[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Reactions of Group IV R_4M Compounds with Silver and Copper Salts[1]

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Unsymmetrical organometallic compounds like R_3MR' are generally more reactive than the symmetrical (R_4M) types. For example, it has been reported that R_4Sn and R_4Pb compounds do not react with silver nitrate, whereas triphenylethyltin and triphenylethyllead are cleaved by silver nitrate to give phenylsilver or its complex with silver nitrate.[2]

$$(C_6H_5)_3SnC_2H_5 + AgNO_3 \longrightarrow (C_6H_5Ag)_2 \cdot AgNO_3$$

This particular illustration of the otherwise well-supported generalization concerning the greater reactivity of unsymmetrical organometallic compounds is not so valid now[3] for we have shown that tetraphenyltin and tetraphenyllead are readily cleaved by silver nitrate.

$$(C_6H_5)_4Pb + AgNO_3 \longrightarrow (C_6H_5)_3PbNO_3 + [C_6H_5Ag] \longrightarrow C_6H_5 \cdot C_6H_5$$

Copper nitrate also cleaves the R_4Sn and R_4Pb compounds.

The fate of the radicals varies with the kind of R_4M compound. With tetraphenyltin and silver nitrate the predominant product is benzene, and only a small quantity of biphenyl is formed. However, with tetraphenyllead and silver nitrate, the chief product is biphenyl.

The fate of the radical is also influenced by the nature of the inorganic salt used in the cleavage. Whereas tetraphenyllead is cleaved by silver nitrate to biphenyl, the same R_4Pb compound with copper nitrate gives largely benzene and only a trace of biphenyl. It is probable that the kind of cleavage product is influenced by the reaction medium.

Under corresponding conditions, tetraphenylsilicon and tetraphenylgermanium undergo no reaction with silver nitrate. These results are hardly unexpected in view of the known lesser reactivity of organosilicon and organogermanium compounds.

We have also examined the reactions of silver nitrate and copper nitrate with tetramethyllead and tetraethyllead, respectively. Details on the reaction between silver nitrate and some tetralkyllead compounds have just been published by Semerano and co-workers.[4] In our reaction between copper nitrate and tetramethyllead we have demonstrated that the highly unstable methylcopper is formed as an intermediate. The methane isolated in the gases from the copper nitrate–tetramethyllead reaction may be due to the hydrolysis[5] of methylcopper, for other experiments have shown that methylcopper in dry ether gives ethane almost exclusively.

Experimental

Tetraphenyllead with Silver Nitrate.—Twelve and nine-tenths grams (0.025 mole) of tetraphenyllead was added to a suspension of 5.1 g. (0.03 mole) of pulverized silver nitrate in 75 cc. of absolute ethyl alcohol. After stirring for one-half hour there was considerable darkening, and after twelve hours the mixture was distinctly black with a silver mirror appearing on some portions of the flask. The suspension was refluxed for four hours, after which the alcohol was evaporated in a stream of air. The dry residue was carefully extracted with three 75-cc. portions of petroleum ether (b. p., 28–38°). The petroleum ether was distilled and the residue steam distilled. The yield of biphenyl (mixed m. p.) was 1.35 g. (70.2%).

The residue from the biphenyl extraction was apparently a triphenyllead nitrate–metallic silver complex and was insoluble in hot organic solvents. The triphenyllead nitrate was liberated by treatment with cold, moderately dilute nitric acid. It was found that the complex could be decomposed by stirring with 40 cc. of a solution composed of one part concd. nitric acid to four parts water for one-half hour while being cooled by ice. The solid material was removed by filtration and dried. This mixture was extracted with hot ethyl alcohol and the resulting solution boiled with a small amount of Norite and filtered. Upon slow evaporation the triphenyllead nitrate[6] appeared in crystalline form. The yield was 9.28 g. (74.3%).

Anal. Calcd. for $C_{18}H_{15}PbNO_3$: Pb, 41.41. Found: 41.10, 41.42.

A duplicate of the above experiment was carried out and the yield of biphenyl was 1.30 g. (67.5%) and the yield of triphenyllead nitrate was 9.60 g. (76.8%).

Tetraphenyllead with Copper Nitrate.—In this experiment 38.6 g. (0.075 mole) of tetraphenyllead was added to a solution of 11.9 g. (0.0495 mole) of $Cu(NO_3)_2 \cdot 3H_2O$ in 75 cc. of absolute alcohol and the mixture refluxed for ten

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[1] Paper XLIX in the series "Relative Reactivities of Organometallic Compounds." The preceding paper is THIS JOURNAL, **65**, 122 (1943).

[2] Krause and Schmitz, *Ber.*, **52**, 2150 (1919).

[3] See p. 455 of Gilman, "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1938.

