oxygen had been passed into the mixture, a further 0.03 mole of aliphatic Grignard was added, and the oxidation carried to completion. The reaction mixture was decomposed as usual. No attempt was made to recover the isopropyl alcohol. The α-naphthol was obtained as in the previous experiments. The yield was 15.2 g. or 70% of the amount calculated. Small amounts of naphthalene and carbinol were also present; these products were not worked up quantitatively.

Summary

1. The catalytic effect of cobaltous halide upon the oxidation of aliphatic and aromatic Grignard reagents has been studied. With aliphatic Grignard reagents, the effect is small; but with aromatic Grignard reagents, high yields of biaryls are obtained instead of the normal oxidation products.

2. Aromatic Grignard reagents have been oxidized in the presence of aliphatic Grignard reagents to give high yields of the corresponding phenols.

3. Mechanisms for the normal and catalyzed oxidations and for the oxidation of mixtures are suggested.

Factors Influencing the Course and Mechanisms of Grignard Reactions. XI. The Effect of Metallic Halides on the Reaction of Grignard Reagents with Vinyl Halides and Substituted Vinyl Halides

BY M. S. KHARASCH AND CHARLES F. FUCHS[1]

The results obtained by the action of Grignard reagents on organic halides, aromatic ketones, unsaturated ketones, etc., in the presence of small quantities of the halides of cobalt, nickel, chromium and iron, have been described.[2] The present paper describes a new type of catalytic effect exercised by cobalt and chromium halides in the condensation of Grignard reagents with vinyl and substituted vinyl halides.

No reference to condensations of vinyl halides with Grignard reagents is recorded in the literature, and numerous attempts in this Laboratory to effect such condensations without catalysts have been of little avail. It has been found, however, that, in the presence of small quantities (5 mole per cent.) of the metallic halides mentioned above (cuprous salts have only a slight effect), reactions of the following type readily take place.

$$C_6H_5MgBr + HC=CH \cdot Cl \xrightarrow{CoCl_2} C_6H_5 \cdot CH=CH_2 + MgBrCl$$
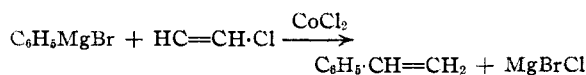
In the particular reaction cited, the yield of styrene is 50–75%. At the same time biphenyl (6–18%) and some polymeric hydrocarbons (7–25%) are formed. In similar reactions, corresponding biaryls are produced.

According to experience so far obtained, the given reaction is applicable to the condensation of vinyl halides (or substituted vinyl halides) with most aromatic or aryl-aliphatic Grignard reagents (phenylmagnesium bromide, naphthylmagnesium bromide, benzylmagnesium chloride). Small to negligible yields are obtained from cyclohexylmagnesium chloride and aliphatic Grignard reagents (Table I). Comparison of the reactions of vinyl bromide, of vinyl chloride, of 1-bromopropene-1, 2-bromopropene-1, of trimethylbromoethylene, and triphenylbromoethylene leads to the conclusion that condensation occurs readily when the unsaturated carbon atom carrying the halogen atom also carries a hydrogen atom, but not when this carbon atom carries a hydrocarbon radical. With the halides of the latter type, because of the catalytic effect of the metallic halides, the rate of the competitive chain-reaction which results in the formation of biaryls[3] is greater than the rate of the so-called normal condensation, and accordingly large quantities of biaryls, but no terphenyl or other phenylated benzene derivatives, are formed. This last finding is in complete agreement with previous observations that biaryls (but no higher phenylated benzene hydrocarbons) are formed from aromatic Grignard reagents and alkyl halides in the presence of the metallic halides mentioned.[3]

(1) The authors are indebted to Dr. S. Archer for some preliminary studies here recorded.

