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Correlation of Oxidation and Reduction Potentials of Reactants with Product Distribution in the Reactions of Various Organomagnesium Reagents with Aromatic Carbonyl and Nitro Compounds

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In the electron transfer initiated fifteen reactions of five organomagnesium reagents, a semiquantitative relationship between the product distribution and the electron-donating and -accepting abilities (EDA and EAA) of reactants was obtained. The EDA was estimated by cyclic voltammetry of oxidation peak potentials of reagents and/or by the product distribution in their reactions, the decreasing order of EDA being: ArMgBr > ArSMgBr > ArNHMgBr > ArN(MgBr)$_2$ > ArOMgBr. The EAA of six quinones, eight nitroarenes, eleven aromatic ketones and an imine, and five azoxyarenes were similarly estimated by their reduction potentials (redox) in THF. The values of differences between the oxidation peak and reduction potentials were taken as an estimate of the relative efficiency of electron transfer, and were correlated to the distribution of normal (addition, condensation, replacement, and azoxy-deoxygenation) and abnormal (radical) products. Some exceptional cases were explained by modifying EDA and/or EAA based on the effect of coordination of substrate's oxygen to reagent's Mg atom.

Carbon-carbon bond formation with the use of Grignard addition to carbonyl compounds has been thoroughly investigated. In our laboratory, the methods for the formation of nitrogen-carbon and nitrogen-nitrogen double bonds based on the condensation of aryliminodimagnesium reagents (ArN(MgBr)$_2$, aryl-IDMg) with aromatic carbonyl[1] and nitro[2] compounds have been developed. A qualitative classification of reactions of the two magnesium reagents on the basis of the distribution of normal and abnormal products in terms of the combination of electron-donating and -accepting abilities(EDA and EAA) of reactants was previously proposed.[3] The lower EDA of IDMg than that of ArMgBr suggested from the product distribution[3] was established by comparing their polarographic oxidation peak potentials;[4] the reactions of these reagents with benzophenones were mechanistically distinguished.[5] The product distribution in C-C, C-S, and C-N bond formations with the use of the replacement of bromo and methoxyl groups on the β-position of α,β-enone and α,β-eneimine by ArMgBr(***C***), ArSMgBr(***S***), ArNHMgBr(***NH***), ArN(MgBr)$_2$(***N***), and ArOMgBr(***O***) was correlated to the relative EDA: ***C>S>NH>N>O***.[6] The product distribution in the deoxygenation of azoxyarenes by IDMg was also explained on the basis of relative EAA's estimated by reduction potentials.[7]

These results suggest the general applicability of the EDA-EAA concept independently of reaction manners; a quantitative basis is needed. In this study, the EAA's of aromatic nitro and carbonyl compounds were estimated from their reduction potentials(redox) measured by cyclic voltammetry in THF used as reaction solvent. The values of differences between the oxidation peak and reduction potentials were correlated to the previously given classification,[3] and the EDA-EAA concept was established semiquantitatively. The results will be described in the following.

Results and Discussion

Reduction and Oxidation Potentials of Substrates and Reagents in Tetrahydrofuran. Cyclic voltammetry by polarography was carried out in THF using n-Bu$_4$NClO$_4$ as the supporting electrolyte. The positive and negative limits of the potential window of this system are +1.5 and −2.1V, respectively. The observed reduction potentials (redox) of substrates were normalized by use of bisbiphenylchromiun(I) tetraphenylborate (BCTB) as internal reference,[8] and are summarized in the following. The negative large values indicate weak EAA.

I Quinones

1)	2,6-Cl$_2$-1,4-benzoquinone	−0.443V
	2-Br-4-t-Bu-1,4-benzoquinone	−0.568V
	2-Me-1,4-benzoquinone	−0.787V
2)	2-Me-1,4-naphthoquinone	−0.935V
	2-MeO-1,4-naphthoquinone	−0.957V
3)	9,10-Anthraquinone	−1.074V

II Nitroarenes

1)	4-MeO-nitrobenzene	−1.608V
	4-Me-nitrobenzene	−1.418V
	4-Cl-nitrobenzene	−1.254V
2)	4-Nitrobenzothiazole	−1.314V
	5-Nitrobenzothiazole	−1.299V
	6-Nitrobenzothiazole	−1.220V
	7-Nitrobenzothiazole	−1.142V
3)	Nitroferrocene	−1.693V

