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REACTION OF ARYLIMINODIMAGNESIUM WITH DIPHENYL DIKETONES: HEAT EVOLUTION ACCOMPANYING SINGLE ELECTRON TRANSFER AND CHELATE FORMATION, AND PRODUCT DISTRIBUTION*

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Reaction of diphenyl diketones (benzils) with aryliminodimagnesium [ArN(MgBr)$_2$, IDMg], a magnesium reagent having condensation ability, was investigated. By comparison of the relative amounts of heat evolved in the reactions of IDMg (mildly electron donating) and ArMgBr (strongly electron donating) with some carbonyl and nitro compounds, results were obtained supporting the reported correlation of the relative yields of normal and abnormal (radical) products with single electron transfer (SET) efficiency estimated by the oxidation and reduction potentials of reactants. A sole exceptional result, i.e. the great heat evolution caused by the combination of benzil and IDMg, was attributed to the generation of tightly chelated radicals via SET. The involvement of stepwise SET was confirmed by ESR. On the basis of these results, substituent effects of benzil and mono-condensation products on their reduction potentials and on the relative yields of normal (mono- and di-condensation) and abnormal (dimerization) products were examined. All the results were consistently explained in terms of the relative efficiency of chelation (or σ-complexation) and SET in two main processes. The role of the initial stages involved in the processes governing the final product distribution is discussed.

INTRODUCTION

Single electron transfer (SET) is involved in the course of Grignard reactions with diaryl mono- and diketones leading to 'normal' addition products, and the precise mechanism is under investigation.[2] In the past decade, a variety of reactions of aryliminodimagnesium [ArN(MgBr)$_2$, IDMg], a magnesium reagent capable of converting aromatic carbonyl and nitro compounds into $>C{=}NAr$ and $-N(O){=}NAr$ products via condensation,[3] has been developed. The involvement of SET in IDMg reactions studied by ESR[3d] has been reported. In terms of the principle that both normal and 'abnormal' (radical) products (observed under ordinary conditions of reactions of magnesium reagents) are formed via common intermediate radicals generated by SET independent of the normal mode of reaction, the types and relative yields of products in fifteen reactions of magnesium reagents were correlated with the relative SET efficiencies estimated by the difference (ΔE) between the oxidation and reduction potentials (E_{ox} and E_{red}) of the reactants.[3e] The governing role of the initial stage of reactions evaluated from electron-donating and -accepting abilities (EDA and EAA) of reactants is proposed.

According to the electron donating/accepting ability (EDA–EAA) approach based on the weaker EDA of IDMg[3c] than that of ArMgBr, modification factors reflected in the product distribution in mild IDMg reactions were derived,[1,3f,3g] viz. the factors due to effects of the formation of a σ-complex and a reagent aggregate. Concerning the reactions of a bifunctional diphenyl diketone (benzil) involving stepwise SET,[2a,3a] however, its IDMg reaction C2 is distinct from Grignard reaction A3 with respect to the types and relative yields of products (Scheme 1): A3 gives exclusively a stepwise addition product[2a] and C2 gives an abnormal radical product (**3**) in reasonable yield.[3a] The behaviour of benzil in the two reactions remains to be examined.

In this study, new evidence supporting the role of an EDA–EAA correlation was obtained by comparison of the relative amounts of heat evolved in eight typical combinations of reagents and substrates (including benzil) selected from the four given classes of reactions.[3e]

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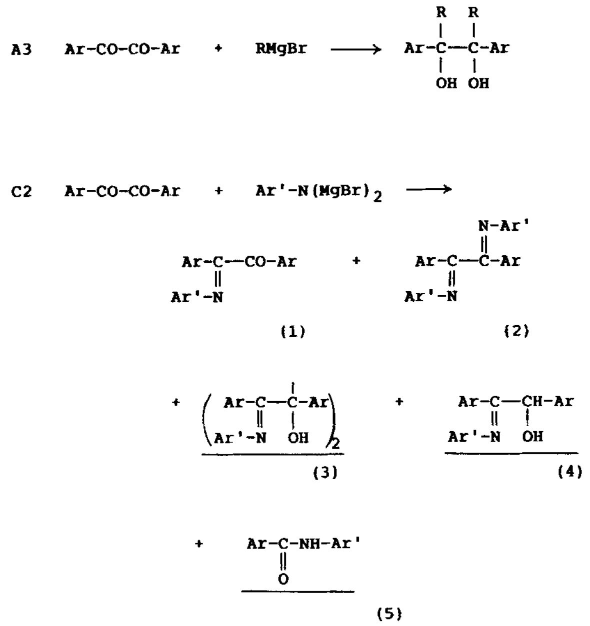
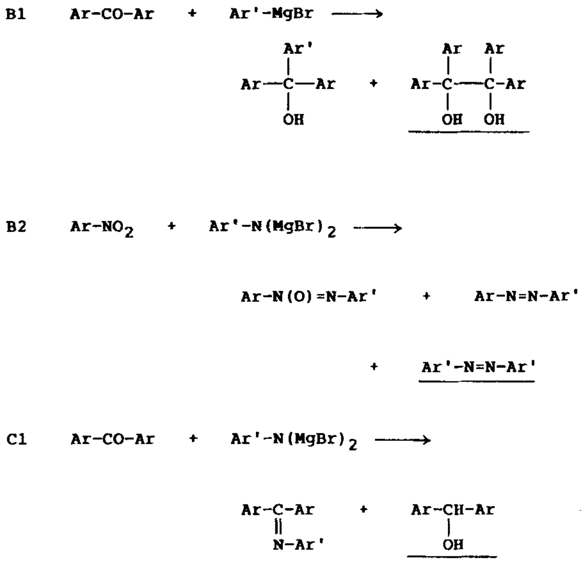


Scheme 1

Among these, the reaction of IDMg with benzil gave an exceptionally large evolution of heat, attributed to cooperative effects of SET and chelation. On the basis of this and measurement of the E_{red} values of benzils and monoimines (**1**) in tetrahydrofuran (THF) and observation of intermediate radicals by ESR, the distribution of products in reaction C2 was explained by relative effects of SET efficiency and chelation (or σ-complexation) cooperating to different extents in the two main processes.

