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REACTION OF DIALKYLMAGNESIUM WITH CARBON MONOXIDE AND NITROSODURENE

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Summary

Reaction between diethylmagnesium and carbon monoxide gives rise to the formation of pentanone-3, pentanol-3, 3-ethylpentanol-3,3-ethyl-3-hydroxyhexanone-4 and 3-ethylhexanone-4. The use of ^{13}CO and application of ^{13}C NMR spectroscopy revealed that $C_2H_5COCH(C_2H_5)_2$ arose after hydrolysis of $C_2H_5COC(C_2H_5)_2MgC_2H_5$. Reaction between $(C_2H_5)_2Mg$ and nitrosodurene proceeds according to the nitrene-radical mechanism and the EPR spectrum presents a signal derived from $Me_4Ph\dot{N}\text{-}N(PhMe_4)OMgC_2H_5$. Upon this basis a carbene-radical mechanism is proposed for the reaction between carbon monoxide and diethylmagnesium.

Introduction

The reaction of carbon–carbon bond formation can be realized in different ways. One of these is the reduction of a CO molecule with the alkali metals in liquid ammonia [1,2] or tetrahydrofuran [3]. Such reaction yields the radical anions $CO^{\cdot-}$, which could react either mutually or with carbon monoxide to form C–C bonds. CO reacts also with nucleophilic species, e.g. in the reaction between phenyllithium PhLi and CO, namely: benzophenone, Ph_2CO, benzoine, PhCH(OH)COPh and α,α'-diphenylacetophenone $Ph_2CHCOPh$ - which is the main product formed there [4]. Such reactions often have radical character, and for that reason their course in tetrahydrofuran is somewhat different. The reaction of RMgX and R_2Mg with carbon monoxide in tetrahydrofuran [5], in the presence of transition metal compounds, forms $R^{\cdot}$ radicals, which next react with tetrahydrofuran to produce the RH hydrocarbon and the new C_4H_7O radicals; the latter react with $CO^{\cdot-}$.

We have used the dialkylmagnesium compounds as the nucleophilic species in reaction with carbon monoxide. These compounds could be obtained readily from

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the reaction between magnesium hydride [6,7] and olefins [8]. It is known that R_2Mg in solvents having the donor properties undergoes dissociation [9].

$$2R_2Mg \overset{Et_2O}{\rightleftharpoons} R_3Mg^- + RMg^+ \qquad (1)$$

The R_3Mg^- anion formed is the potential source of electrons for reduction of carbon monoxide.

Results and discussion

Diethylmagnesium, $(C_2H_5)_2Mg$, in diethyl ether was stirred under carbon monoxide. After 2 h, at room temperature at 1.4 mol/1 concentration, ca. 1.8 CO/Mg was fixed. The reaction mixture was hydrolyzed and the composition of products was established by GC-MS.

$$R_2Mg + CO \xrightarrow[1\ \text{bar};293\ \text{K}]{Et_2O} RCOCHR_2 + R_2COHCOR + R_2CO + R_2CHOH + R_3OH \qquad (2)$$

$R = C_2H_5$

The percentage composition of the compounds formed in reaction 2 depends mainly on the $(C_2H_5)_2Mg$ concentration in Et_2O. 3-Ethylhexanone-4 is the main reaction product (see Table 1).

To elucidate the reaction mechanism, the reaction between $(C_2H_5)_2Mg$ and ^{13}CO was examined. The $^{13}C\{^1H\}$NMR spectrum is presented in Fig. 1, and exhibits first of all two doublets at 150.3 (1), 147.0 (2) and 112.6 (5), 109.5 ppm(6). The $J(^{13}C-^{13}C)$ constant is equal to 83.3 Hz and is characteristic of sp^2-sp^3 type coupling. No $^1J(^{13}C-H)$ type splitting was observed, which excluded the possibility of $^{13}C-H^\cdot$ bonding. However, the signals point of a $^2J(^{13}C-H)$ hyperfine structure equal to 5.0 Hz. The hyperfine structure appears to be due to the interaction of ^{13}C with C_2H_5 methylene protons.

Analysis of the ^{13}C $\{^1H\}$NMR spectrum revealed that the observed signals 1,2,5 and 6 derive from $^{13}C-^{13}C$ coupled carbon atoms. The sp^2-sp^3 hybridization of the carbon atoms, the $^2J(^{13}C-H)$ constant and the formation of $C_2H_5COCH(C_2H_5)_2$ as the main hydrolysis product allow us to attribute the observed signals to $C_2H_5COC(C_2H_5)_2MgC_2H_5$, which after hydrolysis produced 3-ethylhexanone-4. The signals 3 and 4 (Fig.1) have not been fully explained yet and are the subject of further investigations.