III Carbonyl Compounds and an Imine

1)	Benzophenone	−1.989V
	Xanthone	Unobservable
	1-Br-9-fluorenone	−1.337V
	N-(1-Br-9-fluorenylidene)-p-methylaniline	−1.604V

2) p-R^{1}C$_6$H$_4$CH=CHCOC$_6$H$_4$R^2-p

R^1	R^2	
H	H	−1.586V
Cl	MeO	−1.590V
MeO	Cl	−1.606V
CN	Me$_2$N	−1.491V

	Me$_2$N	CN	−1.527V
3)	p-MeO, p-Me, and p-Cl-benzoylferrocenes		Unobservable
4)	p,p'-Me$_2$-benzil		−1.386V
IV	Azoxyarenes(Ar^1-N(O)=N-Ar^2)		
	Ar^1	Ar^2	
1)	4-MeC$_6$H$_4$	4-MeOC$_6$H$_4$	−1.786V
	C$_6$H$_5$	C$_6$H$_5$	−1.596V
	C$_6$H$_5$	4-ClC$_6$H$_4$	−1.423V
2)	4-ClC$_4$H$_4$	2-(4-Me)pyridyl	−1.312V
3)	Ferrocenyl	4-ClC$_4$H$_4$	−1.640V

In each group of substrates, the electron-repelling substituents give larger negative potentials[9] indicative of a weaker EAA. Taking the effect of a π-electron rich ferrocenyl group into account, the larger negative potentials (weaker EAA's) of nitro- and benzoylferrocenes than those of nitrobenzene and benzophenone, respectively, are reasonable. The potentials of the latter were unobservable since they are located out of the potential window. Also, the potential of xanthone is located out of the window due to the effect of electron-repelling resonance effect of ethereal oxygen atom.

The oxidation peak potentials, including those reported previously,[4] observed in the same solvent system were normalized by the use of ferrocene as an internal reference, and are summarized in the following. The electrode process was irreversible, and no reduction peak was observed. The positive large values are indicative of weak EDA.

C	ArMgBr[4]		
	Ar= 4-MeOC$_6$H$_4$	4-MeC$_6$H$_4$	4-ClC$_6$H$_4$
	0.749V	0.819V	0.897V
S	ArSMgBr	Unobservable	
NH	ArNHMgBr[4]		
	Ar= 4-MeC$_6$H$_4$	0.883—0.901V	
N	ArN(MgBr)$_2$		

