APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 9, 285–289 (1995)

Detection of Intermediates in Grignard Reaction on the Magnesium Surface

Anatoly M. Egorov and Alexander V. Anisimov*
Department of Chemistry, Moscow State University, 119899 Moscow, Russia

Benzyl radicals and ion–radical pairs ($RHal^{\cdot-} \ldots Mg_n^{\cdot+}$) have been detected on a magnesium surface by electron spin resonance (ESR) spectroscopy during benzyl halide reactions with magnesium at low temperatures. The ratio of these intermediates depends on the carbon–halogen bond energy in the starting benzyl halide, the nature of the magnesium surface and the degree of magnesium aggregation. Polymagnesiumbenzyl chlorides were formed in small amounts and only monomagnesium organic compounds were formed from benzyl bromide and benzyl iodide.

Keywords: benzyl halide; magnesium; radical; ion-radical pairs; detection; ESR

INTRODUCTION

The capture of radical intermediates in a solution by radical traps is an inconvenient technique for detection and identification of intermediates upon the magnesium surface in the Grignard reaction.[1–3] It is well known that ESR study of organic reactions is the most reliable evidence for the existence of paramagnetic particles as intermediates and one of the most convenient methods for their detection. Despite their stability, thermally produced benzyl radicals are indetectable by ESR spectroscopy.[4] Although the stream method[4,5] and use of an adamantane matrix[6] have been applied for this purpose, none of them was reliable for studies of the heterogeneous formation of Grignard reagents. Recently ion–radical pairs $RX^{\cdot-} \ldots Mg_n^{\cdot+}$ have been detected in some cases, together with $R^{\cdot}$ radicals, by ESR studies of low-temperature reactions.[7–9] The ratio of these intermediates depends on the carbon–halogen bond energy in the original organic halide. We report here the results of an investigation by ESR spectroscopy of low-temperature reactions of benzyl halides with magnesium.

EXPERIMENTAL

Equipment and analytical measurements

ESR spectra were recorded at 77 K on a Rubin radiospectrometer in films of magnesium co-condensates with 50–100-fold excess of benzyl halides according to the literature[7,8] at 9 GHz frequency in the absence of saturation and amplitude broadening. Quantitative analysis of liquid products was performed by GC with a Zvet 162 instrument using a 2.5 m glass column packed with 18% Apiezon L on Chromaton N-AW and 10% PEG-20M on Chromaton N-AW (with a flame ionization detector) and for hydrogen detection using a 2.0 m steel column packed with molecular sieves 4A (thermal conductivity detector was used). The amount of reacting magnesium was determined by ion chromatography techniques with a Zvet 3006 instrument using a Diakat-3 column (Elsiko, Moscow), with a conductivity detector. A water solution 1.5 mM in ethylenediamine, 3.5 mM in citric acid and 3.5 mM in tartaric acid was employed as the eluent.

Grignard reactions

All compounds used were obtained from commercial sources. Benzyl halides were purified via distillation prior to use. The cryosyntheses of organomagnesium compounds were performed in vacuum apparatus by co-condensation of magnesium and a 50–100-fold excess of benzyl halide onto the surface of a thin-walled mobile part of the reactor at 77 K during continuous evacuation (10^{-4} mm Hg) for 2 h as described earlier.[7] Benzyl halides were evaporated at 0–35 °C and the magnesium was sublimated from the quartz crucible at 640–670 K. Chestnut-coloured films of co-condensates were obtained and they were located on the reactor surface. These films were decolourized at the melting points of the hydrocarbons produced during warming.

Carbon tetrachloride (CCl_4)-containing sam-

---

* Author to whom correspondence should be addressed.

CCC 0268–2605/95/030285–05

Received 27 May 1994
Accepted 27 November 1994

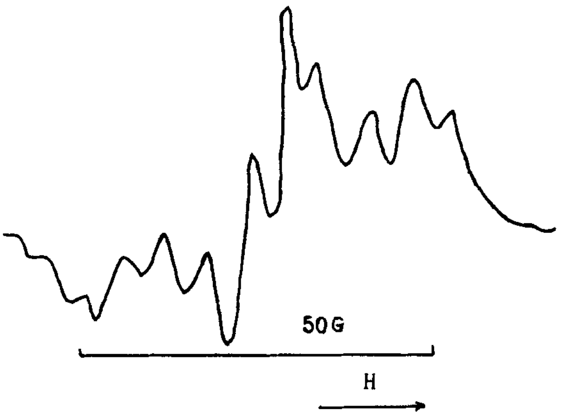


Figure 1 ESR spectrum of magnesium co-condensed with benzyl bromide at 77 K.

ples were prepared by co-condensation of organomagnesium compounds and CCl_4 in excess. The reaction mixture was kept for 1 h under vacuum at 77 K, then it was reacted with ethanol. The ethanolysis was performed by condensation of ethanol in excess on to the reaction mixture film at 77 K. Ethers were not found in the reaction products.

