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A new method for preparation of organocalcium halides by cocondensation of calcium vapor with solvents

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Abstract

Calcium vapor (atom) when cocondensed with various solvents at 77 K was found to be very reactive toward alkyl and aryl halides. A series of organocalcium halides was prepared in good yields by addition of alkyl or aryl halides to the resultant calcium atom-solvent slurries at ambient temperatures.

Introduction

In contrast to organomagnesium halides (Grignard reagents) and organolithium reagents, the chemistry of organocalcium halides has been little investigated owing to a lack of useful preparative methods [1]. A major problem in the preparation of organocalcium halides is inhibition of the reaction by the impurities on the calcium surface. Much effort has been directed at activating calcium metal, these include: treatment of calcium metal with iodine [2] and Grignard reagent [3], amalgamation of calcium metal [4,5], the use of calcium-magnesium alloy [4] and the use of very pure calcium metal [6–8]. Recently, we succeeded in the preparation of organocalcium halides in high yields using calcium atoms (or clusters) [1] and ultrafine calcium particles [9].

However, numerous publications reporting the unusual activity and chemistry of reactive metal surfaces (slurries in solution) have appeared [10–12].

Here we report on a new method for preparing organocalcium halides using calcium atom-solvent cocondensates (slurries).

Results and discussion

The reactive calcium metal surface was conveniently produced by the cocondensation of calcium vapor with solvents and by use of essentially the same apparatus and conditions described previously [1]. Calcium metal (granules, 99% pure) was

Table 1

Reactions of calcium atom-solvent slurries with octyl bromide [a]

Halide (RX)	Solvent	Products (Yield, %) [b]	
		R–H	R–R
$C_8H_{17}Br$	THF	80.9	18.3
$C_8H_{17}Br$	hexane	48.2	16.0
$C_8H_{17}Br$	DME	44.6	17.0
$C_8H_{17}Br$	benzene	15.2	5.8

[a] Reactions were performed at 50 °C for 2 h under argon. [b] Yields of products are based on amount of calcium metal used.

evaporated at a temperature of ca. 900 °C using a tungsten filament in vacuo (ca. 5×10^{-3} Torr) at a rate of ca. 20 mg min^{-1}. At the same time a large excess of solvent, which had been admitted through an inlet tubes, condensed on to the walls of a quartz flask containing the tungsten crucible. Calcium atoms that cocondensed with the solvent were allowed to warm to room temperature. The ensuing calcium atom-solvent slurry was found to react with organic halides under argon *.

The formation of organocalcium halides was identified by hydrolysis or deuterolysis of the products, yielding RH or RD ** [13].

$$R\text{–}X + Ca \rightarrow RCaX \xrightarrow{H_2O\ (\text{or } D_2O)} R\text{–}H\ (\text{or } R\text{–}D) \qquad (1)$$

Effect of solvent

Reactions of calcium atom-solvent slurries with organic halides were examined using various solvents. The results of the reactions with octyl bromide are summarized in Table 1. Octyl bromide readily reacts with these calcium atom-solvent slurries at 50 °C. The yield of the octylcalcium halide varied from 15.2 to 80.9% depending on the solvent employed, whereas with commercially available calcium metal, there was no reaction with octyl bromide under the same reaction conditions. The yields of octylcalcium bromide decreased in the order: THF > hexane ≈ DME > benzene for the solvent employed. This is similar to that reported for nickel and other metal atoms [14]. The yield of octylcalcium bromide was extremely low when a calcium atom-benzene slurry was used. This may have resulted from the strong interaction of the calcium atoms with benzene. In fact, octylbenzene was formed in only 5–10% yields *** [15].

The reaction is accompanied by the production of some amount of the coupling product (hexadecane) (5.8–18.3%). The coupling product might arise from the free radical process since the amount of 2,3-dimethyl-2,3-diphenylbutane increases as the amount of coupling product decreases in the reaction of calcium atom-solvent slurries with organic halides, in the presence of cumene as a radical scavenger.

