CALCIUM, STRONTIUM AND BARIUM

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Activity in the organometallic chemistry of the alkaline earth metals has been increasing over the past few years, but no obvious advantages over the analogous organomagnesium reagents have become apparent. Thus far, the organic derivatives of Ca, Sr and Ba are only of "academic' interest.

In the past few years several groups have studied the reactions of organic halides with calcium metal in organic solvents. Another report has appeared which describes the preparation of RCaX reagents in THF in higher yields than reported previously by others (Table 1) (1). The most important factor in achieving these high yields was considered to be the higher purity of the calcium metal used. Organic iodides are preferred in these reactions; however, some bromides and chlorides reacted with calcium as well, but gave lower RCaX yields. While primary and secondary alkyl halides reacted smoothly with calcium, the $Me_3CX + Ca$ reaction was accompanied by extensive side-reaction to give $Me_2C{=}CH_2$ and Me_3CH. With benzyl iodide the major process which occurred was Wurtz coupling to give bibenzyl. With alkyl (but not aryl) halides, such reactions to give RCaX reagents also could be effected in good yield in hydrocarbon (toluene or cyclohexane) medium (Table 2) (2). A less successful reaction of n-hexyl iodide with calcium in THF (which gave 25-30% RCaI and 60-70% R-R) was investigated in detail by French workers (3). Evidence for radical intermediates and their attack on the solvent was cited.

Table I. Preparation of RCaX in Tetrahydrofuran (Ref. 1)[a]

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

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

[b] Based on the organic halide.

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

Table 2. Preparation of RCaX in Hydrocarbon Solvents (Ref. 2)[a]

Halide, RX	Solvent	Temp, °C	Time, hr	Yield,[b] %
CH_3I	Toluene	40	25.5	61-68
CH_3I	Toluene	40	43	77-84
CH_3I	Cyclohexane	40	43	71-76
C_2H_5I	Toluene	60	27	64
C_2H_5I	Cyclohexane	60	45	70
n-C_3H_7I	Toluene	95	41	88
n-C_3H_7I	Cyclohexane	75	44	77
n-C_3H_7Br[c]	Toluene	65	29	72
n-C_3H_7Br[d]	Toluene	65	48	Trace
n-C_3H_7Cl[c]	Toluene	45	45	50
n-C_3H_7Cl[d]	Toluene	45	48	Trace
i-C_3H_7I	Toluene	85	28	78
i-C_3H_7Br[c]	Toluene	55	45	75
i-C_3H_7Br[d]	Toluene	55	48	66
i-C_3H_7Cl[c]	Toluene	33	47	75
t-C_4H_9I	Toluene	95	17	0
t-C_4H_9Cl[c]	Toluene	70	19	0
$C_6H_5CH_2I$	Benzene	90	99	6
$C_6H_5CH_2Br$[c]	Benzene	90	145	6
$C_6H_5CH_2Cl$[c]	Benzene	90	94	2
C_6H_5I	Toluene	120	96	3
C_6H_5I	Toluene	160	46	3
C_6H_5I	Tetralin	180	30	15
C_6H_5Br[c]	Toluene	160	45	5
C_6H_5Cl[c]	Toluene	130	43	3

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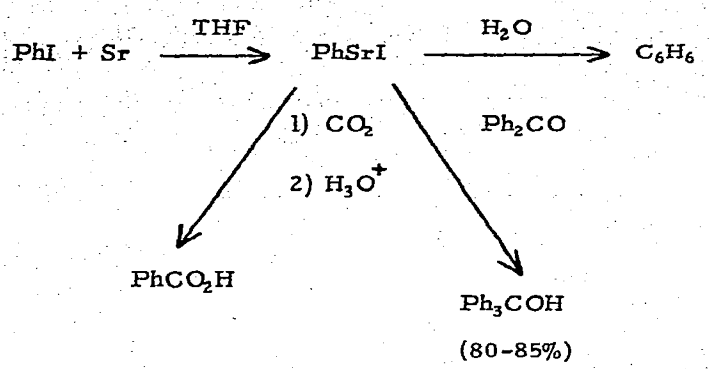
[a] Reaction conditions: organic halides, 5.0 mmol; calcium, 6.5 mmol; solvent, 10 ml.