RESULTS AND DISCUSSION

The reactions of the three different benzyl halides with magnesium were investigated by ESR in the benzyl halide matrix at 77 K as described previously.[7–9] The ESR spectrum of magnesium co-condensate with benzyl bromide at 77 K in a solid matrix is a triplet of quartets with whole width 50 G and g-factor 2.002 (Fig. 1). The spectrum of the co-condensate of magnesium with benzyl iodide at 77 K is similar to the same spectrum of the co-condensate with benzyl bromide but it has not so high a resolution.

The parameters of the spectrum obtained and literature data for the benzyl radical spectrum are listed in Table 1. The ESR spectrum of benzyl radical in solution is usually well resolved. It has three triplets with intensity ratio 1:2:1 and a doublet ($a^H = 6.3$ G) with g-factor 2.0026.[4,5] There is a triplet of quartets with whole width about 50 G in the spectrum of the benzyl radical in a solid matrix at 80–100 K.[10,11] The last fact can be explained by broadening of the lines.[10,11] Comparison of the spectra obtained and literature data[10,11] allows us to attribute the spectra of magnesium co-condensed with benzyl bromide and benzyl iodide to the ESR spectrum of the benzyl radical generated upon abstraction of the halogen atom from the original benzyl halide by magnesium. Signals of isomerization products of the benzyl radical were not detected.

Table 1 Electron spin resonance hyperfine splitting constants for the benzyl radical

g-factor	$a^H_{CH_2}$	a^H_o	a^H_m	a^H_p	Ref.
2.002 ± 0.001	16.4 ± 0.5	5.5 ± 0.5		5.5 ± 0.5	This work
2.0026	16.34	5.13	1.77	6.17	5
—	16.4	5.1	1.6	6.3	4
—	16.5	6.0	—	6.0	10
—	16.5 ± 1.0	5.5 ± 0.5	—	5.5 ± 0.5	11

The ESR spectrum of magnesium co-condensed with benzyl chloride is a superposition of the triplet of quartets (which is similar to the spectrum of magnesium co-condensed with benzyl bromide and benzyl iodide) and a singlet with a half-width of 8 ± 2 G (Fig. 2). It is well known that the radical $\mathrm{M\dot{g}Cl}$ cannot be recorded under experimental conditions by means of ESR techniques and it should be supposed that the singlet could be assigned to an ion–radical pair of the $RX^{\cdot-} \ldots Mg^{\cdot+}$ type. The absence of hyperfine structure seems to be caused by exchange processes.[7,8]

Temperature increase in the benzylmagnesium halide cryosynthesis gradually reduces the intensity of ESR signals. The signal of the ion–radical pair (singlet) in the benzyl chloride–magnesium

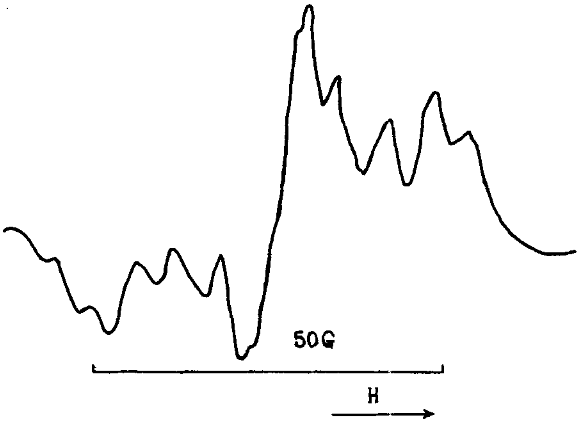


Figure 2 ESR spectrum of magnesium co-condensed with benzyl chloride at 77 K.

system decreases faster than that of the benzyl radical. The reason for this observation could be increase in ion–radical pairs $RX^{\cdot -} \ldots Mg_n^+$ recombination and decomposition rates, leading to the formation of $R^\bullet$ and $\mathrm{M\dot{g}X}$ radicals upon the magnesium surface. The paramagnetic particles disappear with melting of the samples. Thus it is quite possible to assume that radicals and ion–radical pairs are stable from 77 K to the melting point of the mixture of the hydrocarbons produced (1,2-diphenylethane and toluene). The spectra obtained show that ion–radical pairs and radicals are possible intermediates in the formation of Grignard reagents from benzyl derivatives. The reaction mechanism, however, seems to be dependent on the type of halogen in the benzyl halide.

