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PREPARATION OF ORGANOCALCIUM HALIDES

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Abstract—The reaction of organic halides with calcium metal in THF was found to give the corresponding organocalcium halides in much better yields than those available in the literature. The key ingredient appeared to be the availability of higher purity Ca metal than was previously obtainable. The lower content of Na in Ca metal seemed to be an important factor in this improvement. The reaction is not restricted to aryl and primary alkyl iodides contrary to the description in the literature. Bromides and chlorides also afforded organocalcium halides, although yields were generally lower. The reaction proceeded smoothly with secondary alkyl halides, and the yields of isopropylcalcium halides were better than those of the corresponding n-propylcalcium halides. Metallic Ca reacted easily with tertiary alkyl halides, but the yields of t-butylcalcium halides were low, and the disproportionation to form the corresponding alkane and alkene was an important side-reaction in this case.

Although organocalcium compounds would be interesting in terms of physical properties and chemical reactivity, the available data in the literature is limited.[1] The slow progress in this area could be due to the lack of a simple method to prepare organocalcium compounds.

The formation of organocalcium halides from Ca metal and organic halides has been reported.[2-9]

$$RX + Ca \longrightarrow RCaX \qquad (1)$$

Recently, Kocheshkov *et al.*[8,9] prepared phenyl-, *o*-tolyl-, *m*-tolyl- and n-butylcalcium iodides but the reaction appeared to be restricted to aryl and primary alkyl iodides,[3,4] and yields were generally low especially in the aliphatic series (7% or less in THF)[6] although tritylcalcium chloride was obtained in a quantitative yield from trityl chloride and amalgamated calcium.[7] The use of Ca amalgam or Ca–Mg alloy improved the yield,[5,7] but some organomercury or organomagnesium compounds would be mixed with these organocalcium halides. The reaction tended to be slow, erratic, sluggish and difficult to initiate. The most troublesome side-reaction was the Wurtz-type coupling to form R—R and CaX_2.

Payne and Sanderson[10] reported the preparation of dimethylcalcium by the reaction of methyl iodide and calcium in pyridine without giving details. Kaufmann *et al.*[11] doubted the purity of this dimethylcalcium. Although calcium apparently is unable to displace Hg from organomercury,[12] Kocheshkov *et al.*[13] prepared and isolated di-*p*-tolylcalcium in 98% yield by the reaction of di-*p*-tolylmercury with calcium. The reaction is, however, undesirable on account of the toxicity of organomercury.

Fischer and Stölzle[14] obtained biscyclopentadienylcalcium from cyclopentadiene and calcium in 27% yield but the reaction of calcium hydride with cyclopentadiene at 400° gave the compound only in 9% yield.[14]

Several workers have prepared $CaZnR_4$ compounds by the reaction of calcium with dialkylzinc.[15] The property of the complex would be considerably different from that of dialkylcalcium or alkylcalcium halide and would be classified as an organozinc complex like Li_2ZnR_4 rather than an organocalcium compound.

An important factor in the preparation of organocalcium compounds could be impurities in the metallic Ca. Although the presence of such metallic impurities as Hg and Mg may occasionally contribute to ease of initiation of reaction,[5,7] it is generally desirable to employ pure Ca. Bryce-Smith and Skinner[5] have reported that the Ca metal containing $< 0{\cdot}5\%$ of Mg and $< 0{\cdot}2\%$ of Na was the purest material obtainable by them at that time, and suspected that the yields of organocalcium halides could be improved and the range of suitable halides extended if Na-free calcium were used. Recently, calcium metal of higher purity became commercially available, atomic absorption spectroscopic analyses showing only 0·493% of Mg and 0·0019% of Na.

Using this purer Ca metal, we found that reaction (1) proceeded smoothly like the preparation of a Grignard reagent when used under N_2. Activation of calcium metal† was not necessary. The reaction

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†Various efforts of activation of Ca metal were described in the literature. For example, treatment of Ca metal with iodine,[3] that with Grignard reagent,[4] amalgamation of Ca,[5,7] the use of Ca-Mg alloy,[5] or heating of Ca metal with iodine under an argon atmosphere.[9]

proceeded smoothly even at low temperature, and the Wurtz-type coupling was relatively less important under these conditions. Yields of organocalcium halides were much better than those available in the literature, *e.g.*, methyl-, ethyl-, n-propyl- and phenylcalcium iodides were obtained in 91–93% (lit.[6] 7%), 64–68% (lit.[6] 4%), 54–55% (lit.[6] 5%) and 97% (lit.[9] 70–80% in ether) yields, respectively.

