complexation (Character B and Figure 4) shown by the highest yield from Cl (the strongest charge among five IDMgs) and by the second highest yield from Me. The MeO having a strong EDA and weakest charge is least favourable for condensation with electron-deficient



The abnormal nature of Py is described later.

The distinct behaviours of BQ and AQ due to small and large ΔE s, respectively, are demonstrated by features (5) and (6). Feature (5) reflects the 'very efficient SET' due to the small ΔE without participation of σ -complexation (Figure 4), while feature (6) implies 'mild SET inside σ -complex' (Character B; see IDMg reactions of benzophenone^{2d} and benzonitrile^{3c}). Obviously, the fused benzene ring acts as the electron supply favouring σ -complexation to lead to condensation. Owing to the much large ΔE , AQ is inert toward weak Py and Cl (runs 27 and 28).

The relative ease in oxidative self-coupling of IDMg is indicated by feature (7). As proposed previously,^{1f,5c} the reactants of small ΔE 'pre-interact to cause dynamic self-aggregation of reagent molecules' (Character A), favouring the formation of 9. The aggregation of IDMg is preferred by the adjacent



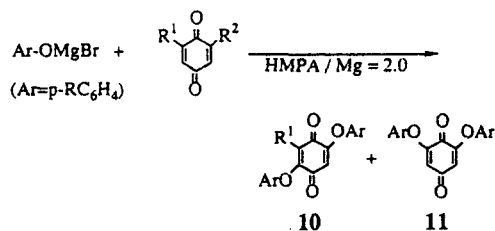
and MeO groups of MeOBQ and MeONQ [cf. Scheme 3(b) and (c)]. The yield of 9 is also higher in reactions of *o*-methoxy- and *o*-halonitrobenzenes.^{1c}

O-Mg with a BQ of strong EAA

The ArOMgBr (O-Mg reagents) having the weakest EDA are incapable of SET toward most of the ketones and nitroarenes so far examined for IDMg reactions. The large positive E_{ox} values of O-Mgs (located at the outside of the potential window of the Bu_4NClO_4 -THF system; see Experimental) were undetermined, but the relative order of the EDA of *p*- $\text{RC}_6\text{H}_4\text{OMgBr}$ ($\text{R}: \text{MeO} > \text{Me} > \text{Cl}$) was determined from the relative velocity in the generation of the semiquinone radical of 2,6- Cl_2 -BQ having a much stronger EAA ($E_{\text{red}} = -0.443 \text{ V}$).^{5a}

In contrast to exclusive Hq (or Dc) formation on IDMg treatment of the cited BQ, treatment with *p*- $\text{RC}_6\text{H}_4\text{OMgBr}$ having two moles of hexamethylphosphoramide [HMPA; tightly coordinating on Mg instead of THF (strong coordination of HMPA is expected from the largest donor number¹⁰)] leads to substitution and replacement products (10 and 11, Table 3). Replacement of the Cl substituent evokes the $\text{S}_{\text{N}}\text{Ar}$ reaction of strongly electron-accepting 2,4-dinitrochlorobenzene,¹¹ but the highest combined yield from *p*- $\text{ClC}_6\text{H}_4\text{OMgBr}$ implies the role of a strong posi-

Table 3. Yields of products in reactions of O-Mg reagents with BQs in the presence of HMPA^a



Run no.	R	R ¹ (E_{red}/V)	R ²	Reaction temperature (°C)	Yield (%)	
					10	11
1	MeO			55	—	13
2	MeO			r.t. ^b	—	7
3	Me	Cl	Cl	55	6	11
4	Me	(-0.443)		r.t.	2	2
5	Cl			55	13	81
6	Cl			r.t.	1	10

^a Reagent/BQ = 2.0; reaction time, 1 h. No quinones were recovered.

