

amounts of tin in the presence of large amounts of lead.

The diffusion current constant $i_d/(Cm^{3/4}t^{1/4})$ of the bromostannate ion at 25° in 4 *M* ammonium bromide in the presence of 0.005% gelatin was found to be 6.52 (total double wave), and hence virtually the same as that of the chloro complex in a similar concentration of ammonium chloride.

Summary

In the presence of a very large concentration of chloride ion stannic tin produces a well developed doublet wave, the first part of which results from reduction of the chlorostannate ion to the stan-

nous state and the second corresponds to reduction of the stannous complex to the metal. In a supporting electrolyte composed of 4 *M* ammonium chloride, 1 *N* hydrochloric acid, and 0.005% gelatin, the half-wave potentials of the doublet wave are -0.25 and -0.52 v. vs. the saturated calomel electrode, and the total diffusion current constant $i_d/(Cm^{3/4}t^{1/4})$ is 6.55 at 25°. The characteristics of the wave are well suited to the polarographic determination of tin.

Stannic tin also produces a well-defined double wave in 4 *M* ammonium bromide as a supporting electrolyte.

CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 20, 1945

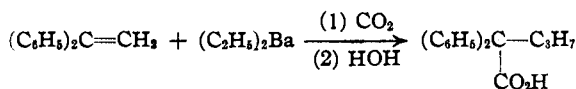
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Organocalcium, -Strontium and -Barium Compounds¹

BY HENRY GILMAN, A. H. HAUBEIN, GORDON O'DONNELL AND LAUREN A. WOODS

The recent availability of organostrontium² and organobarium³ compounds makes it possible to compare some reactions of these compounds as well as the organocalcium compounds.

Addition to Olefinic Linkage.—Diethylbarium like diethylstrontium² adds readily to 1,1-diphenylethylene. The mode of addition was established by carbonation.



However, diethylbarium did not add to stilbene, in contrast to the known addition of *n*-butyllithium⁴ and phenylisopropylpotassium⁵ to this compound.

Diethylbarium and ethyllithium, but not diethylstrontium, add to a limited extent to styrene, and the acid obtained subsequent to carbonation is α -phenyl-*n*-valeric acid.

Addition to Benzophenone-anil.—The Grignard reagent reacts very slowly with benzophenone-anil, and when the reaction is forced the special type of lateral-nuclear 1,4-addition occurs.^{6a} However, the more reactive phenylalkali compounds show 1,2-addition to the azomethylene linkage to give triphenylmethylaniline.^{6b} As might have been predicted, diethylstrontium and diethylbarium, like ethyllithium, add to the azomethylene linkage.

(1) Paper LVIII in the series: "The Relative Reactivities of Organometallic Compounds": the preceding paper with L. A. Woods in *THIS JOURNAL*, **67**, 520 (1945).

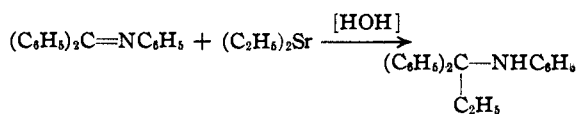
(2) Gilman, Meals, O'Donnell and Woods, *ibid.*, **65**, 268 (1943).

(3) Gilman and Woods, *ibid.*, **67**, 520 (1945).

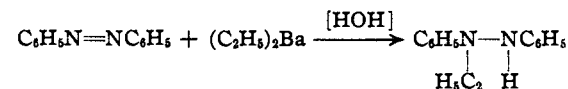
(4) Ziegler, Crössmann, Klein and Schäfer, *Ann.*, **473**, 35 (1929).

(5) Ziegler and Bähr, *Ber.*, **61**, 253 (1928).

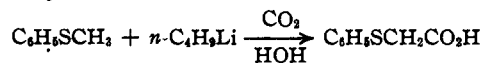
(6) (a) Gilman, Kirby and Kinney, *THIS JOURNAL*, **51**, 2252 (1929); (b) Gilman and Kirby, *ibid.*, **63**, 2046 (1941); (c) Gilman and Bailie, *J. Org. Chem.*, **2**, 84 (1937).



