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Aryliminodimagnesium Reagents. IX. The Reaction with Benzophenones. The Mechanism of Coordination and Electron Transfer Processes Distinct from That of Grignard Reaction

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In the reaction of aryliminodimagnesium reagents($ArN(MgBr)_2$, Ar=C_6H_5, *p*-MeC_6H_4, and *p*-$MeOC_6H_4$) with some *p*-substituted benzophenones, the arylaminyl radicals($Ar\dot{N}MgBr$) derived from the reagents were detected by ESR in low concentrations and identified by computer simulation. From comparison of all the itemized facts characteristic of the reaction with those of Grignard reaction of the same substrates, the mechanisms of initial coordination and electron transfer of the two reactions were distinguished.

Aryliminodimagnesium reagents($ArN(MgBr)_2$, aryl-IDMg) condense with diaryl ketones.[1,2] When the reagent has *o*-Me group, diarylmethanol is obtained as the sole abnormal product arising from ketyl radical *via* hydrogen abstraction from solvent.[2] In this paper, the identification of arylaminyl radical produced from IDMg reagent in the reaction with *p*-substituted benzophenones will be described first. On the basis of the fact that electron transfer is involved in both IDMg and Grignard[3] reactions with benzophenones, all the facts characteristic of each reaction will be itemized and compared. The distinctive mechanisms, consistent with the respective facts, for the initial processes of the two reactions will be proposed.

Results and Discussion

Identification of Arylaminyl Radicals. The ESR measurements were carried out at room temperature under the conditions similar to those of preparative reactions.[1,2] The benzophenones used are 4,4′-disubstituted ones, the substituents being Me_2N, MeO, Me, and Cl groups. The concentration of unsubstituted and *p*-substituted phenyl-IDMg reagents was 0.02 M[†] and the molar ratio of reagent to substrate was 2:1. The degassed and sealed solutions of reagent and substrate in tetrahydrofuran(THF) were mixed by breaking the seal.[3] The radical concentrations observed in this study were quite lower compared with those observed in the reactions with ArMgBr;[3] a high microwave power and a large modulation width(2.00 G, G=10^{-3} T) were supplied for obtaining the sufficient intensity of signals. The typical spectra obtained in the reactions of 4,4′-bis(dimethylamino)benzophenone with phenyl- and *p*-methoxyphenyl-IDMg are shown in Figs. 1a₁ and 1b₁, respectively. The spectra are incompletely resolved and slightly anisotropic, and the resolution was unimproved by dilution in the evacuated sample cell.

For the analysis of spectra 1a₁ and 1b₁, computor simulation with half width of 3.5 G was carried out by use of Lorentzian curve. The Mg-ketyl of the ketone was prepared by use of Mg–Hg amalgam; its ESR signal, observed under the same conditions of measurement, was simulated and overlapped with the simulated spectra of arylaminyl π-radicals,[4] $C_6H_5\dot{N}X$ and *p*-$MeOC_6H_4\dot{N}X$: The resultant spectra are shown

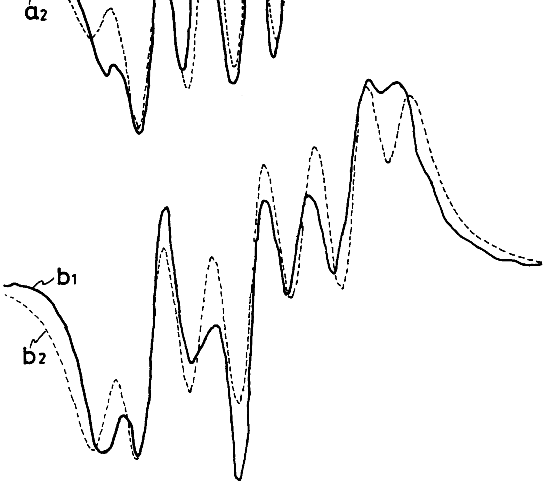


Fig. 1. ESR spectra of the mixtures of arylaminyl and ketyl radicals formed in the reaction of *p,p*′-$(Me_2N)_2$-benzophenone with IDMg reagents.
a_1: Observed in the reaction with C_6H_5–IDMg,
a_2: Simulated without 3.0 G shift of Mg–ketyl signal,
b_1: Observed in the reaction with *p*-$MeOC_6H_4$–IDMg,
b_2: Simulated without 3.0 G shift of Mg–ketyl signal.

[†] 1 M=1 mol dm^{-3}.

in Figs. 1a$_2$ and 1b$_2$, respectively. In both cases, the remarkable deviations are observed in two areas: The one at the left near to the center and the other near to the right end of each spectrum. The former deviation is ascribed to the slightly different *g*-factor of IDMg–ketyl from that of Mg–ketyl, since the best fits of 1a$_2$ and 1b$_2$ with 1a$_1$ and 1b$_1$, respectively, are obtained when the simulated signal of Mg–ketyl is shifted to the lower field by 3.0 G: The difference of *g*-factor originates from the presence of bromine atom combined to Mg atom of IDMg–ketyl. The latter deviation is ascribed to the decay of radicals during the course of scanning.

