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CLEAVAGE OF THE ETHEREAL BOND

XI *. THE REACTION OF ALLYLIC ORGANOMAGNESIUM HALIDES WITH 1,3-BENZOXATHIOLE AND 1,3-BENZODIOXOLE

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Summary

Some reactions of 1,3-benzoxathiole and 1,3-benzodioxole with allylic Grignard reagents have been examined and found to give cleavage of the ether bond to form substitution products with almost complete allylic rearrangement.

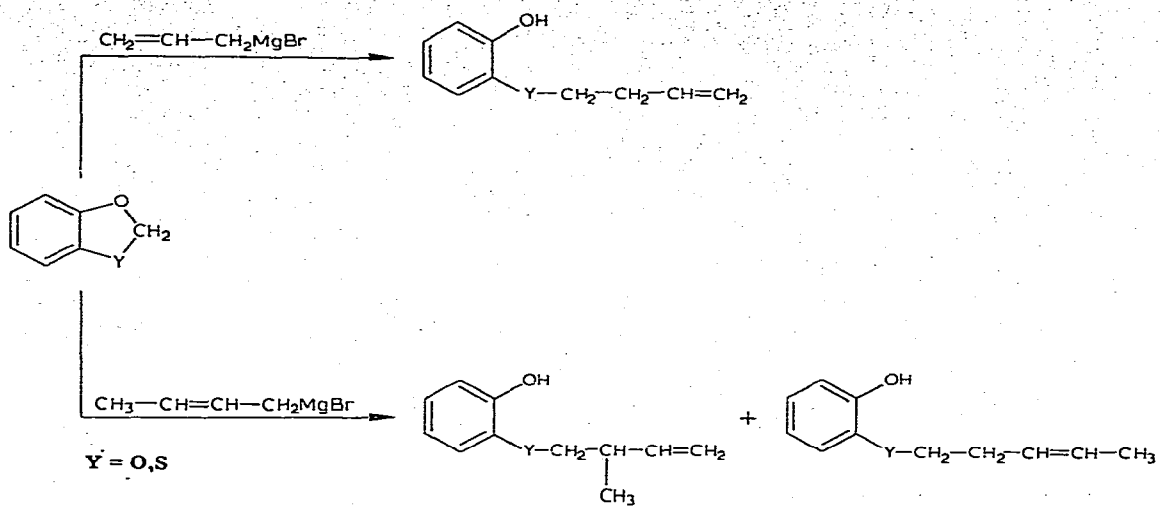
Introduction

Allylic organomagnesium compounds, in contrast to saturated Grignard reagents, do not react with carbonyl compounds to give reduction or enolization products, but generally form alcohols of structure resulting from allylic rearrangement [1—3]. We previously described the cleavage of ether and thioether bonds in 1,3-benzodioxoles and 1,3-benzoxathioles by organometallic compounds [4—6], and we have now extended our studies to include allylic organomagnesium reagents.

Results and discussion

The reactions between the heterocyclic compounds listed in Table 1 and allyl- and crotyl-magnesium bromide have been studied. The products were identified by gas-liquid chromatography (GLC) and compared with authentic samples obtained by monoalkylation of bifunctional phenols with the appropriate alkenyl halides.

* For part X, see ref. 5.



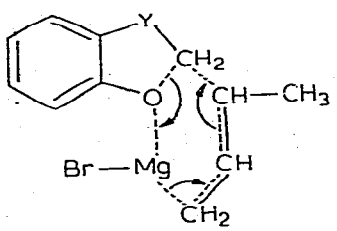
As expected, in all the reactions selective cleavage of the ethereal bond in the heterocyclic ring and formation of a substitution product was observed. In the case of crotylic magnesium compound, the substitution involved almost complete allylic rearrangement.

This rearrangement is most probably a consequence of the following equilibrium:

$$CH_3—CH=CH—CH_2MgBr \rightleftharpoons \underset{\displaystyle MgBr}{CH_3—CH—CH=CH_2}$$

(a) (b)

in which form (a), responsible for the formation of branched chain products, predominates [7—11].



Experimental

NMR spectra were determined on a Varian Ha spectrometer at 100 MHz with hexamethyldisiloxane as internal standard. The infrared spectra were obtained on a Perkin—Elmer 325 spectrophotometer using neat liquids between potassium bromide mulls. GLC analyses were performed on a Perkin—Elmer 881 gas-chromatograph, equipped with a flame detector, and a polyethylene glycol 20M column, using N_2 as the carrier gas. Microanalyses for C and H were carried out on a Perkin—Elmer model 240 Elemental Analyzer; analyses for S were performed by a published procedure [12,13].

