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SOME ORGANO-COMPOUNDS OF CALCIUM, STRONTIUM AND BARIUM

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SUMMARY

Bis(2-phenylethynyl)calcium, Ca(C≡CPh)$_2$, and the corresponding strontium and barium compounds have been isolated as thermally stable solids. Some of their properties and reactions are described.

INTRODUCTION

There is apparently a considerable loss in stability in the metal–carbon bond in passing from beryllium and magnesium to calcium, strontium and barium. This is to be expected from a simple consideration of electronegativity differences and ionic radii but appears nevertheless to be more marked than in neighbouring groups of the periodic table. Thus, while alkyls and phenyls of potassium[1], scandium[2], and titanium[3] have been isolated in the solid state (though these compounds are as expected unstable to hydrolysis and in the case of titanium, to heat), calcium is apparently represented only by its triphenylmethyl derivatives $Ca(CPh_3)Cl$[4] and $Ca(CPh_3)_2$[5], both isolated as etherates. Several organo–calcium compounds are known to exist in solution as attested[6] by isolation of their derivatives after Grignard-type reactions. We now wish to report the isolation of 2-phenylethynyl compounds of calcium, strontium and barium. Failure, however, attended our repeated efforts to isolate simple alkyls and phenyls of calcium.

RESULTS AND DISCUSSION

Metallic calcium was allowed to dissolve in liquid anhydrous ammonia (at −78° to minimise amide formation) and the solution was treated at −78° with the theoretical quantity of phenylacetylene. After the rapid exothermic reaction had ended, tetrahydrofuran was added and the ammonia was removed. The solid product was collected by filtration, washed, and dried at reduced pressure and room temperature. Analysis indicated the formulation $Ca(C{\equiv}CPh)_2 \cdot (NH_3)_x$ where x lies between

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1 and 2. More stringent drying produced the unsolvated product as a white microcrystalline powder.

The corresponding strontium and barium compounds were prepared similarly. However, the products were partly soluble (Sr) or soluble (Ba) in tetrahydrofuran and were precipitated therefrom, solvated by tetrahydrofuran, by addition of n-hexane. Evacuation gave the unsolvated compounds. Bis(2-phenylethynyl)strontium was obtained as a white powder and bis(2-phenylethynyl)barium as a pale yellow powder.

These products are stable indefinitely in nitrogen but decompose at once in moist air. They are quite stable at raised temperatures, decomposition points (0.1 mm) being 320° (Ca), >360° (Sr), and 195° (Ba). When thermal decomposition sets in, it is very rapid and leaves a voluminous black residue which in the barium case gave phenylacetylene and acetylene on hydrolysis and was pyrophoric in air. All three compounds gave a positive colour test with Michler's ketone in the cold but $Ca(C{\equiv}CPh)_2 \cdot (NH_3)_x$ gave a colouration only when boiled.

Reactions of the 2-phenylethynyl compounds

When the compounds were carboxylated with carbon dioxide at $-78°$ in diethyl ether or tetrahydrofuran solution, 30–65% yields of phenylpropynoic acid were obtained. $Ca(C{\equiv}CPh)_2$ in benzene suspension reacted readily with benzophenone to give the expected diphenyl(2-phenylethynyl)methanol in 60% yield. When $Ca(C{\equiv}CPh)_2$ was treated with an equimolar quantity of mercuric chloride in tetrahydrofuran solution, an 80% yield of bis(2-phenylethynyl)mercury resulted.

As a means of comparing the electrophilic reactivities of the calcium, strontium and barium derivatives, they were separately boiled with benzene solutions of benzonitrile (2 moles in 0.05 *M* solution). The times which elapsed before a negative colour test was observed with Michler's ketone were: Ca, 120 h; Sr, 100 h; Ba, 25 h. From this we conclude that these compounds are moderately reactive and that the sequence of reaction rates reflects the presumed increase of bond polarity, and therefore of carbanionic nature of the organic radical, along the series Ca, Sr, Ba.