TABLE 1

REACTION OF DIETHYLMAGNESIUM WITH CARBON MONOXIDE IN Et_2O

Products	$(C_2H_5)_2Mg$ mol/1		
	0.46	0.82	1.40
$(C_2H_5)_2CO$	12.1	5.2	4.4
$(C_2H_5)_2CHOH$	6.4	–	–
$(C_2H_5)_3COH$	0.6	6.8	4.9
$C_2H_5COCH(C_2H_5)_2$	56.6	75.8	89.4
$(C_2H_5)_2COHCOC_2H_5$	24.3	12.1	23.3

The data in Table 1 reveal, that at lower concentrations a larger quantity of ketone, and as well as of binary and ternary alcohols and hydroxyketone, is formed; at higher concentrations mainly 3-ethylhexanone-4. This could point to the radical character of the reaction. To find out whether reaction 2 was really radical, we decided to carry it out in the presence of a radical trap, such as nitrosodurene,

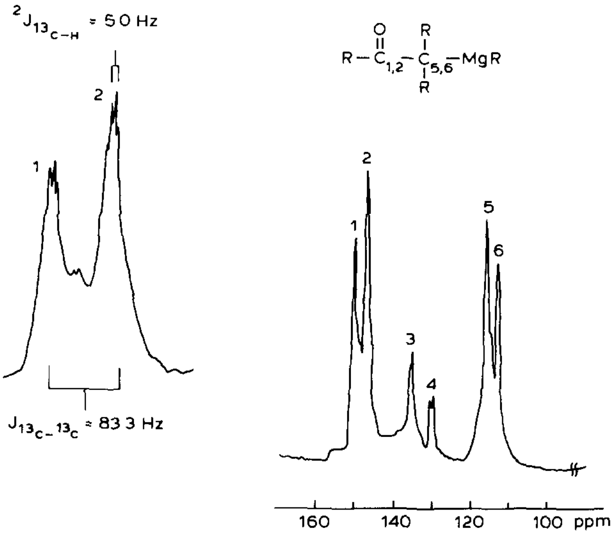


Fig. 1. The ^{13}C {^{1}H} NMR spectrum of the product formed in the reaction between $(C_2H_5)_2Mg$ and ^{13}CO.

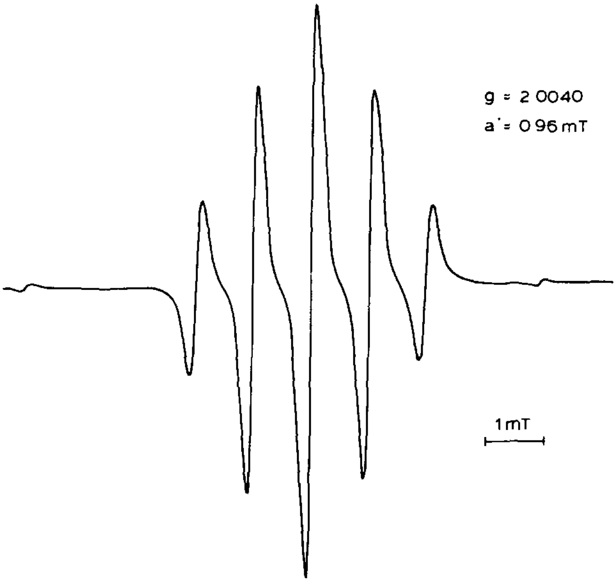


Fig. 2. The EPR spectrum of $Ph\dot{N}-N(PhMe_4)OMgC_2H_5$ formed in the reaction between $(C_2H_5)Mg$ and nitrosodurene.

Me_4PhNO. The EPR spectrum of the reaction product is presented in Fig. 2. It was discovered that the carbon monoxide has no influence on the shape of the spectrum. No matter whether the reaction was carried out under argon or CO, the same spectrum was obtained.

Thus, the reaction between $(C_2H_5)_2Mg$ and nitrosodurene is competitive with the reaction with CO. The explanation could be found in the fact that Me_4PhNO is present in solution, and that carbon monoxide is sparingly soluble in Et_2O. For that reason the reaction between diethylmagnesium and Me_4PhNO is much faster than that with the carbon monoxide. The EPR spectrum consists from five lines, in a 1 : 2 : 3 : 2 : 1 ratio. This spectrum is characteristic of interaction of one unpaired electron with two nuclei of nitrogen atoms. The EPR spectrum for such a case presents $2(I_1 + I_2) + 1$ resonance line. Since the spin of ^{14}N nitrogen is equal to $I_1 = I_2 = 1$, and for that reason the observed signals could be assigned to the $R\dot{N}-N(R)OMgR$ radical. The reaction between diethylmagnesium and Me_4PhNO is accompanied by the formation of $Me_2PhN{=}NPhMe_4$ and liberation of hydrocarbons: ethane and ethylene. The reaction course could be written as follows;

$$R_3Mg^- + MgR^+ + Me_4PhNO \xrightarrow[293\ K]{Et_2O} [R_3Mg \leftarrow ONPhMe_4]MgR \rightarrow$$
$$Me_4Ph\dot{N}-OMgR + R_2Mg + R^\cdot \qquad (3)$$

