

FACTORS DETERMINING THE COURSE AND MECHANISM OF GRIGNARD REACTIONS. XVIII. THE EFFECT OF METALLIC HALIDES ON THE REACTIONS OF GRIGNARD REAGENTS WITH 1-PHENYL-3-CHLOROPROPANE, CINNAMYL CHLORIDE, AND PHENYLETHYNYL BROMIDE

M. S. KHARASCH, FRANK L. LAMBERT, AND W. H. URRY

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To extend the study of free hydrocarbon radicals in solution, several organic halides (1-phenyl-3-chloropropane, cinnamyl chloride, and phenylethynyl bromide) were treated with Grignard reagents both in the presence and in the absence of cobaltous chloride.

TABLE I
COBALTOUS-CHLORIDE-CATALYZED REACTION BETWEEN 1-PHENYL-3-CHLOROPROPANE AND GRIGNARD REAGENTS

	GRIGNARD REAGENT	
	Methylmagnesium Bromide	Butylmagnesium Bromide
Amounts of reagents (moles)		
1-Phenyl-3-chloropropane.....	1.89	1.36
Grignard reagent.....	2.07	1.51
Per cent reaction.....	99	93
Products (yield in per cent of calculated amount)		
<i>n</i> -Propylbenzene.....	17.5	46
β -Methylstyrene.....	39.0	24
Gaseous products.....	89.4 ^a	82 ^b
Higher-boiling products.....	37.2 ^c	15 ^d

^a A mixture of 90% methane, 5% ethane, and 5% ethylene.

^b A mixture of 50% butane and 50% butene. The butene is about 70% *trans*-butene-2.

^c A heterogeneous mixture of higher polymers. For details, see Table II.

^d Primarily *n*-heptylbenzene and 1,6-diphenylhexane. No solid derivatives suitable for identifying these substances are described in the literature. Satisfactory derivatives were obtained by condensing *n*-heptylbenzene with tetrachlorophthalic anhydride and by condensing 1,6-diphenylhexane with phthalic anhydride. When authentic condensates of these substances were mixed with the analogous condensates of the presumed *n*-heptylbenzene and 1,6-diphenylhexane obtained from the higher-boiling products, no depressions of the melting points were observed.

Reactions of Grignard reagents with 1-phenyl-3-chloropropane. When 1-phenyl-3-chloropropane is heated, even for a long time, with Grignard reagents in ether solution, there is no reaction; all the organic halide is recovered unchanged. However, when about 5 mole per cent of cobaltous chloride is added to the reaction mixture, an energetic reaction occurs, and the organic halide is almost

completely consumed. When cobaltous chloride is present, significant differences are found between the reaction of 1-phenyl-3-chloropropane with butylmagnesium bromide and its reaction with methylmagnesium bromide. Quantitative details with regard to these experiments are given in Tables I and II.

TABLE II
HIGH-BOILING PRODUCTS FROM THE REACTION BETWEEN METHYLMAGNESIUM BROMIDE AND 1-PHENYL-3-CHLOROPROPANE

FRACTION NUMBER	WEIGHT (G.)	REFRACTIVE INDEX n_D^{20}	AVERAGE MOLECULAR WEIGHT	AVERAGE NUMBER OF DOUBLE BONDS PER MOLECULE
1	7.2	1.5360	223	0.81
2	10.5	1.5478	268	0.58
3	21.0	1.5573	366	0.31
4	13.2		480	
5	18.5		471	
6	5.0		510	

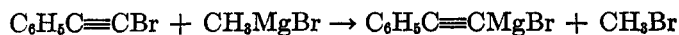
TABLE III
EFFECT OF METALLIC HALIDES ON THE REACTION BETWEEN METHYLMAGNESIUM BROMIDE AND CINNAMYL CHLORIDE^a

METALLIC HALIDE (5 MOLE %)	YIELD, PER CENT OF CALCULATED AMOUNT		
	Addition Product $C_6H_5CH=CHC_2H_5$	Coupling Products	
		1,6-Diphenylhexa- diene-1,5	1,4-Diphenylhexa- diene-1,5
None.....	89	1	5
Cu_2Cl_2	94	0	0
$FeCl_3$	77	6	9
$MnCl_2$	71	7	11
$CrCl_3$	19	20	44
$NiCl_2$	16	30	31
$CoCl_2$	12	30	40

^a Cinnamyl chloride was added to a mixture of the metallic halide in methylmagnesium bromide at 5°.

