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ORGANOCALCIUM IODIDES

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Introduction

In connection with studies on the mechanism of some reactions involving organomagnesium halides it is necessary to replace the —MgX group of the intermediate compound by another in order to get a compound that lends itself to ready identification. Unfortunately this is not always possible. Accordingly, a study has been made of the related organocalcium iodides in order to determine whether the —CaI group is more suitable for such replacements than is the —MgX group.

Beckmann[1] has made the only extensive study of organocalcium halides. Dufford, Nightingale and Calvert[2] investigated the luminescence of phenylcalcium and ethylcalcium iodides, and Gilman and Pickens[3] used phenylcalcium iodide in a study of the mechanism of the reduction of azobenzene by organometallic halides.

A number of experiments have shown that the organocalcium halides are generally devoid of any promise in the reactions that have made the organomagnesium halides so useful. First, the formation of organocalcium halides appears to be restricted to iodides. Second, only primary alkyl iodides undergo reaction with calcium. Even in this limited category there is an exception, for benzyl iodide gave no positive test to indicate the formation of benzylcalcium iodide. Third, the reaction between the alkyl iodide and calcium is quite sluggish and irregular and not always certain. Fourth, the yields of organocalcium iodides are far from satisfactory. This is due in part to a pronounced coupling side reaction leading to the formation of R–R compounds. Fifth, the organocalcium iodides are less reactive generally than the corresponding organomagnesium halides.

Contrary to the results of Beckmann,[1] the organocalcium iodides are not sparingly soluble in ether. The solid compound invariably deposited during the preparation of organocalcium iodide is not the organometallic halide. Instead it is very probably the di-etherate of calcium iodide.

Experimental Part

Preparation of Organocalcium Iodides.—The start and progress of the reaction between calcium and iodide vary with the kind of calcium and the degree of fineness. A variety of rasped calcium obtained from Kahlbaum was somewhat less active than shavings freshly turned from sticks of calcium. Even a given type of calcium gave irregular results, depending

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[1] Beckmann, *Ber.*, **38,** 904 (1905).

[2] Dufford, Nightingale and Calvert, This Journal, **47,** 95 (1925).

[3] Gilman and Pickens, *ibid.*, **47,** 2406 (1925).

in large part on exposure to the atmosphere. The material was always covered, prior to use, with kerosene. However, even such covered calcium tarnished when the containers were loosely stoppered. The tarnished material entered very sluggishly into reaction with the iodides and therefore was not used.

It is necessary to use a higher concentration of iodine in ether to catalyze reactions with calcium than is needed with magnesium. The beginning of reaction between calcium and the organic iodide is shown by the disappearance of the free iodine used to catalyze the reaction, followed by the formation of a light gray or white precipitate. At times the reaction is brisk enough to cause the ether to reflux gently. These changes cannot be taken as absolute criteria for the formation of organocalcium iodides, inasmuch as the organocalcium iodides appear to have a pronounced tendency to couple with the excess of alkyl or aryl iodide that is generally present. The color test with Michler's ketone, previously described by Gilman and Schulze,[4] is reliable.

The reaction between calcium and the alkyl or aryl iodide in ether can be carried out in the conventional three-necked flask provided with a mechanical stirrer, or the reactants can be sealed in a glass container that is shaken mechanically at room temperature. The latter arrangement offers certain advantages in some preparations. Reaction between ethyl iodide in ether and calcium started in various experiments over a time range of 15 minutes to six hours. *n*-Butyl iodide started to react after ten hours, and in one experiment after 48 hours. However, the same halide when shaken in a sealed tube gave a positive test[4] after two hours. *n*-Octyl iodide gave a positive test after being shaken for 24 hours in a sealed glass container. Iodobenzene, when stirred with ether, a little iodine and calcium in a three-necked flask, gave a positive test in some cases after two hours and in others up to seven and one-half hours. In one experiment, when stirring was not used, a positive test was obtained only after 72 hours.

Ethyl bromide, *iso*propyl iodide, *tert.*-butyl iodide, benzyl bromide and benzyl iodide gave no positive tests after being shaken with calcium. The *tert.*-butyl iodide underwent a reaction but there was no positive test for the corresponding organocalcium iodide.[5] Benzyl iodide when shaken

[4] Gilman and Schulze, THIS JOURNAL, **47,** 2002 (1925). Unpublished work on calcium, barium and strontium dialkyls and diaryls shows that all of these organometallic compounds give positive tests. The color test with beryllium diaryls is not conclusive.

