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The Metalation of Fluorene by Means of the Diethylmagnesium-Hexamethylphosphoramide System

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The metalation of fluorene by means of the Et_2Mg–HMPA system was investigated. The reaction scarcely occurred at all when the mole ratio of HMPA: Et_2Mg fell below 1 : 1, but it proceeded easily when the ratio was over 1 : 1, and a solvent-separated ion pair of magnesium fluorenide was formed. When the ratio was 2 : 1, the order of reaction was unity in both fluorene and Et_2Mg. It was demonstrated by the kinetic and NMR studies that the active species of metalation in such a case was not Et_2Mg but the Et_2Mg–HMPA complex, in which two molecules of HMPA are coordinated to Et_2Mg.

In recent years dipolar solvents, especially dipolar aprotic solvents, have frequently been used as media or reactants for organic reactions. Previously we[1)] ourselves reported that Grignard's reagent (RMgX) could not polymerize styrene in toluene, but that high-molecular polystyrene could be obtained when hexamethylphosphoramide (HMPA) existed in over twice the molar quantity of RMgX. It was demonstrated that RMgX was changed to an ionic form, *i.e.*, carbanion, by the coordination of HMPA, and that the initiation reaction proceeded by means of the addition of the carbanion to the styrene monomer. In this paper, the metalation of fluorene by means of the diethylmagnesium–HMPA system will be investigated in order to make clear the role of HMPA in organomagnesium compound–HMPA systems. Normant[2)] has already reported the metalation of fluorene by isopropylmagnesium chloride in HMPA, but the mechanism of the reaction has not yet been studied.

Experimental

Reagents. Fluorene (FL) was purified by recrystallization from ethanol. A solution of diethylmagnesium (Et_2Mg) was prepared by adding dioxane to an ether solution of ethylmagnesium bromide. The concentration of the solution of Et_2Mg was determined by acid-base titration.[3)] HMPA was refluxed and distilled over calcium hydride *in vacuo*.

Metalation Reaction. The reaction of FL with Et_2Mg was done in 0.2 cm optical cells under an atmosphere of nitrogen. Et_2Mg in ether was added to a toluene solution of FL, and at last HMPA in toluene was introduced into the reaction system. Within two min of the mixing of the reagents, the cell was placed in a Hitachi EPS-3T recording spectrophotometer and the optical density at 373 nm was monitored as a function of the time. The absorption at this wavelength is due to the product, fluorenyl carbanion.

Measurement of the NMR Spectrum. The NMR spectrum of the Et_2Mg–HMPA system in ether was taken with a JNM C-60H spectrometer at room temperature, using teramethylsilane as the internal standard.

Results and Discussion

Electronic Spectrum of the Reaction Product. In the absence of HMPA, scarecely no reaction of FL and Et_2Mg in toluene or tetrahydrofuran (THF) occurred. However, the reaction easily proceeded in the presence of HMPA, and fluorenyl carbanion (FL^-) was formed. Figure 1 shows the spectra of the reaction product and fluorenyllithium in THF. The absorption spectrum of magnesium fluorenide has a peak at 373 nm. This peak has been assigned by Hogen-Esch and Smid[4)] to the solvent-separated ion pair of alkali fluorenides in ethereal solvents. The spectrum of magnesium fluorenide in the visible region was similar to that of the solvent-separated ion pair of fluorenyllithium. These results indicate that the magnesium fluorenide produced in the presence of HMPA exists as a solvent-separated ion pair.

The NMR spectrum[5)] of magnesium fluorenide produced by the reaction of FL with equimolar quantities of Et_2Mg at $[HMPA]/[Et_2Mg]=3$ indicated that the

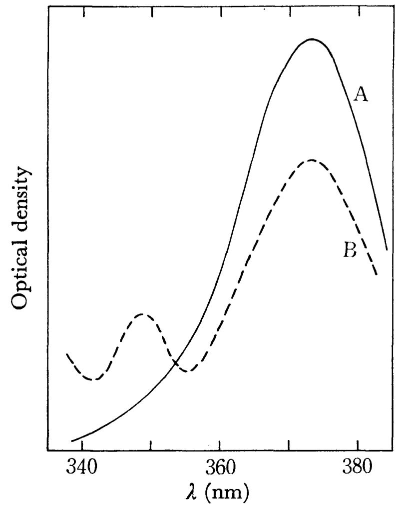

Fig. 1. Absorption spectra of lithium and magnesium fluorenides.
A: Magnesium fluorenide produced by the reaction of FL with Et_2Mg at $[Et_2Mg]/[HMPA]=2$,
B: Fluorenyllithium in THF, Temp.: 15.0 °C.