Starting materials

1,3-Benzoxathiole (I), and 1,3-benzodioxole (II) were prepared by known methods [14,15].

Authentic samples

o-(3-Butenylthio)phenol (IIIa). 2-Hydroxythiophenol (0.07 mol), 4-bromo-1-butene (0.07 mol) [16], anhydrous potassium carbonate (0.075 mol) and dry acetone (25 ml) were refluxed together under nitrogen for 15 h. The mixture was then poured into water and the organic products extracted with diethyl ether. The *o*-(3-butenylthio)phenol was extracted with 10% aqueous sodium hydroxide, liberated with 10% sulphuric acid, and extracted with diethyl ether. The ethereal solution was dried with anhydrous sodium sulphate, the solvent evaporated and the residue distilled. Yield 48%, b.p. 95—97°C/5 mmHg, n_D^{19} 1.5908. (Found: C, 66.56; H, 6.65; S, 17.65. $C_{10}H_{12}OS$ calcd.: C, 66.63; H, 6.71; S, 17.78%.) ^{1}H NMR (CCl_4): δ 6.90 (m, 4 Harom), 6.50 (s, 1 H, OH, deuterium oxide exchanged), 5.65 (m, 1 H, —C<u>H</u>=CH_2), 4.95 (m, 2 H, —CH=C<u>H</u>$_2$), 2.60 (t, 2 H, —S—C<u>H</u>$_2$—CH_2—) and 2.20 ppm (m, 2 H, —S—CH_2—C<u>H</u>$_2$—). IR: 3400 (OH), 1640 and 920 (CH=CH_2) and 1240 cm^{-1} (C—O).

In this manner were obtained:

o-(3-Pentenylthio)phenol (IIIb). This was obtained from 2-hydroxythiophenol and 5-bromo-2-pentene [17]. Yield 40%, b.p. 148—150°C/12 mmHg, n_D^{25} 1.5634. (Found: C, 67.84; H, 7.18; S, 16.33. $C_{11}H_{14}OS$ calcd.: C, 68.00; H, 7.26; S, 16.50%.) ^{1}H NMR (CCl_4): δ 7.15 (m, 4 Harom), 6.90 (s, 1 H, OH, deuterium oxide exchanged), 5.60 (m, 2 H, —C<u>H</u>=C<u>H</u>—), 2.90 (t, 2 H, —S—C<u>H</u>$_2$—CH_2—), 2.45 (m, 2 H, —S—CH_2—C<u>H</u>$_2$—) and 1.90 ppm (m, 3 H, —C<u>H</u>$_3$). IR: 3390 (OH), 1240 (C—O) and 960 cm^{-1} (CH=CH).

o-[(2-Methyl-3-butenyl)thio]phenol (IIIc). This was made from 2-hydroxythiophenol and 4-bromo-3-methyl-1-butene [18]. Yield 44%, b.p. 160—163°C/30 mmHg, n_D^{25} 1.5744. (Found: C, 67.88; H, 7.21; S, 16.31. $C_{11}H_{14}OS$ calcd.: C, 68.00; H, 7.26; S, 16.50%.) ^{1}H NMR (CCl_4): δ 6.90 (m, 4 Harom), 6.45 (s, 1 H, OH, deuterium oxide exchanged), 5.60 (m, 1 H, —C<u>H</u>=CH_2), 4.90 (m, 2 H, —CH=C<u>H</u>$_2$), 2.50 (d, 2 H, —S—C<u>H</u>$_2$—CH<), 2.10 (m, 1 H, —CH_2—C<u>H</u><) and 0.95 ppm (d, 3 H, >CH—C<u>H</u>$_3$). IR: 3400 (OH), 1635 and 915 (CH=CH_2) and 1240 cm^{-1} (C—O).

o-(3-Butenyloxy)phenol (IVa). This was obtained from 1,2-dihydroxybenzene and 4-bromo-1-butene [16]. Yield 43%, b.p. 98—100°C/12 mmHg, n_D^{22} 1.5390. (Found: C, 73.05; H, 7.31. $C_{10}H_{12}O_2$ calcd.: C, 73.14; H, 7.37%.) ^{1}H NMR (CCl_4): δ 6.60 (m, 4 Harom), 6.45 (s, 1 H, OH, deuterium oxide exchanged), 5.30 (m, 1 H, —CH_2—C<u>H</u>=CH_2), 5.00 (m, 2 H, —CH=C<u>H</u>$_2$), 3.85 (t, 2 H, —O—C<u>H</u>$_2$—CH_2—) and 2.35 ppm (m, 2 H, —O—CH_2—C<u>H</u>$_2$—). IR: 3410 (OH), 1640 and 915 (CH=CH_2) and 1250 cm^{-1} (C—O).

