and eight-tenths grams of tetrakis(hydroxymethyl)phosphonium chloride dissolved in 100 cc. of water was boiled with 19 g. of barium hydroxide for several hours until the evolution of hydrogen ceased. The barium was then removed with a slight excess of sulfuric acid and the hydrochloric acid with silver carbonate. From the filtrate, dissolved silver was precipitated with hydrogen sulfide. The filtrate was then evaporated on the water-bath to a sirup and the heating continued for some time to drive off any formic acid which might have resulted from the action of barium hydroxide on formaldehyde. The acid was then converted into the barium salt by boiling with water and barium carbonate, the filtrate evaporated to small bulk and allowed to crystallize. The crystals were washed with a little water. The mother liquor seemed to contain caramel-like substances formed by the action of barium hydroxide on formaldehyde. The product consisted of well-developed crystals, moderately soluble in water, insoluble in alcohol.

Anal. Calcd. for $C_4H_{12}O_6P_2Ba$: Ba, 35.4; P, 16.02. Found: Ba, 35.2; P, 15.68.

Summary

The action of alkali on tetrakis(hydroxymethyl)phosphonium chloride has been shown to take place in two stages, giving first tris(hydroxymethyl)phosphonium oxide and finally bis(hydroxymethyl)phosphinic acid and liberating one molecule of hydrogen at each stage. With a neutral carbonate the action stops at the oxide stage.

Tetrakis(chloromethyl)phosphonium chloride was prepared from the corresponding hydroxy derivative by treating with phosphorus pentachloride. This was converted into tris(chloromethyl)phosphine and the latter to tris(chloromethyl)phosphine oxide.

A crystalline barium salt of bis(hydroxymethyl)phosphinic acid was obtained.

The work is being continued.

KEW GARDENS, NEW YORK

[CONTRIBUTION FROM THE LABORATORIES OF THE SHELL DEVELOPMENT COMPANY]

TRIORGANO THALLIUM COMPOUNDS. THALLIUM TRIETHYL AND THALLIUM DIETHYL TRIPHENYLMETHYL

BY H. P. A. GROLL

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The only organo thallium compounds known are of the type R_2TlX,[1] *i. e.*, salts of the bases R_2TlOH first isolated by R. J. Meyer and A. Bertheim.[2] Many alkyl and aryl compounds of this type have been prepared by D. and A. E. Goddard,[3] E. Krause and A. v. Grosse.[4] F. Hein and E. Markert[5] and A. E. Goddard[3] attempted without success to prepare TlR_3 or $(Tl(C_2H_5)_2)_2$.

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[1] Hansen, *Ber.*, **3**, 3 (1870); Hartwig, *ibid.*, **7**, 298 (1874).

[2] Meyer and Bertheim, *ibid.*, **37**, 2051 (1904).

[3] Goddard and Goddard, *J. Chem. Soc.*, **119**, 672, 1310 (1921); **121**, 36, 256, 482 (1922).

[4] Krause and Grosse, *Ber.*, **58**, 272, 1933 (1925).

[5] Hein and Markert, *ibid.*, **61**, 2255 (1928).

A. v. Grosse[6] in his article "The Periodic System and the Alkyl Compounds of the Elements" predicts the existence of true thallium trialkyls from theoretical considerations of the atomic structure. In fact, no reason can be discerned why triorgano thallium compounds should not be stable provided the combination of the third valency of thallium with an organic radical can be achieved. The strongly alkaline character of dialkyl thallium hydroxide suggests that the third valency may be difficult to combine with an alkyl group, but as alkyls even of the alkali metals are known, it should not be impossible. The most promising method of combining the third valency with an alkyl group seemed to be reaction between thallium dialkyl chloride and an alkali metal alkyl, *e. g.*

$$(C_2H_5)_2TlCl + NaC_2H_5 = (C_2H_5)_3Tl + NaCl \qquad (1)$$

This reaction is analogous to Schlenk's synthesis of tetramethyl triphenylmethyl ammonium, and other penta-organo nitrogen compounds.[7] As both sodium ethyl and thallium diethyl chloride are insoluble in any indifferent solvent, this reaction presents many technical difficulties. Accordingly, lithium ethyl, which is soluble in petroleum ether, was chosen for the reaction. The reaction between lithium ethyl and thallium diethyl chloride occurs slowly with good yields and comparative freedom from side reactions at room temperature. Heating of the reaction mixture if only to 50° is unfavorable, as much metallic thallium is then formed.

Thallium triethyl is a heavy mobile liquid resembling lead tetraethyl in its odor and in many other characteristics. It differs in appearance from the lead compound in its bright golden yellow color, which becomes more intense at increased temperatures. At the temperature of carbon dioxide–acetone mixture the liquid is still yellow, but at liquid-air temperature it crystallizes to almost white crystals.

