Preparation of Organocalcium Halides Using Calcium Ultrafine Particle

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Synopsis. Organocalcium halides were prepared from organic halides and calcium ultrafine particle in good yields.

In contrast to the organomagnesium halides (Grignard reagents), the preparations and chemical reactivities of organocalcium halides have been little studied.[1] This slow progress could be due to the lack of a useful method to prepare organocalcium halides.

The formation of organocalcium halides from organic halides and calcium metal has been reported. An important problem in the preparation of organocalcium halides is the impurities in the calcium metal. Various efforts to activate calcium metal have been described.[2–4] Kawabata and co-workers have reported the preparation of organocalcium iodides and bromides by using higher-purity calcium metal than was previously available.[5–7] The reactivities of organocalcium halides, thus prepared, seem to resemble those of organolithium reagents than Grignard reagents.[7] Recently, we have reported the preparation of solvent-free organocalcium halides using calcium atoms.[1] Solvent-free organocalcium halides are highly reactive solids.

On the other hand, there are many articles in the literature concerning the unusual reactivity and chemistry of ultrafine particles (UFP).[8] These active UFP have been easily produced using a heated tungsten basket. Therefore, calcium UFP is expected to be useful for the preparation of various organocalcium halides which are unobtainable by other methods, or which can be prepared only in low yields.

In this paper, we report on a new method for the preparation of organocalcium halides from the corresponding organic halides and calcium UFP produced by a heated tungsten basket.

Results and Discussion

Calcium UFP was conveniently produced by a heated tungsten-wire basket (ca. 900 °C) in an evacuated vessel (ca. 10^{-2}—10^{-3} Torr, 1 Torr=133.322 Pa).[9] After the preparation of the calcium UFP, a desired amount of the calcium UFP was transfered to a reaction flask in an argon-filled glove box. To this reaction flask, organic halides and solvents were syringed in. All manipulations were carried out under an argon atmosphere.

The hydrolysis of the products from the reactions of calcium UFP with organic halides (RX) gave reduction products (RH) and coupling products (R-R) as the main products. These results are summarized in Table 1. It is known that the reduction product is formed quantitatively by the hydrolysis of organocalcium halides.[10,11] Therefore, the yield of the reduction product can be regarded as that of organocalcium halides.

The calcium UFP produced by a heated tungsten-wire basket is useful for the preparation of organocalcium halides in tetrahydrofuran (THF) shown in Table 1. The reaction proceeded smoothly, even at low temperatures, and the Wurtz-type coupling was relatively less important under these conditions. Yields of organocalcium halides were better than those described in the literature.[1]

The reactions of calcium UFP with octyl iodide and bromide, respectively, afforded the corresponding organocalcium halides in high yields (Runs 1 and 3). On the other hand, the reaction was restricted to octyl chloride (Run 5). The ease of reaction with calcium UFP follows the order octyl iodide>octyl bromide≫octyl chloride. The reactivity of octyl halides shown in Table 1 is consistent with that published by Bryce-Smith and Skinner,[2] and Kawabata and coworkers.[5] As shown in Table 1, the preparation of octylcalcium bromide using calcium UFP in the absence of THF was extremely difficult (Run 4). Thus, the reaction of calcium UFP with octyl bromide in toluene at 100 °C for 2 h resulted in a poorer yield. This result is clearly different from that of Kawabata and co-workers.[5–7] These authors described the reactions of alkyl halides with higher-purity calcium metal as proceeding smoothly in toluene. An initiation of the reaction was not necessarily when calcium UFP was used. Thus, calcium UFP reacted with octyl bromide in THF at −5 °C to give a 41.0% yield of octylcalcium bromide in 2 h (Run 2). This reaction started immediately at −5 °C, and was even produced at temperature as low as −78 °C in a 6.4% yield. The yields of the products from reactions of calcium UFP with octyl halides are almost constant within the temperature range examined (10—50 °C).

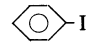
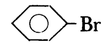
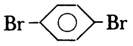
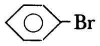
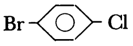
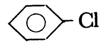
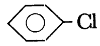
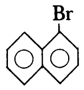
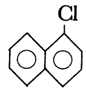
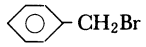
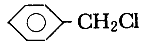
Calcium UFP easily reacted with cyclohexyl halides (Table 1), but the yields of cyclohexylcalcium halides were lower, as expected, than those of octylcalcium halides (Runs 6—8).