GENERAL ASPECTS AND RELATIVE AMOUNTS OF HEAT EVOLVED

The classification and characterization of fifteen reactions of magnesium reagents with aromatic substrates in terms of ΔE values[3e] are summarized in Table 1. Except for class D, involving no SET, small and large ΔE values (A < B < C) indicate more and less efficient SET, respectively.[3e] Of thirteen of the reactions (A1, A2, B1–B9, C1 and C2) examined, the mechanistically important ones (Scheme 2; abnormal products underlined) are Grignard reaction with benzophenone (B1), reaction of IDMg with nitrobenzene (B2) and reaction of IDMg with benzophenone (C1). Grignard reaction A3 is numbered by considering its ΔE value, whereas IDMg reaction C2 was numbered[3a,3e] by considering the substituent effect on the product distribution, resembling that of C1 described below.



Scheme 2

Substituents of substrates favourable for intermediate radical generation and/or yield improvement are shown in Table 2. In reactions B1 and B2, weaker EAA and

Table 1. Classification and characterization of reactions of magnesium reagents including ArMgBr and ArN(MgBr)$_2$

		Relative yield of products			Mechanistic features			
						Favourable substituent[b]		
Units of ΔE	Class	Normal	Abnormal	Character of reaction	Rate-determining step[a]	Substrate	Reagent	Mode of SET[c]
<2·2	A	Minor	Main	Vigorous SET	SET	—	*p*-MeO	Outer-sphere
2·2–2·8	B	Main	Minor	SET efficiency controlled	SET	*p*-F, *p*-Cl	*p*-MeO	Medium
2·9–3·1[d]	C	Main	Minor	Complexation-controlled SET	Complexation	*p*-MeO	*p*-MeO	Inner-sphere
>3·1[d]	D	No reaction		Only complexation (no SET)		—	—	—

[a] *In the initial* stage.

[b] See text.

[c] See text.

[d] Actual highest and lowest limits of class C and D are larger than the cited value, which corresponds to the available potential limit (window) of THF solution.

Table 2. Reaction numbers, ΔE values, substituent effects on relative yields of products and explicit observation of reagent radicals in reactions of ArMgBr and ArN(MgBr)$_2$ given in Schemes 1 and 2

Reaction No.	Mean ΔE	Substituent and product yield			ESR observed [reagent]˙	Ref.
		Reagent	Substrate[a]	Product yield		
A3	2·1	—	—	No abnormal product	No	2a
B1	2·7	*p*-Me	***p*-Cl**	(More rapid SET)	No	16
		p-Me	*p*-MeO	(Less rapid SET)		
B2	2·4	*p*-MeO	***p*-Cl**	Azoxy < azo	No	3b
		p-Cl	*p*-MeO	Azoxy > azo		
C1	2·9	*p*-Me	*p*-Cl	Lower[b]	Yes	3d
		p-Me	***p*-MeO**	Higher[b]		
C2	2·4	*p*-MeO	***p*-MeO**	$1 \ll 2+3$	Yes/no	3a
		p-MeO	*p*-Cl	$1 \gg 2+3$		

[a] Substituent favourable for reaction (see text) is designated by bold type.

[b] Higher concentration of intermediate radical from *p*-MeO substrate was also observed.

stronger EDA due to a *p*-MeO group are reflected in the product yield and ease of radical generation.[3d,3e] The slightly favourable effect of the *p*-MeO group of benzophenone on ketyl generation and/or yield improvement in IDMg reaction C1[3d] indicates that rate-determining σ-complexation of carbonyl oxygen with the Mg atom of the reagent is favoured by the group; the HOMO and LUMO energy levels of the ketone in the σ-complex are lowered to facilitate SET[3d] in spite of the large ΔE value. The role of the initial stage will be discussed later.

Classification of ΔE and relative amounts of heat evolved

Holm[4a] proposed a prototype of the EDA–EAA concept. He estimated the relative SET rate in reaction B1 for a variety of alkyl Grignard reagents (RMgBr) with benzophenone by measuring the heat evolved in the initial stage by means of a 'flow method.'[4b] The rate was correlated with the electrolysability (identical with EDA) of RMgBr[4a] (recently confirmed[2b]) and with the product distribution. However, an attempt to observe heat evolution in IDMg reaction C1 using his flow system[4c] encountered difficulties. The difficulties arose from the applied flow-rate, which was suitable and unsuitable for reactions B1 and C1, respectively, because the rate-determining step in the initial stage of B1 (strong EDA and small ΔE) is SET and that in C1 (weak EDA and large ΔE) is σ-complexation[3c,3d] (Table 2).

An unconventional simple batch method was used for the present purpose of approximately comparing the relative amounts of heat evolved in combinations of reactants selected from the given classes A–D.[3e] In order to compare the amount of heat evolved accompanying almost solely the initial stage, a 1 : 1 molar ratio of reagent to substrate was used (the use of a large proportion

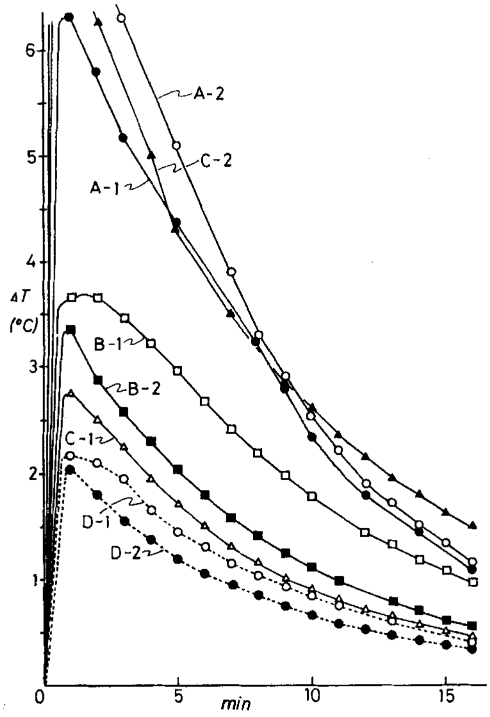


Figure 1. Temperature–time plots obtained in the typical eight combinations of reactants independent of reaction modes.

