CALCIUM, STRONTIUM AND BARIUM

ANNUAL SURVEYS COVERING THE YEARS 1975 and 1976

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Activity in this area of organometallic chemistry continues at a low level. This probably will continue to be the case as long as no applications of the organic derivatives of calcium, strontium and barium are found which find no counterpart in organoalkali chemistry. The organometallic chemistry of the alkaline earth metals has been reviewed (1). The present still undeveloped state of this area is shown by the fact that only 173 references are cited.

Gowenlock and his coworkers (2) prepared several alkylstrontium iodides and ethylbarium iodide and isolated them as their THF adducts:

$$\mathrm{RI} + \mathrm{Sr\ (finely\ divided)} \xrightarrow{\mathrm{THF},\ -78^\circ} \mathrm{RSrI} \quad (70\text{-}87\%)$$

(R = Me, Et, n-Pr, n-Bu)

$$\mathrm{EtI} + \mathrm{Ba} \xrightarrow{\mathrm{THF},\ -78^\circ} \mathrm{EtBaI} \quad (86\%)$$

The di- or tri-tetrahydrofuranates were isolated as microcrystalline solids of limited stability at room temperature. Attempted IR and NMR studies were of little success and initial studies of the synthetic applications of CH_3SrI did not seem promising. Kocheshkov and his coworkers (3,4) have prepared arylstrontium iodides by the reaction of aryl iodides with strontium, preferably activated with mercury (4), although this is not necessary (3):

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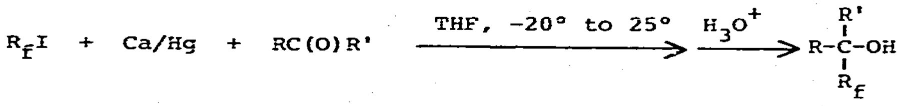
$$\mathrm{Ar\text{-}I} + \mathrm{Sr/Hg} \xrightarrow{\mathrm{THF}} \mathrm{ArSrI} \qquad (\mathrm{Ar} = \mathrm{Ph},\ o\text{-},\ m\text{-},\ p\text{-}\mathrm{CH_3C_6H_4},\ \alpha\text{-}\mathrm{C_{10}H_7}\ \text{and}\ \alpha\text{-thienyl})$$

These compounds also were isolated as their mono- or di-tetrahydrofuranates. They underwent Grignard reagent-like reactions with carbon dioxide and benzophenone and were found to be much more stable than alkylstrontium iodides.

The analysis of organocalcium halides and of diarylcalcium compounds has received attention. Kawabata et al. have found that the Gilman double titration procedure used for organolithium reagents can be applied to the analysis of RCaI (R = Me, n-Pr, Ph) (5). Of the organic halogen compounds tested, chloroform appeared to give the best results. The Kocheshkov group prefers to use reaction gas chromatography for the determination of ArCaI (6), Ar_2Ca (7) and ArSrI (4) in which a sample of the reagent is hydrolyzed in the reactor chamber of a gas chromatograph.

