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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

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (1)$$

TABLE 1

ACTION OF GRIGNARD REAGENTS ON 2,3-DIHYDROBENZOFURAN DERIVATIVES[a]

Starting material	Grignard reagent	Products	Fraction (%)	Material balance (%)
2,3-Dihydrobenzofuran	CH_3MgI	*o*-propylphenol	79	45
		phenol	21	
		propene		
	C_6H_5MgBr	*o*-phenethylphenol	85	33
		phenol	15	
		styrene		
2-Methyl-2,3-dihydrobenzofuran	CH_3MgI	*o*-isobutylphenol	51	51
		o-propenylphenol	27	
		phenol	22	
		2-methylpropene		
2-Phenyl-2,3-dihydrobenzofuran	$(CH_3)_2CHMgBr$	*o*-phenethylphenol	40	31
		2-hydroxy-β-phenylstyrene	39	
		phenol	21	
		styrene		
o-*t*-Butylanisole	$(CH_3)_2CHMgBr$	o-*t*-butylphenol	82	22
		phenol	18	
		2-methylpropene		
	$MgBr_2$	o-*t*-butylphenol	80	25
		phenol	20	
		2-methylpropene		
o-*t*-Butylphenol	$MgBr_2$	phenol	100	12
		2-methylpropene		

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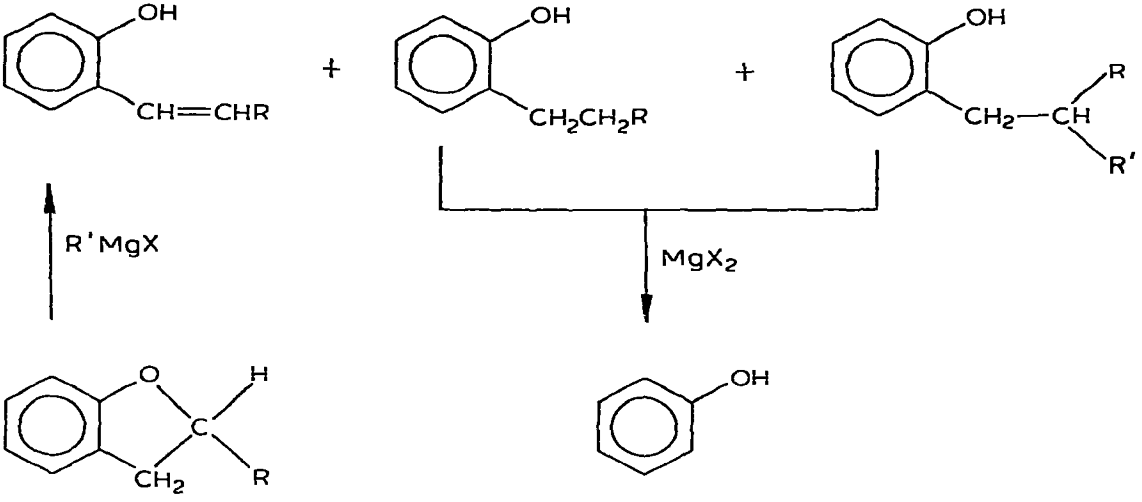
[a] All percentages were obtained by GLC analysis. Material balance = percentage of reacted starting material. The gaseous alkenes were characterized as dibromo-derivatives and are in equimolar amounts with respect to phenol.

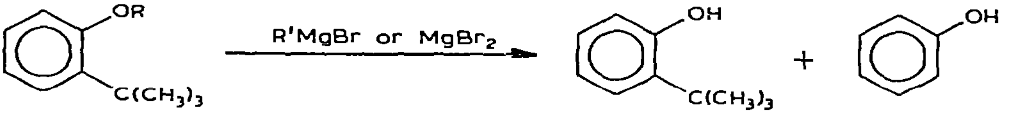
reaction, promotes side-chain dealkylation following cleavage of the ethereal bond (Scheme 1). The formation of an olefin, arising from the alkyl substituent, supports this hypothesis.

SCHEME 1



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

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.



(2)

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

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-β-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.

Acknowledgement

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