$R = C_2H_5$

In the first reaction step the Me_4PhNO is coordinated by a R_3Mg^- anion, and, as a result, the transition compound $[R_3Mg \leftarrow ONPhMe_4]MgR$ is formed. In the next stage the nitrosodurene molecule undergoes reduction to produce the $Ph\dot{N}-OMgR$ radical [10–12]. Such a radical, as it follows from our investigations, is unstable and undergoes subsequent reactions.

$$2Me_4Ph\dot{N}-OMgR \rightarrow 2Me_4PhN + 2MgO + 2C_2H_5^\cdot \rightarrow$$
$$Me_4PhN{=}NPhMe_4 + C_2H_6 + C_2H_4 \qquad (4)$$

The products of this reaction are MgO, nitrene Me_2PhN and C_2H_5 radicals. The nitrenes formed undergo recombination to produce $Me_4PhN{=}NPhMe_4$ and react with $Me_4Ph\dot{N}-OMgR$

$$Me_4PhN + Me_4Ph\dot{N}-OMgR \rightarrow Me_4Ph\dot{N}-N(PhMe_4)OMgR \qquad (5)$$

The $Me_4Ph\dot{N}-N(PhMe_4)OMgR$ radical gives EPR signals and its spectrum is shown in Fig. 2. $C_2H_5^\cdot$ radicals undergo recombination leading to the formation of ethane and ethylene [13,14].

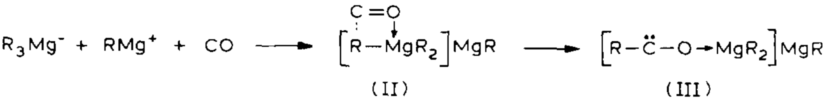
$$2C_2H_5^\cdot \rightarrow C_2H_6 + C_2H_4 \qquad (6)$$

The reaction between nitrosodurene and another reducing agent, e.g. metallic sodium, is different [11,12].

$$Me_4PhNO + Na \rightarrow Me_4Ph\dot{N}-ONa \qquad (7)$$

The $Me_4Ph\dot{N}-ONa$ radical is relatively stable. The difference in reactivity follows from the presence of the magnesium atom in $Me_4Ph\dot{N}$-OMgR, which on homolytic cleavage of the Mg–R bond has one electron, sufficient for the break of the nitrogen–oxygen bond; this results in formation of MgO and Me_4PhN.

The $^{13}C\{^1H\}$NMR spectrum (Fig. 1) points to the formation of $C_2H_5COC(C_2H_5)_2MgC_2H_5$ in the reaction between diethylmagnesium and carbon monoxide. The explanation could be given in the reaction:

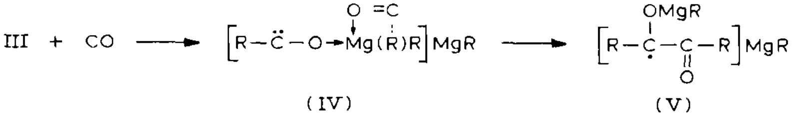


$$R_3Mg^- + RMg^+ + CO \longrightarrow \left[R-\overset{C=O}{\overset{\downarrow}{Mg}}R_2\right]MgR \longrightarrow \left[R-\ddot{C}-O\rightarrow MgR_2\right]MgR \qquad (8)$$

(II) (III)

$(R = C_2H_5)$

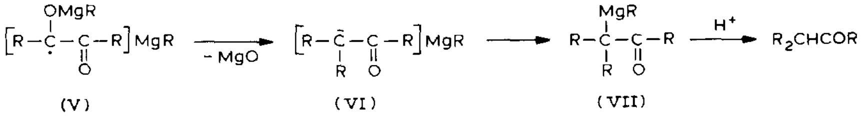
The CO molecule forms with diethylmagnesium the intermediate compound II, which in the nucleophilic reaction between R^- and CO will produce the carbene compound III. In this compound the R_2Mg molecule is bonded to the remaining part of compound via the oxygen. In our opinion, it is important for the further reaction course, because the magnesium atom could subsequently react with a second CO molecule.



$$III + CO \longrightarrow \left[R-\ddot{C}-O\rightarrow \overset{O=C}{\overset{\downarrow}{Mg}}(\dot{R})R\right]MgR \longrightarrow \left[R-\overset{OMgR}{\dot{C}}-\underset{O}{\overset{}{C}}-R\right]MgR \qquad (9)$$

(IV) (V)

Homolytic cleavage of one Mg–R bond in IV and the bonding of the radical formed to CO gives rise to the formation of compound V. This compound, as the result of an intramolecular rearrangement yields compounds VI and VII, observed in the ^{13}C NMR spectrum.