Sergeev *et al.* have shown that the mechanism of the reaction of butyl halides and phenyl halides with magnesium depends on the carbon–halogen bond strength.[7–9] Radicals in these reactions were observed for the bromide and iodine derivatives (carbon–halogen bond energy 276 and 240 kJ $\mathrm{mol^{-1}}$); ion–radical pairs were detected for chloride and fluorine compounds (carbon–halogen bond energy 340–490 kJ $\mathrm{mol^{-1}}$). In this study we have obtained similar results for the cases of benzyl bromide and benzyl iodide (radicals as intermediates) and for benzyl chloride (radical and ion–radical pairs as intermediates). The total amounts of paramagnetic particles at 77 K in these samples were 7%, 12% and 15% for $PhCH_2Cl$, $PhCH_2Br$ and $PhCH_2I$ respectively in accordance with ESR data from the number of magnesium atoms deposited.

It is well known that the carbon–halogen bond strength in allyl and benzyl halides is weaker than in other alkyl halides. The bond energy in benzyl chloride approaches that found in alkyl(aryl) bromides rather than in the corresponding chlorides.[12] Consequently, if the reaction pathway of magnesium with benzyl halides depended only on the carbon–halogen bond strength, the radical intermediate $C_6H_5CH_2$ would be the only particle in the benzyl chloride–magnesium system. The detection of ion–radical pairs $C_6H_5CH_2Cl^{\cdot -} \ldots Mg_n^+$ and radicals $C_6H_5\dot{C}H_2$ suggests that another factor affecting the reaction mechanism is the stabilization of ion–radical pairs on the magnesium surface.

ESR study of magnesium co-condensed with benzyl chloride at 77 K shows that the intensity of the ion–radical pair singlet decreases by 30% as the ratio RX/Mg increases from 50 to 100. At 298 K the yield of the recombination product, namely 1,2-diphenylethane, doubles and reaches 8% (in accordance with GC data, Table 2).

While excess of benzyl halide is settling on to the magnesium film surface (the thickness of the film is about 10^{-4} mm), UHF power dissipation increases. The consequent decrease of ESR spectrum resolution can be attributed to increase in the magnesium film electroconductivity. The paramagnetic particles appearing in benzyl halide–compact magnesium systems are identical to the particles formed when atomic magnesium films are used.

ESR spectra in the cases of benzyl bromide and benzyl iodide condensation on to compact magnesium film at 77 K, are similar to those of co-

Table 2 Yield of products in the reaction of atomic magnesium with benzyl halides after ethanolysis of the reaction mixture

Halide	Ratio RX/Mg	Temp. of ethanolysis (K)	Yield (%) 1,2-Diphenylethane	$PhCH_3$	H_2	Ratio $Mg/PhCH_3$	Ratio Mg/H_2	n[a]
$PhCH_2Cl$	50	160	1.0	98.8	0.2	1.1	11	1.1
	50	298	4.0	96.0	—	1.0	—	1.0
	100	160	2.2	97.7	0.1	1.04	26	1.04
	100	298	8.0	92.0	—	1.0	—	1.0
$PhCh_2Br$	50	160	3.0	97.0	—	1.0	—	1.0
	50	298	6.3	93.7	—	1.0	—	1.0
	100	160	4.0	96.0	—	1.0	—	1.0
	100	298	8.3	91.7	—	1.0	—	1.0
$PhCH_2I$	50	160	4.5	95.5	—	1.0	—	1.0
	50	298	11.0	89.0	—	1.0	—	1.0

[a] n = Average number of magnesium atoms in organomagnesium compound molecule.

condensates of benzyl bromide with atomic magnesium. The ESR spectrum has poor resolution and low intensity in the latter case. That of benzyl chloride–compact magnesium film is similar to the low-intensity spectrum of magnesium cocondensate with benzyl chloride, with the ratio singlet : triplet of quartets being increased by 3–4-fold. The main cause of this increase is the stabilization of ion–radical pairs by charge distribution among the whole group of magnesium atoms.

