CLXX.—*Chelate Compounds of Thallium Dialkyl.*

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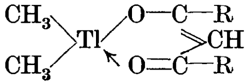
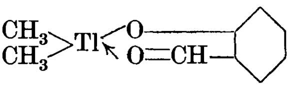
The known thallium dialkyl compounds are the salts of a strong univalent base $Alk_2Tl{\cdot}OH$. We have prepared a series of derivatives of the dimethyl and diethyl bases with β-diketones, acetoacetic ester, and salicylaldehyde, in order to see whether the products were chelate compounds or salts. The presence of the two alkyl groups would give the thallium in a monochelate derivative the stable covalency of 4, and hence these bases should form such derivatives more readily than the alkali metals (see Sidgwick and Brewer, J., 1925, **127**, 2379). The compounds are easily formed by three reactions: (1) by double decomposition of the thallium dialkyl halides with thallous acetylacetone and similar compounds, (2) by the action of crude thallium dialkyl ethoxide (from the iodide or bromide and thallous ethoxide) on the diketone, (3) from thallium dialkyl carbonate and the diketone. The products, which are of the type Alk_2TlA (where A is the radical of the diketone or similar substance), have unusual properties. They are crystalline solids, which can be sublimed with ease under reduced pressure and are readily soluble in benzene and even in hexane. This indicates that they are not ionised, and so they may be assumed to be chelate compounds of types I and II (below):

(I.) 

 (II.)

In water on the other hand, with the exception of the benzoylacetone compounds, they are extremely soluble (which this structure would not lead us to expect), and they are clearly ionised, since the solution has a strong alkaline reaction (containing the salt of a strong base and a weak acid) and can be titrated quantitatively with acid and methyl-red, and it gives a precipitate of the sparingly

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* This work was carried out independently by one of us (R. C. M.) at Bristol, and the rest at Oxford. The simplest course seems to be to publish the combined results as a single paper.

soluble thallium dialkyl iodide with potassium iodide. Thus in water they pass (like hydrochloric acid and stannic chloride) from the covalent to the ionised state. *Dimethyl* and *diethyl thallium benzoylacetone* dissolve in water very slowly even on boiling; their alcoholic solutions, however, remain clear on mixing with much water, and can then be titrated quantitatively; ether extracts from the diluted solution a substance which contains thallium dialkyl.

EXPERIMENTAL.

The thallium dialkyl halides were made by treating thallic chloride (dehydrated with copper sulphate) with excess of the Grignard reagent (Meyer and Bertheim, *Ber.*, 1904, **37**, 2051; Goddard, J., 1921, **119**, 672). The carbonate was obtained from the iodide by treatment with silver oxide and evaporation of the filtrate in an open vessel, or by double decomposition with thallous carbonate. The ethoxide was made by double decomposition with thallous ethoxide in absolute alcohol. These materials were used in the crude state. The thallium was estimated by titration with acid and methyl-red, or gravimetrically, after decomposition of the compound, either as chromate or as iodide (Meyer and Bertheim, *loc. cit.*; Goddard and Goddard, J., 1922, **121**, 488).

Thallium Dimethyl Acetylacetone.—Thallium dimethyl iodide (3·7 g.) was boiled in alcohol with thallous acetylacetone (3 g.) until a sample when filtered gave with potassium iodide a white precipitate free from yellow, thallous iodide. The hot liquid after filtering gave on cooling crystals of *thallium dimethyl acetylacetone*: more was obtained from the mother-liquor. Yield, 64%. M. p. (from benzene) 214—215° with some decomposition (Found: Tl as chromate 61·6, as iodide 61·1, by titration 61·0; C, 25·0; H, 3·9. $C_7H_{13}O_2Tl$ requires Tl, 61·3; C, 25·2; H, 3·9%). It is sparingly soluble in normal hexane and readily soluble in hot toluene and benzene, in methyl iodide (with which it seems to react slowly), and in warm carbon disulphide, the solution in which turns yellow on standing. The compound sublimes under atmospheric pressure, or better in a water-pump vacuum, at about 170°. It can also be made from the carbonate and acetylacetone in aqueous alcohol. Like all the other chelate compounds described in this paper, except those of benzoylacetone, it dissolves slowly in cold water and readily in hot. The solution has an alkaline reaction, and gives a precipitate of thallium dimethyl iodide with potassium iodide.

Thallium diethyl acetylacetone was made in the same way from the bromide (4 g.) and thallous acetylacetone (3 g.) in absolute alcohol. Yield, 81% (Found: Tl as chromate 57·1, by titration

56·7; C, 30·7; H, 5·0. $C_9H_{17}O_2Tl$ requires Tl, 56·5; C, 29·9; H, 4·7%). It is soluble in *n*-hexane, cold toluene, and cold methyl iodide.