Reaction modes: Ad = addition; Cd = condensation, Cp = σ-complexation. A1 (Cd), 2-Me-1,4-naphthoquinone + *p*-MeOC$_6$H$_4$-IDMg;[3a,6] A2 (Ad), *p*-MeOC$_6$H$_4$NO$_2$ + *p*-MeOC$_6$H$_4$MgBr;[7] B1 (Ad), *p,p'*-(MeO)$_2$-benzophenone + *p*-MeC$_6$H$_4$MgBr;[2b,3d] B2 (Cd), *p*-MeOC$_6$H$_4$NO$_2$ + *p*-MeC$_6$H$_4$-IDMg;[3b] C1 (Cd), *p,p'*-(MeO)$_2$-benzophenone + *p*-MeOC$_6$H$_4$-IDMg;[3d] C2 (Cd), benzil + *p*-MeC$_6$H$_4$-IDMg;[3a] D1 (Cp), *N*-(9-fluorenylidene)-*p*-MeO-aniline + *p*-MeC$_6$H$_4$-IDMg;[8] D2 (Cp), xanthone + *p*-ClC$_6$H$_4$-IDMg[9] of reagent will cause considerable heat evolution accompanying the final recombination of intermediate radicals, and the use of a smaller proportion leads to the possibility of the formation of unusual products from the substrate[5]). This increase in temperature caused by mixing of the reactants under fixed conditions was plotted against time (see Experimental); the heat of dilution may be cancelled between one experiment and another. Typical combinations (including benzil), class numbers, normal reaction modes and the plots obtained are shown in Figure 1.

The area enclosed by each curve in Figure 1, representing the relative amount of heat evolved, was converted into a dimensionless value (ΔH) according to the procedure described under Experimental. With the sole exception of the reaction of IDMg with benzil (C2), the decreasing order of ΔH values (A > B > C > D) is in accord with the classification.

The weakly exothermic nature of σ-complexation (see D1 and D2) indicates that the heat of σ-complexation contributes to the ΔH value, which therefore shows a poor linear relationship with ΔE. The relative proportions of the heat of σ-complexation in the ΔH values of A–C can be estimated qualitatively from the characterization (Table 1). In class A, the proportion must be negligible, reflecting the substantial formation of radical products arising from vigorous SET without the assistance of σ-complexation.[3a] The proportion must be small in B1 and B2, involving loose σ-complexation[3d,3e] or complex formation after SET.[2c] A large proportion in C1, comparable to the amount of heat observed in D1 and D2, is in accord with a σ-complexation-controlled character;[3d] a small proportion is assignable to SET in a σ-complex (i.e. inner-sphere SET[10,11]).

The rate of the step succeeding SET, i.e. radical transfer, in Grignard reactions of benzil and benzophenone[2d] (A3 and B1) was estimated spectroscopically to be much lower than the rate of SET. Determination of the rate of the succeeding step in the IDMg reaction is difficult because of deep coloration of the mixture due to rapid oxidation of reagent molecules,[12] and whether or not the succeeding step in the IDMg reaction involves simple transfer of arylaminyl radical $\text{Ar}\dot{\text{N}}\text{MgBr}$[3d]) is undetermined. However, the proposed governing role of the initial stage is confirmed by the correlation of classification by ΔE with heat evolution independent of the mechanism of succeeding steps. The steps probably progress in the inside of aggregates composed of intermediate radicals and reagent molecules; indirect but supporting evidences are the dimerization of RMgBr cation radicals,[2a,b] oligomerization of RMgX molecules in the presence of substrate[13] causing dimerization of benzophenone ketyl[3d] and cooperation of IDMg molecules in the reaction with nitroarenes.[1,14]

The evolution of heat in C2 is comparable to those in A1 and A2, regardless of ΔE, comparable to that of class B reactions, and is ascribed to the substantial participation of chelation, as shown by the effects of four substrates (used for plots A–C) on the heat of adduct formation with equimolar anhydrous $MgBr_2$ (Figure 2, plots E–H; diethyl ether used for solubilization of $MgBr_2$). The great evolution of heat caused by benzil (plot E) indicates stabilization by chelation in accord with the reported elevation of E_{red} by interaction with $MgBr_2$.[3e] The slightly endothermic adduct formation with nitrobenzene (plot H) is unexpected, but may be reflected in the mechanism of B2[3b] and its smaller ΔH than that of B1.

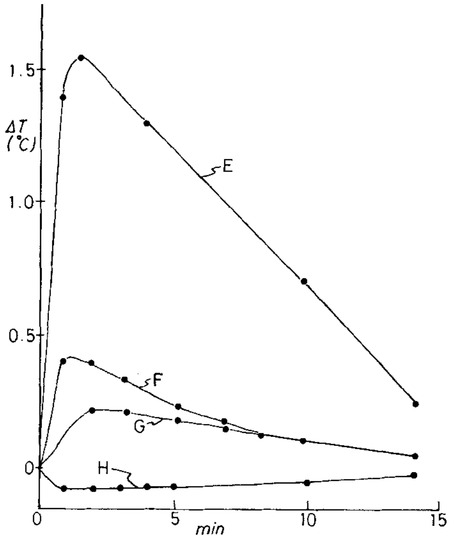


Figure 2. Temperature–time plots obtained by mixing anhydrous $MgBr_2$ with four substrates in diethyl ether: E, benzil; F, 2-Me-1,4-naphthoquinone; G, p,p'-$(MeO)_2$-benzophenone; H, p-MeO-$C_6H_4NO_2$

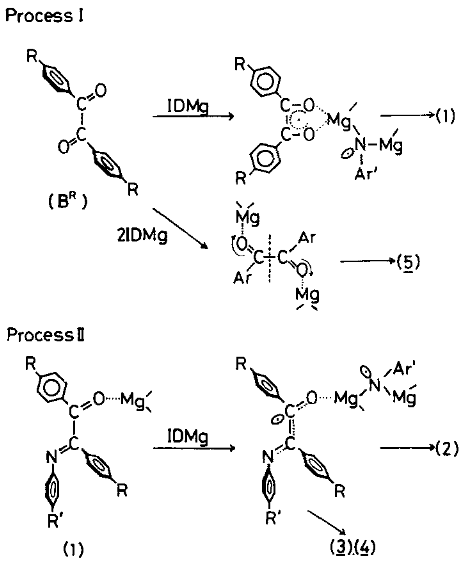
CHARACTERISTICS OF IDMG REACTION WITH BENZILS

For comparison of substituent effects on reaction C2 (Scheme 1), $\mathbf{B}^{R}$ (Ar = p-RC_6H_4; R = MeO, Me, H, Cl) and $\mathbf{N}^{R'}$ (Ar' = p-$R'C_6H_4$; R' = MeO, Me, Cl) were used. Some isolated **1**s were submitted to E_{red} measurement and IDMg reaction. Reaction C2 on a 10^{-3} mol scale was carried out by use of 2·5 and 5·0 molar equivalents of $\mathbf{N}^{R'}$, and the mixtures were heated in THF under fixed conditions. The yields of the main products **1**–**3** and the recovery are affected by the substituents of the reactants and the molar ratio: see Figure 3 [S-series (2·5 mol: S1–S11) and L-series (5·0 mol: L1–L11)].