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1) M. Tomoi and H. Kakiuchi, *Kogyo Kagaku Zasshi*, **73**, 2367 (1970).

2) T. Cuvigny and H. Normant, *Bull. Soc. Chim. Fr.*, **1964**, 2003.

3) H. Gilman, E. A. Zoellner, and J. B. Dickey, *J. Amer. Chem. Soc.*, **51**, 1576 (1929).

4) T. E. Hogen-Esch and J. Smid, *ibid.*, **88**, 307 (1966).

5) M. Tomoi, T. Yoneyama, and H. Kakiuchi, Abstracts, SPSJ 21th Annual Meeting, Tokyo, May 25, 1972, p. 310.

product consisted of equimolar amounts of fluorenyl and ethyl groups. The fluorenyl part of the NMR spectrum of the product was similar to that of fluorenyllithium in THF.⁶⁾ Moreover, the chemical shift of methylene protons, δ_{CH_2}, in the product was -1.1, while the value of δ_{CH_2} in Et_2Mg was -0.88 at $[HMPA]/[Et_2Mg]=3$ (see below). This fact indicates that the diamagnetic anisotropy induced by the aromatic ring strongly shields the ethyl protons. Consequently, the metalation seems to proceed as is shown in Reaction (1), and ethylfluorenylmagnesium (FL^-Mg^+Et) is formed:

$$FL + Et_2Mg \longrightarrow FL^-Mg^+Et + EtH \qquad (1)$$

$$2FL^-Mg^+Et \rightleftarrows (FL^-)_2Mg^{2+} + Et_2Mg \qquad (2)$$

The mixed reagent (FL^-Mg^+Et) may coexist at equilibrium, as is shown in Reaction (2). The NMR data, however, indicate that the structure of the magnesium fluorenide produced is a mixed reagent rather than a mixture of difluorenylmagnesium ($(FL^-)_2Mg^{2+}$) and Et_2Mg. It has been reported by House *et al.*⁷⁾ that a similar mixed reagent was formed when dicyclopentadienylmagnesium and diethylmagnesium were mixed in ether. Since a large excess of Et_2Mg over FL was used in the kinetic experiment, the equilibrium could be considered to lie far to the left.

We allowed a reaction system to come to the steady state and then diluted it with various quantities of toluene, measuring the optical density of the solution at each stage. This showed that Beer's law was accurately obeyed; the extinction coefficient of magnesium fluorenide was $\varepsilon_{373}=9900$.

Kinetic Studies. In a previous paper,¹⁾ we reported that the molar ratio of HMPA to a organomagnesium compound was a significant factor in the polymerization of styrene by the RMgX–HMPA. In this paper, the molar ratio, α, is defined as follows:

$$\alpha = \frac{[HMPA]}{[\text{Organomagnesium compound}]} \qquad (3)$$

Figure 2 shows the variation in the optical density of the reaction system with the time at $\alpha=2$. The optical density increased with the time and became a constant value after about 20 hr. In the absence of HMPA ($\alpha=0$), the optical density remained zero, even after about 22 hr. Since a large excess of Et_2Mg over FL was used in this experiment, the order of the reaction in the latter reagent could be obtained from an analysis of the optical density-time curve.⁸⁾ In this manner, we found the order of the reaction in FL to be 1.0. Thus, we may write:

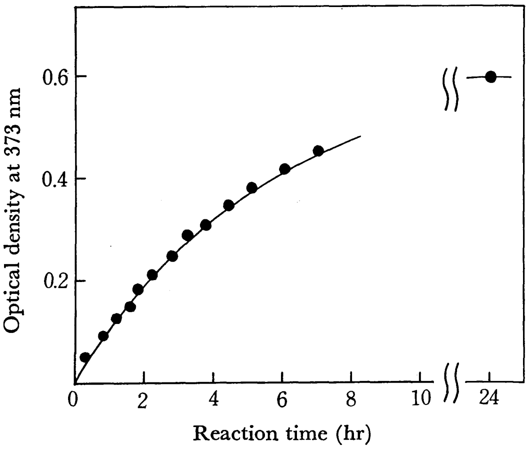

Fig. 2. A typical reaction rate plot.
$[FL]_0=3.04\times10^{-4}$ M, $[Et_2Mg]_0=2.37\times10^{-2}$ M, $[HMPA]_0=4.75\times10^{-2}$ M, Temp.: 19.0 °C.

$$\text{Rate of production of } FL^- = dFL^-/dt = k[FL] \qquad (4)$$

where k is the first-order rate constant.

