434. *The Action of Ethylmagnesium Bromide on Thallous Chloride and on Thallous Ethoxide.*

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The action of the Grignard reagent on lead dichloride gives lead tetra-alkyls or tetra-aryls (Grüttner and Krause, *Ber.*, 1916, **49**, 1420; Pfeiffer and Truskier, *ibid.*, 1904, **37**, 1127), half of the lead being reduced to the metal: $2PbCl_2 + 4RMgBr \longrightarrow PbR_4 + Pb + 4MgClBr$. Mercury diphenyl and mercury are similarly formed from mercurous chloride and phenylmagnesium bromide (*idem*, *ibid.*, p. 1126): $2HgCl + 2MgPhBr \longrightarrow HgPh_2 + Hg + 2MgClBr$.

Meyer and Bertheim (*Ber.*, 1904, **37**, 2061), on the other hand, failed to alkylate thallous chloride by the action of magnesiumalkyl halides, only thallium being isolated. Hein and Segitz (*Z. anorg. Chem.*, 1924, **141**, 224), using a lead anode, obtained lead tetraethyl by the electrolysis of a solution of sodium ethyl in zinc diethyl, and found later (*ibid.*, 1927, **158**, 162) that on using a thallium anode a darkening of the whole electrolyte, accompanied by a fall in the electrical resistance, rapidly took place. They suggested that the first action was formation of thallous ethyl, followed by that of thallium triethyl and the metal, $3TlEt \longrightarrow TlEt_3 + 2Tl$,[*] the liberated metal accounting for the lowered resistance. They do not, however, record the isolation of any alkylated thallium compound. More recently, Groll (*J. Amer. Chem. Soc.*, 1930, **52**, 3000) obtained thallium triethyl in small yield by direct action between ethyl chloride and alloys of thallium with sodium.

We now find (Expt. I) that on heating 1 mol. of thallous chloride with an ethereal solution of *ca.* 2 mols. of ethylmagnesium bromide under reflux for 3 hours, spongy metallic thallium is obtained quantitatively; but if the heating is omitted (Expt. II) 12·4% of the thallium is recovered as diethylthallium bromide, only 28·1% being reduced to the metal.

Thallous chloride is not soluble in organic solvents, and the reaction between it and the Grignard reagent is probably slow, thus subjecting the portion initially alkylated to the reducing action of excess of the reagent. We find that treatment of an ethereal solution of thallous ethoxide, which is miscible with ether in all proportions, with 2 equivs. of ethylmagnesium bromide

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[*] This reaction and the similar reactions of lead dialkyl and mercury monophenyl, which are probably the first products in the above actions, resemble the well-known behaviour of the monochloride of gold (Diemer, *J. Amer. Chem. Soc.*, 1913, **35**, 552) and indium (Nilson and Pettersen, *Z. physikal. Chem.*, 1888, **2**, 664) ($3XCl \longrightarrow XCl_3 + 2X$), and that of cuprous sulphate ($Cu_2SO_4 \longrightarrow CuSO_4 + Cu$) (Recoura, *Compt. rend.*, 1909, **148**, 1105; *Ann. Reports*, 1909, **6**, 47) and mercurous salts [*e.g.*, $2HgOAc \rightleftharpoons Hg(OAc)_2 + Hg$] (Garot, *J. Pharm.*, 1826, **12**, 457) under the influence of water. All the metals whose compounds undergo this type of change are easily reduced and also form co-ordinate compounds very readily, so that the energy given out by one atom in forming co-ordinate linkages may be available to reduce its neighbours to the metallic state. The change of type of compound suffering self reactions of this nature with change of metal is, however, difficult to explain.

(Expts. IV, V, and VI) leads to an immediate alkylation of 22—24% of the metal originally present in the ethoxide. Approximately half the thallium present was reduced to metal (Expt. V). The maximum possible alkylation according to the equations suggested is 33·3%. A larger ratio of Grignard reagent (3 : 1, Expt. IX) does not lead to any increase in the proportion of the metal alkylated (22·2%), while a smaller ratio (1 : 1, Expts. VII and VIII) gives smaller proportions (6·8% and 8·9%).

In all the cases where thallous chloride and ethoxide were used, the alkylated thallium was found before addition of water almost entirely dissolved in the ethereal solution, and little, if any, in the dark grey precipitates formed on addition of the thallous compound to the Grignard solution. With thallic chloride, however, direct conversion into the diethylthallium halide took place (Expt. X), the ethereal layer yielding only a negligible amount.

Diethylthallium bromide is insoluble in ether, and is at once precipitated if the ethereal solutions in question are treated with aqueous acetic acid and sodium bromide. Thallium triethyl (Groll, *loc. cit.*), however, is soluble in ether.

The observed facts and yields are satisfactorily explained if it be assumed that thallous chloride and ethylmagnesium bromide react according to the equation $3TlCl + 3EtMgBr \longrightarrow TlEt_3 + 2Tl + 3MgBrCl$, a reaction comparable with those of lead chloride and mercurous chloride (p. 2863). The thallium triethyl thus formed would remain dissolved in the ether. One of its three ethyl groups has been shown by Groll to be very reactive, so it would be converted by aqueous acetic acid into diethylthallium acetate and ethane, the sparingly soluble diethylthallium bromide being precipitated from the former by sodium bromide by double decomposition.

It also seems probable that the initial reaction between thallous ethoxide and ethylmagnesium bromide is double decomposition, with formation of thallous bromide, unchanged Grignard reagent then reacting with the newly formed, finely divided thallous bromide. The low yields of diethylthallium bromide obtained when only 1 equiv. of ethylmagnesium bromide is taken support this view.