In comparison with typical reactions (Scheme 2), reactions of benzil (Scheme 1) are unique with respect to the relationship between the mean ΔE value and product yield and the effect of substituents favourable for radical generation and/or yield improvement (indicated in bold type) (see Tables 1 and 2). Whereas comparable ΔE values for B1, B2 and C2 are responsible for the comparable yields of abnormal products,[3e] the higher combined yield of **2** plus **3** in C2 using $\mathbf{B}^{\mathrm{MeO}}$ than those obtain from $\mathbf{B}^{\mathrm{H}}$ and $\mathbf{B}^{\mathrm{Me}}$ indicates class C character.[3a] Reaction A3, in contrast to the examined class A reactions which have comparatively small ΔE values,[3e] gives no abnormal products.[2a] The types of products and results of E_{red} and ESR measurements are described prior to discussion of yield variations.

Types of products in IDMg reactions

Reaction C2 of bifunctional benzil is divided into two main processes, I and II. Their initial stages, involving intermediate radicals, are depicted in Scheme 3. Process I leads to **1** and process II leads to **2** (diimine), **3** and **4** (hydroxyimine); **3** and **4** arise from typical radical pathways (dimerization and abstraction of hydrogen from the solvent) via dissociation of the intermediate radical pair generated by SET to **1**. The yield of **4** (in S8, L8 and L11) is lower than 6%.



Scheme 3

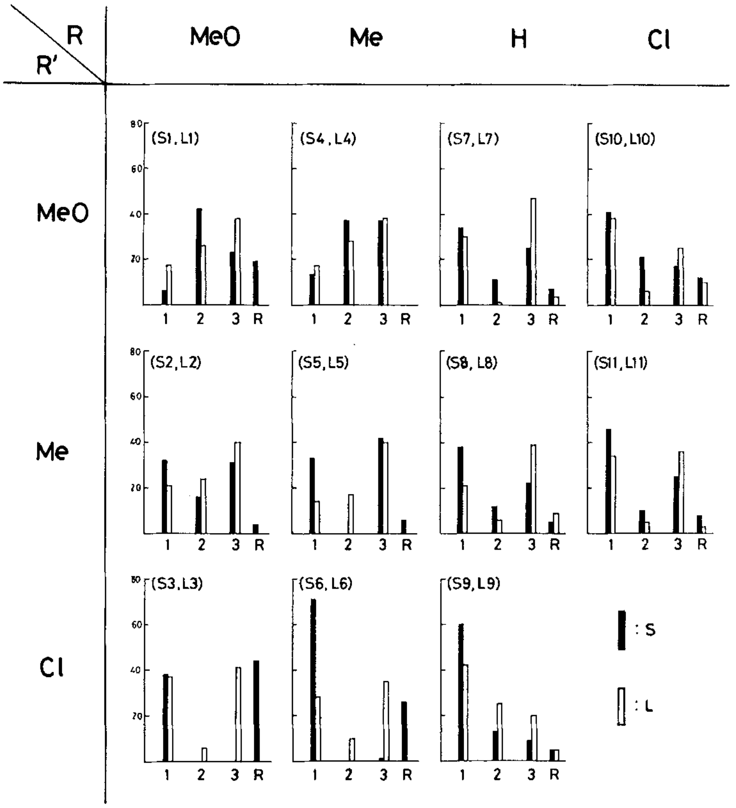


Figure 3. Schematic diagram of relative percentage yields of major products (1–3) (ordinate) and recoveries (abscissa). Runs of S- and L-series are given in the text. Substituents of substrate and reagent are indicated by R and R', respectively

Similarly to reaction A3,[2a] benzoin (or its dimer), expected to arise from benzil itself via a typical radical pathway, was absent. Another type of abnormal product, **5**, in a yield below 10% arising via a bypass of process I, was observed in S7–S11 and L7–L11. The bypass implies double complexation of two oxygen atoms of benzil with Mg atoms of different IDMg molecules; the electron density of the central C—C bond is thus reduced and broken to give **5**. It was undetected when **1** derived from $\mathbf{B}^{\mathbf{H}}$ and $\mathbf{N}^{\mathbf{MeO}}$ was added in a 'normal' manner to a solution of the same reagent, and its yield was lower when 1·5 molar equivalent of $\mathbf{N}^{\mathbf{MeO}}$ was added in a 'reverse' manner to a solution of $\mathbf{B}^{\mathbf{H}}$.

Substituent effect on reduction potentials

The E_{red} (redox) values of $\mathbf{B}^{\mathbf{R}}$ and **1**, measured in THF according to the reported method,[3e] are given below; the reported oxidation (peak) potentials (E_{ox}) of IDMg[3c] are listed for comparison. The smaller negative and positive potential values indicate stronger EAA and EDA, respectively.

$\mathbf{B}^{\mathbf{R}}$ (E_{red}):
R = Me, − 1·43 V; H, − 1·41 V; MeO, − 1·26 V; Cl, − 1·21 V (2,2′-dipyridyl, − 1·41 V);
$\mathbf{N}^{\mathbf{R}'}$ (E_{ox}):[3c]
R′ = MeO, + 0.91 V; Me, + 0.94 V; Cl, + 1·45 V;
1 (E_{red}):
R = R′ = Cl, − 1·45 V;
R = MeO, R′ = CL, − 1·43 V;
R = Cl, R′ = Me, − 1·38 V
R = Me, R′ = Cl, − 1·33 V
R = R′ = Me, − 1·21 V.