^b Room temperature.

tive charge on Mg atom favouring σ -complexation^{3b,12} (Character B). The result gives a rough estimate of ΔE of ca 3.7 V for this reaction and E_{ox} ca 2.7 V for *p*- $\text{ClC}_6\text{H}_4\text{OMgBr}$, the latter being larger by more than 1.0 V than E_{ox} of *p*- ClC_6H_4 -IDMg (Scheme 1).

Without HMPA, the O-Mg treatment led to Hq in a small amount. The effect of HMPA promoting the chemical combination of components resembles the IDMg reaction of nitrobenzene, leading to an increase in azoxy yield.^{5c} When the IDMg reaction in run 6 (Table 1) is carried out in the presence of HMPA, the yield of 2 increases by 15%, accompanied by a slight decrease in the yield (3%) of 3 and recovery of MeNQ. Probably, tightly coordinating HMPA facilitates the reagent with a 3d orbital electronic field feasible for the radical migration to give the product.^{3c,5c}

Relative amounts of heat of reaction

The relative amounts of heat (ΔH) evolved by mixing the reactants in 1:1 molar ratio were obtained from temperature-time plots by means of a simple batch method.^{5b} Figure 5 shows the plots obtained by mixing Py with six quinones and Me with four quinones. Similar plots were obtained with the use of MeO, F and Cl. In Table 4, the dimensionless ΔH values, linear to the highest temperature (ΔT_{max}), and ΔE values are summarized.^{5b} By comparing the combinations of weaker electron-donating Py and Cl with MeBQ to those of stronger electron-donating MeO and Me with NQs, it is clear that a large ΔH reflects efficient SET^{5b}

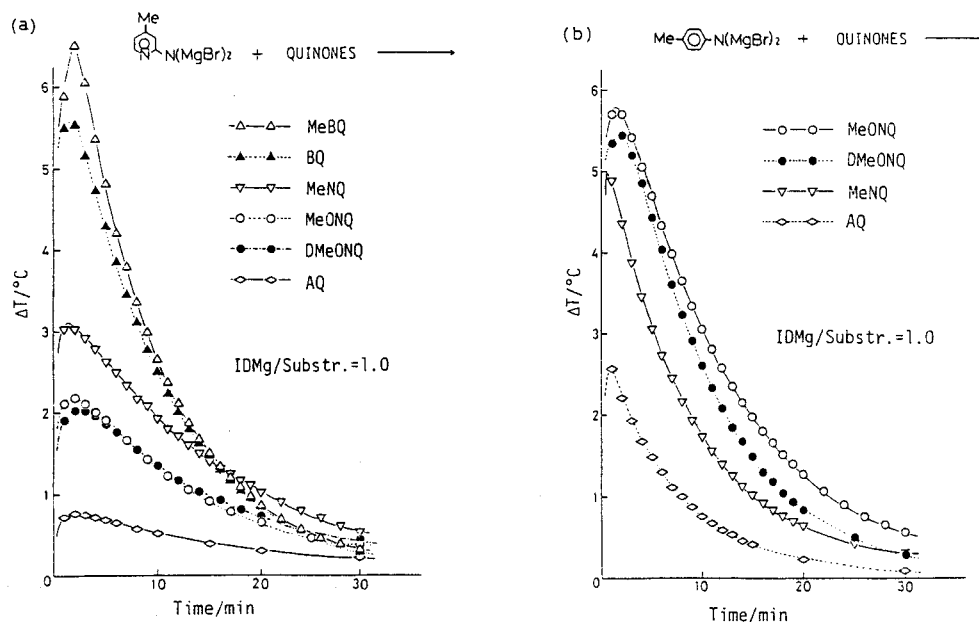


Figure 5. Temperature-time plots obtained in IDMg reaction with quinones: (a) reagent Py with six quinones; (b) reagent Me with four quinones

