CHEMISTRY LETTERS, pp. 731-734, 1987.

Direct Evidence Supporting a Dimer Structure of Stable Radical Intermediate Appeared in the Grignard Reaction

Kazuhiro MARUYAMA* and Toshimasa KATAGIRI
Department of Chemistry, Faculty of Science, Kyoto University,
Sakyo-ku, Kyoto 606

A pink colored intermediate radical which appeared in the Grignard reaction of 2-methylbenzophenone in THF showed a well-resolved ESR spectrum of 2-methylbenzophenone anion radical at room temperature and a clear ESR spectrum of triplet radical pair in rigid state, which suggested that this radical species consisted of two 2-methylbenzophenone anion radicals and a dimer di-cation of Grignard reagent.

It has been gradually disclosed that the Grignard reaction of ketones proceeds by an initial electron transfer from Grignard reagent followed by subsequent alkyl (or aryl) radical transfer.[1-6] Recently, we reported the reaction mechanism of benzil with Grignard reagents,[1a] where we proposed the structure of stable intermediate radicals, which are in the state of aggregated dimer. However, even at the present stage whether such a state is special or general in the Grignard reaction of ketones remains to be clarified.[7]

In the Grignard reaction of benzophenone occurrence of two different kinds of intermediate radicals has been reported by us.[1b] From kinetic investigations of the decay (blue colored) and the growth (pink colored) processes, short-lived blue colored species (λ_{max}: 600 nm) was identified to the monomeric radical anion - radical cation pair, and stable "long-lived" pink colored species (λ_{max}: 540 nm) which showed well-resolved ESR signal to the dimer of the blue colored species. As in the case of benzil in the dimer the two cation moieties of Grignard reagent could aggregate to cancel their magnetic effect toward surrounding anion radicals as shown in structure 1,8) but we hardly succeeded in observing a magnetic evidence for the dimer formation in this case, because of lower concentration of the pink colored "stable" radical in a 2-methyltetrahydrofuran solution.1b)

In the reaction of 2-methylbenzophenone in 2-methyltetrahydrofuran, however, we succeeded in observing the unambiguous triplet ESR signal of the aggregated dimer of pink colored intermediate radical (Fig. 1) in rigid state at 77 K. This finding could confirm the dimer structure of stable radical intermediate, indicating the generality of the structure proposed previously in the Grignard reaction of benzil or benzophenone.1a,b)

From the fine structure, we can determine the energy parameter D' as

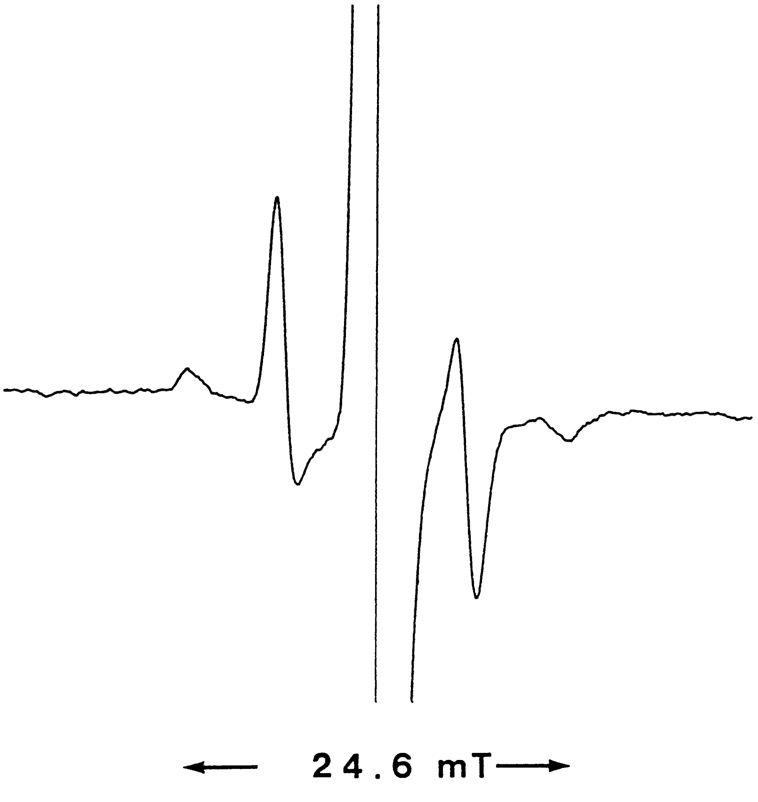
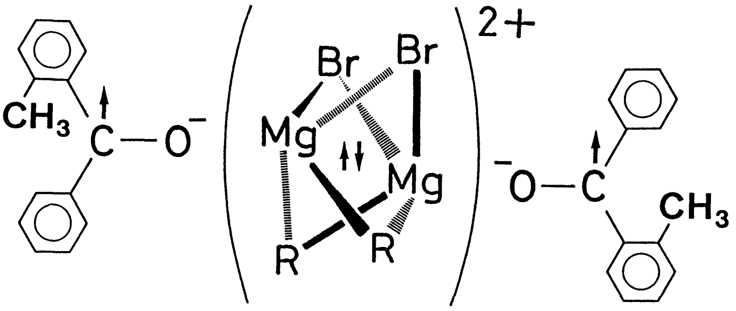


Fig. 1. The triplet ESR signal of pink colored species in rigid media in the reaction of "EtMgBr" with 2-methylbenzophenone in 2-methyltetrahydrofuran at 77 K.

