Journal of Organometallic Chemistry, 235 (1982) 295—300
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE APPLICATION OF FREE RADICALS TO THE CATALYTIC SYNTHESIS OF CARBON MONOXIDE DERIVATIVES

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(Received March 30th, 1982)

Summary

The chemical reactions of carbon monoxide with $(C_2H_5)_2Mg$ and C_2H_5MgBr in the presence of the carbonyls $Mo(CO)_6$, $W(CO)_6$, $Co_2(CO)_8$ and $Fe_2(CO)_9$ in tetrahydrofuran have been examined. Catalytic reaction produced a series of compounds. The tetrahydrofuranyl-2-ethyl ketone was the main reaction product, indicating the radical character of the reaction.

Introduction

The formation of a carbon—carbon bond in the presence of transition metal compounds, a very important procedure in organic chemistry, is based mainly upon "two-electron" component steps such as oxidative addition, migratory insertion and reductive elimination [1—8]. The mechanism of those processes raises the question of whether it would be possible to obtain, for example, ketones from carbon monoxide in a two-electron step by step process. Such a process could be described by the equation:

$$2\,R^{\cdot} + CO \underset{h\nu}{\overset{M}{\rightleftharpoons}} R_2CO \qquad (1)$$

M = transition metal compound

This equation suggests that ketone could be obtained from carbon monoxide from reaction of CO with two radicals. Such a process can proceed readily the other way round under irradiation [9].

From the reaction of organomercurial halides or diorganomercurials with carbon monoxide in the presence of dicobalt octocarbonyl, ketones were formed in excellent yield (eq. 2) [10]. However, the reaction did not proceed

$$R_2Hg + CO \xrightarrow[THF]{Co_2(CO)_8} R_2CO + Hg \qquad (2)$$

0022-328X/82/0000—0000/$02.75

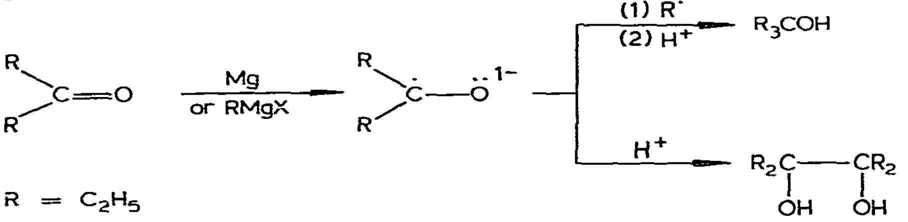
according to the free radical mechanism because of the heterolytic decomposition of R_2Hg into RHg^+ and R^-; RHg^+ and R^- reacted with cobalt compounds $THFCo(CO)_4^+$ and $Co(CO)_4^-$, formed from $Co_2(CO)_8$ dissociation in tetrahydrofuran, and the products of these reactions reacted with CO.

Results and discussion

In our studies we have used as source of radicals RMgX and R_2Mg, which in a solvent cage and on diffusion from a solvent cage react via the single electron transfer (SET) pathway [11,12]. We chose the compounds C_2H_5MgBr and $(C_2H_5)_2Mg$ because the ethyl group exhibits moderate electronegativity as well as intermediate addition velocity, and a reducing tendency. Common carbonyls such as $Mo(CO)_6$, $W(CO)_6$, $Co_2(CO)_8$ and $Fe_2(CO)_9$ were used as precursors of catalysts. $Mo(CO)_6$ (2.64×10^{-3} g; 1×10^{-5} mol) was dissolved in tetrahydrofuran (THF 30 cm^3) under carbon monoxide and an excess of a diethyl ether (Et_2O) solution of C_2H_5MgBr or $(C_2H_5)_2Mg$ (10 cm^3; 4.3×10^{-3} mol) was added under stirring. In 2 min the reaction solution changed its color from light yellow to brown with simultaneous carbon monoxide fixation. After 15 min, $MgBr_2$-$(THF)_2$ (for the case of C_2H_5MgBr) and after another couple of minutes alkoxydes (Table 1) precipitated from the solution. The reaction proceeded as long as the ratio of carbon monoxide fixed to magnesium compound, $CO/(C_2H_5)_2Mg$ or $2\ C_2H_5MgBr \approx 0.97$. The reaction was accompanied by the liberation of small amounts of hydrocarbons (C_2H_6, C_2H_4 and C_4H_{10} in the ratio 9.5 : 1, 6 : 1). When the reaction had ceased (2 h), the entire mixture was treated with 20 cm^3 5% HCl solution, THF was distilled off and the remnants were extracted with Et_2O (3×20 cm^3). The compounds were separated by the GLC method and identified on a mass spectrometer.

An identical procedure was applied in reactions with $W(CO)_6$, $Co_2(CO)_8$ and $Fe_2(CO)_9$. The observations were similar. Analysis revealed the formation of over ten products. The qualitative and quantitative results gathered in Table 1 revealed that the nature of our reactions was similar to that of reaction 1, but more complicated.