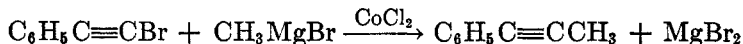
Reaction of methylmagnesium bromide with cinnamyl chloride. Metallic halides exert a profound effect on the reaction between methylmagnesium bromide and cinnamyl chloride. The percentage yields of the various products obtained are given in Table III.

Reaction of methylmagnesium bromide with phenylethynyl bromide. Methylmagnesium bromide reacts with phenylethynyl bromide as follows:



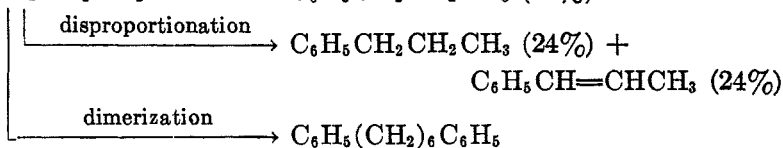
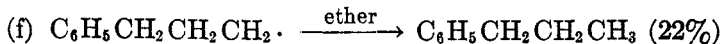
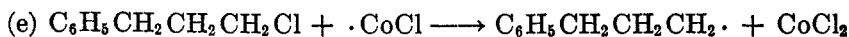
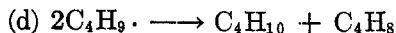
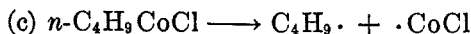
This exchange reaction accounts for the formation of phenylacetylene or phenylpropynoic acid when the reaction mixture is decomposed with water or carbon dioxide, respectively. However, when 5 mole per cent of cobaltous chloride is

added to the Grignard reagent and then phenylethynyl bromide is added to the mixture, a 62% yield of 1-phenyl-2-methylacetylene is obtained along with a considerable quantity of tar.



DISCUSSION

When 1-phenyl-3-chloropropane is treated with Grignard reagents in the presence of cobaltous chloride, the quantitative differences in the reaction products (*n*-propylbenzene, β -methylstyrene, higher-boiling materials) when methyl- or butyl-magnesium bromide is used, are of significance. These differences may be explained by assuming for the reaction with butylmagnesium bromide, the following mechanisms:

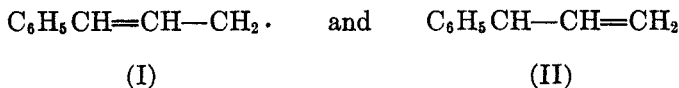


The reaction when methylmagnesium bromide is used is similar, but the free methyl radical, because of its greater reactivity, also attacks the molecule of 1-phenyl-3-chloropropane. Hence, much more β -methylstyrene and higher-boiling products (see Tables I and II) are obtained with the methyl Grignard reagent. Furthermore, as would be expected, the compositions of the gases formed in the two reactions are different. The gas obtained in the reaction with butylmagnesium bromide is exclusively an equimolecular mixture of butane and butene. This fact indicates that the free butyl radical does not attack the solvent (ether) either by removing hydrogen atoms from it or by breaking the carbon-to-oxygen bond. In the reaction with methylmagnesium bromide, the gas formed contains 90% of methane, 5% of ethane, and 5% of ethylene. This proportion of methane is far higher than that usually found in reactions in which free methyl radicals react only with ethyl ether, namely 66% methane, 17% ethane, and 17% ethylene. These findings indicate that the free methyl radicals remove hydrogen atoms competitively from ethyl ether and from 1-phenyl-3-chloropropane (or the free radical formed from it).

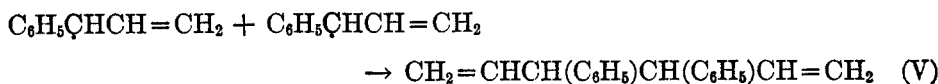
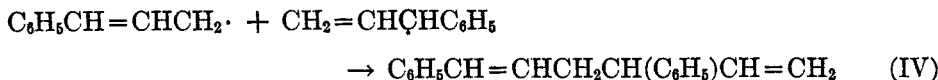
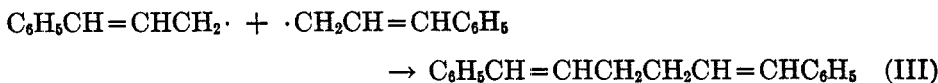
The disproportionation products, of both the free phenylpropyl radical (Equation f) and the free *n*-butyl radical (Equation d) are of considerable theoretical

interest. *A priori*, one might expect the unsaturated products of these disproportionations to be allylbenzene and butene-1, respectively. However, *trans*- β -methylstyrene (see Experimental Part) and butene-2 (predominantly the *trans* form) were actually obtained. Both of these products indicate the migration of a hydrogen atom in the free radical during disproportionation.

