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Mechanism of the Grignard Reaction. Reaction of Benzil

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Abstract: The mechanism of the reaction between a Grignard reagent and benzil was investigated by using EPR and stopped-flow techniques. Two stable radical species, the concentrations of which were dependent upon the molecular ratio of Grignard reagent (G) and benzil (B), were invariably observed: a purple colored (PCR) ion-paired monoanion radical of benzil and a golden colored (GCR) ion-paired monoanion radical of the α-alkyl (or aryl-)-substituted benzoin magnesium salt. It was established that the two anion radicals are ion-paired with the dimeric counter cation of the Grignard reagent and that the resulting ion pairs exist as a dimeric species. From decay kinetics of the PCR followed by a stopped-flow method we conclude that the observed pseudo-first-order decay-rate constants are proportional to the initial concentrations of the Grignard reagent. This fact indicates that assistance by another neutral molecule of Grignard reagent is necessary for an alkyl (or aryl) group transfer within the PCR, to complete the addition reaction.

A radical pathway for a Grignard reaction was proposed tentatively in 1929 by Blicke and Powers who detected reduction byproducts in the reactions between Grignard reagents and benzophenone.[1] However, it was generally believed that the Grignard reaction proceeded via ionic intermediates[2] until investigations using the EPR technique disclosed the formation of radical species in the reactions of benzophenone and its substituted derivatives.[3,4] Since then, evidence indicating participation of radicals in Grignard reactions have accumulated.[5-10]

The Grignard reaction mechanism still remains to be clarified since there is almost no definite information on the mechanism by which an alkyl or aryl group transferred to the initially formed anion radical, although a few proposals[7j-l,n,8d,9b] have been made.

We have considered the mechanism of the Grignard reaction of benzil. Benzil has two neighboring carbonyl groups and affords a stable intermediate anion radical and, thus, may be suitable for investigating the details of the reaction. In the reactions of benzil, we have found two different kinds of persistent anion radicals. Although we know by preliminary investigations that other ketones such as 3,3-dimethyl-1-phenylbutane-1,2-dione, benzophenone, acetophenone, cyclohexanone, and 2-butanone behave similarly to benzil in the Grignard reactions, this paper will deal solely with the reaction of benzil.[11]

Table I. Hyperfine Coupling Constants of Benzil Anion Radicals (mT)[b]

counter cation	*o*-, *p*-	*m*-	others
K^+ (rt)	0.092	0.035	
(−20 °C)	0.092	0.035	
Na^+ (rt)	0.091	0.036	Na($^3/_2$) 0.054
(−20 °C)	0.094	0.036	0.057
Mg^{2+} (rt)	0.102	0.041	
$(EtMgBr)_2{}^{2+}$ (rt)[a]	0.099	0.041	

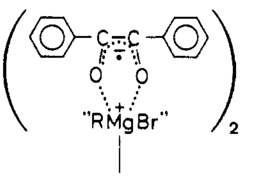
[a] See text. [b] In THF.

In this report we will demonstrate that two stable paramagnetic species participate as true reaction intermediates and that the Grignard reaction proceeds stepwise {initial electron transfer to benzil → alkyl (or aryl) radical transfer to the anion radical → second electron transfer → second alkyl (or aryl) radical transfer} to give the pinacol or the final product.

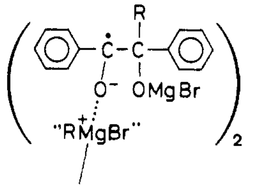
Results and Discussion.

I. Formation of Two Radicals. Reaction of Benzil. Phenylmagnesium bromide (PhMgBr) dissolved in tetrahydrofuran (THF) was allowed to react with benzil (B) with various benzil/Grignard reagent ratios (B/G) under dry and strictly deaerated conditions. Two different radical species were identified whose concentrations were dependent on the B/G ratios. These two radicals were both quite stable at room temperature.[12] They showed well-resolved EPR spectra as given in Figure 1A.

In the range B/G > 1.0 a purple colored radical (PCR, λ_{max} 515 nm) was observed, which was assigned to the ion-paired monoanion radical (see section II) of benzil (**1**). The hyperfine splitting constants (hfsc) and the splitting patterns of the anion radical allowed us to reach an unambiguous structural assignment



1 (PCR)



2 (GCR)

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[1] Blicke, F. F.; Powers, L. D. *J. Am. Chem. Soc.* **1929**, *51*, 3378.

[2] For example, *Organic Chemistry, An Advanced Treatise*; Gilman, H. Ed., Wiley: 1950; Vol II, p 1880.

[3] (a) Maruyama, K. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 897. (b) Maruyama, K. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1013.

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[5] For example, see: (a) Blomberg, C.; Grootveld, H. H.; Gerner, T. H.; Bickelhaupt, F.; *J. Organomet. Chem.* **1970**, *24*, 549. (b) Blomberg, C.; Salinger, R. M.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2385. (c) Blomberg, C.; Mosher, H. S. *J. Organomet. Chem.* **1968**, *13*, 519.

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[7] (a) Ashby, E. C.; Walker, F. W.; Neumann, H. M. *Chem. Commun.* **1970**, 330. (b) Ashby, E. C.; Laemmle, J.; Neumann, H. M. *J. Am. Chem. Soc.* **1971**, *93*, 4601. (c) Ashby, E. C.; Laemmle, J.; Neumann, H. M. *J. Am. Chem. Soc.* **1972**, *94*, 5421. (d) Ashby, E. C.; Laemmle, J.; Neumann, H. M. *Acc. Chem. Res.* **1974**, *7*, 272 and references cited therein. (e) Ashby, E. C.; Wiesemann, T. L. *J. Am. Chem. Soc.* **1974**, *96*, 7117. (f) Ashby, E. C.; Neumann, H. M.; Walker, F. W.; Laemmle, J.; Chao, L. C. *J. Am. Chem. Soc.* **1973**, *95*, 3330. (g) Ashby, E. C.; Lopp, I. G.; Buhler, J. D. *J. Am. Chem. Soc.* **1975**, *97*, 1964. (h) Lopp, I. G.; Buhler, J. D.; Ashby, E. C. *J. Am. Chem. Soc.* **1975**, *97*, 4966. (i) Ashby, E. C.; Buhler, J. D.; Lopp, I. G.; Wiesemann, T. L.; Bowers, J. S., Jr.; Laemmle, J. T. *J. Am. Chem. Soc.* **1976**, *98*, 6561. (j) Ashby, E. C.; Bowers, J. S., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 8504. (k) Ashby, E. C.; Wiesemann, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 189. (l) Ashby, E. C.; Bowers, J. R., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 2242. (m) Ashby, E. C.; Goel, A. B. *J. Am. Chem. Soc.* **1981**, *103*, 4983. (n) Ashby, E. C. *Pure Appl. Chem.* **1980**, *52*, 545.

[8] (a) Holm, T.; Crossland, I. *Acta Chem. Scand.* **1971**, *25*, 59. (b) Holm, T. *Tetrahedron Lett.* **1966**, *28*, 3329. (c) Holm, T. *J. Organomet. Chem.* **1971**, *29*, C45. (d) Holm, T. *Acta Chem. Scand., Sec. B* **1983**, *B37*, 567.

[9] (a) Ōkubo, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2057. (b) Ōkubo, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2379.

[10] (a) Eistert, B.; Klein, L. *Chem. Ber.* **1968**, *101*, 900. (b) Rells, H. M. *J. Org. Chem.* **1969**, *34*, 3687. See 5b, too.

[11] These ketones produce radicals in the Grignard reactions and behave similar to benzil in their EPR and stopped-flow examinations. Maruyama, K.; Hayami, J.; Katagiri, T. *Chem. Lett.* **1986**, 601.

