CALCIUM, STRONTIUM AND BARIUM

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The bis-phenylethynyl compounds of calcium, strontium and barium have been prepared by reaction of a liquid ammonia solution of the appropriate metal with phenylacetylene (1). All three could be isolated in the unsolvated form as thermally stable microcrystalline powders. The evidence obtained suggested that $Ca(C{\equiv}CPh)_2$ is polymeric in the solid state. It appears to dissolve initially in THF as a low polymer and depolymerizes slowly in THF solution, giving predominantly a dimeric species. The chemistry of these compounds was investigated:

$$(PhC{\equiv}C)_2M + CO_2 \xrightarrow{-78^{o}} \xrightarrow{H_3O^+} PhC{\equiv}CCO_2H$$

$$(PhC{\equiv}C)_2Ca + Ph_2C{=}O \longrightarrow \xrightarrow{H_3O^+} PhC{\equiv}CC(Ph)_2OH$$

$$(PhC{\equiv}C)_2Ca + HgCl_2 \longrightarrow (PhC{\equiv}C)_2Hg + CaCl_2$$

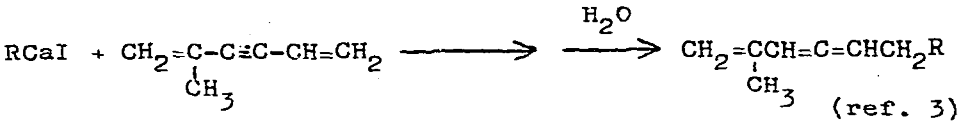
$$(PhC{\equiv}C)_2Ca + 2\ C_5H_6 \longrightarrow Ca(C_5H_5)_2 + 2\ PhC{\equiv}CH$$

The rate of reaction of these phenylethynyl compounds with Micheler's ketone decreased in the order Ba > Sr > Ca.

Further examples of the addition of organocalcium iodides to vinylacetylenes have been reported by Russian workers:

$$RCaI + CH_2{=}CHC{\equiv}CR' \xrightarrow{Et_2O} \xrightarrow{H_2O} RCH_2CH{=}C{=}CHR' \quad \text{(ref. 2)}$$

(R = Et, Pr, Bu, n-C_5H_{11}, i-C_5H_{11}, Ph, m-MeC_6H_4; R' = Me, Et, Pr, t-Bu)



$$RCaI + CH_2{=}C(CH_3){-}C{\equiv}C{-}CH{=}CH_2 \longrightarrow \xrightarrow{H_2O} CH_2{=}C(CH_3)CH{=}C{=}CHCH_2R \quad \text{(ref. 3)}$$

(R = Et, Pr, Bu, i-Bu, n-C_5H_{11}, Ph, m-MeC_6H_4)

$$RCaI + CH_2{=}CHC{\equiv}CSiMe_3 \longrightarrow \xrightarrow{H_2O} RCH_2CH{=}C{=}CHSiMe_3 + RCH_2CH_2C{\equiv}CSiMe_3 \quad \text{(ref. 4)}$$

(R = Et, Pr, Bu)

$$RCaI + CH_2{=}CHC{\equiv}CSR' \longrightarrow \xrightarrow{H_2O} RCH_2CH{=}C{=}CHSR' \quad \text{(ref. 5)}$$

(R = Et, Pr, Bu, Ph, m-MeC_6H_4; R' = Me, Et)

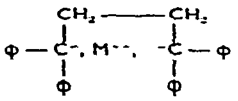
$$RCaI + CH_2{=}CHC{\equiv}CCMe_2OH \longrightarrow \xrightarrow{H_2O} RCH_2CH{=}C{=}CHCMe_2OH \quad \text{(ref. 6)}$$

(R = Et, Pr, C_5H_{11}, Ph, m-MeC_6H_4)

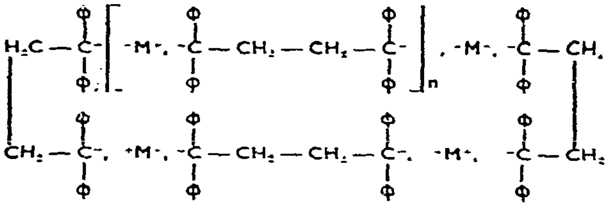
The alkyl- and arylcalcium iodides used in these studies were prepared by reaction of calcium shavings (activated by heating with magnesium and mercury at 150° under argon) with the respective organic iodide in refluxing diethyl ether (initiation with I_2).

The reaction of metallic calcium with dibutylzinc in diethyl ether gave $CaZnBu_4$ (7). This compound reacted with α,β-unsaturated ketones to give 1,4 conjugate addition and hydrogen abstraction, but no 1,2 C=O addition.

A new technique for preparation of alkaline earth adducts of activated olefins involves the use of a flow reactor for the continuous preparation of finely divided alkaline earth metals by cooling a mixture of metal vapor and argon (8). The diphenylethylene-barium adduct was prepared in this way in THF. The uv spectra of diphenylethylene solutions in THF over mirrors of sublimed calcium, strontium or barium were studied (9). The presence of dimeric species such as $\boxed{1}$, or more likely, $\boxed{2}$ (M = Ca, Sr, Ba), more highly polymerized aggregates, was indicated. Such solutions initiated the polymerization of 2-vinylpyridine.



$\boxed{1}$



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