o-(3-Pentenyloxy)phenol (IVb). This was obtained from 1,2-dihydroxybenzene and 5-bromo-2-pentene [17]. Yield 46%, b.p. 132—134°C/15 mmHg, n_D^{26} 1.5291. (Found: C, 74.02; H, 7.85; $C_{11}H_{14}O_2$ calcd.: C, 74.13; H, 7.92%.) ^{1}H NMR (CCl_4): δ 6.90 (m, 4 Harom), 6.00 (s, 1 H, OH, deuterium oxide exchanged), 5.60 (m, 2 H, —C<u>H</u>=C<u>H</u>—), 4.05 (t, —O—C<u>H</u>$_2$—CH_2—), 2.60 (m, —CH_2—C<u>H</u>$_2$—CH=) and 1.85 ppm (m, 3 H, =CH—C<u>H</u>$_3$). IR: 3420 (OH), 1230 (C—O) and 965 cm^{-1} (CH=CH).

TABLE 1

ACTION OF ALLYLIC ORGANOMAGNESIUM ON 1,3-BENZOXATHIOLE AND 1,3-BENZODIOXOLE [a]

Starting material	Grignard reagent	Products	Fraction (%)	Material balance (%)
1,3-Benzoxathiole (I)	CH_2=$CHCH_2MgBr$	*o*-(3-Butenylthio)phenol (IIIa)	100	51
	CH_3CH=$CHCH_2MgBr$	*o*-(3-Pentenylthio)phenol (IIIb)	5	47
		o-[(2-Methyl-3-butenyl)thio]-phenol (IIIc)	95	
1,3-Benzodioxole (II)	CH_2=$CHCH_2MgBr$	*o*-(3-Butenyloxy)phenol (IVa)	100	54
	CH_3CH=$CHCH_2MgBr$	*o*-(3-Pentenyloxy)phenol (IVb)	3	49
		o-[(2-Methyl-3-butenyl)oxy]-phenol (IVc)	97	

[a] Material balance = percentage of starting material reacted. All percentages were obtained by GLC analysis.

o-[(2-Methyl-3-butenyl)oxy]phenol (IVc). This was prepared from 1,2-dihydroxybenzene and 4-bromo-3-methyl-1-butene [18]. Yield 30%, b.p. 102—104°C/4 mmHg, n_D^{21} 1.5190. (Found: C, 73.98; H, 7.87. $C_{11}H_{14}O_2$ calcd.: C, 74.13; H, 7.92%.) ^{1}H NMR (CCl_4): δ 6.65 (m, 4 Harom), 6.35 (s, 1 H, OH, deuterium oxide exchanged), 5.60 (m, 1 H, —C<u>H</u>=CH_2), 4.95 (m, 2 H, —CH=C<u>H</u>$_2$) 3.80 (d, 2 H, —O—C<u>H</u>$_2$—CH<), 2.05 (m, 1 H, —CH_2—C<u>H</u><) and 1.00 ppm (d, 3 H, >CH—C<u>H</u>$_3$). IR: 3400 (OH), 1620 and 915 (CH=CH_2) and 1260 cm^{-1} (C—O).

Procedure for cleavage reactions

Allyl (or crotyl) bromide (5 ml) in anhydrous diethyl ether (100 ml) was brought into reaction with activated magnesium (285 mmol) under nitrogen. Allyl (or crotyl) bromide (100 mmol) in anhydrous $(C_2H_5)_2O$ (65 ml) was added during two hours. The mixture was then stirred for one hour, warmed for thirty minutes, then decanted rapidly into another flask through a coarse filter to remove unreacted metal. The yield of Grignard reagent, estimated by titration against hydrochloric acid [19] was 71%.

The diethyl ether was then evaporated off under vacuum and replaced by anhydrous toluene (100 ml). The 1,3-benzodioxole (or the 1,3-benzoxathiole) (26 mmol) was added and the mixture refluxed with vigorous stirring for about eight hours. The mixture was poured into ice-water, acidified with 10% aqueous sulfuric acid, and extracted with diethyl ether. After drying of the ethereal solution over anhydrous sodium sulphate, the mixture was analyzed by GLC, authentic samples being available for comparison.

The results are listed in Table 1.

Acknowledgement

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