Bis(2-phenylethynyl)calcium effects an exchange with cyclopentadiene. Thus when cyclopentadiene monomer was boiled in tetrahydrofuran solution with $Ca(C{\equiv}CPh)_2$ and then carboxylated, dicyclopentadienedicarboxylic acid was produced in 80% yield. This indicates that the equilibrium:

$$Ca(C{\equiv}CPh)_2 + 2\,C_5H_6 \rightleftharpoons Ca(C_5H_5)_2 + 2\,HC{\equiv}CPh$$

lies well to the right (and may well provide a ready synthesis for dicyclopentadienylcalcium). An alternative explanation in terms of preferential carbonation of a minority of $Ca(C_5H_5)_2$ or $Ca(C_5H_5)(C{\equiv}CPh)$ seems less likely.

Solvates are formed readily. Thus, when $Ca(C{\equiv}CPh)_2$ or $Ba(C{\equiv}CPh)_2$ was treated with tetrahydrofuran or 1,2-bis(dimethylamino)ethane, solid amorphous products were formed which were stable to pumping at room temperature, gave a positive test with Michler's ketone, and showed strong solvent absorptions in the infrared.

Infrared spectra

These were obtained from Nujol mulls and the principal absorptions are as follows (cm^{-1}):

Bis(2-phenylethynyl)calcium: 3064 w, 3026 w, 2036 m, 1952 w, 1886 w, 1602 w, 1581 w, 1493 m, 1448 m, 1275 w, 1192 m, 1177 m, 1155 w, 1069 m, 1025 m, 911 m, 767 (sh), 750 s, 686 s, 539 m, 491 m.

Bis(2-phenylethynyl)strontium: 3058 w, 3018 w, 2023 w, 1943 w, 1876 w, 1605 w, 1580 w, 1497 s, 1446 m, 1185 w, 1173 m, 1149 w, 1066 m, 1021 m, 909 m, 762 (sh), 748 s, 687 s, 535 m, 480 m.

Bis(2-phenylethynyl)barium: 3052 w, 3012 w, 2017 w, 1947 w, 1886 w, 1597 m, 1568 w, 1497 s, 1443 m, 1245 w, 1191 m, 1179 m, 1158 w, 1072 m, 1028 m, 1000 w, 913 m, 895 (sh), 866 w, 794 w, 765 (sh), 755 s, 694 s, 540 m, 484 m.

The spectra are closely similar to those previously observed[7] for the alkali metal derivatives $M(C{\equiv}CPh)$ where M = Na, K, Rb, Cs. They show the characteristic frequencies of a phenylethynyl derivative, *e.g.* for the calcium compound: CH stretch at 3064, 3026; CH out-of-plane bend at 750 and 687; CH in-plane bend at 1070, 1025; CC stretch (ring) at 1602, 1581 (conjugation band), 1493; and CC acetylenic stretch at 2036 (all cm^{-1}). Comparison of the acetylenic C≡C stretching frequency with that of phenylacetylene is difficult as in the latter compound there must be strong coupling with the CH stretching mode. However, it is of interest that there is a decrease in frequency of about 20 cm^{-1} along the series $M(C{\equiv}CPh)_2$ (M = Ca→Ba) in accord with a gradual increase in the importance of the ionic contribution M^{+}-$(C{\equiv}CPh)^{-}$.

The intensity of the C≡C stretching mode, weak in phenylacetylene itself, is greatly reduced again in the Ca, Sr and Ba derivatives, as it is in NaC≡CPh. It is accompanied, in the spectra of all four metal compounds, by two further bands, equalling it in intensity, at rather longer wavelengths. Thus $Ba(C{\equiv}CPh)_2$ absorbs at 1947 and 1886 cm^{-1}, in addition to 2017 cm^{-1}'.

The far infrared spectra show medium intensity absorptions at 378 (Ca), 353 (Sr) and 347 cm^{-1} (Ba), together with a broad absorption at around 240 cm^{-1} in all three cases. The calcium compound alone shows a strong band at 324 cm^{-1} which is presumably associated with a Ca–C stretching mode, as this type of vibration is the only one expected to show a strong dependence on the nature of the metal. A comparison spectrum of NaC≡CPh showed only bands at 353 cm^{-1} and ~250 cm^{-1}.