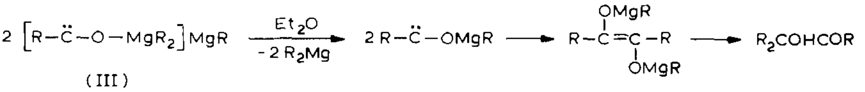
$$\left[R-\overset{OMgR}{\dot{C}}-\underset{O}{C}-R\right]MgR \xrightarrow[-MgO]{} \left[R-\underset{R}{\ddot{C}}-\underset{O}{C}-R\right]MgR \longrightarrow R-\underset{R}{\overset{MgR}{C}}-\underset{O}{C}-R \xrightarrow{H^+} R_2CHCOR \qquad (10)$$

(V) (VI) (VII)

In the reaction with carbon monoxide, as in the reaction with Me_4PhNO it is essential that the R_2Mg molecule is a part of the transition compound III. In consequence, it may cause the bonding of a second carbon monoxide molecule, and in subsequent reactions produce compound VII. For this reason the course of the reaction with PhLi is somewhat different [4]. In the first stage of the reacction the carbene compound $Ph-\ddot{C}-OLi$ is formed, which yields benzoine after dimerization and hydrolysis. The reaction yielding the main product, α,α-diphenylacetophenone, may be written as follows:

$$2Ph-\ddot{C}-OLi + PhLi \xrightarrow[-Li_2O]{} Ph_2C{=}C(Ph)OLi \xrightarrow{H_2O} Ph_2CHCOPh \qquad (11)$$

The relationship between 3-ethylhexanone and 3-ethyl-3-hydroxyhexanone-4 is given in Table 1. Independently of the concentration, the total yield of both compounds always exceeds 80%. The amount of $(C_2H_5)_2COHCOC_2H_5$ increases with dilution of $(C_2H_5)_2Mg$, which may be explained as follows:



$$2\left[R-\ddot{C}-O-MgR_2\right]MgR \xrightarrow[-2R_2Mg]{Et_2O} 2R-\ddot{C}-OMgR \longrightarrow R-\overset{OMgR}{C}{=}\underset{OMgR}{C}-R \longrightarrow R_2COHCOR \qquad (12)$$

(III)

The donor strength of the Et_2O molecule exceeds that of the carbonyl or alkoxy groups [15]. This being so, at lower concentrations, R_2Mg would be coordinated by

Et_2O, which makes possible the dimerization of carbene molecules and the formation of $R_2COHCOR$ after hydrolysis.

The rate of reaction 2 was found to be very temperature sensitive. Temperature increase accelerated the reaction rate. Kinetic studies of this reaction as well as the mechanism of formation of R_2CO, R_2CHOH and R_3COH will be the subject of a separate publication.

Experimental

All experiments were carried out under dinitrogen, using Schlenk and dry box techniques. Diethyl ether was distilled under N_2 from sodium and benzophenone. Diethylmagnesium and nitrosodurene were obtained by literature methods [15–17]. Reaction products before identification were separated by preparative chromatography. The compounds were identified by GLC analyses on an ELPO chromatograph. GC/MS was performed on a LKB 1000 equipped with a gas-chromatograph coupled to a mass spectrometer equipped with a computer. The ^1H and ^{13}C NMR spectra were recorded on a Jeol JNM-PS-100 spectrometer, and the IR spectra on a Perkin-Elmer 180 spectrophotometer. Quantitative analysis was performed on an ELPO 52OH chromatograph, equipped with a 1.8 m column, filled with 3% SE 30 on Chromosorb W, at 343–493 K.

Reaction of diethylmagnesium with carbon monoxide

A solution of 15 mmol of $(C_2H_5)_2Mg$ in 25 cm^3 diethyl ether was stirred under CO. After 3 h, at room temperature and under normal pressure 500 cm^3 of carbon monoxide was taken up. Next, 10 cm^3 of 5% HCl were added to the reaction mixture; the ether phase was separated and the water layer was extracted additionally with 3×15 cm^3 Et_2O. The ether fractions were combined and dried with $MgSO_4$. The ether solution was condensed under a rectification column to a volume of 5 cm^3 and separated by means of preparative chromatography.

Reaction of diethylmagnesium with nitrosodurene

Nitrosodurene (0.1 mmol) was dissolved in Et_2O (10 cm^3) under N_2 and $(C_2H_5)_2Mg$ (0.1 mmol) in 5 cm^3 H_2O was added. Under stirring the solution turned dark yellow and gaseous products (ethane and ethylene) were liberated. The solution was examined by EPR. $Me_4PhN{=}NPhMe_4$ isolated from the reaction with nitrosodurene was identified by thin-layer chromatography (TLC) by comparison with an authentic sample.

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