[12] The radicals were so stable that they still showed strong EPR signals even after 2 years.

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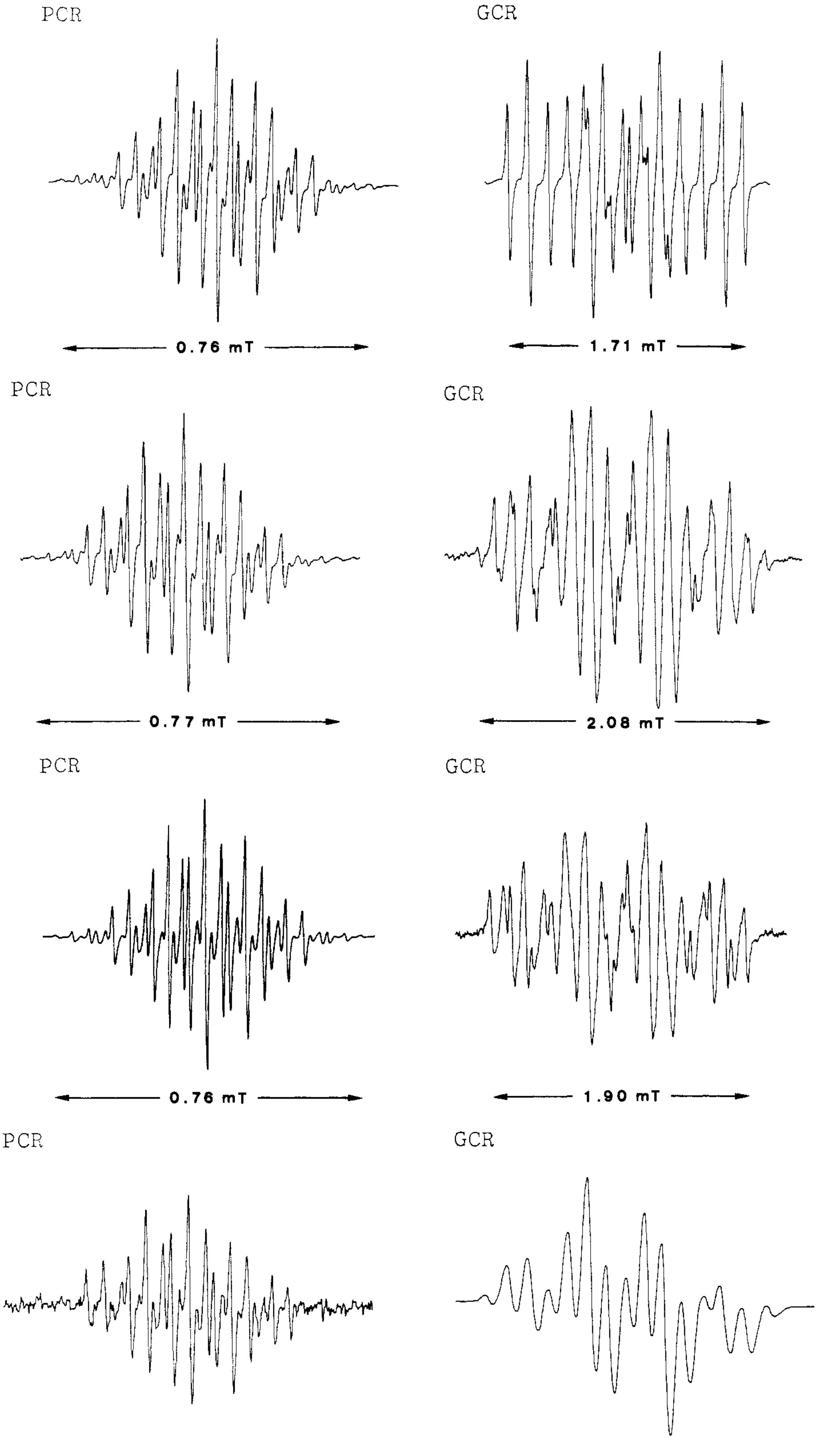

Figure 1. EPR spectra of the two different radical intermediates (PCR and GCR[55]) formed in the Grignard reactions in THF at room temperature: (A) reaction of PhMgBr with benzil, (B) reaction of MeMgBr with benzil, (C) reaction of EtMgBr with benzil, (D) reaction of *i*-PrMgBr with benzil.

for PCR (see Table I). In the B/G < 1.0 range, a golden colored radical (GCR, λ_{max} 472 nm) was observed. The GCR (see structure **11**) was compatible with the ion-paired anion radical of the α-phenylbenzoin salt **2**, because we observed the formation of the same radical in the reaction of 2 mol of ethylmagnesium bromide (EtMgBr) with 1 mol of α-phenylbenzoin in THF under dry and deaerated conditions. With a change in B/G, none of the reaction mixtures showed the concurrent existence of both radicals.

Methylmagnesium bromide (MeMgBr), ethylmagnesium bromide (EtMgBr), and isopropylmagnesium bromide (*i*-PrMgBr) were also reacted with benzil. Again, two corresponding radicals appeared. Their concentrations in solution were also dependent on the B/G ratios.[13] Their EPR spectra are shown in Figure

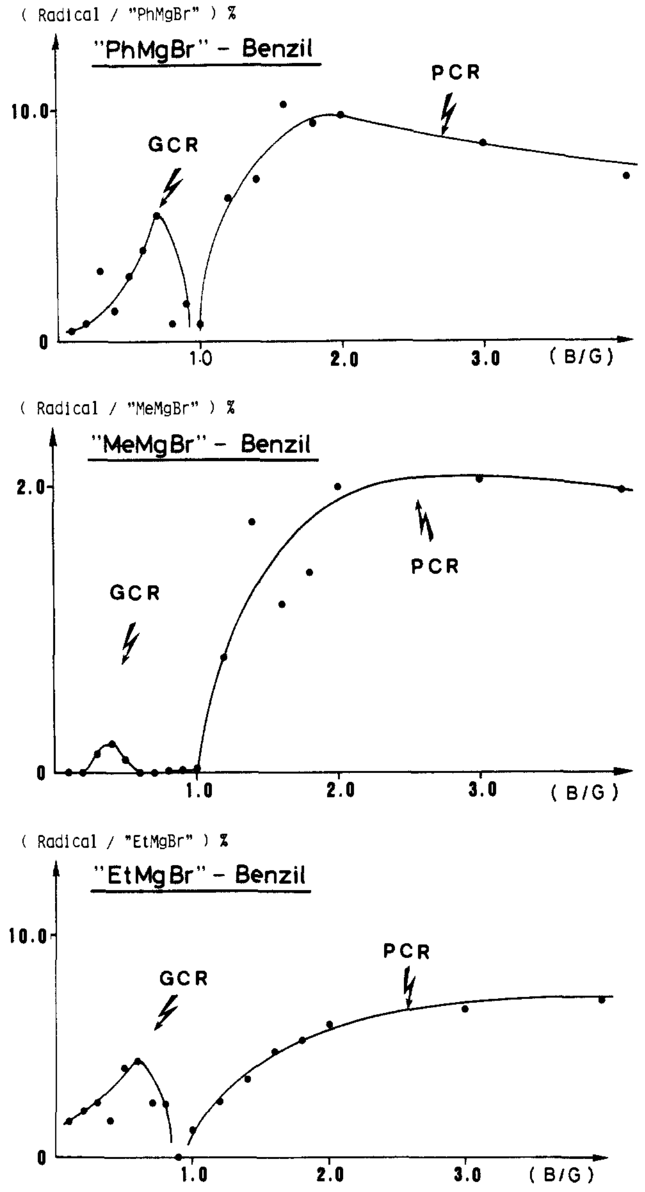

Figure 2. Radical concentrations as determined by EPR in the Grignard reaction at various B/G ratios in THF at room temperature: (A) reaction of PhMgBr with benzil, (B) reaction of MeMgBr with benzil, (C) reaction of EtMgBr with benzil.

