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## DEALKYLATION REACTIONS CATALYZED BY GRIGNARD REAGENTS

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#### Summary

Some reactions of 2,3-dihydrobenzofuran derivatives with Grignard reagents were re-examined in order to account for discrepancies between the yields of starting materials and reaction products. Phenol was found to be present in addition to the products previously described. On the basis of the results it is assumed that phenol results from dealkylation of *o*-alkylphenol, catalyzed by the magnesium halide moiety of the Grignard reagent.

## Introduction

1,3-Benzodioxoles and 1,3-benzoxathioles are known to undergo selective cleavage of C—O bonds by the action of Grignard reagents, resulting in substitution, elimination and reduction products [1, 2] whilst with 2,3-dihydrobenzofurans the product yields were lower than expected [1].

## **Results and discussion**

To account for these apparently anomalous facts, we have examined the reaction between certain Grignard reagents and the 2,3-dihydrobenzofurans listed in Table 1. Solutions containing the reaction products were directly analyzed by gas—liquid chromatography (GLC) and compared with authentic samples. The gaseous olefins were characterized as dibromo-derivatives.

From the results (Table 1) it can be seen that phenol is present among the products of all reactions together with the expected o-alkyl- and o-alkylidene-phenols. The unexpected presence of phenol depends most likely on the action of magnesium halide arising from the Schlenk equilibrium, eqn. 1 [3, 4]. This halide, behaving as a Lewis acid in an "inverted" Friedel—Crafts  $2RMgX \Rightarrow R_2Mg + MgX_2$ 

3.3-Dihydrobenzo- furan CH <sub>3</sub> Mg1 c o-propulptenol propene 70 pitenol 70 21 45   Autan C <sub>6</sub> H <sub>3</sub> Mg1 o-propene 21 85 33   Propene o-propenylphenol 15 33   Arbuzofuran CH <sub>3</sub> Mg1 o-propenylphenol 27 51   Arobenzofuran CH <sub>3</sub> Mg1 o-reobnylphenol 27 51   Arobenzofuran CH <sub>3</sub> Mg1 o-reopnylphenol 27 51   Arobenzofuran CH <sub>3</sub> Mg1 o-reopnylphenol 27 51   Arobenzofuran CH <sub>3</sub> Mg1 o-reopnylphenol 21 31   Arobenzofuran CH <sub>3</sub> Mg1 o-reutylphenol 21 31   Arobenzofuran CH <sub>3</sub> Mg1 o-reutylphenol 21 31   Arobenzofuran CH <sub>3</sub> J <sub>2</sub> CHMgBr o-reutylphenol 21 22   Arobenzofuran GH <sub>3</sub> J <sub>2</sub> CHMgBr o-reutylphenol 21 22   Arobenzofuran GH <sub>3</sub> J <sub>2</sub> CHMgBr o-reutylphenol 22 22   Arobenzofuran GH <sub>3</sub> J <sub>2</sub> CHMgBr o-reutylphenol 22 22   Arobenzofuran GH <sub>3</sub> J <sub>2</sub> CHMgBr o-reutylphenol 20 26   Arobenzofuran GH <sub>3</sub> J <sub>2</sub> CHMg1 D-reutylphenol 20 26 </th <th>Starting material</th> <th>Grignard reagont</th> <th>Products</th> <th>Fraction (%)</th> <th>Materia] balance (%)</th>	Starting material	Grignard reagont	Products	Fraction (%)	Materia] balance (%)
C6H5MBH 0-pinenthylphenol 86 33   2Medry1-2,3-dihy- C4JaMB 0-siobutylphenol 16 61   2Medry1-2,3-dihy- CH3MB 0-siobutylphenol 27 61   2Pheny1-2,3-dihy- CH3MB 0-siobutylphenol 27 61   2Pheny1-2,3-dihy- CH3MB 0-siobutylphenol 27 61   2Pheny1-2,3-dihy- CH3MP 0-siobutylphenol 27 61   2Pheny1-2,3-dihy- CH3/2CHMBP 0-siobutylphenol 27 61   drobenzohran 2-siydroxy-2-phenylstyrene 29 21 71   drobenzohran 2-sivdroxy-2-phenylstyrene 21 21 21   drobenzohran 2-sivdroxy-2-phenylstyrene 21 21 21   drobenzohran 2-sivdroxy-2-phenylstyrene 21 21 22   drobenzohran 2-sivdroxy-2-phenylstyrene 21 22 22   MeBr3 0-sivelylpropene 18 22 22   MeBr3 0-sivelylpropene 2 22 22   MeBr3 0-sivelylpropene 2 22 22   MeBr3 0-sivelylpropene 2 2 22   MeBr3 0-sivelylpropene 2 2	2.3.Dihydrobenzo- furan	CH <sub>3</sub> Mg1	o-propylphenol phenol propene	79 21	46
2.Methyl-2.3-dihy- CH <sub>3</sub> Mg1 o-isobutylphenol E1 E1   drobenzofuran 27 27 27   drobenzofuran 22 27 27   2.Phenyl-2.3-dihy- CH <sub>3</sub> J <sub>2</sub> CHMgBr o-propenylphenol 22   2.Phenyl-2.3-dihy- CH <sub>3</sub> J <sub>2</sub> CHMgBr o-phenethylphenol 23   2.Phenyl-2.3-dihy- CH <sub>3</sub> J <sub>2</sub> CHMgBr o-phenethylphenol 23   2.Phenyl-2.3-dihy- CH <sub>3</sub> J <sub>2</sub> CHMgBr o-phenethylphenol 23   drobenzofuran CH <sub>3</sub> J <sub>2</sub> CHMgBr o-phenethylphenol 21   drobenzofuran CH <sub>3</sub> J <sub>2</sub> CHMgBr o-t-butylphenol 21   of-Butylanisole (CH <sub>3</sub> ) <sub>2</sub> CHMgBr o-t-butylphenol 82 22   MgBr <sub>2</sub> o-t-butylphenol 18 22   MgBr <sub>2</sub> o-t-butylphenol 80 26   of-Butylphenol MgBr <sub>3</sub> 0-t-butylphenol 20		C <sub>6</sub> H <sub>5</sub> MgBr	o-phenethylphenol phenol styrene	85 16	33
2-Phanvi-2,3-dihy- (CH <sub>3</sub> ) <sub>2</sub> CHMgBr o-phenethylphenol 40 31 drobenzofuran C(H <sub>3</sub> ) <sub>2</sub> CHMgBr 2-hydroxy-4-phenylstyrene 39 phenol 21 o-t-Butylanisole (CH <sub>3</sub> ) <sub>2</sub> CHMgBr 0-t-butylphenol 82 2-methylpropene 80 25 phenol MgBr <sub>2</sub> 0-t-butylphenol 80 25 o-t-Butylphenol 80 20 2-methylpropene 100 12 2-methylpropene 100 12	2.Methyl-2,3-dihy- drobenzofuran	CH <sub>3</sub> MgI	o-isobutyIphenol o-propenyIphenol phenol 2-methyIpropene	61 27 22	61
o-t-Butylanisole (CH <sub>3</sub> ) <sub>2</sub> CHMgBr o-t-butylphenol 82 22 phenol 18 2 2-methylpropene 80 25 phenol 20 25 2-methylpropene 80 25 2-methylpropene 20 25 2-methylpropene 100 12 2-methylpropene 100 12	2.Phenyl-2,3.dihy- drobenzofuran	(CH <sub>J)2</sub> CHMgBr	o-phenethylphenol 2-hydroxy-ß-phenylstyrene phenol styrene	40 39 21	31
MgBr2 o-t-butyIphenol 80 25 phenol 20 2-methyIpropene 100 12 0-t-ButyIphenol MgBr2 phenol 2-methyIpropene 100 12 2-methyIpropene	o-(-Butylanisole	(CH <sub>3</sub> ) <sub>2</sub> CHM <b>g</b> Br	o-t-butyJphenol phenol 2-methyJpropene	82 18	22
o-t-Butylphenol MgBr2 phenol 100 12 2-methylpropene		MgBr <sub>2</sub>	o-t-butylphenol phenol 2-methylpropene	80 20	26
	o-t-Butylphenol	MgBr <sub>2</sub>	phenol 2-methylpropeno	100	12

