

CCC.V.—*Applications of Thallium Compounds in Organic Chemistry. Part VI. Thallium and Dialkylthallium Derivatives of Tetra-acetylene and Tetra-acetylpropane.*

By ROBERT CHARLES MENZIES and ERNEST REX WILTSHIRE.

SIDGWICK and BREWER (J., 1925, **127**, 2381) pointed out that compounds of the alkali metals with β -diketones and kindred substances might be divided into three classes: (1) salts, insoluble in organic solvents, and charring without melting on being heated; (2) intermediate compounds, soluble in organic solvents immediately on formation, but reverting on isolation to class (1); (3) chelate compounds, soluble in organic solvents, and having definite m. p.'s. A number of derivatives of dialkylthallium were later described (J., 1928, 1288) which displayed the properties of class (3), and, moreover, were in most cases easy to sublime. They were also soluble in water, forming alkaline solutions in which the thallium could be accurately titrated with standard acid, methyl-red being used as indicator. It is now pointed out that this combination of properties is shared by corresponding compounds of non-alkylated thallium (Christie and Menzies, J., 1925, **127**, 2372). In contrast to compounds of the alkali metals with β -diketones, which Sidgwick and Brewer (*loc. cit.*, p. 2381) state generally to belong to class (1), those of thallium and of dialkylthallium belong generally to class (3). The strong tendency of the metal to form compounds of this type is also shown by the properties of thallos ethoxide, which is a liquid at ordinary temperatures and completely miscible with benzene (see Sidgwick and Sutton, J., 1930, 1461), and of dimethylthallium ethoxide (*ibid.*, p. 1573), which, in addition, is volatile, a behaviour quite different from that of the alcoholates of the alkali metals.

In this paper, it is shown that the dithallium derivative of tetra-acetylene (I) belongs quite definitely to class (1), that the



corresponding dimethylthallium compound also approximates in behaviour to this type, as does the diethylthallium compound, though less closely; on the other hand, the dithallium and tetramethyl-dithallium compounds of tetra-acetylpropane (II), although very unstable, behave as chelate compounds belonging to class (3). Other observations on thallium and dialkylthallium compounds are included.

The *thallium*, *dimethylthallium*, and *diethylthallium* derivatives of tetra-acetylene were all prepared by treating hot solutions of the latter in benzene or toluene with the corresponding ethoxide. In each case, the compounds obtained were immediately precipitated indicating their slight solubility in these solvents. None of them possessed a definite m. p., but they decomposed on heating, often with a slight explosion. The solubility in water decreases, and that in benzene and toluene increases, in the order thallium, dimethylthallium, and diethylthallium tetra-acetylene, as shown in the following scheme :

Solvent.	Tl.	$(\text{CH}_3)_2\text{Tl}$.	$(\text{C}_2\text{H}_5)_2\text{Tl}$.
Water	Soluble	Soluble	Soluble (on heating)
Benzene	Insoluble	Insoluble	Slightly soluble
Toluene	Insoluble	Soluble (on heating)	Soluble

It thus appears that the thallium derivative is a simple salt of tetra-acetylene belonging to class (1), but that a tendency to pass into the form soluble in organic solvents (class 3) becomes apparent as we pass from the left to the right of the table. This corresponds to the greater tendency of the dialkylthallium ion, already containing four electrons in its outer sheath, to complete a stable octet by co-ordinate attachments to the two oxygen atoms.

The dialkylthallium derivatives are also much more stable than that of thallium. For instance, after being kept in a sealed tube for 4 months, the latter had changed to a dark brown mass, whereas the dialkyl compounds were unaltered. This difference is more pronounced in the tetra-acetylpropane derivatives (see below).

Another interesting gradation in this series of compounds is observed in the decrease of colour. Whereas the thallium compound is a distinct yellow, the dimethyl compound is much paler, and the diethyl compound is almost white. This is a general effect, and obtains with most coloured thallium and dialkylthallium derivatives, especially if the thallium compound itself is highly coloured, as in the nitrophenol derivatives. It thus appears that the decrease in colour is associated with the attachment to the thallium atom of inert radicals.

Attempts to prepare the corresponding derivatives of tetra-acetylpropane in the same way as had been adopted for those of tetra-acetylene proved unsuccessful, but by using cold benzene solutions, followed by evaporation in a vacuum, the *dimethylthallium* derivative could be obtained as a light yellow compound which remained unchanged in a desiccator, but soon changed to a dark brown mass when left in a stoppered tube.

The non-alkylated thallium derivative was later obtained in the same way by evaporation of the benzene solution, but was so unstable

that it changed to a black resinous mass immediately it was isolated.

The increased stability of the dialkyl compound as compared with the thallium one is a general result, numerous, but much less marked examples, having been observed; *e.g.*, the thallium derivative of salicylaldehyde decomposes, while those of acetoacetic ester and acetylacetone frequently darken on keeping, but the corresponding dialkylthallium compounds appear to keep indefinitely. Moreover, chelate thallos compounds are very easily hydrolysed in solution with splitting of the diketone, and require much more care in their preparation and recrystallisation than the chelate dialkyl compounds; indeed, solutions of the latter can often be boiled almost to dryness on a red-hot wire gauze, a proceeding which would be unwise in the case of the simple thallos compounds.

It is suggested, therefore, that many reactions may be preceded by the reacting molecules becoming co-ordinately attached to the same atom, and that the greater the co-ordinating action of any atom the more likely it is to promote chemical change. If anything be done to reduce the co-ordinating power of any atom, as in the case in point, by filling two of the co-ordinated positions of thallium with inert and firmly attached molecules, its power to promote change is diminished, and consequently the stability of compounds into which it enters is increased.

