Reactions of Methylcalcium Iodide

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Methylcalcium iodide was shown to be a useful organometallic reagent in several fundamental organic reactions in tetrahydrofuran. Reactions at −30° with benzaldehyde, acetone, benzophenone, methyl acetate, and diethyl carbonate gave the corresponding addition products in good yields. In the reaction with methyl crotonate, the carbonyl addition much predominated over the 1,4 addition. Both the coupling and the addition reactions were observed in the reactions with acid halides. The reagent gave the corresponding ketones in low yields by the reaction with nitriles, reacted but slowly with benzyl chloride and 1,1-diphenylethylene, and did not react with cyclohexene.

The development of organocalcium chemistry has been very slow when compared with that of other organometallic areas. The slow progress could have been due to the lack of a simple method to prepare organocalcium compounds. In a previous paper,[1] we demonstrated that the reaction of organic halides with calcium metal in tetrahydrofuran gave the corresponding organocalcium halides in much better yields than those available in the literature, and the range of suitable halides was extended (eq 1). The

$$\mathrm{RX + Ca \longrightarrow RCaX} \qquad (1)$$

key ingredient appeared to be the availability of higher purity calcium metal than was previously obtainable. In the present study, we aimed to elucidate the property of methylcalcium iodide in several fundamental organic reactions in tetrahydrofuran.

Although reactions of organocalcium iodides have been studied,[2-20] the available data in the literature are limited. An important problem that troubled the previous authors was the low yield of organocalcium halides. Nevertheless, reactions of arylcalcium iodides were relatively well investigated. Reaction of phenylcalcium iodide with benzophenone anil gave triphenylmethylaniline in 78% yield;[4] with benzoyl chloride, ethyl benzoate and benzophenone gave triphenylmethanol in 94, 80, and 80% yields, respectively;[7] that with α-bromonaphthalene gave after carboxylation α-naphthoic acid in 98% yield;[7] that with pyridine gave a mixture of mono- and diphenylated pyridine.[7] Metalation of fluorene, indene, triphenylmethane, pentafluorobenzene and thiophene by phenylcalcium iodide gave the expected products in 10–53% yields.[10,16] Examples of the addition of arylcalcium iodides to vinylacetylenes have been reported.[9,11,12,14,15] Yields of products were low or were not given in the reactions of arylcalcium iodides with benzaldehyde,[2] phenyl isocyanate,[3] benzonitrile,[4] dibenzofuran,[4] dibenzothiophene,[5] and anisol.[7]

On the other hand, only a very few data are available in the literature on the reaction of aliphatic organocalcium halides. Moreover, yields of products were generally low in these cases. Contrary to the case of arylcalcium iodides,[7,10,16] carboxylation of alkylcalcium iodides did not quantitatively give the corresponding carboxylic acids.[6,7] The reaction of methylcalcium iodide with benzaldehyde gave α-methylbenzyl alcohol in only 10% yield;[7,17] reaction with thiophene gave after carboxylation thiophene-2-carboxylic acid in 21% yield.[7] Bogatskii and coworkers[8] reported that methylcalcium iodide promoted the aldol condensation of acetone and other carbonyl compounds, and that it did not undergo the addition reactions to these carbonyl compounds. Chastrette and Gauthier[18] reported that a solution of methylcalcium iodide in tetrahydrofuran underwent only addition to diisopropyl ketone to give α,α-diisopropylethanol, while the solid methylcalcium iodide underwent only reduction of the ketone. Cherkasov and coworkers[9,11-15,19,20] reported examples of the addition of alkylcalcium iodides to vinylacetylenes. Metalation of carbon acids by alkylcalcium iodides was reported to result in low yields of the expected products.[10]

Judging from these limited results reported by previous authors, organocalcium halides seem to resemble organolithium reagents and should be useful in organic syntheses. However, available data in the literature are limited and yields of products by previous authors were generally low especially in the aliphatic series. If the limitation is due to difficulties in the preparation of organocalcium halides, and their low yields are derived from some impurities contained in the calcium metal and/or the organocalcium reagents, organocalcium halides might yet be useful in organic syntheses if these factors could be overcome. These difficulties have been overcome,[1]

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and in this paper we examined the utility of methylcalcium iodide in several fundamental organic reactions.

