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TWO INTERMEDIATES OBSERVED IN THE GRIGNARD REACTION WITH BENZOPHENONE

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Intermediates in the reaction of Grignard reagent with benzophenone in THF were investigated by both ESR and stopped-flow techniques. The short-lived (blue colored) and other long-lived (pink colored radical) intermediates were observed. The pink colored radical intermediate could be in a state of dimeric aggregate of benzophenone anion radicals ion-paired with Grignard cation ["RMgBr"]$^{\dot{+}}$ in solution.

In 1964, unambiguous appearance of radical species in the Grignard reaction with benzophenone and its substituted derivatives was first reported by K.Maruyama.[1)] Recently, the Grignard reactions with ketones have been outlined to proceed via an initial electron transfer from Grignard reagent to ketones and subsequent alkyl (or aryl) radical transfer.[2)] However, the detailed reaction mechanism is still hidden in a veil. Especially, the true structure of the "intermediate" anion radical, probably being ion-paired with Grignard cation ["RMgBr"]$^{\dot{+}}$ and how alkyl (or aryl) radical does transfer to the anion radical are not known. This paper will deal with these problems.

When Grignard reagents were allowed to react with benzophenone in a tetrahydrofuran (THF) solution under dry and strictly deaerated conditions, blue and pink colored species appeared. The one (pink colored) of the two species showed quite well-resolved ESR spectra, but decayed rather slowly, and the other (blue colored) could not be observed by ESR because of its extremely short life-time. The color and the proton hyperfine coupling constants (hfcc) of pink colored species are given in Table 1, together with those of benzophenone magnesium mono-halide ketyl, and magnesium mono-alkyl ketyls.

Table 1.

Hyperfine Coupling Constants of Benzophenone Anion Radicals [a)]

(mT)

	Counter cations	o-	m-	p-	Color
1	$(\text{"MeMgBr"})_2^{2+}$	0.290	0.104	0.357	pink
2	$(\text{"EtMgBr"})_2^{2+}$	0.291	0.107	0.357	pink
3	$(\text{"i-PrMgBr"})_2^{2+}$	0.289	0.105	0.357	pink
4	$(\text{"n-BuMgBr"})_2^{2+}$ b)	-	-	-	no color
5	$(\text{"PhMgBr"})_2^{2+}$	0.288	0.106	0.357	pink
6	$(\text{BrMg})_2^{2+}$ c)	0.295	0.108	0.357	purple
7	$(\text{BrMg})_2^{2+}$ d)	0.295	0.108	0.357	pink
8	$(\text{BrMg})_2^{2+}$ e)	0.295	0.108	0.357	pink
9	$(\text{EtMg})^{+}$ f)	0.294	0.108	0.357	blue
10	$(\text{PhMg})^{+}$ g)	0.294	0.108	0.358	blue

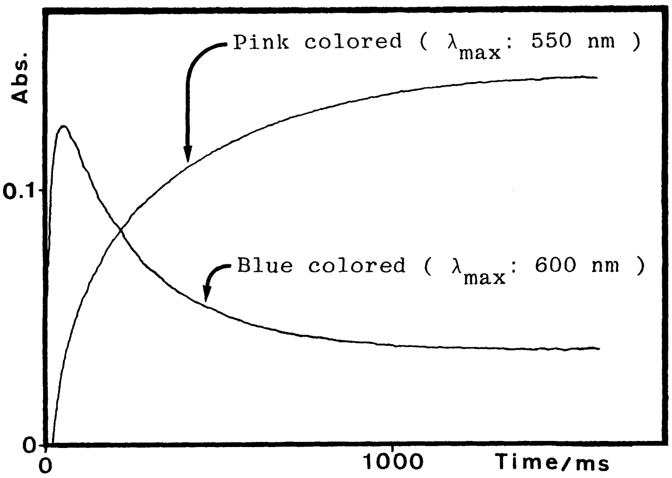
a) The value of hfcc is an average of three experiments at 25 °C in THF. Standard deviation of the values was smaller than 0.001 mT.
b) The radical was too short lived to be measured. c) Generated by the reaction of $MgBr_2$ with benzophenone potassium ketyl.[5)] d) Generated by the reaction of "EtMgBr" with 1,1,2,2-tetraphenylethane-1,2-diol (TPEG).[8)] e) Generated by the reaction of "PhMgBr" with TPEG.[8)] f) Generated by the reaction of "Et_2Mg" with TPEG.[8)]
g) Generated by the reaction of "Ph_2Mg" with TPEG.[8)]

As shown in Table 1, there is an unambiguous difference in the hyperfine coupling constants (hfcc's) between anion radicals observed in the Grignard reactions (column 1-5) and the benzophenone magnesium mono-halide ketyl (column 6-8) or magnesium mono-alkyl ketyls (column 9,10). In addition, the hfcc values are varied with size of the alkyl (or aryl) groups in the Grignard reagents (column 1-5). The latter is a clear indication of "tight" ion-pair formation between benzophenone anion radical and Grignard cation $[\text{"RMgBr"}]^{+\bullet}$. In benzophenone ketyl, the smaller proton hfcc's of o-hydrogens are generally observed in the case of the ketyl "tight" ion-paired with a large cation, compared with that associated with a smaller size cation.[3)] Consulting to the results given in Table 1, we arrive to the following conclusions; Grignard cation "tight" ion-paired with benzophenone anion radical is different from simple magnesium mono-halide cation $(\text{BrMg})_2^{2+}$ or magnesium mono-alkyl cations $(\text{RMg})^{+}$. Our experiments indicate further that the addition reaction of Grignard reagent to benzophenone proceeds stepwise; i.e., initial electron transfer and subsequent alkyl (or aryl) radical transfer.