Thallium triethyl is soluble in ether, petroleum ether and alcohol, but is insoluble in water. Under atmospheric pressure it decomposes spontaneously at 129° before reaching its boiling point and liberates metallic thallium. Under a pressure of 1.5 mm. of mercury it boils unchanged at 54.8°, but it was observed that the compound decomposed if the temperature of the glass walls of the distilling flask rose to 90–100°.

The chemical properties differ more widely from those of the corresponding lead compound. Thallium triethyl is more reactive. While it is stable toward dry oxygen, it is decomposed readily by water to thallium diethyl hydroxide and ethane.

$$Tl(C_2H_5)_3 + H_2O = Tl(C_2H_5)_2OH + C_2H_6 \qquad (2)$$

This decomposition is comparatively slow, as the reaction occurs only at the interface between the two immiscible liquids. That the slow reaction is not due to inactivity of the thallium triethyl is shown by the fact that

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[6] Grosse, *Z. anorg. allgem. Chem.*, **152**, 133 (1926).

[7] W. Schlenk and J. Holtz, *Ber.*, **49**, 603 (1916); **50**, 274, 276 (1917).

a much more rapid reaction occurs with alcohol, in which it is soluble. The compound is violently decomposed by absolute alcohol with evolution of heat and gas; also, when shaken with water it reacts much more rapidly, and in moist air emits white fumes due to reaction of its vapor with the water vapor.

For preliminary information prior to the preparation of thallium triethyl, thallium diethyl triphenylmethyl was prepared from thallium diethyl chloride and sodium triphenylmethyl, which latter is soluble in ethyl ether. The reaction occurred in the same way as with lithium ethyl. Thallium diethyl triphenylmethyl was obtained as a yellow sirup which did not crystallize. It therefore could not be separated from impurities such as triphenylmethyl carbinol and triphenylmethane. The sirup has properties similar to those of thallium triethyl. It is soluble in ether and petroleum ether, but insoluble in water. In moist air the sirup becomes coated with a skin of crystals which were shown to contain thallium. These crystals dissolve in water to give a solution with a strongly alkaline reaction, but are insoluble in ether or petroleum ether. They effervesce with acid and are obviously thallium diethyl carbonate. With water the sirup decomposes slowly without evolution of gas, the water becoming alkaline, and the sirup, originally clear and yellow, becoming cloudy and discolored. This indicates a decomposition to thallium diethyl hydroxide and triphenylmethane.

$$(C_2H_5)_2TlC(C_6H_5)_3 + H_2O = (C_2H_5)_2TlOH + HC(C_6H_5)_3 \qquad (3)$$

Thallium diethyl triphenylmethyl was not further examined since only a small quantity of it was prepared as a step toward the synthesis of thallium triethyl, the latter being the main object of this investigation.

Finally, it was found that thallium triethyl may also be prepared by direct reaction between ethyl chloride and alloys of thallium with sodium. Finely divided alloys containing 7, 10 and 15% of sodium were shaken for several hours with ethyl chloride. The reaction was very slow at room temperature. Small amounts of thallium triethyl were formed in each experiment but no way has been found to increase the yield.

Experimental

In the preparation of thallium triethyl from thallium diethyl chloride and lithium ethyl, oxygen and moisture must be rigorously excluded. The technique and apparatus used by Schlenk and Holtz[7,8] for the preparation of lithium ethyl were, with minor modifications, found suitable also for the preparation of the thallium triethyl. The thallium diethyl chloride must be as pure as possible. When the Grignard synthesis of the compound is carried out correctly, one recrystallization from ammonia is suf-

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[8] Schlenk and Holtz, *Ber.*, **50**, 262 (1917). Houben-Weyl, "Die Methoden der organischen Chemie," Vol. IV, 2d ed., p. 959.

ficient; otherwise, a recrystallization in the dark from absolute alcohol, using conveniently a Soxhlet extractor, is necessary to provide a product pure enough for the synthesis. The lithium ethyl prepared by the reaction of finely granulated lithium with mercury diethyl was isolated by crystallization, weighed, and used as solid in order to ensure freedom from mercury diethyl, which would contaminate the thallium triethyl and be difficult to separate. This precaution is unnecessary if the solution of lithium ethyl as obtained by the synthesis is free from mercury. Lithium metal is prepared in a finely granulated form by melting lithium in white paraffin and stirring rapidly. Using such finely divided lithium, the yield of lithium ethyl with respect to mercury diethyl is practically quantitative.

