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FACTORS INFLUENCING THE COURSE AND MECHANISM OF GRIGNARD REACTIONS. XX. THE CLEAVAGE OF ETHERS BY GRIGNARD REAGENTS IN THE PRESENCE OF COBALTOUS HALIDES

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The methods employed for the cleavage of the oxygen-to-carbon bond in ethers have been discussed and classified by Lüttringhaus and Sääf (1). Considerable interest attaches to the use of Grignard reagents in the demethylation of certain synthetic oestrogens (2), and the degradation of certain natural products, *e.g.*, the cleavage of the oxide ring in thebaine and related compounds (3).

In the cleavage of ethers by Grignard reagents, the general procedure is to add the ether to be cleaved to an ethyl ether solution of the Grignard reagent, remove the solvent, and heat the mixture to 160–200° for a suitable length of time (the aryl allyl ethers are an exception). Some of the results recorded in the literature are collected in Table I.

Grignard attempted to explain the cleavage reaction by assuming the formation of ether-complexes (4); his formulation was supported by Stadnikow (5). Schönberg and Moubasher (6), however, argue that the magnesium halide is the reagent responsible for the cleavage.

There are certain noteworthy aspects of the cleavage in question: (a) the reaction proceeded very slowly, if at all, at the boiling point of ethyl ether (phenyl allyl ether is an exception, Table I), a temperature of 160–200° was usually required; (b) the reagent RMgI was more effective than the corresponding bromide or chloride (7); (c) the cleavage of *n*-butyl benzhydryl ether with methylmagnesium iodide gave appreciable amounts of symmetrical tetraphenylethane (8).

The facts cited suggest a free-radical mechanism for the cleavage of ethers at high temperatures. Moreover, the reactions of Grignard reagents with organic halides in the presence of cobaltous salts have been successfully explained by assuming such mechanisms. Consequently, the reactions of certain types of ethers with Grignard reagents in the presence of metallic halides (particularly cobaltous chloride) have been investigated.

GENERAL PROCEDURE

The procedure (except where otherwise indicated) was to add the cobaltous chloride (in small portions) over a three-hour period to an ethyl ether solution of the Grignard reagent containing the ether to be cleaved. After the addition was complete, the mixture was heated (30 minutes) to the boiling point of the ethyl ether, and then allowed to cool. The details of the further procedure are given in the experimental part. Under the experimental conditions just described, neither the Grignard reagent nor cobaltous chloride, when these reagents are used separately, cleaves any one of the ethers studied. Thus, benzyl phenyl ether, phenyl ether, benzyl ether, and isopropyl phenyl ether were recovered unchanged after being boiled for four hours with *n*-butyl- or ethyl-magnesium bromide in ethyl ether. These ethers were also unaffected when boiled in ether solution with *n*-butylmagnesium bromide and a large amount of magnesium.

Cleavage of ethers by Grignard reagents (in ethyl ether) and cobaltous halides. The cleavage of the following types of ether by Grignard reagents and cobaltous halides was investigated: (A) benzyl aryl and benzyl alkyl ethers; (B) phenyl allyl ether; (C) diaryl ethers; (D) aryl alkyl ethers. Each of these types reacts in a distinctive way.

TABLE I

REACTIONS OF ETHERS WITH GRIGNARD REAGENTS

	ETHER, ROR'		GRIGNARD, R''MgX	HOURS	TEMP., °C.	PRODUCT(S)
	R	R'				
1.	C_6H_5	CH_3	CH_3MgI	8	200	ROH (85%)[a]
2.	C_6H_5	C_2H_5	CH_3MgI	1	230	ROH (85%)[a]
3.	C_6H_5	$C_6H_5CH_2$	C_2H_5MgBr	15	180	ROH (49%)[b] + R'R'' (50%)
4.	C_6H_5	$C_6H_5CH_2$	*n*-C_4H_9MgBr	16	80	ROR' recovered (90%)[c]
5.	C_6H_5	$CH_2{=}CHCH_2$	*n*-C_4H_9MgCl	5	79	ROH (74%)[c]
6.	C_6H_5	$CH_2{=}CHCH_2$	*n*-C_4H_9MgBr	140	17	ROH (43%)[d]
7.	$C_6H_5CH_2$	$C_6H_5CH_2$	CH_3MgI	12	160	ROH (60%) + RR'' (55%)[b]
8.	C_6H_5	C_6H_5	C_2H_5MgBr	15	190	ROH (31%)[b]

[a] Simonis and Remmert, *Ber.*, **47**, 269 (1914). [b] Späth, *Monatsh.*, **35**, 319 (1914). [c] Lüttringhaus, Sääf, and Hauschild, *Ber.*, **71**, 1673 (1938). [d] Ref. (1).

