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Ether cleavage by activated metals

II *. Cleavage of allyl and benzyl ethers by activated magnesium

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Abstract

Activated magnesium (prepared by reduction of magnesium halides with potassium) reacts with allyl and benzyl ethers to give the corresponding allyl or benzyl magnesium compounds.

Introduction

The standard procedure for the synthesis of organometallic compounds (e.g. of lithium or of magnesium), i.e. the reaction of organic halides with the metals, frequently cannot be used for the preparation of allyl or benzyl metal derivatives; the latter are often consumed rapidly by reaction with the starting halides to give the products of Wurtz coupling [2]. This undesired reaction can be avoided by using allyl or benzyl ethers instead of the halides [3]; for example, the cleavage of allyl phenyl ether by lithium provides the easiest and most efficient route to allyllithium [4]. Similarly organomagnesiums can be prepared by reaction of allyl ethers with magnesium [5]. However, this method has so far been restricted to unsubstituted and aryl substituted compounds, and gives only low yields (if it works at all) with ethers bearing alkyl substituents in the allyl group, or with benzyl ethers. These drawbacks now can be avoided by the use of an activated form of magnesium prepared as described by Rieke by reduction of magnesium halide with potassium [6] (Other types of activated magnesium, such as those obtained by cocondensation methods [7] or by thermal decomposition of magnesium compounds [8] have not been tested for this purpose, but may well behave similarly).

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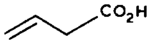
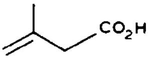
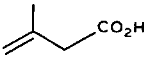
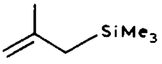
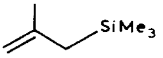
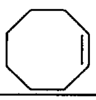
Results and discussion

In general, allyl and benzyl ethers are cleaved fairly well by 'Rieke-magnesium' (Scheme 1). This is evident even with allyl methyl ether (**1a**), which is only slowly attacked by ordinary magnesium (15% cleavage after 56 h refluxing in THF [5a]); with Rieke-magnesium considerable conversion was achieved even after 8 h (see Table 1). Methallyl and benzyl phenoxide (**1c**, **2b**) as well as benzyl methoxide (**2a**), all of which are essentially unreactive towards normal magnesium powder, can also be cleaved at reasonable rates; the yields level off at about 65% after 24 h refluxing when the metal and the ether are employed in equimolar amounts (see entries 4, 7, and 9 in Table 1). When a 50–100% excess of activated metal is used there is almost quantitative conversion of the ethers (entries 5, 8, and 10). The results indicate, incidentally, that the activated magnesium is not completely homogeneous but

Table 1

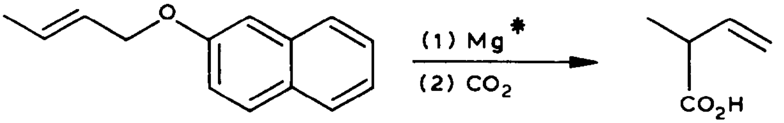
Reactions of some allyl and benzyl ethers with activated magnesium

Entry	Ether	Molar ratio Mg/ ether	Reaction time (h)	Electro- phile	Product	Yield (%)	
						Isolated	GLC
1	**1a**	1	8	CO_2		55	–
2	**1b**	1	24	CO_2		33	–
3	**1b**	3	70	CO_2		77	–[a]
4	**1c**	1	24	Me_3SiCl		–	61
5	**1c**	2	24	Me_3SiCl		69	89[a]
6	**1d**	2	24	CO_2	**3**	79	–[a]
7	**2a**	1	24	D_2O	$PhCH_2D$	51	65
8	**2a**	2	24	D_2O	$PhCH_2D$	–	88[a]
9	**2b**	1	24	D_2O	$PhCH_2D$	49	64
10	**2b**	1.5	24	D_2O	$PhCH_2D$	–	91[a]
11	**4**	1	24	H_2O		–	3.5

[a] The ether was consumed completely during reaction (as indicated by GLC).

consists of particles of various reactivities; about one third is evidently no more reactive than ordinary magnesium.