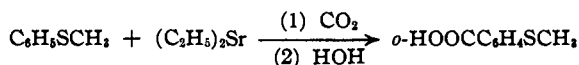
Addition to Azobenzene.—Several products are formed by the reaction of azobenzene with RM compounds, and the relative reactivity of the organometallic compound determines rather uniquely the nature of the product, the very reactive types giving hydrazines.^{6c} Diethylstrontium and diethylbarium add to give 1-ethyl-1,2-diphenylhydrazine, which was identified after rearrangement, as *N*-ethylbenzidine.



Metalation.—Diethylbarium metalates anisole in the ortho-position to give, subsequent to carbonation, *o*-methoxybenzoic acid. However, the metalation of methyl phenyl sulfide by diethylstrontium and diethylbarium was unusual. It has been shown that the metalation of methyl phenyl sulfide by *n*-butyllithium takes place laterally⁷



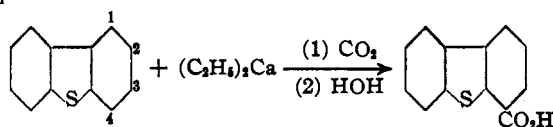
No lateral metalation was observed with diethylstrontium and diethylbarium; instead ortho-nuclear metalation occurred



An equally unexpected metalation occurred in the reaction between dibenzothiophene and di-

(7) Gilman and Webb, *THIS JOURNAL*, **62**, 987 (1940).

ethylcalcium. It was shown earlier^{8a} that although RLi and RK compounds, as well as diethylstrontium,² metalated dibenzothiophene in the 4-position, phenylcalcium iodide effected metalation in the 3-position.^{8b} However, diethylcalcium metalates dibenzothiophene in the 4-position.

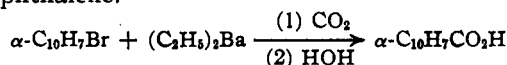


In general, there are no essential differences in reaction of a simple (R_2M) compound and a mixed (RMX) compound, where M is the same metal.⁹

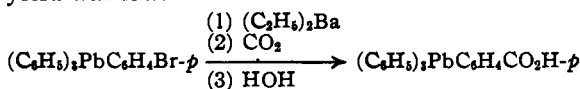
The metalation of the analogous dibenzofuran in the 4-position by diethylbarium was normal, for this position has invariably been involved in metalations irrespective of the metalating agent (metals, inorganic salts like mercuric acetate or organometallic compounds).

Triphenylmethane has an acidic lateral hydrogen which is readily replaced by lithium. This reaction which takes place with most RLi compounds is the basis of color test II.^{11b} A replacement of the lateral hydrogen in a reaction with diethylbarium was expected; however, practically all of the triphenylmethane was recovered.

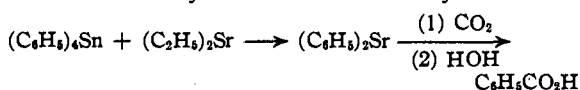
Halogen-Metal Interconversions.—Diethylbarium, like diethylstrontium, underwent a halogen-metal interconversion reaction with α -bromonaphthalene.



A particularly promising halogen-metal interconversion reaction was observed with triphenyl-*p*-bromophenyllead. This reaction extends the possibility of introducing water-solubilizing groups in some organometallic compounds. When it was observed (see below) that there was no metal-metal interconversion reaction between diethylbarium and tetraphenyllead, the way appeared open to the formation of a C-Ba bond in an organolead compound. The C-Ba linkage would then make possible the introduction of a water-solubilizing group like the carboxyl. Although the halogen-metal interconversion reaction did take place the yield was low.



Metal-Metal Interconversions.—Tetraphenyltin undergoes smooth metal-metal interconversions with diethylstrontium and diethylbarium.

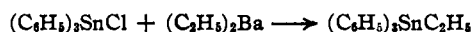


(8) (a) Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); (b) Gilman, Jacoby and Pacevitz, *ibid.*, **3**, 120 (1938).

(9) See, Gilman, "Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1943, Vol. I, p. 517.

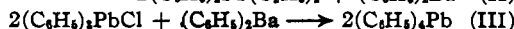
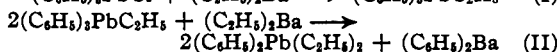
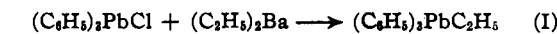
Under corresponding conditions, there is no metal-metal interconversion with tetraphenylsilicon, tetraphenylgermanium, or tetraphenyllead.