The free cinnamyl radical (I) formed in the reaction between methylmagnesium bromide and cinnamyl chloride in the presence of cobaltous chloride is a resonance-hybrid of the free phenylvinylmethyl radical (II).



These free radicals (I and II) are not very reactive. Hence, they do not attack the solvent (ether) to yield β -methylstyrene or allylbenzene; instead, they dimerize.



It is of interest that 1,6- and 1,4-diphenylhexadiene-1,5 (III and IV) are formed, but not the 3,4- isomer (V). No undue importance, however, should be attached to this finding, until the structure of the high-boiling non-distillable material is ascertained. This material may have been formed by removal of a hydrogen atom from 3,4-diphenylhexadiene-1,5 by free methyl radicals (formed in the reaction) and subsequent dimerization of the free radical thus produced. However, if any of the 3,4-isomer is formed, its amount cannot exceed 10%. This finding suggests that a steric factor may also play an important part in the dimerization of the free cinnamyl radicals.

The catalysis by cobaltous chloride of the normal condensation of phenylethyne bromide (and presumably other ethynyl bromides) with Grignard reagents is most important from a synthetic standpoint. The role of cobaltous chloride in this reaction is similar to its role in the condensation of vinyl halides with Grignard reagents (1).

EXPERIMENTAL PART

Reaction of 1-phenyl-3-chloropropane with n-butylmagnesium bromide in the presence of cobaltous chloride. n-Butylmagnesium bromide (2) (1.51 moles dissolved in one liter of ether) was placed in a dried, nitrogen-swept 3-liter, 3-necked flask provided with ground-glass joints. A condenser, a dropping-funnel, and a mercury-sealed stirrer were attached. An ice-bath was placed around the reaction flask, and the Grignard reagent was stirred. When the solution had cooled to 0°, cobaltous chloride (6 g.) was added.

1-Phenyl-3-chloropropane (210 g., 1.36 moles, n_D^{20} 1.5225) in an equal volume of anhydrous ether was dropped into the vigorously stirred Grignard solution over a period of three hours. Two further portions of cobaltous chloride (3 g. each) were added to the reaction mixture, the first after one-half of the halide had been introduced, and the second after the addition of the halide was complete. Then the reaction mixture was allowed to warm to room temperature. A vigorous evolution of dissolved gas ensued. This gas was passed through the condenser into a large trap immersed in a dry ice-acetone bath; here the gas condensed. The reaction and the evolution of gas were completed by refluxing the ether solution for three hours.

Excess Grignard reagent was decomposed and magnesium salts were dissolved by adding dilute acetic acid to the mixture. The two liquid phases of the resulting mixture were separated, and the ether layer was extracted twice with water, twice with 10% potassium carbonate solution, and then once again with water. The aqueous layer was extracted with ether, and the resulting ether solution was washed as above. The combined ether solutions were dried over anhydrous sodium sulfate. The aqueous extracts were combined and diluted to a known volume. The halide ion content (Volhard) of this solution indicated that 93% of the organic halide had reacted.

The ether was distilled from the dried solution just described, and the lower-boiling substances were distilled *in vacuo* (major fraction collected at 42–50°/3 mm.) until the distillation temperature reached 75°/3 mm. A high-boiling residue (19 g.) remained in the flask. The lower-boiling reaction products were fractionally distilled at 42 mm. through a 100-plate Podbielniak Heligrid column.

Careful examination of the successive fractions collected indicated the following products:

- (a) *n*-Propylbenzene (69.0 g., 0.575 mole; 46% yield); n_D^{20} 1.4922; b.p. 69.5–70°/42 mm.
- (b) β -Methylstyrene (35.9 g., 0.305 mole; 24% yield); n_D^{20} 1.5494; b.p. 87.5°/42 mm.
- (c) 1-Phenyl-3-chloropropane (13.9 g., 0.090 mole; 7% recovery); n_D^{20} 1.5225; b.p. 81°/6 mm.