The spectrum observed in the reaction of the same ketone with *p*-methylphenyl–IDMg was simulated similarly. The values of splitting constans and *g*-factors given in Table 1 are reasonable as compared to those of various types of arylaminyl π-radicals($Ar\dot{N}X$: Ar=*t*-Bu, O-*t*-Bu, and H) reported previously.[5–7] The attempt to observe triplet state at 77 K was unsuccessful: The observed spectra are assignable to the mixtures of arylaminyl($Ar\dot{N}MgBr$) and ketyl ($Ar'_2\dot{C}OMgBr$) radicals interacting, if any, quite weakly with each other.

When the substituent on reagent is fixed, the shape of spectrum remains almost independent of the substituent on substrate, which, however, causes the gradual decrease in the signal strength according to the order: $Me_2N>MeO>Me>H>Cl$.[8] Since no diarylmethanol was detected, the observation implies that the electron-repelling substituent assists the substrate in rate-determining coordination of carbonyl oxygen to Mg atom of reagent and the resultant acceleration of electron transfer leads to the effective condensation(*vide infra*).[2,9]

Mechanistic Distinction between Grignard and IDMg Reactions. The electron transfer from reagent to substrate is involved in pathways for the formation of normal products in the reactions of benzophenone with both ArMgBr(***C***) and $ArN(MgBr)_2$(***N***): This is revealed not only by ESR measurement but also by use of *o*-Me-substituted reagents, which give rise to the increase in yields of abnormal products.[2,3] The coordination of carbonyl oxygen to Mg atom of reagent (or σ-complex formation, process I) due to the strong affinity of magnesium for oxygen, in addition to the subsequent electron transfer (process II), is also common to the two reactions. Accordingly, the itemized facts characteristic of the reactions observed in the previous and present studies (Table 2,

TABLE 1. HYPERFINE SPLITTING CONSTANTS AND *g*-FACTORS OF ARYLAMINYL RADICALS DERIVED FROM IDMg REAGENTS IN THE REACTION WITH 4,4′-BIS(DIMETHYLAMINO)BENZOPHENONE

Reagents	hfs/G (G = 10^{-3} T)					*g*-factors
	a_N	$a_{p\text{-}H}$	$a_{o\text{-}H}$	$a_{m\text{-}H}$	a_{CH_3}	
$C_6H_5N(MgBr)_2$	9.80	5.75	5.20	0.73	—	2.0031
p-$CH_3C_6H_4N(MgBr)_2$	10.50	—	5.20	1.10	5.20	2.0031
p-$CH_3OC_6H_4N(MgBr)_2$	11.00	—	5.00	0.50	—	2.0031

TABLE 2. ITEMIZED FACTS CHARACTERISTIC OF THE REACTIONS OF BENZOPHENONE WITH IDMg AND GRIGNARD REAGENTS

	Items	$ArN(MgBr)_2$ (***N***)	ArMgBr (***C***)
[*a*]	Manner of Reaction	Condensation	Addition
[*b*]	Classification[i]	Type C	Type B
[*c*]	Favorable Substituents on Substrate	*p*-Me_2N, *p*-MeO	*p*-F, *p*-Cl
[*d*]	Abnormal Products		
	from Substrate	Diarylmethanol	TPE-diol[iv]
	from Reagent	Aniline	Biaryl
[*e*]	Character of Reagent		
	Oxidation Peak Potential[ii]	High	Low
	EDA	Weak	Strong
[*f*]	Radicals Observed at r.t.		
	from Substrate	Ketyl ○	Ketyl ◎
	from Reagent	Arylaminyl ○	Aryl ×
	Concentration	Low	High
[*g*]	Rate-determining Process[iii]	Coordination	Electron Transfer

i) Type A includes the reactions which are hardly controllable due to vigorous electron transfer.[9] ii) Ref. 11). iii) See text. iv) 1,1,2,2-Tetraphenylethan-1,2-diol.