[5] *tert.*-Butyl bromide in ether reacts with *magnesium.* However, a positive test is obtained only when the Michler's ketone solution[4] is added in the early part of the vigorous reaction. When the ether has ceased to boil no positive test is obtained. Preliminary experiments indicate that the *tert.*-butylmagnesium iodide that is first formed undergoes dissociation to magnesious bromide (—MgBr) and the *tert.*-butyl radical [$(CH_3)_3C$-]. The radical then appears to undergo a considerable disproportionation to trimethylmethane [$(CH_3)_3CH$] and *iso*butylene [$(CH_3)_2C = CH_2$]. Gomberg has given an excellent proof for existence of the magnesious halides [*Chem. Rev.*, **2**, 301

in a sealed bottle for two to three weeks also underwent a reaction but gave no positive test.

It was hoped that the secondary reaction between organocalcium iodides and alkyl iodides could be overcome by removing the organocalcium halide as fast as it formed. For this purpose, advantage was taken of the very suggestive experiments made by Gilliland and Blanchard.[6] They prepared phenylmagnesium bromide by allowing an ethereal solution of bromobenzene to descend through a column of magnesium turnings, the solution being highly diluted, before reaching the column, by the ether condensed from the vapors of the solution boiling in the receiving flask. In this manner there is a minimal contact between the organometallic halide and the organic halide from which it is prepared. However, the same principle when extended to the preparation of ethylcalcium iodide was found to be unsuccessful. When an ethereal solution of ethyl iodide was percolated through a column of calcium shavings contained in a tube 20 cm. long and 1.5 cm. in diameter, the reaction could be started only by using a concentrated solution of iodide in ether. The reaction, once started, was quite irregular. When the concentration of ethyl iodide was low, the reaction stopped altogether; when the solution was sufficiently concentrated to insure a continuous reaction, very little ethylcalcium iodide formed, probably as a result of the coupling reaction mentioned above. It is, of course, possible that the ethylcalcium iodide owes its gradual disappearance to a partial dissociation of the kind described in Ref. 5. A further difficulty in the use of the column of calcium is the marked clogging due to the deposition of the di-etherate of calcium iodide. Quite probably there is an effective concentration of ethyl iodide to warrant the use of the column, but such optimal conditions were not further investigated.

Ethylcalcium Iodide.—The white precipitate that forms when calcium reacts with ethyl iodide in ether was analyzed by Beckmann,[1] and he concluded that it was the mono-etherate of ethyl-calcium iodide, $C_2H_5CaI.(C_2H_5)_2O$. This formula is very probably incorrect, for apparently the same compound is formed when calcium undergoes reaction with any alkyl iodide. In no case did it give a positive color test[4] for an organocalcium iodide after being filtered and washed with anhydrous ether. When organocalcium iodides were shown to be present by the preparation of characteristic derivatives, the perfectly clear supernatant liquid always gave a positive color test, whereas the precipitate never gave a test. Evidently the few organocalcium iodides that were studied are soluble in ether. However, since they never were obtained in high yields no reasonable predictions can be made concerning their solubility in more concentrated solutions.

(1925)] and a study in this Laboratory of the mechanism of the reduction of azobenzene by organomagnesium halides and magnesious iodide supports his results.

References to other mechanisms for the diminution in yield of organomagnesium halides are given in Ref. 2 of a paper by Gilman and Kirby [THIS JOURNAL, **48,** 1733 (1926)].

[6] Gilliland and Blanchard, *ibid.*, **48,** 410 (1926).

It is difficult to obtain a perfectly pure sample of the white precipitate.[7] The compound is usually contaminated with bits of unaltered calcium, calcium oxide, basic calcium iodide and possibly calcium hydroxide. Because of these impurities not much reliance can be placed on the calcium analysis made by Beckmann,[1] and the only quantitative analysis he made was for calcium. A fairly homogeneous sample was obtained by treating calcium with a liberal excess of ethyl iodide in a dry atmosphere. The material was rapidly filtered, washed with anhydrous ether, transferred to a glass-stoppered weighing bottle and dried in a vacuum desiccator.

A sample prepared in this manner for analysis contained 58.18 and 57.97% of iodine. The compound that best agrees with such results is the di-etherate of calcium iodide, $CaI_2.2(C_2H_5)_2O$, which contains 57.4% of iodine. Beckmann's ethylcalcium iodide mono-etherate, $C_2H_5CaI.(C_2H_5)_2O$, contains 46.9% of iodine. A gas is evolved when this solid is treated with water. Beckmann stated that the gas was ethane contaminated with some ether. The gas was not unsaturated, and its characteristic ethereal odor coupled with its complete solubility in concd. sulfuric acid indicated that it was ether and not ethane. Two samples were analyzed.

Anal. Subs., 0.3382, 0.2944: 37.3, 32.7 cc. of gas (corr.). Calcd. for $CaI_2.2(C_2H_5)_2O$: 34.2, 29.8 cc.

The small amount of ethylcalcium iodide present accounts in part for the lack of success in obtaining characteristic anilides with phenyl- and naphthylisocyanates. However, another alkylcalcium iodide (*n*-butyl) gave the characteristic anilide with α-naphthylisocyanate.