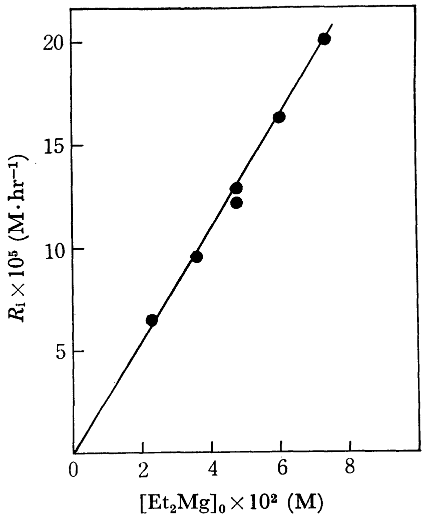

Fig. 3. Dependence of initial rate on initial diethylmagnesium concentration.
$[FL]_0=3.40\times10^{-4}$ M, $[HMPA]_0/[Et_2Mg]_0=2.0$, Temp.: 19.0 °C.

Figure 3 shows the dependence of the initial rate (R_i) on the initial diethylmagnesium concentration $[Et_2Mg]_0$ at $\alpha=2$. This finding indicates the order of the reaction in Et_2Mg to be 1.0. Consequently, the rate of the production of FL^- at $\alpha=2$ may be written as follows:

$$dFL^-/dt = k'[Et_2Mg][FL] \qquad (5)$$

where k' is the second-order rate constant.

Effect of the Molar Ratio of HMPA to Et_2Mg (α). Figure 4 shows the dependence of the initial rate (R_i) on the molar ratio of HMPA to Et_2Mg (α) at a constant Et_2Mg concentration. When α is less than about unity, the rate of metalation is zero, while the reaction is significantly promoted when α is more than about unity. The relationship between R_i and α is indicated by the two straight lines, the slopes of which are dependent on the range of α. One is the range in α from about unity to about two, while the other is in the α range over about two. The increment of the rate was larger in the former range than in the latter.

The dependence of R_i on $[Et_2Mg]_0$ at a constant concentration of HMPA is shown in Fig. 5. When α was less than about two, the rate decreased greatly in spite of the increase in the concentration of Et_2Mg.

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6) R. H. Cox, *J. Phsy. Chem.*, **73**, 2649 (1969).

7) H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, **32**, 2481 (1967).

8) See *e.g.*, A. G. Evans, and N. H. Rees, *J. Chem. Soc.*, **1963**, 6039.

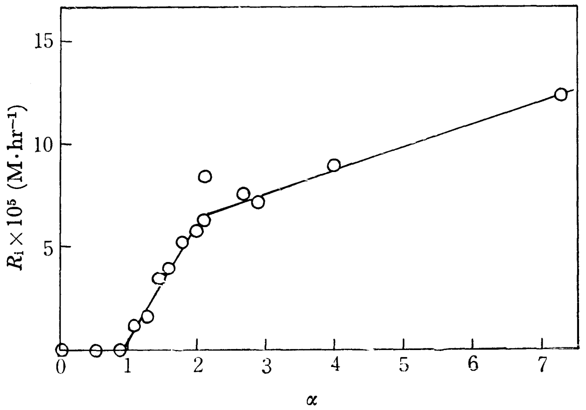


Fig. 4. Dependence of initial rate on α at a constant diethylmagnesium concentration.
$[FL]_0=2.80\times10^{-4}$ M, $[Et_2Mg]_0=3.95\times10^{-2}$ M, Temp.: 15.0 °C.

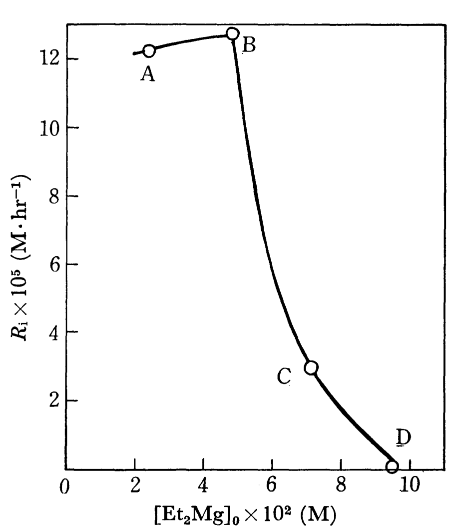


Fig. 5. Dependence of initial rate on initial diethylmagnesium concentration at a constant HMPA concentration.
$[FL]_0=3.40\times10^{-4}$ M, $[HMPA]_0=9.50\times10^{-2}$ M, Temp.: 19.0 °C.
The values of α are as follows;
A: 4.0, B: 2.0, C: 1.33, D: 1.0.

