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CALCIUM, STRONTIUM AND BARIUM

ANNUAL SURVEY COVERING THE YEARS 1977 AND 1978[*]

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Progress in the organic chemistry of the heavier alkaline earth metals, calcium, strontium and barium, has been slow during the past two years. The applications of the organic derivatives in synthesis offer no advantages over those of analogous lithium and magnesium reagents and, in fact, in many cases are less advantageous.

Gowenlock, Lindsell and Singh have studied the preparation of compounds of type RMI (R = Me, Et, n-Pr, n-Bu; M = Sr and Ba) in THF medium at -78°C and isolated their solid THF solvates (1). The finely divided metals reacted as well as the amalgamated metals (5% Hg). These products are very reactive and are rapidly decomposed by atmospheric moisture. They decompose slowly in vacuo at room temperature. At room temperature they also attack THF. Cocondensation of alkyl halides in large excess with calcium, strontium and barium vapor at -196°C in vacuo produced solvent-free RMX species in 10-25% yield after the RX/metal matrices has been warmed to 10-20° below their melting points. Also prepared in yields of 90-100% by such cocodensation techniques were the dicyclopentadienyl and diindenyl compounds of these metals. The dicyclopentadienyl compounds are quite insoluble in THF and their proton NMR spectra were measured in HMPA solution.

Russian workers have prepared solutions of arylstrontium iodides in diethyl ether and benzene solutions which contained only a small amount of THF by the reactions of aryl iodides with amalgamated strontium at room temperature (2). Prepared in this

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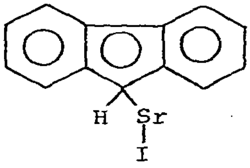
[*] Previous survey see J. Organometal. Chem., Vol. 143 (1977) p. 141-151.

manner were PhSrI, m- and p-$CH_3C_6H_4SrI$, 2-thienyl-SrI and 1-$C_{10}H_7SrI$. Carboxylation of these solutions gave the expected benzoic acids. Another Russian group has described in detail its studies of the preparation of alkyl and aryl-calcium derivatives by the reactions of organic iodides with calcium metal (3). Factors such as the purity of the calcium, the donor solvent or additive used and the temperature were investigated and the reactions could be optimized so that generally acceptable yields of RCaI could be obtained in the case of primary alkyl and aryl iodides: CH_3CaI, 66%; EtCaI, 66%; n-C_3H_7CaI, 73%; n-C_4H_9CaI, 68%; n-$C_7H_{15}CaI$, 40%; C_6H_5CaI, 97%; 1-$C_{10}H_7CaI$, 94%. Poorer yields were obtained with secondary alkyl iodides and tert-butyl iodide. Stable THF, 1,4-dioxane and triethylamine adducts of some of these RCaI were prepared. Dicyclopentadienylcalcium also was prepared by reaction of cyclopentadiene with calcium metal in THF and was isolated as the 2THF solvate. It was found to react in THF solution with isopropyl bromide in the presence of $BF_3 \cdot OEt_2$ to give a diisopropyl derivative, i-$Pr_2C_{10}H_8Ca$, of undetermined structure in 50% yield.

The dibenzyl compounds of calcium, strontium and barium have been prepared by the mercurial route and their ^1H and ^{13}C NMR and electronic spectra in the visible region have been

$$(PhCH_2)_2Hg + M \xrightarrow{THF} (PhCH_2)_2M + Hg \qquad (M = Ca, Sr, Ba)$$

studied (4). A high degree of carbanionic character was indicated. In such benzylic derivatives, $(PhCH_2)_nM$, the ionic nature increases in the order: Mg<Ca<Sr<Li<Ba<K. Fluorenylstrontium iodide, 1, has been prepared by the metalation of fluorene with PhSrI·½TMED in THF (5).



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Diverse reactions of organic derivatives of the heavy alkaline earth metals have been studied.

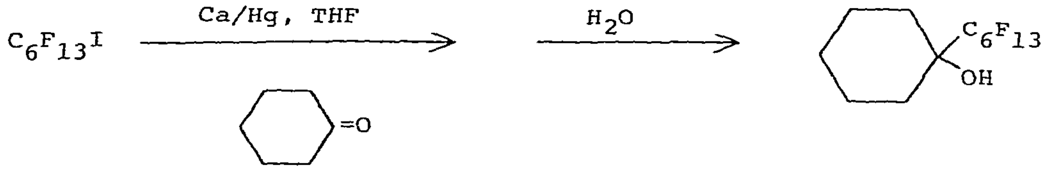
1) Addition to enynes

$$CH_2{=}CH{-}C{\equiv}CSiMe_3 + EtBaI \xrightarrow[\text{(ref.6)}]{} \xrightarrow{H_2O} EtCH_2CH{=}C{=}CHSiMe_3$$
$$+ EtCH_2CH_2C{\equiv}CSiMe_3 \quad \text{(1:1 ratio)}$$

