## SHORT COMMUNICATIONS

# *The Appearance of Free Radicals during Grignard Reactions*

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Although ionic mechanisms are generally assumed for most Grignard reactions, I have been able to observe free radicals during the course of the addition of Grignard reagents to certain ketones by ESR techniques. Such aromatic ketones as benzophenone, 4-chlorobenzophenone, 4-aminobenzophenone, 4-methoxybenzophenone, 4, 4′-dimethoxybenzophenone, acetophenone and *p*-bromoacetophenone produce free radicals in their reactions with $C_2H_5MgI$, $C_6H_5MgBr$ and *p*-$CH_3C_6H_4MgBr$ in tetrahydrofuran (THF).1) Some aliphatic ketones (such as pentamethylacetone and hexamethylacetone) and benzonitrile also produce free radicals in the reaction.

The ESR measurements were carried out as follows: The carbonyl compounds and the Grignard reagent (each at about $10^{-3}$ mol.) were mixed at a dry-ice-acetone temperature in the absence of air and moisture. The sapmle was then inserted into a cavity which had previously been cooled with a stream of boiling liquid nitrogen, and the ESR spectrum was measured.

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1) The Grignard reagents were prepared from reagent grade magnesium turnings for a Grignard reagent and the corresponding halides.

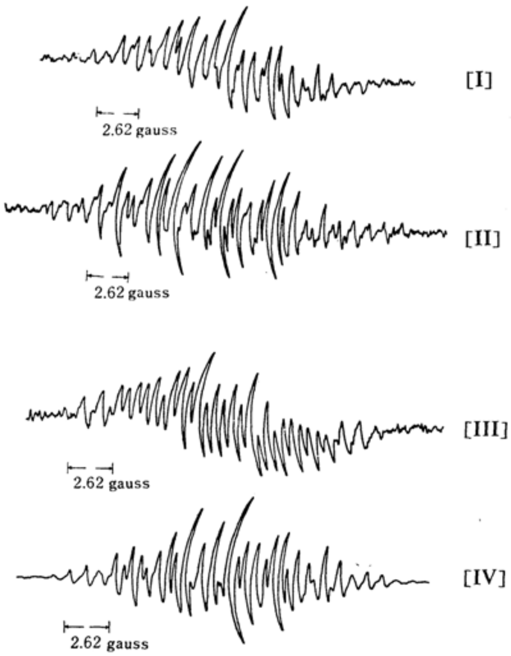

Fig. 1. The ESR spectra obtained during the course of some Grignard reaction.
[I] Benzophenone/phenylmagnesium bromide reacting system at −25°C
[II] Benzophenone/*p*-tolylmagnesium bromide reacting system at −25°C
[III] *p*-Chlorobenzophenone/phenylmagnesium bromide reacting system at −20°C.
[IV] Benzophenone-magnesium ketyl at −20°C

TABLE I. ABSORPTION MAXIMUM IN THE VISIBLE ABSORPTION SPECTRA OF CARBONYL/GRIGNARD REACTING SYSTEMS AND OF THE CORRESPONDING KETYLS

| Carbonyl compound | Carbonyl/ Grignard system in THF | Ketyl in THF |
|---|---|---|
| Benzophenone | 555 mμ | 615 mμ |
| 4-Chlorobenzophenone | 570 mμ | 623 mμ |

Benzophenone and 4-chlorobenzophenone give well-resolved hyperfine spectra during the course of the reactions with the Grignard reagents mentioned (Fig. 1). The other compounds give a single line. Although it is clear that the free radical in each Grignard reaction is not the ketyl which is obtained through the reduction of the corresponding carbonyl compound with Mg/Hg, a comparison of their ESR spectra and visible absorption spectra indicate that they are quite similar.

It was also found that the amount of the free radical which is produced in the course of the Grignard reaction depends on the concentration of the Grignard reagent (Table II).

Although the mechanism of the free radical formation can not be clarified by only the ESR technique, the facts described above seem to suggest that the free radical is of the ketyl type and that it is produced through the reduction of ketone by a species such as $(MgX)_2(RMgX)_n$ or $(MgR)_2(RMgX)_n$ which might exist in the Grignard reagent.2)

The scope of the formation and the problem of the structure of such free radical species are now under study.

TABLE II. CONCENTRATION OF FREE RADICALS PRODUCED IN THE COURSE OF REACTION BETWEEN $C_6H_5COC_6H_5$ AND $C_6H_5MgBr$

| Benzophenone[*2] (B) mol. | Phenylmagnesium[*1] bromide (G) mol. | Mol. ratio (B/G) | Maximum concn. of[*2] free radicals (%) |
|---|---|---|---|
| $1.8\times10^{-3}$ | $1.9\times10^{-3}$ | 1 | 3.4 |
| $4.5\times10^{-4}$ | $11.3\times10^{-4}$ | 1/ 3 | 3.7 |
| $3.8\times10^{-5}$ | $7.5\times10^{-4}$ | 1/20 | 24.0 |

[*1] Dissolved in 10 ml. of THF.
[*2] Calculated value based on the amount of benzophenone.

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2) There is no conclusive information about the components of Grignard reagents. The existence of an equilibrium such as $2RMgX \rightleftarrows RMgR\ MgX_2 \rightleftarrows RMgR+MgX_2$ is generally believed in, but this is not enough to explain the complex behavior of Grignard reagents. See H. Gilman "Organic Chemistry," Vol. 1, John Wiley & Sons, New York (1949), p. 489; A. D. Vreugdenhill and C. Blomberg, *Rec. trav. chim.*, **28**, 453 (1963); N. M. Bikales and E. I. Becker, *Can. J. Chem.*, **41**, 1329 (1963); K. Maruyama, a paper which will soon appear in this Bulletin; A. F. Scott "Survey of Progress in Chemistry," Vol. 1, Academic Press, New York (1963), p. 300, etc.