

256. Application of Thallium Compounds in Organic Chemistry. Part XI.*

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A summary is given of earlier work on the thallium method of alkylating sugars and its more recent extensions. It is pointed out that entry of thallium into carbohydrate molecules, controlled by Purves by varying the sizes of the molecules carrying the ethoxide in solution, can also be controlled by varying the effective size of the thallium atom by anchoring it by attached alkyl groups. A case of methylation by boiling a diethylthallium derivative with methyl iodide is also described.

ALKYLATIONS by reaction between thallos compounds and alkyl iodides were first described by Fear and Menzies (*J.*, 1926, 937), *o*-methoxybenzaldehyde, dimethyl hydroxymethoxy-succinate, and a mixture of trimethyl methylglucosides being obtained from thallos salicylaldehyde, tetrathallium tartrate, and trithallium methylglucoside. Twelve years later Purves and Hudson (*J. Amer. Chem. Soc.*, 1937, 59, 49) methylated by this method α -methyl- and α -benzyl-fructofuranosides, both obtained by them from the uncrystallised mixture of isomeric methylfructofuranosides first prepared by the author (*J.*, 1922, 121, 2238). Later, Hirst, Jones, and others (*J.*, 1938, 497; 1939, 458, 1482, 1867, 1884; 1942, 76; 1946, 506) described the thallation and initial methylation of an arabo-pectic acid complex and a number of vegetable gums, thus altering their solubilities so that methylation could be completed by Purdie's reaction. Hirst and Jones also showed (*J.*, 1938, 1695) that the action of methyl iodide on trithallium methylglucoside gave a mixture of 50% of 2 : 4 : 6-, 36% of 2 : 3 : 6-, 10% of 3 : 4 : 6-, and 4% of 2 : 3 : 4-trimethyl methylglucosides, so that positions 2, 3, 4, and 6 were methylated in 90, 50, 64, and 96% respectively of the whole product, positions 2 and 6 being methylated simultaneously in 86%, but positions 3 and 4 were only methylated together to the extent of 14%.

Purves later (*J. Amer. Chem. Soc.*, 1944, 66, 59) investigated the distribution of amorphous and crystalline material in cellulose by treating it with thallos ethoxide dissolved in organic solvents of different molecular sizes.

Thallation followed by treatment with methyl iodide thus affords a method of initial partial methylation capable of being used in non-aqueous solvents, occasionally applicable where sodium hydroxide and methyl sulphate are ineffectual. Purves and Hudson's preparation of dimethyl methyl- and benzyl-fructosides and Hirst and Jones's preparation of partly methylated methylglucosides indicate that thallation can be controlled and used in the preparation of partly methylated sugars.

These authors have laid stress on results rather than on experimental methods. A recapitulation and extension of published and unpublished observations on the thallos derivatives of some of the more simple sugars and allied substances may therefore be of use.

Treatment of substances containing carboxyl or hydroxyl groups with aqueous thallos hydroxide generally results in replacement of the labile hydrogen by the metal. Where hydroxyl hydrogen is replaced, the metal can be accurately titrated with standard acid; it is also converted into thallos carbonate by passing carbon dioxide through the solution. The first compound described in which both replacements occur in the same molecule was tetrathallium tartrate (Part II). Hexathallium gluconate in which five of the six metallic atoms can be titrated was described in Part IV. *Tetrathallium mesotartrate*, *dithallium glycollate*, and *dithallium lactate* are described below. *Trithallium glycerol* and *tetrathallium erythritol* are both sparingly soluble, separating slowly on mixing solutions of the parent compound with aqueous thallos hydroxide. Hexathallium sorbitol was described in Part IV. Many of these and other thallium compounds crystallise well (cf. *Nature*, 1931, 907) so the recognisable patterns formed by mixing drops of the reacting solutions or on allowing their hot solutions to cool on a microscope slide are suitable for identification purposes. So far as is known all hydroxyl hydrogen atoms in straight-chain compounds can be substituted by the metal. When, however, the compound contains a pyranose, furanose, or an attached benzene ring, substitution may be incomplete. For instance, methylaraboside (Part IV) gives a trithallium derivative, but so, under similar conditions, does methylglucoside (Part III). Sucrose, with eight hydroxyl groups, and salicin, with five, give *tetrathallium sucrose* and *trithallium salicin*. It is only in

* Previous parts of this series published in the *Journal* are : I, 1924, 125, 1148; II, 1925, 127, 2369 III, 1926, 937; IV, 1928, 186; V, 1930, 1571; VI, 1931, 2239; VII, 1932, 2604; VIII, 1932, 2734 IX, 1933, 21; X, 1936, 1678.

rings containing an oxygen atom that incomplete thallation has been observed. Inositol, in which all six hydroxyl groups are secondary, forms sparingly soluble *hexathallium inositol*.

Replacement of hydrogen by the metal in certain cases is thus incomplete. Incomplete also may be subsequent replacement of the metal on treatment with methyl iodide. The attempted methylation of tetrathallium tartrate gave, for instance, after 100 hours, a syrup whose methoxyl content indicated that only three of the metallic atoms had reacted (Part III).