Further proof of the identity of the *n*-propylbenzene was obtained by converting a sample of the material to the *p*-acetamido derivative (3). The melting point observed for this derivative was 95–96° (recorded m.p. 96°). The dibromide of β -methylstyrene was prepared (m.p. 64–66°; recorded m.p. 66.5°) (4). The constant indices of refraction of the various β -methylstyrene fractions indicate that the β -methylstyrene here isolated was one pure form, probably the *trans* form.

Previous workers (5) have not mentioned the fact that there are two possible β -methylstyrenes—*cis* and *trans*. The reported properties of β -methylstyrene range from those observed by Campbell and O'Connor (b.p. 166.7°/746 mm.; n_D^{20} 1.5420) to those originally observed by Klages (b.p. 176–178°; n_D^{20} 1.5492) which check closely with the values here obtained. Campbell and O'Connor prepared their β -methylstyrene by low-pressure hydrogenation of phenylmethylacetylene over Raney nickel. No attempt was made by these workers to establish the configurations of their product, but one observation—the formation of isostilbene from diphenylacetylene—indicates that hydrogenations of the type mentioned probably involve *cis* addition of one molecule of hydrogen to the triple bond. Hence, Campbell and O'Connor's β -methylstyrene was probably the *cis* modification.

The high-boiling residue (19 g.; 15% yield) from the distillation described was molecularly distilled. Three fractions were collected. The average molecular weights of these materials were determined in a Swietoslowski ebullioscope (6) using carbon tetrachloride as solvent.

FRACTION	REFRACTIVE INDEX n_D^{20}	FRACTION WEIGHT	AVERAGE MOLECULAR WEIGHT
1	1.5060	7.1 g.	169
2	1.5237	5.4 g.	221
3	1.5370	4.9 g.	289

Samples of these three fractions were shown to be saturated: they did not decolorize a solution of bromine in carbon tetrachloride.

The molecular weight and the refractive index of Fraction 1 indicated that it probably contained 1-phenyl-3-chloropropane and *n*-heptylbenzene in about equal quantities. Accordingly, to remove the halide, part of the fraction was refluxed with alcoholic silver nitrate for one hour. The silver chloride which precipitated was collected on a filter, and the ethyl alcohol in the filtrate was evaporated on a steam-bath. The residue from the evaporation was treated with water and extracted with ligroin (60°). The ligroin solution was extracted twice with water, twice with concentrated sulfuric acid, and once again with water. It was dried by standing overnight with Drierite, and the ligroin was removed first by distillation and finally by pumping under high vacuum. The residue was converted to its tetrachloro-*o*-benzoylbenzoic acid derivative (7). This derivative, after one recrystallization from ethyl alcohol (70%), melted at 117–120°. *n*-Heptylbenzene (b.p. 115–116°/14 mm.; n_D^{20} 1.4879) prepared by the Clemmensen reduction of phenyl hexyl ketone was treated in the same way. The derivative obtained melted at 117–120°. The melting point of a mixture of the two substances was 117–120°.

A part of Fraction 2 was treated with phthalic anhydride and aluminum chloride. The method used was that of Underwood and Walsh (procedure II) except that a 4-fold excess of hydrocarbon was used. The solid derivative obtained melted, after one recrystallization from ethyl alcohol (80%), at 92–94°. 1,6-Diphenyl-*n*-hexane (b.p. 142–144°/1 mm.; n_D^{20} 1.5500) was prepared by the reaction of 1-phenyl-3-chloropropane with sodium in ethyl ether (8). The *o*-benzoylbenzoic acid derivative of this substance melted at 92–94°. (Neutralization equivalent: observed, 381; calc'd for $C_{26}H_{28}O_3$, 386.) A mixture of the two substances melted at 92–94°.

Study of gaseous reaction products. The mixture of gaseous products was liquefied at -80° in a dry ice-acetone bath. A 20% solution of bromine in carbon tetrachloride was added drop by drop to the condensate. Almost at once a yellow solid began to precipitate. The bromine solution was added until the persistence of the bromine color indicated that the addition of bromine was complete.

An efficient condenser was attached to the flask containing the brominated mixture. A rubber tube led from the top of the condenser to a large trap immersed in a -80° bath. The reaction mixture was warmed slowly until its boiling point was reached. During this operation a distillate (46.9 g.) collected in the cold trap. A sample of this distillate was transferred to a vacuum line where, in order to remove ether, it was bubbled repeatedly through a trap containing concentrated sulfuric acid. The unabsorbed residue was passed through a trap held at -80° until all the carbon tetrachloride had been condensed. Weighing the sample before and after these treatments showed that the distillate contained butane (26.2 g., 0.45 mole; mol. wt.: calc'd, 58.1; found, 59.7).