Reactions with Triarylmethyl Chlorides.—The following expected reaction took place in good yield



However, the related triphenyllead chloride gave not only triphenylethyllead, but also an appreciable quantity of tetraphenyllead.

The tetraphenyllead may owe its formation to the following sequence of reactions



That is, the relatively reactive, unsymmetrical and soluble triphenylethyllead formed in (I) underwent a metal-metal interconversion reaction (II) to give diphenylbarium which then reacted with some of the triphenyllead chloride suspension in accordance with (III). A separate experiment confirmed Reaction (II), and the diphenylbarium was identified by carbonating to benzoic acid. It is not excluded that part of the 19.4% yield of tetraphenyllead may have come from a disproportionation or redistribution reaction under the experimental conditions.¹⁰

In connection with diphenylbarium it might be mentioned that this compound was prepared independently by interaction of diphenylcadmium with barium. Interestingly enough, the closely related diphenylzinc did not form diphenylbarium under essentially the same conditions. Diethylcalcium, -strontium and -barium were all made from diethylzinc and the corresponding metal; and di-*n*-butylbarium was prepared from di-*n*-butylzinc and barium.

Experimental

Preparation of Organostrontium and Organobarium Compounds.—General directions have been given for the preparation of diethylstrontium^{2,3} and diethylbarium.³ Schlenk tubes are unnecessary, and the preparations can be carried out conveniently in conventional three-necked flasks, using an atmosphere of dry, oxygen-free nitrogen. A small wood rasp was used to prepare the finely-divided metals which were caught directly in benzene contained in a suitable vessel like a casserole.

No appreciable quantities of diethylbarium were obtained in corresponding experiments in which triethylboron and tetraethyllead were used in place of diethylzinc.

Diphenylbarium was prepared by heating at reflux, with stirring, a mixture of 3.4 g. (0.025 g. atom) of barium in 20 cc. of benzene with 10.3 g. (0.039 mole) of diphenylcadmium for five hours. At the end of this time, the benzene was removed by distillation and replaced by 15 cc. of xylene. This mixture was refluxed for four hours, and assumed a gray color. After adding ether to the cooled mixture, carbonation was carried out to yield 4.2% of benzoic acid. Under corresponding conditions no benzoic acid was isolated from attempted preparations of diphenylbarium in which diphenylzinc, and triphenylantimony were used.

(10) See Calingaert and Beatty in Chap 24 of the citation given in ref. 9.

It was observed that diethylbarium and diethylstrontium gave positive color tests I^{11a} and IV,^{11a} but a negative color test II.^{11b} Diphenylbarium gave positive color tests I, III,^{11c} and IV, but a negative color test II.

Addition to Olefinic Linkages (1) **Styrene**.—A solution of 0.02 mole of diethylbarium in 64 cc. of ether was added, during twenty minutes, to a stirred solution of 4.2 g. (0.04 mole) of styrene in 25 cc. of ether. A deep red solution and a red precipitate were formed. After stirring and refluxing at room temperature for fifty-five minutes, the mixture was carbonated by addition to an ether-Dry Ice slurry. The quantity of α -phenyl-*n*-valeric acid¹² isolated was 0.04 g. (0.6%). Under essentially corresponding conditions, the yield of α -phenyl-*n*-valeric acid from a reaction between styrene and ethyllithium was 1.7%, and this acid showed no depression in a mixed m. p. determination with the acid obtained using diethylbarium. Under similar conditions, diethylstrontium did not give any apparent addition product with styrene.

(2) **1,1-Diphenylethylene**.—To diethylbarium prepared in the usual manner, by reaction of 6.9 g. (0.05 g. atom) of finely-rasped barium and 12.3 g. (0.1 mole) of diethylzinc in 5 cc. of benzene and the subsequent addition of 75 cc. of ether, was added a solution of 9 g. (0.05 mole) of 1,1-diphenylethylene in 25 cc. of ether. The mixture was refluxed for three hours (a deep red suspension being formed), and then carbonated by Dry Ice. The yield of α,α -diphenylvaleric acid was 5.5 g. (21.6%). There was no depression in a mixed m. p. determination with a sample of the acid prepared in accordance with the procedure of Ziegler and co-workers.⁴

(3) **Stilbene**.—Under essentially corresponding conditions, no acid was isolated subsequent to carbonation of a reaction mixture of diethylbarium with stilbene. It appeared that polymerization was the chief reaction.