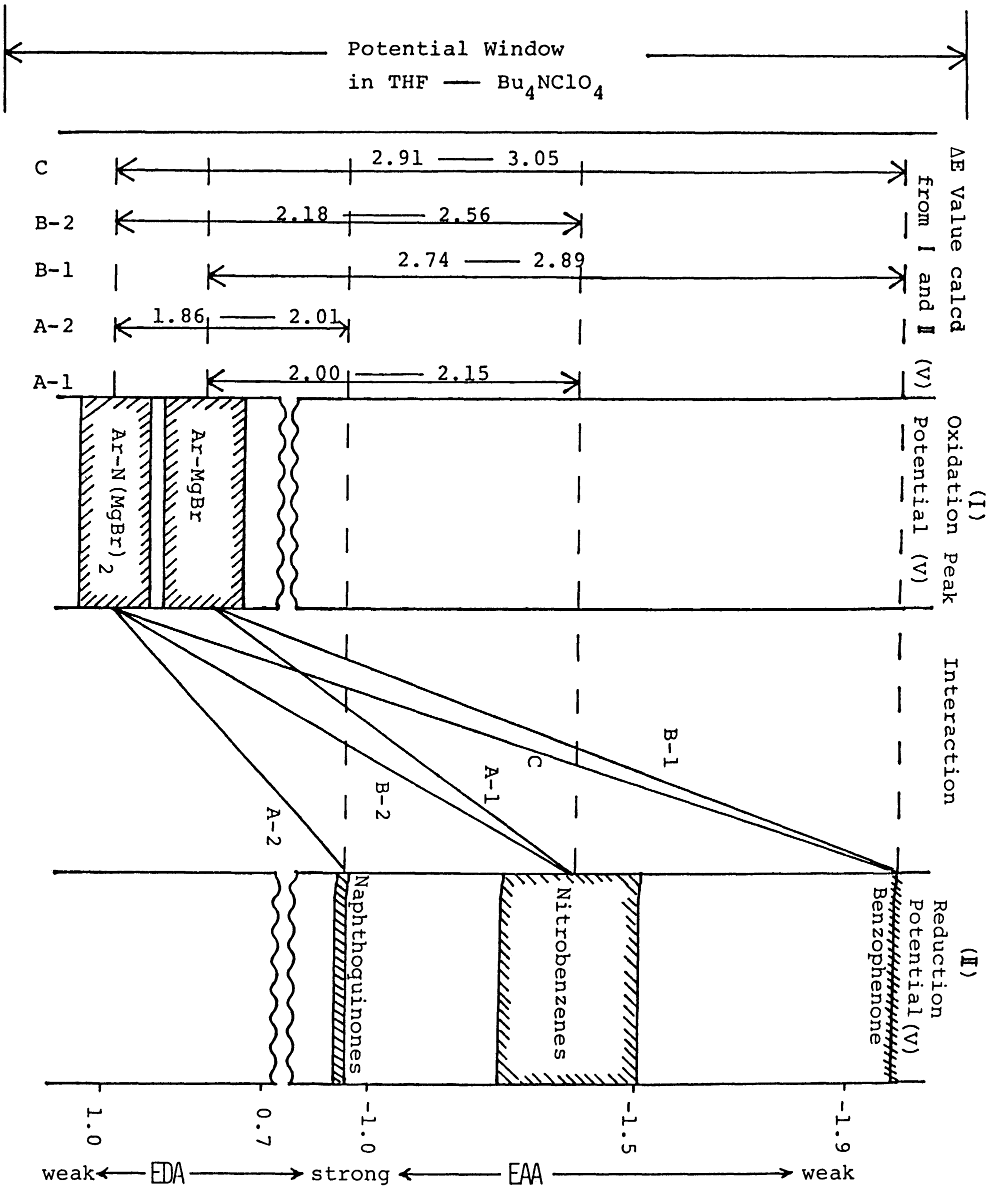


Fig. 1. Correlation of oxidation peak and reduction potentials with classes of reactions of ArMgBr and ArN(MgBr)$_2$.

1)[4]	Ar= 4-MeOC$_6$H$_4$ 0.912V	4-MeC$_6$H$_4$ 0.941V	4-ClC$_6$H$_4$ 1.056V
2)[7]	Ar= 2-(4-Me)pyridyl	1.295V	
NN	Ph(Me)N-N(MgBr)$_2$	Undetermined	
O	ArOMgBr	Unobservable	

The lower oxidation peak potential of ***C*** than that of ***N*** was reported previously.[4] In both cases, the electron-repelling substituents gave smaller positive potentials[9] indicating stronger EDA. The large positive potential of 2-pyridyl-IDMg is responsible for its low reactivity observed in condensation with diaryl ketones.[1] The unsuccessful observation of the oxidation peak potential of aryloxyl reagent(***O***) derived from phenol is due to its much larger potential located out of the potential window. The reason for the unsuccessful observation of the oxidation peak potential of ***S*** is equivocal. Probably, the long and weak S-Mg bond will be responsible for the electron transfer followed by an extraordinarily quick dimerization. This is shown not only by the previous result involving a replacement reaction[6] but also by many examples concerning the one-electron oxidation of sulfide anions.[10] The oxidation peak potential of ***S*** is suggested to be located between those of ***C*** and ***NH***,[6] and to have an approximate value of 0.86V. The oxidation peak potential of the IDMg-type reagent ***NN***, which was derived from 1-methyl-1-phenylhydrazine,[1] shifts from ca. 1.0 to 1.9V during the course of repeated measurements: The reason is equivocal.

Correlation of Relative Value of Difference between Oxidation Peak and Reduction Potentials with Product Distribution in Addition, Condensation, Replacement, and Azoxy-Deoxygenation. The relative efficiency of electron transfer in individual reactions depends on the combination of EDA and EAA of reactants. It is thus reasonable that the relative values of differences (ΔE) between oxidation peak and reduction potentials are correlated to the distribution of normal and abnormal (radical) products. Previously, five reactions of ***C*** and ***N*** with some carbonyl and nitro compounds were classified into Classes A, B, and C on the basis of the product distribution.[3] As shown in Fig. 1, the three classes proved to be correlated to the relative ΔE values.