Three features of substituent effects on the E_{red} values reflected in the two processes are as follows. (i) The E_{red} values of **1**, comparable as a whole to those of $\mathbf{B}^{\mathbf{R}}$, indicate the comparable SET efficiencies in processes I and II. (ii) The E_{red} value of $\mathbf{B}^{\mathbf{R}}$ varies according to Hammett's σ_m-like order (p-Cl > p-MeO > H > p-Me), which is distinct from the σ_p-like effect of the E_{ox} values of $\mathbf{N}^{\mathbf{R}'}$ (p-Cl > p-Me > p-MeO) and the E_{red} value of nitrobenzenes (p-MeO > p-Me > p-Cl).[3c,3e] (iii) The larger negative E_{red} values of **1**s derived from $\mathbf{B}^{\mathbf{MeO}}$ and $\mathbf{B}^{\mathbf{Cl}}$ *than that of* **1** *derived from* $\mathbf{B}^{\mathbf{Me}}$ *indicate* the participation of resonance due to the better planarity of the p-R^1-benzoyl group of **1** than the same group on the parent $\mathbf{B}^{\mathbf{R}}$. In the intermediate radical generated from **1**, fair planarity of the imino and carbonyl groups is shown by the considerable coupling of unpaired electrons with the imino nitrogen (see below).

Intermediate radicals and stepwise SET (cf. Scheme 3)

Stepwise SET was confirmed by ESR observation of the first and second radicals generated successively in processes I and II, respectively; $\mathbf{B}^{\mathbf{R}}$ (R = H, Me, MeO) and C_6H_5-IDMg ($\mathbf{N}^{\mathbf{H}}$) were used. Signals of the first radicals appeared just after mixing the degassed THF solutions of $\mathbf{B}^{\mathbf{H}}$ and $\mathbf{B}^{\mathbf{Me}}$ with 1·0 or 2·0 molar equivalents of $\mathbf{N}^{\mathbf{H}}$ by breaking the seal at room temperature, the signals (Figure 4a and c) being observable for ca 30 min after mixing. The hyperfine splitting constants (a_H, Table 3) are smaller than those of benzophenone ketyls[2a,15],

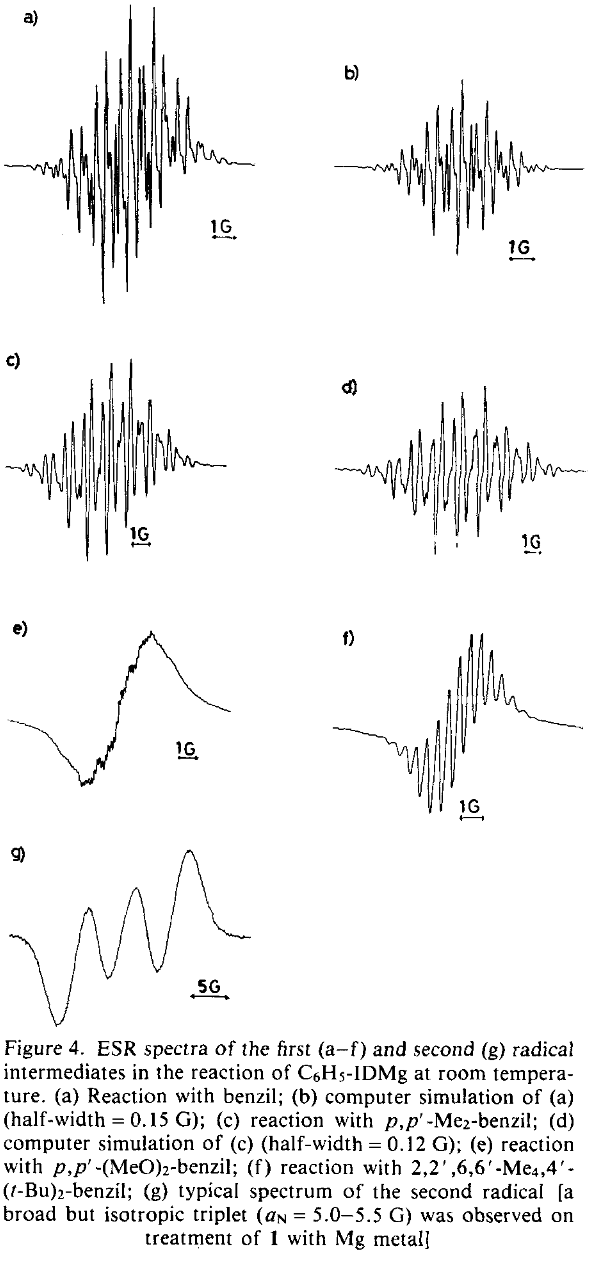


Figure 4. ESR spectra of the first (a–f) and second (g) radical intermediates in the reaction of C_6H_5-IDMg at room temperature. (a) Reaction with benzil; (b) computer simulation of (a) (half-width = 0.15 G); (c) reaction with p,p'-Me$_2$-benzil; (d) computer simulation of (c) (half-width = 0.12 G); (e) reaction with p,p'-(MeO)$_2$-benzil; (f) reaction with 2,2′,6,6′-Me$_4$,4′-(t-Bu)$_2$-benzil; (g) typical spectrum of the second radical [a broad but isotropic triplet (a_N = 5.0–5.5 G) was observed on treatment of **1** with Mg metal]

Table 3. Hyperfine splitting constants (HFS) of first radicals generated in the reactions of benzils (**B**^{H} and **B**^{Me}) with C_6H_5-IDMg (**N**^{H})

	HFS (G)			
Benzils	a_p	a_o	a_m	a_{Me}
Unsubstituted (**B**^{H})	0·98	0·98	0·40	—
p,p′-Me$_2$-(**B**^{Me})	—	0·95	0·40	1·08

indicating the reduced and elevated densities of unpaired electrons on the aryl and —CO—CO— groups, respectively, and are assigned to chelated radicals.

The first radical generated from **B**^{MeO} gave a broad spectrum (Figure 4e) unresolved even on extreme dilution of the sample solution, and no splitting assignable to a_H was observed; the breadth was attributable to overlap of a signal of a slightly dissociated arylaminyl radical (see later).[3d] Instead, the weak and narrow sextets observed are assigned to the coupling with an Mg atom ($a_{Mg} = 0{\cdot}15$ G; G = 10^{-4} T). Its observation is due to tighter chelation that those of the first radicals generated from **B**^{H} and **B**^{Me}.

