

PREPARATION AND REACTIONS OF SOLVENT-FREE ARYLCALCIUM HALIDES, ArCaX ($\text{X} = \text{F}, \text{Cl}, \text{Br}$)

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Summary

Reactions of aryl halide vapor and calcium metal vapor were found to give the corresponding arylcalcium halides, ArCaX ($\text{X} = \text{F}, \text{Cl}$, and Br). Phenylcalcium halides, PhCaX ($\text{X} = \text{F}$ and Cl), reacted with trimethylchlorosilane to give phenyltrimethylsilane. The reactions of phenylcalcium halides with acetone and benzaldehyde readily gave good yields of 1-methyl-1-phenylethanol and diphenylmethanol, respectively. Phenylcalcium halides reacted slowly with acetonitrile to afford acetophenone in poor yields. With ethyl acetate, phenylcalcium halides gave a mixture of 1,1-diphenylethanol and acetophenone.

Introduction

Considering the position of calcium in the Periodic Table, it is interesting to study the chemical reactivity and physical properties of arylcalcium halides in comparison with those of the corresponding Grignard reagents and reagents of the other Group 2A metals. However, arylcalcium halides have not been studied sufficiently because of the lack of a useful method to prepare them [1–18].

The formation of arylcalcium halides from the corresponding aryl halides and calcium metal in solutions has been reported. An important factor in the preparation of arylcalcium halides is the impurities in the calcium metal. Various efforts to activate calcium metal have been described [1,4,8]. Recently, Kawabata and co-workers have prepared arylcalcium iodides and bromides in high yields by using higher purity calcium metal than was previously available [2,3].

On the other hand, the co-condensation procedure has been recently with much success to prepare main group and transition metal compounds which are unobtainable by other methods, or which are prepared only in low yields in solution [19–22].

In this paper, we report the preparation of arylcalcium halides, ArCaX ($\text{X} = \text{F}, \text{Cl}$, and Br), from the corresponding aryl halide vapor and calcium metal vapor. Reactions of solvent-free phenylcalcium halides, PhCaX ($\text{X} = \text{F}$ and Cl), with

trimethylchlorosilane, carbonyl compounds and other organic substrates are also described.

Results and discussion

The apparatus described in the Experimental section was used. Calcium metal (granule, 99% pure) was vaporized at a temperature of ca. 900°C using a filament of tungsten in vacuo (ca. 5×10^{-3} Torr) at a rate of ca. 20 mg min⁻¹. During the vaporization of calcium metal, excess aryl halides were introduced, as vapor, into the reaction vessel. Arylcalcium halides prepared from calcium metal vapor and excess of aryl halide vapor were condensed on the wall of the reaction vessel which was cooled to 77°K with liquid nitrogen. The color of arylcalcium halides thus prepared is reddish brown. Solvent-free arylcalcium halides are very reactive solids and ignite in air. The normal organocalcium halides are also reactive and decompose rapidly in a moist atmosphere [1,22].

Hydrolysis of the products from the reactions of calcium metal vapor with aryl halide vapor gave the reduction product, ArH, as the main product. A small quantity of the Wurtz-type coupling product, Ar-Ar, and unknown products were also detected. The results are summarized in Table 1. It is known that the reduction product is formed quantitatively by hydrolysis of arylcalcium halides [10,22]. Therefore, the yield of reduction product can be regarded as that of arylcalcium halides.

Bryce-Smith and Skinner obtained a 45% yield of phenylcalcium bromide and a < 1% yield of phenylcalcium chloride from the corresponding phenyl halides and amalgamated calcium metal (the calcium metal contained < 0.5% magnesium and < 0.2% sodium) in tetrahydrofuran (THF) [1]. Kawabata, Matsuura, and Yamashita reported 45–55% yields of phenylcalcium bromide and 3–14% yields of phenylcalcium chloride from the corresponding phenyl halides and higher purity calcium

TABLE 1

PRODUCTS FROM THE REACTIONS OF CALCIUM METAL VAPOR WITH ARYL HALIDE VAPORS^a

Ar-X	Yields of products (%)	
	Ar-H	Ar-Ar
C ₆ H ₅ F	38.4	2.9
<i>o</i> -CH ₃ C ₆ H ₄ F	47.5	3.4
<i>m</i> -CH ₃ C ₆ H ₄ F	46.6	1.9
<i>p</i> -CH ₃ C ₆ H ₄ F	49.6	1.8
C ₆ H ₅ Cl	42.3	trace
<i>o</i> -CF ₃ C ₆ H ₄ Cl	5.9	trace
<i>m</i> -CF ₃ C ₆ H ₄ Cl	8.6	trace
<i>p</i> -CF ₃ C ₆ H ₄ Cl	6.6	trace
C ₆ H ₅ Br	48.8	10.1

^a An average of at least 2 or 3 determinations. Based on the calcium metal consumed.

metal than was previously available in THF or toluene [2,3]. The yields of phenylcalcium bromide and chloride obtained in this work are better than those in the literature. The formation of arylcalcium fluorides is a first example.

The yields of arylcalcium halides as shown in Table 1 were almost constant except for trifluorotolylcalcium chlorides, regardless of the nature of the halogen and the position of the group. The low yields of trifluorotolylcalcium chlorides may be due to the difficulty of introducing the corresponding aryl chlorides as vapor into the reaction vessel.