TABLE II

REACTION OF PHENYL BENZYL ETHER WITH *n*-BUTYLMAGNESIUM BROMIDE (4 Moles) IN THE PRESENCE OF METALLIC HALIDES (2 Moles)[a]

METALLIC HALIDE	PHENOL, %
$CoCl_2$	86
$NiCl_2$	68
$FeCl_3$	65
$CuCl_2$	10
Cu_2Br_2	0
$MnCl_2$	0
$AlCl_3$[b]	3

[a] The gaseous products of these reactions were always collected but were not analyzed, unless otherwise indicated. [b] Aluminum chloride, in the absence of a Grignard reagent, gives about 25% phenol under the experimental conditions here used (four hours at room temperature and 30 minutes heating to the boiling point of ether).

(A) Cleavage of benzyl ethers. Table I shows that phenyl benzyl ether is decomposed when heated with a Grignard reagent for 15 hours at 180°, but not when heated for 16 hours at 80°. Since the reactions here described were carried out

TABLE III

Cleavage of Phenyl Benzyl Ether (1 Mole) with Grignard Reagents (4 Moles) and Cobaltous Chloride (2 Moles) in Ethyl Ether[a]

R (in RMgBr)	PHENOL, %
CH_3	35
C_2H_5	48
i-C_3H_7	80
n-C_4H_9	86
sec-C_4H_9	82
tert-C_4H_9	92
C_6H_5[b]	<8[b]

[a] See footnote (*a*) Table II. [b] After correction for phenol formed from the Grignard reagent.

TABLE IV

Cleavage of Phenyl Benzyl Ether (1 Mole) with Grignard Reagents and Metallic Halides[a]

GRIGNARD REAGENT		METALLIC HALIDE		PHENOL, %
R (in RMgBr)	Moles		Moles	
C_2H_5	2	$CoCl_2$	0.3	9
C_2H_5	2	$CoCl_2$	2	18
C_2H_5	4	$CoCl_2$	2	48
C_2H_5	2	$FeCl_3$	0.3	8
sec-C_4H_9	2	$CoCl_2$	1	66
sec-C_4H_9	4	$CoCl_2$	2	82
tert-C_4H_9	4	$CoCl_2$	2	92

[a] See footnote (*a*) Table II.

TABLE V

The Cleavage of Benzyl Ethers by Grignard Reagents and Cobaltous Chloride[a]

R'OR''		RMgBr		$CoCl_2$ (MOLES)	CLEAVAGE, %
R'	R''	R	Moles		
$C_6H_5CH_2$	α-$C_{10}H_7$	CH_3	4	2	31
$C_6H_5CH_2$	α-$C_{10}H_7$	*n*-C_4H_9	2	1.1	40
$C_6H_5CH_2$	α-$C_{10}H_7$	*n*-C_4H_9	4	2	81
$C_6H_5CH_2$	β-$C_{10}H_7$	*n*-C_4H_9	2	1.1	35
$C_6H_5CH_2$	$C_6H_5CH_2$	*n*-C_4H_9	4	2	88
$C_6H_5CH_2$	CH_3	*n*-C_4H_9	4	2	90
$C_6H_5CH_2$	*p*-$CH_3OC_6H_4$	*i*-C_3H_7	4	2	82
$C_6H_5CH_2$	*p*-$CH_3OC_6H_4$	C_6H_5	4	2	10

[a] See footnote (*a*) Table II.

at room temperature, this particular ether appeared to be a useful test object with which to investigate the influence of (a) the metallic halide and (b) the structure of the Grignard reagent.

The effect of various metallic halides (2 moles) in the cleavage of phenyl benzyl ether by *n*-butylmagnesium bromide (4 moles) is given in Table II.

Grignard reagents, in the presence of cobaltous chloride, differ considerably in their properties as cleavage agents. Some of the results obtained are assembled in Table III.