Table 4. ΔE , $\Delta T_{\max}$ and ΔH values of individual reactions

Quinone	IDMg	ΔE (V)	ΔH	$\Delta T_{\max}$ ($^{\circ}\text{C}$)
MeBQ	<u>Py</u>	2.08	6.0	6.5
MeBQ	<u>Cl</u>	2.27	6.2	5.3
MeNQ	<u>MeO</u>	1.85	6.3	6.2
MeNQ	<u>Me</u>	1.88	4.1	5.0
MeNQ	<u>F</u>	1.99	2.5	1.9
MeNQ	<u>Py</u>	2.23	4.2	3.0
MeNQ	<u>Cl</u>	2.42	2.3	1.8
MeONQ	<u>MeO</u>	1.87	6.2	6.4
MeONQ	<u>Me</u>	1.90	6.5	5.8
MeONQ	<u>F</u>	2.01	5.4	5.4
MeONQ	<u>Py</u>	2.25	2.9	2.2
MeONQ	<u>Cl</u>	2.44	4.0	3.4
AQ	<u>MeO</u>	1.99	2.5	3.0
AQ	<u>Me</u>	2.02	1.9	2.6
AQ	<u>F</u>	2.13	0.9	1.1
AQ	<u>Py</u>	2.37	1.2	0.7
AQ	<u>Cl</u>	2.56	0.7	0.7

(small ΔE). In the combinations of F, Py and Cl, the slightly larger ΔH from MeONQ than that from MeNQ reflects the participation of MeO oxygen (and/or pyridyl nitrogen; see below) for complexation. The results support the above discussion. The structural effect of diphenyl diketone (benzil), favouring chelation (very tight complexation; Character B) for IDMg condensation, was supported by heat measurements.^{5b}

CONCLUSION

Owing to the use of IDMg and O-Mg having mild EDA ('less reactive, more selective'), the validity of Characters A and B, i.e. aggregation and SET, is established even in the present reactions of small ΔE (Figure 1). The common behaviours displayed in reactions of magnesium reagents are based on the EDA order ($\text{C-Mg} > \text{N-Mg} > \text{O-Mg}$), reflecting simple electronegativity of the adjacent atoms. The specific natures of the heteroatoms (usually recognized when they are bound with carbon atoms) are reduced owing to the 'strong polarizing ability' Mg^{2+} arising from its small size and double charge.

REMARKS

Unified view of reactions of carbonyl compounds

Structural requirements for IDMg condensation with all types of carbonyl substrates are illustrated in Figure 6, implying that the reaction mode depends on two functions: (a) electron acceptance and (b) σ -complexation. For 1,4-quinones having two



groups fixed in opposite directions, function (b) is usually reduced by a small ΔE and function (a) participates exclusively. However, as Figure 6 illustrates, function (b) operates with the assistance of electron

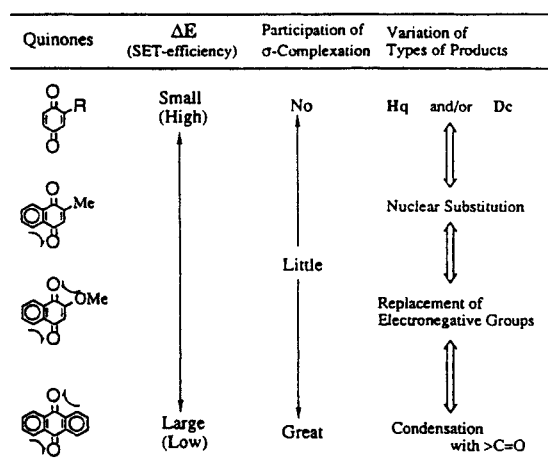


Figure 6. Illustration: structural requirement of quinones and modes of reactions. Curved arrows indicate the role of groups as electron supply favouring σ -complexation

supply (fused benzene ring and MeO group; Character B) and also the previously introduced $\text{ArN}(\text{MgBr})$ group (Character A). For diary ketones (weak EAA^{2d}), function (b) strongly participates to lead to condensation. For benzils (medium $\text{EAA}^{5b,5c}$), strong participation of (b) (tight chelation with Mg atom) overcomes that of (a) to tend to condensation.