(2) For earlier references, see Kharasch, Lewis and Reynolds, THIS JOURNAL, 65, 493 (1943)

(3) Kharasch and Fields, ibid., 63, 2316 (1941)

TABLE I

REACTION OF GRIGNARD REAGENTS WITH VINYL HALIDES AND THEIR SUBSTITUTION PRODUCTS

	Grignard reagent	Vinyl halides	Metallic halide (5 mole %)	Ionic halogen from vinyl halide	% Yield of condensation product[a]	% Yield of polymer	% Yield of biaryl[a]
1.	Phenylmagnesium bromide (1.68 N)	CH_2=CHBr	$CoCl_2$	81	56	11	17
2.	Phenylmagnesium bromide	CH_2=CHBr	$CrCl_3$	66	38	25	18
3.	Phenylmagnesium bromide	CH_2=CHBr	Cu_2Cl_2		11		
4.	Phenylmagnesium bromide	CH_2=CHBr	None		5	Polyvinyl polymer	None
5.	Phenylmagnesium bromide	CH_2=CHCl	$CoCl_2$	64	56	7	6
6.	Cyclohexylmagnesium bromide (2.38 N)	CH_2=CHBr	$CoCl_2$	96	7		Cyclohexane Cyclohexene dicyclohexyl
7.	Phenylmagnesium bromide (2.31 N)	CH_3—CH=CHBr	$CoCl_2$	88	51	14	33
8.	Phenylmagnesium bromide	CH_3CBr=CH_2	$CoCl_2$	71	23	33	57
9.	Phenylmagnesium bromide	$(CH_3)_2C$=$CBrCH_3$[c]	$CoCl_2$	46	7	22	75
10.	Benzylmagnesium bromide (1.05 N)	CH=CHBr	$CoCl_2$	100	75	Dibenzyl	
11.	Benzylmagnesium bromide	CH=CHBr	None		No reaction		
12.	Phenylmagnesium bromide	$(C_6H_5)_2C$=$CBr·C_6H_5$[c]	$CoCl_2$[d]	99	Triphenylethylene 82	18	86
13.	Butylmagnesium bromide (2.0 N)	$(C_6H_5)_2C$=$CBrC_6H_5$[c]	$CoCl_2$	99	Triphenylethylene (42)	56	
14.	Butylmagnesium bromide	$(C_6H_5)_2C$=$CBrC_6H_5$[c]	None		No reaction		
15.	Naphthylmagnesium bromide (0.93 N)	CH=CHBr	$CoCl_2$	75	61		30

[a] Calculated as per cent. of Grignard reagent. [b] The reaction mixture was kept in a sealed tube for 56 days. [c] A 20% excess of Grignard reagent was used. Yields calculated on the basis of vinyl halide used. [d] Two mole % of $CoCl_2$ was used.
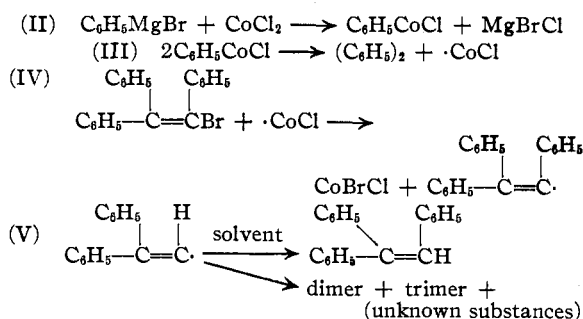
The reaction of n-butyl- and phenylmagnesium bromides with triphenylbromoethylene illustrates (within the limits of the equilibrium given in Equation I) a new type of reaction of substituted bromoethylenes; it was, therefore, studied in some detail. In the absence of metallic halides, triphenylbromoethylene does not react with phenyl- or butylmagnesium bromides even after three hours of heating at the temperature of boiling ether. In the presence of small quantities of cobaltous chloride (0.5–1 mole per cent.), the following equilibrium is reached at 0° some ten to fifteen minutes after the reagents are mixed.

$$C_6H_5—C(C_6H_5)=C(C_6H_5)—Br + RMgX \rightleftarrows$$
$$C_6H_5—C(C_6H_5)=C(C_6H_5)—MgX + RBr$$
$$(I)$$
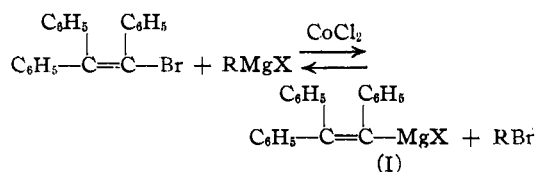
This equilibrium was demonstrated by treating the reaction mixture with carbon dioxide and also by isolating the resultant organic halide.[4] The position of this equilibrium probably accounts for the differences in the yields of triphenylethylene and its polymers observed when butyl- or phenylmagnesium bromides are treated with triphenylbromoethylene in the presence of 2–5 mole per cent. of cobaltous chloride. There are at least two reaction mechanisms whereby triphenylethylene and its polymers may be formed.

