

Strontium and barium reacted in a manner similar to that of calcium, and the yields of diphenylethane were 20 and 70%, respectively; the yields of 1,1,4,4-tetraphenylbutane were 14 and 35%, respectively.

Reactions with 1,1,2-Triphenylethylene.—The triphenylethylene was prepared in accordance with the directions of Hell and Wiegandt.⁶ The same general procedure was used as with 1,1-diphenylethylene, and the organometallic compounds formed in liquid ammonia were red. The yields of 1,1,2-triphenylethane from experiments with calcium, strontium and barium were 40, 61 and 48%, respectively. The authentic specimen used for characterization of the products from the liquid ammonia reactions was prepared by the addition of phenyllithium to 1,1-diphenylethylene in ether.

Reaction with Triphenylmethane.—Six grams of barium in 200 cc. of liquid ammonia was treated with 9.8 g. of triphenylmethane to give a red solution. This was forced into a three-necked flask and 50 cc. of ether was added. After the ammonia had evaporated, powdered carbon dioxide was added. From the mixture was isolated triphenylacetic acid (mixed melting point). From a second

(6) Hell and Wiegandt, *Ber.*, **37**, 1431 (1904).

experiment in which the red ammonia solution was poured upon solid carbon dioxide there was again isolated a very small quantity of triphenylacetic acid, and the yield of recovered triphenylmethane was 83%.

Summary

Lithium, calcium, strontium and barium add, in liquid ammonia, to the olefinic linkage of 1,1-diphenylethylene to give the corresponding red colored organometallic compounds. These when ammonolyzed yield 1,1-diphenylethane and 1,1,4,4-tetraphenylbutane. Calcium, strontium and barium add, under corresponding conditions, to 1,1,2-triphenylethylene to give 1,1,2-triphenylethane. The significance of these experiments on the addition of the corresponding RM compounds to an olefinic linkage is pointed out.

Barium reacts with triphenylmethane in liquid ammonia to give traces of triphenylmethylbarium.

AMES, IOWA

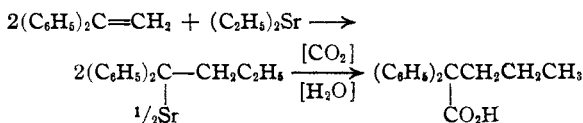
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Organostrontium Compounds¹

BY H. GILMAN, R. N. MEALS, G. O'DONNELL AND L. WOODS

This report describes some reactions of a new class of organometallic compounds, the organostrontium compounds. Perhaps the most interesting reaction is the addition to an olefinic linkage. Diethylstrontium adds to the olefinic linkage of 1,1-diphenylethylene to give another R_2Sr compound, which was identified by carbonation to a known acid.



It has not been established definitely whether the diethylstrontium adds as $[2C_2H_5][Sr]$ or as $[C_2H_5][SrC_2H_5]$; however, it appears more likely that the former mode of addition takes place.

The addition of diethylstrontium to an olefinic linkage serves to classify organostrontium compounds with the very highly reactive organoalkali compounds, and supports the prediction (see preceding paper²) of such high reactivity.

(1) Paper XLVII in the series, "Relative Reactivities of Organometallic Compounds." The preceding paper is THIS JOURNAL, **65**, 267 (1943).

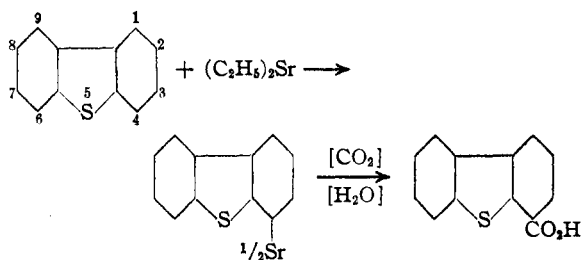
(2) Gilman and Bailie, *ibid.*, **65**, 267 (1943).

Metalation.—Nuclear metalation is a reaction which is generally characteristic of the more reactive RM types. Diethylstrontium metalates anisole in the expected *ortho*-position to give di-*o*-anisylstrontium, identified as *o*-anisic acid, subsequent to carbonation. Dibenzofuran was also metalated in the expected 4-position, a position invariably involved irrespective of the kind of metalating agent (metals, inorganic salts like mercuric acetate or organometallic compounds). However, metalation of the related dibenzothiophene was, in a sense, quite anomalous.

It was shown earlier^{3a} that although RLi and RK compounds metalated dibenzothiophene in the 4-position, phenylcalcium iodide effected metalation in the 3-position.^{3b} It seemed altogether reasonable to expect that organostrontium compounds would, like the presumably very closely related organocalcium compounds, also metalate in the 3-position. This was not the case, however, for the only metalation product

(3) (a) Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); (b) Gilman, Jacoby and Pacevitz, *ibid.*, **3**, 120 (1938); (c) Krause and von Grosse, "Die Chemie der metall-organischen Verbindungen," Gebrüder Borntraeger, Berlin, 1937, p. 123.