Tables II and III show the results obtained when four moles of Grignard reagent and two moles of cobaltous, ferric, or nickel chloride were used per mole of phenyl benzyl ether. Table IV contains the results obtained when smaller amounts of these reagents were used. The lower yields of phenol in the latter case indicate that a large excess of these two reagents is advisable.

The results obtained in the cleavage of benzyl ethers (other than phenyl are given in Table V.

TABLE VI

REACTIONS OF ETHERS (1 MOLE) WITH GRIGNARD REAGENTS IN THE PRESENCE OF COBALTOUS CLORIDE IN ETHYL ETHER[a]

R'OR''		RMgBr		$CoCl_2$ (MOLES)	CLEAVAGE, %
R'	R''	R	Moles		
C_6H_5	Allyl	n-C_4H_9	1.2	0.01	89
C_6H_5	CH_3	n-C_4H_9	4	2	0
C_6H_5	C_2H_5	n-C_4H_9	4	2	0
C_6H_5	i-C_3H_7	n-C_4H_9	4	2	5
C_6H_5	$C_6H_5CH_2CH_2$	n-C_4H_9	4	2	49
p-$CH_3OC_6H_4$	i-C_3H_7	n-C_4H_9	4	2	0
α-$C_{10}H_7$	C_2H_5	n-C_4H_9	4	2	0
C_6H_5	C_6H_5	C_2H_5	4	2	42
C_6H_5	C_6H_5	n-C_4H_9	4	2	43
C_6H_5	C_6H_5	n-C_4H_9	6	2.5	72
C_6H_5	C_6H_5	*tert*-C_4H_9	4	2	58
C_6H_5	α-$C_{10}H_7$	n-C_4H_9	6	2.5	52[b]
C_6H_5	p-$CH_3OC_6H_4$	n-C_4H_9	6	2.5	33[c]

[a] See footnote (*a*) Table II. [b] Phenol (36%), α-naphthol (16%). [c] Mostly phenol.

The results obtained in the cleavage of the other ethers here investigated are assembled in Table VI.

DISCUSSION

The reactions of ethers with Grignard reagents depend largely on the presence or absence of cobaltous chloride: (a) the reactions induced by cobaltous chloride take place at low temperatures; they are very fast and give high yields of the cleavage products. Note, for instance, that whereas phenyl ether (Table I) yields 31% of phenol when heated with ethylmagnesium bromide for 15 hours at 190°, this same ether yields 42% of phenol when treated with ethylmagnesium bromide at room temperature in the presence of cobaltous chloride.

(b) Whereas the reaction of an ether with a Grignard reagent at high temperature, in the absence of cobaltous chloride, is best represented by the equation

$\mathrm{ROR'} + \mathrm{R''MgX} \rightarrow \mathrm{ROMgX} + \mathrm{R'R''}$ (Table I), this same reaction in the presence of cobaltous chloride is best represented by the equation, $\mathrm{ROR'} + \xrightarrow[\mathrm{R''\ MgX}]{\mathrm{CoCl_2}} \mathrm{ROMgX} + \mathrm{R'H} + \mathrm{R''_{-H}}$.

Thus, in the presence of cobaltous chloride, phenyl benzyl ether gives phenol and toluene; phenyl allyl ether gives phenol and propylene. (See experimental part. In the reaction between laurylmagnesium bromide and phenyl allyl ether in the presence of cobaltous chloride, the gas formed was practically pure propylene). No coupled product $\mathrm{R'R''}$ was ever found. The formation of the olefins ($\mathrm{R''_{-H}}$) could in certain instances be demonstrated by appropriate experiments.

Phenyl allyl ether behaves uniquely. High yields of phenol (and propylene) are obtained when only traces (0.01 mole or less) of cobaltous chloride are used. All other ethers require large amounts of cobaltous chloride (at least two moles for four moles of Grignard reagent). In some instances (the diaryl ethers) better yields are obtained with still larger amounts of Grignard reagent and cobaltous chloride. Note that phenyl allyl ether reacts faster and requires less of the Grignard reagent and of the cobaltous chloride than does phenyl benzyl ether. Contrary results have been noted in the cleavage of these ethers by hydrobromic acid; the benzyl ether is cleaved about 50 times as rapidly as the allyl ether (9).