Preparation of Thallium Triethyl.—Thirty-two and one-half grams (0.11 mole) of dry thallium diethyl chloride was put into a 200-cc. bulb of the type described by Schlenk with a neck wide enough to fill in the solid lithium ethyl by introducing the neck of the closed filter or storage bulb in which the lithium compound was weighed. Enough petroleum ether of 30–50° boiling range was added to cover the thallium diethyl chloride completely and to expel any air included by the powder. A stream of dry, highly purified nitrogen was passed through the bulb until all air was displaced. The bulb was inserted into a mixture of ice and salt to prevent reaction during the operation of filling. Six grams (0.16 mole) of lithium ethyl was added and washed down with petroleum ether, the bulb finally being filled to about two-thirds of its capacity. The neck and the side tubes were then sealed quickly, the stream of nitrogen being maintained as long as possible. For ease of operation in an inert atmosphere it is very convenient to use reaction bulbs with two side tubes set at 90° to each other instead of the bulbs with single tubes as described by Schlenk. The bulb was taken out of the ice and carefully shaken by hand for about twenty minutes. The temperature of the reaction mixture must not be allowed to rise above room temperature. Occasional cooling with ice was advisable during this period as the reaction sometimes started too rapidly. The bulb was then shaken in a shaking machine in the dark.

The liquid soon began to turn yellow and at the same time lithium chloride began to appear as a very fine light sludge, slightly discolored by traces of metallic thallium; the heavy powder of thallium diethyl chloride slowly disappeared. Completion of the reaction required twenty-four to forty-eight hours at room temperature, the time depending mainly on the fineness of the thallium diethyl chloride.

The bulb was opened in a stream of dry nitrogen and the liquid decanted into centrifuge tubes shaped at the top like a Schlenk bulb with a side tube for the nitrogen current. After centrifuging, the liquid was decanted from solid matter into another bulb. Any residual lithium ethyl was destroyed by passing through the solution a stream of dry air free from carbon dioxide. The liquid was filtered in a well-dried atmosphere and the petroleum ether removed by evaporation on a water-bath below 100°. This evaporation may be accelerated by evacuating, a lower temperature being then maintained to prevent loss of thallium triethyl. The residue is pure thallium triethyl. The yield was 25 g. of $Tl(C_2H_5)_3$, *i. e.*, 79% of the theoretical. The product was distilled under vacuum and the constant-boiling fraction analyzed.

Analysis.—A weighed quantity (1.7144 g.) of substance was hydrolyzed with water and the amount of ethane formed according to Equation 2 measured. The solution was divided into five equal parts, one of which was titrated with 0.1 *N* hydrochloric acid to determine thallium diethyl hydroxide, while the other four were used for the gravimetric estimation of thallium as thallous iodide. The following gravimetric method was used.

The solution of $Tl(C_2H_5)_2OH$ was neutralized with dilute sulfuric acid and evaporated to dryness. The organic salt was decomposed by carefully adding fuming nitric acid and heating on a water-bath until no more red fumes were evolved. The solution was again evaporated to dryness, the residue dissolved in water, reduced with ammonium bisulfite and dilute sulfuric acid, and evaporated to dryness. The thallous sulfate was converted to thallous iodide as described by Fresenius.[9]

Anal. Subs., 1.7144: C_2H_6, 0.1753. Subs., 0.3429: 11.5 cc. of $N/10$ HCl. Subs., 0.3429: TlI, 0.3897, 0.3857, 0.3907, 0.3889; av., 0.3888. Calcd.: C_2H_6, 0.1767; 11.76 cc. of $N/10$ HCl; TlI: 0.3898.

Physical Properties.—Specific gravity, $S^{21.4}_{21.4}$, 1.971; b. p. 54.6–54.8° at 1.50–1.55 mm.; m. p. below −80 and above −183°.

Thallium Diethyl Triphenylmethyl.—Two and four-tenths grams of dry thallium diethyl chloride was put into a bulb of the type already described. The air was then displaced from the bulb by dry nitrogen, 107 cc. of 0.075 N solution of sodium triphenylmethyl in ether was added and the mixture shaken until the red color of the sodium triphenylmethyl had disappeared. This took about twenty hours. The solution was separated from the precipitate by centrifuging in the manner already described and the ether evaporated.

The yield was about 4 g. of a yellow sirup, which contained much thallium. It was soluble in petroleum ether and in ether, and insoluble in water. It slowly decomposed in the presence of water without gas formation. After decomposition by water the extract with ether or petroleum ether contained no thallium, whereas the extract with water was strongly alkaline and gave all reactions of thallium diethyl hydroxide. From this behavior and analogy with thallium triethyl it is concluded that the sirup is or contains thallium diethyl triphenylmethyl. It was not further examined.

Summary

1. Thallium triethyl has been synthesized by the reaction of thallium diethyl chloride with lithium ethyl.
2. The chemical and physical properties of thallium triethyl are described.
3. Thallium diethyl triphenylmethyl has been synthesized from thallium diethyl chloride and sodium triphenylmethyl.

EMERYVILLE, CALIFORNIA

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[9] Fresenius, *Z. anal. Chem.*, **29–30**, 342 (1891).