BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (3), 1057—1058 (1975)

Ketyl Radical Formed in the Grignard Reaction of 2-Methylbenzophenone

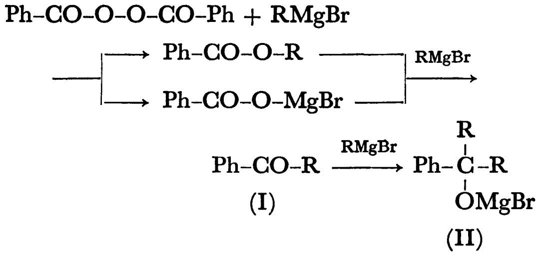
Masao Ōkubo

Department of Chemistry, Faculty of Science and Engineering, Saga University, Honshō-chō, Saga 840

(Received December 6, 1973)

Synopsis. The radical in the title reaction gave an ESR spectrum different from that of potassium-ketyl. From studies using the deuterium label technique, the reason for this difference was ascribed to the suppression of the twisting vibration caused by aggregate-formation.

The scheme for the reaction of Grignard reagents with benzoyl peroxide in tetrahydrofuran (THF) was recently established to be that shown in formula 1.[1]



$$\mathrm{Ph\text{-}CO\text{-}O\text{-}O\text{-}CO\text{-}Ph + RMgBr} \longrightarrow \left\{\begin{array}{l}\mathrm{Ph\text{-}CO\text{-}O\text{-}R}\\ \mathrm{Ph\text{-}CO\text{-}O\text{-}MgBr}\end{array}\right\} \xrightarrow{\mathrm{RMgBr}}$$

$$\underset{\text{(I)}}{\mathrm{Ph\text{-}CO\text{-}R}} \xrightarrow{\mathrm{RMgBr}} \underset{\text{(II)}}{\mathrm{Ph\text{-}\overset{\displaystyle R}{\underset{\displaystyle OMgBr}{C}}\text{-}R}} \qquad (1)$$

In the course of a study of this reaction, a large excess of *o*-tolyl-MgBr was found to change the reaction solution from colorless to purple and an exceptionally long-lived radical species was detected.[2] As this radical is considered by the author to be related to the ketone (I, R=*o*-tolyl in formula 1), the radical produced in the Grignard reaction of 2-methylbenzophenone itself was studied in detail.

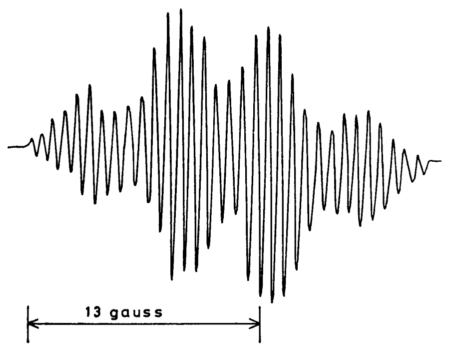


Fig. 1. ESR spectrum (A) of the radical species obtained in the reaction of 2-methylbenzophenone with *o*-tolyl-MgBr in THF.

The ESR spectrum (A) obtained in the reaction of I with *o*-tolyl-MgBr is shown in Fig. 1. As the spectrum obtained in the reaction of I with phenyl-MgBr was identical with spectrum A, the radical seemed to be a ketyl-type.[3] This radical existed even after the evacuated sample solution had been allowed to stand for several months at room temperature. This Grignard-ketyl, if that is what it is, is anomalous because of its long life[4] in comparison with the Grignard-ketyl of benzophenone which gave a measurable (by ESR) radical concentration only at temperatures lower than −20 °C.[5,6] Considering this anomaly, one might suspect that spectrum A is not that of a ketyl radical but that of triarylmethyl radical derived from the final product (II). The latter possibility, however, can be excluded by examining the calcium-ketyl of I prepared by using Ca-amalgum in THF. Spectrum B shown in Fig. 2 was obtained when the solution of Ca-ketyl was not fully diluted. Resemblance of spectrum A to B is obvious.

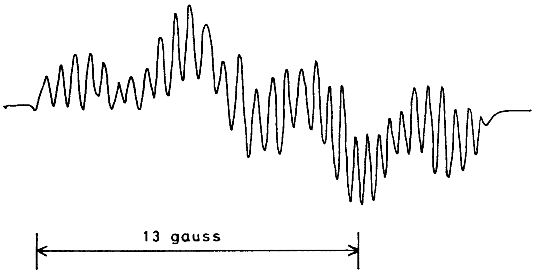
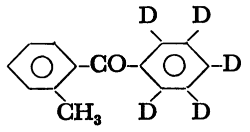
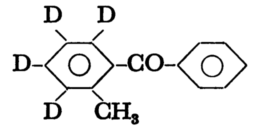


Fig. 2. ESR spectrum (B) of Ca-ketyl of 2-methylbenzophenone prepared in THF.