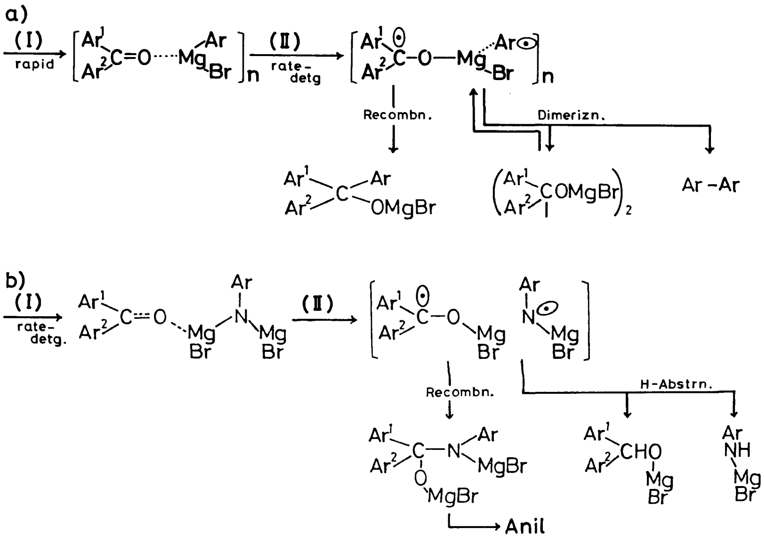
[*a*—*g*]) are helpful in distinguishing the mechanisms from each other.

The fundamental fact for the distinction is that *one of the two initial processes is rate-determining*[*g*] and the subsequent ones for product formation are not. The rate-determining nature of process II in the reaction of ***C***[*g*] established by the thermochemical study of Holm[10] was confirmed by acceleration of ketyl formation by *p*-F- and *p*-Cl-substituents on benzophenone[*c*].[3,9] The rate-determining nature of process I in the reaction of ***N***[*g*] is suggested from the fact that *p*-Me$_2$N and *p*-MeO substituents on benzophenone favor the formation of products[*c*],[2,9] and is verified by the substituent effect on radical concentration. The rate-determining process moves between I and II depending on the electron-donating abilities(EDA) of reagents:[9] The weaker EDA of ***N*** than that of ***C***[*e*] is estimated by polarographic measurement of oxidation potentials.[11] On this basis, the mechanism of initial processes leading to the *monomeric* diarylmethanol in IDMg reaction is distinguished from that leading to the *dimeric* 1,1,2,2-tetraphenylethan-1,2-diol(TPE-diol) in Grignard reaction[*d*].

Since process II of the reaction of ***C*** is rate-determining, process I proceeds rapidly but incompletely. The "incomplete coordination" is substantiated by considering the two previous observations: The oligomeric aggregation of reagent molecules in the presence of oxygen-containing substances[12] and the presence of equilibrium between Grignard-ketyl and Mg–TPE–diolate[3,13] (Scheme 1a). The aggregation is best ascribed to the prior interaction of benzophenone molecules with ***C*** having strong EDA[*e*], and *the electron transfer from aggregated reagent molecules* give rise to production of Grignard-ketyls in the neighborhood of each other. This favors the formation of Mg–TPE–diolate[*d*], the equilibration with it being responsible for the ESR observation of long-lived Grignard-ketyl in moderately high concentration[*f*]. Aryl radicals, produced inside the reagent aggregate, are hardly observable by ESR[*f*] due to the favorable formation of biaryl[*d*] and also probably due to the delocalization of unpaired electrons in the aggregate.

In the reaction of ***N***, process II proceeds after the rate-determining σ-complex formation (process I) has been at least nearly completed[*g*]. The complex formation assists the substrate in lowering its HOMO and LUMO energy levels[8,14] and accepting electrons from ***N*** having weak EDA[*e*]. From the "complete σ-complex" surrounded by solvent molecules, both IDMg–ketyl and arylaminyl radicals are produced in monomeric states: They are thus short-lived and detectable in quite low concentration[*f*]. Most part of the two kinds of radicals recombine with each other leading to the formation of anil[1,2] (Scheme 1b), but a part of them abstracts hydrogen from solvent[*d*] especially when the radical recombination is retarded by *o*-Me substituent.[2]

The essential roles of processes I and II in the reactions of ***N*** and ***C***, respectively, are exemplified by the distinctive behaviors of the reagents towards sterically hindered 2,3,5,6-tetramethylbenzophenone. On the treatment with ***N***, neither ESR signal nor coloration of the mixture indicative of σ-complex formation is observed and the ketone is recovered unchanged. On the treatment with ***C***, in contrast, the ketyl accumulates gradually up to a very high concentration.[3] Whereas ***N*** having weak EDA is unable to transfer electrons *because the σ-complex formation is inhibited,* ***C*** having strong EDA transfers electrons *even though the coordination is incomplete.* The previous postulate on the possibility of produc-



Scheme 1.

tion of "benzophenone anion radical" prior to the O–Mg bond formation in the reaction of ***C*** resembles the discussion given above. However, the aggregate formation, supposed in the earliest paper on Grignard-ketyls,[16] is verified to be essential in the reaction of ***C*** due to its strong EDA.

Experimental

Materials and Procedures. Benzophenone and aniline as well as their substituted derivatives were commercially available, and were purified by recrystallization or distillation if necessary. The preparation of stock solutions of reagents[1] and ESR measurements[3,16] were carried out according to the reported procedures.

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