EXPERIMENTAL.

To allow for loss of EtBr and for incomplete dissolution of the Mg, these reagents were taken in 10% excess in each case.

After the reaction, and decantation of the ether, the solid remaining consisted of a mixture of Tl, TlCl (or TlBr), and $TlEt_2Cl$ (or $TlEt_2Br$). The last dissolved on boiling with NH_3 aq. A smaller amount of TlCl (or TlBr) also dissolved and was conveniently pptd. as Tl_2CrO_4. $(TlEt_2)_2CrO_4$ (Goddard, J., 1921, **119**, 675) is not pptd., as it is readily sol. in H_2O.

Expt. I. (TlCl : Mg = 1 : 2). 27·3 G. of TlCl (0·114 mol.) were added in small portions to the solution obtained by dissolving 6 g. of Mg (0·25 mol.) in 27·2 g. of EtBr (0·25 mol.) in dry Et_2O at room temp. with vigorous stirring, and the mixture was refluxed on a water-bath for 3 hr. Only a negligible amount of $TlEt_2Br$ was obtained. The ppt. remaining (24 g.) was almost completely sol. in H_2SO_4 aq. containing a trace of $PtCl_4$ (which greatly accelerates the dissolution of Tl in H_2SO_4). The Tl content of the TlCl originally taken is 23·3 g.

Expt. II. The same materials and the same wts. were taken as in Expt. I, but after addition of the TlCl to the Et_2O solution, the mixture was not heated, HOAc aq. and NaBr aq. being added to the ethereal layer after decantation from the dark grey solid. 4·3 G. of $TlEt_2Br$ were obtained from the ether; a further 0·5 g. was obtained from the grey solid by boiling it with NH_3 aq. and by the removal of univalent Tl as Tl_2CrO_4.

The total (4·8 g.) contains 2·88 g. of Tl, equiv. to 12·4% of that present in the TlCl taken. The solid insol. in NH_3 weighed, after drying, 15·65 g., of which 6·55 g. dissolved in boiling H_2SO_4 aq. This is 28·1% of the total Tl taken.

Expt. III. A repetition of Expt. II with 203·5 g. of TlCl, stirred for 1 hr. at room temp. with the Grignard reagent (from 29·5 g. of Mg), gave a smaller percentage yield, 12·5 g. of crude $TlEt_2Br$ being obtained. The bromide was converted into the iodide by addition of KI to its aq. solution, and thence into the chloride by treatment with Ag_2O in boiling H_2O and addition of HCl to the filtered solution (Found : Cl, 11·9. Calc. for $TlEt_2Cl$: Cl, 11·9%). Hot aq. solutions of all three halides, when cooled on a slide, gave microscopic pattern effects characteristic of lower $TlAlk_2$ halides (cf. for $TlMe_2I$, Menzies, *Nature*, 1931, **128**, 907).

Expts. IV and V. (Tl : Mg = 1 : 2). In each of these expts., EtMgBr, prep. from 6 g. of Mg and 27·2 g. of EtBr (0·25 mol.), was added with vigorous stirring to an ice-cooled solution of 28·4 g. (0·114 mol.) of TlOEt in Et_2O. In both cases, a white ppt. formed in the ethereal solution while it was being decanted from the dark grey ppt. formed on addition of the Grignard solution (*i.e.*, after exposure of the ethereal solution to moist air). From the ethereal solutions and white ppts. were obtained : in IV, 8·75 g. of $TlEt_2Br$ (= 5·25 g. of Tl, or 22·6% of the total Tl originally taken), and in V, 10·9 g. of $TlEt_2I$ (= 5·71 g. of Tl, or 24·5% of the total). In neither case was any appreciable amount of $TlEt_2$ halide obtained by extracting the dark grey ppt. with hot dil. aq. NH_3.

In Expt. V, 11·8 g. of this grey ppt. dissolved in H_2SO_4 aq., indicating that 50·7% of the Tl taken had been reduced to the metal.

Expt. VI. The method and quantities used were the same as in Expts. IV and V, except that the TlOEt solution was run into the Grignard solution. This did not alter the yield, 10·25 g. of $TlEt_2I$ (= 5·38 g. of Tl) being obtained, an alkylation of 23·1% of the total metal taken.

Expts. VII and VIII. (Tl : Mg = 1 : 1). In Expt. VII, 5·3 g. of $TlEt_2Br$ (6·8%), and in VIII, 7·9 g. of $TlEt_2I$ (8·9% of the total Tl taken), were obtained from 56·8 g. (0·228 mol.) of TlOEt, 6 g. of Mg, and 27·2 g. (0·25 mol.) of EtBr. In Expt. VIII, 45·9 g. of TlBr (= 70·9% of the Tl originally taken) were also obtained. The formation of this large amount of TlBr indicates that the immediate action of EtMgBr on TlOEt is a double decomp., with formation of TlBr.

Expt. IX. (Tl : Mg = 1 : 3). From 0·25 mol. of EtMgBr and 18·9 g. (0·076 mol.) of TlOEt, 6·55 g. of $TlEt_2I$ (= 3·44 g. Tl) were obtained : hence 22·2% of the Tl was ethylated.

Expt. X. Comparative experiment with thallic chloride. 17·7 G. (0·057 mol.) of solid $TlCl_3$ were added in small portions to 0·25 mol. of EtMgBr; 9·2 g. of $TlEt_2Br$ (= 47·5% of Tl taken) were extracted from the ppts. insol. in Et_2O.

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