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Aryliminodimagnesium Reagents. VI. The Reactions with Conjugated Carbonyl Compounds. The Initial Coordination and the Electron-transfer in the Reactions of Organomagnesium Reagents

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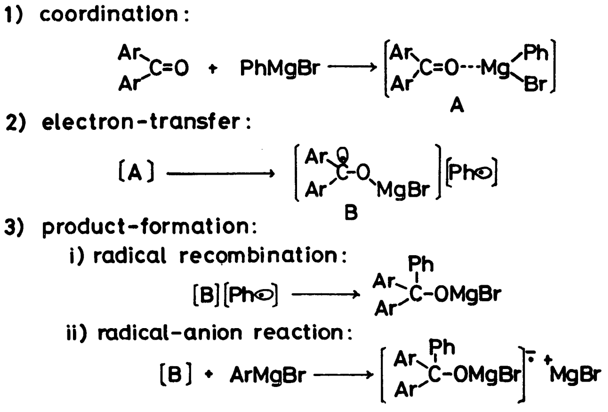
The reactions of aryliminodimagnesium reagents ($ArN(MgBr)_2$) with benzylideneacetophenones, quinones, and benzils were examined. Among the product-distributions in the reactions with the enones and the α-diketones, some examples in which *p*-MeO-substituted substrates gave higher yields of condensation products were obtained. The results are in contrast with the product-distributions in the reaction of ArMgBr with Ar^1COAr^2 and that of $ArN(MgBr)_2$ with Ar^1NO_2: *p*-Cl-Substituted substrates are advantageous for the formation of addition and/or condensation products. These reactions of the two organomagnesium reagents were classified into "coordination controlled" and "electron-transfer controlled" ones on the basis of the combination of electron-donating ability of reagents with the electron-accepting ability of substrates. The classification was illustrated also on the basis of the relative difference of the energy levels of HOMO's and LUMO's of the reactants.

The sequence of the Grignard reaction of benzophenone is formulated as shown in Scheme 1. In general, the initial coordination process is quite rapid and the subsequent electron-transfer process is rate-determining.[1–3] The two types of elementary reactions, i) and ii), are possible for the product-formation process: An evidence for the radical recombination was reported on the basis of product analysis,[4] while another evidence was obtained by ESR on the replacement of electronegative substituents.[2]



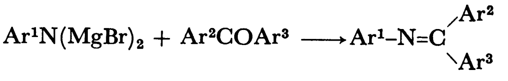
Scheme 1.

The rate-determining electron-transfer process of the reaction of Scheme 1 is accelerated by the electron-attracting *p*-halogeno substituents of the substrate and also by the electron-repelling *p*-methoxyl substituent of the reagent.[2,3] The similar type of the electronic effect of substituents was observed in the product-distribution obtained on the condensation of aryliminodimagnesium reagents ($ArN(MgBr)_2$, aryl–IDMg) with nitroarenes (Scheme 2): A high combined yield of unsymmetical and symmetrical azoarenes was obtained when Ar^1 had *p*-MeO and Ar^2 had *p*-Cl substituents, while a high yield of azoxyarene was obtained when the reactants were reversely substituted.[3,5] Though the detailed mechanism of the IDMg reaction remains to be studied, the similar type of the electronic effect of substituents found in the reactions of Schemes 1 and 2 will allow the present authors to compare the reactivities of the two organomagnesium reagents in the common elementary processes, *i.e.*, the initial coordination of the substrate to the Mg atom of the reagent and the subsequent electron-transfer.

$$Ar^1N(MgBr)_2 + Ar^2NO_2 \longrightarrow Ar^1\text{–}N{=}N(O)\text{–}Ar^2$$
$$+ Ar^1\text{–}N{=}N{=}Ar^2 + Ar^1\text{–}N{=}N\text{–}Ar^1$$

Scheme 2.

A different type of substituent effect was reported previously on the condensation of aryl–IDMg with diaryl ketones (Scheme 3): even the least electron-accepting bis(*p*-dimethylamino)benzophenone gave a sufficient yield of the anil,[6,7] and a higher combined yield of products was obtained in the reaction with 1-methoxy-9-fluorenone than that with 1-halogeno-9-fluorenone.[8]


$$Ar^1N(MgBr)_2 + Ar^2COAr^3 \longrightarrow Ar^1\text{–}N{=}C\begin{matrix}\diagup Ar^2\\ \diagdown Ar^3\end{matrix}$$

Scheme 3.