As expected, we obtained the diethyl ketone as well as the other compounds formed in the subsequent reaction of $(C_2H_5)_2CO$ with diethylmagnesium or with ethylmagnesium bromide, e.g. the products of the reduction, addition and dimerization reactions. The carbonyl group in ketones readily undergoes reduction, e.g. in solution the reduction reaction proceeds by transfer of an electron to give the radical anion [11,12], which dimerizes and after protonation forms pinacol [13].



(3)

(4)

The radical anion may also react with $R^{\cdot}$ to produce, after hydrolysis, the tertiary alcohol. The secondary alcohol may be formed as the result of magnesium hydride formation in solution [14]. Tetrahydrofuranyl-2-ethyl ketone is the main product of these reactions, which is evidence for the radical character of those reactions. The solvent tetrahydrofuran contains a partially positively charged hydrogen atom which is easily removable by ethyl radicals [15,16]. As the result the tetrahydrofuranyl $R_1^{\bullet}$ radicals are formed.

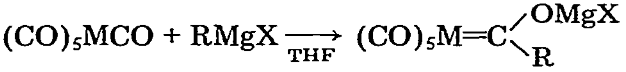
(5)

That the $R_1^{\bullet}$ radical is the component of the main reaction product may be explained by the fact that the stability of the tetrahydrofuranyl radical exceeds that of the ethyl radical, and may also be due to the radical combination rate constant *k*, which generally appears to decrease as the size of the radical increases from the correlation between radical molecular weight and log *k* [17]. The other products, containing $R_1^{\bullet}$ and $R^{\bullet}$, are direct a statistic consequence of their cross-combination reactions. Liberation of hydrocarbon, ethylene and ethane during the reaction is further confirmation of the formation of radicals in the reaction medium [18,19].

$$C_2H_5^{\bullet} + C_2H_5^{\bullet} \rightarrow C_2H_4 + C_2H_6 \qquad (6)$$

We also expected the presence of cross-combination compounds, like R_1R_1 and R_1R, in the reaction mixture. However, such compounds were not detected and the reactions seem to be more complicated. Most probably they produce high molecular weight materials (ca. 5—10%) which are observed but not separated by GC/MS.

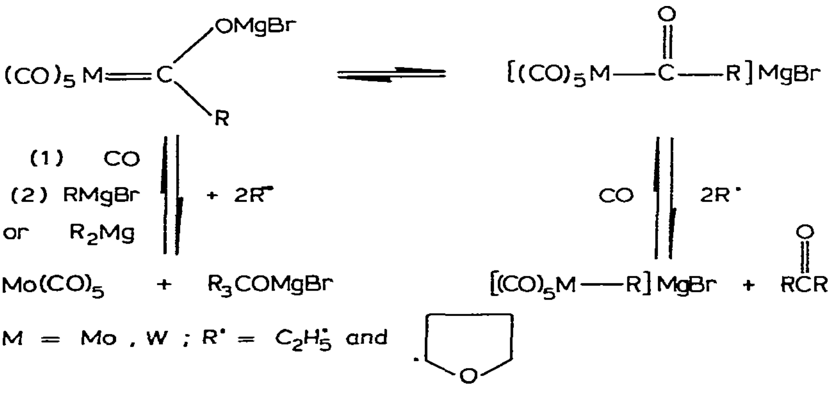
The reaction between metal carbonyls and a Grignard compound is well known. As the result of direct nucleophilic attack on a positively charged carbonyl carbon, a carbene complex is formed [20,21].



$$(CO)_5MCO + RMgX \xrightarrow[THF]{} (CO)_5M{=}C\begin{matrix}\nearrow OMgX \\ \searrow R\end{matrix} \qquad (7)$$

(I)

Under reaction conditions the carbene group coexists simultaneously with the acyl group [22]. Both groups seem to play an essential role in the catalytic synthesis of ketones and their derivatives eq. 8.



(8)

TABLE 1

COMPOSITION OF THE PRODUCTS FORMED IN CATALYTIC REACTION BETWEEN DIETHYLMAGNESIUM OR ETHYLMAGNESIUM BROMIDE WITH CARBON MONOXIDE IN TETRAHYDROFURAN IN THE PRESENCE OF CARBONYL COMPOUNDS

Reactions[a]	Catalyst precursor	Products (%)							
		R_2CO	R_2CHOH	R_3COH	$RCOC(OH)R_2$	$R_2C(OH)C(OH)R_2$	$RCH(OH)C(OH)R_2$	R_1COR	$R_1CH(OH)R$
R_2Mg + CO	$Mo(CO)_6$	8,7	4,9	17,3	5,5	1,0	—	41,5	—
R_2Mg + CO	$W(CO)_6$	2,3	3,0	10,2	10,5	—	13,7	27,0	4,0
R_2Mg + CO	$Co_2(CO)_8$	4,8	15,4	5,7	4,5	—	10,1	27,3	—
R_2Mg + CO	$Fe_2(CO)_9$	4,6	—	29,2	9,4	—	—	22,7	—
RMgBr + CO	$Fe_2(CO)_9$	3,5	11,4	0,8	5,7	5,4	—	58,2	—
RMgBr + CO	$Co_2(CO)_9$	5,2	9,3	1,9	9,1	3,0	—	65,4	—
RMgBr + CO	$Mo(CO)_6$	2,7	3,7	20,3	36,9	5,0	—	13,8	—
RMgBr + CO	$W(CO)_6$	4,2	4,6	25,8	31,4	4,0	—	13,2	—