Reaction with Benzophenone.—To diethylbarium, prepared from 6.9 g. (0.05 g. atom) of barium and 12.3 g. (0.1 mole) of diethylzinc, was added (during one-half hour with stirring) 9.1 g. (0.05 mole) of benzophenone in 25 cc. of ether. Previously 75 cc. of ether had been added to the diethylbarium which was prepared in 5 cc. of benzene. Color test I was negative, and the cooled reaction mixture was hydrolyzed immediately by a solution of ammonium chloride. The yield of pure diphenylethylcarbinol was 7.9 g. (74.5%). A mixed m. p. determination was made with a sample prepared by the procedure of Hell and Bauer.¹³

To a solution of diethylstrontium, prepared from 8.5 g. (0.097 g. atom) of strontium and 12 g. (0.097 mole) of diethylzinc in 50 cc. of benzene, was added at room temperature a solution of 16.4 g. (0.09 mole) of benzophenone in 50 cc. of benzene. The reaction mixture was stirred for three hours and then hydrolyzed with iced ammonium chloride. (A control experiment with just diethylzinc and benzophenone showed no reaction at room temperature.) From the hydrolyzate there was first removed a small quantity of benzophenone by treatment with hydroxylamine. The solid remaining from this operation weighed 14.6 g. and melted in the range 50–56°. The separation of benzohydrol and diphenylethylcarbinol was patterned after some unpublished studies by C. E. Arntzen. It was based on the observation that the reaction product of benzohydrol and phenylmagnesium bromide is insoluble in a mixture of ether and benzene, whereas the corresponding product from diphenylethylcarbinol is soluble. The yield of benzohydrol was 6 g. (36.2%), and the yield of diphenylethylcarbinol was 7.5 g. (39.4%). Each of the compounds was identified by mixed m. p. determinations with authentic specimens. A mixture of equal parts of the two carbinols melted at 50–55°, or essentially the same temperature range of product after treatment with hydroxylamine.

(11) (a) Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925); (b) Gilman and Swiss, *ibid.*, **62**, 1847 (1940); (c) Gilman and Yablunsky, *ibid.*, **63**, 839 (1941); (d) Gilman and Woods, *ibid.*, **65**, 33 (1943).

(12) Rossolymo, *Ber.*, **22**, 1275 (1889).

(13) Hell and Bauer, *ibid.*, **37**, 231 (1904).

Addition to Benzophenone-anil.—To a suspension of 11 g. (0.043 mole) of benzophenone-anil in 100 cc. of ether was added 0.05 mole of ethyllithium in 100 cc. of ether over a one-half hour period. The warm mixture was stirred for an additional one-half hour, and then hydrolyzed by pouring into an iced ammonium chloride solution. After the ether layer had been separated, the solvent was removed under reduced pressure to give a dark reddish-brown glass. Isolation was effected by forming the hydrochloride from an ether solution, decomposing the hydrochloride with sodium hydroxide, extracting with ether, and then distilling. The 1-anilino-1,1-diphenylpropane distilled at 153.6–154° (1 mm.) with a bath temperature of 188–195°. The compound crystallized on standing to give 7.5 g. (52.3%) of white product melting at 72–73°.

Anal. Calcd. for C₂₁H₂₁N: N, 4.87. Found: N, 4.67.

The same compound (mixed m. p.) was obtained in 3.6% yield from a reaction between 10 g. (0.039 mole) of benzophenone-anil and diethylstrontium prepared from 4.4 g. (0.05 g. atom) of strontium and 12.3 g. (0.1 mole) of diethylzinc.

In a comparable experiment, the same compound (mixed m. p.) was obtained in a 36.9% yield from 10.2 g. (0.04 mole) of benzophenone-anil and diethylbarium prepared from 6.9 g. (0.05 g. atom) of barium and 12.3 g. (0.1 mole) of diethylzinc.