In order to find the reason for the apparent contradiction, the reaction of aryl–IDMg with some other types of carbonyl compounds was investigated. In this paper, the product-distribution obtained in the IDMg reaction with benzylideneacetophenones, quinones, and benzils will first be described, and compared with that obtained in the Grignard reaction with the same substrates, respectively. On the basis of the comparison, the role of the initial coordination in the IDMg reaction with carbonyl compounds, including diaryl ketones, will be emphasized. The types of the electronic substituent effects found in the reactions of the two organomagnesium reagents with nitro and carbonyl compounds will be classified and discussed in terms of the electron-accepting and -donating abilities of the reactants.[8]

Results and Discussion

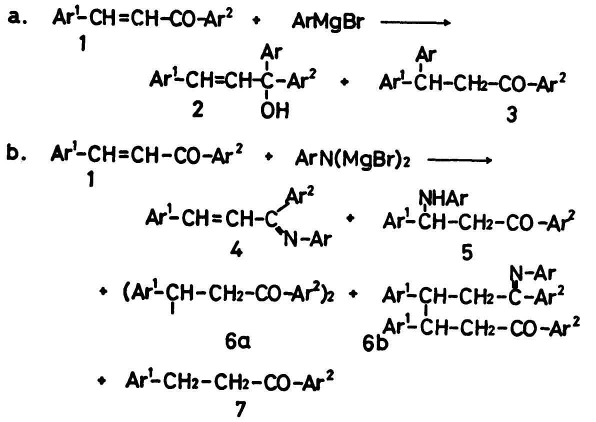
IDMg Reaction with Benzylideneacetophenones. In the Grignard (ArMgBr) reaction of benzylideneaceto-

Table 1. Product-distribution in the IDMg reaction with benzylideneacetophenones (Scheme 4b)

Expt No.	Ar^1	Ar^2	Ar	[IDMg]/[Enone]	Product	
					Type[b)]	Yield/%
1	2,4,6-$Me_3C_6H_2$	C_6H_5	4-MeC_6H_4	1.2	**4**	42—64
2	2,4,6-$Me_3C_6H_2$	C_6H_5	4-$MeOC_6H_4$	1.2	**4**	43
3	4-ClC_6H_4	4-ClC_6H_4	4-$MeOC_6H_4$	1.2	**4**	20
4	4-ClC_6H_4	4-MeC_6H_4	4-$MeOC_6H_4$	1.2	**5**	7.5
5	4-$MeOC_6H_4$	C_6H_5	4-MeC_6H_4	1.2	**6a** **6b**	37 12
6	4-$MeOC_6H_4$	C_6H_5	4-MeC_6H_4	3.0	**6a**	74
7	4-$MeOC_6H_4$	DMB[a)]	4-MeC_6H_4	1.2	**7**	10
8	4-$MeOC_6H_4$	DMB[a)]	4-MeC_6H_4	5.0	**7**	59

a) DMB=2,6-Me_2-4-*t*-BuC_6H_2. b) Types of products are given in Scheme 4b.

phenones, **1**, the normal 1,2-addition product, **2**, and the conjugate 1,4-addition product, **3**, are obtained when an excessive molar equivalent of the reagent is used (Scheme 4a): The product **3** is obtained usually in yields higher than 90% almost independently of the electronic effect of substituents of the enones.[9)] When a deficient equivalent of the reagent was used, a product due to the radical dimerization at the the β-position of the enone was isolated.[10)] The high spin densities on the carbonyl and the β-positions were observed[11,12)] and the electron-transfer mechanism for the 1,4-addition and the dimerization was proposed.[2)]



Scheme 4.

In contrast, the IDMg reaction with the same substrate gave an appreciably different product-distribution (Scheme 4b and Table 1): The types of products, **4**—**7**, and their yields were specified dramatically by the electronic and steric effect of the benzylidene and benzoyl moieties, Ar^1 and Ar^2, respectively.

The hindered Ar^1 and the unhindered Ar^2 lead to a moderate yield of the normal condensation product **4** (Expts 1 and 2): A low yield of **4** was obtained when both Ar^1 and Ar^2 had the electron-attracting *p*-Cl substituent (Expt 3). A low yield of the 1,4-addition product **5** was obtained only when Ar^1 had *p*-Cl substituent and Ar^2 had *p*-Me substituent (Expt 4). The reductive dimerization product **6a** and the condensation-dimerization product **6b**, both of which were indicative of the existence of the electron-transfer process, were obtained in fair yield when Ar^1 had *p*-MeO substituent (Expts 5 and 6): A high yield of **6a** was obtained when a larger excess of the reagent was used (Expt 6). The reduction product **7** was formed when the enone had hindered Ar^2 (Expts 7 and 8): The comparison of the results of Expts 5 and 6 with those of Expts 7 and 8 shows that the bulkiness of the substrate is in favor of hydrogen abstraction from the solvent molecule by the intermediate radicals but not of their dimerization. No product other than the unreacted enones and the products **4**—**7** were detected in Expts 1—8.