(c) All of the benzyl ethers (Table V) are cleaved by Grignard reagents and cobaltous chloride at room temperature. The results are similar [except as noted in (b)] to those obtained by heating these same ethers to higher temperatures with the Grignard reagent alone (Table I). However, the alkyl aryl ethers and the diaryl ethers differ markedly in their behavior under these two conditions. Anisole is said to yield 80% of phenol when heated with methylmagnesium bromide for eight hours at 200° (or one hour at 230°); no alkyl aryl ether (anisole, phenetole, isopropyl phenyl ether, *p*-anisyl isopropyl ether) is cleaved by a Grignard reagent and cobaltous chloride. On the other hand, the diaryl ethers, which withstand heating to 250° with hydrobromic or hydriodic acid (9, 10), are cleaved at room temperature by a Grignard reagent and cobaltous chloride. Similarly, *p*-anisyl ether when heated with hydrobromic and acetic acid (or with aluminum chloride) is demethylated (11), but phenyl *p*-anisyl ether when treated with a Grignard reagent and cobaltous chloride gives phenol (31%).[1]

(d) Grignard reagents, in the presence of cobaltous chloride, differ considerably in their effectiveness as cleavage agents (Tables III, IV, V and VI). *tert*-Butylmagnesium halide is undoubtedly the most effective reagent yet found when used in conjunction with cobaltous chloride. The ethyl and methylmagnesium halides are less effective, and phenylmagnesium halides are almost without effect.

The data at hand are insufficient to justify the formulation of a precise mechanism for the cleavage of ethers by Grignard reagents and cobaltous (or ferric or nickelous) halides. Obviously, the reaction is not of the ionic type. In many respects the results here obtained are similar to those obtained in the hydrogenolysis of ethers in the presence of Raney nickel (12). Thus, the alkyl aryl ethers do

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[1] Note that phenyl *p*-anisyl ether is more stable than phenyl ether under the conditions cited [for comparison *cf*. Sartovetto and Sowa, *J. Am. Chem. Soc.*, **59**, 603 (1937)].

not undergo hydrogenolysis even when heated in the presence of Raney nickel, although they may be hydrogenated under these conditions. Dialkyl ethers are stable even when heated with hydrogen over nickel at 250°. Raney nickel and hydrogen cleave benzyl ethers at low temperatures (100–150°); diaryl ethers over nickel undergo hydrogenolysis at 150–200°. It would appear, therefore, that cobaltous chloride may act as follows (schematic representation):[2]

1. $RMgX + CoX_2 \rightarrow RCoX + MgX_2$
2. $RCoX \rightarrow R\bullet + (CoX)\bullet$
3. $R\bullet \rightarrow R_{-H} + H\bullet$

According to this scheme the radicals which are most readily stabilized by decomposition into an olefin and a hydrogen atom should be most effective in cleavage of ethers.[3] The action of *sec*-butylmagnesium bromide in the presence of cobaltous chloride on isosafrole supports the suggestion just made. In this reaction large quantities (50%) of dihydrosafrole were obtained; the other reaction products were not identified. The hydrogenation of an olefin under the conditions cited is perhaps further presumptive evidence in favor of the hypothesis that hydrogen atoms are involved in the cleavage of ethers. Additional work is under way to test more fully the mechanism here suggested.

EXPERIMENTAL

Reagents. The anhydrous metallic salts of cobalt, nickel, and manganese were obtained from the hydrated salts by heating *in vacuo*. The ferric and aluminum chlorides were sublimed prior to use.

The Grignard solutions were prepared in the usual way in ethyl ether, filtered under nitrogen pressure, and the concentrations of the reagents were determined by titration of aliquot portions with standard hydrochloric acid.

The following ethers were prepared by the procedure described in *Organic Syntheses* (13): benzyl phenyl, α- and β-naphthyl benzyl, benzyl methyl, allyl phenyl, isopropyl phenyl, *p*-anisyl isopropyl, *p*-anisyl benzyl, α-naphthyl ethyl.

Benzyl ether was prepared by dehydration of benzyl alcohol (14); α-naphthyl phenyl and phenyl *p*-anisyl ethers as described by Ullmann and Sponagel (15) and Lea and Robinson (16), respectively.