Reaction with Azobenzene.—Diethylbarium was prepared from 6.9 g. (0.05 g. atom) of barium, and 12.3 g. (0.1 mole) of diethylzinc in 5 cc. of benzene; then 75 cc. of ether was added. To this ether suspension was added, over a forty-minute period, a solution of 9.1 g. (0.05 mole) of azobenzene in 25 cc. of ether. After stirring for four hours, hydrolysis was effected by a solution of 4 g. of ammonium chloride in 15 cc. of water. The ether layer was separated after filtration; the ether was removed by distillation under reduced pressure; and the oily residue that remained was taken up in 50 cc. of petroleum ether (b. p., 28–38°). From this solution there separated on standing 2.72 g. (29.6%) of hydrazobenzene. The petroleum ether filtrate was evaporated to give an oily residue which resisted crystallization. The oil was mixed with 10 cc. of methanol, cooled by ice, and then a solution of 7 cc. of methanol and 7 cc. of concd. hydrochloric acid added. An intermediate green color was noted; then, after adding 30 cc. of water and cooling, the mixture was filtered to give 1.4 g. (15.5%) of azobenzene. The filtrate was made basic to the appearance of a precipitate; this was removed and treated with 25 cc. of ether and 20 cc. of 10% potassium hydroxide; and, then, removal of the ether left a solid which on crystallization from ethanol yielded 0.89 g. (8.3%) of *N*-ethylbenzidine¹⁴ melting at 72–73°.

From a reaction between 9.1 g. (0.05 mole) of azobenzene in 25 cc. of ether and 0.025 mole of diethylstrontium in 120 cc. of ether there was isolated 0.5 g. (4.7%) of *N*-ethylbenzidine (mixed m. p. with product from the diethylbarium reaction).

Metallations: (1) **Anisole**.—A solution of 2.2 g. (0.02 mole) of anisole and diethylbarium, prepared from 2.8 g. (0.02 g. atom) of barium metal and 2.4 g. (0.02 mole) of diethylzinc in 10 cc. of benzene, was refluxed for fourteen hours. After carbonation in the usual manner, there was isolated 0.36 g. (11.8%) of *o*-methoxybenzoic acid.

(2) **Methyl Phenyl Sulfide**.—A solution of 6.2 g. (0.05 mole) of methyl phenyl sulfide in 100 cc. of ether was added to a suspension of diethylbarium prepared from 6.9 g. (0.05 g. atom) of barium and 18.5 g. (0.015 mole) of diethylzinc. The mixture was refluxed for nineteen hours and at the end of this time there was a strong color test I. Carbonation, by pouring into a mixture of ether and Dry Ice, gave 0.1 g. (1.2%) of methyl *o*-carboxyphenyl sulfide. The mixed melting point determination was made with an authentic specimen prepared in accordance with the directions of Friedlaender.¹⁵ From the ether solutions there was recovered 4.4 g. (71%) of methyl phenyl sulfide.

(14) Rassow, *J. prakt. Chem.*, **84**, 349 (1911).

(15) Friedlaender, *Ann.*, **381**, 401 (1907).

A mixture of 6.9 g. (0.05 g. atom) of finely-rasped barium, 50 cc. of ether and 6.2 g. (0.05 mole) of methyl phenyl sulfide was refluxed, with stirring, for twenty-four hours and then poured on an ether-Dry Ice slurry. At no time did the mixture give a positive color test I; no carboxylic acid was isolated; and the recovery of methyl phenyl sulfide was 90.3%.

A mixture of 6.2 g. (0.05 mole) of methyl phenyl sulfide in 100 cc. of ether and diethylstrontium prepared from 4.4 g. (0.05 g. atom) of strontium and 12.3 g. (0.1 mole) of diethylzinc in 5 cc. of benzene was refluxed for nineteen hours. The supernatant ether gave a strong color test I, and after carbonation there was obtained 0.06 g. (0.7%) of methyl *o*-carboxyphenyl sulfide.