The notably different profiles of the reaction of Scheme 4b from those of Scheme 4a are explained in terms of the moderate reactivity[3,6)]—electron-donating ability—of aryl–IDMg compared with that of ArMgBr and also in terms of the initial coordination of substrate to the Mg atom of the reagent. The first factor, the moderate reactivity of aryl–IDMg, is responsible for the unexpectedly enhanced selectivity observed in the reaction of Scheme 4b. The second factor, the effective initial coordination, is responsible for the high yields of the typical radical products in Expts 5—8 in comparison with the low yields of condensation or addition products in Expts 3 and 4: The *p*-MeO substituent of the substrate is advantageous for the coordination and facilitates the subsequent electron-transfer and the product-formation. The attempt to detect the intermediate radicals by ESR at room temperature was unsuccesful: No sufficient accumulation of them is due to the weakly electron-donating ability of the reagent. The role of the initial coordination will be discussed again in the final section.

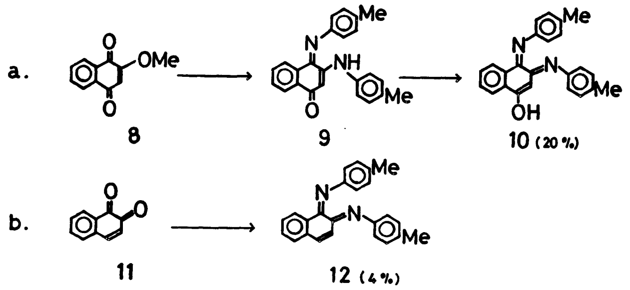
IDMg Reaction with Quinones. The reaction of PhMgBr with quinones under the ordinary reaction conditions lead to the formation of hydroquinone and biphenyl,[13)] their formation indicating the existence of the electron-transfer process. Some products due to radical substitution were also reported,[14)] and the detection of the semiquinone radical by ESR was successful only by use of a fully diluted reaction mixture.[15)]

The reactions of aryl–IDMg with 2-methyl- and 2-methoxy-1,4-naphthoquinones were clearly different from that with 9,10-anthraquinone. In the reactions with the naphthoquinones, complex mixtures containing large amounts of quinhydrone-like products and hardly soluble black materials were obtained: The normal condensation products, quinone imines, were isolated only in low yields (10—20%). In the reaction with anthraquinone, in contrast, good yields of the quinone imines were obtained and no formation of unidentifiable products was observed. The results of the individual reactions will be described first, and a summary discussion will be given in terms of the electron-accepting ability of the quinones.

In the reactions of 2-methyl-1,4-naphthoquinone with 4—6 molar equiv. of *p*-Me- and *p*-MeO-C_6H_4-IDMg, a lower than 10% yield of dark red products—quinone mono- and diimines—was isolated from the complex mixture. The quinone imines show the ^{1}H-NMR spectra having more than two Me- and MeO-proton signals probably due to the geometrical isomerism around the $>C=N-$ groups: The separation of the isomers was unsuccessful.

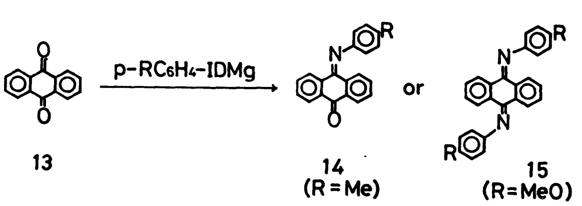
In the reaction of 2-methoxy-1,4-naphthoquinone, **8**, with *p*-Me-C_6H_4-IDMg (4 molar quiv., Scheme 5a), a dark red product which had more than two *p*-Me-C_6H_4 groups but no MeO group was isolated from the complex mixture. The ^{1}H-NMR spectrum has three or four signals at the range of δ=2.3—2.4: The splitt pattern, which indicates that the isolated product is a mixture, changes gradually, during the repeated treatment on silica gel, into another pattern consisting of two signals at δ=2.40 and 2.36. The final product, **10**, shows ν_{OH} absorption band at 3350 cm^{-1} (mp 136 °C). In the reaction with 1,2-naphthoquinone, **11** (Scheme 5b), the quinone diimine, **12** (mp 175 °C), isolated in 4% yield shows two Me-proton signals at δ=2.36 and 2.30: The splitt pattern resembles closely that of **10**. The structure of the primary product in the reaction of **8** is thus assigned to the condensation-replacement product, **9** (yield: 20%), which isomerizes into **10** during the quenching with aqueous NH_4Cl and the subsequent treatment with moist silica gel.