Apparatus. The apparatus consisted of a three-necked flask, fitted through ground-glass joints, with a mercury-sealed stirrer, a graduated dropping-funnel, and a reflux condenser connected through a calcium chloride tube to a gas outlet, which provided for collection of the gases formed in the reaction.

Procedure. A typical experiment was conducted as follows. Benzyl phenyl ether (5 g.,

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[2] The schematic representation outlined in equations 1 to 3 should not be interpreted as necessarily implying the spontaneous dissociation of a radical $R\cdot$, into an olefin molecule R_{-H}, and a free hydrogen atom $H\cdot$. On the whole it would appear more probable that such a process would be an induced decomposition in which a hydrogen acceptor (in this case the ether which is being cleaved) participates. In any event, the breakdown into steps of the ether cleavage process is artificial, and is done here to bring out the essential prerequisites for these reactions. Mechanistically, the process is probably a concerted (free radical) displacement reaction involving an ethereal complex.

[3] The effectivensss of methylmagnesium halides is probably due to an indirect action. The free methyl radicals generated in the reaction attack the ether to give methane and free ethyl radicals and these give in the reaction hydrogen atoms and ethylene.

0.027 mole) was dissolved in anhydrous ethyl ether (50 ml.), and an ethereal solution of *n*-butyl magnesium bromide (1.97 *N*; 56 ml., or 0.11 mole) was added (normality of the solution with respect to the Grignard reagent was therefore 1 *N*), and the air in the apparatus was displaced by nitrogen gas. Anhydrous cobaltous chloride (7.0 g., 0.054 mole) was then added (in 12 portions) at intervals of 15 minutes to the well-stirred mixture (*ca.* 3 hours). Evolution of gas took place after each addition of the metallic halide, and there was a slight rise in temperature (5 to 10°). After all the cobaltous chloride had been added, stirring was continued for one-half hour, and the mixture was finally warmed to gentle reflux for another half-hour. Usually, a heavy black sludge settled to the bottom of the flask. The mixture was decomposed with ice and hydrochloric acid (acetic acid was used for allyl phenyl ether), the product was taken up in ether, and the ethereal solution was extracted four times with 5% aqueous sodium hydroxide (total 100 ml.). The alkaline extract was washed twice with 25-ml. portions of ether and warmed to remove the dissolved ether. It was then divided into two portions (*a*, *b*).

(*a*) After acidification the liberated phenol was titrated with a 10% solution of bromine in aqueous potassium bromide. The precipitated tribromophenol was collected and crystallized from aqueous ethanol. Identification was made by melting point and the non-depression of the melting point of an authentic sample. Comparison with a blank titration experiment performed with a known quantity of phenol, under approximately the same conditions, made it possible to estimate the yield of phenol resulting from the cleavage of benzyl phenyl ether (84% of the theoretical).

(*b*) The second portion of the alkaline extract was benzoylated, and the resulting phenyl benzoate was crystallized from ethanol and identified by melting point and mixture melting point. A blank experiment here also permitted an estimate of the yield of phenol (89%).

The ethereal extract, which contained the alkali-insoluble materials was dried, and concentrated, and then distilled. The material boiling at 109–111° (756 mm.) was shown to be toluene. The 2,4-dinitro derivative of this material did not depress the melting point of a known sample of 2,4-dinitrotoluene.

The gaseous products were collected. The analyses, whenever made, were by the method described by Kharasch, Lewis, and Reynolds (17).

The above procedure was used with the ethers which upon cleavage gave phenol (benzyl phenyl, allyl phenyl, alkyl phenyl, phenethyl phenyl, and phenyl). *p*-Anisyl benzyl ether gave the corresponding substituted phenol, which was identified as the benzoate, and estimated in the same way as phenol. With the α- and β-naphthyl benzyl ethers, the resulting α- or β-naphthols were isolated and weighed as such. Benzyl methyl ether gave toluene; benzyl ether yielded approximately equal quantities of toluene and benzyl alcohol, both of which were identified (the benzyl alcohol in the form of its 3,5-dinitrobenzoyl derivative). The amount of ether unchanged, if any, served as a further check on the extent of cleavage.