Results and Discussion

We prepared methylcalcium iodide in tetrahydrofuran according to the procedure reported previously.[1] Owing to the poor solubility in tetrahydrofuran, the methylcalcium iodide was obtained as a suspension. The suspension was used for further reactions without the isolation of the methylcalcium iodide. We added a tetrahydrofuran solution of various reactants to this suspension at −30°. Yields of products were, therefore, calculated based on the amount of methyl iodide used in the preparation of methylcalcium iodide. We also estimated the yields of products based on methylcalcium iodide and gave these in parenthesis in the text. This estimation was based on the result that the yield of methylcalcium iodide in tetrahydrofuran was generally 91–93% based on methyl iodide.[1]

We used calcium metal of higher purity than was available before. This made several improvements upon the experimental procedure of the reaction of organocalcium halides. Bryce-Smith and Skinner[7] as well as Chastrette and Gauthier[18,21] activated calcium by amalgamation, and Cherkasov and coworkers[9,11–15,19,20] activated calcium by heating with magnesium and mercury. Therefore, there would be some organomercury or organomagnesium compounds mixed in their organocalcium iodides, and their experimental results could be influenced by the presence of these impure organometallic compounds. Since the activation was not necessary when calcium metal of higher purity was used, the effect of such impure organometallics would be minimized.

The yields of alkylcalcium iodides by previous workers were generally very low, and a considerable amount of calcium iodide produced by the Wurtz-type coupling, the most important side-reaction of reaction 1, was present. The presence of such a by-product might exert some influence upon the organic reactions of alkylcalcium iodides, since the presence of lithium halides was reported to exert a large influence upon the reaction of lithium carbenoids,[22] and the presence of magnesium halides was also reported to produce a remarkable effect on the reactions of organozinc[23,24] and organocadmium compounds.[25,26] We obtained methylcalcium iodide 91–93% yield using the higher purity calcium metal, and the influence of calcium iodide would be minimized.

Reaction of methylcalcium iodide with acetone gave *tert*-butyl alcohol in 49–51% (53–56%) yield. We also observed the formation of methane in 37–39% (40–43%) yield during the reaction. The result is in a striking contrast to that reported recently by Bogatskii and coworkers.[8] They observed only the aldol condensation of acetone to diacetone alcohol. We feel some doubt on the purity of their methylcalcium iodide. Calcium metal and methylcalcium iodide are sensitive to atmospheric oxygen and moisture. When the calcium metal and/or methylcalcium iodide were improperly treated, oxide and hydroxide of calcium would be introduced to the reaction system. These compounds are strong inorganic bases and would facilitate the aldol condensation, but would not give *tert*-butyl alcohol by the reaction with acetone.

Reaction of methylcalcium iodide with an excess of benzophenone gave α,α-diphenylethanol in 76% (82–84%) yield. When a nearly equimolar amount of benzophenone was used, the yield of α,α-diphenylethanol was lower, and a part of methylcalcium iodide remained unchanged in the reaction system. The result was due to the fact that we used an excess of calcium metal in the preparation of methylcalcium iodide. The reaction of metallic calcium with benzophenone to form benzophenone calcium ketyl seemed to be much faster than the addition reaction of methylcalcium iodide with benzophenone.

Reaction of methylcalcium iodide with benzaldehyde gave α-methylbenzyl alcohol in 55–64% (59–70%) yield. Meanwhile Bryce-Smith and Skinner[7] as well as Bogatskii and coworkers[17] obtained the alcohol only in 10% yield by the same reaction in tetrahydrofuran at −50°. The discrepancy could be ascribable to the difference in the purity of methylcalcium iodide.

The reaction of methylcalcium iodide with methyl acetate gave *tert*-butyl alcohol in 70–71% (75–78%) yield. During the reaction, we observed the formation of methane in 17–21% (18–23%) yield. The reaction with diethyl carbonate gave *tert*-butyl alcohol and acetone in 68–73% (73–80%) and 3–6% (3–7%) yields, respectively. The reaction with an α,β-unsaturated ester, methyl crotonate, gave the carbonyl adducts, 2-methyl-3-penten-2-ol and ethylideneacetone, in 50% (54–55%) and 4% (4%) yields, respectively, together with a small amount of methyl isovalerate. During the reaction, we observed the formation of methane in 17% (18–19%) yield. Thus the carbonyl addition predominated over the 1,4 addition. This result forms a marked difference with the case of the reaction of calcium zinc tetrabutyl with α,β-unsaturated ketones. The latter reaction was reported to show 1,4 addition and hydrogen abstraction without carbonyl addition.[27]