All the first radicals decayed gradually in 30–60 min at room temperature, and a signal of the second radical having a broad triplet (Figure 4g) appeared; the triplet are assigned to coupling with the imino nitrogen of **1**. The a_N value (5·0–5·5 G) is distinctly smaller than those reported for arylaminyl radicals ($a_N = 9{\cdot}8$–$11{\cdot}0$ G),[3d] and slightly anisotropy of the signals indicates overlap of the weak signal of arylaminyl radical. The second radicals were observable for 3–5 h by use of 2·0–3·0 mol of IDMg, whereas 5·0 mol caused fairly rapid decay.

Crowded 2,2′,6,6′-Me$_4$-4,4′-(*t*-Bu)$_2$-benzil gave **1** quantitatively on treatment with 2·5 mol of **N**^{H} and **N**^{Cl}. A spectrum having thirteen lines (Figure 4f; $a_H = 0{\cdot}40$ G) due to equal coupling with four Me groups indicates that the first radical participates in normal product formation. The second radical, also giving a broad triplet signal, did not decay to reach a high concentration. The succeeding step is sterically inhibited, similarly to the case with Grignard ketyls generated from crowded benzophenones.[16]

Product yield governed by SET efficiency and chelation

The roles of E_{red} and σ-complexation are discussed first. The σ_m dependence of E_{red} of **B**^{R} indicates a lack of electron-repelling resonance due to a *trans* and non-planar conformation in the free state. For the generation of a more or less resonance-stabilized chelated radical from **B**^{R}, a conformational change accompanying SET is required. The substituent shift of E_{red} of **B**^{R} caused by adduct formation with $MgBr_2$[3a] was undetermined because the adduct precipitated; however, in the case of **B**^{MeO}, strong EAA and resonance stabilization must cooperate in the initial stage of process I.

Chelation, i.e. fairly efficient σ-complexation, assists condensation in process I at the expense of abnormal products. In process II, however, only one oxygen atom of **1** is available for σ-complexation, giving rise to the frequent formation of **3** (cf. Scheme 3), similarly to typical reactions in Scheme 2. In contrast, reaction A3 is assisted throughout by chelation with unremoved oxygen, leading to complete stepwise addition[2a] regardless of the small ΔE. A hybrid ⟨A + C⟩ character could be ascribed to A3 and ⟨B + C⟩ to C2. Pinacol formation from ketone solely by Mg metal is evoked.

The variation of the yields of **1**–**3** (Figure 3) can be explained. The combined yield of **2** plus **3** versus **1** reflects the actual efficiency of SET and σ-complexation in the two processes, and the relative yield of **2** versus **3** reflects the tightness of σ-complexation responsible for condensation in process II. Four features of the variations in yield are noted, as follows. (a) The major product in run S1 is **2** whereas that in run S10 is **1**, indicating that condensation in process II is more favoured by the *p*-MeO than the *p*-Cl group of **1**, regardless of the comparable E_{red}. (b) The high yield of **2** obtained by use of reactants having MeO and/or Me groups (S1 and S4) indicates cooperation of tight σ-complexation and the small ΔE required for stepwise condensation. (c) Weakening of EDA by the change in the substituent in IDMg from MeO via Me to Cl in both the L- and S-series leads to an increase in the relative yield of **1** versus **2** plus **3** at the expense of the yield of **2** versus **3**.[3c] (d) The higher yield of **3** versus **2** in the L-series than that in the S-series is due to the more efficient SET from the large amount of IDMg causing too rapid consumption of **1** in process II.

The behaviour of **1** in process II is more or less modified by the effect of some *a priori* bound Mg salts, as indicated by comparison with the results of the reaction of three isolated **1**s (R=MeO, R′=Cl; R=R′=Me; R=R′=Cl) with 2·5 mol of IDMg having a substituent with the same R′. The recovery of **1** and the yields of **2** and **3** were 0, 81, 0%; 0, 21, 65%; and 95, 0, 0%, respectively: first, almost exclusive formation of **2** due to efficient σ-complexation with the *p*-MeO-benzoyl oxygen of **1** regardless of the large ΔE (S3 and L3: considerably modified); second, no recovery of **1** and efficient formation of **3** over **2** due to the strong EDA and EAA (S5 and L5: slightly modified); and third, nearly complete recovery of **1** due to weak EDA and EAA.

Additional remarks

Explicit ESR observation and no observation of reagent radicals under ordinary conditions in class C and B reactions, respectively, have been described. Previous results are listed in Table 2. In A3 and B1, a reagent radical was explicitly unobservable, and the formation of an aggregate including a diamagnetic dimer of RMgBr cation radical was concluded from the effect of the bulkiness of the Grignard alkyl group on a_H values of intermediate ketyl radicals.[2a,2c] Also in B2, an arylaminyl radical is explicitly unobservable.[3b] Overlap of the signal of the arylaminyl radical in C2 is suggested above, and the same radical was explicitly observed in C1 although in low concentration.[3d] The existence and non-existence of pre-interaction between reactants due to small and large ΔE in B1 and C1, respectively, were proposed to relate the results obtained with the different types of abnormal products.[3d] ⟨B1⟩: pre-interaction → oligomer $(RMgX)_n$ formation → SET from oligomer → 'free spin delocalization in oligomer' (no explicit observation of reagent radical) → dimeric $(AR_2C(OH){-})_2$. ⟨C_1⟩: no pre-interaction → σ-complex formation → SET in σ-complex → dissociation of radical pair (explict observation of reagent radical) → monomeric Ar_2CHOH.

The suggestion of free spin delocalization[3d] is revised by cation radical dimer formation,[2a] which is still explainable by the 'pre-interaction prior to SET'. In any event, a 'σ-complexation-controlled character' (Table 1) is required for ESR observation of reagent radicals, although in low concentration. The hybrid character of C2 is reflected in overlap of the signal of the aminyl radical being seemingly dependent on the tightness of the chelate or σ-complex.

2,2′-Dipyridyl, having a larger negative E_{red} value than expected from the effect of the electron-deficient pyridine ring,[17] behaves in the IDMg reaction in line with the above discussion. Under the conditions of the S- and L-series using $\mathbf{N}^{\mathbf{Me}}$, a large amount of unidentified black material was formed owing to vigorous SET (cf. Table 1); solely pyridine-2-*N*-(*p*-methylphenyl) carboxamide (ca 35%) corresponding to **5** was identified. Vigorous SET, reflecting the effect of the pyridine ring, arises from conformational changes, probably via double chelation by the two sets of carbonyl oxygen and pyridyl nitrogen (similar to the double complexation proposed in Scheme 3), leading to facile C—C bond breaking. The monoimine corresponding to **1** was obtained under mild conditions using 'reverse addition' of 1·25 molar equivalent of $\mathbf{N}^{\mathbf{Me}}$ to a solution of dipyridyl at −20 °C followed by stirring at 0–15 °C.