(3) **Dibenzothiophene.**—A solution of 0.027 mole of diethylcalcium³ in 85 cc. of ether was added to 9.2 g. (0.05 mole) of dibenzothiophene in 25 cc. of ether. The ether was distilled off and the oily residue heated at 100–105° (bath temperature) for five hours and then poured on a Dry Ice–ether slurry. The yield of 4-dibenzothiophenecarboxylic acid was 0.08 g. (0.7%). The acid was converted to the corresponding methyl ester by means of diazomethane, and the methyl ester (as well as a mixture with an authentic specimen) melted at 92–94°. Diethylcalcium was without action on dibenzothiophene in ether solution at room temperature.

A mixture of 3.7 g. (0.02 mole) of dibenzothiophene and diethylbarium, prepared from 3 g. (0.022 g. atom) of barium and 4 g. (0.032 mole) of diethylzinc, was refluxed for three hours and then carbonated. The small quantity (about 0.1 g.) of 4-dibenzothiophenecarboxylic acid was converted to the methyl ester by means of diazomethane, and this ester was identified by a mixed m. p. determination.

(4) **Dibenzofuran.**—A mixture of 3.4 g. (0.02 mole) of dibenzofuran and diethylbarium, prepared from 3 g. (0.022 g. atom) of barium and 3.5 g. (0.028 mole) of diethylzinc, was refluxed fourteen hours and then carbonated. The yield of 4-dibenzofurancarboxylic acid, melting at 207–209°, was 0.29 g. (8.8%).

(5) **Triphenylmethane.**—A reddish-brown solution of 0.015 mole of diethylbarium in 60 cc. of ether was added to a stirred solution of 7.3 g. (0.03 mole) of triphenylmethane in 60 cc. of ether. There was no color change, and no gas was evolved. Also no gas was evolved while being heated at reflux for twenty-four hours. Then the ether was distilled off and the residue heated at 55–60° for fourteen hours. No appreciable amount of gas was evolved at any time, and the solution gave a strong color test. Subsequent to carbonation by Dry Ice there was recovered 7.2 g. (98.7%) of triphenylmethane (mixed m. p.). Acidification of the basic extract gave a cloudy suspension, but no solid material could be isolated.

Halogen–Metal Interconversions: (1) **α -Bromonaphthalene.**—To a filtered solution of diethylbarium, prepared from 4 g. (0.029 g. atom) of barium and 3.6 g. (0.029 mole) of diethylzinc, was added 4.1 g. (0.02 mole) of α -bromonaphthalene. The mixture was refluxed for two hours and then carbonated to yield a very small quantity of α -naphthoic acid (mixed m. p.).

(2) **Triphenyl-*p*-bromophenyllead.**—A solution of 0.015 mole of diethylbarium in 65 cc. of ether was added quickly to a stirred suspension of 5.9 g. (0.01 mole) of triphenyl-*p*-bromophenyllead in 25 cc. of ether. The organolead compound dissolved and then a flocculent precipitate appeared. After two and one-fourth hours there was a considerable quantity of yellow precipitate. The mixture was stirred for an additional twenty-two hours and then carbonated by Dry Ice. The carbonation residue was cooled by an ice-bath, and carefully hydrolyzed with 10 cc. of water followed by 50 cc. of 10% hydrochloric acid. Practically clear ether and aqueous layers resulted. The ether layer was separated and extracted with 25 cc. of 10% potassium hydroxide; some precipitate appeared in the basic layer. The aqueous layer was removed, filtered, cooled by an ice-bath and acidified to give a viscous oil. This was dissolved in 25 cc. of 10% potassium hydroxide, a milky suspension appearing which could

not be filtered clear. The mixture was acidified, and on standing overnight the oil (0.35 g.) solidified. Methylation by means of diazomethane gave a 1.5% yield of *p*-carbomethoxyphenyl-triphenyllead melting at 124–126°. A mixed m. p. determination with an authentic specimen prepared by D. S. Melstrom¹⁶ melted at 124–126°.

Metal–Metal Interconversions: (1) **Triphenylethyllead.**—A solution of 0.03 mole of diethylbarium in 75 cc. of ether was added to 4.2 g. (0.009 mole) of triphenylethyllead in 30 cc. of ether. The cloudy mixture was stirred at room temperature for four hours and then carbonated by Dry Ice. After the usual procedures, there was isolated 0.1 g. (9.1%) of benzoic acid.