This fact indicates that, in the course of the reaction the important factor is not the Et_2Mg concentration, but the molar ratio of HMPA to Et_2Mg, this is, α.

NMR Spectrum of the Et_2Mg-HMPA System. The chemical shift of the methyl protons in Et_2Mg, δ_{CH_3}, was 1.17 in ether, while that of the methylene protons, δ_{CH_2}, was −0.65. The value of δ_{CH_2} was dependent on α. However, δ_{CH_3} scarcely changed in the presence of HMPA. Figure 6 shows the dependence of δ_{CH_2} on α. The change in δ_{CH_2} was small when α was less than about unity. The δ_{CH_2}, however, shifted upfield with an increase in α when α was between about unity and about two. When α was over about two, the magnitude of the decrease in δ_{CH_2} was small.

It is known that an approximately linear relationship exists between the internal chemical shift in ethyl compounds and the electronegativity of the substituent or the metal atom.[9] We could study the change in the electronegativity of magnesium metal in diethylmagnesium upon coordination with HMPA by using the relationship proposed by Narasimhan and Rogers:[10]

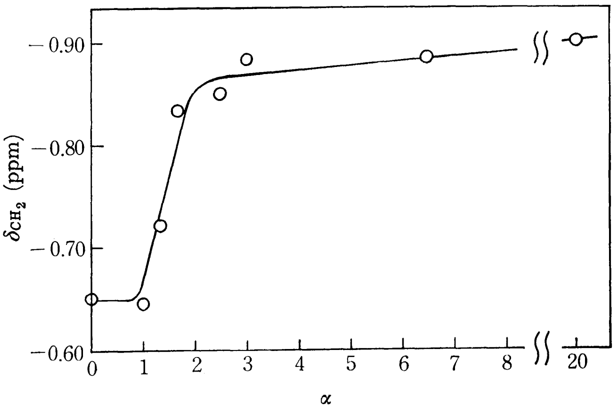
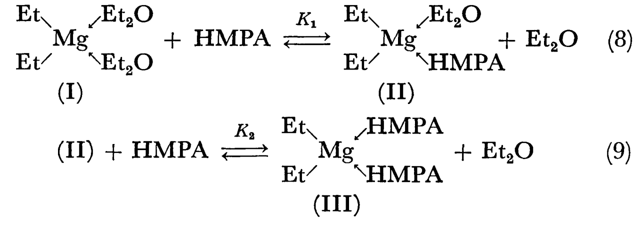


Fig. 6. Variation of δ_{CH_2} in Et_2Mg with α.
Solvent: ether, $[Et_2Mg]=0.50$—0.88 M.

$$\text{Electronegativity} = 0.62(\delta_{CH_2}-\delta_{CH_3}) + 2.07 \quad (6)$$

where $\delta_{CH_2}-\delta_{CH_3}$ is the internal chemical shift in ethyl compounds. The electronegativity of magnesium in Et_2Mg was 0.94 (δ_{CH_2}, −0.65; δ_{CH_3} 1.17) in the absence of HMPA in ether. When α was equal to 3, the electronegativity of magnesium changed to 0.79 (δ_{CH_2}, −0.88; δ_{CH_3}, 1.17). In the presence of THF ($[THF]/[Et_2Mg]=3$), it was 0.89 (δ_{CH_2}, −0.74; δ_{CH_3}, 1.17).[5] This result indicates that the electronegativity of magnesium in Et_2Mg decreases upon coordination with HMPA or THF, and that HMPA coordinates to magnesium more strongly than THF, as is to be expected from the donicities of these solvents.[11] Our result is in agreement with that recently reported by Ducom,[12] who investigated the same system in benzene. Similar conclusions have been obtained in triethylalminium–donor[13,14] and diethylzinc–donor[14] systems.