We observed both coupling and addition reactions between methylcalcium iodide and acid chlorides. The reaction of methylcalcium iodide with benzoyl chloride gave α-methylstyrene in 70% (75–77%) yield, together with a small amount of acetophenone and α,α-dimethylbenzyl alcohol. The reaction of methylcalcium iodide with acetyl chloride gave *tert*-butyl alcohol and *tert*-butyl acetate in 22–31% (24–34%) and 19–26% (20–29%) yields, respectively, together with a small amount of acetone. During the reaction, we observed the formation of methane in 25–26% (27–29%) yield.

Reaction of methylcalcium iodide with acetonitrile gave acetone only in 9–14% (10–15%) yield, and methane formed in 60% (64–66%) yield during the reaction. The hydrogen abstraction reaction predominated over

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TABLE I

REACTIONS OF METHYLCALCIUM IODIDE WITH VARIOUS COMPOUNDS IN TETRAHYDROFURAN[a]

Registry no.	Compd	Mmol	Ca, mmol	CH_3I, mmol	THF,[b] ml	Products (yield, %[c])
67-64-1	CH_3COCH_3	5.1	7.1	5.0	12	$(CH_3)_3COH$ (49), CH_4 (39)
	CH_3COCH_3	4.9	5.9	4.5	10	$(CH_3)_3COH$ (51), CH_4 (37)
119-61-9	$C_6H_5COC_6H_5$[d]	6.2	8.5	5.7	15	$CH_3C(C_6H_5)_2OH$ (32)
	$C_6H_5COC_6H_5$	16.8	9.1	5.9	17	$CH_3C(C_6H_5)_2OH$ (76)
100-52-7	C_6H_5CHO	6.6	7.9	5.9	15	$C_6H_5CH(CH_3)OH$ (64), $C_6H_5CH{=}CH_2$ (trace)
	C_6H_5CHO	12.0	9.2	6.2	15	$C_6H_5CH(CH_3)OH$ (55), $C_6H_5CH{=}CH_2$ (trace)
79-20-9	CH_3COOCH_3	3.4	7.7	6.0	14	$(CH_3)_3COH$ (71), CH_4 (21)
	CH_3COOCH_3	3.3	7.5	6.0	14	$(CH_3)_3COH$ (70), CH_4 (17)
105-58-8	$(C_2H_5O)_2CO$	1.8	7.1	5.1	12	$(CH_3)_3COH$ (68), CH_3COCH_3 (3)
	$(C_2H_5O)_2CO$	2.2	8.0	6.0	14	$(CH_3)_3COH$ (73), CH_3COCH_3 (6)
18707-60-3	$CH_3CH{=}CHCOOCH_3$	6.6	9.4	6.0	15	$CH_3CH{=}CHC(CH_3)_2OH$ (50), $CH_3CH{=}CHCOCH_3$ (4), $(CH_3)_2CHCH_2COOCH_3$ (trace), CH_4 (17)
98-88-4	C_6H_5COCl	6.0	8.0	5.8	15	$CH_2{=}C(CH_3)C_6H_5$ (70), $C_6H_5COCH_3$ (trace), $C_6H_5C(CH_3)_2OH$ (trace)
75-36-6	CH_3COCl	3.4	8.1	6.0	14.5	$(CH_3)_3COH$ (31), $CH_3COOC(CH_3)_3$ (19), CH_3COCH_3 (trace), CH_4 (25)
	CH_3COCl	6.2	7.4	5.9	14	$(CH_3)_3COH$ (22), $CH_3COOC(CH_3)_3$ (26), CH_3COCH_3 (2), CH_4 (26)
75-05-8	CH_3CN	6.5	8.5	5.9	14	CH_3COCH_3 (14), CH_4 (60)
	CH_3CN	6.2	9.6	6.0	14	CH_3COCH_3 (9), CH_4 (60)
100-47-0	C_6H_5CN	6.1	8.6	6.0	15	$C_6H_5COCH_3$ (18)
	C_6H_5CN	6.6	7.6	5.9	15	$C_6H_5COCH_3$ (21)
	C_6H_5CN	6.6	8.6	5.9	15	$C_6H_5COCH_3$ (21)

[a] Reactions were carried out at −30° under a nitrogen atmosphere. [b] Tetrahydrofuran. [c] Based on CH_3I. [d] 27% of methylcalcium iodide remained unchanged.

the addition reaction. The reaction with benzonitrile gave acetophenone in 18–21% (19–23%) yield. Distillation of the reaction products left a viscous undistillable residue, apparently polymeric.