It should be noted here briefly that the formation of the oxidative coupling product, 4,4′-dimethylazobenzene, in the reaction of *p*-Me-C_6H_4-IDMg is associated with the structure of quinones. The azoarene was isolated in 8% yield in the reaction with **11**. The azoarene is the sole identifiable product (yield: 19%) in the reaction with 9,10-phenanthraquinone, which also gave large amounts of unidentifiable black materials and no condensation product. The formation of symmetrical azoarenes is unavoidable in the IDMg reaction with nitroarenes (Scheme 2).[3] The oxidative coupling of the IDMg molecules is thus ascribed to the structural resemblance of the *ortho*-quinones and nitroarenes, those having the similarly oriented two oxygen atoms.



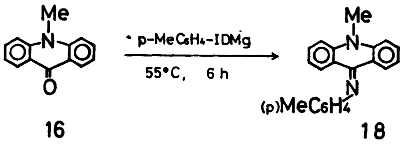
Scheme 5.

In contrast to the poor yields of the condensation products in the reactions of the naphthoquinones and phenanthraquinone, anthraquinone gave good yields of the quinone mono- and diimine depending clearly upon the electron-donating abilities of the reagents, *p*-Me- and *p*-MeO-C_6H_4-IDMg (Scheme 6 and Table 2). The less electron-donating former reagents gave the monoimine, **14** (R=Me), even by use of the reagent in a large excess, whereas the more electron-donating latter reagent gave the diimine, **15** (R=MeO).



Scheme 6.

The inertness of **14** (R=Me) towards *p*-Me-C_6H_4-IDMg is understood by considering the intramolecular charge separation as depicted by the structure, **14a**, which is more favorable for the initial coordination to the reagent's Mg atom but is less favorable for the subsequent electron-transfer. In order to check the electron-repelling resonance effect, *N*-methylacridone, **16**, was treated with the same reagent (Scheme 7): The yield of the corresponding imine, **18**, was 28% by use of 1.2 molar equiv. of the reagent (recovery of **16**: 56%) but the yield was improved to 94% by use of four molar equivalents. The reaction of xanthone, **17**, with aryl-

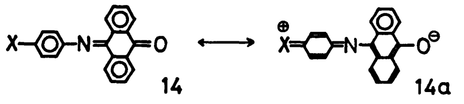


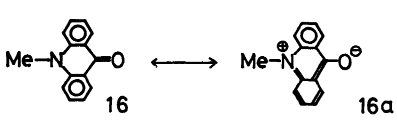
Scheme 7.

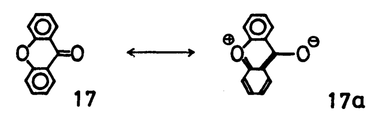
Table 2. Product-distribution in the IDMg reaction with anthraquinone (Scheme 6)

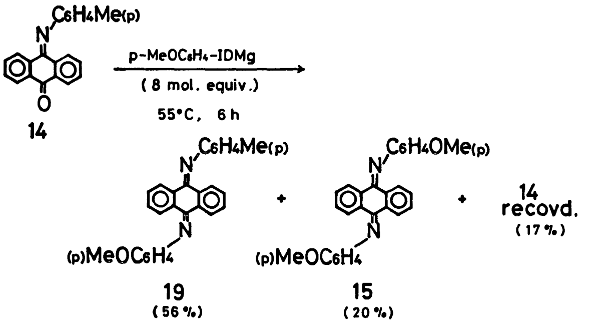
Expt No.	[IDMg]$^{a)}$/[Substrate]	R	Amount of THF/ml	Reaction time at 55 °C h	Yield/% 14	15	Azo	Recovered
9	4	Me	195	1	16	—	1.8	58
10	8	Me	100	6	68	—	1.3	Yes
11	16	Me	65	48	44	—	2.6	Yes
12	8	MeO	100	6	—	41	2.0	23

a) Sixteen millimols of IDMg reagents were used.







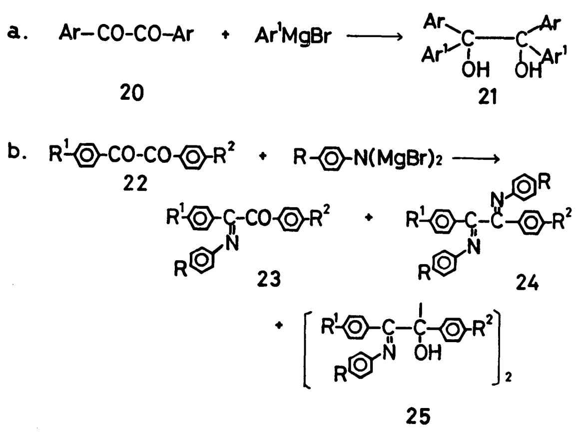


Scheme 8.

IDMg was reported.[5] On the basis of these results, **14** was treated with the more electron-donating *p*-MeO–C_6H_4–IDMg (8 molar equiv.): The expected mixed diimine, **19** and the exchange product, **15** (R=MeO), were obtained (Scheme 8).