[4] Semerano, Riccoboni and Götz, *Z. Elektrochem.*, **47**, 484 (1941) [*C. A.*, **36**, 4089 (1942)]; Semerano and Riccoboni, *Ber.*, **74**, 1089 (1941) [*C. A.*, **36**, 4801 (1942)]; Semerano, Riccoboni and Callegari, *Ber.*, **74**, 1297 (1941) [*C. A.*, **36**, 4802 (1942)].

[5] Gilman and Straley, *Rec. trav. chim.*, **55**, 821 (1936).

[6] This compound had previously been prepared by Robert Leeper.

hours. The solvent was distilled from the reaction mixture under a pressure of 40–50 mm. The receiver for the distillation was cooled in a dry ice–acetone bath. The residue was maintained at a temperature of 70–80° for one hour. The benzene in the filtrate was separated as *m*-dinitrobenzene in the following manner. The filtrate from the distillation was slowly treated, while being maintained at −15°, with 100 g. of powdered anhydrous calcium chloride. The benzene, along with some alcohol, was distilled at 40–50 mm. pressure into a receiver cooled by a dry ice–acetone bath. The calcium chloride mixture was heated on a water-bath at 70–80° for forty-five minutes to remove the benzene. The distillate was diluted with 55 cc. of water and the benzene layer separated and added dropwise through a condenser attached to a 125-cc. acetylating flask containing a mixture of 20 cc. of fuming nitric acid and 10 cc. of concd. sulfuric acid cooled to 0°. After the addition was complete the mixture was maintained at room temperature for one-half hour, the flask being cooled with ice if heat was generated too rapidly. The mixture was then heated on a boiling water-bath for one and one-half hours with frequent shaking. After being cooled to room temperature the solution was hydrolyzed by ice and the acid almost neutralized with concd. potassium hydroxide. The *m*-dinitrobenzene was extracted with ether and the product isolated by distilling off the ether. The yield was 10.9 g. (86.5%).

Triphenyllead nitrate was separated and purified as described previously. The yield was 25.4 g. (66.8%).

A trace of biphenyl was isolated.

Methylcopper with Benzoyl Chloride.—A solution of 0.05 mole of methyllithium in 50 cc. of anhydrous ether was added during one hour to a stirred suspension of 10.5 g. (0.055 mole) of cuprous iodide in 50 cc. of ether cooled to −15°. The yellow mixture was then stirred at 0° for ten hours. A 3-cc. aliquot of the supernatant solution gave a negative Color Test I. After cooling the above mixture to −15°, 7.0 g. (0.05 mole) of benzoyl chloride in 25 cc. of ether was slowly added dropwise. After warming to room temperature and stirring for one-half hour the mixture was hydrolyzed with 10% hydrochloric acid. The acetophenone was separated and identified as the oxime. The yield was 3.82 g. (56.5%).

Tetramethyllead with Cupric Nitrate in the Presence of Benzoyl Chloride.—A solution of 20.0 g. (0.075 mole) of tetramethyllead in 15 cc. of absolute alcohol was added during fifteen minutes to a solution of 12.1 g. (0.05 mole) of $Cu(NO_3)_2 \cdot 3H_2O$ in 25 cc. of absolute alcohol cooled to −70°. A flocculent yellow suspension formed. Then 7.0 g. (0.05 mole) of benzoyl chloride was added slowly. The mixture was allowed to warm slowly to room temperature, at which it was kept for twelve hours. The alcohol was removed by evaporation. Ten cc. of concd. hydrochloric acid was slowly added and the resulting mixture steam distilled. The distillate was extracted with 100 cc. of ether, the ether distilled off and the residue treated with 6 cc. of 3.6 *M* alcoholic hydroxylamine hydrochloride and 30 cc. of 2.5 *M* alcoholic potassium hydroxide and boiled for ten minutes. This mixture was cooled, diluted with 100 cc. of water and extracted with 50 cc. of ether. This last ether extraction was discarded. The aqueous solution was saturated with carbon dioxide and a milky suspension appeared. This was extracted with 75 cc. of ether and after the ether evaporated, the residual oil solidified by cooling on ice. The yield of dry acetophenone oxime was 0.3 g. (3.0%, based on one methyl group from the tetramethyllead).

A known mixture of acetophenone and ethyl benzoate was carried through the steam distillation and subsequent procedures and a 92% recovery of the ketone as the oxime was realized.

A blank run was carried out with the tetramethyllead and the benzoyl chloride under the same conditions as the above experiment but no acetophenone oxime could be isolated.

