CALCIUM, STRONTIUM AND BARIUM

ANNUAL SURVEY COVERING THE YEAR 1974

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I. PREPARATION OF ORGANOALKALINE EARTH COMPOUNDS

More examples of the reaction of diorganomercury compounds with alkaline earth metals have been published (eq. 1). In some cases the

$$Ar_2Hg + Ca \xrightarrow{\text{THF, } 40°} Ar_2Ca + Hg \qquad (1)$$

unsolvated diarylcalcium compounds were obtained directly, in others, tetrahydrofuran complexes were isolated. These could be desolvated in vacuo (1). The preparation of dimethylcalcium, diethylcalcium and -strontium, diallyl-, dibenzyl-, di-p-tert-amylbenzyl-, diphenyl- and diphenylethynyl-calcium, -strontium and -barium, dicyclopentadienyl- and diindenyl-calcium and -strontium and bis(vinylcarboranyl)-calcium by this procedure was described by West and Woodville in a patent (2). The NMR spectra of these products and other spectroscopic data are given.

Reactions of aryl iodides with strontium amalgam in THF were used to prepare arylstrontium iodides, ArSrI (Ar = Ph, o- and p-tolyl, α-naphthyl, α-thienyl) (3).

+Calcium, strontium and barium, Annual Survey covering the year 1973 see J. Organometal. Chem., 75(1974)5-12.

As might have been expected, organic derivatives of the alkaline earths metalate relatively acidic hydrocarbons, thus providing new organic compounds of these metals (2,4-6). The reaction of diphenylcalcium with indene, fluorene, triphenylmethane and diphenylmethane in THF gave di(indenyl)calcium, di(fluorenyl)calcium, bis(triphenylmethyl)calcium and bis(diphenylmethyl)calcium, respectively (2, 4). Methylcalcium iodide metalated fluorene in similar fashion in THF at -30° (5). Treatment of the fluorenylcalcium reagent thus generated with carbon dioxide at -70°, followed by acidic work-up, gave 9-fluorenecarboxylic acid in 93% yield. Similar metalation of indene with CH_3CaI, followed by carboxylation of the new calcium reagent, gave 3-indenecarboxylic acid (5). Triphenylmethylcalcium chloride also served as a metalating agent in THF solution, converting indene, cyclopentadiene, phenylacetylene and fluorene to the respective organocalcium species, R_2Ca or $RCaCl$ (6).

The factors important in the preparation of complexes of type $M(AlEt_4)_2$ (M = Ca, Sr, Ba) by reaction of triethylaluminum with the respective alkaline earth metal (degree of comminution and surface treatment of the metal M, nature of M, temperature, solvent) have been studied in some detail by Russian workers (7, 8).

2. REACTIONS OF ORGANOALKALINE EARTH COMPOUNDS

Kawabata and his coworkers have continued their studies of the reactions of methylcalcium iodide with an investigation of its action as a metalating agent, its carboxylation and its reactions with aromatic halides (5):

$$CH_3CaI + CO_2 \xrightarrow{-70^\circ} \xrightarrow{H_3O^+} CH_3CO_2H\ (57\%) + (CH_3)_2CO\ \ (17\%) + (CH_3)_3COH\ \ (11\%)$$

$$\mathrm{CH_3CaI + PhCl} \xrightarrow[\text{2) } \mathrm{CO_2}]{\text{1) THF, 25°, 49h}} \mathrm{PhCO_2H}\ \ (21\%)$$

$$\mathrm{CH_3CaI + PhBr} \xrightarrow[\text{2) } \mathrm{CO_2}]{\text{1) THF, 25, 49.5h}} \mathrm{PhCO_2H}\ \ (42\%)$$

$$\mathrm{CH_3CaI + PhI} \xrightarrow[\text{2) } \mathrm{CO_2}]{\text{1) THF, 25°, 49.5h}} \mathrm{PhCO_2H}\ \ (38\%)$$

n-Propylcalcium was much more effective:

$$\underline{n}\text{-}\mathrm{C_3H_7CaI + PhBr} \xrightarrow[\text{2) } \mathrm{CO_2}]{\text{1) THF, 20°, 40h}} \mathrm{PhCO_2H}\ \ (80\%)$$

French workers have examined reactions of organocalcium iodides with ketones in THF. The insoluble part of the reagent causes only reduction to the secondary alcohol which is the major product. The soluble portion of the reagent has Grignard-type reactivity, giving the respective tertiary alcohol (9). Addition is the favored process when the Barbier procedure is used (addition of the organic iodide and the ketone simultaneously to metallic calcium in THF). Improved yields and larger $C = O$ addition/reduction ratios were obtained when the hybrid reagents $\mathrm{CaZnR_4}$ (R = Me, Et, n-Pr) and $\mathrm{CaAl_2Et_8}$ were used instead of RCaI (10). Further examples of additions of organoalkaline earth reagents to enynes have been reported:

$$\mathrm{Et_2Ca + CH_2 = CH{-}C \equiv CR} \longrightarrow \xrightarrow{\mathrm{H_2O}} \mathrm{EtCH_2CH = C = CHR}$$

(25-30%)

(R = Me, Et, Ph, Vi, (ref. 11)
CH = CHMe, CMe = CH$_2$)