Interaction of HMPA with Et_2Mg, and the Mechanism of the Metalation Reaction. It has been reported by Walker and Ashby[15] that Et_2Mg is predominantly monomeric in ether (degree of association=∼1.3 at $[Et_2Mg]$=∼1M). The dietherate species (I), therefore, must have changed to Species (II)—(IV) on the addition of HMPA to this system:



$$Et_2Mg(Et_2O)_2\ (\text{I}) + HMPA \underset{}{\overset{K_1}{\rightleftarrows}} Et_2Mg(Et_2O)(HMPA)\ (\text{II}) + Et_2O \quad (8)$$

$$(\text{II}) + HMPA \overset{K_2}{\rightleftarrows} Et_2Mg(HMPA)_2\ (\text{III}) + Et_2O \quad (9)$$

$$(\text{III}) + m\text{HMPA} \overset{K_3}{\rightleftarrows} \underset{(\text{IV})}{Et^-Mg^+Et(2+m)\text{HMPA}} \quad (10)$$

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[9] B. P. Dailey and J. N. Shoolery, *J. Amer. Chem. Soc.*, **77**, 3977 (1955).

[10] P. T. Narasimhan and M. T. Rogers, *ibid.*, **82**, 5983 (1960).

[11] V. Gutmann, *Angew. Chem.*, **82**, 858 (1970).

[12] J. Ducom, *Bull. Soc. Chim. Fr.*, **1971**, 3523.

[13] K. Hatada and H. Yuki, *Tetrahedron Lett.*, **1968**, 213.

[14] M. Ikeda, T. Hirano, and T. Tsuruta, *Makromol. Chem.*, **150**, 127 (1971).

[15] F. Walker and E. C. Ashby, *J. Amer. Chem. Soc.*, **91**, 3845 (1969).

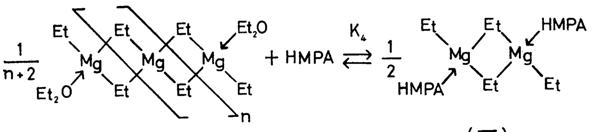
where K_1, K_2, and K_3 are the equilibrium constants in the three reactions.

The fact that the chemical shift, $\delta_{\mathrm{CH_2}}$, changed continuously suggests that the exchanges of these species are rapid at room temperature. If $K_1 > K_2 \gg 1$ and $K_3 \ll 1$ in these equilibria, Species (I) and Species (II), which is coordinated by one HMPA and one ether, coexist at equilibrium when α is less than unity. When α is between about unity and about two, Species (III), which is coordinated by two HMPA molecules, coexists with Species (II). The monomeric species (III) seems to change to an ionic form (IV) with the additional coordination of HMPA when $\alpha > 2$. As the $\delta_{\mathrm{CH_2}}$ is considered to shift more upfield with an increase in the number of HMPA molecules coordinated to Mg, it is reasonable that the $\delta_{\mathrm{CH_2}}$ of these species decreases in this order:

$$\delta_{\mathrm{CH_2}}(\mathrm{I}) > \delta_{\mathrm{CH_2}}(\mathrm{II}) > \delta_{\mathrm{CH_2}}(\mathrm{III}) > \delta_{\mathrm{CH_2}}(\mathrm{IV}).$$

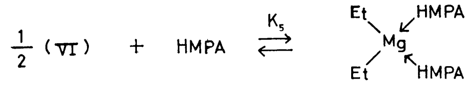
A similar order has been suggested by Parris and Ashby in the case of dimethylmagnesium in THF.[16] The fact that the $\delta_{\mathrm{CH_2}}$ shifted upfield with the increase in α at $1 < \alpha < 2$ is considered to be due to the increase in the concentration of Species (III). It can be explained that, because of the low concentration of Species (IV) formed in Reaction (10), the $\delta_{\mathrm{CH_2}}$ decreased gradually at $\alpha > 2$.

The metalation reaction was done in a mixture of solvents of toluene and a small amount of ether. It could be assumed that Et_2Mg is present as aggregated forms (V) in a toluene–ether mixture rather than as a monomeric form. These aggregates must have been dissociated into less aggregated or monomeric forms on the addition of HMPA:



(11)

(V) (VI)



(12)

(III)

where K_4 and K_5 are the equilibrium constants in Reactions (11) and (12). The dimeric species (VI), which is coordinated by one HMPA molecule per Mg atom, seems to be present in this system. However, the monomeric form (II) shown in Reaction (8) may also coexist with Species (VI). The species which are coordinated by one HMPA per Mg must, in any event, have been changed to Species (III) coordinated with two HMPA molecules (Reactions (9) and (12)). Furthermore, Species (III) seems to change to the ionic species (IV), as is shown in Reaction (10).