CONCLUSION

In terms of the EDA–EAA concept regarding the initial stages of the main processes of the reaction of IDMg with benzil, the characteristics governing the relative yields of the products are as follows: (i) the reaction involves two SET steps having medium efficiency corresponding to that of typical class B reactions; and (ii) as the modification factor depends on substituent effects, class C character operates strongly in process I and moderately or weakly in process II.

The Marcus approach, based on kinetic measurements, is useful for evaluating SET reactions in terms of ΔG^0 values estimated from oxidation and reduction potentials of the reactants.[10] Usually in a Marcus plot, log k vs ΔG^0 is linear for small ΔG^0 values and deviates parabolically downwards at large ΔG^0 values according to a 'reorganization factor'.[4a,10] The EDA–EAA approach based on product analyses has an identical basis, i.e. ΔE value, and the modification in terms of class C character (participation of σ-complexation) in the high ΔE region (cf. C1) corresponds to a Marcus deviation. An example of modification in the low ΔE region is presented. The initial and later stages of the reactions of magnesium reagents should be estimated separately, and the kinetic features of A3 and B1 (lowest rate of radical transfer)[2b] should not be oversimplified. Whether or not the chelation (or σ-complexation) precedes SET in the initial stages was undetermined, but the elaborated EDA–EAA approach plays a role in the field of structure–reactivity relationships concerning reactions involving SET.

EXPERIMENTAL

Materials and procedures. Symmetrical benzils having methyl and methoxy substituents were prepared by benzoin condensation of the corresponding benzaldehydes followed by oxidation using copper(ii) sulphate in pyridine.[18] 4,4′-Dichlorobenzil was prepared by the Friedel–Crafts reaction of 4-chlorophenylacetyl chloride with chlorobenzene followed by oxidation with SeO_2.[19] 2,2′6,6′-Me_4-4,4′-(*t*-Bu)$_2$-benzil was prepared by the coupling reaction of the corresponding acid chloride using 2-propylmagnesium iodide.[20] The Grignard and IDMg reagents and $MgBr_2$ etherate were prepared in the usual manner. The substrates used in the heat measurements were commercially available and/or previously prepared (cf. D1[8]).

The IDMg reactions were carried out by adding benzils (0.002 mol) dissolved in THF (10 ml) to a given amount of IDMg in the same solvent (30 ml), and the mixture was stirred at 55 °C for 6 h. After quenching at 0 °C with concentrated aqueous NH_4Cl, the product mixture was separated by column chromatography on silica gel (Wako Gel C-200, C-300 and FC-40). The elemental analyses of the products gave satisfacotyr results; the melting points (uncorrected) and ^{1}H NMR data are summarized in Table 4.

The reduction potentials of benzils and monoimines were determined in THF by cyclic voltammetry by use of platinum and silver electrodes, bis(biphenyl)chromium(I) tetraphenylborate (BCTB) as an internal standard and Bu_4NClO_4 as supporting electrolyte.[3c,3e] ESR

Table 4. Melting points and ^{1}H NMR data of products formed in reaction C2 (Scheme 1: Ar = p-RC$_6$H$_4$; Ar′ = p-R′C$_6$H$_4$)