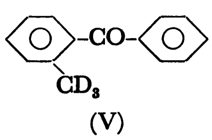
Spectrum A (total width 23.5 G) consists of four broad lines (a_1=5.86 G), each of which splits into eight lines (a_2=0.73 G). This spectrum differs from that of the potassium-ketyl of the same ketone, which is known to give a spectrum made up of only four broad lines.[7] In order to explain why the hyperfine splittings are observed in the Grignard reaction and not observed in the alkali metal reduction, the assignment of the splitting constants a_1 and a_2 is necessary. As no fruitful result is obtained if the numbers of equivalent hydrogen atoms are taken into account, the deuterium label technique was applied. When d_5-phenyl *o*-tolyl ketone (III) was treated with phenyl-MgBr, a broad single line with the total width of 9.4 G was observed. The splitting constant a_1 is thus ascribed to the equivalent coupling of the two *ortho-* and one *para*-hydrogen atoms of the phenyl group with the free electron.[7] 2-Methyl-3,4,5,6-d_4-phenyl phenyl ketone(IV) gave four broad lines. In the case of 2-(d_3-methyl)phenyl phenyl ketone (V), spectrum C, composed of 32 lines, was observed but the relative strength of each line varied as shown in Fig. 3. The hyperfine splitting constant a_2 can thus be assigned mainly to the coupling of the nuclear



(III)



(IV)



(V)

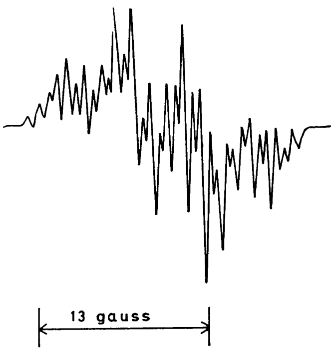


Fig. 3. ESR spectrum (C) of radical species obtained in the reaction of 2-(d_3-methyl)phenyl phenyl ketone with PhMgBr.

hydrogen atoms of the *o*-tolyl group and partly to that of the *o*-methyl hydrogen atoms with free spins.

The difference between the spectrum of the Grignard-ketyl and that of the K-ketyl can be ascribed to "aggregate-formation". The divalent calcium ion favors the formation of dimeric ketyl, which may aggregate further when the solution is less than fully diluted. During the dilution of the solution of the Grignard-ketyl in an evacuated sample tube, a portion of the deeply colored concentrated solution was observed to form a heavy layer at the bottom of the tube and some difficulty was found in obtaining a homogeneously diluted solution. This must be due to the formation of dimeric or polymeric aggregates. Resemblance of spectrum A to B suggests that the Grignard–ketyl exists in an aggregated state even in a fully diluted solution, although a description of this state cannot be given at present. The dimer- or aggregate-formation may suppress the twisting vibration of the *o*-tolyl group out of the plane of the benzoyl group, and thus the interaction of *o*-tolyl hydrogen atoms with free spins can be observed even though the spin density on the *o*-tolyl group is low. In the case of the K-ketyl, in which aggregate formation is not favored at low concentrations, the twisting vibration of the *o*-tolyl group may be rapid and the interaction of its hydrogen atoms with free spins could not be observed.

The large effect of deuterium label of the phenyl group on the total width of the Grignard-ketyl spectrum is remarkable. The spectrum width is reduced from 23.5 to 9.4 G while that of the K-ketyl is reduced from 21.7 to 18.5 G.[7] This indicates that the free spin density on the phenyl group is much higher in the Grignard-ketyl than in the K-ketyl. It is therefore concluded that the twisting angle of the *o*-tolyl group is larger in the former and the twisting vibration of the *o*-tolyl group is more rapid in the latter.

The reason for the exceptionally long life of the Grignard-ketyl is not yet clear, and further studies of Grignard-ketyls of 2-substituted benzophenones are now in progress.

Experimental

Materials. 2-Methylbenzophenone was prepared as usual. The ketone III was prepared from *o*-tolyl chloride and benzene-d_6 in CS_2 using $AlCl_3$. The ketone IV was prepared by the reaction of PhCOCl with the Grignard reagent derived from 2-methyl-3,4,5,6-d_4-phenyl bromide, which was obtained by repeated treatment of *o*-bromotoluene with 95% D_2SO_4.[9] The ketone V was prepared by the reaction of PhCOCl with the Grignard reagent derived from 2-(d_3-methyl)phenyl bromide, which was obtained from the following sequence of reactions. Anthranilic acid was converted to *o*-bromobenzoic acid by Sandmeyer reaction. By treatment of the acid with $LiAlD_4$, *o*-bromo-α,α-d_2-benzyl alcohol was obtained. The alcohol was then converted to the chloride by treatment with $SOCl_2$, and the Cl-atom was replaced by deuterium by using Zn-powder and CH_3COOD. Grignard reagents in THF were prepared as usual and transferred under N_2 to storage bottles.

ESR Measurement. Evacuated samples were prepared as previously described.[8] The molar ratio of phenyl-MgBr to ketones was 5: 1. After mixing by breaking the seal, the resulting purple solution was diluted by low-temperature-distillation in order to obtain a sufficiently resolved spectrum. A JEOL JES-ME-3X ESR spectrometer was used.

References

1) M. Ōkubo, K. Maruyama, and J. Ōsugi, This Bulletin, **44**, 125 (1971).

2) See foot-note 3) of Ref. 1.

3) If these spectra are not identical with each other, the possibility of formation of a triarylmethyl-type radical should be considered. See the following discussions.

4) E. C. Ashby, J. Laemmle, and H. M. Neumann, *J. Amer. Chem. Soc.*, **94**, 5421 (1972).

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7) K. Maruyama, R. Tanikaga, and R. Gotō, This Bulletin, **36**, 1141 (1963).

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