(4) Various additional examples of this type of equilibrium have subsequently been studied in this Laboratory; in a later paper they will be reported in detail

In the first case, the following chain reaction occurs.

(II) $C_6H_5MgBr + CoCl_2 \longrightarrow C_6H_5CoCl + MgBrCl$
(III) $2C_6H_5CoCl \longrightarrow (C_6H_5)_2 + ·CoCl$
(IV) $C_6H_5—C(C_6H_5)=C(C_6H_5)Br + ·CoCl \longrightarrow$
$CoBrCl + C_6H_5—C(C_6H_5)=C(C_6H_5)·$
(V) $C_6H_5—C(C_6H_5)=C(C_6H_5)(H)· \xrightarrow{\text{solvent}} C_6H_5—C(C_6H_5)=CH$
$\longrightarrow$ dimer + trimer + (unknown substances)

At the same time, triphenylvinylmagnesium bromide (I) undoubtedly reacts with cobaltous chloride as follows

(VI) $C_6H_5—C(C_6H_5)=C(C_6H_5)—MgBr + CoCl_2 \longrightarrow$
$C_6H_5—C(C_6H_5)=C(C_6H_5)—CoCl + MgBrCl$
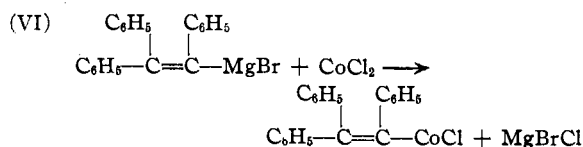
The organo-cobaltous compound may decompose into the triphenylvinyl free radical or into di- and trimeric triphenylethylenes and cobalt subhalide. Since the exchange (Equation I) proceeds further with the butyl Grignard reagent than with the corresponding phenyl compound, Reaction V probably results in formation of triphenylethylene, whereas Reaction VI is responsible for the polymers of this substance. This interpretation is in accord with the formation of 86% of triphenylethylene, 18% of polymer and 86% of biphenyl when phenylmagnesium bromide is treated with triphenylbromoethylene in the

presence of cobaltous chloride, as compared with 45% of triphenylethylene and 56% of the polymer when butylmagnesium bromide is used.

The term "polymer of triphenylethylene" is here applied to the yellow amorphous material formed in the above mentioned reaction. This material contains some diphenylbutadiene, and also a trimer, as indicated by analyses and molecular weight determinations. The substance may be the same as the "yellow, ether-soluble, glassy substance" reported to be obtained by treatment of triphenylvinylmagnesium bromide with triphenylchloromethane.[5]

Experimental Part

Preparation of the Metallic Salts.—The anhydrous metal chlorides, used as catalysts, were prepared from their hydrates by dehydration in a stream of dry hydrogen chloride gas. They were finally dried *in vacuo* at 200°.

Reaction of Grignard Compounds with Vinyl Halides in the Presence of Metallic Salts.—To a measured amount of ethereal Grignard reagent under dry nitrogen, a weighed amount (*e. g.*, 5 mole per cent. of the Grignard reagent used) of metallic halide was added. The mixture was stirred until the development of the black or dark color which indicates reaction between the Grignard reagent and the metallic halide. To the reaction mixture, which was constantly stirred and cooled, an excess of dry gaseous vinyl halide was then added. The vinyl halide was dispensed from a calibrated test tube in which it had been liquefied. Before entering the reaction flask, it passed through a calcium chloride drying tube. The rate of addition was adjusted to keep the reaction from becoming too vigorous. Approximately twice the theoretical amount of vinyl halide was used. A reaction between the components was noticeable when only a fraction of the vinyl halide had been added. After the addition of all the vinyl halide, the mixture was allowed to stand at room temperature for twelve hours. It was then heated for thirty minutes, again cooled, and finally poured into a mixture of 100 g. of ice and 200 ml. of distilled water. Glacial acetic acid (10 ml.) and ethyl ether (about 100 ml.) were then added. The ether and water layers were separated, and the water layer extracted twice with ether. The combined ethereal extracts were then washed with a 5% sodium bicarbonate solution to remove all acetic acid. The bicarbonate solution was added to the water layer; the aqueous solutions were combined, filtered and made up to 1000 ml. From this solution, aliquots were withdrawn for halogen ion determination. The total halogen ion found, minus the halogen ion corresponding to the amount of Grignard reagent and the metallic halide used, indicated how much vinyl halide had reacted. The residue left, after distilling the ether from the ether extract, was steam-distilled. The oily fraction of the distillate was separated from the crystalline fraction (biphenyl). All distilled fractions, as well as the non-distillable residue, were quantitatively collected, dried and weighed. The liquid frac-