[b] Based on the organic halide.

[c] In these cases, reaction 1 was initiated by the addition of 1 mol % of the corresponding iodides, respectively.

[d] The initiation by the addition of the corresponding iodides was not adopted.

Strontium (activated by mercury) was found to react with iodobenzene in THF to give phenylstrontium iodide in high yield (4). The solid mono-tetrahydrofuran adduct of this reagent was isolated.



The reaction of diarylmercurials with metallic calcium in THF gives diarylcalcium compounds (5). Compounds of type Ar_2Ca where Ar = Ph, o-, m- and p-MeC_6H_4, p-$MeOC_6H_4$, 2-thienyl, 1-$C_{10}H_7$, inden-1-yl, fluoren-9-yl, Ph_3C, Ph_2CH) were prepared in 40-68% yield by this procedure. Complexes of such diarylcalcium compounds with THF were isolated. Allyl and benzyl compounds of calcium, strontium and barium also have been prepared by metal displacement from the appropriate tetraorganolead (6) or -tin (7) compounds:

$$(PhCH_2)_4Pb + 2\,M \xrightarrow{\text{THF, room temp.}} 2\,(PhCH_2)_2M + Pb$$
$$(M = Ca,\ Sr)$$

$$(CH_2{=}CHCH_2)_4Sn + 2\,M \xrightarrow[(HgBr_2)]{\text{THF}} 2\,(CH_2{=}CHCH_2)_2M + Sn$$
$$(M = Ca,\ Sr,\ Ba) \qquad\qquad (\sim 90\%)$$

The products were found to be initiators of anionic polymerization of styrene. (Another study (8) showed organobarium compounds to be initiators of anionic polymerization in donor solvents). Dicyclopentadienylcalcium has been prepared by reaction of cyclopentadiene with calcium metal in THF and the unsolvated material was obtained by vacuum sublimation (9). Various adducts with Lewis bases, $(C_5H_5)_2Ca\cdot C_5H_5N$ and $(C_5H_5)_2Ca\cdot L\text{-}L$ (L-L = TMED, bipy, DME, phen) were prepared and studied (in particular, ^1H NMR and IR). Dicyclopentadienylcalcium is a

Table 3. Reactions of Methylcalcium Iodide (Ref. 10)[a]

Compound	Products (yield, %[c])
CH_3COCH_3	$(CH_3)_3COH$ (49), CH_4 (39)
CH_3COCH_3	$(CH_3)_3COH$ (51), CH_4 (37)
$C_6H_5COC_6H_5$[d]	$CH_3C(C_6H_5)_2OH$ (32)
$C_6H_5COC_6H_5$	$CH_3C(C_6H_5)_2OH$ (76)
C_6H_5CHO	$C_6H_5CH(CH_3)OH$ (64), $C_6H_5CH=CH_2$ (trace)
C_6H_5CHO	$C_6H_5CH(CH_3)OH$ (55), $C_6H_5CH=CH_2$ (trace)
CH_3COOCH_3	$(CH_3)_3COH$ (71), CH_4 (21)
CH_3COOCH_3	$(CH_3)_3COH$ (70), CH_4 (17)
$(C_2H_5O)_2CO$	$(CH_3)_3COH$ (68), CH_3COCH_3 (3)
$(C_2H_5O)_2CO$	$(CH_3)_3COH$ (73), CH_3COCH_3 (6)
$CH_3CH=CHCOOCH_3$	$CH_3CH=CHC(CH_3)_2OH$ (50), $CH_3CH=CHCOCH_3$ (4), $(CH_3)_2CHCH_2$-$COOCH_3$ (trace), CH_4 (17)
C_6H_5COCl	$CH_2=C(CH_3)C_6H_5$ (70), $C_6H_5COCH_3$ (trace), $C_6H_5C(CH_3)_2OH$ (trace)
CH_3COCl	$(CH_3)_3COH$ (31), $CH_3COOC(CH_3)_3$ (19), CH_3COCH_3 (trace), CH_4 (25)
CH_3COCl	$(CH_3)_3COH$ (22), $CH_3COOC(CH_3)_3$ (26), CH_3COCH_3 (2), CH_4 (26)
CH_3CN	CH_3COCH_3 (14), CH_4 (60)
CH_3CN	CH_3COCH_3 (9), CH_4 (60)
C_6H_5CN	$C_6H_5COCH_3$ (18)
C_6H_5CN	$C_6H_5COCH_3$ (21)
C_6H_5CN	$C_6H_5COCH_3$ (21)