The reaction of methylcalcium iodide with olefins appeared to be very slow. The calcium compound did not react with cyclohexene in tetrahydrofuran even at 20° for 60 hr. According to the descriptions in the literature, however, organocalcium iodides undergo addition reactions with vinylacetylenes,[9,11–15,19,20] and alkylcalcium iodides can initiate polymerization of conjugated dienes in the presence of hexamethylphosphoramide,[28,29] and copolymerization of styrene and butadiene.[30] Thus, organocalcium halides seem to react with conjugated olefins to some extent. However, we found that methylcalcium iodide was poorly reactive toward 1,1-diphenylethylene in tetrahydrofuran. When 1,1-diphenylethylene was added to the suspension of methylcalcium iodide in tetrahydrofuran, a dark red color developed but the yield of 1,1-diphenylpropane was negligible even after 60 hr at 20°.

The rapid reaction of organolithium compounds with benzyl chloride is the basis for a quantitative analysis of organolithium compounds by double titration.[31] On the other hand, the procedure was reported to give unpromising results with organocalcium halides.[7] We observed that the reaction of methylcalcium iodide with benzyl chloride was slow. When the reaction was carried out for 1 hr at 20°, ethylbenzene was obtained only in 6% (6–7%) yield, and 46% (49–51%) of methylcalcium iodide remained unchanged in the reaction system. The yield of ethylbenzene was only 13% (14%) even after 17 hr at 20°.

When one attempts to carry out the reaction of organocalcium halides in ethereal media, particular attention should be given to the reaction of the reagents with the solvent. Although tetrahydrofuran and other ethereal solvents are convenient media for the preparation of organocalcium halides, they are readily cleaved by organocalcium reagents. Bryce-Smith and Skinner[7] described that the half-life of methylcalcium iodide in tetrahydrofuran at 20° was 13 days. However, we observed that methylcalcium iodide was much less stable. The half-life in tetrahydrofuran at 20° was ~10 hr. Although the calcium compound was somewhat more stable at lower temperature, it was necessary to use the reagent for further reactions immediately after the preparation. The cleavage reaction is significant in the slow reactions of the organocalcium reagents, *e.g.*, reactions of methylcalcium iodide with benzyl chloride and olefins.

Results are summarized in Table I.

Judging from the above results, we can confirm the similarity[7] of organocalcium halides with organolithium reagents in several fundamental organic reactions. Methylcalcium iodide undergoes addition reactions with various carbonyl compounds to give the expected products in good yields. In the reaction with an α,β-unsaturated ester, the carbonyl addition much predominated over the 1,4 addition. Thus, organocalcium halides would be useful in organic syntheses, although methylcalcium iodide gave the corresponding ketones in

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low yields by the reaction with nitriles, and reacted very slowly with olefins. The characteristic nature of organocalcium halides in organic reactions remains to be revealed in the future.

Experimental Section

Gas chromatographic analyses were carried out on a Shimadzu GC-4A or GC-4B gas chromatograph. Infrared spectra were recorded on a Japan Spectroscopic Co. Model 402G spectrometer.

Materials.—Methylcalcium iodide was prepared in tetrahydrofuran according to our procedure reported previously.[1] Tetrahydrofuran was purified by distillation in the presence of benzophenone sodium ketyl under a nitrogen atmosphere. Nitrogen was purified by passing through a tube containing copper turnings in a furnace at 170° followed by drying with phosphorus pentoxide. Methyl iodide, acetone, benzophenone, benzaldehyde, benzoyl chloride, acetyl chloride, methyl acetate, diethyl carbonate, methyl crotonate, acetonitrile, benzonitrile, benzyl chloride, cyclohexene, and 1,1-diphenylethylene were purified by usual methods.[32] Authentic samples of 2-methyl-3-penten-2-ol and α,α-diphenylethanol were prepared by the reactions of methylmagnesium iodide with *n*-butyl crotonate and benzophenone, respectively. 1,1-Diphenylpropane was prepared by a conventional procedure.[33,34] Other authentic samples and chemicals were commercial products and were used without further purification.