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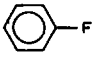
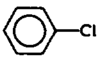
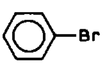
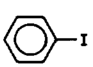
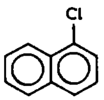
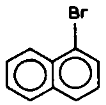
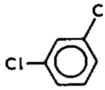
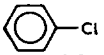
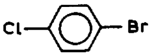
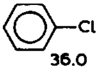
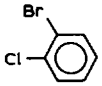
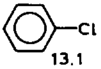
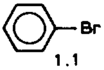
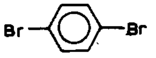
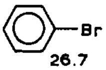
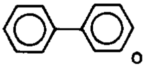
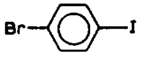
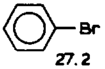
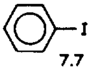
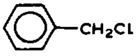
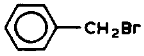
* The size of particles in the calcium atom-THF slurry was measured by a General Automatic Particle Analyzer, Horiba Co., Ltd.. More than 80% of the calcium particles thus prepared were smaller than 1 μm.

** About 70–80% of the yields of reduction products contained deuterium by deuteriolysis.

*** We did not observe (by GLC) any reaction between calcium metals and solvents such as THF, hexane or DME during the cocondensation process.

Table 2. Reactions of calcium atom-THF slurry with organic halides [a]

Halide (RX)	Products (Yield, %) [b]		
	R-H	R-R	R(-H)
$C_5H_{11}Cl$	48.2	13.1	
i-$C_5H_{11}Cl$	35.7	15.0	trace
$C_8H_{17}Cl$	58.2	4.8	
$C_8H_{17}Br$	80.9	18.3	
$C_8H_{17}I$	98.6	20.3	
c-$C_6H_{11}Cl$	33.9	1.2	
c-$C_6H_{11}Br$	28.4	14.7	16.1
	no reaction		
	32.4	2.9	
	68.7	4.4	
	98.0	5.6	
	26.3	0.2	
	42.2	0.3	
	 19.5	 trace	
	 36.0		
	 13.1	 1.1	
	 26.7	 1.5  0.6	
	 27.2	 7.7  trace	
	5.3	58.8	
	15.0	60.0	

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[a] Reactions were performed at 50 °C for 2 h under argon. [b] Yields of products are based on amount of calcium metal used.

Preparation of organocalcium halides using calcium atom-THF slurry

Table 2 summarizes the results of the reactions of this active calcium atom-THF slurry with various organic halides.

The reactions of a calcium atom-THF slurry with octyl iodide and bromide at 50 ° C for 2 h afforded the corresponding organocalcium halides in 81–99% yields. Initiation of the reaction with octyl iodide and bromide was not necessary when the calcium atom-THF slurry was employed. Thus, it reacts with octyl bromide even at − 5 ° C to give octylcalcium bromide in 66% yield in 2 h. Octyl and pentyl chlorides also afforded organocalcium chlorides, although yields were relatively low. Fluorides on the other hand were completely inert. Thus, the ease of reaction of organic halides with calcium atom-THF slurry falls in the order: iodides > bromides > chlorides ≫ fluorides. The reactivity observed for primary halides is consistent with that found by Bryce-Smith and Skinner [4] and Kawabata and co-workers [6]. The yield of isopentylcalcium chloride was lower than that of the corresponding n-pentylcalcium chloride. The reaction of calcium atom-THF slurry with secondary alkyl chlorides more closely resembles that of amalgamated calcium metal reported by Bryce-Smith and Skinner [4], than that of highly pure calcium metal reported by Kawabata and co-workers [6]. The calcium atom-THF slurry readily reacts with cyclohexyl halides, however, the yields of the cyclohexylcalcium halides were lower than those of the octylcalcium halides. Cyclohexene was also formed in the reaction with the bromide.