The residue in the reaction flask was washed with water, sodium bisulfite solution (10%), sodium bicarbonate solution (10%) and again with water. It was then dried over anhydrous calcium chloride and distilled. After the ether and carbon tetrachloride had been removed, a mixture of dibromobutanes was collected (102 g.; b.p. 72–78°/50 mm.; n_D^{20} 1.5123). These dibromobutanes had been formed by the addition of bromine to a mixture of butenes (27.5 g., 0.49 moles). Part of the mixture of the dibromobutanes (70.2 g.) was fractionally distilled through a 100-plate Podbielniak column at a pressure of 50 mm. The refractive indices of the various fractions collected indicate the following products:

1. Meso-2,3-dibromobutane (48 g. = 69%) b.p. 72.5–73°/50 mm., n_D^{20} 1.5116.
2. Racemic 2,3-dibromobutane (22 g. = 31%) b.p. 75.5–76°/50 mm., n_D^{20} 1.5147.

The physical constants of the products are close to those observed by Dillon, Young, and Lucas (9). In order to check the identity of these products, careful density determinations were made, and the values thus obtained were corrected to a vacuum. The density of a middle fraction of 1. was determined in a 10-ml. pycnometer. The value of d_4^{20} thus obtained was 1.7825; the value given for meso-2,3-dibromobutane is 1.7829 (9). The density of a middle fraction of 2. was determined in a 5 ml. pycnometer. The value of d_4^{20} thus obtained was 1.7916; this value is identical with that given (9) for racemic 2,3-dibromobutane.

Two other dibromobutane mixtures were studied. One was prepared in the manner described above from the gaseous product of the reaction between *n*-butylmagnesium bromide and *n*-butyl bromide in the presence of cobaltous chloride. The refractive indices for the various fractions of this dibromobutane mixture indicate that the mixture contained 80% meso-2,3-dibromobutane and 20% racemic 2,3-dibromobutane. The other dibromobutane mixture was prepared as described from the gaseous products of the reaction between phenylmagnesium bromide and *n*-butylmagnesium bromide in the presence of cobaltous chloride. This mixture contained about 70% of meso-2,3-dibromobutane and 30% of racemic 2,3-dibromobutane.

Reaction of 1-phenyl-3-chloropropane with methylmagnesium bromide in the presence of cobaltous chloride. 1-Phenyl-3-chloropropane (292 g., 1.89 moles) in an equal volume of ether was treated with methylmagnesium bromide (2) (2.07 moles dissolved in 1500 ml. of ether) in the presence of cobaltous chloride (16 g., 0.12 mole). The procedure used was the same as that already described. The gas evolved during the reaction (37.8 l. S.C.; 1.69 moles; 89% yield) was passed through a trap held at -80° and then collected over water. This gas [analyzed by the method of Kharasch, Lewis, and Reynolds (10)] had an average molecular weight of 17.4; it contained 5.4% of unsaturated hydrocarbons. These figures indicate that the gas contained methane (89%), ethane (5.5%), and ethylene (5.5%). Volhard titration of the aqueous washings of the reaction mixture indicated that the reaction was about 99% complete.

The liquid reaction product was distilled (as above) *in vacuo* to remove the lower-boiling components. A fraction boiling from 35° to 70° at 3 mm. was collected. This mixture of lower-boiling compounds was distilled at a pressure of 35 mm. through a 100-plate column. The refractive indices of the various fractions indicate the following products:

n-Propylbenzene (39.5 g., 0.33 mole; 17.5% yield) b.p. $66-67^{\circ}/35$ mm.; n_D^{20} 1.4922.

β -Methylstyrene (87.7 g., 0.743 mole; 39% yield) b.p. $86^{\circ}/35$ mm.; n_D^{20} 1.5496.

The *n*-propylbenzene was further identified by the melting point ($95-96^{\circ}$, uncorr.) of its *p*-acetamido derivative. β -Methylstyrene was converted to its dibromide (m.p. $65-66^{\circ}$, uncorr.).

The high-boiling residue (70.4 g.) was molecularly distilled. The average molecular weights of the fractions were determined in a Swietoslowski ebullioscope, using carbon tetrachloride as solvent. The degree of unsaturation of the first three fractions was determined by bromate-bromide titration (11). The findings are given in Table II.