1B–D. In the reaction of benzil with alkyllithium (or aryllithium) the corresponding PCR and GCR were also observed. This implies that the mechanism of reaction of alkyllithium (or aryllithium) is essentially the same as that for Grignard reagents.

The absolute quantities of the two radicals at the different B/G ratios were determined by using EPR spectroscopy. The results are shown in Figure 2. In the phenylmagnesium bromide (PhMgBr)–benzil system at B/G = 1.8, the amount of PCR was measured to be as high as about 10% of the PhMgBr used. At B/G = 0.7, that of GCR reached about 5%. Figure 2 clearly shows the existence of a boundary relevant to the two radicals with change of the B/G ratios. A narrow region where no radical was observed appeared near B/G $\simeq$ 1.0 in the cases of methylmagnesium bromide (MeMgBr) and ethylmagnesium bromide (EtMgBr). These observations were also confirmed by means of the electronic spectra of the reacting mixtures, since both the PCR and the GCR have characteristic visible spectra.

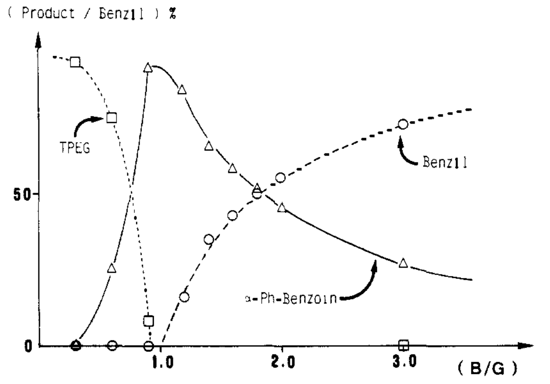

Figure 3. Products distributions in the reaction of PhMgBr with benzil at various B/G ratios as determined by ^{13}C NMR; TPEG: 1,1,2,2-tetraphenylethane-1,2-diol.

Irrespective of the structure of the Grignard reagent, we observed the same EPR signals due to PCR in the range B/G $\geq$ 1.2. This means that the structure of the PCR is independent of the alkyl or aryl part of the Grignard reagent. In addition, the EPR signal due to the PCR is quite similar to that of the alkali metal ion pairs of benzil semidione.[14] Therefore, the PCR is assigned to a benzil anion radical ($a_{(6H)}$ = 0.099 mT and $a_{(4H)}$ = 0.041 mT) ion paired with the Grignard cation. Here, we will designate the cation ([RMgBr]$^{\bullet+}$ of Grignard regaent from which an electron was released as the Grignard cation. In general, it is believed that organometallic cation radicals such as $R_4Sn^{\bullet+}$ and $R_4Pb^{\bullet+}$ are short-lived because of their tendency to cleave the metal–carbon bond.[15] As described below, the cation radicals derived from the Grignard reagent could be short-lived in monomeric state, but they could be stabilized in solution as a diamagnetic aggregate (see section II).

Stable reaction products obtained after hydrolyzing a reaction mixture of PhMgBr and benzil in the range B/G > 1.0 consisted of a mixture of α-phenylbenzoin and benzil (see Figure 3). By careful examination of the reaction product we did not find any appreciable amount of self-coupling product of the free alkyl (or aryl) radicals, i.e., the bialkyl or biphenyl, originating from the Grignard reagent.[16] Upon decreasing B/G to 0.8 ~ 1.2, a narrow region where no radical was detectable appeared in every case (see Figure 2). However, upon decreasing the B/G ratio further, other golden colored radical species (GCR), appeared in the reacting solutions. Similar to the PCR, the GCR species showed well-resolved EPR spectra. However, their hyperfine structures were dependent on the alkyl or aryl part of the Grignard reagents used.[33] The EPR spectra of GCRs given in Figure 1 reflect these features clearly. After decomposing a reaction mixture of benzil and PhMgBr containing the GCR with water, we obtained 1,1,2,2-tetraphenylethane-1,2-diol, α-phenylbenzoin, and trace amounts of benzil (see Figure 3). Again we did not find any appreciable amount of dimerization product of the free phenyl radical originating from the Grignard reagent. These facts suggest that the GCR is an anion radical of an α-alkyl(or aryl)substituted benzoin magnesium salt.[33] As described above, when we added 2 equiv amounts of a Grignard reagent to a THF solution of

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[13] When we used *tert*-butylmagnesium bromide (*t*-BuMgBr) in THF, PCR was observed similarly in the region of B/G > 1.0. However, we could not recognize the corresponding GCR in the region of B/G < 1.0 by means of EPR spectroscopy.

[14] Luckhurst and Orgel reported the EPR hfcc of benzil sodium ketyl as $a_{(6H)}$ = 0.102 mT and $a_{(4H)}$ = 0.041 mT. Luckhurst, G. R.; Orgel, L. E. *Mol. Phys.* **1963**, *7*, 297.

[15] Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790.

[16] Investigators of the Grignard reactions often argued on formation of the free alkyl (or aryl) radical as a key component of reacting intermediates. See, for example, ref 5a and 7l. With these facts in mind, we inspected very cautiously self-coupling of free alkyl (or aryl) in the reaction mixture by column chromatography and other spectroscopic devices (IR, NMR, etc.) using internal standard. After quenching the reaction mixtures under strictly deaerated conditions with saturated aqueous NH_4Cl solution, we examined the products. With repeated examinations we found (a) in a reaction mixture containing PCR, less than 0.3% of biphenyl (based on used Grignard reagent), (b) in a reaction mixture containing GCR, less than 0.3% of biphenyl, and (c) after decomposition of PhMgBr, less than 0.1% of biphenyl. Also we could not detect the reduced byproduct, benzoin, by means of ^{13}C NMR spectroscopy.

Table II. Optical Absorption Maxima of Benzil Anion Radicals[b]

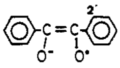
counter cation	λ_{max} (nm)	ν (cm^{-1})	color
K^+	610	16400	blue
Na^+	575	17400	blue
Mg^{2+}	520	19200	purple
$(EtMgBr)_2^{2+}$ [a]	515	19400	purple

[a] See text. [b] At 25 °C, in THF.

α-substituted benzoin such as α-phenylbenzoin or α-methylbenzoin, we obtained the same GCRs as from benzil and PhMgBr or MeMgBr, respectively.

II. Structure of the Radical Ion Pair Derived from Benzil and the Grignard Reagent. The PCR derived from benzil must be ion paired with some cation derived from the Grignard reagent. However, we have no clear indication regarding the formation of the cation radical. Only in a very few instances[17] are both anion and cation radical pairs persistent enough to be observed simultaneously under stationary conditions. Recently, W. Kaim[17] observed clear and overlapping broad EPR signals due to both the anion and cation radicals in the reaction of 1,4-bis(trialkylsilyl)-1,4-dihydropyrazines and TCNE. It must be noted here that additional features in the EPR spectra of ketyls have recently led Ashby and co-workers to claim radical anion/radical cation pairs as long-lived intermediates.[7m] However, Kaim has indicated reservations about this assignment.[18] The PCR shows a well-resolved EPR signal which can be easily analyzed in terms of the hyperfine splitting constants (hfsc) of the benzil anion radical. In Table I the hfsc of the benzil anion radicals produced by reduction with alkali or alkali earth metals are compared with that of the PCR formed in the Grignard reaction. The hfsc of an anion radical is, in general, known to be sensitive to environmental perturbations; i.e., interionic distance, solvent, and temperature.[19] Thus, from the results given in Table I, we may estimate the interionic distance of ion radical pairs. The resulting proton hfsc changes can be qualitatively understood in terms of valence bond pictures.[19a]