Bryce-Smith and Skinner[5] obtained phenylcalcium iodide in 68–72% yield from iodobenzene and amalgamated Ca, (the Ca metal* contained $<0.5\%$ Mg and $<0.2\%$ Na). We obtained the compound in 97% yield using Ca containing about 0·5% Mg and about 0·002% Na. Bryce-Smith and Skinner[5] stated that the use of Na alloys led to lower and the Mg alloys to higher yields of organocalcium halides.

Contrary to the literature,[3,4] the reaction is not restricted to aryl and primary alkyl iodides. Bromides and chlorides also afforded organocalcium halides, although yields were generally lower than those of the corresponding reactions with iodides.

Gilman and Schulze[3] reported that isopropyl iodide does not react with Ca. Glacet[4] found that the introduction of a Grignard reagent as an initiator did not improve the low reactivity of isopropyl and sec-butyl iodides with Ca. Bryce-Smith and Skinner[5] failed to react secondary alkyl halides even with amalgamated Ca. However, when the Ca metal of higher purity was used, reaction (1) proceeded smoothly with secondary alkyl halides. Yields of isopropylcalcium halides were better than those of the corresponding n-propylcalcium halides. These results could be due to the difficulty of the Wurtz-type coupling by a steric requirement in this case.

Metallic Ca reacted easily with tertiary alkyl halides, but the yields of t-butylcalcium halides were low, and the disproportionation to form the corresponding alkane and alkene was an important side-reaction.

Reaction of Ca metal with benzyl iodide gave benzylcalcium iodide in low yield on account of Wurtz-type coupling as a side-reaction.

Some of the main results are given in Table 1.

Table 1. Preparation of organocalcium halides by reaction (1) in tetrahydrofuran[a]

Halide, RX	Temp. (°C)	Time (hr)	Yield (%)[b]	n[c]
MeI	−70	3	91–93	3
EtI	−70	2	64–68	2
EtI	−30	3	25	1
EtBr[d]	−30	7	35	1
n-PrI	−70	2	54–55	2
n-PrBr[d]	−70	3	45	1
n-PrCl[d]	0	4	29	1
i-PrI	0	2	67	1
i-PrI	−70	2	57	1
i-PrBr[d]	0	3	78	1
i-BuI	−30	7	27	1
t-BuI	0	7	1	5
t-BuBr[d]	−10	7	14	1
$C_6H_5CH_2I$	−70	4	13	1
$C_6H_5CH_2I$	0	3	10	1
PhI	−30	9	97	1
PhBr[d]	0	9	55	1
PhCl[d]	0	9	14	1

[a]Reaction conditions: Organic halides, 5·0 mmole; Ca, 6·5 mmole; THF as solvent, 10 ml.

[b]Based on the organic halide.

[c]Number of repeated runs.

[d]In these cases, reaction (1) was initiated by the addition of 1 mole% of the corresponding iodides, respectively.

EXPERIMENTAL

VPC analyses were performed on a Shimadzu GC-4A gas chromatograph. NMR spectra were obtained with a Varian HA-100 spectrometer using $CDCl_3$ as the solvent and TMS as an internal standard. Atomic absorption spectroscopic analyses of metallic Ca were performed at the Chemical Analyses Center of Yanagimoto Ltd., Kyoto.

Materials. t-Butyl and benzyl iodides were prepared by a conventional procedure.[16] Commercial materials of other organic halides were purified by usual methods.[17] Ca metal of higher purity was provided by Mitsuwa Chemicals, Ltd., Osaka. The Ca was rasped in dry liquid paraffin. N_2 was purified by passing through a tube containing Cu turnings in a furnace at 170° followed by drying with P_2O_5. THF was purified by distillation in the presence of benzophenone sodium ketyl under N_2. Other chemicals were commercial products and were used without further purification.

General procedure. The reaction vessel was a 2-necked flask equipped with two 3-way cocks. Each 3-way cock was connected with a N_2 inlet and a rubber serum cap. The rasped Ca metal was placed in the flask. The reaction vessel was evacuated and filled with dry N_2, and the Ca was washed with THF under N_2.

In the preparation of organocalcium iodides, about 1% of a soln of organic iodide (5·0 mmole) in THF (3·0 ml) was added *via* a hypodermic syringe at −3° or at room temp to this rasped Ca (0·26 g, 6·5 mmole) in THF (5·0 ml) without stirring. The mixture immediately showed a brown color. Reaction (1) commenced within several min, which was perceived by bubbling of gas and/or disappearance of the brown color followed by formation of a small amount of a white ppt. Immediately after the initiation, the mixture was cooled to the prescribed temp, and 2·0 ml of THF was added. The rest of the organic iodide soln was then added *via* a hypodermic syringe over a period of 1 hr while stirring at the same temp. Stirring was continued for several hr at this temp. After the preparation, organocalcium iodide was decomposed by addition of MeOH (in the case of Me, Et, Pr and benzyl derivatives), AcOH (in the case of phenyl derivatives), or 2:1 mixture (volume ratio) of water and EtOH (in the case of Bu derivatives) to the mixture, and the products were analysed. In the case of Me, Et, and Pr