Product				
No.	R	R′	Mp (°C)	^{1}H NMR: δ (ppm)
1	MeO	MeO	Oil	7·84–7·64(4H, m), 6·92–6·56(8H, m), 3·77(3H, s), 3·72(3H, s), 3·60(3H, s)
	MeO	Me	Oil	7·82–7·56(4H, m), 6·92–6·64(8H, m), 3·78(3H, s), 3·73(3H, s), 2·17(3H, s)
	MeO	H	Oil	8·06–7·66(5H, m), 7·25–6·62(8H, m), 3·75(3H, s), 3·68(3H, s)
	MeO	Cl	Oil	7·98–7·69(4H, m), 7·12–6·43(8H, m), 3·80(3H, s), 3·76(3H, s)
	Me	MeO	Oil	7·92–7·64(4H, m), 7·32–7·08(4H, m), 6·92 and 6·66(4H, ABq, J = 8·0 Hz), 3·63(3H, s), 2·38(3H, s), 2·30(3H, s)
	Me	Me	Oil	7·90–6·80(12H, m), 2·47(3H, s), 2·40(3H, s), 2·27(3H, s)
	Me	H	85·6–86·0	7·79–6·60(13H, m), 2·36(3H, s), 2·28(3H, s)
	Me	Cl	100·0–101·0	7·81–6·90(12H, m), 2·38(3H, s), 2·33(3H, s)·
	H	MeO	121·0–121·5	7·88–6·81(14H, m), 3·68(3H, s)
	H	Me	113·0–114·0	7·88–6·79(14H, m), 2·18(3H, s)
	H	Cl	87·5–88·0	7·88–7·39(10H, m), 7·09 and 6·82(4H, ABq, J = 8·8 Hz)
	Cl	MeO	Oil	7·78 and 6·69(4H, ABq, J = 9·2 Hz), 7·67 and 7·31 (4H, ABq, J = 8·6 Hz), 7·39 and 6·88(4H, ABq, J = 8·5 Hz), 3·69(3H, s)
	Cl	Me	Oil	7·79 and 7·41(4H, ABq, J = 8·5 Hz), 7·67 and 7·31(4H, ABq, J = 9·2 Hz), 6·95 and 6·79(4H, ABq, J = 8·2 Hz), 2·20(3H, s)
2	MeO	MeO	143·2–145·0	7·86 and 6·89(8H, ABq, J = 8·4 Hz), 6·69(8H, s), 3·83(6H, s), 3·73(6H, s)
	MeO	Me	152·3	7·80 and 6·80(8H, ABq, J = 8·8 Hz), 6·73 and 6·14(8H, ABq, J = 8·8 Hz), 3·78(6H, s), 2·24(6H, s)
	MeO	H	149·0–149·2	7·96–7·69(4H, m), 7·26–6·85(12H, m), 6·56–6·45(2H, m), 3·84(6H, s)
	MeO	Cl	139·0–140·0	7·78 and 6·82(8H, ABq, J = 8·8 Hz), 7·00 and 6·37(8H, ABq, J = 8·4 Hz), 6·50–6·40(4H, m), 3·82(6H, s)
	Me	MeO	160·1–163·4	7·86 and 7·22(8H, ABq, J = 8·0 Hz), 6·64(8H, s), 3·66(6H, s), 2·34(6H, s)
	Me	Me	146·0–148·0	7·74 and 7·10(8H, Abq, J = 8·0 Hz), 6·84 and 6·44(8H, ABq, J = 8·0 Hz), 2·47(6H, s), 2·33(6H, s)
	Me	H	145·0–146·0	7·84–6·34(18H, m), 2·39(6H, s)
	Me	Cl	215·0–215·5	7·78 and 7·22(8H, ABq, J = 8·0 Hz), 7·06 and 6·46(8H, ABq, J = 8·4 Hz), 2·20(6H, s)
	H	MeO	166·0–167·0	7·87–6·61(18H, m), 3·82(6H, s)
	H	Me	—	—
	H	Cl	168·0–168·5	7·87–7·32(10H, m), 7·05 and 6·45(8H, ABq, J = 8·8 Hz)
	Cl	MeO	167·0–167·5	7·76 and 7·32(8H, ABq, J = 8·8 Hz), 6·72 and 6·65(8H, ABq, J = 8·8 Hz), 3·72(6H, s)
	Cl	Me	172·0–172·5	7·77 and 7·34(8H, ABq, J = 8·8 Hz), 6·90 and 6·53(8H, ABq, J = 8·3 Hz), 2·25(6H, s)
3	MeO	MeO	183·0	8·10–7·95(4H, d), 7·50–7·22(8H, m), 6·90–6·70(14H, m), 3·86(6H, s), 3·82(6H, s), 3·73(6H, s)
	MeO	Me	152·3	7·88(4H, d), 7·36–7·12(8H, m), 7·00–6·64(14H, m), 3·77(6H, s), 3·74(6H, s), 2·20(6H, s)
	MeO	H	211·0–212·0	8·64(4H, d), 8·10–6·85(24H, m), 3·90(12H, s)
	MeO	Cl	214·0–215·0	7·92–7·82(4H, m), 7·32–7·08(14H, m), 6·83–6·69(8H, m), 3·82(6H, s), 3·78(6H, s)
	Me	MeO	233·1–236·5	7·96(4H, d), 7·52–7·10(16H, m), 6·88–6·74(4H, m), 3·77(6H, s), 3·35(6H, s), 2·31(6H, s)
	Me	Me	218·0–221·0	8·95–8·83(2H, m), 7·97–7·83(3H, m), 7·36–6·92(18H, m), 6·68–6·59(3H, m), 2·34(6H, s), 2·26(6H, s), 2·20(6H, s)
	Me	H	201·0–203·0	7·80–7·20(28H, m), 2·27(6H, s), 2·33(6H, s)
	Me	Cl	—	—
	H	MeO	189·0 (sublm.)	8·01–6·81(28H, m), 6·96(2H, s), 3·75(6H, s)
	H	Me	178·0 (sublm.)	8·09–7·11(28H, m), 6·96(2H, s), 2·29(6H, s)
	H	Cl	195·0 (sublm.)	7·97–7·21(28H, m), 7·12(1H, s), 7·11(1H, s)
	Cl	MeO	206·0 (sublm.)	7·90–6·76(24H, m), 6·69(1H, s), 6·68(1H, s), 3·75(6H, s)
	Cl	Me	226·0 (sublm.)	7·92–7·01(24H, m), 6·94(2H, s), 2·29(6H, s)

(*Continued*)

Table 4. (*continued*)

Product				
No.	R	R′	Mp (°C)	^{1}H NMR: δ (ppm)
4	H	Me	144·0–144·5	8·00–6·54(14H, m), 6·00(1H, s), 5·25(1H, s), 2·19(3H, s)
5	H	MeO	161·0–161·5	13·8(1H, s), 8·99–6·69(18H, m), 3·74(3H, s), 3·67(3H, s), 1·60(1H, s)
	H	Me	194·0–195·0	14·0(1H, s), 8·92–6·57(18H, m), 2·24(3H, s), 2·20(3H, s), 1·59(1H, s)
	H	Cl	202·0–202·5	13·8(1H, s), 9·02–6·64(18H, m), 1·57(1H, s)
	Cl	MeO	179·0–180·0	13·7(1H, s), 8·92–6·63(16H, m), 3·78(3H, s), 3·70(3H, s)
	Cl	Me	202·5–203·0	13·9(1H, s), 8·88–6·57(16H, m), 2·28(3H, s), (2·22(3H, s)

spectra of intermediate radicals were recorded according to the reported method,[3d] and hyperfine splitting constants of the first radicals generated from benzil and *p,p′*-Me_2-benzil (Table 3) were determined by computer simulation.

Heat measurements. The temperature–time plots shown in Figures 1 and 2 were obtained by use of an apparatus for the measurement of freezing-point depressions for molecular weight determinations. An air-jacketed sample tube equipped with a Beckmann thermometer was purged with nitrogen and placed in a water-bath. Its temperature was maintained at ca 15 ± 0·01 °C using a circulating thermostat. A 0·003-mol amount of substrate dissolved in 15 ml of THF was introduced into the sample tube and 15 ml of the reagent solution (0·30 M) were introduced into a purged reservoir tube and placed in the same water-bath. After the temperature of the two solutions had equilibrated by standing for about 40 min, a 10-ml portion of the reagent solution was quickly removed under nitrogen and added to the sample tube with vigorous stirring. The temperature shown by the thermometer was recorded at time intervals of 30 s.

The plots in Figure 1 were treated as follows. The area enclosed by each curve, copied on paper of good quality, was cut out and weighed. The weight was normalized by use of a reference obtained by weighing an arbitrary area of the same paper. The dimensionless values of ΔH thus obtained were taken as the relative amounts of heat evolved in the individual combinations of reactants. For simplicity, the greatest ΔH value was defined to be 7·0, the same as the maximum temperature (ΔT_{max}), both being observed in the A2 combination. For all the plots, ΔH showed a satisfactorily linear relationship with ΔT_{max} values.

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