In Table 1, fifteen reactions of ***C***, ***S***, ***NH***, and ***N***, including not only addition and condensation but also replacement and azoxy-deoxygenation, are summarized. The three classes given above are designated. The ΔE values listed in the Table are approximate and were calculated using the oxidation peak potentials of *p*-Me-substituted reagents and mean values of reduction potentials of nitrobenzenes (A-1 and B-2), naphthoquinones (A-2), azoxybenzenes (B-6), and nitrobenzothiazoles (B-9) cited above. The applied reaction conditions are usual and are similar to each other, as reported previously.[1-7,11,13-15]

In Class A reactions, the ΔE values smaller than 2.2 as well as the formation of large amounts of abnormal (radical) products at the expense of normal ones are in accord with the previous characterization, i.e., "hardly controllable reactions due to a vigorous electron transfer."[3] The reduction potential of 1,3-diaryl-3-MeO-2-propen-1-one(β-MeO-α,β-enone) used in A-3 (and also in B-5) reactions[6] could not be determined. The potential was estimated with use of the ΔE values to be −1.3—−1.5 V, comparable to those of nitro-

Table 1. Correlation of Classes of Reactions, Potential Differences, and Distribution of Normal and Abnormal Products

Class of reacn	Reagent	Substrate[a]	Manner of reacn[b]	Approx. ΔE/V[c]	Product Yield/% Normal	Product Yield/% Abnormal	Ref.
A-1	***C***	ArNO$_2$	A	2.2	ca. 50	ca. 60	2
A-2	***N***	NQ	C	1.9	10—20	ca. 80	3
A-3	***S***	MeOChl	R	—	5	95	6
A-4	***N***	Azx-Py	D	2.0—2.1	<30	>70	7
B-1	***C***	Ar$_2$CO	A	2.8	90	5	5
B-2	***N***	ArNO$_2$	C	2.3	85	10—20	2
B-3	***S***	BrFl	R	2.2	80	—	6, 15
B-4	***C***	BrFl-An	R	2.4	65—90	0—25	6, 15
B-5	***N***(***NH***)	MeOChl	R	—	85—92	0	6
B-6	***N***	Azx-Bz	D	2.5	75—90	0—21	7, 11
B-7	***N***	AQ	C	2.0[d]	>70	0	3
B-8	***N***	NBT	C	2.0—2.2	50—60	15—28[d]	13
B-9	***NN***	Xnt	C	—	90	5	3
C-1	***N***	Ar$_2$CO	C	2.9	60—90	10[d]	1, 5
C-2	***N***	Bzl	C	2.4	50—60	0[d]	3, 14

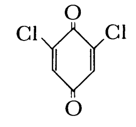
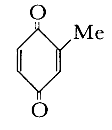
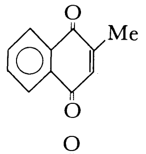
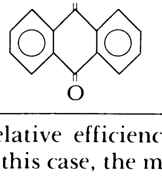
a) Abbreviations. NQ=1,4-naphthoquinones, MeOChl=β-MeO-chalcone (α-benzylideneacetophenone), Azx-Py=Azoxypyridine, BrFl=1-Br-9-fluorenone, BrFl-An=*N*-(1-Br-9-fluorenylidene)aniline, Azx-Bz=azoxybenzenes, AQ=9,10-anthraquinone, NBT=nitrobenzothiazoles, Xnt=xanthone, Bzl=benzil. b) Abbreviations. A=addition, C=condensation, R=replacement, D=deoxygenation. c) Calculation of approximate ΔE values is given in the text. d) The seemingly exceptional results are discussed in the text.

benzenes. The yields of normal products could be improved using lower temperatures (−20—−40 °C), which suppress the electron transfer (as confirmed by the present authors in A-3 reaction[6] and also by Bartoli in A-1 reaction[12]).