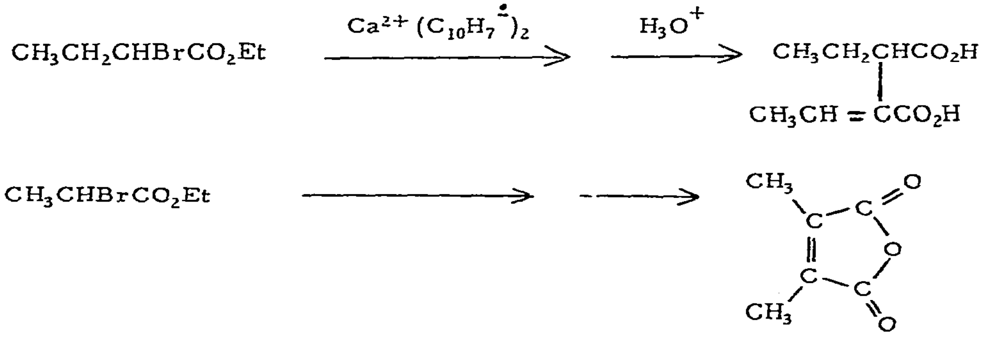
$$\mathrm{Et_2Ba + CH_2=CH-C\equiv CSR \longrightarrow \xrightarrow{H_2O} EtCH_2CH=C=CHSR}$$

$$(35\text{-}40\%)$$

$(\mathrm{R = Me, Et})$ (ref. 12)

Such double bond additions can initiate anionic polymerization of some olefins (2). In another study, polymerization of methyl methacrylate in 1, 2-dimethoxyethane was effected by triphenylmethylcalcium chloride, fluorenylcalcium chloride, diindenylcalcium, dicyclopentadienylcalcium and diphenylcalcium (13). Both homogeneous and heterogeneous processes were demonstrated to occur. Triphenylmethylcalcium chloride also initiated polymerization of styrene. A Russian group has evaluated organobarium compounds (barium diphenylethylenide (14) and $\mathrm{BaZnR_4}$ (R = Et, n-Bu) (15) and also strontium diphenylethylenide (16) as initiators for diene polymerization and copolymerization.

Reactions of calcium naphthalenide in liquid ammonia with α-bromoalkanoic acid esters gave unsaturated "dimers" (17):



3. OTHER STUDIES

The structural investigation of dicyclopentadienylcalcium by X-ray diffraction brought a surprising result: the coordination sphere about the calcium atom consists of two $\underline{h}^5$-C_5H_5, one $\underline{h}^3$-C_5H_5 and one $\underline{h}^1$-C_5H_5 ring (Fig. 1) (18). The overall crystal structure is shown in Fig. 2. Three crystallographically unique bridging cyclopentadienyl rings link the calcium atoms in the lattice. The mass spectrum of

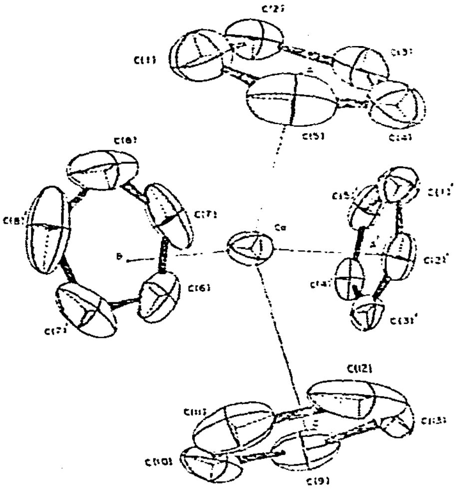


Fig. 1 The molecular geometry of $(C_5H_5)_2Ca$ (from ref. 18)

dicyclopentadienylcalcium (at 280°) showed not only R_2Ca^+ and RCa^+ species, but also $R_2Ca_2^+$ and $R_3Ca_2^+$ ions ($R = C_5H_5$) (18). The latter result from ion-molecule reactions in the mass spectrometer, e.g.:

$$(C_5H_5)_2Ca + C_5H_5Ca^+ \longrightarrow (C_5H_5)_3Ca_2^+$$

The complexes of difluorenylbarium with crown ethers and glycol ethers in THF were studied by optical spectroscopy. Complexes of type (Fl^-, Ba^{2+}, crown, Fl^-) and (Fl^-, crown, Ba^{2+}, crown, Fl^-) were observed (19).

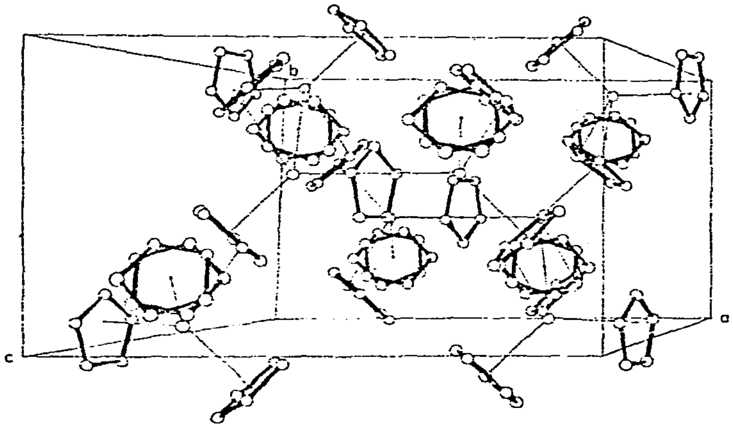


Fig. 2 The ab projection of the unit cell of $(C_5H_5)_2Ca$ (from ref. 18)

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