(5) Koelsch, This Journal, **54**, 2045 (1932).

tion of the steam distillate was extracted twice with ether, the ether solution dried with sodium sulfate, and the reaction product (*e. g.*, styrene) isolated by fractional distillation. The vinyl derivative was identified by its physical constants and/or by converting it into some well defined derivative, such as the dibromide. All crystalline substances were identified by their melting points and the melting points of mixtures made with pure materials.

When higher boiling substituted vinyl halides (2-bromo-propene-1,1-bromopropene-1 or trimethylbromoethylene) were used, the liquid halide was diluted with an equal volume of dry ether and the solution run into the reaction flask through the dropping funnel. Otherwise, the method of experimentation was identical with the one already described.

Preparation of 1-Bromopropene-1 and 2-Bromopropene-1.—A mixture of these bromopropenes was prepared from propylene dibromide by the action of one mole of sodium ethoxide on one mole of propylene dibromide. The compounds were then separated by fractional distillation through a Podbielniak column of 100 plates. The 2-bromopropene-1 fraction (boiling from 47–49° cor.) and the 1-bromopropene-1 fraction (a mixture of the *cis* and *trans* isomers with a boiling range from 59° to 63° cor.) were used.

Reaction of Triphenylbromoethylene and Phenylmagnesium Bromide.—Powdered triphenylbromoethylene (16.9 g., 0.05 mole) was suspended in 180 cc. of dry ether; this suspension was added through a dropping funnel to the reaction mixture. The remainder of the experiment was conducted essentially in the manner already described. The following vacuum distillation fractions were obtained: (1) 5.5 g. biphenyl (b. p. 105–110 at 1–2 mm.). The compound was identified by melting point and the fact that it did not depress the melting point of pure biphenyl, (2) 10.6 g. of a light yellow oil (b. p. 170–175° at 1–2 mm.). This oil crystallized when treated with about 10 ml. of ethyl alcohol. It was identified as triphenylethylene by the usual method. (3) In the flask, there remained 2.4 g. of an orange-yellow brittle substance easily soluble in chloroform, acetone, or ether, but only slightly soluble in alcohol. This amorphous material is probably a polymer of triphenylethylene.

Reaction between Triphenylbromoethylene and *n*-Butylmagnesium Bromide.—To an ice-cooled ether solution containing 0.08 mole of *n*-butylmagnesium bromide, 5 mole per cent. of cobaltous chloride was added. To this freshly prepared reaction mixture was added 0.039 mole of triphenylbromoethylene dissolved in a mixture of 30 ml. of dry ether and 70 ml. of pure, dry benzene. The entire mixture was stirred for one hour at 0°, for two hours at room temperature, and finally allowed to stand for twelve hours at room temperature. The product was treated as previously described. Triphenylethylene (4.5 g.) was isolated. The dry residue from the vacuum distillation weighed 5.7 g. By solution of this residue in a small amount of ether and evaporation of the ether under reduced pressure, there was obtained a porous, brittle, amorphous mass which was easily pulverized. Of this substance, one gram was dissolved in 20 ml. of ether. The solution was filtered, and the filtrate was mixed with 100 ml. of ethyl alcohol. From the clear orange-yellow solu-

tion, four fractions were obtained by slow concentration under slightly reduced pressure. Molecular weights (Rast) of the different fractions were 748, 750, 573 and 612.