(2) **Tetraphenyllead.**—A mixture of 0.01 mole of diethylbarium and 10.3 g. (0.02 mole) of tetraphenyllead in 250 cc. of ether was stirred at room temperature for twenty-four hours. Subsequent to carbonation there was recovered 9.4 g. (91.2%) of tetraphenyllead (mixed m. p.) but no benzoic acid.

(3) **Tetraphenyltin.**—A solution of 0.01 mole of diethylstrontium in 40 cc. of ether was added to a stirred suspension of 8.5 g. (0.02 mole) of tetraphenyltin in 27 cc. of ether. After stirring at room temperature for twenty-four hours, the mixture was carbonated to yield 0.26 g. (10.7%) of benzoic acid together with a recovery of 75.3% of tetraphenyltin.

Under corresponding conditions, a solution of 0.01 mole of diethylbarium in 41 cc. of ether was added to a stirred suspension of 8.5 g. (0.02 mole) of tetraphenyltin in 250 cc. of ether, and the resulting mixture was stirred for twenty-four hours at room temperature prior to carbonation. The products isolated were 32% of benzoic acid and 57.5% of tetraphenyltin.

(4) **Other RM Compounds.**—No benzoic acid was isolated when a solution of 0.03 mole of diethylbarium was first refluxed in benzene for thirteen hours with an equivalent quantity of either tetraphenylsilicon or tetraphenylgermanium and then carbonated.

Reactions with Triarylmethyl Chlorides.—A solution of 0.01 mole of diethylbarium in 44 cc. of ether was added, over a one-hour period, to a stirred suspension of 9.5 g. (0.02 mole) of triphenyllead chloride in 75 cc. of ether. Reaction occurred, as evidenced by a darkening of the mixture which was then stirred for an additional three hours. A color test was weakly positive. Hydrolysis of the cooled mixture by an ammonium chloride solution gave, subsequent to drying and removal of the ether under reduced pressure, an oil which crystallized after standing for several hours. This was triphenylethyllead (mixed m. p.) and the yield was 4.6 g. (49.2%). The residue, which was obtained by filtration immediately after the hydrolysis, was extracted with boiling chloroform from which solution was isolated 2 g. (19.4%) of tetraphenyllead (mixed m. p.).

Under conditions essentially like those described above, 0.01 mole of diethylbarium and 7.7 g. (0.02 mole) of triphenyltin chloride gave 6.5 g. (85.8%) of triphenylethyltin.

Carbonations: (1) **Diethylbarium.**—Carbonation of diethylbarium prepared from 10.3 g. (0.075 g. atom) of barium and 12 g. (0.098 mole) of diethylzinc gave, subsequent to treatment with silver nitrate, 2.02 g. (14.9%) of silver propionate. 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., 99.5–101°).

(2) **Di-*n*-butylbarium.**—A mixture of 3.7 g. (0.027 g. atom) of barium and 5 g. (0.028 mole) of di-*n*-butylzinc in 10 cc. of benzene was refluxed for ten hours. The resulting jet-black mixture gave an immediate color test I. Subsequent to carbonation, the resulting valeric acid was distilled and the distillate titrated with standard thallous hydroxide for the purpose of using the thallous salt as a derivative.¹⁷ On evaporation, the thallous valerate crystallized out in shiny, white crystals and the yield was 13%. Neither the thallous valerate prepared in this

(16) Melstrom, *Iowa State Coll. J. Sci.*, **18**, 65 (1943).

(17) Gilman and Abbott, *This Journal*, **65**, 123 (1943).

manner, nor the thallos valerate prepared by R. K. Abbott from other valeric acid, had a definite melting point. Accordingly the salt was heated with *p*-bromophenacyl bromide to give the corresponding ester (m. p. 67.5–69.5°), which was identified by comparison with an authentic specimen. The *p*-bromophenacyl ester was prepared in another experiment in which the valeric acid was isolated in a 17.5% yield by way of the silver salt.

Summary

A comparison has been made of some reactions of organocalcium, -strontium, and -barium compounds. The recently available organostrontium and organobarium compounds show reactions with some olefins, benzophenone-anil and azobenzene characteristic of the highly reactive organoalkali compounds.