This inhibition of chemical activity by inert hydrocarbon radicals firmly attached to the central co-ordinating atom may be related in its mechanism to the inhibition of chemical reactions occurring on surfaces by a coating of paraffin wax, as, *e.g.*, in the effect of this substance in decreasing the speed of combination between chlorine or bromine and ethylene (Norrish and Jones, J., 1926, 55).

An indication that not only the number but also the size of the co-ordinated groups may influence this effect, is given by the observation that solid dimethylthallium tetra-acetylene dissolves in and reacts quickly with standard sulphuric acid, a good end-point being obtained on titration in the cold almost at once. Similar cold titration of diethylthallium tetra-acetylene also gives a good end-point, but takes about an hour, constant shaking being necessary to effect solution. Dimethylthallium and diethylthallium acetylacetone show the same difference in behaviour on titration.

The smaller stability of the thallium derivatives of tetra-acetylene and of tetra-acetylpropane as compared with the parent substances can also be attributed to the above cause, since the thallium atom can form co-ordinated links much more readily than the hydrogen which it replaces.

Dimethylthallium tetra-acetylpropane is soluble in benzene and in alcohol, and has a definite m. p. : these are the properties of a chelate compound (class 3). Like all the other dialkylthallium chelate compounds referred to above, it also dissolves in water to give an alkaline solution, and thus, like them, it appears to pass from the covalent to the ionised state in water. Although thallium tetra-acetylpropane was not obtained in a condition in which it could be handled, the fact that it is soluble in benzene makes it appear that this also belongs to class (3).

Summarising, it may be said (i) that the thallium and dialkylthallium derivatives of tetra-acetylene are salts belonging to class (1), whereas those of tetra-acetylpropane are chelate compounds belonging to class (3); (ii) that the greater stability of chelate compounds of dialkylthallium in comparison with those of the non-alkylated metal may be due to a diminution of the labile co-ordinating capacity of the metal.

EXPERIMENTAL.

Tetra-acetylene.—This was prepared by acting on sodium acetylacetone with iodine (Zanetti, *Gazzetta*, 1893, **23**, ii, 305); m. p. 188° (Zanetti gives 187°) (Found: C, 60.1; H, 7.4. Calc.: C, 60.6; H, 7.1%).

Thallium Tetra-acetylene.—Tetra-acetylene (1 g.) and thallium ethoxide (2.5 g.) were dissolved separately in hot toluene and mixed; the resulting yellow precipitate was filtered off [Found: C, 19.1; H, 2.0; Tl (by titration), 66.0. $C_{10}H_{12}O_4Tl_2$ requires C, 19.8; H, 2.0; Tl, 67.6%]; yield 73%. The compound, which shows no definite m. p. but chars on heating, is soluble in water, but not in benzene or toluene. White crystals, which separated during the titration of thallium tetra-acetylene, were filtered off, dried, and identified as tetra-acetylene, m. p. 189°.

Dimethylthallium Tetra-acetylene.—The calculated quantity of dimethylthallium ethoxide solution was added to tetra-acetylene (1 g.) dissolved in warm benzene, and the pale yellow precipitate was filtered off; yield 97% [Found: C, 25.2; H, 3.7; Tl, 61.7. $C_{10}H_{12}O_4Tl_2(CH_3)_4$ requires C, 25.3; H, 3.6; Tl, 61.5%]. The compound decomposes when heated.

Diethylthallium tetra-acetylene was obtained in the same way (yield 96%) from tetra-acetylene (1 g.) and diethylthallium ethoxide solution [Found: C, 29.9; H, 4.6; Tl, 58.8. $C_{10}H_{12}O_4Tl_2(C_2H_5)_4$ requires C, 30.0; H, 4.4; Tl, 58.9%]; it decomposes on heating.

Tetra-acetylpropane.—Acetylacetone (10 g. 2 mols.) was warmed on a water-bath with 1.5 g. (1 mol.) of finely powdered para-formaldehyde, with the addition of 4 drops of piperidine, until

all the paraformaldehyde had dissolved (compare Knoevenagel, *Ber.*, 1903, **36**, 2154). The reddish-brown solution obtained was kept at room temperature, 20 drops of piperidine being added at intervals. A thick syrup was formed from which a sufficient quantity of crystals was obtained only after 4 months' standing (Knoevenagel gives 6 days). These were separated by means of a filter pump, and thus obtained as pale yellow crystals after repeated recrystallisations from ether; m. p. 87° (Found: C, 61.9; H, 7.5. Calc.: C, 62.2; H, 7.6%).

Thallium Tetra-acetylpropane.—The theoretical quantity of thallium ethoxide in benzene was added to a hot solution of tetra-acetylpropane (0.5 g.). A yellow colour was produced, which rapidly turned red, and a brown substance was precipitated, which changed to a resinous mass when filtered off. In other experiments with cold solvents, evaporation of the benzene in a vacuum desiccator yielded light brown or light yellow residues which also rapidly darkened, and the mother-liquors yielded similar unstable materials.

Dimethylthallium Tetra-acetylpropane.—When the preparation was attempted in hot benzene, the results were similar to those above. From cold solvent, however, a light yellow substance was obtained on evaporation of the mixed solutions of tetra-acetylpropane and dimethylthallium ethoxide. This was filtered off and dried; m. p. 98° [Found: (by titration), Tl, 44.3; (by precipitation as iodide in solution after titration), Tl, 59.9. $C_{11}H_{14}O_4Tl_2(CH_3)_4$ requires Tl, 60.2%]. This compound is soluble in water, alcohol, and benzene (on heating).

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