Abnormal IDMG and quinones

The effect of the weak EDA of Py (Scheme 1) observed in reaction of nitrobenzene has been reported,¹³ but the effect on the reaction of NQs shows some anomaly in the relative yields of products. Condensation is preceded by replacement but not by substitution [cf. features (1)–(3)] as given in the product yields from MeONQ (Table 1, runs 18 and 20; cf. 14, 16, 17 and 21) and those from MeNQ (runs 9–12; cf. 6–8 and 13). The anomaly is not simply related to the smaller E_{red} of 2 and 4 (having an electron-deficient pyridylaminyl group) than those of parent NQs (Table 2), and may be

Table 5. Melting points and ^1H NMR data of products

Product			
No. ^a	Parent quinone	M.p. ($^{\circ}\text{C}$)	δ (ppm)
2 ^{Py}	MeBQ	150 ^b	8.21 (1H, d), 7.70 (1H, s), 6.78 (1H, d), 6.75 (1H, s), 2.34 (3H, s), 2.17 (3H, s)
2 ^{Cl}	MeBQ	—	7.18–7.02 (7H, m), 6.52 (1H, s), 6.07 (1H, s)
1 ^{Cl}	MeOBQ	—	7.36 and 7.15 (4H, ABq, $J = 8.5$ Hz), 6.04 (1H, d), 5.84 (1H, d), 3.83 (3H, s)
2 ^{Cl}	MeOBQ	—	7.54 (1H, s), 7.36 and 7.15 (4H, ABq, $J = 8.5$ Hz), 5.86 (1H, s), 3.87 (3H, s)
1 ^{Py}	MeNQ	—	8.50–8.35 (2H, m), 8.20–8.14 (1H, m), 7.75–7.62 (2H, m), 7.06 (1H, m), 6.96 (1H, d), 6.86 (1H, s), 2.42 (3H, s), 2.09 (3H, s)
1 ^{Cl}	MeNQ	—	8.43–8.39 (1H, m), 8.19–8.16 (1H, m), 7.73–7.62 (2H, m), 7.38 and 6.84 (4H, ABq, $J = 8.1$ Hz)
2 ^{MeO}	MeNQ	177.5–178.0	8.12–8.04 (2H, m), 7.74–7.60 (2H, m), 7.36 (1H, s) 6.97 6.86 (4H, ABq, $J = 8.6$ Hz), 3.81 (3H, s), 1.70 (3H, s)
2 ^{Me}	MeNQ	143.5–144.5	8.13–8.07 (2H, m), 7.75–7.62 (2H, m), 7.37 (1H, s), 2.34 (3H, s), 1.74 (3H, s)
2 ^F	MeNQ	171.5–172.0	8.17–8.07 (2H, m), 7.78–7.62 (2H, m), 7.33 (1H, s), 7.08–6.95 (4H, m), 1.75 (3H, s)
2 ^{Py}	MeNQ	160 ^b	8.18–8.07 (3H, m), 7.76–7.63 (2H, m), 7.57 (1H, s), 6.77 (1H, d), 6.55 (1H, s), 2.33 (3H, s), 1.96 (3H, s)
2 ^{Cl}	MeNQ	189.0–191.0	8.14–8.07 (2H, m), 7.74–7.66 (2H, m), 7.32–7.26 (3H, m), 6.90 (2H, d), 1.76 (3H, s)
3 ^{MeO}	MeNQ	—	8.17–8.15 (2H, m), 7.48–7.41 (1H, t), 7.20–7.14 (2H, m), 7.00–6.82 (8H, m), 3.85 (3H, s), 3.50 (3H, s), 1.76 (3H, s)
3 ^{Me}	MeNQ	134.5–136.5	8.18–8.15 (1H, m), 7.48–7.41 (1H, m), 7.20–7.10 (6H, m), 6.90 (2H, d), 6.76 (2H, d), 2.39 (3H, s), 2.33 (3H, s), 1.79 (3H, s)
3 ^F	MeNQ	272.0–273.0	8.83–8.80 (1H, m), 8.33–8.26 (1H, m), 7.92–7.86 (1H, m), 7.76–7.65 (2H, m), 7.46–7.37 (5H, m), 7.03–6.96 (1H, m), 6.52–6.48 (1H, m), 1.51 (3H, s)
3 ^{Cl}	MeNQ	213.3–214.1	8.17 (1H, d), 8.03 (1H, s), 7.50 (1H, t), 7.39–7.15 (6H, m), 6.91 (2H, d), 6.6.82 (2H, d), 1.81 (3H, s)
7 ^{Me}	MeNQ	206.5–208.0	8.91–8.88 (1H, m), 8.37–8.34 (1H, m), 7.83 (1H, d), 7.77–7.69 (2H, m), 7.38–7.26 (5H, m), 7.12 (1H, d), 6.71 (1H, s), 2.50 (3H, s), 2.33 (3H, s), 1.54 (3H, s)
7 ^{Cl}	MeNQ	225.5–227.0	8.87–8.83 (1H, m), 8.35–8.32 (1H, m), 7.86 (1H, d), 7.79–7.72 (2H, m), 7.60 and 7.38 (4H, ABq, $J = 8.5$ Hz), 7.28–7.24 (1H, m), 6.85 (1H, s), 1.55 (3H, s)

