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Synthesis of organomagnesium β-diketonates and alkoxides

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Abstract

Phenyl- and butyl-magnesium β-diketonates, [R–Mg–(R′–C(O)=C(H)=C(O)–R″)] · THF (where R = C_6H_5 or C_4H_9; R′ and R″ = C_6H_5 or CH_3) have been made by the reaction of phenyl- or butyl-magnesium bromide with sodium β-diketonates and Cu^{II} β-diketonates. Phenyl- and butyl-magnesium alkoxides [R–Mg–OR‴] (where R‴ = CH_3, C_2H_5, $^iC_3H_7$, $^iC_4H_9$, $^tC_4H_9$) have been made by treatment of phenyl- or butyl-magnesium bromide with the appropriate sodium alkoxides.

1. Introduction

The chemistry of Grignard reagents has been extensively studied, and most of the reactions have been found to involve the Mg–C bond rather than the Mg–X bond (X = halogen) [1].

Reactions of the Mg–X bond are of interest because they give organomagnesium species that may perhaps be isolable in an unsolvated form. Kapoor *et al.* [2] treated phenyl-magnesium bromide with sodium carboxylates and isolated phenyl-magnesium carboxylate. THF adducts in 90% yield.

There seem to have been no reports of attempts to synthesize organomagnesium β-diketonates. We therefore decided to study the reactions of phenyl- and butyl-magnesium bromide with sodium β-diketonates or Cu^{II} β-diketonates and also to make organomagnesium alkoxides by reaction of Grignard reagents with sodium alkoxides.

2. Experimental section

All reactions were carried out under nitrogen in Schlenk tubes on a vacuum line. Phenyl- and butyl-magnesium bromide and Cu^{II} β-diketonate, sodium β-diketonate and sodium alkoxides were prepared by published methods [3–6]. IR spectra were recorded as KBr discs or Nujol mulls on a Perkin-Elmer 842 grating spectrophotometer in the range 4000–400 cm^{-1}. The ^1H NMR spectra were recorded on a Perkin-Elmer R-32, 90 MHz spectrometer. Concentrations of Grignard reagent were determined by the Gilman method [7]. Magnesium was determined by the EDTA method with Erio-chrome Black T as indicator [8]. Analysis for ethoxy and isopropoxy groups was by the oxidometric method [9,10].

2.1. *Preparation of phenylmagnesium acetylacetonate · tetrahydrofuran*

(a) Sodium acetylacetonate (1.26 g) was added to a solution of phenyl-magnesium bromide in THF (5 ml, 2.06 M) and the mixture stirred at room temperature for 10–12 h. The colour of the solution changed from light green to light yellow. The precipitated sodium bromide was filtered off, dried and weighed to confirm the completion of reaction. The solvent was removed from the filtrate under reduced pressure and the pale yellow solid residue was recrystallized from n-hexane-THF mixture. Yield 90%.

(b) Copper (II) acetylacetonate (1.35 g) was added to a solution of phenyl-magnesium bromide in THF (5 ml, 2.06 M) and the mixture was stirred at room temperature; the reaction was highly exothermic. The green colour changed to brown during stirring for 10–12 h. The solvent was removed from solution under reduced pressure, and the brown solid residue was treated with 15–20 ml of benzene and the mixture was stirred for 5–6 h then filtered. The filtrate was evaporated to dryness under reduced pressure, and the light yellow solid residue recrystallized from n-hexane-THF mixture. Yield 50%.

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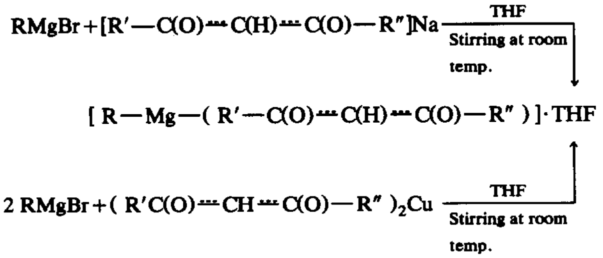
Details of other reactions are summarized in Table 1.

2.2. *Preparation of phenyl- and butyl-magnesium alkoxides*

These alkoxides were made essentially by the procedure described above but by the reaction of phenyl- or butyl-magnesium bromide with the sodium alkoxide at low temperature (0–5°C) (Table 2). The products were recrystallized from benzene-heptane mixture.