The reactions of calcium UFP with aryl iodides and bromides, respectively, afforded the corresponding arylcalcium halides in high yields (Runs 9, 10, and 14). A higher reaction temperature (50 °C) was necessary to obtain arylcalcium halides in high yields. Calcium UFP reacted selectively with the bromo substituent of *p*-dibromobenzene and *p*-bromochlorobenzene to give bromobenzene and chlorobenzene, respectively (Runs 11 and 12). No reactions of calcium UFP with chlorobenzene and 1-chloronaphthalene took place (Runs 13 and 15).

The reaction of calcium UFP with benzyl bromide gave the corresponding organocalcium halide in low yield on account of a Wurtz-type coupling as a side reaction (Run 16). The reaction was restricted to benzyl chloride (Run 17).

Although organocalcium halides are useful reagents for alkylation and arylation, the following points can be made about the usefulness of the calcium UFP method.

Table 1. Products from the Reactions of Calcium UFP with Organic Halides[a]

Run	R-X	Solvent	Conditions	Products, Yield/%[b]	
				R-H	R-R
1	$n\text{-}C_8H_{17}I$	THF	10°C, 2h	95.3	
2	$n\text{-}C_8H_{17}Br$	THF	−5°C, 2h	41.0	
3	$n\text{-}C_8H_{17}Br$	THF	10°C, 2h	70.2	
4	$n\text{-}C_8H_{17}Br$	Toluene	100°C, 2h	0.5	
5	$n\text{-}C_8H_{17}Cl$	THF	50°C, 2h	0.4	
6	$c\text{-}C_6H_{11}I$	THF	10°C, 2h	39.4	
7	$c\text{-}C_6H_{11}Br$	THF	10°C, 2h	44.9	
8	$c\text{-}C_6H_{11}Cl$	THF	50°C, 2h	5.1	
9		THF	50°C, 2h	65.6	6.7
10		THF	50°C, 2h	58.7	7.8
11		THF	10°C, 2h	 26.7	
12		THF	10°C, 2h	 20.0	
13		THF	50°C, 2h	no reaction	
14		THF	50°C, 2h	69.9	
15		THF	50°C, 2h	no reaction	
16		THF	50°C, 2h	3.0	42.0
17		THF	50°C, 2h		trace

a) Typical reaction conditions: Organic halides, 30 mmol, Ca UFP, 10.0 mmol; THF as solvent, 20 cm^3. b) Based on the calcium UFP.

(a) Reactions of calcium UFP with various organic iodides and bromides proceed smoothly under an argon atmosphere.

(b) Yields of organocalcium halides are better than those published by other workers.

(c) Low temperatures and short times are required in these reactions.

Experimental

GLC analyses were performed on a Shimadzu GC-6A or 8A gas chromatograph. NMR spectra were obtained with a Varian FT-80 A spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard.

Materials. Calcium metal (granules, 99% pure, Wako Chemicals), organic halides, and other chemicals were commercially available. THF was distilled from benzophenone ketyl immediately prior to use.

Preparation of Calcium UFP. In a typical calcium UFP preparation, calcium metal (300 mg, 7.5 mmol) was vaporized in 30 min, from an aluminum oxide crucible in a tungsten filament (ca. 900°C). This apparatus was contained in a vacuum vessel (ca. 10^{-2}—10^{-3} Torr). The calcium UFP was deposited (vessel immersed in liquid nitrogen). Upon completion of a deposition, the vessel was isolated from the vacuum pump and allowed to become room temperature. The calcium UFP was weighed in an argon-filled glove box.

Reactions of Calcium UFP with Organic Halides. As a typical example, the reaction of calcium UFP with octyl bromide is described. Calcium UFP (9.0 mmol) was transferred to two-necked 50 cm^3 flask equipped with a serum cap and reflux condenser. Then, THF (20 cm^3) and octyl bromide (27.0 mmol) were syringed in. The reaction mixture was stirred at 10°C for 2 h under argon. After hydrolysis of the reaction mixture with dilute HCl, the organic layer was extracted with ether.

References

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9) The diameter of calcium particle produced by a heated tungsten-wire basket was 70—100 nm.

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