continued

Table 5. (Continued)

Product			
No. ^a	Parent quinone	M.p. (°C)	δ (ppm)
1 ^{MeO}	MeONQ	—	7.95–7.90 (2H, m), 7.77–7.68 (2H, m), 7.35 and 7.02 (4H, ABq, $J = 8.5$ Hz), 6.17 (1H, s), 3.84 (3H, s), 3.73 (3H, s)
2 ^{MeO}	MeONQ	—	8.10–8.02 (2H, m), 7.75–7.59 (2H, m), 7.51 (1H, s) 7.07 and 6.86 (4H, ABq, $J = 9.2$ Hz), 3.82 (3H, s), 3.44 (3H, s)
2 ^{Me}	MeONQ	—	8.11–8.03 (2H, m), 7.78–7.62 (2H, m), 7.50 (1H, s), 7.10 and 6.96 (4H, ABq, $J = 8.6$ Hz), 3.50 (3H, s), 2.34 (3H, s)
2 ^F	MeONQ	122.0–123.0	8.14–8.02 (2H, m), 7.80–7.61 (2H, m), 7.48 (1H, s), 7.20–6.98 (4H, m) 3.54 (3H, s)
2 ^{Py}	MeONQ	~130 ^c	8.17–8.06 (3H, m) 7.76–7.65 (2H, m), 7.45 (1H, s), 6.80 (1H, d), 6.63 (1H, s), 3.75 (3H, s), 2.34 (3H, s)
2 ^{Cl}	MeONQ	—	8.12–8.04 (2H, m), 7.76–7.62 (2H, m), 7.26 and 6.98 (4H, ABq, $J = 8.6$ Hz), 7.14 (1H, s), 3.56 (3H, s)
3 ^F	MeONQ	—	8.20–8.15 (1H, m), 7.82 (1H, s), 7.55–7.47 (1H, m), 7.20–6.80 (10H, m), 3.50 (3H, s)
4 ^{MeO}	MeONQ	155.5–157.0	8.90 (2H, d), 7.75–7.64 (2H, m), 7.46 (1H, s), 7.19 and 6.94 (4H, ABq, $J = 6.7$ Hz), 3.83 (3H, s)
4 ^{Me}	MeONQ	205.5–206.0	8.14–8.09 (2H, m), 7.79–7.64 (2H, m), 7.52 (1H, s), 7.22 and 7.16 (4H, ABq, $J = 8.5$ Hz), 2.37 (3H, s)
4 ^F	MeONQ	248.5–249.0	8.14–8.10 (2H, m), 7.80–7.68 (2H, m), 7.42 (1H, s), 7.30–6.98 (4H, M), 6.27 (1H, s)
4 ^{Py}	MeONQ	243.0–244.0	8.26 (1H, d), 8.12 (2H, d), 7.99 (1H, s), 7.93 (1H, s), 7.79–7.65 (2H, m), 6.83 (2H, s), 2.36 (3H, s)
4 ^{Cl}	MeONQ	265.5–266.5	8.15–8.10 (2H, m), 7.81–7.65 (2H, m), 7.52 (1H, s), 7.40 and 7.25 (4H, ABq, $J = 9.2$ Hz), 6.37 (1H, s)
5 ^{MeO}	MeONQ	—	8.14–8.10 (2H, m), 7.42 (1H, t), 7.26–7.12 (4H, m), 6.95–6.81 (6H, m), 6.11 (1H, s), 3.82 (3H, s), 3.80 (3H, s)