In the case of benzil, the ground state of the anion radical is approximately represented by a linear combination of the wave functions including structures **3**–**9**. As the perturbations of the cation on the carbonyl oxygen increase, structures **3**, **4**, **6**, and **7** become more favorable than structures **5**, **8**, and **9**. Therefore, the larger spin densities at the carbons 4′ and 2′, i.e., the larger hfsc's of H_p and H_o, are expected with an increasing interionic interaction between the anion radical and the cation. We can arrive at the same conclusion by using a simple HMO calculation.[20] The hfsc values (H_p, H_o, 0.099 mT; H_m, 0.041 mT) of the ion paired benzil anion radical (PCR) observed in the Grignard reaction are very close to that (H_p, H_o, 0.102 mT; H_m, 0.041 mT) of the magnesium metal ketyl of benzil. From these hfsc values we can estimate the interionic distance between the benzil anion radical and the Grignard cation ($[EtMgBr]^{\bullet+}$) to be about 3.0 Å. A similar conclusion was obtained from the visible absorption spectra of the PCR and benzil metal ketyls. McClelland had studied the metal ketyls of benzophenone, fluorenone, and benzil and showed that the frequency of the visible absorption maximum shifted toward red as the radius of the metal cation (r_c) increased. There were linear relationships between ν and $1/(r_c + r_a)$, where r_a is the radius of an anion radical.[21] He used r_a = 2.0 Å for the metal ketyls of benzophenone, fluorenone, and benzil. Applying this r_a value, we can estimate r_c from the visible spectrum of the PCR. The data of visible spectra of the PCR along with that of other benzil metal ketyls are given in Table II. Actually, the ν values produce a good linear plot against $1/(r_a + r_c)$. From the relationship, the r_c value of Grignard cation ($[RMgBr]^{\bullet+}$) was estimated to be 0.7 Å. This result is consistent with that of the EPR hfsc. This means that the radical ion pair formed in the Grignard reaction is in the state of a "tight" ion pair. The following experimental evidence supports further this concept. The PCR formed in a PhLi–benzil system showed a well-resolved EPR signal with a characteristic lithium hyperfine structure (H_o, H_p, 0.097 mT; H_m, 0.039 mT; ^7Li, 0.005 mT).[22] This is an unambiguous indication of "tight" ion pair formation between anion radical and phenyllithium cation.



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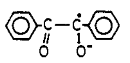

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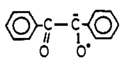

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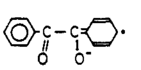

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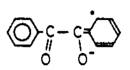

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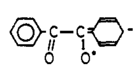

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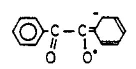

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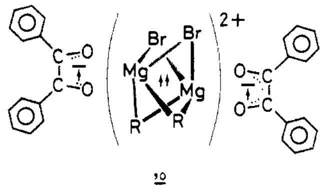
If the Grignard cation were in a state of monomeric $[RMgBr]^{\bullet+}$ and in a "tight" ion pair with PCR, such a situation should be reflected in the EPR signal of PCR (or GCR), i.e., on the g value or on the line width (broadening). Moreover, the EPR signal of $[RMgBr]^{\bullet+}$ should also be observed. However, this is not the case. The PCR showed a well-resolved EPR signal in the region g = 2.0046. Therefore, the Grignard cation or phenyllithium cation may be in a dimeric state so as to produce a homogeneous diamagnetic field. The radical ion pair could be represented as structure **10**[23] in which paired antiparallel arrows indicate spin-paired electrons. If this is true, we should be able to observe the triplet EPR signal of the PCR dimer in a glassy state. Actually, we succeeded in observing a clear EPR signal of the triplet radical pair. The weak, but unambiguous, triplet EPR signal was observed in the regions $g \simeq 2.0$ and 4.0 in a 2-methyltetrahydrofuran (MTHF) solution of an EtMgBr–benzil system at 77 K, and the strong triplet EPR signal in a PhLi–benzil system in the regions $g \simeq 2.0$ and 4.0 (Figure 4).[24] From these data, we can evaluate the distance of the two free spins in the dimeric radical ion pair to be about 5.0 Å.[25] Thus, it is reasonable to conclude that the radical ion pair formed in the Grignard reaction exists in a dimeric form (see structure **10**). The dimeric forms of alkali or alkali earth metal ketyls and semidiones in solutions were well-known.[26]



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III. How Does Alkyl (or Aryl) Radical Transfer to Anion Radical? When a constant amount of Grignard reagent was mixed

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[17] (a) Kaim, W. *Angew. Chem.* **1984**, *96*, 609; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 613. (b) Emori, S.; Weir, D.; Wan, J. K. S. *Chem. Phys. Lett.* **1981**, *84*, 512.

[18] Kaim, W. *Acc. Chem. Res.* **1985**, *18*, 160.

[19] (a) Hirota, N. *Radical Ions*; Kaiser, E. T.; Kevan, L. Eds., Interscience: New York, 1968; Chapter 2. (b) Takeshita, T.; Hirota, N. *J. Am. Chem. Soc.* **1971**, *93*, 6421. (c) Hirota, N.; Weissman, S. I. *J. Am. Chem. Soc.* **1964**, *86*, 2537. (d) Hirota, N.; Weissman, S. I. *J. Am. Chem. Soc.* **1964**, *86*, 2538.

[20] According to McClelland's approximation, perturbation energy in ion pair was assumed as $V = -e^2/r$, where r = interionic distance. McClelland, B. J. *Trans. Faraday Soc.* **1961**, *57*, 1458.

[21] Carter, H. V.; McClelland, B. J.; Warhurst, E. *Trans. Faraday Soc.* **1960**, *56*, 455.

[22] There appeared a characteristic hyperfine splitting into 4 equivalent lines, due to $^3/_2$ nuclear spin of ^7Li atom of phenyllithium cation.

[23] Of course, this structure may be a representative of possible other structures which could include solvent and other ions as $(MgX)^+$ in the aggregation. See ref 25.

[24] Emori et al. claimed observation of triplet radical ion pair in solid state in a THF solution of 2,5-diphenyl-p-benzoquinone and organotin upon irradiation. Emori, S.; Weri, D.; Wan, J. K. S. *Chem. Phys. Lett.* **1981**, *84*, 512.

[25] Figure 4B suggests the presence of three major components (D'_1 = 26.7, D'_2 = 22.9, D'_3 = 17.9 mT) in the triplet state. From these we can evaluate the distances ($r_{12} = (2D'/3g\beta)^{-1/3}$) of two spins of each component as 4.7, 5.0, and 5.4 Å, respectively. McGarrity, J. F.; Ogle, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 1805.

[26] (a) Russell, G. A.; Lawson, D. F.; Malkus, H. L.; Stephens, R. D.; Underwood, G. R.; Takano, T.; Malatesta, V. *J. Am. Chem. Soc.* **1974**, *96*, 5830. (b) Russell, G. A.; Gerlock, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 5838.