*Designated as calcium "A" by the authors.[5]

derives, the total amount of the gas evolved after the decomposition was determined by a gas burette. The gas was analyzed by VPC. The gas usually contained a small amount (less than 1 mole %) of H_2. In other cases, the amount of hydrocarbon evolved after the decomposition was determined by VPC. Yield of organocalcium iodide was determined by the amount of hydrocarbon evolved after the decomposition. Kocheshkov *et al.*[9] ascertained the nearly quantitative formation of benzene by hydrolysis of phenylcalcium iodide.

Preparation of organocalcium bromides and chlorides in THF was performed in a similar manner except for the initiation. The reaction of calcium with organic bromide and chloride appeared to be more difficult. Therefore, we initiated by the addition of 1 mole % of the corresponding iodide.

Methylcalcium iodide. Preparation of methylcalcium iodide was carried out at −70°. Although the Wurtz-type coupling was less important at low temp, the initiation was difficult so we added 1% MeI at −3° as 0·5% was insufficient for the purpose. Addition of more MeI at −3° resulted in a decreased yield of methylcalcium iodide due to the Wurtz-type coupling. Three runs of the preparation at −70° for 3 hr gave MeCaI in 91, 93 and 91% yields, respectively. The preparation at −70° for 2·5 hr gave the compound in 78% yield. Three runs of the preparation at −70° for 2 hr gave the compound in 42, 47 and 46% yields, respectively.

Ethyl- and n-propylcalcium halides. Preparation of ethyl- and n-propylcalcium iodides was carried out in a similar manner. The preparation of EtCaBr was conducted at −30° after the addition of 1 mole % EtI at −3° in order to initiate the reaction. The yield was 35%. Preparation of n-PrCaBr and chloride was carried out in a similar manner.

Isopropylcalcium halides. Preparation of isopropylcalcium iodide at 0° for 2 hr after the initiation at room temp gave the title compound in 67% yield. The reaction was not difficult to initiate. The preparation at −70° for 2 hr after the initiation at −3° gave the compound in 57% yield. Preparation of i-PrCaBr was carried out at 0° for 3 hr after the initiation by the addition of 1 mole % i-PrI at room temp. The yield was 78%.

t-Butylcalcium halides. Preparation of t-BuCaI was carried out at 0° for 7 hr after the initiation at room temp. The reaction proceeded smoothly. After the preparation, a 2:1 mixture (volume ratio) of water and EtOH was added, giving isobutane and isobutene in 48 and 47% yields, respectively. Experiments were repeated 5 times, but much the same results were obtained. In an experiment, a mixture of D_2O and EtOD was added to the mixture after the preparation. The mixture of isobutane and isobutene was separated by VPC. NMR spectrum of the mixture in $CDCl_3$ showed that deuterium was scarcely contained in the isobutane. The result indicated that the yield of t-BuCaI was negligible and the disproportionation to form isobutane and isobutene was an important side-reaction. The yield of t-BuCaI was estimated as the subtraction of the yield of isobutene from that of isobutane.

Preparation of t-BuCaBr was conducted at −10° for 7 hr after the initiation by the addition of 1 mole % t-BuI at room temp. Addition of water and EtOH to the mixture at −70° after the preparation gave isobutane and isobutene in 55 and 41% yields, respectively. The estimated yield of t-BuCaBr was 14%. The disproportionation was again an important side-reaction.

Isobutylcalcium iodide. Preparation of i-BuCaI was carried out at −30° for 7 hr after the initiation at −3°. Addition of water and EtOH to the mixture gave isobutane and isobutene in 37 and 10% yields, respectively. The yield of i-BuCaI estimated as the subtraction of the yield of isobutene from that of isobutane was 27%. Both the Wurtz-type coupling and the disproportionation were important side-reactions.

Benzylcalcium iodide. Preparation of benzylcalcium iodide was carried out at −70° for 4 hr after the initiation at −3°. The yield was 13%. The preparation at 0° for 3 hr after the initiation at room temp gave the compound in 10% yield. The Wurtz-type coupling seemed to be an important side-reaction.

Phenylcalcium halides. Preparation of PhCaI was carried out at −30° for 9 hr after the initiation at −3°. The yield was 97%. When the reaction time was 2 hr, the yield was 65%. Preparation of PhCaBr and chloride was conducted at 0° for 9 hr after the initiation by the addition of 1 mole % of iodobenzene at −3°. The yields were 55 and 14%, respectively.

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