Reaction of cinnamyl chloride with methylmagnesium bromide in the presence of metallic halides. In a typical experiment, cinnamyl chloride (12) (20 g., 0.13 mole) was slowly added to a mixture of methylmagnesium bromide (0.23 mole in 100 ml. of ether) and 5 mole per cent of the metallic halide. The reaction products were recovered in the manner already described. In all experiments, Volhard titration for halide ion indicated that the reaction was 100% complete.

In the distillation of the reaction product, the first fraction was 1-phenylbutene-1 distilling at $63-64^{\circ}/6$ mm. In most instances, two other fractions were taken; one boiled at $170-180^{\circ}/6$ mm., the other at $180-200^{\circ}/5$ mm. The lower-boiling of these two fractions was usually an oil; the higher-boiling one was a mixture of an oil and a solid. The solid material was separated by filtration. After it had been crystallized from ethyl alcohol, it melted at $81-82^{\circ}$. The melting point of bicinnamyl (1,6-diphenylhexadiene-1,5) is reported to be $81-82^{\circ}$ (13). This substance was converted to its tetrabromide (m.p. $191-193^{\circ}$) by the method of Rupe and Burgin (13). When this solid was treated with 1,3,5-trinitrobenzene, a crystalline addition product melting at $145-146^{\circ}$ was obtained. Kuhn (14) reports that bicinnamyl forms such a compound melting at 145.5° .

The oil was redistilled and found to boil at $180-185^{\circ}/8$ mm.; its index of refraction was n_D^{20} 1.5890. The oil was therefore 1,4-diphenylhexadiene-1,5 (n_D^{20} 1.5885) (15). The yields of the products mentioned which were obtained when various metallic halides were used as catalysts are shown in Table III.

Reaction of phenylethynyl bromide with methylmagnesium bromide. Phenylethynyl bro-

amide (16) (18 g., 0.097 mole) dissolved in 20 ml. of ether was added to methylmagnesium bromide (0.16 mole in 75 ml. of ether). After the mixture had been stirred for one hour, it was treated with dilute acetic acid. Aqueous washings of the reaction mixture were found by Volhard titration to contain 0.16 equivalents of halide ion. Distillation of the reaction mixture yielded phenylacetylene (8.8 g., 89% yield; b.p. 43–44°/18 mm.).

In a second experiment with the same quantities of reagents, dry carbon dioxide was passed into the reaction mixture after it had been refluxed for one hour. Distillation of the reaction mixture yielded phenylacetylene (1.9 g., 21% yield; b.p. 140°) and phenylpropynoic acid (7.2 g., 55% yield; m.p. 136–137°).

The same reaction was then carried out in the same manner except that 5 mole per cent of cobaltous chloride was added to the methylmagnesium bromide solution before the phenylethynyl bromide was dropped in. The reaction mixture was refluxed for one hour and then decomposed with dilute acetic acid. The aqueous washings were found to contain 0.281 equivalents of halide ion, indicating a 100% reaction.

Phenylmethylacetylene (7.2 g., 62% yield; b.p. 75–78°; n_D^{20} 1.5600) was obtained by distilling the reaction mixture. Some tar was also formed.

SUMMARY

1. In the absence of a catalyst, neither methyl- nor butyl-magnesium bromide reacts with 1-phenyl-3-chloropropane. In the presence of cobaltous chloride, these reagents react with 1-phenyl-3-chloropropane to give *n*-propylbenzene, β -methylstyrene, *n*-heptylbenzene, 1,6-diphenylhexane, some unsaturated polymers, and a gaseous product. When methylmagnesium bromide is used, the gas is a mixture of methane (90%), ethane (5%), and ethylene (5%). When *n*-butylmagnesium bromide is used, the gas is an equimolecular mixture of butane and butene-2 (mostly the *trans* form).

2. Cuprous chloride does not affect the normal reaction between cinnamyl chloride and methylmagnesium bromide by which β -ethylstyrene is formed. Ferric, manganous, chromic, nickel, and cobaltous chlorides give progressively larger amounts of 1,6- and 1,4-diphenylhexadiene-1,5.

3. A free radical mechanism is suggested for the reactions described in 1 and 2.

4. Phenylethynyl bromide, when treated with methylmagnesium bromide, exchanges its bromine atom for the -MgBr group. In the presence of cobaltous chloride, phenylmethylacetylene is formed.

CHICAGO, ILL.

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