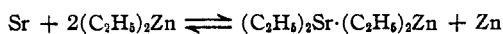
isolated showed that metalation must have taken place in the 4-position.



The differences in metalation behavior of phenylcalcium iodide and diethylstrontium may possibly be due to the presence of halogens in one of these RM compounds but not in the other. However, with dibenzofuran the presence or absence of halogens in the organometallic compound has not influenced the position of metalation.

Experimental

Preparation of Diethylstrontium.—Numerous unpublished experiments were made in this and other laboratories to prepare organostrontium compounds by various procedures.^{3c} Our present method involves the reaction of strontium metal with diethylzinc.⁴ The reaction appears to result in an equilibrium with the diethylstrontium forming a complex with diethylzinc.



A mixture of 12 g. (0.097 mole) of diethylzinc and 8.49 g. (0.097 g. atom) of finely rasped strontium metal in 20 cc. of sodium-dried benzene was heated in a Schlenk tube which had been thoroughly flushed out with nitrogen. Heating was effected at 90° in an oil-bath, and after five hours refluxing the clear solution had given way to a dark chocolate brown. This and all subsequent reactions were carried out under nitrogen. The solution was filtered through a sintered glass plate from the solid metals, and the excess diethylzinc and the benzene removed under vacuum at room temperature. The yield of crystalline diethylstrontium–diethylzinc complex was 6.65 g. or 51%.

In a similar experiment the filtered solution was reduced to half its original volume and the resulting transparent, reddish brown crystals filtered off on a sintered glass plate. These crystals decompose at 170° with the deposition of a metallic mirror, liberation of diethylzinc and considerable gas evolution. They are extremely sensitive to air, being rapidly changed to the metallic oxides. They are easily redissolved by benzene, but an attempt to wash them with petroleum ether (b. p. 65–68°) changed them to an amorphous white powder.

Color test I^{5a} gives a very strong reaction. Color test IV^{5b} was positive, giving a bright red solution on addition of 2 or 3 drops of the diethylstrontium solution.

(4) It is interesting to note that di-*n*-butylstrontium has not yet formed under conditions for the preparation of di-*n*-butylbarium from barium and di-*n*-butylzinc.

(5) (a) Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925); (b) Gilman and Woods, *ibid.*, **65**, 33 (1943).

Under corresponding conditions, triethylboron does not react with strontium to give diethylstrontium.

Reaction with 1,1-Diphenylethylene.—To a solution of diethylstrontium prepared from 2.2 g. (0.025 g. atom) of strontium metal and 3.5 g. (0.028 mole) of diethylzinc in 10 cc. of benzene, was added 3.5 g. (0.02 mole) of 1,1-diphenylethylene, and the solution was refluxed eight hours. The hot solution was carbonated with a finely powdered carbon dioxide–petroleum ether slurry. Subsequent to hydrolysis and working up by customary procedures there was obtained 1.0 g. (20%) of α,α -diphenylvaleric acid. After two crystallizations from absolute alcohol the acid melted at 154–155°. Identification was completed, as was done in the case of all solids described in this paper, by the method of mixed melting points with an authentic specimen. The α,α -diphenylvaleric acid was prepared by the method of Ziegler.⁶ *Neutral equivalent*: calculated 254, found 250.

It should be mentioned that parallel experiments were carried out with diethylzinc and each of the reactants described in this report. No reaction product was isolated in these control experiments with diethylzinc alone. Organozinc compounds are known to have a low order of reactivity.⁷

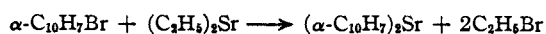
Metalations

(1) **Anisole.**—A solution of 2.16 g. (0.02 mole) of anisole and diethylstrontium, prepared from 1.76 g. (0.02 g. atom) of strontium metal and 2.44 g. (0.02 mole) of diethylzinc in 10 cc. of benzene, was refluxed fourteen hours, and then carbonated by pouring on a slurry of crushed, solid carbon dioxide and petroleum ether. After working up the reaction products in the customary way, there was obtained *o*-anisic acid, melting at 99–100° after recrystallization from hot water.

(2) **Dibenzofuran.**—A solution of 3.86 g. (0.02 mole) of dibenzofuran and diethylstrontium, prepared from 2.5 g. (0.028 g. atom) of strontium metal and 3.5 g. (0.028 mole) of diethylzinc in 10 cc. of benzene, was refluxed for fourteen hours, and carbonated by pouring on a crushed solid carbon dioxide–petroleum ether mixture. After working up the reaction products by conventional procedures there was isolated 0.26 g. of 4-dibenzofurancarboxylic acid; m. p. 207–209° after recrystallization from dilute ethanol.