In Class B reactions, the medium ΔE values (2.2—2.8) are responsible for the yields of normal products higher than 65% and those of abnormal ones lower than 28%. The previously given "electron transfer controlled" character of Class B reactions is based on the fact that in B-1 and B-2 reactions the electron-attracting substituents of substrates and electron-repelling ones of reagents accelerate electron transfer leading to the higher concentration of intermediate radicals[3,5] and, consequently to a better yields of normal products. In kinetic terms, the B-1 reaction proceeds via a rapid but incomplete coordination and rate-determining electron transfer.[5] The B-2 reaction proceeds step by step via condensation and subsequent deoxygenation.[2,11] The comparable reduction potentials of nitro- and azoxybenzenes cited above may be responsible for the dependence of the final distribution of products simply on the relative EAA of substrate. The 65—90% yields of replacement products are obtained in B-3, B-4, and B-5 reactions.[6] The ΔE value in the B-5 reaction is estimated to be 2.3—2.5 (vide supra). The effect of EAA on the deoxygenation of azoxybenzenes (B-6) and an azoxypyridine (A-4) was recently reported.[7,11] In condensation reactions B-7 and B-8,[13] good yields of normal products were obtained in spite of the small ΔE values comparable to those of Class A reactions. The precise results concerning product distribution in a B-8 reaction will be reported elsewhere, but the reduction of EDA of p-MeC$_6$H$_4$-IDMg due to the coordination of thiazolyl group to Mg atom of reagent was confirmed.[13] In the B-9 reaction of ***NN*** with xanthone, the corresponding hydrazone was obtained in good yield.[1] The high yield and the observed manner of fluctuation of oxidation peak potential (vide supra) suggest that the actual potential of ***NN*** is lower than 0.8V (which is responsible for an efficient electron transfer to xanthone having weak EAA).

Even in the C-1 reaction having a ΔE value larger than 2.9 (which seems to be unfavorable for electron transfer), the condensation product was obtained in good yield.[5] In this reaction, the substituent effect of substrate appears in the manner reverse to that of the B-1 reaction (vide supra). The electron-repelling substituents favor the σ-complex formation by the rate-determining coordination of carbonyl oxygen to Mg atom of reagent, the reaction being thus characterized as "coordination controlled" one.[3] The weak EDA and EAA of reactants of C-1 reflect their low HOMO and high LUMO levels, respectively, but the σ-complex formation assists the substrate in lowering its HOMO and LUMO levels and in accepting electrons from the mild reagent.[3] The good yield of the normal product in C-1 is, thus, reasonable. The mechanisms of initial steps of C-1 distinct from those of B-1 were proposed for elucidating the formation of dimeric and monomeric types of abnormal products, respectively.[5]

Table 2. Relative Efficiency of Electron Transfer from ArOMgBr to Quinones Depending on EDA and EAA

ArOMgBr Quinone		p-RC$_6$H$_4$OMgBr (R)		
	strong ←	MeO	Me (EDA)	Cl → weak
	↑	○○○○[a)] 0 °C immediate	○○○ 0 °C immediate	○○ 55 °C 10 min
		○○○ 0 °C 5 min	○○ 55 °C 20 min	○ 55 °C 40 min
	(EAA)	△[b)] complex formation	×	×
	↓ weak	×	×	×

a) Relative efficiency of electron transfer is indicated by number of circles, and no color change by X. b) In this case, the mixture turned yellow-brown but no radical species was detected by ESR. The coloration is ascribed to σ-complex formation.[3,5]

Irrespective of the small ΔE value comparable to that of B-2, the reaction of *p*-substituted benzils with IDMg reagent is characterized as C-type because the reaction is accelerated by the *p*-MeO-substituent of substrate.[3] The anomaly in C-2 reaction, however, is understood by a measurement of reduction potential of benzil in the presence of an equimolar amount of anhydrous $MgBr_2$. The potential becomes large at least in ca. 0.2V. The reduction of EAA is ascribable to chelate formation by the coordination of α-dicarbonyl oxygen atoms to Mg atom of the reagent. The actual ΔE value in the C-2 reaction may be larger than 2.5. The precise results of the study of substituent effect will be reported elsewhere.[14]

Undoubtedly, the Grignard addition to carbonyl compounds owes its great success about eighty years ago to the lucky selection of Class B combination of reactants.

Electron Transfer from Aryloxymagnesium Reagents to Quinones. Among the reagents examined, aryloxymagnesium (***O***) is suggested to be the weakest electron donor because it is unable to react with monofunctional carbonyl compounds.[6] Its oxidation peak potential was undetermined in the present measurements (vide supra), but it donates electrons to benzoquinones having strong EAA. When *p*-$MeOC_6H_4O$-MgBr was allowed to react with a sixth molar amount of 2-Br-5-*t*-Bu-1,4-benzoquinone, ca. 80% of the quinone was recovered unchanged but a small amount of quinhydrone was obtained. No replacement product was detected. Also, in the reaction with 2-MeO-5-*t*-Bu-1,4-benzoquinone, the results were similar. The precise results on product distribution will be reported elsewhere.