Unlike *n*-butyllithium which metalates methyl phenyl sulfide laterally, diethylstrontium and -bar-

ium effect nuclear metalation. The metalation of dibenzothiophene in the 4-position by diethylcalcium was equally unexpected because the 3-position is involved when phenylcalcium iodide is used.

Water-solubilizing groups can be introduced in tetraphenyllead by means of a halogen-metal interconversion reaction between triphenyl-*p*-bromophenyllead and diethylbarium. This novel reaction is made possible by a highly subordinated metal-metal interconversion reaction.

The anomalous formation of tetraphenyllead from triphenyllead chloride and diethylbarium appears to be due primarily to a metal-metal interconversion reaction between the reactive, intermediately-formed triphenylethyllead and diethylbarium.

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RECEIVED MARCH 19, 1945

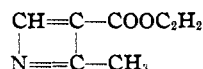
[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES OF MONSANTO CHEMICAL COMPANY]

Esters of β -Cyanocrotonic Acid

BY DAVID T. MOWRY AND ALFRED G. ROSSOW

In connection with certain investigations in progress in these Laboratories, authentic samples of some esters of β -cyanocrotonic acid were prepared.

Ethyl β -cyanocrotonate was one of several possible structures proposed by Pinner^{1,2} for a compound, m. p. 70–71°, resulting from the action of formamidine on acetoacetic ester. Although at first¹ he reported it to be identical with a compound obtainable from acetoacetic ester and hydrogen cyanide or ammonium cyanide, he later² disclosed his inability to obtain the supposed β -cyanocrotonate by this latter method. Later, Shestakove and Kazakov³ expressed considerable doubt that ethyl β -cyanocrotonate was the correct structure of Pinner's product and favored instead a four-membered ring compound of the possible structure

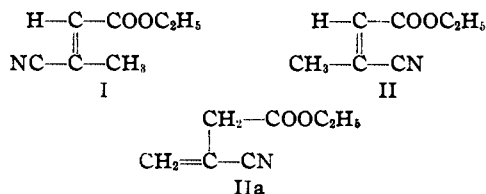


Furthermore, since the ethyl esters of crotonic acid containing either chloro⁴ or phenyl⁵ substituents in the β -position are mobile liquids at room temperature, it appeared that a melting point of 70–71° was abnormally high for the cyano derivative.

Of several methods attempted, for the preparation of ethyl β -cyanocrotonate, the dehydration of acetoacetic ester cyanohydrin by means of thionyl

chloride proved to be the most successful. Two isomers resulted: I, b. p. 94° (24 mm.), f. p. –14°, and II, b. p. 120° (24 mm.), f. p. –40°, having the same composition, C₇H₉NO₂. That the compounds were esters of a β -cyano unsaturated acid was shown by the formation of mesaconic acid on long hydrolysis with aqueous alkali.

Three isomers, then, were possible from this dehydration, *viz.*, the *trans* (I)⁶ and *cis* (II) ethyl β -cyanocrotonates and, less probably, ethyl β -cyano- β -butenoate (IIa).



A compound possessing the latter methylene structure (IIa) would be an α -substituted acrylonitrile and should polymerize readily. Neither isomer developed any trace of polymer on standing for one week at 65° in the presence of 0.1% of benzoyl peroxide, whereas both acrylonitrile and methacrylonitrile polymerized completely in a few hours under similar conditions.

A comparison (see Table I) of the boiling points, densities, refractive indices and molecular refractions of the two isomers with the corresponding known values of analogous compounds, involving the same kinds of isomerism, indicated that the

(1) Pinner, *Ber.*, **18**, 2846 (1885).

(2) Pinner, "Die Imidoether und ihre Derivate," Robert Oppenheim (Gustav Schmidt), Berlin, 1892, pp. 105–107.

(3) Shestakove and Kazakov, *J. Russ. Phys.-Chem. Soc.*, **44**, 1312–20 (1912).

(4) Autenrieth, *Ber.*, **29**, 1655 (1896).

(5) Schroeter and Wulfing, *ibid.*, **40**, 1593 (1907).

(6) It should be noted that this structure has been called *trans* because it is a derivative of mesaconic acid although it is at the same time a derivative of iso-crotonic acid, the *cis* acid. This election was made because it was felt that the cyano group was of greater import than the methyl group.