Anal. (Mol. wt. 748) Calcd. for $(C_{20}H_{16})_n$: C, 93.71; H, 6.29. Found: C, 93.59; H, 6.38.

Summary

1. In the presence of halides of cobalt or chromium, aromatic Grignard reagents react with vinyl halides and substituted vinyl halides to yield normal condensation products.

2. The effect which substituents in the vinyl halide molecule exercise on the yield of the condensation product has been determined.

3. Phenylmagnesium bromide and triphenyl-bromoethylene react to give an equilibrium mixture of two Grignard reagents.
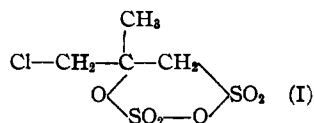

The Sulfonation of Methallyl Chloride. Mobility of the Olefinic Linkage in Unsaturated Sulfonic Acids

BY C. M. SUTER AND FREDERICK G. BORDWELL

It has long been known[1] that the action of sulfur trioxide upon ethylene gives a cyclic anhydride, carbyl sulfate. More recently it has been shown[2] that dioxane sulfotrioxide reacts readily with propylene and other straight-chain *alpha* olefins resulting in similar products.[3] On the other hand, isobutylene[4] and styrene[5] give for the most part olefinic mono and disulfonic acids through substitution reactions. Because of these varied results it seemed of interest to investigate the sulfonation of methallyl chloride in order to determine the influence of the chlorine on the nature of the reaction products. The major part of the investigation has dealt with the dioxane sulfotrioxide sulfonation, but the behavior of sodium chlorosulfonate[6] and a solution of sulfur trioxide in ethylene chloride received some study.

The sulfonation of methallyl chloride by dioxane sulfotrioxide in ethylene chloride solution proceeds smoothly at 0°. In contrast to isobutylene, no polymerization was observed and the products were substantially the same whether the methallyl chloride was added to the sulfonating agent or the reverse. Since the addition of water and alkali (even at a low temperature) to the reaction mixture resulted in the formation of chloride ion, a better method of isolating the components of the mixture was sought. The best results were obtained by the addition of aniline which precipitated a mixture of anilinium chloroisobutylenesulfonates, anilinium sulfate, and probably anilinium phenylsulfamate. The yield of this mixture is practically quantitative based on the sulfur trioxide. The probable presence of anilinium sulfate and anilinium phenylsulfamate in this product was indicated by the fact that about 18% of the total sulfur present was precipitated, after acid digestion, as barium sulfate. This sulfate seemed most logically to be derived from products of the anilinolysis of an intermediate of the carbyl sulfate type, I. Fortunately it was possible to isolate this intermediate, β-chloromethyl-β-methylethionic anhydride (I), in crystalline form by using sulfur tri-

oxide dissolved in ethylene chloride as a sulfonating agent. When methallyl chloride was added to this reagent in the ratio of one mole of olefin to two of sulfur trioxide at 0°, the reaction was almost exclusively addition of the sulfur trioxide to the double bond, as indicated by the amount of sulfate ion formed by the hydrolysis of the product. Treatment of a solution of I in chloroform with aniline gave about a 25% yield of anilinium sulfate, and small amounts of a compound which has been tentatively identified as anilinium phenylsulfamate, thus confirming

(1) Regnault, *Ann. chim. phys.*, **45**, 98 (1838); *Ann.*, **27**, 11 (1838); **26**, 32 (1838); Michael and Weiner, THIS JOURNAL, **58**, 294 (1936).

(2) Suter, Evans and Kiefer, *ibid*, **60**, 538 (1938).

(3) It has been observed by Mr. Kaplan in this Laboratory that some unsaturated sulfonic acid is formed when propylene is sulfonated.

(4) (a) Suter and Malkemus, THIS JOURNAL, **63**, 978 (1941); (b) Suter, Malkemus and Archer, *ibid.*, **63**, 1594 (1941).

(5) J. M. Holbert, Ph.D. Thesis, Northwestern University, 1941.

(6) We are indebted to Dr. S. Archer of this Laboratory for the report on experiments with this reagent.