Tetraethyllead with Silver Nitrate.—A solution of 24.2 g. (0.075 mole) of tetraethyllead in 40 cc. of absolute ethyl

TABLE I

REACTION OF R_4Sn AND R_4Pb COMPOUNDS WITH SILVER AND COPPER NITRATES

R_4M Compound	Salt	Products (yields, %)
$(C_6H_5)_4Pb$	$AgNO_3$	$C_6H_5 \cdot C_6H_5$ (70.2, 67.5) $(C_6H_5)_3PbNO_3$ (74.3, 76.8)
$(C_6H_5)_4Pb$	$Cu(NO_3)_2 \cdot 3H_2O$	*m*-$C_6H_4(NO_2)_2$ (86.5) $C_6H_5 \cdot C_6H_5$ (trace) $(C_6H_5)_3PbNO_3$ (66.8, 76.0)
$(C_6H_5)_4Sn$[a]	$AgNO_3$	*m*-$C_6H_4(NO_3)_2$ (80.6) $C_6H_5 \cdot C_6H_5$ (5.2)
$(CH_3)_4Pb$[b]	$AgNO_3$	CH_4 (4.0), C_2H_4 (2.1), C_2H_6 (98.3), $(CH_3)_3PbNO_3$ (82.7)
$(CH_3)_4Pb$[c]	$Cu(NO_3)_2 \cdot 3H_2O$	CH_4 (21.1), C_2H_6 (74.6), $(CH_3)_3PbI$ (71.3)
$(C_2H_5)_4Pb$	$AgNO_3$	C_2H_4 (15.5), C_2H_6 (27.8), C_4H_{10} (52.0), $(C_2H_5)_3PbCl$ (72.7)
$(C_2H_5)_4Pb$[d]	$Cu(NO_3)_2 \cdot 3H_2O$	C_2H_4 (16.7), C_2H_6 (26.3), C_4H_{10} (52.5), $(C_2H_5)_3PbCl$ (75.7)

[a] In this reaction 10.7 g. (0.025 mole) of tetraphenyltin was added to a suspension of 5.1 g. (0.03 mole) of silver nitrate in 75 cc. of absolute alcohol and refluxed for four hours. The benzene was isolated and identified as described above. After removing the biphenyl by the petroleum ether extraction, the residue was found to be insoluble in hot organic solvents and amounted to 6.2 g. An analysis showed that this solid mixture contained 45.0% tin. This accounted for 94.2% of the total tin. The yields in this reaction are calculated on the basis of 4 phenyl groups. [b] Twenty grams (0.075 mole) of tetramethyllead was used. The reaction was carried out at a temperature of −70°. The trimethyllead nitrate was purified by crystallization from alcohol. This compound is sparingly soluble in ether, moderately soluble in alcohol or water, and insoluble in petroleum ether fractions. It slowly decomposes on being heated in a capillary tube but does not melt. *Anal.* Calcd. for $C_3H_9PbNO_3$: Pb, 65.93. Found: Pb, 66.22. The excess over one hundred per cent. yield for the total gas evolution was probably due to a slight thermal decomposition of tetramethyllead. [c] Due to the lack of success of separating the excess copper nitrate from the trimethyllead nitrate, the latter compound was converted to the water insoluble trimethyllead iodide by means of sodium iodide in a dilute alcohol solution. [d] In this reaction the amount of copper nitrate used was 12.1 g. (0.05 mole) and the temperature of addition was −70°.

alcohol was added, over a period of twenty-five minutes, to a suspension of 17.0 g. (0.1 mole) of pulverized silver nitrate in 25 cc. of absolute alcohol at a temperature of −70°. A pale yellow suspension was formed which turned black quite rapidly. The mixture was allowed to warm slowly to room temperature, and was then stirred for two hours after which it was refluxed for fifteen minutes. An analysis of the evolved gases gave 0.0208 mole (27.8%) of ethane, 0.0116 mole (15.5%) of ethylene, and 0.0195 mole (52.0%) of butane. The yields are based on the cleavage of one ethyl group.

The residual suspension was filtered and evaporated in a stream of air to a volume of about 50 cc. Then 100 cc. of water was added followed by 30 cc. of 10% hydrochloric acid. During the addition, the mixture was stirred while being cooled in an ice-bath. The large amount of white precipitate was filtered; dissolved in 100 cc. of ether; and the ether solution allowed to evaporate spontaneously almost to dryness. White needles were formed which were washed with 10 cc. of petroleum ether (b. p., 28–38°) and dried. The yield of triethyllead chloride was 18.0 g. (72.7%).

The general results are given in Table I. Gases were analyzed by conventional procedures. All of the organolead products were analyzed, but analytical results are given only for the new organolead compounds. The percentages of *m*-dinitrobenzene are those obtained incidental to the isolation and characterization of the benzene.

Silver Nitrate with Tetraphenylsilicon and Tetraphenylgermanium.—Tetraphenylsilicon was refluxed with an alcoholic suspension of silver nitrate for one hundred and forty-four hours. There was no evidence of reaction, and the RM compound was recovered.