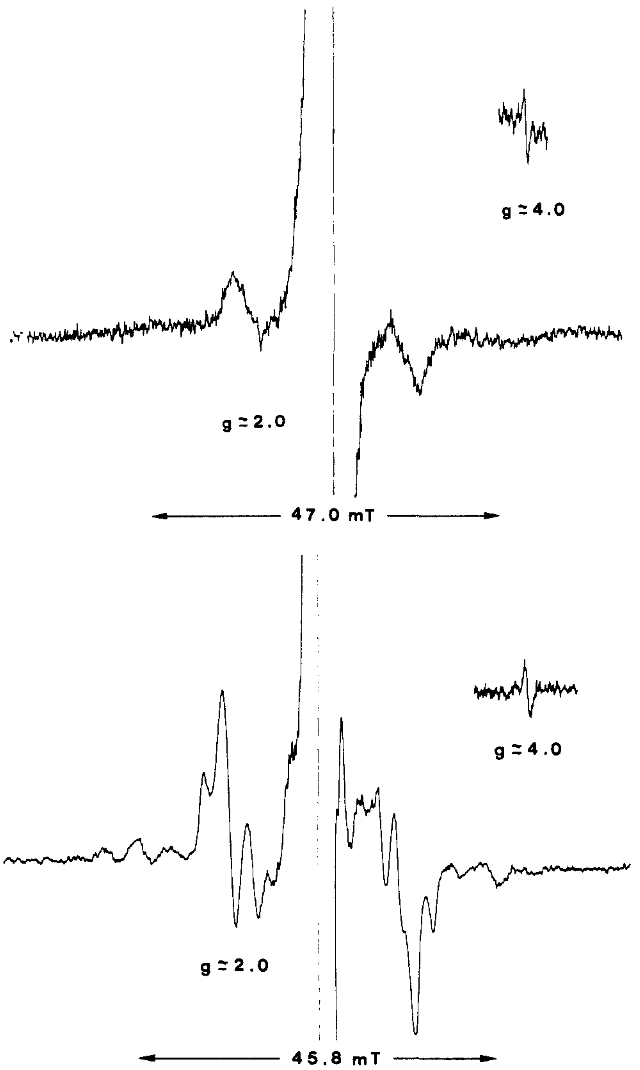


Figure 4. Rigid media EPR spectra of PCR dimers in MTHF at 77 K: (A) EPR spectra of PCR in the reaction of EtMgBr with benzil and (B) EPR spectra of PCR in the reaction of PhLi with benzil.

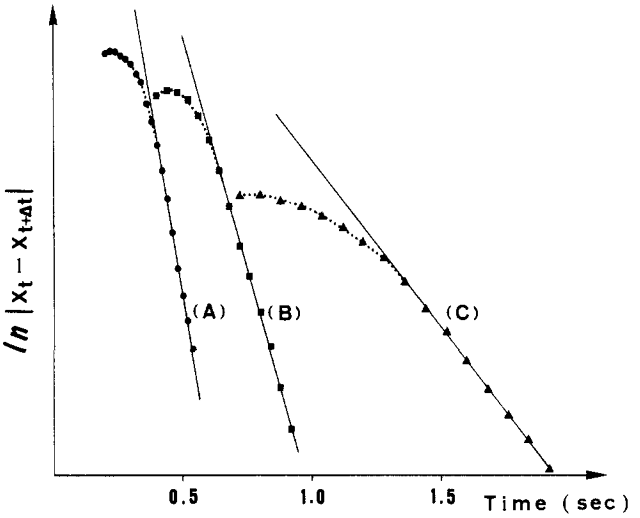


Figure 5. Guggenheim plot for the decay of PCR in the reaction between PhMgBr and benzil with B/G = $^1/_{10}$, at 25/°C in THF: (A) [PhMgBr] = 0.19 M k = 16 s^{-1}, (B) [PhMgBr] = 0.09 M k = 9 s^{-1}, (C) [PhMgBr] = 0.05 M k = 4 s^{-1}.

Table III. Decay Rate Constant of PCRs Benzil–RMgBr[a] (B/G = $^1/_{10}$)

RMgBr M,	decay rate const, s^{-1}
PhMgBr	
0.19	16
0.09	9
0.05	4
EtMgBr	
0.16	2000
0.08	1000
0.04	500
MeMgBr	
0.32	150
0.16	60
0.08	30

[a] Stopped-flow, 25.0 °C, under a N_2 atmosphere, observed at 610 nm, in THF.

Scheme I[a]

$$\mathrm{B + G \xrightarrow{k_1} MIP} \tag{1}$$

$$\mathrm{2MIP \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} D} \quad (K_2 = k_2/k_{-2}) \tag{2}$$

$$\mathrm{D + G \xrightarrow{k_3} [D{\cdot}G]^{+} \longrightarrow A + MIP + G} \tag{3}$$

[a] B, benzil; G, Grignard reagent; MIP, monomer ion-radical pair; D ≡ PCR, triplet radical dimer; A, adduct; α-alkyl (or aryl) substituted benzoin neutral salt.

with different amounts of benzil in THF at room temperature under strictly deaerated conditions, two radicals were produced as described in section I. The species and the amounts of the two radicals corresponded to the B/G as shown in Figure 2. Upon decreasing benzil from B/G $\simeq$ 3.0 to B/G = 1.0, the PCR was always observed in the reacting solution, in which the PCR survived for at least 2 years under strictly deaerated conditions even at room temperature.

When Grignard reagent was added to a solution containing a known amount of PCR, there was observed a sudden decrease in the radical concentration, a complete disappearance of the PCR, or the appearance of the GCR corresponding to the amount of the added Grignard reagent. The results suggest that the participation of another molecule of neutral Grignard reagent is necessary for an alkyl (or aryl) radical ($R^{\bullet}$) transfer from the ion-paired Grignard cation to the anion radical of benzil to form an α-alkyl(or aryl)-substituted benzoin anion (ion-paired with $MgBr^+$). Actually, we examined the reaction by using a stopped-flow method and confirmed that the (pseudo)-first-order decay rate constants of the PCRs were proportional to the initial concentrations of Grignard reagents.

Kinetic Evidence for an R$^{\bullet}$ Transfer. We applied a large excess of a Grignard reagent over benzil (B/G = $^1/_{10}$) to simplify the situation and traced the amount of PCR which appeared first and vanished within a few seconds before the appearance of GCR. This was done with the aid of the stopped-flow method. The obtained decay curve of the PCR fitted well with the (pseudo)-first-order decay curve and was analyzed by a Guggenheim plot (Figure 5) to determine the first-order decay rate constant. The results are shown in Table III.

In every reaction, we confirmed that the observed decay rate constants were proportional to the initial concentration of Grignard reagents. In other words, the decay rate constants obey pseudo-first-order kinetics. This can be rationalized as shown in Scheme I.

According to Scheme I, under pseudo-first-order conditions, the reaction rate should be expressed as, from eq 1

$$d[B]/dt = -k_1[G]_0[B] \tag{4}$$

($[G]_0$, initial concentration of Grignard reagent $[G] \simeq [G]_0 \gg [B]$) from eq 2

$$K_2 = k_2/k_{-2} = [D]/[MIP]^2 \tag{5}$$

(provided that $k_2 \gg k_3$) from eq 3

$$d[A]/dt = k_3[G]_0[D] \tag{6}$$

where,

$$[B] + [MIP] + 2[D] + [A] = [B]_0$$

If it is assumed that

$$d[B] + d[MIP] + 2d[D] + d[A] = 0 \qquad (7)$$

from eq 1, 2, 3, and 5

$$d[MIP]/dt = k_1[G]_0[B] - 2k_2[MIP]^2 + 2k_{-2}[D] + k_3[G]_0[D] = k_1[G]_0[B] + k_3[G]_0[D] \qquad (8)$$

from eq 4, 6, and 8

$$d[MIP]/dt + d[B]/dt = k_3[G]_0[D] = d[A]/dt \quad \therefore d[MIP] + d[B] = d[A] \qquad (9)$$

from eq 7 and 9

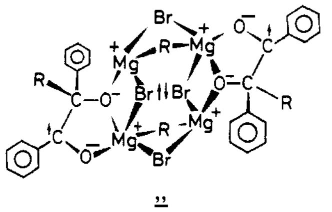
$$2d[D] + 2d[A] = 0 \qquad \therefore d[D]/d[A] = -1 \qquad (10)$$

$$d[D]/dt = (d[D]/d[A])\cdot(d[A]/dt) = -k_3[G]_0[D] = -k_{obsd}[D] \qquad (11)$$

Equation 11 predicts that the pseudo-first-order decay rate constant of the triplet radical dimer (**D** ≡ PCR) should be proportional to the initial concentration of Grignard reagent ($[G]_0$). This agrees well with the experimental results given in Table III.