ACTION OF GRIGNARD REAGENTS ON 2,3-DIHYDROBENZOFURAN DERIVATIVES<sup>a</sup>

TABLE 1

<sup>a</sup> All percontages were obtained by GLC analysis. Material balance = percentage of reacted starting material. The gaseous alkones were characterized as dibromo-derivatives and are in equimolar amounts with respect to phenol.

reaction, promotes side-chain dealkylation following cleavage of the ethereal bond (Scheme 1). The formation of an olefin, arising from the alkyl substituent, supports this hypothesis.



# $R = H, CH_3, C_6H_5$ $R' = CH_3, (CH_3)_2CH, C_6H_5$

The fact that analogous results are obtained either by reaction of o-t-butylanisole, o-t-butylphenol or the alkyl phenols in Scheme 1 with organomagnesium reagent or magnesium bromide (eqn. 2) is further proof of this hypothesis.



# Experimental

Analytical GLC was carried out with a Carlo Erba Fractovap C gas chromatograph equipped with a flame ionization detector, and a 10% SE 30 column, using  $N_2$  as the carrier gas. All compounds were pure by GLC.

## Starting materials

2,3-Dihydrobenzofuran, 2-methyl- and 2-phenyl-2,3-dihydrobenzofuran and o-t-butylanisole were prepared by known literature methods [5-8]. Commercial o-t-butylphenol was used as supplied (Schuchardt).

# Authentic samples

o-Propyl-, o-phenethyl-, o-isobutyl-, o-propenylphenol, 2-hydroxy- $\beta$ -phenylstyrene and 1,2-dibromo-2-methylpropane were prepared by known literature methods [9-14]. Commercial phenol, styrene and 1,2-dibromopropane were used (Schuchardt).

## Common procedure of cleavage reactions

The reactions were performed as previously described [2, 15]. The products were analyzed by GLC and compared with authentic samples. The results are listed in Table 1.

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