The Wurtz-type coupling reaction was relatively unimportant in the preparation of arylcalcium fluorides and chlorides, while the yield of the Wurtz-type coupling product was relatively high in the preparation of phenylcalcium bromide. The yields of arylcalcium halides are based on the amount of consumed calcium metal, assuming that all calcium metal except for that remaining in the crucible reacted with the aryl halides. Taking into consideration that unreacted calcium metal may also be consensed on the wall of the reaction vessel, the yield of arylcalcium halides as shown in Table 1 may be underestimated.

Reactions of solvent-free arylcalcium halides thus prepared with trimethylchlorosilane, acetone, benzaldehyde, acetonitrile, and ethylacetate were investigated. Bryce-Smith and Skinner [1] and Kawabata and coworkers [23] have pointed out that organocalcium halides resemble organolithium compounds more than Grignard reagents chemically. It is interesting to examine the chemical behavior of solvent-free phenylcalcium fluoride and chloride, which has not been studied up to now, in comparison with that of organocalcium halides prepared in solutions.

Phenylcalcium fluoride and chloride reacted with trimethylchlorosilane to give phenyltrimethylsilane in ca. 40% and ca. 50% yields, respectively. Phenylcalcium

TABLE 2

REACTIONS OF PHENYLCALCIUM CHLORIDE AND FLUORIDE WITH VARIOUS ORGANIC SUBSTRATES ^a

C_6H_5Ca-X	Substrates	Products yield (%)
F	$(CH_3)_3SiCl$	$C_6H_5Si(CH_3)_3$, 38.9
Cl	$(CH_3)_3SiCl$	$C_6H_5Si(CH_3)_3$, 47.2
F	$(CH_3)_2CO$	$C_6H_5(CH_3)_2COH$, 53.6
Cl	$(CH_3)_2CO$	$C_6H_5(CH_3)_2COH$, 70.1
F	C_6H_5CHO	$(C_6H_5)_2CHOH$, 42.6
Cl	C_6H_5CHO	$(C_6H_5)_2CHOH$, 64.9
F	CH_3CN	$C_6H_5COCH_3$, 9.4
Cl	CH_3CN	$C_6H_5COCH_3$, 15.4
F	$CH_3CO_2C_2H_5$	$C_6H_5COCH_3$, 30.5
		$(C_6H_5)_2(CH_3)COH$, 7.2
Cl	$CH_3CO_2C_2H_5$	$C_6H_5COCH_3$, 42.6
		$(C_6H_5)_2(CH_3)COH$, 6.4

^a An average of at least 2 determinations. Based on the concentrations of phenylcalcium halides. Reactions performed at room temperature for 1 h.

fluoride and chloride reacted with acetone to give 1-methyl-1-phenylethanol in ca. 55% and 70% yields, respectively. Mesityl oxide prepared by aldol condensation of acetone was also obtained as a minor product. The reactions of phenylcalcium fluoride and chloride with benzaldehyde gave diphenylmethanol in ca. 45% and 65% yields, respectively. The reactions of phenylcalcium fluoride and chloride with acetonitrile gave acetophenone in poor yields. With ethyl acetate, phenylcalcium fluoride and chloride afforded acetophenone as a major product and 1,1-diphenylethanol as a minor product. The results are summarized in Table 2.

In general, the yield of products in this work is lower than that of products from the corresponding Grignard reagents and organolithium reagents [24]. The low yield of products may be due to the reaction conditions we employed, where an excess of organic substrate was introduced as vapor into the reaction vessel containing phenylcalcium halide. The mixture was allowed to stand to room temperature for 1 h.

Thus, judging from the results as shown in Table 2, we cannot discuss the similarities between solvent-free arylcalcium halides and organolithium reagents or Grignard reagents. Furthermore, we cannot compare solvent-free arylcalcium halides with arylcalcium halides in solutions. However, solvent-free arylcalcium halides should also be useful in organic syntheses with arylcalcium halides in solutions.

Experimental section

Materials

Calcium metal (granules, 99% pure, Wako Chemicals), aryl halides, and other chemicals were commercially available. Phenyltrimethylsilane, b.p. 72°C/27 mmHg [25], diphenylmethanol, b.p. 180°C/20 mmHg [26], and 1,1-diphenylethanol, b.p. 190°C/12 mmHg [27] were prepared according to literature methods.

Preparations of arylcalcium halides

The apparatus used was similar to that described by Timms, Green, and other workers [20]. A typical reaction is described below. Calcium metal (0.5 g, 12.5 mmol) was vaporized in ten minutes from an aluminum oxide crucible in a tungsten wire heater at 4.0 volts, 15 amps, which was connected to copper electrodes. This apparatus was put in a vacuum vessel (ca. 5×10^{-3} Torr) made of quartz glass. During the vaporization of calcium metal, fluorobenzene (ca. 5.0 ml, 52.0 mmol) was introduced, as a vapor, through the organic substrate inlet tube into the reaction vessel immersed in the liquid nitrogen. Upon completion of introduction, the vessel was allowed to warm under argon to room temperature.

Reactions of arylcalcium halides with organic substrates

As a typical example, the reaction of phenylcalcium fluoride with acetone is described. Dry acetone (10 ml) was introduced, as a vapor, through the organic substrate inlet tube into the reaction vessel containing phenylcalcium fluoride. The reaction vessel was isolated from the vacuum line and allowed to warm to room temperature and was left to stand for 1 h. After hydrolysis of the reaction mixture with dilute HCl, the organic layer was extracted with ether.

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