It should be noted that one molecule of the Grignard reagent is enough for one-electron transfer from the Grignard reagent to a substrate. However, the assistance ("boosting") by another molecule of a Grignard reagent is necessary for an alkyl (or aryl) group transfer (see eq 2 and 3). The assumption of eq 3 is of considerable interest in regard to the mechanism of the Grignard reaction. After completion of an addition reaction one molecule each of A, MIP, and G are released. However, as is clear from equations given in Scheme I, this does not imply that 2 equiv of Grignard reagent are necessary for completion of an addition reaction. After completion of the addition reaction an excess of Grignard reagent is able to participate in the other reactions.

Formation and decay processes of GCR may essentially proceed similar to those of PCR. However, we realized from a diagnosis of the processes by stopped-flow technique that these processes are rather complicated. This complication may be brought about by bulkier complexes formed by the reacting species. Actually, in a glassy state we observed again unambiguous triplet EPR signals of GCR at about $g \simeq 2.0$ and 4.0 as shown in Figure 6. From the result we estimated average distance of two electron spin as 5.9 Å. The greater distance of two spins compared with that of PCR (5.0 Å) reflects the bulkier complex. An aggregation of GCR could be depicted as in structure **11**,[27] in which paired antiparallel arrows represent spin-paired electrons. It is rational to consider that electron transfer should take place to α-alkyl(or aryl)-substituted benzoin magnesium salt, and the successive alkyl (or aryl) group transfer might proceed through more complex aggregation among α-alkyl(or aryl)-substituted benzoin magnesium salt, dimer dication of Grignard reagent, and neutral Grignard reagent. In this complex, alkyl (or aryl) group transfer process would require presence of a rather larger amount of neutral Grignard reagent. This may be the reason why some GCR's remain still below B/G ≃ 0.5. These processes are now under investigation.



11

IV. Conclusion. Benzophenone[11] has been previously used for investigation of the mechanism of the Grignard reaction. In the reaction the rate-determining step involves an electron transfer, and available information concerning an alkyl group transfer step has been limited to that obtained from the byproduct distributions.[7m,n,8d,9b]

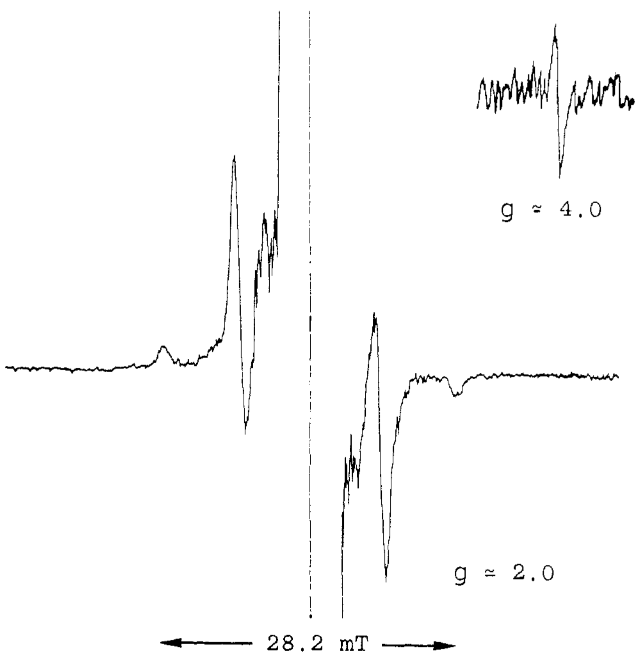
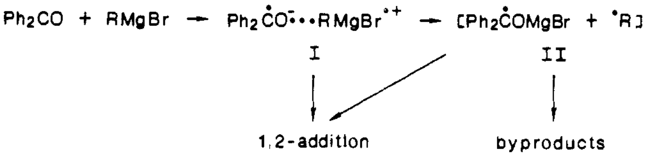
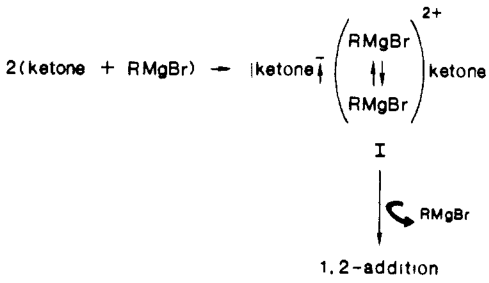


Figure 6. Rigid media EPR spectra of GCR dimer in MTHF at 77 K; EPR spectra of GCR in the reaction of EtMgBr with benzil.

Scheme II



Scheme III



According to a previously proposed mechanism, for example, the whole reaction system can be summarized in Scheme II.[7f-m]

Our probe using benzil as a substrate, however, was successful in stabilizing sufficiently an intermediate which we designated PCR. This fact enabled us to study the alkyl (or aryl) group transfer step in the 1,2-addition reaction of benzil. Preliminary investigations of the Grignard reactions of 3,3-dimethyl-1-phenylbutane-1,2-dione and benzophenone by similar techniques suggest the occurrence of the similar processes occurring by the process outlined in Scheme III.

Experimental Section

1. Materials and Methods. Benzil prepared by air oxidation of benzoin[28] was recrystallized from carbon tetrachloride [mp 95.2 °C; IR (KBr) 1670 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR ($CDCl_3$) δ 7.4–7.7 (m, 6 H), 8.0 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 128.8, 129.7, 132.8, 134.7, 194.3]. Commercially available pure tetrahydrofuran (THF), ethyl ether, and 2-methyltetrahydrofuran (MTHF) were distilled under nitrogen before use

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[27] Of course, this structure may be a representative of possible other structures including solvents or other ions in the aggregation.

[28] *Organic Synthesis*: Wiley: New York, Collect. Vol. 1, p 87.

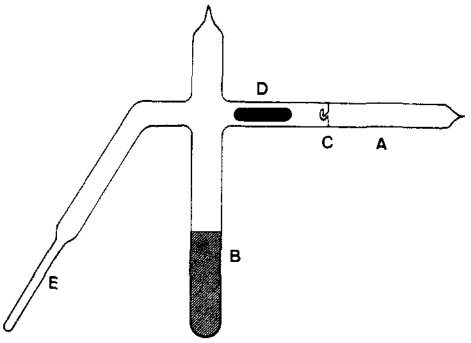

Figure 7. Reaction vessel: (A) Grignard reagent, (B) benzil in THF, (C) breakable seal, (D) hammer, (E) EPR quartz cell.

from respective reservoirs containing sodium benzophenone ketyl. Commercially available extra pure grade bromobenzene, ethyl bromide, *tert*-butyl bromide, and isopropyl bromide stored, respectively, on anhydrous magnesium sulfate were distilled just prior to use, but guaranteed reagent grade gaseous methyl bromide was used without further purification. Magnesium turnings for Grignard reaction grade (Mg > 99.5%, Fe < 0.01%) and Merck lithium wire for synthetic grade (Li > 99%) were used. Every Grignard reagent was prepared in a flask containing a 30–100% excess of magnesium under a high purity argon. The prepared Grignard reagents were analyzed by Gilman's method,[29] stored in round flasks with three-way stop cocks, and kept dark in a desiccator. An ethyl ether solution of phenyllithium was prepared in a similar manner as Grignard reagents.