12.3 mT, which enables us to estimate that the distance between two free spins on two anion radicals is 6.1 Å. The evaluated distance is close to the reported values on benzophenone sodium (6.5 Å) and lithium (5.9 Å) ketyl dimers.[9)]



Structure 1

In the reaction of ethylmagnesium bromide ("EtMgBr") with 2-methylbenzophenone in THF under strictly dry and deaerated conditions, the pink colored radical species (λ_{max}: 540 nm) appeared in the solution, which showed well-resolved ESR spectra at room temperature (Fig. 2). When we used methylmagnesium bromide ("MeMgBr") as well as n-butylmagnesium bromide ("n-BuMgBr") instead of "EtMgBr", the same ESR signals with the same hyperfine structures were observed. From the detailed analysis of hyperfine splitting constants of the ESR signals, these radicals are identified to an anion radical of 2-methylbenzophenone ($a_{(1H)}$ = 0.540 mT, $a_{(2H)}$ = 0.481 mT, $a_{(2H)}$ = 0.193 mT, $a_{(5H)}$ ≈ 0.057 mT, and $a_{(2H)}$ ≈ 0.019 mT).

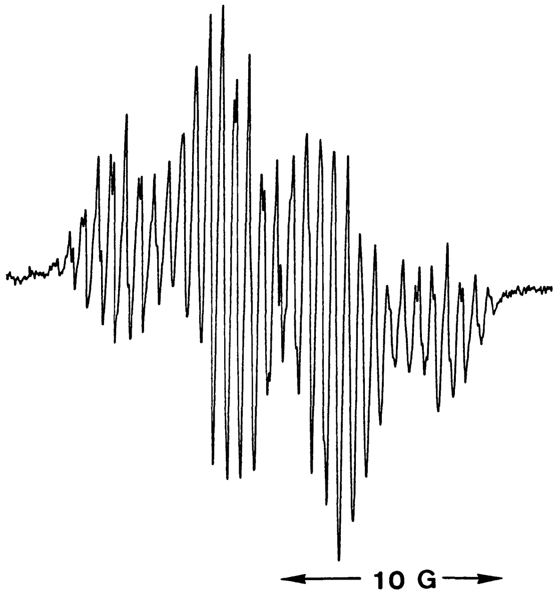


Fig. 2. The ESR spectrum observed in the reaction of "EtMgBr" with 2-methylbenzophenone in THF at 25 °C.

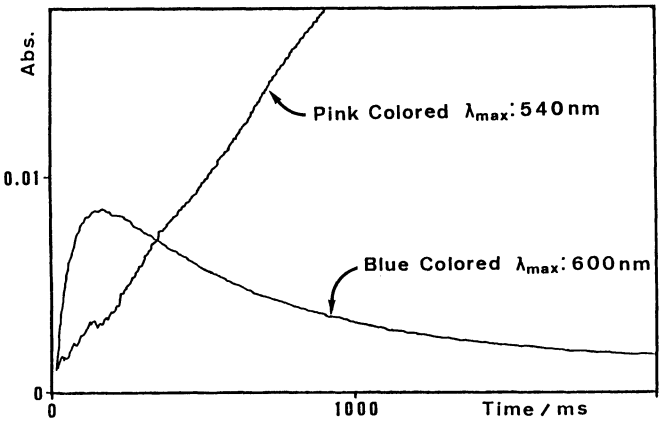


Fig. 3. Initial stage of the radical formations, in the reaction of "EtMgBr" with 2-methylbenzophenone in THF at 25 °C under N_2, followed by stopped-flow method.

The dimer formation is sufficiently faster compared with the initial electron transfer. Thus, we observed only a trace amount of the blue colored species which could be a monomer ion-radical pair at the initial stage of the radical formations by stopped-flow method (Fig. 3).

References

1) a) K.Maruyama and T.Katagiri, J.Am.Chem.Soc., 108, 6263 (1986); b) K. Maruyama, J.Hayami, and T.Katagiri, Chem.Lett., 1986, 601; c) K.Maruyama, Bull.Chem.Soc.Jpn., 37, 897 (1964); d) K.Maruyama, ibid., 37, 1013 (1964).

2) T.Holm and I.Crossland, Acta Chem.Scand., 25, 59 (1971); T.Holm, J.Organomet.Chem., 29, C45 (1971); T.Holm, Acta Chem.Scand., Ser.B, 37, 567 (1983).

3) E.C.Ashby and J.S.Bowers,Jr. J.Am.Chem.Soc., 99, 8504 (1977); E.C.Ashby and J.S.Bowers,Jr. ibid., 103, 2242 (1981); E.C.Ashby and A.B.Goel, ibid., 103, 4983 (1981); E.C.Ashby, Pure Appl.Chem., 52, 545 (1980).

4) G.A.Russell, E.G.Janzen, and E.T.Storm, J.Am.Chem.Soc., 86, 1807 (1964).

5) C.Blomberg and H.S.Mosher, J.Organomet.Chem., 13, 519 (1968).

6) M.Ōkubo, Bull.Chem.Soc.Jpn., 48, 2057 (1975); M.Ōkubo, ibid., 50, 2379 (1977).

7) W.Kaim, Acc.Chem.Res., 18, 160 (1985).

8) We had shown recently that alkyl or aryl group was kept in the cation moiety of Grignard reagent, see Ref. 1b.

9) N.Hirota, "Radical Ions," ed by E.T.Kaiser and L.Kevan, Interscience, New York (1968), Chap. 2; N.Hirota, J.Am.Chem.Soc., 89, 32 (1967).

(Received January 30, 1987)