Molecular weight and solubility measurements

The compounds are insoluble in benzene but are soluble in tetrahydrofuran, in which well-dried solvent ebullioscopic molecular weight determinations were performed on $Ca(C{\equiv}CPh)_2$ under a nitrogen atmosphere. Addition of the solid $Ca(C{\equiv}CPh)_2$ to the boiling solvent, in which it rapidly dissolved, did not at once produce any elevation in boiling-point, but a gradual asymptotic rise was observed which reached a steady value after about 40 min. When an additional quantity was added, equilibrium was again not reached for a similar period. The final equilibrium values approximately corresponded with a dimeric species (molecularity 1.9 in 0.013 *M* and 2.2 in 0.032 *M* solutions). When the solvent was removed under reduced pressure from a freshly made solution, the unsolvated compound remained. A solution, however, which had been boiled under reflux for some hours gave a tetrahydrofuran-solvated residue on evaporation, the infrared spectrum being similar to that of the starting material except for the addition of peaks assignable to coordinated tetrahydrofuran. The inference must be that $Ca(C{\equiv}CPh)_2$ is polymeric in the solid state, dissolves as a low polymer, and is slowly depolymerised by solvation possibly giving a predominant dimer. The solid polymeric $Ca(C{\equiv}CPh)_2$ may well have a structure similar to that established[8] for dimethylberyllium.

It is noteworthy that an "aged" solution dissolves further solid only very slowly, but solutions of concentration up to at least 0.4 *M* can be obtained if prepared in a single operation. X-ray powder photographs showed apparent isomorphism between the Ca, Sr and Ba compounds so that the latter two compounds are also presumably polymeric in the solid state.

EXPERIMENTAL

Details of solvent purification and nitrogen supply are as previously given[2]. Calcium and strontium were supplied by Koch-Light Ltd. and barium by Hopkin and Williams Ltd.; they were used as obtained. Ammonia was dried, as a liquid, by sodium and was then distilled directly into the reaction vessel. Phenylacetylene was distilled under reduced pressure, dried with calcium hydride and redistilled before use.

Calcium and strontium were estimated by EDTA titration. Barium was determined by X-ray fluorescence by Mr. K. Leen, whom we thank. The 2-phenylethynyl radical was estimated spectrophotometrically at 246 nm as phenylacetylene after hydrolysis and extraction with cyclohexane, the spectrum of the cyclohexane solution in the region 200–300 nm being identical with that obtained from an authentic solution of phenylacetylene.

All operations involving the compounds $M(C{\equiv}CPh)_2$ were carried out in a nitrogen atmosphere or under vacuum.

Preparation of bis(2-phenylethynyl)calcium

Calcium (2.0 g; 0.05 mole) was dissolved in liquid ammonia (200 ml) in a two-necked flask fitted with an ammonia condenser and dropping funnel, the apparatus being connected with a low pressure nitrogen supply. The flask was cooled in a carbon dioxide/acetone bath. Phenylacetylene (11.0 ml; 0.1 mole) was added dropwise with magnetic stirring. The vigorous reaction was accompanied by evolution of gas and deposition of a white solid. The blue colouration of the solution was discharged when about one quarter of the acetylene had been added but reaction continued until complete addition. On warming to −33° the white bis(2-phenylethynyl)calcium dissolved but was reprecipitated on the addition of tetrahydrofuran (150 ml). The ammonia was allowed to evaporate and the tetrahydrofuran-insoluble material was collected by filtration and washed with n-hexane before overnight evacuation at room temperature to produce a bis(2-phenylethynyl)calcium–ammonia adduct. The complex, on exposure to air, smelled strongly of phenylacetylene and ammonia and gave a dark green colouration with Michler's ketone only when boiled with the latter before hydrolysis and oxidation. The ammonia content of the complex was quite variable, the formulations $(C_6H_5C{\equiv}C)_2Ca \cdot 0.9\ NH_3$, 1.6 NH_3 and 1.8 NH_3 being obtained from estimations on samples obtained from different experiments, each having been subjected to similar evacuation procedures. The ammonia was estimated by alkali back-titration of the dilute acid in which the ammonia, removed from the complex by alkaline hydrolysis or prolonged high vacuum treatment at 100°, had been absorbed. Evacuation of the ammonia complex at 95° for 3 h produced the pure unsolvated compound which readily gave the Michler's ketone test in the cold. (Found: Ca, 16.6 and 16.4; $C_6H_5C{\equiv}C$, 80.1. $C_{16}H_{10}Ca$ calcd.: Ca, 16.5; $C_6H_5C{\equiv}C$, 83.5%.)