Gaseous products were obtained with the aliphatic Grignard reagents. Phenylmagnesium bromide and benzylmagnesium chloride gave rise to biphenyl and bibenzyl respectively. These products were separated from the unchanged benzyl phenyl ether by steam-distillation, followed by hydrolysis with a mixture of hydrobromic and glacial acetic acids, which cleaved the ether but did not affect the hydrocarbons. After removal of the cleavage products of the ether (by alkali extraction and distillation) the pure biaryl or biaralkyl was obtained on recrystallization. (In the case of bibenzyl, a chromatographic separation was resorted to in the final stage of purification.)

The reaction of phenyl allyl ether with Grignard reagents. It has been found that the cleavage of this ether with Grignard reagents alone can be effected at a comparatively low temperature (34°), although a long time is required. Thus, 40 hours were required for 61% cleavage, and less than 2% was effected in three hours. However, the addition of a "catalytic" amount of anhydrous cobaltous chloride brought the reaction to completion in a matter of minutes at room temperature. Thus, when one mole-% of the metallic salt was added to a solution of allyl phenyl ether dissolved in an ethereal solution of *n*-butylmagnesium bromide, a violent evolution of gas took place, and the reaction was over in about five minutes. A nearly quantitative yield of phenol was obtained. In fact it was found necessary to operate at 0°, in order to insure proper control of the reaction.

In the cleavage of benzyl phenyl ether, the benzyl group gave rise to toluene in the reaction product. The allyl group in allyl phenyl ether should therefore by analogy give rise to propylene, which, however, could not be readily identified when it was mixed with the low-boiling hydrocarbons (butane and butenes, etc.) resulting from the use of butyl Grignard reagent. An experiment was therefore carried out with this ether, laurylmagnesium bromide, and cobaltous chloride.

Allyl phenyl ether (0.09 mole, 12 g.) was dissolved in an ethereal solution of laurylmagnesium bromide (0.1 mole, in 120 ml. ether), and the solution was cooled to 0°. Cobaltous chloride (0.001 mole, 0.13 g.) was then added, and stirring was begun. After an induction period of about five minutes, evolution of gas started, becoming quite vigorous after two minutes. The reaction subsided in about three minutes, and stirring was continued for one-half hour. The phenol (77%) was isolated in the usual manner. The gas was collected and analyzed. It was found to have a molecular weight of 44.2 (calc'd for C_3H_6, 42.0) and to be 95% unsaturated.

An experiment was performed to ascertain whether the coupled product RR′ (heptene) was formed when a phenyl allyl ether is treated with *n*-butylmagnesium bromide in the presence of cobaltous chloride. The result was negative.

The reaction of isosafrole with Grignard reagents. (*a*) *sec*-Butylmagnesium bromide does not react when heated with isosafrole for many hours at the boiling point of ethyl ether. All the isosafrole was recovered unchanged. (*b*) The reaction between isosafrole (n_D^{20} 1.5781) and a mixture of *sec*-butylmagnesium bromide (4 moles) and cobaltous chloride (2 moles) gave rise to a product which boiled at 59–59.5°/1 mm. (50% on the basis of the isosafrole used). From the refractive index of this material (n_D^{20} 1.5220) it was estimated that it consisted of about 90% of dihydrosafrole (n_D^{20} 1.5153) and about 10% of isosafrole (n_D^{20} 1.5781). Some phenolic material (15%) was also formed. Since the separation of isosafrole and dihydrosafrole was impracticable, the mixture was converted to the catechol, 3,4-dihydroxypropylbenzene, in the manner described by Delange (18) and identified as the bis(3,5-dinitrobenzoate) of 3,4-dihydroxypropylbenzene. For comparison isosafrole was hydrogenated (19) and similarly converted to 3,4-dihydroxypropylbenzene. The 3,5-dinitrobenzoates of the two substances thus obtained had the same melting point and mixture melting point.

SUMMARY

1. Benzyl alkyl, benzyl aryl, aryl allyl, and diaryl ethers are cleaved (at room temperature) by Grignard reagents in the presence of cobaltous halides.

2. Alkyl aryl ethers are not cleaved by Grignard reagents and cobaltous chloride, but phenyl β-phenethyl ether undergoes cleavage.

3. Phenol and toluene and phenol and propylene are formed in the cleavage of benzyl phenyl and allyl phenyl ethers, respectively.

4. Isosafrole is hydrogenated to dihydrosafrole when treated with a Grignard reagent in the presence of cobaltous chloride.

5. A mechanism is proposed which accounts for the difference in effectiveness of the Grignard reagents.

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