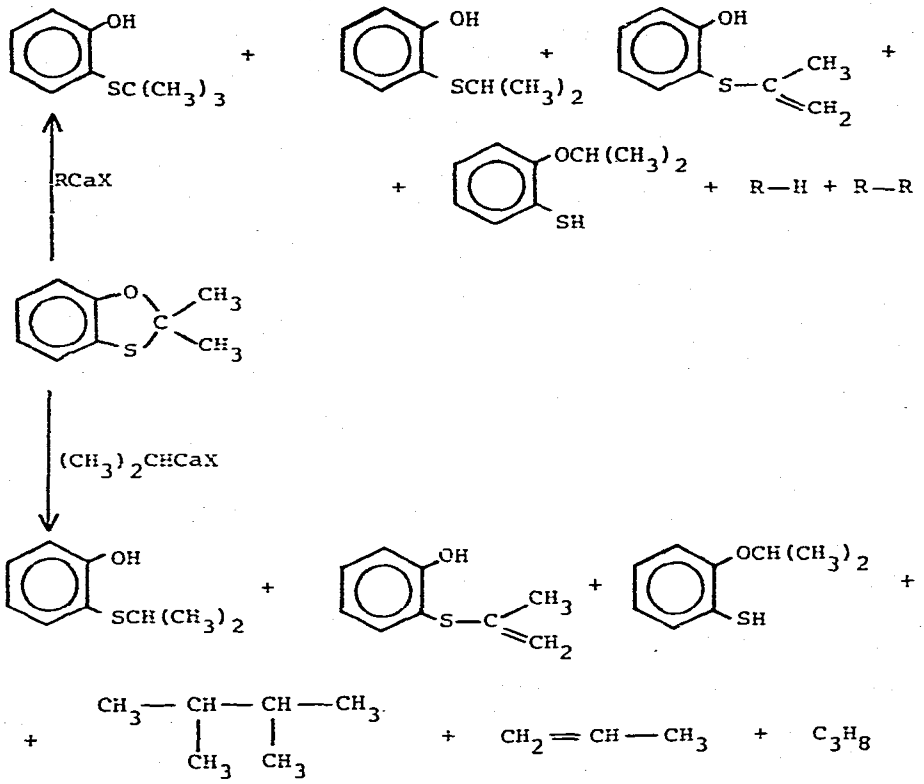
A Barbier reaction of perfluoroalkyl iodides (R_fI, R_f = C_2F_5 and $n\text{-}C_6F_{13}$) with calcium and carbonyl compounds gave the expected tertiary alcohols (8):



$$\mathrm{R_fI} + \mathrm{Ca/Hg} + \mathrm{RC(O)R'} \xrightarrow{\mathrm{THF},\ -20°\ \text{to}\ 25°} \xrightarrow{\mathrm{H_3O^+}} \mathrm{R}\text{-}\overset{\mathrm{R'}}{\underset{\mathrm{R_f}}{\mathrm{C}}}\text{-}\mathrm{OH}$$

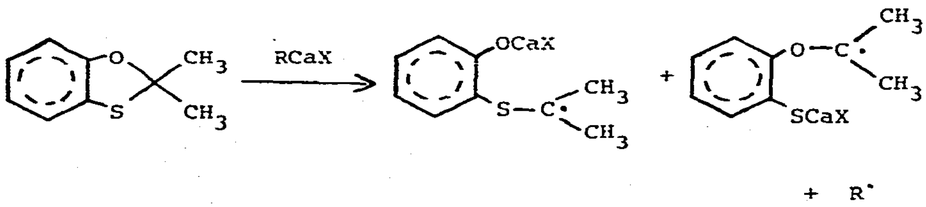
$RC(O)R'$ = Et_2CO, cyclohexanone, $i\text{-}Pr_2CO$,
PhC(O)Me, Me_2CO, EtC(O)Me, PhCHO

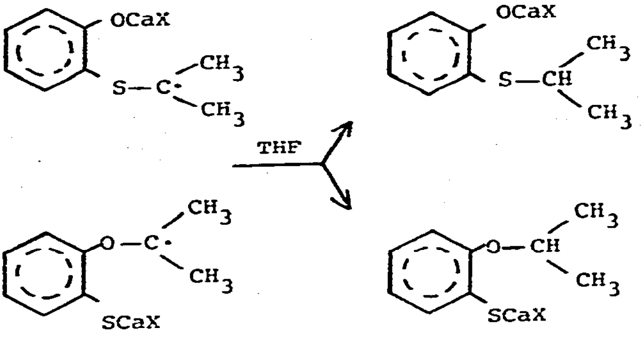
The product yields were variable and ketolization by-products were formed. Formation of the R_fCaI reagent prior to its reaction with the carbonyl compound was less satisfactory. The reaction of alkylcalcium iodides with 1,3-benzoxathiole and 1,3-benzodioxole derivatives gave products derived from substitution, elimination and reduction which resulted from initial ether cleavage. The following reaction course was suggested (9).