3. Results and discussion

The reactions of phenyl- and butyl-magnesium bromide with sodium β-diketonates, Cu^{II} β-diketonates (*viz*., acetylacetonate, benzoylacetonate and dibenzoylmethonate) and sodium alkoxides are represented by the following general equations:



$$\mathrm{RMgBr+[R'{-}C(O)\cdots C(H)\cdots C(O){-}R'']Na}\xrightarrow[\text{Stirring at room temp.}]{\text{THF}}\mathrm{[R{-}Mg{-}(R'{-}C(O)\cdots C(H)\cdots C(O){-}R'')]\cdot THF}$$

$$\mathrm{2\,RMgBr+(R'C(O)\cdots CH\cdots C(O){-}R'')_2Cu}\xrightarrow[\text{Stirring at room temp.}]{\text{THF}}\mathrm{[R{-}Mg{-}(R'{-}C(O)\cdots C(H)\cdots C(O){-}R'')]\cdot THF}$$

$$\mathrm{RMgBr + R'''ONa}\xrightarrow[\text{Initial stirring (0–5°C) followed by stirring at room temp.}]{\text{THF}}\mathrm{RMgOR'''}$$

where $R = C_6H_5$ or C_4H_9; R′ and $R'' = C_6H_5$, CH_3; CH_3, CH_3; and C_6H_5, C_6H_5; $R''' = CH_3$, C_2H_5, $^iC_3H_7$ and $^tC_4H_9$

The products are pale to brownish-yellow solids, susceptible to hydrolysis, and soluble in common organic solvents such as C_6H_6, DMF, DMSO and THF.

The IR spectra of phenyl-/butyl-magnesium β-diketonates show characteristic bands for ν(C⩦O), ν(C⩦C) and ν(C–O)Mg (Table 1). The bands due to ν(C⩦O) at 1610–1595 cm^{-1} are in the same region as those in the free ligands, clearly indicating that β-diketonates are bonded to magnesium through the two carbonyl groups and not through the carbon [11]. The C–O–C vibrational band which appears at 1075 cm^{-1} in the spectrum of free THF has been shifted to 1035 cm^{-1} in the solids, indicating that the THF is coordinated to magnesium [12].

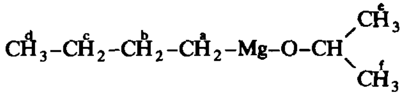
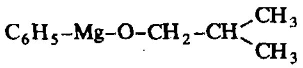
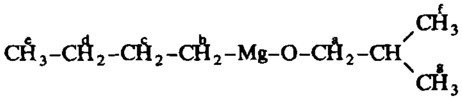
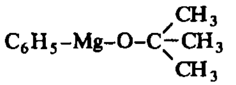
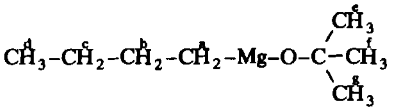
The IR spectra of the phenyl- and butyl-magnesium alkoxides show the characteristic band for ν(C–O) stretching vibrations at 1180–1070 cm^{-1} [13]. The strong band at 950–930 cm^{-1} can be assigned to ν(C–O) bridging alkoxy group [13]. The presence of both terminal and bridging alkoxy groups suggests an oligomeric nature for the alkoxides. The band at ~ 1385 cm^{-1} in the IR spectra of phenyl- or butyl-magnesium isopropoxide can be assigned to the *gem*-dimethyl moiety of the isopropoxy group [13]. The band at 1210 and 1170 cm^{-1} observed for phenyl- and butyl-magnesium tert-butoxide may arise from skeletal vibrations of tert-butoxy group.

