CCII.—*Application of Thallium Compounds in Organic Chemistry. Part V. Thallous Ethoxide and Dimethylthallium Ethoxide.*

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The following preparations of thallium salts starting from thallic oxide may prove useful to others interested in the metal.

The first reaction described probably takes place according to the equation $Tl_2O_3 + 2H{\cdot}CHO \longrightarrow 2H{\cdot}CO{\cdot}OTl + H_2O$: the others are double decompositions.

In the preparations of thallous ethoxide advantage is taken of the fact that the reaction between thallous ethoxide and water with formation of thallous hydroxide and ethyl alcohol is reversible. The heat given out by the reaction is shown below to be small.

Owing to its complete miscibility with ether, with benzene and with *n*-hexane the ethoxide is a convenient intermediary for the preparation of chelate compounds of thallium such as the acetylacetonate, which can easily be prepared in 90% yield by mixing solutions of the ethoxide and of acetylacetone in dry benzene. The benzene is conveniently purified before use by heating under reflux for 1 hour with a little thallous ethoxide, followed by washing with water, drying over sodium, and distillation. Kurowski (*Ber.*, 1910, **43**, 1079) pointed out that thallous acetylacetonate affords a very delicate test for the presence of sulphur compounds in benzene, and

the author has only once purchased benzene in which this substance dissolves without formation of an orange precipitate on heating.

After the preliminary treatment described above, benzene may be used for recrystallisation of thallous acetylacetonate without development of any colour or precipitate. Orange-coloured precipitates are formed if traces of carbon disulphide are added, and yellow precipitates, darkening slightly on heating, by ethyl mercaptan. Dark discolorations occur on the surface of the tube on heating solutions of thallous ethoxide in benzene thus purified, but these discolorations are dissolved to a colourless solution by water or by alcohol and are probably due to decomposition of thallous ethoxide with formation of thallous oxide on the metal.

On addition of a little carbon disulphide to a cold solution of thallous ethoxide in benzene the whole sets to a stiff jelly. Traces of carbon disulphide give a light-coloured precipitate which on heating becomes black. This black precipitate is insoluble in water or in alcohol but is rapidly dissolved by hydrogen peroxide, and is indistinguishable in appearance and in its behaviour towards the above reagents from that obtained by heating commercial benzene with a little thallous ethoxide and which liberates hydrogen sulphide on treatment with hydrochloric acid.

Ethyl mercaptan added to a solution of thallous ethoxide in purified benzene gives a yellow precipitate which becomes orange on heating.

Both the acetylacetonate and the ethoxide give yellowish discolorations on heating with thiophen, but only slowly; small quantities of thiophen added to their solutions in purified benzene have little if any effect.

It is thus probable that thallous ethoxide is as delicate a test for some sulphur compounds as is the acetylacetonate. The matter is being further investigated.

The preparation of *dimethylthallium ethoxide* in solution has already been described (J., 1928, 1288), but not that of the pure liquid.

Thallous formate. Formaldehyde (180 c.c., $d^{19°}$ 1·084) was warmed gently in a large evaporating basin after 456 g. (1 g.-mol.) of thallic oxide had been stirred in. A vigorous reaction soon began, the mixture boiling and frothing with much vaporisation of formaldehyde. On its completion the mixture was diluted with water and filtered, 96 g. of apparently unchanged thallic oxide being recovered. From the faintly alkaline filtrate, after neutralisation with a few drops of formic acid, 350 g. of thallous formate, m. p. 103—104°, were obtained (yield, 89%) (Found: Tl, 82·15; C, 4·9; H, 0·8. Calc.: Tl, 81·95; C, 4·8; H, 0·4%).

Thallous hydroxide. To 1000 c.c. of solution containing 752 g.

of thallous formate prepared from 695 g. of thallic oxide and 345 c.c. of formaldehyde as described above were added 200 g. of sodium hydroxide dissolved in 300 c.c. of water. The mixture was brought to the boiling point and filtered. On cooling, 337 g. of crude thallous hydroxide crystallised, and a further 200 g. were obtained by concentration of the mother-liquor (yield, 80%).

Thallous ethoxide. (1) 337 G. of crude moist thallous hydroxide were shaken in a stout-walled flask with 100 c.c. of commercial absolute alcohol at 20°. The temperature rose to 23° and the crystalline hydroxide sintered. After 10 minutes, as much of the alcohol as possible was decanted and a further 100 c.c. of alcohol were added. On shaking, the temperature rose to 25° and the solid sintered still more. On again decanting and again shaking with 100 c.c. of alcohol, the temperature did not quite reach 25° and the solid appeared to melt; after a final treatment with 50 c.c. of alcohol the thallous ethoxide was tapped off in a separating funnel (yield, after filtration, 288 g. or 76%) (Found by titration: Tl, 82·8. Calc.: Tl, 81·95%).

(2) 50 G. of thallous formate, dissolved in its own weight of water, were boiled with a solution of 8 g. of sodium in 150 c.c. of commercial absolute alcohol. The whole was filtered into a separating funnel and 41·1 g. of thallous ethoxide were tapped off (yield, 82%). Thallous ethoxide thus prepared probably contains a little sodium ethoxide. The crude liquid gave a titration value corresponding to 83·8% Tl, which fell to 82·9% after shaking with decolorising carbon and filtration.

Dimethylthallium ethoxide. 24·1 G. of thallous ethoxide and 34·2 g. of dimethylthallium bromide were refluxed in dry ether till a filtered portion of the solution gave a white precipitate with potassium iodide. On removal of the solvent 23 g. of crude dimethylthallium ethoxide remained as a yellow oil [Found by titration: Tl, 73·8. $(CH_3)_2Tl{\cdot}O{\cdot}C_2H_5$ requires Tl, 73·1%]. 15·35 G. of the crude product were then distilled at 110—120°/15 mm., 12·5 g. of the pure substance being obtained (Found by titration: Tl, 73·2, 73·2%). The freshly distilled liquid is water-white and very mobile, but rapidly becomes cloudy on exposure to air. A glass rod dipped in the liquid fumes on exposure to air. The substance is completely miscible with water, methyl alcohol, ether, and *n*-hexane, and is altogether more quickly reactive than thallous ethoxide.

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