5 ^{Me}	MeONQ	165.0–166.0	8.16–8.11 (2H, m), 7.44 (1H, s), 7.21–7.12 (8H, m), 6.77 (2H, d), 6.25 (1H, s), 2.40 (3H, s), 2.36 (3H, s)
5 ^F	MeONQ	155.0–156.0	8.17–8.11 (2H, m), 7.52–7.46 (1H, m), 7.30–7.18 (8H, m), 6.90–6.85 (2H, m), 6.16 (1H, s)
5 ^{Py}	MeONQ	~165 ^b	8.74 (1H, s), 8.412 (1H, s), 8.26 (1H, d), 8.19 (1H, d), 7.94 (1H, s), 7.52 (1H, t), 7.22 (1H, t), 6.99 (1H, d), 6.97–6.79 (3H, m), 6.64 (1H, s), 2.37 (3H, s), 2.33 (sH, s)
5 ^{Cl}	MeONQ	187.5–188.5	8.18–8.08 (2H, m), 7.54–7.17 (9H, m), 6.85 (2H, d), 6.23 (1H, s)
6 ^{Me}	MeONQ	184.5–185.0	8.16 (2H, d), 8.02 (1H, s), 7.43 (1H, t), 7.31–7.13 (4H, m), 6.82–6.71 (7H, m), 6.38 (2H, d), 2.39 (3H, s), 2.20 (3H, s), 2.18 (3H, s)
8 ^{Py}	DMeONQ	>300	9.27 (2H, d), 8.31–8.22 (4H, m), 7.82–7.68 (6H, m), 7.07 (2H, d), 2.55 (6H, s)
1 ^{MeO}	AQ	—	8.50–8.43 (1H, d), 8.32–8.22 (1H, d), 7.80–7.60 (2H, m), 7.52 (1H, t), 7.35–7.36 (3H, m), 6.90 and 6.79 (4H, ABq, $J = 8.8$ Hz), 3.83 (3H, s)
1 ^{Me}	AQ	165.0–168.5	8.36–8.24 (2H, m), 7.70–7.36 (6H, m), 7.16 and 6.76 (4H, ABq, $J = 7.9$ Hz), 2.40 (3H, s)
1 ^F	AQ	—	8.50–8.25 (3H, m), 7.76–7.50 (3H, m), 7.35–7.25 (2H, m), 7.10–7.04 (2H, m), 6.83–6.77 (2H, m)
10 ^{Me}	Cl ₂ BQ	131.5–132.0	7.22 and 6.99 (4H, ABq, $J = 8.1$ Hz), 7.08 and 6.86 (4H, ABq, $J = 8.1$ Hz), 5.66 (2H, s), 2.37 (3H, s)
10 ^{Cl}	Cl ₂ BQ	153.5–155.0	7.43 and 7.08 (4H, ABq, $J = 8.8$ Hz), 7.27 and 6.91 (4H, ABq, $J = 8.8$ Hz), 5.68 (1H, s)
11 ^{MeO}	Cl ₂ BQ	150.0–150.5	7.01 and 6.95 (8H, ABq, $J = 8.8$ Hz), 5.63 (2H, s), 3.82 (6H, s)
11 ^{Me}	Cl ₂ BQ	160.0–161.0	7.21 and 7.00 (8H, ABq, $J = 8.1$ Hz), 5.64 (2H, s), 2.37 (6H, s)
11 ^{Cl}	Cl ₂ BQ	215.0–217.0	7.41 and 7.08 (8H, ABq, $J = 8.8$ Hz), 5.68 (2H, s)