R = CH_3, C_6H_5

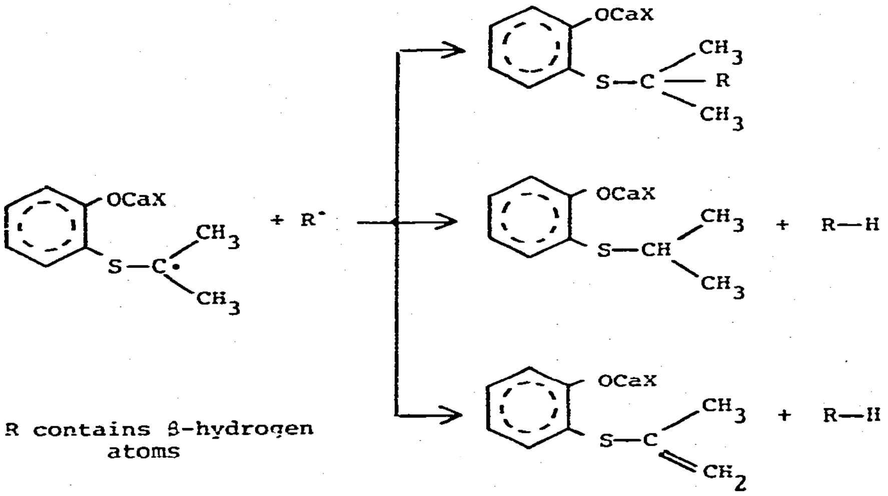
<u>via</u>:





R does not contain β-hydrogen atoms

and:



R contains β-hydrogen atoms

Methylenedicalcium diiodide has joined other methylene dimetallics (CH_2Li_2, $CH_2(MgX)_2$, $CH_2(ZnI)_2$) which react with carbonyl compounds to give olefins (10):

$$CH_2I_2 + Ca \xrightarrow{THF,\ -30°} CH_2(CaI)_2 \qquad (\sim 17\%)$$

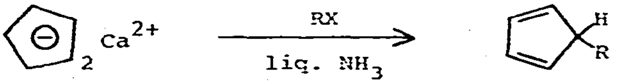
$$CH_2(CaI)_2 + RCH{=}O \longrightarrow RCH{=}CH_2 \qquad (53\text{-}94\%)$$

(R = Ph, p-MeC_6H_4, trans-MeCH=CH, n-C_4H_9)

This reagent also could be carboxylated:

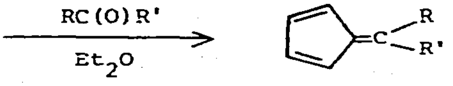
$$CH_2(CaI)_2 \xrightarrow{CO_2} \quad \xrightarrow{H_3O^+} CH_2(CO_2H)_2 \qquad (12\%)$$

The low yields of $CH_2(CaI)_2$ obtained, however, preclude any useful applications in synthesis. Diammoniates and di-tetrahydrofuranates of calcium dicyclopentadienide and calcium diindenide have been prepared by metallation of cyclopentadiene and indene with metallic calcium in liquid ammonia and subsequent treatment of the products with THF (11). Spectroscopy (IR and proton NMR) established their ionic structures. Their application in the synthesis of cyclopentadiene and indene derivatives was explored:

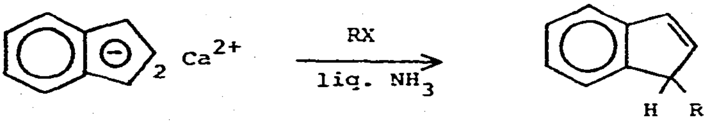


(∿30%)

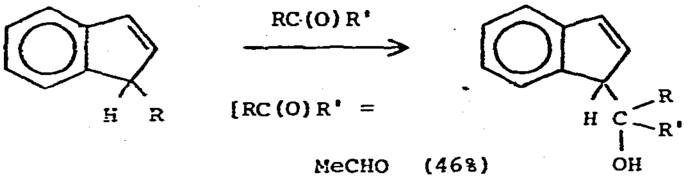
(RX = EtI, $PhCH_2Cl$)



[RC(O)R' =
PhCHO (57%)
Me_2CO (42%)
PhCOMe (36%)]



(RX = EtI, $PhCH_2Cl$)



[RC(O)R' =

MeCHO (46%)
PhCHO (55%)
PhCOMe (47%)]