The reaction with iodobenzene afforded phenylcalcium iodide quantitatively. By contrast, bromo- and chlorobenzene exhibited less reactivity and gave lower yields. No reactions occurred with fluorobenzene. The Wurtz-type coupling reaction was relatively unimportant in the preparation of arylcalcium halides, which is in contrast to that of alkylcalcium halides.

The reactions with dihalobenzenes gave the monocalcium derivatives as main products. Thus, just the chlorine atom of a dichlorobenzene reacted, whereas the chlorine of bromochlorobenzenes was practically unreactive. Similarly, dibromobenzene and bromoiodobenzene gave almost completely the expected (bromophenyl) calcium bromide and iodide, respectively.

With benzyl halides, the corresponding organocalcium halides were obtained only in low yields because of Wurtz-type coupling side-reactions.

Organocalcium halides are expected to be useful reagents for alkylation and arylation, and the following points can be made about the usefulness of the calcium atom-THF slurry method:

(a) Reactions of calcium atom-THF slurries with various organic halides except for fluorides proceed smoothly under argon.

(b) Yields of organocalcium halides thus prepared are better than those obtained by other methods.

(c) Reaction conditions are mild, and manipulations are easy.

Experimental

GLC analyses were performed on a Shimazu GC-6A and 8-A gas chromatograph equipped with a 2m column packed with 20% SE-30 or 30% Apiezon L. Infrared spectra were recorded on a Hitachi 260-10 spectrometer. GC-MASS spectra were obtained with a JEOL JMS-DX 303 mass spectrometer. ^{1}H NMR spectra were recorded on a Varian FT 80A, using tetramethylsilane as internal standard.

Materials

Calcium metal (granules, 99% pure, Wako Chemicals) and the organic halides were commercial products. THF and other solvents were dried over benzophenone ketyl and distilled before use.

Preparation of calcium atom-solvent slurries

Calcium atom-solvent slurries were produced using essentially the same apparatus and conditions described previously [1]. A typical procedure is described below. Calcium metal (0.5 g, 12.5 mmol) was vaporized at a rate of ca. 20 mg min^{-1}, at a temperature of 900–1000 °C using a resistance-heated, alumina-coated tungsten spiral crucible (4.0–5.0 V, 15 A) connected to copper electrodes, in vacuo (ca. 5×10^{-3} Torr). During the vaporization of calcium metal, a large excess of THF (20 cm^3) was introduced as a vapor through a perforated inlet tube. The THF was cocondensed onto the walls of a quartz reaction flask containing the tungsten crucible (crucible was kept at 900–1000 °C). The reaction flask was immersed in liquid nitrogen during the entire operation. Then the reaction flask was allowed to warm to room temperature and left to stand for 1 h. The reaction flask was evacuated and then filled with argon.

Reactions of calcium atom-THF slurry with organic halides

The reaction with octyl bromide is described as a typical example. The calcium atom-THF slurry was shaken vigorously and a given volume of calcium atom-THF slurry was placed quickly in a two-necked 50 cm^3 flask equipped with a serum cap and reflux condenser in an argon-filled glove box. Ten times molar amounts of octyl bromide were then syringed in. The reaction mixture was stirred at 50 °C for 2 h under argon. After the reaction mixture had been hydrolysed with dilute HCl, the organic layer was extracted with ether. The products were identified by comparing their GC-MS and their retention times on GLC with those of authentic samples.

Reaction of calcium atom-THF slurry with octyl bromide in the presence of cumene

Reaction of the calcium atom-THF slurry (7.5 mmol) with octyl bromide (27.0 mmol) in the presence of cumene (20.0 mmol) was carried out at 50 °C for 2 h. After the reaction mixture had been hydrolysed with dilute HCl, octane (79.0%), hexadecane (12.0%), and 2,3-dimethyl-2,3-diphenylbutane (1.0%) were found to have formed.

Acknowledgement

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