TABLE 1. Characterization data

Grignard reagent (ml, molar)	Ligand (g)	Product formed, colour, state, m.p. (°C)	Analysis (%) found (calcd) Mg	IR data (cm^{-1})			
				ν_{sym} (C⩦O)	ν_{sym} (C⩦C)	ν_{asym} (C⩦O)	ν_{asym} (C–O)
PhMgBr (5, 2.06)	NaAcac 1.26	PhMg(Acac).thf brownish yellow solid, 140(d)	8.9(8.9)	1610s	1510s	1395s	1260s
BuMgBr (5, 2.38)	NaAcac 1.45	BuMg(Acac).thf brownish yellow solid, 130(d)	9.8(9.6)	1610s	1510s	1400s	1260s
PhMgBr (5, 2.06)	NaBzac 1.89	PhMg(Bzac).thf brown solid, 70(d)	7.4(7.3)	1595s	1510s	1390s	1280s
BuMgBr (2.5, 2.38)	NaBzac 1.09	BuMg(Bzac).thf dark brown viscous liquid, 62(d)	7.3(7.7)	1600s	1500s	1390s	1280s
PhMgBr (2.5, 2.06)	NaDBzM 1.27	PhMg(DBzM).thf brownish yellow viscous liquid, 162(d)	6.3(6.1)	1600s	1500s	1410s	1280s
BuMgBr (2.5, 2.38)	NaDBzM 1.46	BuMg(DBzM).thf brown viscous liquid, 152(d)	6.6(6.4)	1600s	1500s	1400s	1280s

Acac: acetyacetonate anion; Bzac: benzoylacetonate anion; DBzM: dibenzoylmethanate anion; s = strong.

TABLE 2. Characterization data

Grignard reagent (ml, molar)	Ligand (g)	Product formed, colour, state, m.p. (°C)	Analysis (%) found (calcd)		Structure	NMR data (ppm)			
			Mg	O^iPr/OEt		$-C_6H_5$	$-CH_3$	$-CH_2-$	$>CH-$
PhMgBr (5, 2.4)	NaOMe 0.54	PhMgOMe, yellow solid, 198(d)	18.5 (18.3)	-	$C_6H_5{-}Mg{-}O{-}CH_3$	6.9 m	3.4 s	-	-
BuMgBr (5, 0.9)	NaOMe 0.26	BuMgOMe, white solid, 228(d)	21.5 (21.6)	-	$C\overset{d}{H}_3{-}C\overset{c}{H}_2{-}C\overset{b}{H}_2{-}C\overset{a}{H}_2{-}Mg{-}O{-}C\overset{e}{H}_3$	-	1.3(d) 3.8 s(e)	0 t(a) 0.9 m(b) 1.8 m(c)	
PhMgBr (5, 2.4)	NaOEt 0.81	PhMgOEt, yellow solid, 200	16.4 (16.6)	30.5 (30.7)	$C_6H_5{-}MgOCH_2{-}CH_3$	7.2 m	1.2 t	3.7 q	-
BuMgBr (5, 0.9)	NaOEt 0.33	BuMgOEt, white solid, 240(d)	19.2 (19.2)	35.4 (35.6)	$C\overset{f}{H}_3{-}C\overset{e}{H}_2{-}C\overset{d}{H}_2{-}C\overset{c}{H}_2{-}Mg{-}O{-}C\overset{b}{H}_2{-}C\overset{a}{H}_3$	-	1.1 t(f) 1.3 t(a)	0 t(c) 1.4 m(d) 1.6 m(e) 3.8 q(b)	-
PhMgBr (5, 2.4)	NaO^iPr 0.98	$PhMgO^iPr$, white solid, 175	15.1 (15.1)	36.8 (36.8)	 $C_6H_5{-}MgOCH{<}\begin{array}{l}CH_3\\CH_3\end{array}$	7.0 m	2.1 d	-	2.5 sep
BuMgBr (5, 0.9)	NaO^iPr 0.39	$BuMgO^iPr$, yellow solid, 208(d)	17.0 (17.3)	42.0 (42.0)	 $C\overset{d}{H}_3{-}C\overset{c}{H}_2{-}C\overset{b}{H}_2{-}C\overset{a}{H}_2{-}Mg{-}O{-}CH{<}\begin{array}{l}C\overset{e}{H}_3\\C\overset{f}{H}_3\end{array}$	-	1.2 m(d) 1.8 s,b(e,f)	0.1 t(a) 0.9 m(b) 1.4 m(c)	4.2 sep
PhMgBr (5, 2.4)	NaO^iBu 1.15	$PhMgO^iBu$, yellow solid, 205	13.7 (13.9)	-	 $C_6H_5{-}Mg{-}O{-}CH_2{-}CH{<}\begin{array}{l}CH_3\\CH_3\end{array}$	7.2 m	0.9 d	3.7 d	2.7 m
BuMgBr (5, 0.9)	NaO^iBu 0.46	$BuMgO^iBu$, yellow solid, 201	15.1 (15.7)	-	 $C\overset{e}{H}_3{-}C\overset{d}{H}_2{-}C\overset{c}{H}_2{-}C\overset{b}{H}_2{-}Mg{-}O{-}C\overset{a}{H}_2{-}CH{<}\begin{array}{l}C\overset{f}{H}_3\\C\overset{g}{H}_3\end{array}$	-	1.0 m (g,e,f)	0 m(b) 1.3 m(c) 1.8 m(d) 3.8 s,b(a)	2.3 m
PhMgBr (5, 2.4)	NaO^tBu 1.15	$PhMgO^tBu$, yellow solid, 229	13.8 (13.9)	-	 $C_6H_5{-}Mg{-}O{-}C{\equiv}\begin{array}{l}CH_3\\CH_3\\CH_3\end{array}$	7.4 m	1.2 s	-	-
BuMgBr (5, 0.9)	NaO^tBu 0.46	$BuMgO^tBu$, white solid, 246	15.7 (15.7)	-	 $C\overset{d}{H}_3{-}C\overset{c}{H}_2{-}C\overset{b}{H}_2{-}C\overset{a}{H}_2{-}Mg{-}O{-}C{\equiv}\begin{array}{l}C\overset{e}{H}_3\\C\overset{f}{H}_3\\C\overset{g}{H}_3\end{array}$	-	0.8 t(d) $\left.\begin{array}{l}1.3\ s\\1.7\ s\end{array}\right\}(e,f,g)$	0.1 s,b(a) 2.4–2.5 m(b,c)	-