A JEOL PE-3X ESR spectrometer system with JEOL ES-SCXA X-band microwave unit was used. Absolute amounts of radicals were determined by comparison with standard 1,1-diphenyl-2-picrylhydrazyl (DPPH). To determine the *g* values of radicals DPPH and a Mn^{2+} marker were used. A JEOL JNM-FX400 FT-NMR spectrometer was used for ^{13}C NMR. An Union Giken RA-103 stopped-flow system with gas driving device equipped with an RA-451 data processor was used.

2. Reactions. 2.1. EPR Samples. The EPR measurement of the reaction of Grignard reagent with benzil was carried out as follows: prior to the sealing of part A of the reaction vessel, a solution of Grignard reagent was introduced into A by syringe and deaerated (see Figure 7). Thereafter, part B of the vessel which contained a known amount of weighed crystalline benzil was evacuated under a high vacuum, a known amount of dry THF was distilled into this vessel, and the vessel was sealed off from the vacuum line. Benzil and a Grignard reagent which had been separated from each other by a breakable seal were mixed at room temperature in the absence of air and moisture.

2.2. Reaction of PhMgBr with Benzil. After a THF solution of 0.13 mmol of PhMgBr (0.52 M, 0.25 mL) was mixed with a THF solution of benzil in a reaction vessel, the reacting solution was subjected to EPR observations. In the reaction of excess of Benzil ($B/G > 1.0$), the reacting solutions became deep purple soon after the reactants were mixed together and showed well-resolved EPR spectra of PCR (**1**) with g value of 2.0047. On the contrary, in case of excess of PhMgBr ($B/G < 1.0$), the reacting solutions showed once a pink or pale purple color in a few seconds before the solutions became bright orange. The bright orange colored solutions showed well-resolved EPR spectra of GCR (**2**) with a g value of 2.0031. The curve illustrating the concentrations of radicals vs. B/G is given in Figure 2A. The reaction products are given in section 2.5.

2.3. Reaction of MeMgBr with Benzil. After a THF solution of 0.20 mmol of MeMgBr (0.80 M, 0.25 mL) was mixed with a THF solution of an excess of benzil in a reaction vessel and the reacting solution was subjected to EPR observations, the well-resolved EPR spectra of PCR was observed with a g value of 2.0045. In the reaction of excess of MeMgBr ($B/G < 1.0$), the reacting solutions showed at first a pink or pale purple color due to PCR for only a few seconds. Samples prepared in a region of $0.3 \leq B/G \leq 0.5$ showed well-resolved EPR spectra of GCR with a g value of 2.0031. The reaction products are given in section 2.6.

2.4. Reaction of EtMgBr with Benzil. After a THF solution of 0.11 mmol of EtMgBr (0.42 M, 0.25 mL) was mixed with a THF solution of an excess of benzil in a reaction vessel and the reacting solution was subjected to EPR observations, the well-resolved EPR spectra of PCR was observed with a g value of 2.0046. However, in the reactions of excess of EtMgBr ($B/G < 0.8$), the reacting solutions became bright orange as soon as the reactants were mixed together and showed well-resolved EPR spectra of GCR with a g value of 2.0031. A sample prepared at $B/G = 0.9$ did not produce any radical in the solution. Product analyses of the reactions, however, indicated that reactions other than 1,2-addition to the carbonyl had occurred. Reaction products consisted of a mixture of α-ethylbenzoin and *d,l*- and *meso*-3,4-diphenylhexane-3,4-diol accompanied by an ethyl benzoate and benzaldehyde.

Table IV. Product Distributions (%)

				2,3-diphenylbutane-2,3-diol	
run	B/G ratio	benzil	α-methylbenzoin	d,l	meso
1[a]	2.0	52	47	1	<0.2
2[a]	1.0	6	91	3	<0.5
3[a]	0.5	0	26	63	11

[a] Mean values of two runs.

2.5. Products in the Reaction of PhMgBr with Benzil. To 2.5 mmol of benzil (525 mg) dissolved in a dearated and dried THF solution (20 mL) were added 0.83 mmol, 2.8 mmol, 4.2 mmol, and 8.3 mmol of PhMgBr to make the reacting solutions which are corresponding to the values of $B/G = 3.0$, 0.9, 0.6, and 0.3, respectively. The reactions were started at water–ice cooled temperature and continued for 48 h at room temperature (25 °C). The reacting solutions were quenched and hydrolyzed with 2 mL of saturated aqueous NH_4Cl solutions under strictly deaerated conditions. The hydrolyzed mixtures were extracted with ether, washed with saturated aqueous NaCl solutions, and dried over anhydrous magnesium sulfate.

The ^{13}C NMR analysis of the samples obtained above were performed by adding the expected products as internal standards. Two characteristic ^{13}C NMR signals (δ 194.3 and 200.7 ppm) due to two carbonyl carbons in benzil and α-phenylbenzoin and two other characteristic signals corresponding to hydroxylated carbons (δ 82.9 and 84.9 ppm) were used for the product determinations. Even by very careful examination we did not find any appreciable amount of biphenyl.[16]

Benzil: mp 95.2 °C; IR (KBr) 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.4–7.7 (m, 6 H), 8.0 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 128.8, 129.7, 132.8, 134.7, and 194.3 ppm.

α-Phenylbenzoin: mp 87.5–88.5 °C; IR (KBr) 1663 ($\nu_{C=O}$), 3490 (ν_{OH}) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.0–7.8 (m, 15 H), 3.0 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 84.9, 128.0, 128.1, 128.2, 130.6, 132.8, 135.0, 141.8, and 200.7 ppm; mass spectrum, *m/z* (rel intensity) 288 (3), 184 (13), 183 (81), 182 (11), 105 (100), 77 (55), 51 (14), 44 (93).

1,1,2,2-Tetraphenylethane-1,2-diol: mp ~200 °C dec (lit.[30] 188–190 °C dec); IR (KBr) 3550–3580 (ν_{OH}) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.0–7.6 (m, 20 H), 3.0 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 82.9, 126.8, 127.1, 128.4, and 144.0 ppm; mass spectrum, *m/z* (rel intensity) 182 (3), 181 (20), 122 (100), 121 (100), 107 (30), 105 (40), 78 (24), 77 (47).

Some samples used for EPR observations were quenched in the same way and analyzed by means of high pressure liquid chromatography. Reliable results were obtained for the samples prepared in the range of $B/G > 1.2$, but not for the samples prepared in $B/G < 1.0$ because of the small amount of the samples.

2.6. Products in the Reaction of MeMgBr with Benzil. To 1.0 mmol of benzil (210 mg) dissolved in strictly deaerated and dried THF was added a calculated amount of MeMgBr solution. After mixing and standing for 2 days, the mixture was quenched with saturated aqueous NH_4Cl solution under strictly deaerated conditions. Product distributions according to change of the B/G ratio were cautiously examined by ^{1}H NMR and UV.

α-Methylbenzoin: mp 66–67 °C (lit.[31] 68–69 °C); IR ($CDCl_3$) 1663 ($\nu_{C=O}$), 3440 (ν_{OH}) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.2–7.9 (m, 10 H), 4.8 (s, 1 H), 1.9 (s, 3 H); mass spectrum, *m/z* (rel intensity) 226 (8), 208 (8), 122 (100), 121 (100), 120 (100), 105 (100), 78 (100), 77 (100).

2,3-Diphenylbutane-2,3-diol (mixture of d,l and meso compound): mp 116–118 °C (lit.[32] d,l 122–124 °C, meso 115–117 °C); IR (KBr) 3500 (ν_{OH}, br) cm^{-1}; ^{1}H NMR ($CDCl_3$) d,l compound δ 1.6 (s, 6 H), 2.3 (s, 2 H), 7.2–7.3 (s, 10 H), meso compound δ 1.5 (s, 6 H), 2.6 (s, 2 H),

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(33) We recognized hfs's due to hydrogen atom of Me (0.14 mT), Et (0.15 mT), and *i*-Pr (0.16 mT) groups originated from respective Grignard reagents on the EPR spectra of GCR's. In the cases of PhMgBr, Ph-d_5-MgBr, and *p*-TolMgBr we found none of such splittings on the corresponding EPR spectra of the GCR's. These facts substantiate the structure of the GCR.