[a] Reactions were carried out at -30° under a nitrogen atomosphere.

[b] Tetrahydrofuran.

[c] Based on CH_3I.

[d] 27% of methylcalcium iodide remained unchanged.

reactive C_5H_5 source and was useful in the preparation of ferrocene, titanocene dichloride and dicyclopentadienylmercury. An attempt to prepare C_5H_5CaCl by reaction of $(C_5H_5)_2Ca$ with HCl in DME was unsuccessful.

Japanese workers (10) have investigated the reactions of methylcalcium iodide in some detail (Table 3) (10). Additions to carbonyl compounds occurred readily and in good yield at -30° in THF. 1,2-Addition was favored in the case of methyl crotonate. Reactions with acid chlorides and with nitriles were less satisfactory. In contrast, observations made by French workers suggested that the Barbier procedure gives better results in such organocalcium chemistry than does the use of preformed RCaX reagents (11). This conclusion, however, probably is not valid, since it was these workers who were not able to achieve good yields of n-$C_6H_{13}CaI$ (3).

The preparation of RBaI by the reaction of organic iodides with barium metal in diethyl ether or in THF gave only low yields (20-30%) (R = Me, Et, n-Pr, n-Bu, n-C_5H_{11}, Ph) (12). In reactions of these reagents with benzophenone, only PhCaI gave the expected triphenylcarbinol in 65% yield. With alkylbarium iodides, an olefin was formed e.g.:

$$C_2H_5BaI + Ph_2CO \longrightarrow Ph_2C{=}CHCH_3 \quad (70\%)$$

presumably via decomposition of the $Ph_2C(CH_2R)OBaI$ intermediate.

Further reactions of alkaline earth organic compounds with enynes have been reported:

$$RCaI + CH_2{=}CHC{\equiv}CCH{=}CHMe \xrightarrow{Et_2O} \xrightarrow{H_2O}$$

(R = Et, Pr, Bu)

$$RCH_2CH{=}C{=}CHCH{=}CHMe \ (25\%)$$

(ref. 13)

$$RCaI + CH_2{=}CHC{\equiv}CCH_2NEt_2 \xrightarrow{Et_2O} \xrightarrow{H_2O}$$

(R = Et, Pr, i-Pr)

$$RCH_2CH{=}C{=}CHCH_2NEt_2 \ (25\text{-}30\%)$$

(ref. 14)

$$Et_2Sr + CH_2{=}CHC{\equiv}CEt \xrightarrow{Et_2O} \xrightarrow{H_2O} EtCH{=}C{=}CHPr\text{-}n \ (40\text{-}50\%)$$

(ref. 15)

$$Et_2Ba + CH_2{=}CHC{\equiv}CR \xrightarrow{Et_2O} \xrightarrow{H_2O} RCH{=}C{=}CHPr\text{-}n \ (45\text{-}50\%)$$

(R = Me, Et, Pr, Me_3C)

(ref. 16)

$$Et_2Ba + CH_2{=}CHC{\equiv}CR \xrightarrow{Et_2O} \xrightarrow{H_2O} n\text{-}PrCH{=}C{=}CHR$$

$(R = CH_2{=}CH,\ MeCH{=}CH)$ (ref. 17)

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