The profiles of the IDMg reaction with the quinones described above can be understood by taking their reduction potentials (E_0/V)[16] into account: 1,2-Naphthoquinone (0.58)>1,4-naphthoquinone (0.48)> 9,10-phenanthraquinone (0.46)≫9,10-anthraquinone (0.15). The order of the values seems to be correlated to the following series of the yields of the condensation products: No formation of 9,10-phenanthraquinone imines, the poorest yield 1,2-naphthoquinone diimine (**12**), the 10% yield of 2-methyl-1,4-naphthoquinone imines, the 20% yield of the condensation-replacement product **9**, and the good yields of 9,10-anthraquinone imines (**14** and **15**). The fact that the IDMg reaction with the least electron-accepting (*i.e.*, oxidizing) quinone proceeds most smoothly is indicative of the important role of the combination of electron-donating and -accepting abilities of the reactants.

IDMg Reaction with Benzils. The reaction of benzil and its derivatives, **20**, with excessive amounts of ArMgBr was utilized for preparing substituted benzopinacols, **21**[17] (Scheme 9a): The by-products and the mechanism of the reaction have not been studied extensively, but the ESR evidence for the electron-transfer was reported very recently.[18]



Scheme 9.

The reaction of *p*-substituted benzils with excessive equivalents of aryl–IDMg gave monoimine, **23**, diimine, **24**, and the condensation-dimerization product, **25**, in high combined yields (Scheme 9b and Table 3): The appreciable formation of **25** is reasonable since the higher electron-accepting ability of α-dicarbonyl compound[12] causes a rapid electron-transfer even from the moderately electron-donating reagent.

The distribution of the three types of products was varied but not so dramatically by the reaction conditions (Expts 13—15) and also by the substituents of both substrate and reagent (Expts 14, 16, and 17). The much smaller variation of product-distribution than that of the reaction of Scheme 4b is attributed to the higher electron-accepting ability of benzils: The electronic effect upon the product-distribution is not enhanced but reduced. The intermediate radical derived from 4,4'-dimethylbenzil, **22** ($R^1=R^2=Me$), observed easily at room temperature, gave the ESR spectrum indicating the symmetrical distribution of the free spin on the two *p*-methylbenzoyl moieties ($a^{\rm H}_{\rm Me}=$

Table 3. Product-distribution in the IDMg reaction with benzils (Scheme 9b)

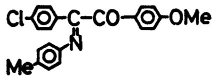
Expt No.	Substrate		Reagent R	[IDMg]/[Substrate]	Yield/%[a)]				
	R^1	R^2			**23**	**24**	**25**	Azo	Recov.
13	Me	Me	OMe	2.5	32	16	32	Trace	4
14	Me	Me	OMe	5.0	21	24	40	—	—
15	Me	Me	OMe	5.0[b)]	34	26	28	Trace	8
16	MeO	MeO	Me	5.0	17	28	38	Trace	—
17	Cl	Cl	Me	5.0	28	10	35	Trace	4
18	Cl	MeO	Me	1.5[c)]	59[d)]	4	25	Trace	10

a) Yields obtained after heating at 55 °C for 6 h. b) The addition was carried out in the "reverse" manner. c) For examining the difference between the reactivities of the two carbonyl groups, a small amount of the reagent was added in the "reverse" manner. d) The constitution of the two isomeric 1 : 1-product is given in the text.

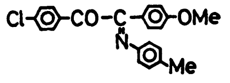
1.2 G, $a^{\mathrm{H}}_{o\text{-}\mathrm{H}}$=2.1 G, 1 G=$10^{-4}$ T).

Though the radical concentration observed in the reaction of 4,4′-dimethoxybenzil, **22** (R^1=R^2=MeO), was remarkably lower than that observed in the reaction of 4,4′-dimethylbenzil, the very similar distribution of the three types of products were obtained (Table 3, Expts 14 and 16). Both the effective electron-transfer from the reagent in Expt 14 and the effective coordination of the substrate to the reagent in Expt 16 are responsible for the closely similar results.

The examination of the reaction with an unsymmetrical benzil, **22** (R^1=Cl, R^2=MeO), gave an explicit evidence for the initial coordination as a governing factor for the product-distribution. In the reaction using one and a half molar equivalents of *p*-Me–C_6H_4–IDMg, a high yield of a mixture of the isomeric monoimines, **23a** and **23b**, was obtained (Expt 18). The chromatographic separation of the isomers was incomplete, but the comparison of the ^{1}H-NMR chemical shifts of the Me- and MeO-protons with those of the monoimines obtained in Expts. 16 and 17 showed that the mixture contained **23a** and **23b** in an approximate molar ratio of 1 : 2. Also the relative yields of mono- and diimines in Expts 16 and 17 reflect the advantage of the substrate's *p*-MeO group over the *p*-Cl group for the product-formation.