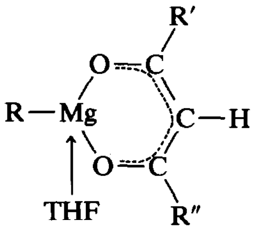
s = singlet; s,b = broad singlet; m = multiplet; t = triplet; q = quartet; sep = septet; d = doublet.

The phenyl- and butyl-magnesium β-diketonates and alkoxides show strong bands at 850–800 cm^{-1} which may be assigned to the (Mg–C) vibration [14]. The presence of a broad band at 580–515 cm^{-1} is indicative of a bridging alkyl group, as noted previously by Ashby [14].

The ^{1}H NMR spectrum of phenyl- and butyl-magnesium β-diktonates in C_6D_6 shows a multiplet in the region δ 7.8–7.4 due to aromatic protons. The tetrahydrofuran protons in these β-diketonates give rise to multiplets in the regions δ 3.8–3.5 and δ 1.9–1.7, attributed respectively to $-CH_2-O-CH_2-$ and $-CH_2-CH_2-$ protons. The methyl protons of β-diketonates derived from benzoylacetone and acetylacetone, however give rise to a singlet in the region δ2.7–2.5.

The ^{1}H NMR spectra of the butyl-magnesium β-diketonates display a triplet at 0.0 ppm due to the CH_2 group directly linked to magnesium. The second and third $-CH_2$ groups give rise to ill-resolved multiplets at δ 0.9 and δ 1.8, respectively, while the methyl protons give a multiplet at δ 1.3.

The ^{1}H NMR spectra of the phenyl- and butyl-magnesium alkoxides display the expected signals, as shown in Table 2. In case of the tert-butoxides, besides the usual signals, there are two signals, at δ 1.3 and δ 1.7, due respectively to terminal and bridging methyl groups [14]. However in the other phenyl- or butyl-magnesium alkoxides, these two signals could not be clearly distinguished because of overlapping with other signals. The presence of two types of tert-butoxy groups—terminal and bridging—suggests that organomagnesium alkoxides probably form oligomers, as reported for MeMgOEt [14].



($R = C_6H_5$ or C_4H_9; R′ and $R'' = C_6H_5$, CH_3; CH_3, CH_3; or C_6H_5, C_6H_5)

Fig. 1.

The presence of the bridging butoxy group indicates that the butoxy oxygen is sufficiently electron-donating to allow isolation of stable unsolvated organomagnesium alkoxides [14].

On the basis of the above studies, the following structure (Fig. 1) is tentatively proposed for the THF complexes of the β-diketonates.

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