Thallium Dimethyl Benzoylacetone.—The reaction of the iodide with thallous benzoylacetone is very slow: the addition of ammonia (to increase the solubility of the iodide) leads to hydrolysis of the diketone and formation of thallium dimethyl acetate [Found: Tl, 69·0. Calc. for $(CH_3)_2Tl{\cdot}O{\cdot}CO{\cdot}CH_3$: Tl, 69·7%]. The desired *compound* can be made by heating the carbonate with benzoylacetone (without solvent) at 150°; but at 100° no reaction occurs. It is better prepared by boiling thallous ethoxide (20 g.) with thallium dimethyl bromide (25·15 g.) in alcohol (300 c.c.), evaporating the filtered solution to small bulk, adding benzoylacetone (13 g.) in the minimum of alcohol, and evaporating the mixture to dryness in a vacuum. Yield, 78·7%. It forms colourless crystals (from ligroin or by sublimation), m. p. 128—129°, sublimes at 120°/20 mm., and is readily soluble in cold methyl iodide, cold ether, hot hexane and hot benzene (Found: Tl by titration 51·5, as chromate 51·4; C, 36·3; H, 4·05. $C_{12}H_{15}O_2Tl$ requires Tl, 51·7; C, 36·4; H, 3·8%).

Thallium Diethyl Benzoylacetone.—A solution of thallium diethyl bromide (19 g.) and thallous ethoxide (12·5 g.) in alcohol (250 c.c.) was boiled, filtered, and evaporated to 20 c.c. Benzoylacetone (8 g.) was added: it dissolved in the hot solution, and on cooling, the required *compound* separated; after recrystallisation from ligroin it was obtained in 72% yield; m. p. 116—118°. It is soluble in methyl iodide, and very soluble in dry ether, from which it crystallises well. 100 G. of a solution in light petroleum (b. p. 40—60°), saturated at 19°, contain 3·29 g. (Found: Tl as chromate 46·5, by titration 48·6; C, 39·5; H, 4·6. $C_{14}H_{19}O_2Tl$ requires Tl, 48·3; C, 39·7; H, 4·5%).

Ethyl Thallium Dimethyl Acetoacetate.—The filtrate from thallous ethoxide (2·5 g.) and thallium dimethyl iodide (3·6 g.) was evaporated to dryness in a vacuum. To the residue, after solution in light petroleum, ethyl acetoacetate (1·3 g.) in light petroleum was added. 1·8 G. of the desired *compound* separated on cooling, and 0·6 g. was got from the mother-liquor. Yield, 66%. It forms thick, colourless prisms, m. p. 128—130°, soluble in the cold in *n*-hexane, benzene, toluene, and methyl iodide (Found: Tl as chromate 55·7, as iodide 56·1, by titration 56·3. $C_8H_{15}O_3Tl$ requires Tl, 56·3%). The compound is also formed by heating the carbonate with ethyl acetoacetate in benzene.

Ethyl Thallium Diethyl Acetoacetate.—Ethyl acetoacetate (4 g.) was added to the concentrated alcoholic solution (20 c.c.) from thallium diethyl bromide (10·3 g.) and thallium ethoxide (7·5 g.), and the liquid evaporated to dryness, finally in a vacuum. The product is difficult to purify on account of its great solubility. It was boiled in ligroin with animal charcoal, and the clear brown filtrate on concentration to small bulk and cooling gave large, almost colourless crystals. Yield of pure product, 58%; m. p. 88—90°. In the cold the *compound* is readily soluble in *n*-hexane and very readily in dry ether and methyl iodide (Found: Tl by titration, 52·2, 52·1. $C_{10}H_{19}O_3Tl$ requires Tl, 52·35%).

Thallium Dimethyl Salicylaldehyde.—Salicylaldehyde (3·66 g.) and crude thallium dimethyl carbonate (7·9 g.) were boiled with pure benzene until the distillate was no longer cloudy, showing that the water formed in the reaction was removed. On cooling, part, and on concentration more, of the product separated. Yield, 63%. It forms lemon-yellow crystals, decomp. 200°, which can be sublimed at 160—170°/20 mm., and is easily soluble in benzene (Found: Tl as chromate 57·5, by titration 57·7; C, 30·5; H, 3·3. $C_9H_{11}O_2Tl$ requires Tl, 57·4; C, 30·4; H, 3·1%).

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