As shown in Table 2, the relative efficiency of electron transfer in cases of benzoquinones and no electron transfer in cases of naphtho- and anthraquinones are in line with the expectation based on the EDA–EAA concept. By mixing the THF solutions of reactants in 1 : 1 molar ratio, the mixture turned deep blue-green due to the formation of semiquinone and aryloxyl radicals. The time given in the Table indicates the period of time needed for obtaining the highest concentration of radicals under the given temperatures. Taking into account the correlation of potential difference shown in Table 1, the results of Table 2 suggest that *p*-RC_6H_4OMgBr has oxidation peak potential higher than 1.6V.

General Discussion. The characteristics of the three typical classes of reactions under usual conditions are summarized in the following.

Class A: High yields of radical products are formed as the result of a vigorous electron transfer. The small ΔE values indicate the strong EDA and/or EAA.

Class B: Good yields of normal products are formed as the result of efficient electron transfer arising from medium ΔE values. The favorable electronic effect of substituents of reactants appears in the manner raising the oxidation potential and lowering the reduction potential, i.e., strengthening both EDA and EAA.

Class C: As far as the initial formation of the σ-complex is not sterically retarded, good yields of products are formed in spite of the large ΔE values. The σ-complex formation is favored by the electron-repelling substituent of the substrates, and assists them in strengthening their EAA, resulting in a mild electron transfer.

The correlation of product distribution with the ΔE value as the first approximation must originate from the remarkable feature of reactions of magnesium reagents. As established in B-1 and C-1 reactions,[3,5] the rate-determining step is located in one of the common initial processes, i.e., the σ-complex formation and the subsequent electron transfer. Due to the strong affinity of magnesium with oxygen, the modification of EDA and/or EAA based on the second important effect of coordination is reasonable.

The EDA–EAA concept is extended further to additional cases, in which no chemical change takes place and no radical species is detected even though the mixture turns yellow-brown indicating the formation of σ-complex: The combination of *N*-(1-Br-9-fluorenylidene)aniline with ***S***,[6] and those of β-MeO-α,β-enone[6] and anthraquinone with ***O*** (Table 2). The much larger ΔE value is responsible for no transfer of electrons, even after the α-complex formation. Similarly, no color change after mixing the components, indicating no interaction, is ascribed to the very large ΔE value as exemplified by the combination of anthraquinone with ***O*** (Table 2) and/or to the steric inhibition of σ-complex formation.[5]

So far, the reactants were confined to aromatic types; the rather simple types of products obtained assisted us in revealing the governing factor. The combination of magnesium reagents with α-benzylideneacetophenones,[16] β-nitrostyrenes,[17] nitro- and benzoylferrocenes,[18] were also studied. These substrates have carbonyl and nitro groups that are not bound directly to the benzene ring; the types of products as well as the effect of substituents are explainable partly on the basis of the EDA–EAA concept. However, some additional factors have to be taken into account.[16,18] The reactions are, thus, excluded from the present classification and will be reported elsewhere.

Electron transfers in organic reactions, including that of a Grignard reagent, have been studied on the general basis of the Marcus theory.[19] Further quantitative studies are needed. However, the present classification will contribute to studies on the mechanisms and molecular orbital picture of electron transfers (vide supra) in the field of organomagnesium chemistry.[20,21] The simple relationship will also be helpful for the selection of reaction conditions and for the expectation of product yields in the synthetic applications of magnesium reagents.

Experimental

Materials, Reaction Procedures, and Measurements. Almost all the quinones, nitrobenzenes, and benzophenone were commercially available. Nitrobenzothiazoles, nitroferrocene, 1-bromo-9-fluorenone, α-benzylideneacetophenones, *p,p′*-dimethylbenzil, and azoxyarenes were prepared according to the manner given in the references. Some references will be given in the forthcomig papers. The preparation of magnesium reagents in THF was reported previously.

The reaction of *p*-$MeOC_4H_4OMgBr$ with 2-bromo-4-*t*-butylbenzoquinone was carried out by heating the mixture at 55 °C for 3 h. The products were separated by column chromatography on silica gel.

Cyclic voltammetry of oxidation peak potentials[4)] and reduction potentials[7)] were reported previously.

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