^a Superscripts indicate IDMg.^b Decomposition.^c Converted into **8**.

attributed to additional aggregation and complexation involving the pyridyl nitrogen of the reagent.

The natures of DMeONQ and 9,10-phenanthraquinone (PQ; 1,2-quinone) are abnormal. The smaller E_{red} of DMeONQ than that of MeONQ (Scheme 1), even with the presence of one more MeO group, may be due to a crowded and distorted structure reducing the electron-repelling resonance of the MeO group. While reactions with electron-donating MeO and Me lead to unidentified Dc, the reaction with less electron-donating Py leads to a 20% yield of mono-replacement product (same with substitution product 2 in run 20 in Table 1), which is also crowded and easily demethanolated (by heating of its crystals) to give 8 (^1H NMR signals of NH and MeO groups absent). Its dimeric dihydrophenazine (not aziridine) structure was identified from mass spectrum.

The reaction of PQ having a strong EAA ($E_{\text{red}} = -0.773$ V, comparable to those of BQs) with a two molar amount of Me (or Cl) led to quinhydrone in a trace (or 22%) amount accompanied by 9 in 10% (or 27%) yield and recovered PQ in 70% (or 46%) yield. Very efficient SET may take place, but the expected steps to give other product may be inhibited by the formation of dimeric quinhydrone (diamagnetic Mg chelate^{7f}) which must be tight and inert toward IDMg.

EXPERIMENTAL

The E_{red} values given in Scheme 1 and Table 2 were determined in THF by cyclic voltammetry^{5a} using bis(biphenyl)chromium(I) tetraphenylborate as internal standard and Bu_4NClO_4 as supporting electrolyte. Procedures of ESR measurements,^{2d} and heat measurement and treatment of the data,^{5b} have been reported previously.

Materials and procedures. MeONQ and DMeONQ were prepared by replacement of the Cl substituent according to the reported procedures,¹⁴ and MeOBQ and ClBQ were obtained by oxidation of the corresponding hydroquinones with Ag_2O . The other quinones were commercially available. The IDMgs were prepared in THF by treating the corresponding anilines with a two molar amount of freshly prepared EtMgBr .^{2a4a} The O-Mgs were similarly prepared.

The IDMg reactions were carried out using 2–3 mmol of reagent and calculated amounts of quinones in THF (50 ml) under the conditions given in the footnotes of Table 1. The reaction mixtures were quenched at 0°C with aqueous ammonium chloride, and the products were separated by column chromatography on silica gel (Wako Gel C-200, C-300 and FC-40). The most probable pathways for the formation of products 1–6, 8 and 9 are described in the text. The product 7 formed from MeNQ (runs 7 and 13) arises from substitution at 3-position (cf. 3) followed by intramolecular attack of a

nitrogen radical on the *ortho*-position of the anilino moiety (the precise mechanism being obscure), and is recognized as a 'substitution' product. Numbers of products, their melting points (uncorrected) and ^1H NMR data are summarized in Table 5.

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