Reactions[a]	Catalyst precursor	Products (%)						
		$R_1COC(OH)R_2$	$R_1CH(OH)C(OH)R_2$	$R_1CR(OH)C(OH)R_2$	$R_1COCH_2R_1$	$R_1CH(OH)CH(OH)R_1$	$R_1CHRCH(OH)R$	$R_1CH(OH)CHRR_1$
R_2Mg + CO	$Mo(CO)_6$	2.3	1.7	1,8	6.1	1,8	—	—
R_2Mg + CO	$W(CO)_6$	7.1	—	—	1.1	3.3	2.9	2.0
R_2Mg + CO	$Co_2(CO)_8$	14.4	—	—	1.8	2.2	5.4	—
R_2Mg + CO	$Fe_2(CO)_9$	2.1	5.0	7.1	—	2.9	1.8	0.9
RMgBr + CO	$Fe_2(CO)_9$	9.9	—	—	—	—	—	—
RMgBr + CO	$Co_2(CO)_9$	3.4	—	—	—	—	—	—
RMgBr + CO	$Mo(CO)_6$	—	3.4	—	6.6	—	—	—
RMgBr + CO	$W(CO)_6$	—	4.1	—	7.0	—	—	—

[a] $R = C_2H_5$; R_1 = 

A tertiary alcohol is formed in the reaction of a radical with the carbene form, and ketones arise in reaction of $R^\bullet$ with the acyl group. Formation of the magnesium bromide is described by the Schlenk equation (eq. 9).

$$2\,RMgBr \rightleftharpoons R_2Mg + MgBr_2 \qquad (9)$$

The reaction equilibrium is shifted towards the right-hand side because of the contribution of R_2Mg to the reaction, which also confirms that for the reaction with C_2H_5MgBr, diethylmagnesium is the main source of radicals [23]. The catalytic reaction reported here was not sensitive to light, which seems to be indicative of the formation of radicals as the result of interaction of some paramagnetic transition metal centre [24]. The compounds formed in the reaction between $(C_2H_5)_2Mg$ and metal carbonyls are the subject of further investigation.

Formation of the R_1-free compounds (Table 1) and liberation of C_2H_4 could be explained also in terms of conventional organometallic reaction such as β-H elimination, oxidative addition-reductive elimination sequences involving transition metal carbene intermediates.

The formation of tetrahydrofuranyl-2-ethyl ketone is difficult to explain by anything other than a radical mechanism. The free radical process discovered by us suggests that such a reaction would also proceed on use of another source of radicals, which would open the new perspectives for organic synthesis.

Experimental

All manipulations were carried out under pure, dry argon and carbon monoxide, using Schlenk-tube and vacuum-line techniques. THF and Et_2O were purified before use by distillation under argon from sodium and benzophenone. Ethyl bromide was distilled over $CaCl_2$. The metal carbonyls $Mo(CO)_6$, $W(CO)_6$, $Co_2(CO)_8$ and $Fe_2(CO)_9$ were obtained commercially from Fluka AG; Grignard Mg turnings and ethyl bromide were obtained from POCh-Gliwice. C_2H_5MgBr and $(C_2H_5)_2Mg$ were obtained by the usual method.

Reaction of diethylmagnesium with carbon monoxide

To a tetrahydrofuran solution (30 cm^3) containing dissolved tungsten hexacarbonyl, $W(CO)_6$ (0.026 g; 7.5×10^{-5} mol) an ether solution of diethylmagnesium (4.95×10^{-3} mol, 10 cm^3) was added with stirring under carbon monoxide. After 2 min the solution changed its colour from light yellow to brown, simultaneous with carbon monoxide uptake (measured by means of the gas burette). The reaction proceeded as long as $CO/(C_2H_5)_2Mg \approx 0.97$. Repeated addition of $(C_2H_5)_2Mg$ or C_2H_5MgBr to the reaction mixture caused each time further CO fixation up to the moment when the total amount of added magnesium compound perreacted. After 2 h when the reaction had ceased the entire mixture was treated with 5% solution (20 cm^3), tetrahydrofuran was distilled off and the residue was extracted with Et_2O (3×20 cm^3). The compounds were identified on a mass spectrometer after chromatographic separation (GLC, 2 m column, 3% OV 225 on GAS-CHROM Q). An identical procedure was applied for reactions with $Mo(CO)_6$, $Co_2(CO)_8$ and $Fe_2(CO)_9$, and also using either $(C_2H_5)_2Mg$ or C_2H_5MgBr. The qualitative and quantitative results are gathered in Table 1. Relative yields of particular compounds were calculated on the assumption of total area under the GLC curves as 100%. Corrections for different numbers of carbon atoms in particular compounds were taken into account.

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