Journal of Organometallic Chemistry, 340 (1988) 1–5
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Reaction of dialkylmagnesium with carbon monoxide. II *

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(Received August 6th, 1987)

Abstract

Reaction of $MgEt_2$ with CO gives Et_2CO, Et_2CHOH, EtCOCH(OH)Et, $EtCOCHEt_2$ and $EtCOC(OH)Et_2$. The qualitative and quantitative composition of the product mixture was found to be dependent on the $MgEt_2$ concentration and the polarity of solvent. The kinetic results reveal that reaction of CO with $MgEt_2$ and with its dissociation product $MgEt_3^-$, followed by the formation of the Et_2CO and $EtCOCHEt_2$, respectively. The other compounds are formed in the subsequent reactions. The rate constants of formation of pentanone-3 and 4-ethylhexanone-3 are equal k_1 0.292 s^{-1} and k_2 0.450 s^{-1}, respectively.

Introduction

In the reaction between diethylmagnesium and carbon monoxide in diethyl ether (Et_2O) several compounds are formed (eq. 1). The percentage composition of the

$$MgR_2 + CO \xrightarrow[1\text{ bar, }293\text{ K}]{Et_2O} RCOCHR_2 + RCOC(OH)R_2 + RCOCH(OH)R$$
$$(R = C_2H_5)$$
$$+ R_2CO + R_2CHOH \quad (1)$$

products is dependent mainly on the MgR_2 concentration. At 1.4 mol/dm^3 the 4-ethylhexanone-3 is formed in ca. 90% yield [1]. The main product $RCOCHR_2$, is probably formed because of nucleophilic attack on the carbon monoxide by MgR_3^-, which is formed under ionisation of MgR_2 in ether solvent R_2O (eq. 2).

$$2\ MgR_2 \rightleftarrows MgR_3^- + MgR^+ \quad (2)$$

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* For Part I see ref. 1.

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$[MgR_2(THF)_2]$ in tetrahydrofuran (THF) is monomeric [2]. Its ionization state is small. However, the number of ions in solution could be increased by addition of e.g. 2,2,1-cryptand, which results in the formation of $[MgR(cryptand)][R_2Mg(\mu\text{-}R)_2MgR_2]$ when $R = C_2H_5$. However, when R = neopentyl (Np), the ions $[MgNp(cryptand)]^+$ and $MgNp_3^-$ arise [3,4]. MgR_3^- ion undergoes dimerisation to give $[R_2Mg(\mu\text{-}R)_2MgR_2]^{2-}$, or association with $[MgR_2(THF)_2]$ to give $[Mg_2R_5]$ anion. It seems however, that without a ligand or an anion to stabilize MgR^+, the latter would undergo solvation in ether solutions, like $MgCl^+$ [5], and thus being unstable undergoes subsequent reaction viz. (eq. 3).

$$[MgR(THF)_5]^+ + [MgR_2(THF)_2] \rightarrow MgR_3^- + [Mg(THF)_6]^{2+} \qquad (3)$$

For this reason, we think that, the ionization process of MgR_2 in THF is best described by eq. 4. We have undertaken kinetic studies to explain which of the

$$3[MgR_2(THF)_2] \rightarrow 2\ MgR_3^- + [Mg(THF)_6]^{2+} \qquad (4)$$

magnesium species described in eq. 2–4 would be involved in reactions with carbon monoxide.

Results and discussion

Solvent polarity greatly affects the position of the equilibrium of reactions 2–4. To confirm this, the influence of the dielectric constant ϵ on the reaction rate k between MgR_2 and CO was examined. The reaction was carried out in a THF and n-hexane solvent mixtures. Variation of the THF/C_6H_{14} molar ratio was found to give the linear relation $\log k = f((\epsilon - 1)/(2\epsilon + 1))$ (Fig. 1). When the dielectric constant was low the main process was found to be reaction between undissociated MgR_2 and CO, to give R_2CO. In polar solvents the reaction between CO and MgR_3^- anion is also possible. If this conclusion is true, the percentage composition of reaction products should also depend on solvent polarity. The results of the direct reaction of $MgEt_2$ with CO in various solvents are given in Table 1. Direct reaction between $MgEt_2$ and CO in n-heptane, in which diethylmagnesium is not dissociated, mainly Et_2CO ketone is formed in 78 and 59% yields. In polar solvents,