Mono- and polyorganomagnesium compounds can be formed as a result of the decay of ion–radical pairs $\mathrm{RX}^{\cdot -}\ldots\mathrm{Mg}_n^{\cdot +}$. The mechanism of this reaction also depends on the bond-breaking energy of the carbon–halogen bond of the starting benzyl halide.[13] The compositions of organomagnesium compounds were determined by ethanolysis of the reaction mixture. The amounts of magnesium, toluene and hydrogen as the products of ethanolysis were estimated both in the frozen samples and in the thawed ones. The low melting point of ethanol (160 K) allowed us to detect polyorganomagnesium compounds, unstable at 298 K, in frozen and in molten samples (Eqn [1]).

$$\begin{aligned}&\mathrm{C_6H_5CH_2Mg_{\mathit{n}}Cl} + (2n-1)\mathrm{C_2H_5OH}\\ &\quad\rightarrow \mathrm{C_6H_5CH_3} + (n-1)\mathrm{Mg(OC_2H_5)_2}\\ &\quad\quad + (n-1)\mathrm{H_2} + \mathrm{MgCl(OC_2H_5)} \qquad [1]\end{aligned}$$

The compositions of reaction products being produced by the ethanolyses of organomagnesium compounds obtained by the co-condensation of magnesium with benzyl bromide and benzyl iodide are listed in Table 2. These data show that organomagnesium compounds contain only one magnesium atom in all cases. Those results are quite different from the literature data on the insertion of two or three magnesium atom clusters into carbon–halogen bonds of methyl and phenyl halides.[13–16] The absence of magnesium atom aggregation in the systems under study seems to be caused by the low bond-breaking energy of the carbon–halogen bond[14] in accordance with the absence of the formation of the ion–radical pairs $\mathrm{RX}^{\cdot -}\ldots\mathrm{Mg}^{\cdot +}$. If benzyl chloride is applied, hydrogen is formed as a by-product of reaction mixture ethanolysis at 160 K (magnesium conversion, 100%). The increase of the magnesium/toluene ratio in this case can be explained by the formation of cluster structures.[13,14] It is known that approximately 15% of the total number of magnesium atoms could be dimeric at the ratio RX/Mg = 100[9] and magnesium clusters with two or three atoms are more reactive than atomic magnesium.[15,16] Thus, the formation of polymagnesium chlorides occurs as in the recombination of ion–radical pairs $\mathrm{C_6H_5CH_2X}^{\cdot -}\ldots\mathrm{Mg}_n^{\cdot +}$ but not as a step-by-step insertion of magnesium atoms into C–X bonds. The presence of a small amount of cluster structures (less than 15%) and their disappearance in the course of ethanolysis at 298 K can be easily explained, either by the degradation of polybenzylmagnesium chlorides at 77 K with the formation of magnesium (Eqn [2]), or by a fast reaction with excess benzyl chloride giving the Grignard reagent (Eqn [3]).

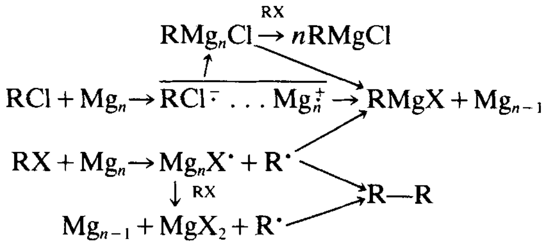
$$\mathrm{C_6H_5CH_2Mg_{\mathit{n}}Cl} \rightarrow \mathrm{C_6H_5CH_2MgCl} + \mathrm{Mg}_{n-1} \qquad [2]$$

$$\begin{aligned}&\mathrm{C_6H_5CH_2Mg_{\mathit{n}}Cl} + (n-1)\mathrm{C_6H_5CH_2Cl}\\ &\quad\rightarrow n\mathrm{C_6H_5MgCl} \qquad [3]\end{aligned}$$

The four-fold increase of the amount of 1,2-diphenylethane in the reaction products in the temperature range 160–298 K is connected with the decay of cluster structures with an increase in the rate of the Wurz reaction and with recombination of free benzyl radicals (Eqn [4]).

$$\begin{aligned}&\mathrm{C_6H_5CH_2Mg_{\mathit{n}}Cl} + \mathrm{C_6H_5CH_2Cl}\\ &\quad\rightarrow \mathrm{C_6H_5CH_2CH_2C_6H_5} + \mathrm{MgCl_2} + \mathrm{Mg}_n \qquad [4]\end{aligned}$$