2) Addition to carbonyl compounds

Reactions of CH_3SrI and CH_3BaI with a variety of substrates (summarized in Table 1) did not look very promising (1). Ethylstrontium iodide di-tetrahydrofuranate was found to polymerize methyl methacrylate at −78°C (1). The reactions of alkyl- and arylcalcium compounds with acetone, benzaldehyde and carbon dioxide were studied by a Russian group (3). Carboxylation occurred in reasonable yields, but additions to acetone occurred in only poor yield because of side reactions which formed acetone condensation products. These side reactions were given special study.

The in situ reactions of perfluoroalkyl iodides, calcium amalgam and various aldehydes and ketones in THF at −20° to −40°C gave alcohols in yields of 20-70% (7), e.g.:



Results of these reactions are given in Table 2. Without doubt, organocalcium intermediates, $C_nF_{2n+1}CaI$, are involved.

Calcium carbide can serve as a reagent in organocalcium syntheses of acetylenic alcohols (8):

$$CaC_2 + KOH + Me_2C{=}O \xrightarrow{\text{benzene}} \xrightarrow{\text{aq.HCl}} HOCMe_2C{\equiv}CCMe_2OH$$
$$(45\%)$$

3) Initiation of anionic polymerization

There has been some interest in the past years in the use of organocalcium, -strontium and -barium compounds in the initiation of anionic polymerization of arylolefins and 1,3-dienes, and a

(Continued on p. 16)

TABLE 1. Organic Reactions of CH_3SrI and CH_3BaI in THF Solution (1)

	Products			
	Reaction with CH_3SrI[b]		Reaction with CH_3BaI[c]	
Reactant	Volatiles formed in reaction	Isolated after hydrolysis[d]	Volatiles formed in reaction	Isolated after hydrolysis[d]
Ph_2CO	CH_4 + other hydrocarbons	$Ph_2C(Me)OH$ (69)	CH_4(31)	$Ph_2C{=}CH_2$(21), [Ph_2CHOH + $Ph_2C(Me)OH$ (2)
PhCHO	n.a.	PhCH(Me)OH(21), $PhCH{=}CH_2$(4) $PhMeC{=}CH_2$(2)	n.a.	PhCH(Me)OH(16), $PhCH{=}CH_2$ (11), $PhCME{=}CH_2$(4)
PhCOCl	CH_4	$PhCMe{=}CH_2$(11)	CH_4	e
PhCN	n.a.	PhCOMe(6), PhCHO(t)	n.a.	PhCOMe(1)
Me_2CO	CH_4(26), C_2H_6(t)	Me_3COH(8)	CH_4(24), C_2H_6 (5)	Me_3COH(18), Me_2CHOH(8)
MeCOCl	CH_4(21)	Me_2CO(t)	CH_4, C_2H_6(mol ratio 5:2)	e
MeCN	CH_4(27)	Me_2CO(t)	CH_4(21), C_2H_6(8)	e
$MeCO_2Me$	CH_4	Me_3COH(3)	CH_4	e

[a] At between -78 and -30°C. n.a. = Not analysed, t=trace. [b] Yields (%) (g.l.c.) given in parentheses were based on the amount of SrMe(I) • 2thf used. [c] Yields (%) (g.l.c.) given in parentheses were based on the amount of MeI used to prepare the organometallic. [d] Starting material (or a hydrolysis product) and volatile hydrocarbons (mainly CH_4 and C_2H_6) were also obtained. [e] No addition or reduction products.

TABLE 2. Alcohol Synthesis by the Reaction of Perfluoroalkyl Iodides, Calcium Amalgam and Aldehydes and Ketones (7)