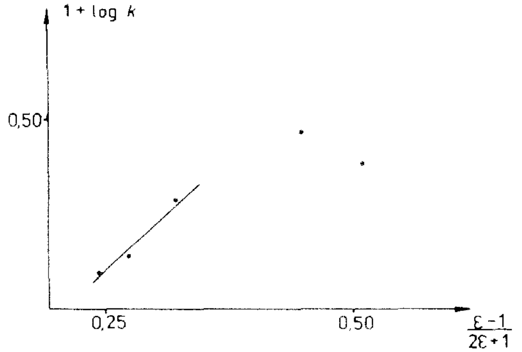


Fig. 1. Plot of log k vs. $(\epsilon - 1)/(2\epsilon + 1)$ for the initial rate of reaction of $MgEt_2$ with CO in THF/hexane solution.

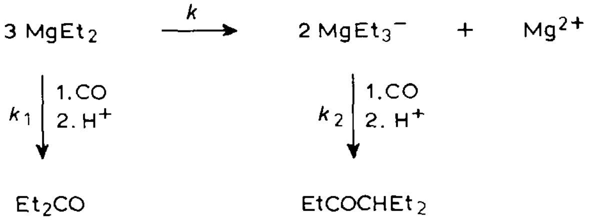
Table 1

Effect of solvent on the proportion in which each of the product was obtained from the reaction of $MgEt_2$ with CO

Products	Solvent [a]				Without solvent
	Et_2O	Pr_2O	$n\text{-}C_7H_{16}$	THF	
Et_2CO	12.1	15.0	59.0	15.5	78.0
Et_2CHOH	6.4	6.2	–	3.6	–
EtCOCHOHEt	0.6	8.2	5.5	5.2	3.3
$EtCOCHEt_2$	56.6	24.1	12.4	26.2	10.0
$EtCOCHEt_2$	24.3	36.0	22.4	30.0	5.2
$[k]$ [b]	0.050	0.072	0.044	0.450	0.005

[a] Initial concentration of $MgEt_2$ was 0.5 M in all cases. [b] Rate constant (pseudo first-order kinetics) with a CO excess versus $MgEt_2$ ($k = k_1 + k_2$).

however, a compound with a carbon–carbon bond, $EtCOCHEt_2$, is formed. The results indicate that both MgR_2 and MgR_3^- ion react with CO (eq. 5).



(5)

The course of reaction 5 is somewhat similar to that of the reaction of Grignard reagent with ketones. Ashby et al. [6], on the basis of kinetic studies have found, that R_2CO in solution reacts with all the Grignard reagent viz. Mg(R)X, MgR_2 and MgX_2.

The initial rates of $MgEt_2$ reactions with CO in THF were measured at various concentrations of diethylmagnesium (Table 1). The investigations were carried out in an excess of CO, and thus the observed reaction rates vary with reagent concentrations in solution. The rate constant k was found to change with concentration of solution (Table 2). Such a relationship indicates that the carbon monoxide molecule reacts with both anion and diethylmagnesium. The observed reaction rates are described by eq. 6.

$$-\frac{d(CO)}{dt} = \left[\alpha k_1 + (1-\alpha)k_2\right] c_{MgEt_2} \tag{6}$$

Table 2

Relationship of the rate constant k of the reaction of $MgEt_2$ with CO in THF, to $MgEt_2$ concentration

c_{MgEt_2}	k [a]
0.78 M	0.436
1.50 M	0.420
2.27 M	0.418
2.75 M	0.414

[a] $k = k_1 + k_2$.

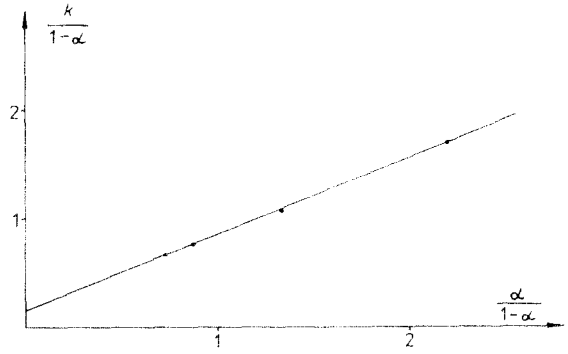


Fig. 2. Plot of $k/(1-\alpha)$ against $\alpha/(1-\alpha)$ for the initial rate of reaction of $MgEt_2$ with CO in THF.