Tetraphenylgermanium was refluxed with silver nitrate, under corresponding conditions. for one hundred and twenty hours. Only a slight darkening of the mixture was apparent and the RM compound was recovered practically quantitatively.

Summary

The fate of the R groups in cleavage reactions of $(C_6H_5)_4Sn$ and $(C_6H_5)_4Pb$ with silver and copper nitrates varies both with the RM compound and the inorganic salt. Tetraphenylsilicon and tetraphenylgermanium are not cleaved, under corresponding conditions, by silver nitrate.

The highly unstable methylcopper has been shown to be an intermediate in the reaction between tetramethyllead and copper nitrate.

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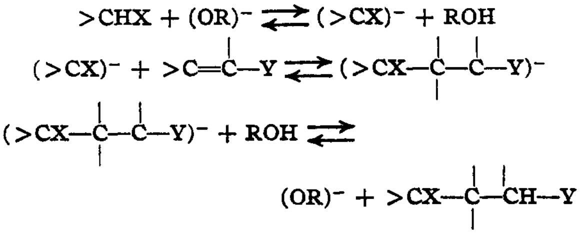
[Contribution from the School of Chemistry of the University of Minnesota]

A Study of Some Michael Reactions

By C. F. Koelsch

When a Michael reaction is brought about by treating a mixture of an α,β-unsaturated compound and a substance containing an active methylene group with an alkoxide, it proceeds through the following stages (X and Y are electrophilic groups)



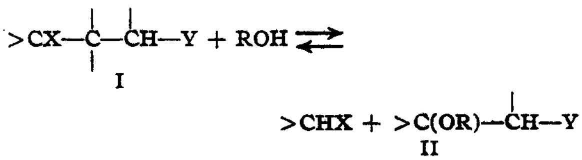
$$>\mathrm{CHX} + (\mathrm{OR})^- \rightleftarrows (>\mathrm{CX})^- + \mathrm{ROH}$$

$$(>\mathrm{CX})^- + >\mathrm{C}{=}\overset{|}{\mathrm{C}}\text{—}\mathrm{Y} \rightleftarrows (>\mathrm{CX}\text{—}\underset{|}{\overset{|}{\mathrm{C}}}\text{—}\overset{|}{\mathrm{C}}\text{—}\mathrm{Y})^-$$

$$(>\mathrm{CX}\text{—}\underset{|}{\overset{|}{\mathrm{C}}}\text{—}\overset{|}{\mathrm{C}}\text{—}\mathrm{Y})^- + \mathrm{ROH} \rightleftarrows$$

$$(\mathrm{OR})^- + >\mathrm{CX}\text{—}\underset{|}{\overset{|}{\mathrm{C}}}\text{—}\overset{|}{\mathrm{C}}\mathrm{H}\text{—}\mathrm{Y}$$

But since not only the anion formed from the active methylene compound but also the alkoxide anion can add to the unsaturated substance, the reaction involves effectively the equilibrium



$$\underset{\mathrm{I}}{>\mathrm{CX}\text{—}\underset{|}{\overset{|}{\mathrm{C}}}\text{—}\overset{|}{\mathrm{C}}\mathrm{H}\text{—}\mathrm{Y}} + \mathrm{ROH} \rightleftarrows >\mathrm{CHX} + \underset{\mathrm{II}}{>\mathrm{C}(\mathrm{OR})\text{—}\overset{|}{\mathrm{C}}\mathrm{H}\text{—}\mathrm{Y}}$$

In most cases the tendency to form an alkoxy compound (II) is relatively small, and the Michael reaction can be carried out successfully in alcoholic solution.[1]

It was found, however, that methyl acrylate and acrylonitrile[2] formed addition products with alcohols with exceptional rapidity. When attempts were made to carry out Michael reactions with these acrylic acid derivatives in alcoholic solutions, only β-alkoxypropionic esters or nitriles were obtained. The following experiments indicate the ease with which alcohol additions took place.

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[1] Reactions between β-hydroxy- or β-halogenated compounds (II, OH or Br in place of OR) and active methylene compounds in the presence of bases lead to I. These transformations are obviously similar to the Michael reaction and do not involve *direct* interchange of OH or Br for >CX— [*Cf.* Ingold, *J. Chem. Soc.*, **119**, 335 (1921)].

[2] The research described in the present paper was undertaken primarily to discover satisfactory conditions for carrying out condensations of benzyl cyanide with methyl acrylate and with acrylonitrile. It was done during the early months of 1940, but since it forms a part of a larger investigation, it was not published. Publication of the work in its present form is, however, now made desirable by the appearance of a paper by Bruson [This Journal, **64**, 2457 (1942)] in which related reactions are described and identical investigations are projected.