***n*-Butylcalcium Iodide.**—When 12 g. (0.3 mole) of calcium was treated with 55.2 g. (0.3 mole) of *n*-butyl iodide in 100 cc. of ether, considerable insoluble material was deposited. During the preparation, about 2 liters of gas was evolved. The gas was saturated, inflammable and insoluble in concd. sulfuric acid. Undoubtedly it was largely *n*-butane, formed by the reaction of a trace of moisture in the reagents with *n*-butylcalcium iodide.

After the reaction had been allowed to complete itself, over two days, the mixture was hydrolyzed with dil. hydrochloric acid. Considerable heat is evolved during the hydrolysis of any organocalcium halide, and a part of this is very probably due to the hydration of calcium iodide. The ethereal layer was separated, dried and 10 g. of liquid was obtained; b. p., 120–130°. If the mixture were entirely *n*-octane this would correspond to a 59% yield. However, *n*-butyl alcohol and *n*-butyl iodide might have been contained in this fraction. Accordingly, the mixture was first refluxed for four hours with 10% sodium hydroxide solution; this was then extracted with ether, the etheral solution carefully shaken with concd. sulfuric acid to remove ether and *n*-butyl alcohol, and finally fractionally distilled. In this way, despite mechanical losses, there was obtained a 29.2% yield of *n*-octane.

In another run the *n*-butylcalcium iodide was characterized by the preparation of *n*-valeryl-α-naphthalide obtained from the reaction with α-naphthylisocyanate.

***n*-Octylcalcium Iodide.**—A mixture of 0.05 mole of calcium and an equivalent amount of *n*-octyl iodide in an excess of ether was shaken for 24 hours in a sealed flask. A heavy, white precipitate formed and the supernatant liquid gave a positive color test for *n*-octylcalcium iodide. After hydrolysis, the ether layer yielded 2 g. or a 17.8% yield of hexadecane, $C_{16}H_{34}$.

Phenylcalcium Iodide.—Phenylcalcium iodide was treated with phenylisocyanate,

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[7] Experiments now in progress show that it is possible to prepare unusually pure, ether-free organomagnesium halides in a special apparatus through which circulates pure, dry hydrogen.

and to the reaction mixture was then added a slight excess of diethyl sulfate. After refluxing for an hour, the mixture was hydrolyzed and then worked up in the customary manner. Some benzanilide, the normal reaction product of phenylcalcium iodide and phenylisocyanate, was obtained. Practically all of the diethyl sulfate was recovered, and there was no indication of the formation of the desired imino ether, $C_6H_5N=C(OC_2H_5)(C_6H_5)$. This ether would have resulted by the replacement of the —CaI group attached to oxygen by an ethyl group of diethyl sulfate.[8]

A vigorous reaction occurs during the addition of an equivalent of benzoyl chloride to phenylcalcium iodide. At the end of the addition there was a strong test for phenylcalcium iodide, and benzoyl chloride was present as evidenced by its characteristic odor. In order to complete the reaction, the mixture was refluxed for 24 hours. Even after this protracted digestion of a 0.1-mole run, there was present in the mixture not only benzoyl chloride, as might have been expected, but also some phenylcalcium iodide. This emphasized in a striking manner the relatively less activity of organocalcium iodides when compared with the corresponding organomagnesium halides.[9] On working up the hydrolyzed reaction products, there were obtained a 35% yield of iodobenzene and 5% of triphenylmethane. The triphenylmethane probably owes its formation to the reduction of triphenylcarbinol when the unaltered calcium reacts with water during hydrolysis.

In another experiment the reaction between phenylcalcium iodide and benzoyl chloride was forced by refluxing for several hours in an ether-benzene solution. Under these conditions the phenylcalcium iodide was used up, and about 1% of triphenylcarbinol was obtained in addition to some unaltered iodobenzene and benzoyl chloride, benzoic acid and a small amount of an apparently intractable tar.

Despite the significant amounts of iodobenzene recovered, it appears that phenylcalcium iodide is obtained in higher yields than the other organocalcium iodides that were studied. With this arylcalcium iodide less of the di-etherate of calcium iodide separates than is the case with the alkyl calcium iodides.

Summary

Organocalcium iodides can be prepared in poor yields from a limited class of iodides. They are soluble in ether and less reactive than the corresponding organomagnesium halides.

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[8] Under like conditions, phenylmagnesium bromide also gives benzanilide and there is no replacement of the —MgX group by an ethyl group. Compare Gilman and Kinney, THIS JOURNAL, **46**, 493 (1924).

[9] In this connection mention should be made of the unreactivity of phenylcalcium iodide towards azobenzene [Gilman and Pickens, *ibid.*, **47**, 2406 (1925)]. Also, unpublished results show that acid chlorides undergo ready reaction with organo-magnesium halides to give good yields of tertiary alcohols.