23a



23b

General Discussion. The significance of the combination of electron-donating ability of reagents with electron-accepting ability of substrates in the reactions of organomagnesium reagents (ArMgBr and ArN-$(MgBr)_2$) was pointed out very recently.[8] Since the new method for preparing unsymmetrical azoxy- and azoarenes by the IDMg reaction with the highly electron-accepting nitroarenes[19,20] owes its success to the moderately electron-donating ability of the reagent,[3,6] it is reasonable to classify the profiles of the reactions of the organomagnesium reagents from the same standpoint. The classification into three types will be given in the following.

The type A represents the "hardly controllable reactions" leading to the formation of large amounts of radical products due to much vigorous electron-transfer. The first example is the reaction of highly electron-donating ArMgBr with highly electron-accepting $PhNO_2$ (A-1). The formation of the three types of products, ArNHPh, ArOH, and Ar–Ar, in comparable yields (50—60%) was reported:[21] The high yield of the biphenyl is the result of efficient oxidative coupling of the reagent molecules. The second example is the reaction of the moderately electron-donating aryl–IDMg with the strongly electron-accepting naphthoquinones (A-2) described above.

The type B represents the "electron-transfer controlled reactions" which involve the moderate electron-transfer followed by efficient formation of normal products due to addition and/or condensation. The reactions of this type are accelerated by the electron-attracting *p*-F and *p*-Cl substituents of substrates and also by the electron-repelling *p*-MeO substituent of reagents. The first example is the well-studied reaction of ArMgBr with the moderately electron-accepting diaryl ketones (B-1; *cf.* Scheme 1). The second example is the IDMg reaction with nitroarenes (B-2; Scheme 2). The reactions B-1 and B-2 involve the rapid coordination followed by the rate-determining electron-transfer[1] and the subsequent product-formation. The more moderate reaction of imino compounds with ArMgBr (B-3) was reported.[8,22]

The type C represents the "coordination controlled reactions," the product-distributions of which are governed by the initial coordination of the substrates to the Mg atom of the reagent: The electron-repelling *p*-MeO substituent of both reactants is favorable for the product-formation. The examples are the IDMg reactions with diaryl ketones (C-1), benzylideneacetophenones (C-2), and benzils (C-3). Though the existence of the electron-transfer process in C-1 and C-2 reactions is indicated by the formation of diarylmethanols[7] and that of **6** respectively, the attempt to detect the ketyl-type radicals by ESR at room temperature is unsuccessful: This fact suggests that the process in these reactions takes place after the initial coordination has been completed. The favorable role of the *p*-MeO-substituted reagent in the type C reactions can be ascribed to the acceleration of the subsequent electron-transfer process. The reaction C-3 involves the most rapid electron-transfer among the three examples: This reaction has the type B character with regard to the substituent effect upon the concentration of radicals (*vide supra*). It is quite reasonable that, as the electron-donating and -accepting abilities of the reactants are lowered, the rate-determining step is shifted to the just initial coordination process (*cf.* Scheme 1).

The electron-accepting ability of substrates should be estimated by comparing the relative values of the reduction potentials:[16,20] The comparison of the published values in detail between the different types of substrates is not always possible at present because the conditions for the measurements have not been generalized.[20] With regard to the electron-donating ability of reagents, the situation is same because any standard method for determining the oxidation poten-

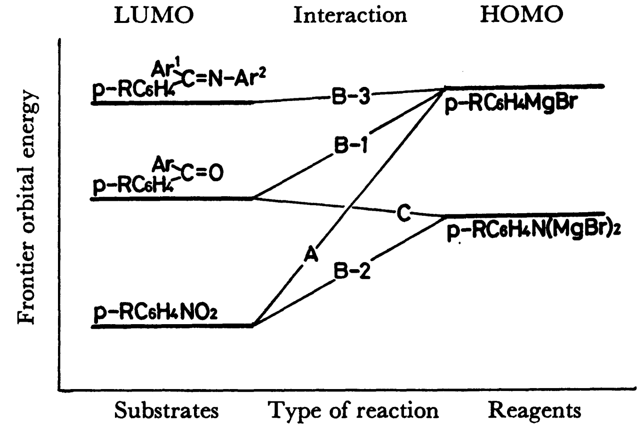


Fig. 1. An illustration diagram for the correlation of frontier orbital energies with reaction profiles.