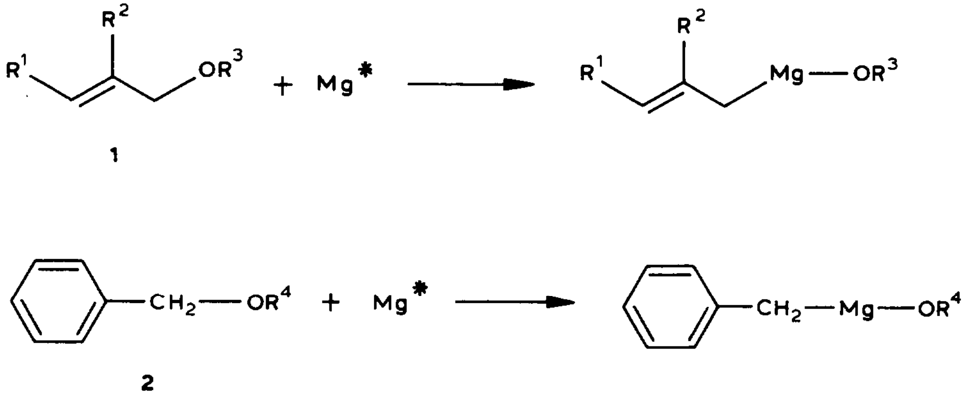
Reaction is observed not only with methallyl ethers but also with ethers having the methyl substituent in the terminal position of the allyl moiety, e.g. 2-buten-1-yl β-naphthoxide (**1d**; entry 6 in Table 1). With an excess of activated metal this ether had completely reacted after 24 h. (However, naphthyl ethers are generally somewhat more reactive than phenyl ethers; e.g. methallyl naphthoxide reacts already with ordinary magnesium, albeit slowly and to give low yields [5b]). It should be noted that after carboxylation the product was not 2-pentenoic acid but exclusively the isomeric 2-methyl-3-butenoic acid (**3**) (see eq. 1); thus there has been complete allylic rearrangement, as in other reactions of carbonyl compounds with magnesium allyls substituted in the 3-position [5c,9].



(1)

1 d **3**

The presence of additional alkyl groups in the allyl ether limits the reactivity even of activated magnesium. This is evident even with methallyl methoxide (**1b**) which reacts markedly more slowly than the corresponding phenoxide (**1c**), though it gave

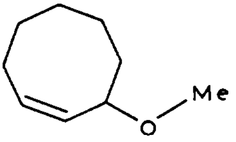


(**1a**: $R^1 = R^2 = H, R^3 = Me$;
1b: $R^1 = H, R^2 = R^3 = Me$;
1c: $R^1 = H, R^2 = Me, R^3 = Ph$
1d: $R^1 = Me, R^2 = H, R^3 = \beta$-naphthyl)

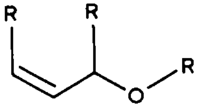
(**2a**: $R^4 = Me$
2b: $R^4 = Ph$)

Scheme 1

good yields when an excess of metal and a prolonged reaction time were used (see entries 2 and 3). However, hardly any reaction was observed with 2-cyclooctenyl methoxide (**4**), in which the allyloxy moiety effect bears three alkyl groups (if the model compound **5**).



4



5

The use of an even more reactive form of magnesium, prepared, as described by Rieke, by reduction of magnesium chloride in the presence of sodium iodide [10], did not bring about any improvement in the latter case (in marked contrast to the increase of reactivity of such magnesium in the synthesis of various Grignard compounds [11] and in the cleavage of THF or other cyclic ethers [12]). An inhibition of the cleavage reaction by traces of protic compounds cannot be excluded. (Only low conversions were observed even with **1a**, **1c**, or **2b**, when protic impurities such as water, phenol, or the respective alcohol, originating from the preparation of the ether, had not been carefully removed). However, the decrease of reactivity on introduction of alkyl groups into the ether seems to be a more general phenomenon, since it was observed even with ordinary magnesium, as mentioned above. The reactivity of magnesium towards organic substrates such as alkyl halides correlates well with the ease of their electrochemical reduction, i.e. with their half-wave potentials [13]. To our knowledge, no polarographic measurements on allyl ethers have been reported, but the introduction of two t-butyl groups into allyl halides shifts the reduction potential by about 0.3 V to more negative values, whereas a phenyl substituent makes the allyl halide more easily reducible by 0.5 V [14]. The effect of small alkyl groups cannot be assumed to be fully similar to that of t-butyl groups, nor can allyl ethers be regarded as fully comparable with allyl halides, but in view of the electrochemical data it is not surprising that whereas allyl methyl ether is cleaved readily by activated magnesium and slowly even by the normal metal, introduction of two additional alkyl groups (structure **5**) makes the ether almost inert, whereas a phenyl substituent in the allyl moiety gives rise to a rapid reaction even with ordinary magnesium. (The fundamental effect of the substituents is, of course, not accounted for by these observations, and is not discussed here). It is clear that Rieke-magnesium not only reacts faster than normal magnesium, but also has a higher reduction potential; in other words: it is not only more reactive kinetically (due to its much larger surface area) but shows also an enhanced reactivity in a thermodynamical sense (due to a higher energy content). Hence a lot reactions so far unknown for magnesium, should become feasible by use of the activated material.