There have been further reports of organoalkaline earth reagent additions to enynes:

$$Et_2Sr + CH_2{=}CH{-}C{\equiv}CR \xrightarrow{Et_2O} \xrightarrow{H_2O} RCH{=}C{=}CHCH_2Et$$

In these experiments R = Me, Et, and n-Pr (12).

$$R'BaI + CH_2{=}CH{-}C{\equiv}CR \xrightarrow{THF} \xrightarrow{H_2O} R'CH_2CH{=}C{=}CHR$$

Ethyl-, n-propyl-, n-butyl- and phenylbarium iodides were allowed to react with enynes where R = Me, Et, Me_3C, $CH_2{=}CH$, MeCH=CH, SMe and SPh. The product yields were in the 15-20% range (13). The action of R'BaI on methylseleno- and methyltellurovinylacetylenes resulted in cleavage of the carbon-chalcogen bonds.

$$Et_2Ba + CH_2{=}CH{-}C{\equiv}CCH_2NR_2 \longrightarrow \xrightarrow{H_2O} EtCH_2CH{=}C{=}CHCH_2NR_2$$

Here R = Me and Et (14).

Related to such additions is the initiation of the anionic polymerization of 1,3-dienes and activated olefins by organoalkaline earth derivatives. Especially organic derivatives of barium have received much attention. Thus, in one study, dibenzylbarium, obtained by reaction of a barium mirror with dibenzylmercury in THF, was used to form a "living" oligomer from α-methylstyrene which then was allowed to react with styrene to give the barium salt of one-ended living polystyrene (15). Conductance and kinetic studies of this salt were carried out.

French workers have investigated the visible spectrum of such a polystyryl-barium in THF (16). Extensive kinetic studies of organobarium-induced anionic polymerization of styrene and 1,3-dienes have been reported (16-27). Among the organobarium initiators used were the following:

$(Ph_3\overset{-}{C})_2Ba^{2+}$ (18, 20), prepared <u>via</u>:

$$"Ph_6C_2" + Ba \xrightarrow{THF} (Ph_3\overset{-}{C})_2Ba^{2+}$$

Dibenzylbarium (22)

$(PhCH_2CH_2\overset{-}{C}Ph_2)_2Ba^{2+}$ (18), prepared <u>via</u>:

$$(PhCH_2)_2Ba + 2\ CH_2{=}CPh_2 \longrightarrow (PhCH_2CH_2\overset{-}{C}Ph_2)_2Ba^{2+}$$

R_2Mg + $Ba(OEt)_2$ combinations, containing, presumably, RBaOEt and R_2Ba ($R = n\text{-}C_4H_9$ and $n\text{-}C_6H_{13}$) (27)

$(Ph_2\overset{-}{C}CH_2CH_2\overset{-}{C}Ph_2)Ba^{2+}$ (23), prepared <u>via</u>:

$$Ph_2C{=}CH_2 + Ba\ mirror \xrightarrow[\text{in vacuo}]{\text{quartz ampoule}} (Ph_2\overset{-}{C}CH_2CH_2\overset{-}{C}Ph_2)Ba^{2+}$$

$Ba(AlR_4)_2$ (R = Et and n-Bu) and $Ca(AlR_4)_2$ (24)

French workers have made a detailed spectral study of $(Ph_2\bar{C}CH_2CH_2\bar{C}Ph_2)Ba^{2+}$ (28) and of the corresponding strontium compound, $(Ph_2\bar{C}CH_2CH_2\bar{C}Ph_2)Sr^{2+}$ (29), in THF medium. These reagents are present in solution as contact ion pairs over a wide temperature range.