Table 4. Analytical data and physical constants of products

Product No.	Mp θ_m/°C	Formula	Found (Calcd) (%)			NMR data δ
			C	H	N	
^{1}**4**	86—87	$C_{25}H_{25}N$	88.65 (88.49)	7.22 (7.37)	4.14 (4.12)	CCl_4, 8.02—6.24 (13H, m), 2.28 and 2.24 (3H, two s lines), 2.16 (3H, s), 2.10 (3H, s)
^{2}**4**	119—120	$C_{25}H_{25}NO$	84.29 (84.50)	6.99 (7.04)	4.04 (3.94)	CCl_4, 8.16—6.46 (13H, m), 3.88 (3H, d), 2.40 (6H, s), 2.36 (3H, s)
^{3}**4**	179	$C_{22}H_{17}Cl_2NO$	69.02 (69.11)	4.57 (4.45)	3.73 (3.66)	$CDCl_3$, 8.00—6.00 (14H, m), 3.81 (3H, s)
^{4}**5**	116—117	$C_{23}H_{22}ClNO_2$	72.79 (72.72)	5.69 (5.79)	3.78 (3.69)	$CDCl_3$, 7.76—6.34 (12H, m), 4.76 (1H, t), 4.16 (1H, broad s), 3.60 (3H, s), 3.26 (2H, d), 2.36 (3H, s); IR: 3390 and 1670 cm^{-1}
^{5}**6a**	An oil	$C_{32}H_{30}O_4$	80.19 (80.33)	6.39 (6.27)		CCl_4, 8.12—6.50 (18H, m), 3.60 (6H, s), 2.90—2.80 (2H, m), 2.28—2.10 (4H, m); IR: 1680 cm^{-1}
^{5}**6b**	An oil	$C_{39}H_{37}NO_3$	82.42 (82.54)	6.72 (6.52)	2.39 (2.47)	CCl_4, 8.02—6.56 (22H, m), 3.65 (3H, s), 3.60 (3H, s), 2.90—2.60 (4H, m), 2.40—2.30 (2H, m), 2.12 (3H, s); IR: 1685 cm^{-1}
^{8}**7**	An oil	$C_{22}H_{28}O_2$	81.57 (81.48)	8.59 (8.64)		CCl_4, 7.16—6.66 (6H, m), 3.64 (3H, s), 2.88 (2H, t), 2.26 (2H, t), 2.16 (6H, s), 1.26 (9H, s); IR: 1695 cm^{-1}
10	135	$C_{24}H_{20}N_2O$	81.79 (81.82)	5.72 (5.68)	7.99 (7.95)	$CDCl_3$, 8.24—8.06 (2H, m), 7.80—7.16 (10H, m), 6.84—6.26 (2H, m), 2.40 (3H, s), 2.36 (3H, s)
12	175	$C_{24}H_{20}N_2$	85.78 (85.71)	5.87 (5.95)	8.35 (8.33)	$CDCl_3$, 8.62—8.20 (2H, m), 7.80—7.60 (2H, m), 7.36—6.70 (10H, m), 2.36 (3H, s), 2.30 (3H, s)
^{10}**14**	165—168.5	$C_{21}H_{15}NO$	84.73 (84.85)	5.14 (5.05)	4.78 (4.71)	$CDCl_3$, 8.36—8.24 (2H, m), 7.70—7.36 (6H, m), 7.20 and 6.76 (4H, ABq), 2.40 (3H, s)
^{12}**15**	183—186	$C_{28}H_{22}N_2O_2$	80.49 (80.38)	5.19 (5.26)	6.61 (6.69)	$CDCl_3$, 8.44—8.28 (2H, m), 7.70—6.90 (6H, m), 6.94 (8H, s), 3.82 (6H, s)
18	86—89	$C_{21}H_{18}N_2$	84.49 (84.56)	6.03 (6.04)	9.48 (9.39)	CCl_4, 7.30—6.64 (12H, m), 3.30 (3H, s), 2.29 (3H, s)
19	79—84	$C_{28}H_{22}N_2O$	84.01 (83.58)	5.39 (5.47)	7.07 (6.96)	CCl_4, 8.42—8.24 (2H, m), 7.56—6.72 (14H, m), 3.74 (3H, s), 2.34 (3H, s)
^{14}**23**	An oil	$C_{23}H_{21}NO_2$	80.41 (80.47)	6.15 (6.12)	4.01 (4.08)	CCl_4, 7.90—7.64 (4H, m), 7.32—6.60 (8H, m), 3.63 (3H, s), 2.38 (3H, s), 2.30 (3H, s)
^{14}**24**	160—163	$C_{30}H_{28}N_2O_2$	80.40 (80.35)	6.19 (6.25)	6.23 (6.25)	CCl_4, 7.82 and 7.18 (8H, ABq), 6.66 (8H, s), 3.68 (6H, s), 2.36 (6H, s)
^{14}**25**	233—236	$C_{46}H_{42}N_2O_4$	80.51 (80.46)	6.02 (6.12)	4.16 (4.08)	$CDCl_3$, 8.04—7.92 (4H, m), 7.50—7.12 (16H, m), 6.90—6.76 (4H, m), 3.76 (6H, s), 2.36 (6H, s), 2.30 (6H, s)
^{16}**23**	An oil	$C_{23}H_{21}NO_3$	76.95 (76.88)	5.79 (5.85)	3.93 (3.89)	$CDCl_3$, 7.92—7.58 (4H, m), 6.92—6.62 (8H,m), 3.78 (3H, s), 3.73 (3H, s), 2.17 (3H, s)
^{16}**24**	195—197	$C_{30}H_{28}N_2O_2$	79.98 (80.35)	6.41 (6.25)	6.21 (6.25)	$CDCl_3$, 7.82 (4H, d), 6.86 (8H, d), 6.48 (4H, d), 3.78 (6H, s), 2.24 (6H, s)
^{16}**25**	>250	$C_{46}H_{42}N_2O_6$	76.71 (76.88)	5.76 (5.84)	3.94 (3.89)	$CDCl_3$, 7.92 and 7.84 (4H, d), 7.34—7.10 (8H, m), 7.00—6.66 (12H, m), 4.08 (2H, broad s), 3.78 (6H, s), 3.74 (6H, s), 2.20 (6H, s)
^{17}**23**	An oil	$C_{21}H_{15}Cl_2NO$	68.62 (68.48)	4.01 (4.07)	3.69 (3.80)	CCl_4, 7.84 and 7.42 (4H, ABq), 7.68 and 7.32 (4H, ABq), 6.86 and 6.76 (4H, ABq), 2.22 (3H, s)
^{17}**24**	Not purified					$CDCl_3$, 7.84 and 7.40 (8H, ABq), 6.98 and 6.62 (8H, ABq), 2.27 (6H, s)
^{17}**25**	>250	scarcely soluble				DMSO-d_6, 8.00—7.90 (4H, m), 7.46—6.90 (20H, m), 2.25 (6H, s)
^{18}**23a**	An oil					CCl_4, 7.77 and 7.37 (4H, ABq), 7.66 (2H, d), 6.98—6.64 (6H, m), 3.83 (3H, s), 2.20 (3H, s)
^{18}**23b**	An oil					CCl_4, 7.88 and 7.43 (4H, ABq), 7.72 (2H, d), 7.04—6.76 (6H, m), 3.78 (3H, s), 2.26 (3H, s)