If $K_4 > K_2 \approx K_5 \gg 1$ and $K_3 \ll 1$ in these reactions, the concentration of the monomeric species (III) at $\alpha \leq 2$ can be given as follows:

$$[\mathrm{Et_2Mg\cdot 2HMPA}] \simeq 0 \quad \text{when } \alpha \leq 1$$

$$[\mathrm{Et_2Mg\cdot 2HMPA}] = [\mathrm{HMPA}] - [\mathrm{Et_2Mg}] \tag{13}$$
$$= [\mathrm{Et_2Mg}](\alpha - 1) \quad \text{when } 1 < \alpha < 2$$

where [HMPA] and $[Et_2Mg]$ are the total concentrations of HMPA and Et_2Mg respectively in the reaction system. The rate of the production of FL^- at $\alpha \leq 2$ can be given as in Eq. (14) by assuming that only Species (III) can react with FL:

$$\mathrm{FL} + \mathrm{Et_2Mg\cdot 2HMPA} \longrightarrow \mathrm{FL^-Mg^+Et\cdot 2HMPA} + \mathrm{EtH}$$

$$\mathrm{dFL^-}/\mathrm{d}t = k_1[\mathrm{Et_2Mg\cdot 2HMPA}][\mathrm{FL}] \tag{14}$$

where k_1 is the second-order rate constant. From Eqs. (13) and (14), we obtain Eqs. (15):

$$\mathrm{dFL^-}/\mathrm{d}t \simeq 0 \quad \text{when } \alpha \leq 1 \tag{15-A}$$

$$\mathrm{dFL^-}/\mathrm{d}t = k_1(\alpha - 1)[\mathrm{Et_2Mg}][\mathrm{FL}] \quad \text{when } 1 < \alpha < 2 \tag{15-B}$$

$$\mathrm{dFL^-}/\mathrm{d}t = k_1[\mathrm{Et_2Mg}][\mathrm{FL}] \quad \text{when } \alpha = 2 \tag{15-C}$$

The dependence of the rate on α at $\alpha < 2$ (Fig. 4) could be explained in terms of Eqs. (15-A) and (15-B). The order of reaction at $\alpha = 2$ is in agreement with the experimental results shown in Eq. (5). These facts support the idea that the reactive species in the metalation reaction is the monomeric species (III) when $\alpha < 2$.

When α is more than two, the ionic species (IV) seems also to react with FL. The concentration of Species (IV) is given as follows:

$$[\mathrm{IV}] = K_3[\mathrm{III}][\mathrm{HMPA_f}]^m \tag{16}$$

where $HMPA_f$ is the concentration of free HMPA and is given by the following equation:

$$[\mathrm{HMPA_f}] = [\mathrm{HMPA}] - 2[\mathrm{Et_2Mg}]$$
$$= (\alpha - 2)[\mathrm{Et_2Mg}] \tag{17}$$

As the concentration of Species (IV) is considered to be low, the concentration of Species (III) is given as follows:

$$[\mathrm{III}] = [\mathrm{Et_2Mg}] - [\mathrm{IV}] \simeq [\mathrm{Et_2Mg}]. \tag{18}$$

From Eqs. (16), (17), and (18), we can obtain Eq. (19):

$$[\mathrm{IV}] = K_3[\mathrm{Et_2Mg}]\{(\alpha - 2)[\mathrm{Et_2Mg}]\}^m$$
$$= K_3(\alpha - 2)^m[\mathrm{Et_2Mg}]^{1+m}. \tag{19}$$

Consequently, the rate at $\alpha < 2$ is given as follows:

$$\mathrm{dFL^-}/\mathrm{d}t = k_1[\mathrm{Et_2Mg}][\mathrm{FL}]$$
$$+ K_3 \cdot k_2(\alpha - 2)^m[\mathrm{Et_2Mg}]^{1+m}[\mathrm{FL}] \tag{20}$$

where k_2 is the rate constant in the reaction of Species (IV) with FL. The fact that a linear relationship exists between R_i and α when $\alpha \geq 2$ can be explained by assuming that m in Eq. (20) is equal to unity. That is to say, Et_2Mg probably changes to the ionic species with the coordination of three HMPA molecules. However, the formation of the ionic species from the organomagnesium compound (R_2Mg, RMgX) is considered to be dependent on the structure of the organic moiety in the compound. The relationship between the ease of carbanion formation from RMgX and the structure of the organic group, R, is now under investigation.

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[16] G. E. Parris and E. C. Ashby, *J. Amer. Chem. Soc.* **93**, 1206 (1971).