(3) **Dibenzothiophene.**—A mixture of 3.7 g. (0.02 mole) of dibenzothiophene and diethylstrontium, prepared from 2.5 g. (0.028 g. atom) of strontium metal and 4.0 g. (0.032 mole) of diethylzinc in 10 cc. of benzene, was refluxed four hours and carbonated. Subsequent to working up in the usual manner there was obtained a trace of 4-dibenzothiophenecarboxylic acid. 4-Carbomethoxydibenzothiophene, prepared from the acid and diazomethane, melting at 93–94° after recrystallization from dilute ethanol, was used to characterize the acid by the usual method of mixed melting points.

Halogen–Metal Interconversion.—The following typical halogen-metal interconversion reaction was effected with α -bromonaphthalene.



and the di- α -naphthylstrontium was characterized by car-

(6) Ziegler and co-workers, *Ann.*, **473**, 7 (1929).

(7) Gilman and Marple, *Rec. trav. chim.*, **55**, 133 (1936).

bonation to the corresponding α -naphthoic acid. A mixture of 4.14 g. (0.02 mole) of α -bromonaphthalene and diethylstrontium, prepared from 0.02 g. atom of strontium metal and 0.02 mole of diethylzinc in 10 cc. of benzene, was refluxed two hours before carbonation. The small quantity of α -naphthoic acid obtained after working up according to the usual procedure melted at 157–159° after crystallization from dilute ethanol.

Reaction with Carbon Dioxide.—A mixture of 12 g. (0.097 mole) of diethylzinc, and 6.6 g. (0.075 g. atom) of finely rasped strontium metal in 20 cc. of benzene, was refluxed with stirring for four hours. The resulting suspension was carbonated by pouring onto a petroleum ether-crushed carbon dioxide slurry. The products were worked up in the customary manner, and the ensuing propionic acid isolated as the silver propionate. The yield was 2.2 g. (16.3%). The silver salt was converted to sodium propionate which was treated with *p*-phenylphenacyl bromide to give the corresponding ester (m. p. and mixed m. p. 98.5–100°).

Reaction with Benzonitrile.—The formation of a normal reaction product (propiophenone) from diethylstrontium

and benzonitrile⁸ indicates that organostrontium compounds will react readily with other functional groups.

Summary

Diethylstrontium has been prepared from strontium and diethylzinc.

In confirmation of an earlier prediction that organostrontium compounds would have the general high reactivity of organoalkali compounds, it has been shown that diethylstrontium adds to the olefinic linkage in 1,1-diphenylethylene.

Metallation of dibenzothiophene by diethylstrontium involves the 4-position. This result was unexpected in view of an earlier observation that the very closely related phenylcalcium iodide metalates dibenzothiophene in the 3-position.

(8) Entemann and Johnson, *THIS JOURNAL*, **55**, 2900 (1933).
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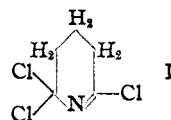
Reaction of Glutarimides with Phosphorus Pentachloride. A New Pyridine Synthesis

BY W. W. CROUCH AND H. L. LOCHTE

Recent studies in this Laboratory of the nitrogen bases from petroleum distillates have led to the isolation of certain compounds which appear to be β -substituted pyridines. Since no reliable method is known for the synthesis of these compounds, it seemed desirable to attempt to find a general procedure by which they could be made. A promising approach appeared to be the reaction of properly substituted glutarimides with phosphorus pentachloride followed by the elimination of the elements of hydrogen chloride to form chloropyridines from which the chlorine atoms could be removed by hydrogenation.

The corresponding reaction of phosphorus pentachloride with succinimide was first studied by Bernthsen,¹ who pointed out that the reaction with glutarimide should yield chloro compounds which could be reduced with zinc dust to form pyridine. A careful study of the reaction with succinimide and related compounds was made by Anschütz² and co-workers who likewise made a brief study of the reaction with glutarimide but reported that this reaction was not so simple as that of succinimide. The reaction of glutari-

imide with phosphorus pentachloride was studied by Bernheimer,³ who isolated a crystalline compound to which he assigned structure I. While



a compound of this structure would be expected to be hydrolyzed with ease, Bernheimer reported that his compound could be purified by steam distillation.

This reaction has now been repeated and a steam-distillable crystalline compound similar to that described by Bernheimer was isolated, but the formula of our compound was found to be $C_5H_2NCl_3$ instead of $C_5H_6NCl_3$. Its hydrogenation to form pyridine showed that it was a trichloropyridine, indicating that the elimination of hydrogen chloride had occurred spontaneously during the reaction. Since its formation from glutarimide requires that two of its chlorine atoms be bonded to carbon atoms 2 and 6 of the pyridine ring, only two molecular structures are possible for the trichloropyridine. Its properties

(1) Bernthsen, *Ber.*, **13**, 1047 (1880).

(2) Anschütz, *Ann.*, **295**, 27 (1897).

(3) Bernheimer, *Gazz. chim. ital.*, **12**, 283 (1882).