The last two processes are the reason for the 2–2.5-fold increase in the amount of 1,2-diphenylethane whilst the ethanolysis temperature of magnesium–benzyl bromide and magnesium–benzyl iodide co-condensation increases from 160 to 298 K. As seen from Table 2, the formation of polyorganomagnesium compounds does not occur for these systems. One of the products of polybenzylmagnesium halide ethanolysis is hydrogen, which is formed by magnesium cluster insertion into C–H bonds of the starting benzyl halide.[14,15] The amount of hydride complexes forming was estimated by $\mathrm{CCl_4}$ condensation on to sample surfaces at 77 K before ethanolysis. According to GC data the amount of chloroform in ethanolysis products was about



R = benzyl
X = Cl, Br, I

Scheme 1

0.1% for the case of magnesium–benzyl chloride co-condensate and less than 0.001% for the case of systems containing benzyl bromide and benzyl iodide.

Thus the interaction of benzyl halides with magnesium proceeds mainly by insertion of magnesium into C–X bonds. The low C–X bond energy values do not allow C–H bond breakage by magnesium and benzylmagnesium hydride is not formed in virtually all the reactions. These studies of the nature of the intermediates and of some mechanism details of Grignard reagent formation at low temperatures allow us to propose the general reaction scheme shown in Scheme 1.

This scheme does not include the reactions of compounds with C–Mg_n–H bonds which were detected in trace amounts, isomerization and recombination of radicals and ion–radical pairs. It is in good agreement with classical mechanisms of Grignard reagent formation by radical and ion–radical pathways.[20]

CONCLUSIONS

It has been shown by ESR studies that benzyl radicals are formed as intermediates in the course of low-temperature reactions of benzyl chloride, benzyl bromide and benzyl iodide with magnesium. Ion–radical pairs and organic polymagnesium compounds were detected in the reaction of benzyl chloride with magnesium as well. Benzyl polymagnesium hydrides are formed only in trace amounts.

REFERENCES

1. L. M. Lawrence and G. M. Whitesides, *J. Am. Chem. Soc.* **102**, 2493 (1980).
2. E. C. Ashby and J. Oswald, *J. Org. Chem.* **53**, 6068 (1988).
3. A. M. Egorov and A. V. Anisimov, *Vestnik Moskovskogo Universiteta, Khimija* **34**, 191 (1993).
4. W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.* 4857 (1964).
5. P. Neta and R. H. Schuler, *J. Phys. Chem.* **77**, 1368 (1973).
6. R. V. Lloyd and D. E. Wood, *Mol. Phys.* **20**, 735 (1971).
7. G. B. Sergeev, V. V. Smirnov and V. V. Zagorsky, *J. Organomet. Chem.* **201**, 9 (1980).
8. G. B. Sergeev, V. V. Zagorsky and F. Z. Badaev, *J. Organomet. Chem.* **243**, 123 (1983).
9. G. B. Sergeev, V. V. Smirnov and V. V. Zagorsky, *Vestnik Moskovskogo Universiteta, Khimija* **21**, 257 (1980).
10. N. Ya. Buben, V. A. Tolkatchev and I. I. Tchcheidze, *Kinet. Katal.* **4**, 683 (1953).
11. V. A. Tolkatchev, I. I. Tchcheidze and N. Ya. Buben, *Dokl. Akad. Nauk SSSR* **147**, 643 (1962).
12. G. O. Bekker, *Vvedenije v Fotochimiju Organitcheskich Soedinenij*, Khimija, Leningrad, 1976, p. 163.
13. L. A. Tyurina, S. V. Kombarova, N. A. Bumagin and I. P. Beletskaja, *Metalloorg. Khim.* **3**, 48 (1990).
14. S. V. Kombarova, L. A. Tyurina and V. V. Smirnov, *Metalloorg. Khim.* **5**, 1038 (1992).
15. K. J. Klabunde and A. Whetten, *J. Am. Chem. Soc.* **108**, 6529 (1986).
16. P. G. Jasien and C. E. Dykstra, *J. Am. Chem. Soc.* **105**, 2089 (1983).
17. W. J. Evans, K. M. Coleson and S. C. Engerer, *Inorg. Chem.* **20**, 4320 (1981).
18. Ch. S. Bagdasarjan, Yu. I. Kiryushina and Z. A. Sinitsina, *Khim. Fiz.* 1666 (1982).
19. A. A. Butchatchenko, *Khimitcheskaja Polyarizatsija Elektronov i Yader*, Nauka, Moscow, 1974, p. 246.
20. H. M. Walborsky, *Acc. Chem. Res.* **23**, 286 (1990).