Then, what is the true structure of Grignard cation in the reacting mixture ? If it were in a state of monomeric cation,[4,5] it should affect the hyperfine line-width of benzophenone anion radical, the lines should be broadened because of strong spin-spin interaction, but this is not the case. Or simply the ESR signal of Grignard cation radical should be observed, but again it is not. In ESR experiments, we observed a stable (pink colored) benzophenone ketyl giving well-resolved hyperfine structure, and could not detect any other "stable" radical or remarkable line-broadening of the ESR signals. In addition, simple organometallic cation radicals are extremely short-lived because of their high tendency to cleave the metal-carbon bond.[6] The answer to this problem may be given from the results of stopped-flow kinetic studies.

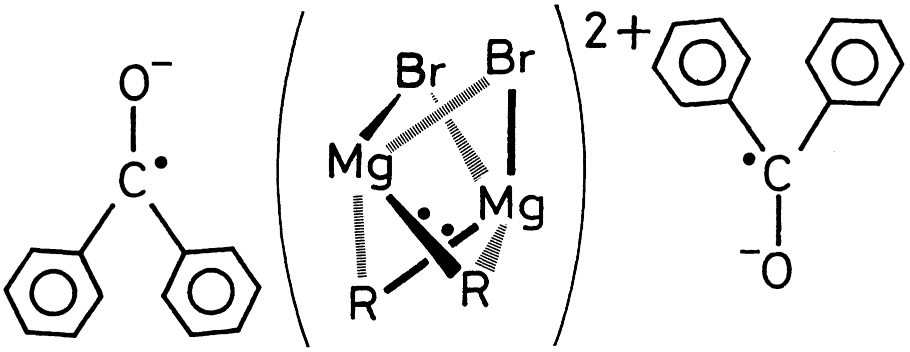
As mentioned above, there appeared two kinds of (blue and pink) intermediates in the initial stage of the reaction. First of all, the blue colored species which has λ_{max} at 600 nm is very short-lived (decay rate: 1.1×10^7 $M^{-1}s^{-1}$ in the reaction of EtMgBr (1 M = 1 mol dm^{-3})). This species may be a monomer ion pair; that is, monomeric benzophenone anion radical ion-paired with Grignard cation, because the λ_{max} of the species is in a good agreement with that of benzophenone magnesium ketyl.[3a] Even in the presence of a large excess of Grignard reagent, the decay of this blue species obeyed good second-order kinetics, suggesting formation of a dimer. The other pink colored species which has λ_{max} at 550 nm appeared in accordance with decay of the blue species, as shown in Fig.1. This pink colored species long-lived (decay rate: 0.07 s^{-1} in the reaction [0.023 M EtMgBr]) is just corresponding to the intermediate studied by ESR technique.[1,4] We could, hence, concluded that the pink species is an aggregate, possibly dimer, of the blue species.[7] Thus, the radical feature of the Grignard cation is extinguished by dimerization. Possible structure of the pink colored radical in solution may be depicted as structure 1.

Summarizing our results, we realized two intermediates (blue colored and pink colored) in the Grignard reaction of benzophenone. The blue colored decays to the pink colored by second order kinetics. The pink colored which is unambiguously fairly stable radical could be in a state of structure 1 in solution, but decayed to give final addition product.



25°C, under N_2.

Fig.1. Decay of blue species and appearance of pink species in the reaction of n-BuMgBr (0.35 M) - $C_6H_5COC_6H_5$ (0.035 M).



Structure 1

References

1) K.Maruyama, Bull.Chem.Soc.Jpn.,37,897 (1964); also see G.A.Russell, et al., J.Am.Chem.Soc.,86,1807 (1964); C.Blomberg and H.S.Mosher, J.Organomet.Chem., 13,519 (1968).

2) For recent review see: T.Holm, Acta Chem.Scand.,Ser.B,37,567 (1983).

3) a) N.Hirota, "Radical Ions," ed by E.T.Kaiser, L.Kevan, Interscience, New York, N.Y.,(1968),Chap.2; b) N.Hirota and S.I.Weissman, J.Am.Chem.Soc., 86,2538 (1964); c) T.Takeshita and N.Hirota, ibid.,93,6421 (1971).

4) E.C.Ashby and A.B.Goel, J.Am.Chem.Soc.,103,4983 (1981).

5) W.Kaim, Acc.Chem.Res.,18,160 (1985); W.Kaim, Angew.Chem.,Int.Ed.Engl.,21,140 (1982).

6) J.K.Kochi, "Organometallic Mechanisms and Catalysis," Academic Press, New York, N.Y.,(1978),Chap.16.

7) We have an umambiguous evidence which indicates dimer formation of benzil anion radical ion-paired with Grignard cation. The results will be soon reported elsewhere.

8) I.G.Lopp, et al., J.Am.Chem.Soc.,97,4966 (1975).

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