The determination of the degree of dissociation α for diethylmagnesium in solution, from the relationship log Λ vs. log c is possible only for tetrahydrofuran solution. In other ethers the determination of the α from the conductivity measurements is practically impossible because of association with organomagnesium species. From eq. 7 (Fig. 2):

$$\frac{k}{1-\alpha} = \frac{k_1}{1-\alpha} + k_2 \tag{7}$$

the reaction rates k_1 and k_2 (in THF) were found to be 0.293 s^{-1} and 0.450 s^{-1}, respectively. From the above data it follows that the proportion in which each of the products was obtained from reaction 1 depends on the degree to which $MgEt_2$ is ionized. It was of interest to find out whether it was possible to obtain with the same $MgEt_2$ concentration different quantities of each product, by attempting to shift the equilibrium of reaction 4 in one solvent, by the addition of e.g. $MgCl_2$. It was expected that addition of $[MgCl_2(THF)_2]$ to $MgEt_2$ solution in THF would result in the formation of $[(THF)_4Mg(\mu\text{-}Cl)_2MgEt_2]$, which could prevent the shift of the reaction equilibrium. In accord with expectations, Et_2CO was formed in the presence of $[MgCl_2(THF)_2]$ in 68% yield. The results presented here confirm unambiguously, that the percent quantity of each product of reaction 1 depends primarily on the ionization degree of $MgEt_2$. In polar solvents with high diethylmagnesium concentrations, mainly products containing a carbon–carbon bond which is formed between two CO molecules are obtained. $MgEt_2$ without solvent, in hydrocarbon or polar solvents (in presence of $MgCl_2$) gave mainly Et_2CO with CO.

Experimental

The quantitative and qualitative analysis of reaction products was carried out with a gas chromatograph ELPO 520 equipped with a 1.8 m column (∅ 4 mm), filled with 3% SE-30 on Chromosorb W, at 343–493 K. The products were identified by comparison with authentic compounds; in doubtful cases compounds were isolated by preparative chromatography and subjected to ^1H NMR spectroscopy. Quantitative measurements of products were carried out chromatographically, using n-decane as internal standard.

Kinetic measurements were carried out in thermostatted reaction flasks, connected to a burette, to measure the amount and rate of CO consumption.

Influence of solvent and dielectric constant ϵ on reaction rate

These investigations were carried out in a solvent mixture of tetrahydrofuran and n-hexane. The value ϵ changed with change in the THF/C_6H_{14} molar ratio. Solutions of 10 mmol of $MgEt_2$ in 5 cm^3 THF were added to several solvent mixtures (20 cm^3) of various THF/C_6H_{14} ratios. Initial reaction rate was determined from the volume of CO consumed. The rate constant of the reaction was calculated from pseudo first-order reaction kinetics the dielectric constant ϵ of the solvent mixture was determined by measuring the electric volume of condensator each time it was filled with a different THF/n-hexane ratio. The results are shown in Fig. 1.

Influence of solvent on the proportion in which each of the products was obtained from the reaction of $MgEt_2$ with CO

A solution of 25 mmol $MgEt_2$ in 5 cm^3 Et_2O (Pr_2O of THF) was placed in a reaction flask under CO and stirred. After 2 h, when carbon monoxide consumption had ceased, 20 cm^3 of 5% HCl was added. Then, the ether phase was separated and the aqueous phase additionally extracted with 3 × 15 cm^3 Et_2O. The ether fractions were combined and reduced in volume to 10 cm^3 under vacuo. The results are given in Table 1.

Kinetics of the reaction between $MgEt_2$ and CO in tetrahydrofuran

The relationship between rate constant k and $MgEt_2$ concentration in THF was examined for the concentration range 0.78–2.75 *M*. The initial reaction rate was determined by measuring the volume CO consumed with time. The reaction rate constant k, k_1 and k_2 were calculated from eq. 6 and 7. Degree of dissociation was calculated from $\alpha = \Lambda/\Lambda_0$. The value for Λ was taken from the literature [7]. The results are presented in Table 2.

Acknowledgement

The authors are grateful to Dr M. Moll, Erlangen-Nürnberg University for recording the ^{13}C NMR spectra (Part I) and for helpful discussions.

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