Preparation of bis(2-phenylethynyl)strontium and bis(2-phenylethynyl)barium

These were prepared using a method similar to that described for the calcium compound. However, because the strontium and barium compounds are soluble in tetrahydrofuran, it was necessary to precipitate them therefrom with n-hexane after removal of the ammonia. The unsolvated compounds were obtained by evacuation (0.1 mm) at 80° for 3 h (Sr) and 50° for 16 h (Ba) to remove tetrahydrofuran. (Found: Sr, 30.4; Ba, 40.4. $C_{16}H_{10}Sr$ and $C_{16}H_{10}Ba$ calcd.: Sr, 30.2 and Ba, 40.4% respectively.)

Carboxylation reactions

Bis(2-phenylethynyl)calcium (1.0 g) in tetrahydrofuran (40 ml) was exposed to CO_2 for 4 h at −78°. The solvent was removed and replaced by diethyl ether. Hydrolysis and separation gave 0.73 g (60%) of phenylpropynoic acid m.p. 136° (lit. m.p. 137°) of identical infrared spectrum with an authentic sample. Carboxylation in diethyl ether gave only 30% yield. Carboxylation of $Sr(C{\equiv}CPh)_2$ in tetrahydrofuran gave 65% yield; $Ba(C{\equiv}CPh)_2$ in diethyl ether gave 30%.

Bis(2-phenylethynyl)calcium and benzophenone

A benzene suspension (80 ml) of bis(2-phenylethynyl)calcium (1.2 g, 0.005 moles) was refluxed with benzophenone (1.8 g, 0.01 moles) for 30 min, the solution clearing immediately on addition of the ketone. Thence hydrolysis followed by filtration, separation of the organic layer, and evaporation produced a yellow oil, which eventually crystallised. The solid was recrystallised from n-hexane to yield diphenyl-(2-phenylethynyl)methanol (1.6 g, 60% yield), m.p. 83.5–84° lit. 82°. (Found: C, 88.7, H, 5.7. $C_{21}H_{16}O$ calcd.: C, 88.7; H, 5.7%.)

Mercuric chloride and bis(2-phenylethynyl)calcium

Bis(2-phenylethynyl)calcium (0.62 g, 0.002 moles) was refluxed with mercuric chloride (0.70 g, 0.002 moles) in tetrahydrofuran (60 ml) for 40 h. Replacement of the THF by ether solution, dilute hydrochloric acid hydrolysis, evaporation and recrystallisation from an ether/hexane mixture produced bis(2-phenylethynyl)mercury (0.83 g) in 80% yield, m.p. 124–124.5° lit. 124.5–125°. (Found: C, 47.7; H, 2.5. $C_{16}H_{10}Hg$ calcd.: C, 47.7; H, 2.5%.)

Cyclopentadiene and bis(2-phenylethynyl)calcium

Freshly cracked cyclopentadiene monomer (3.0 ml, 4 moles) was refluxed with bis(2-phenylethynyl)calcium (2.10 g, 1 mol) in tetrahydrofuran (100 ml) for 18 h. Carboxylation and purification of the hydrolysed product in the manner described previously produced dicyclopentadiene dicarboxylic acid (1.43 g) in 80% yield. After recrystallisation from an ethanol/hexane mixture it had m.p. 211° lit. 204–205°.

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