Carbonyl Compound	Exp. Conditions		Products	Yields (%)
	time (h)	temperature (°C)		
cyclo-$C_6H_{10}O$	8	-20	cyclo-$C_6H_{10}(OH)C_6F_{13}$	58
$CH_3C(O)CH_3$	20	-40	$(CH_3)_2C(OH)C_6F_{13}$ $(CH_3)_2C(OH)CH_2C(CH_3)(OH)C_6F_{13}$	37 28
$CH_3C(O)C_2H_5$	18	-30	$CH_3C(OH)C_2H_5C_6F_{13}$ $CH_3C(OH)C_2H_5CH_2C(OH)C_2H_5C_6F_{13}$	29 10
$C_2H_5C(O)C_2H_5$	8	-40	$(C_2H_5)_2C(OH)C_6F_{13}$	66
$[(CH_3)_2CH]_2C(O)$	18	-40	$C_{12}F_{26}$ $[(CH_3)_2CH]_2C(OH)C_6F_{13}$	31 40
$C_4H_9C(O)C_4H_9$	15	-30	$(C_4H_9)_2C(OH)C_6F_{13}$	22
$CH_3C(O)C_6H_5$	22	-35	$CH_3C(OH)C_6H_5C_6F_{13}$	30
C_6H_5CHO	(a) C_2F_5I 20	-40	$C_6H_5CH(OH)C_2F_5$	69
	(b) $C_6F_{13}I$ 20	-40	$C_6H_5CH(OH)C_6F_{13}$	56
o-OHC_6H_4CHO	20	-40	o-$OHC_6H_4CH(OH)C_6F_{13}$	21

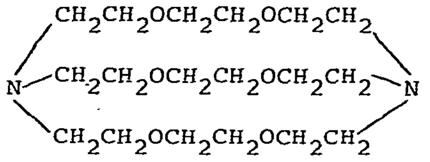
number of papers during the present survey period has dealt with this aspect of organoalkaline earth chemistry.

The organobarium species RBaOEt and R_2Ba, produced by the action of Grignard reagents on barium ethoxide, have been used to initiate the polymerization of 1,2-butadiene (9). These organobarium products were insoluble in benzene and THF, but they dissolved when 1,1-diphenylethylene was added, giving the red, ionic adduct, $(RCH_2CPh_2{}^-)_2Ba^{2+}$. The EtLi/Ba(OR)$_2$ system also initiates polymerization of butadiene (10). Other examples of organobarium initiation of anionic polymerization have been noted in the Russian literature (11,12).

French workers have described a method for the preparation of finely divided (~0.1μ) strontium and barium and reaction of these metal powders with styrene in THF or tetrahydropyran to give oligostyrylstrontium and -barium of DP less than 5 (13,14). Physical and chemical evidence, including results of styrene polymerization initiation, indicated that these oligostyryl alkaline earth species are dicarbanionic. Another group has studied the effect of $Ba(BPh_4)_2$ on the anionic polymerization of the barium salt of one-ended polystyrene in THF (15). The following equilibrium was established:

$$(\sim\sim CH_2CHPh)_2Ba^{2+} + Ba(BPh_4)_2 \rightleftharpoons 2\ (\sim\sim CH_2\bar{C}HPh)BaBPh_4$$

Finely divided metallic barium reacts with naphthalene in THF in the presence of [2.2.2]cryptand 2 at room temperature to give



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relatively stable, paramagnetic, green solutions containing Ba[2.2.2]$^{2+}$ and the naphthalene radical anion (16). The latter was identified by means of its ESR spectrum.

4) Miscellaneous reactions

The reaction of aryl iodides with diborane in THF in the presence of calcium metal, followed by oxidation of the reaction mixture, gave phenols in yields of 30–50% (17). Here also, organocalcium intermediates must be involved:

$$ArI + Ca \longrightarrow ArCaI$$

$$ArCaI + B_2H_6 \longrightarrow Ar_nBH_{3-n}$$

$$Ar_nBH_{3-n} + H_2O_2 \xrightarrow{OH^-} ArOH$$

The polymerization of ethylene oxide can be initiated by diarylcalcium compounds (18).

Organocalcium intermediates could be (but need not be) involved in the reduction of aryl and heterocyclic halides by calcium in methanol (19).

Finally, we note some organic reactions of alkaline earth tetraorganoaluminates, $M[AlR_4]_2$ (M = Ca, Sr, Ba). In reactions of $M[AlEt_4]_2$ with aliphatic aldehydes, four of the eight ethyl groups react. Ethylation of the aldehyde to form the secondary alcohol is the main process (20). Six methyl groups of $Ca[AlMe_4]_2$ and four phenyl groups of $Ca[AlPh_4]_2$ are utilized in reaction with benzophenone (21). A 1:1 intermediate complex, $Ca[AlPh_4]_2 \cdot Ph_2C{=}O$, could be isolated. $Ca[AlR_4]_2$ and $Sr[AlR_4]_2$ reacted with PhC(O)Cl and $(CH_3CO)_2O$ to give the respective ketones, PhC(O)R and $CH_3C(O)R$, as well as their reduction and alkylation products.

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