Experimental

All experiments were carried out under nitrogen using Schlenk techniques.

Materials

THF was dried by refluxing over potassium in the presence of catalytic amounts of phenanthrene or benzophenone and freshly distilled under nitrogen before use.

Allyl, methallyl and benzyl ethers were prepared as described previously [5,15] 2-butenyl-β-naphthyl-ether [16] and 2-cyclooctenyl-methyl-ether [17] were gifts from Prof. R.W. Hoffmann (Marburg). Allyl and methallyl methoxide were distilled twice before use. For purification of the other ethers, the ether was diluted with pentane and the solution washed with several portions of 2*N* NaOH and of water, then dried ($MgSO_4$) and fractionally distilled.

The magnesium chloride used for preparation of activated magnesium was usually prepared in situ. About a quarter of a solution of 5 ml (6.25 g, 63.2 mmol) of 1,2-dichloroethane in 20 ml THF was added to a vigorously stirred suspension of 1.50 g (61.7 mmol) magnesium powder in 50 ml THF. After reaction had started (as indicated by a gas evolution), the mixture was cooled with a water bath (ca. 15 ° C) and the remaining dichloroethane solution was added slowly in such a manner that the reaction and the gas evolution proceeded at a moderate rate. Finally the mixture was refluxed for 1 h.

Ether cleavage

4.85 g (124 mmol) potassium was added to a suspension of $MgCl_2$ prepared as described above; the mixture was heated slowly and cautiously to reflux. After 30 min refluxing the finely divided grey suspension formed was cooled to 40–50 ° C, the ether was added, and the mixture was refluxed (For ratios of components and reaction periods see Table 1). The organomagnesiums formed were characterized by reaction with D_2O, Me_3SiCl, or CO_2.

(a) Deuteration or silylation. The reaction mixture was quenched at -70 ° C by addition of a solution of ca. 5 ml (275 mmol) D_2O in 20 ml of THF or of 20 ml (17.2 g, 158 mmol) chlorotrimethylsilane in 20 ml THF. The mixture was allowed to cool to room temperature and 10 ml pentane were added followed by a mixture of 10 ml of concentrated hydrochloric acid and 30 ml water. The organic layer was separated and the aqueous layer was extracted three times with 25 ml ether. The combined organic solutions were analyzed by gas chromatography or worked up by distillation at ambient pressure: b.p. 110 ° C (α-deuterotoluene [18]) or 111–112 ° C (methallyltrimethylsilane [19]) (yields see Table 1).

(b) Carboxylation. A few pieces of dry ice were added to the reaction mixture cooled to -70 ° C. The mixture was allowed to warm up slowly, then at 0 ° C it was treated with a mixture of 10 ml of concentrated hydrochloric acid and 30 ml water. After ether extracten as above the combined extract was evaporated in vacuo (14 mbar). The residue was dissolved in 25 ml ether and the solution was extracted three times with 25 ml of a saturated aqueous $NaHCO_3$. The combined extracts were washed with 25 ml ether, then acidified with 2*N* hydrochloric acid and extracted four times with 20 ml ether. These ethereal extracts were evaporated in vacuo and the residue was distilled at 14 mbar: b.p. 70–72 ° C (3-butenoic acid [20]), 84–85 ° C (3-methyl-3-butenoic acid [21]), 81–83 ° C (2-methyl-3-butenoic acid (**3**) [22]). ^{1}H-NMR ($CDCl_3$): **3**: $\delta = 1.28$ (d, 3H), 3.17 (m, 1H), 5.12 (d, 1H), 5.15 (d, 1H), 5.8–6.0 (m (ddd), 1H); for comparison 2-butenyl β-naphthyl ether: 1.78 (dd, 3H), 4.56 (dd, 2H), 5.7–6.0 (m, 2H), 7.1–7.5 (m, 4H), 7.65–7.8 (m, 3H).

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