tials of these reagents has not been established.[23] However, the classification of the reaction profiles given above enables us to make qualitative estimates of the reduction potentials of substrates, including nitroarenes and diaryl ketones,[20] and those of the oxidation potentials of the reagents.

Since the oxidation and reduction potentials are correlated to the energy levels of the frontier molecular orbitals of the electron-acceptors and -donors,[24–26] the classification given above can be illustrated in terms of the energy levels of the lowest unoccupied molecular orbitals (LUMO) of substrates and those of the highest occupied ones (HOMO) of reagents as shown in Fig. 1: Only the LUMO's of the typical substrates are designated for simplicity and their levels relative to those of the HOMO's of the reagents are given arbitrarily. The three types of the reaction profiles (A, B, and C) are also designated in the figure.

The discussion and the illustration given above are only qualitative at present, and detailed studies are needed especially for determining the precise mechanisms and the energy levels of the reactants. However, the classification of the reactions into "electron-transfer controlled" and "coordination controlled" ones will provide a clue for understanding the rather complicated profiles of the reactions of organomagnesium reagents.

Experimental

The melting points are uncorrected.

Materials and Procedures. The benzylideneacetophenones were prepared by condensation of the corresponding benzaldehydes and acetophenones in ethanol containing potassium hydroxide. The naphthoquinones, 9,10-anthraquinone, 9,10-phenanthraquinone, and *N*-methylacridone were commercially available. The symmetrical and unsymmetrical benzils were prepared by condensation of benzaldehydes followed by oxidation by copper(II) sulfate in pyridine.[27]

The procedures of the IDMg reaction were reported previously.[3,6,7] The ESR measurements were carried out according to the reported method.[2]

Products. The presence of the quinhydrone-like products in the black mixtures of products obtained in the IDMg reactions with the naphthoquinone and 9,10-phenanthraquinone was suggested from the fact that a part of the starting materials was recovered after the treatment of the mixture with aqueous sodium hydroxide: The black color characteristic to quinhydrones faded to some extent during the treatment.

The melting points, the results of elemental analyses, and the NMR data of the products of IDMg reactions are summarized in Table 4. The products are designated by the numbers given in the reaction schemes (gothic letters) as well as the experiment numbers given in the tables (super-prefixes). The chromatographic separations of the products, ^{17}**24**, ^{17}**25**, ^{18}**23a**, and ^{18}**23b** from the individual reaction mixtures were incomplete, and were not submitted to the elemental analyses: The contents of these products in the mixture (Table 3) were estimated by inspecting the NMR spectra of chromatographic fractions.

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