Procedure.—The reaction vessel was a two-necked flask equipped with two three-way cocks. Each three-way cock was connected with a nitrogen inlet and a rubber serum cap. Methylcalcium iodide was prepared in this flask by the reaction of calcium metal with methyl iodide in tetrahydrofuran at −70°.[1] Various reactants in tetrahydrofuran were added dropwise at −30° to this methylcalcium iodide in the flask over a period of 0.5 hr while stirring at the temperature. Reactons with carbonyl compounds and nitriles were rapid and exothermic, and the stirring was continued for 1 hr at 20° to complete the reaction. Reactions with benzyl chloride, cyclohexene, and 1,1-diphenylethylene were slow and were continued for several hr at 20° after the addition of the reactants. After the reaction, water, methanol, acetic acid, or 6 *N* hydrochloric acid was added to the reaction mixture. The amount of gaseous products evolved during the reaction was determined by a gas burette, and the gas was analyzed by gas chromatography. Qualitative and quantitative analyses of other reaction products were carried out by gas chromatography.

Registry No.—Methylcalcium iodide, 20458-43-9.

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Inversion of Configuration in the Bromination of Vinylic Mercurials[1]

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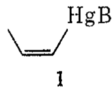
The bromination of *cis*- and *trans*-1-propenyl- and 2-butenylmercury(II) bromide in carbon disulfide occurs with predominant inversion of configuration at the double bond. The rate of bromination of *trans*-2-butenylmercury(II) bromide in carbon disulfide is 75 times as fast as that of *n*-propylmercury(II) bromide. The observed inversion of configuration is consistent with a trans addition of bromine to the carbon–carbon double bond of the vinylic mercurials followed by a trans elimination of mercury(II) bromide. In contrast to the results in carbon disulfide, the bromination of the vinylic mercurials takes place with retention of configuration in pyridine.

A study of the bromination of *cis*- and *trans*-2-butenyl- and 1-propenylmercury(II) bromides (compounds **1**, **2**, **3**, and **4**) in carbon disulfide was initiated in an attempt to generate free propenyl radicals of known stereochemistry and to investigate their stereochemical fate.[2] A free-radical pathway for the bromination of these compounds in carbon disulfide was anticipated at the outset, since Jensen had shown that the bromination of either *cis*- or *trans*-4-methylcyclohexylmercury(II) bromide in degassed carbon disulfide produced the same ratio of *cis*- and *trans*-1-bromo-4-methylcyclohexane and had interpreted the loss of of stereochemistry in terms of a free-radical reaction.[3] The possibility of an alternative pathway involving retention of stereochemistry in the bromination of the vinylic mercurials was also considered, since Jensen[3] had shown that the bromination of the isomeric methylcyclohexyl mercurials in methanol proceeds with 85% retention of stereochemistry. Here, we report the surprising finding that bromination of 1-propenyl and 2-butenyl mercurials leads to propenyl and butenyl bromides of inverted stereochemistry.[4]



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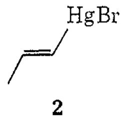

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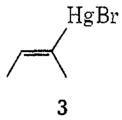

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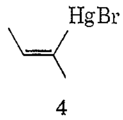

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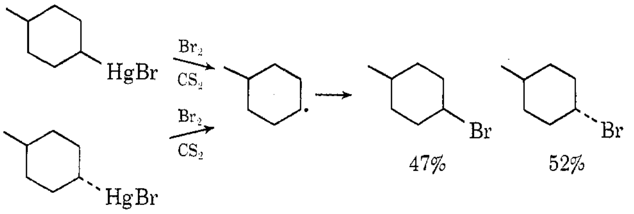

Results

Synthesis and Stereochemistry of Vinylic Mercurials.

—*cis*- and *trans*-1-propenyl- and 2-butenylmercury(II)

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[1] Supported in part by the National Science Foundation, Grants GP-28586X and GP-2018.

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