In another investigation, Szwarc and his coworkers have studied equilibria and kinetics of the disproportionation of the barium salts of the radical anions derived from tetraphenylethylene and tetracene in THF and DME (30), e.g.:

$$Ba^{2+}(Ph_2C{=}CPh_2)^- \quad + \quad (Ph_2C{=}CPh_2)^- \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad Ba^{2+}(Ph_2\overset{-}{C}-\overset{-}{C}Ph_2) \quad + \quad Ph_2C{=}CPh_2$$

This reaction has a very high ($\sim 10^6$) disproportionation constant and a bimolecular rate constant in DME (by flash photolysis techniques) of $\sim 10^7 M^{-1}s^{-1}$. A study of the optical spectrum of $Ba^{2+}(Ph_2\overset{-}{C}-\overset{-}{C}Ph_2)$ suggested an unsymmetrical structure, with the Ba^{2+} ion tightly associated with only one of the Ph_2C^- moieties to form the Ba^{2+}, $-\overset{-}{C}Ph_2$ ion pair.

Diphenylcalcium has been found to initiate the polymerization of propylene oxide, presumably by an anionic mechanism (31). The product was an elastic, non-crystalline material with molecular weight $>10^6$.

Further studies have been carried out by Zakharkin and his coworkers on $M^{II}[AlR_4]_2$ (M^{II} = Ca, Sr, Ba) complexes:

$$M^{II} \quad + \quad Et_2Hg \quad + \quad 2\ Et_3Al \quad \xrightarrow[\text{(ref. 32)}]{} \quad M^{II}[AlEt_4]_2 \quad + \quad Hg$$

and, more generally:

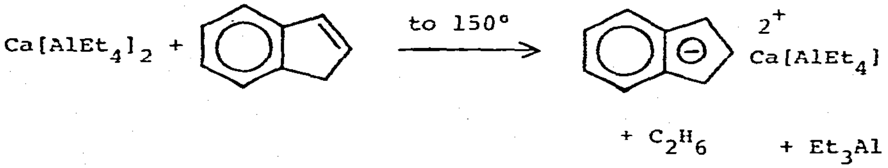
$$M^{II} \quad + \quad R_2Hg \quad + \quad 2\ R'_3Al \longrightarrow M^{II}[AlR'_3R]_2 \quad + \quad Hg$$

(R, R' = alkyl or aryl)

Prepared in this way were: $Ca[Al(n\text{-}C_3H_7)_4]_2$, $Ba[Al(n\text{-}C_3H_7)_4]_2$, $Ca[AlPh_4]_2$, $Sr[AlPh_4]_2$, $Ba[AlPh_4]_2$, $Ca[AlEt_3Ph]_2$, and $Ca[AlEt_3(C_6H_4CH_3\text{-}p)]_2$. A number of solvates was prepared (with diethyl ether, tetrahydrofuran, diglyme, tetramethylethylene diamine, trimethylamine) in which it was the alkaline earth ion which appeared to interact with the Lewis base (32).

$$M^{II}[AlEt_4]_2 \quad + \quad 2n\ RC{\equiv}CH \quad \xrightarrow[\text{(ref. 33)}]{} \quad M^{II}[AlEt_{4-n}(C{\equiv}CR)_n]_2 \quad + \quad 2n\ C_2H_6$$

The displacement of successive ethyl groups took place with increasing difficulty. The final product, obtained at 180-200° after 50 min., was $Ca[AlEt(C{\equiv}CPh)_3]_2$ in the $CaAlEt_4$ + $PhC{\equiv}CH$ reaction. The remaining ethyl group could not be displaced. The reactivity in such metalation of acetylenes decreased in the order $Ba[AlEt_4]_2 > Sr[AlEt_4]_2 > Ca[AlEt_4]_2$. Indene also could be metalated with $Ca[AlEt_4]_2$ (34).



A few miscellaneous items remain:

Calcium and barium hydrides (CaH_2 and $BaH_{1.3}$) were found to catalyze the isomerization of 1-hexene at 100-350° to give trans-2-hexene and lesser amounts of the cis isomer, 3-hexene and hexane. Barium hydride was more active in this application than calcium hydride (35, 36). An organometallic mechanism involving organobarium and -calcium intermediates is a possibility, but it certainly is not required.

The direct synthesis of a strontium intercalation compound of graphite has been effected by French workers (37). A stoichiometry of SrC_6 was established for the first stage. An analogous CaC_6 also was prepared.

The reaction of calcium, strontium and barium halides with Ph_2NK in the presence of dioxane in THF solution gave the respective $M^{II}(Ph_2N)_2$ dioxanates (38).

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