7.2–7.3 (s, 10 H); mass spectrum (mixture), *m/z* (rel intensity) 242 (8), 205–209 (100), 121 (100) (see Table IV).

2.7. Reaction of EtMgBr with α-Phenylbenzoin. A THF solution of 0.11 mmol of EtMgBr (0.42 M, 0.25 mL) was mixed with a THF solution of 0.05 mmol of α-phenylbenzoin (0.5 equiv) in a reaction vessel. The reacting solution became bright orange soon after the reactants were mixed. The EPR spectrum of the solution was the same as that of GCR observed in the reaction of PhMgBr with benzil in the ratios of $B/G < 1.0$.

2.8. Reaction of PhMgBr with α-Methylbenzoin. A THF solution of 0.24 mmol of PhMgBr (0.96 M, 0.25 mL) was mixed with a THF solution of 0.12 mmol of α-methylbenzoin (0.5 equiv) in a reaction vessel. The reacting solution became bright orange soon after the reactants were mixed. The EPR spectrum of the solution was the same as that of GCR observed in the reaction of MeMgBr with benzil mixed in the ratios of $0.3 \leq B/G \leq 0.5$.

2.9. Reaction of PhLi with Benzil. A ethyl ether solution of 0.17 mmol of PhLi (0.66 M, 0.25 mL) was mixed with 6 mL of a THF solution of benzil in a reaction vessel. In the reactions of excess benzil ($B/PhLi > 1.0$), the reacting solution became dark brown as soon as the reactants were mixed together and showed well-resolved EPR spectra of PCR with a g value of 2.0047. In the reactions of excess PhLi ($B/PhLi < 1.0$), the solutions became green soon after the reactants were mixed and showed very complex but well-resolved EPR spectra with a g value of 2.0031.

2.10. EPR Observations at 77 K. A known amount of EtMgBr or PhLi was mixed with a 2-methyltetrahydrofuran (MTHF) solution of benzil in a reaction vessel at room temperature. Then, the EPR quartz cell containing MTHF solution of PCR or GCR was placed in the tip of a quartz Dewar filled with liquid nitrogen, and the tip of the Dewar was inserted into a resonance cavity of EPR. The resulting EPR spectra of the PCRs and GCR at 77 K are shown in Figures 4 and 6, respectively. When we mixed the solvent with ethyl ether, the weak, fine structure of the PCR which appeared in the reaction of EtMgBr with benzil was enhanced; the phenomena might be related to the well-known fact that neutral Grignard reagents prefer to aggregate in ethyl ether.[7d]

2.11. Change of B/G in Situ. At solution B, PCR prepared in the mixing ratio of $B/G = 2.0$ (0.25 mL of a 0.42 M THF solution of EtMgBr was reacted with 2 equiv of benzil dissolved in 6 mL of THF) was left standing for 2 h before the subsequent experiments. When a calculated amount of EtMgBr solution (0.42 M, 0.17 mL) was added to the prepared sample to make the solution correspond to $B/G = 1.2$, the amount of the PCR decreased to 85% of the initial amount. When a calculated amount of EtMgBr solution (0.42 M, 0.38 mL) was added to another prpared sample as described above to give the value of $B/G = 0.8$, the solution became colorless or pale yellow, and the PCR vanished completely. This was confirmed not only by EPR but also by electronic spectra. Further, when into another prepared sample was added a calculated amount of EtMgBr solution (0.42 M, 0.58 mL) to give the value of $B/G = 0.6$, the PCR vanished immediately, and the solution became bright orange, indicating appearance of GCR.

3. Kinetic Observations by Stopped-Flow Method. All of the instruments were dried in vacuo and flushed with high purity argon before use. Samples were prepared in well-dried and argon-flushed vessels sealed with rubber septa. Grignard reagents were diluted with dry THF to $^1/_2$ or $^1/_4$ of the initial concentration. Several THF solutions of benzil of different concentrations were employed, but the B/G ratio was kept constant at $B/G = {}^1/_{10}$. With syringes the reactants were transferred to reservoirs of the equipment which were kept dry with the flow of high purity nitrogen. In every case, the result was accumulated 4–60 times, and the resulted curve was analyzed by inspecting both computer curve fitting and Guggenheim plot. Detailed conditions of the experiments are given in Table III.

Acknowledgment. We are greatly obliged to Professor Noboru Hirota, Kyoto University, for his discussions on the radical ion pair and to Professor Jun-ichi Hayami, Kyoto University, for use of stopped-flow equipment as well as his discussions on the reaction kinetics.

Registry No. 1 (R = Ph), 103852-41-1; **1** (R = Me), 103852-43-3; **1** (R = Et), 103852-49-9; **2** (R = Ph), 103852-45-5; **2** (R = Me), 103852-47-7; **2** (R = Et), 103852-51-3; PhMgBr, 100-58-3; MeMgBr, 75-16-1; EtMgBr, 925-90-6; PhLi, 591-51-5; $Ph_2C(OH)C(OH)Ph_2$, 464-72-2; $PhC(O)C(O)Ph^{-\cdot}/K^+$, 95515-29-0; $PhC(O)C(O)Ph^{-\cdot}/Na^+$, 34508-03-7; $PhC(O)C(O)Ph^{-\cdot}/{}^1/_2Mg^{2+}$, 103852-36-4; $PhC(O)C(O)Ph\cdot{}^3/_2Na$, 103852-37-5; $Ph_2C(OH)C(O)Ph\cdot PhLi$, 103852-38-6; $PhC(O)C(O)Ph\cdot PhLi$, 103852-39-7; benzil, 134-81-6; α-phenylbenzoin, 4237-46-1; α-methylbenzoin, 5623-26-7; (±)-2,3-diphenylbutane-2,3-diol, 22985-90-6; *meso*-2,3-diphenylbutane-2,3-diol, 4217-65-6.

Effect of Cationic Surfactants on the Conformational Transition of Poly(methacrylic acid)

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Received January 13, 1986

Abstract: The interaction between poly(methacrylic acid) and alkyltrimethylammonium bromide, C_nTAB, cationic surfactants has been investigated in aqueous solutions of pH 8, by use of the photophysics of pyrene and its derivatives. Photophysical studies of these fluorescent probes, both steady-state and pulsed laser studies, show that a conformational transition of PMA is induced by C_nTAB. The surfactant induces a coiling up of PMA chains at pH 8, which takes place via a cooperative process. This effect takes places when the concentration of C_nTAB is above a critical aggregate concentration, CAC. The CAC is 1 or 2 orders of magnitude less than the cmc of the corresponding micelle. There is a significant effect of surfactant chain length and PMA concentration on the CAC, which provides information on the nature of the CAC and the mechanism of the PMA transition. A model is suggested for the aggregation of PMA–$C_{10}TAB$ based on experimental data. Studies show that the aggregate consists of about 100 $C_{10}TAB$ molecules and 1 coiled polymer chain.

Considerable interest has developed in polymer–surfactant systems both as models for membrane mimetic chemistry[1] and for the practical uses, e.g., in processes of enhanced oil recovery.[2] Early studies have mainly focused on the interaction between nonionic polymers and surfactants, e.g., poly(ethylene glycol), PEG,[3a] poly(ethylene oxide), PEO,[3b] or poly(*N*-vinylpyrrolidone), PNVP,[3c] and the anionic surfactant, sodium dodecyl sulfate, SDS. A great variety of experimental data exists, but the nature of the

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