The isolation of well-defined thallos derivatives recalls McKenzie's suggestion (*J.*, 1899, 75, 765) that a possible explanation of methylation by the silver oxide method is the intermediate formation of an unstable silver derivative which subsequently undergoes double decomposition with the alkyl halide (see also Lander, *J.*, 1900, 77, 747; 1903, 83, 416); but these intermediate compounds have never been isolated. Many of the thallos compounds are somewhat unstable, but the fact that they can be isolated facilitates more detailed examination of the mechanism of methylation. Both the occasional incomplete thallation and the usual incomplete subsequent methylation are probably partly due to steric hindrance, but this cause does not act alone. There are also to be considered the alkalinity of the metal or organo-metallic group, the dissociation constant of each individual labile hydrogen, the co-ordinating capacity of the metal, and the presence or absence of water, small amounts being occasionally of importance. Information on the above, and reciprocally, on the properties of the sugars, can be obtained by considering the courses of different methods of substitution on the same, and of the same method on different, hydroxyl compounds.

Steric hindrance certainly plays a part. Purves, for instance, has shown that the depth of entry of thallos ethoxide into fibres of cellulose depends, in the case of the ethers, on the lengths of the carbon chains attached to the oxygen of the ethers. Maxted (*J.*, 1937, 1004) showed that the catalytic activity of platinum in hydrogenations is inhibited by alkyl sulphides in proportion to the lengths of the carbon chains attached to the sulphur. The alkyl groups act like umbrellas. Similar protection of derivatives of β -diketones from hydrolysis, increasing with the length of the alkyl groups attached to the metal, was described in Part X (*loc. cit.*, p. 1880). The probable similar mechanism in this case also is made clear by Powell and Crowfoot's observation (*Z. Krist.*, 1934, 87, 370) that the alkyl groups in the dialkylthallos compounds are attached at an angle of 180° . The effective size of the thallos atom may thus be increased in a known way without destroying, but not without altering, its power of replacing labile hydrogen, Berry, Lowry, and Gilbert (*J.*, 1928, 1761) having shown that the dialkylthallonium ions are derived from relatively weak bases. One dialkylthallium group probably does not differ much from another in basicity, so that differences between homologous organometallic derivatives may be mainly of steric origin. The non-alkylated metal, however, is a stronger base. It is shown below that in alkaline solutions, where all four labile hydrogen atoms of tartaric acid are replaced by the metal, only three are replaced by the dialkylthallium group. This difference is probably due to both the two causes indicated above. Both causes are also probably concerned in Brady and Hughes's results. They described both mono- and di-thalliumdiphenol, but only mono(diethylthallium)diphenol (*J.*, 1933, 1228). Whatever the cause and whatever alkylation method be used, it is always the insertion of the last group that is the most difficult. Even the silver oxide method occasionally breaks down. Purdie and Young, for instance (*J.*, 1910, 97, 1524), found that the 3 : 4-dimethyl ether of 2 : 5-dimethylhexane-2 : 3 : 4 : 5-tetraol resisted methylation in this way. McKenzie and Wren (*J.*, 1910, 97, 473) could only methylate the secondary hydroxyl group of triphenylethylene glycol by its means. Other methods break down more easily. Both the methyl sulphate (Haworth, *J.*, 1915, 107, 15) and the thallium method (Part III) give incomplete methylation when applied to tartaric acid; and Schlubach and Firgau (*Ber.*, 1926, 59, 2100) found that, although the potassium salt of 2 : 3 : 6-trimethyl β -methylglucoside gave an 86% yield of tetramethyl β -methylglucoside on treatment with methyl iodide, yet it was unaffected by propyl iodide, benzyl chloride, or acetobromoglucose. The smaller the metal atom or the entering group, and the looser the structure of the metallic derivative, as in Hirst and Jones's preparations of partly methylated methylglucosides and methylarabinosides referred to above, or in Percival's preparation of acetylated trimethyl sucrose (*J.*, 1935, 648), the more likely is substitution of the metal to be complete.

With regard to the varying dissociation of hydrogen from one sugar to another, it is difficult to explain that while the thallation of hexahydroxy-alcohols takes place instantly, that of glycerol and of erythritol takes hours, the solubilities of the resulting thallated derivatives being of the same order, on any other ground than that the lower alcohols must have smaller dissociation constants.

It will also be recalled that the silver oxide method began from following up Purdie and

Pitkeathly's observation (*J.*, 1899, **75**, 153) that in the course of preparation of esters by the action of alkyl halides on silver salts certain anomalous results were encountered, the tartaric esters obtained having abnormally high rotations, and it was ascertained that alkoxy-derivatives were produced during the reaction; *i.e.*, the substitution of silver, known to have a high capacity for forming co-ordination compounds, took place not only on the acid but also on the neighbouring hydroxyl group. This makes it difficult to believe, without further proof, that the replacement of thallium, also a readily co-ordinating element, by other groups always takes place on the same oxygen atom as that to which the metal was attached before reaction with the alkylating agent.

The incomplete thallation referred to above varies in some cases with quite small differences in the conditions of preparation, so that exact repetition of analytical results is occasionally difficult. This difficulty was encountered by Assat, Haas, and Purves (*J. Amer. Chem. Soc.*, 1944, **66**, 61). It is also met with in the analyses of derivatives of sucrose and cellulose and in those of ethylene glycol and of pentaerythritol. In the last two cases the solubility of the derivatives is of the same order as that of thalious hydroxide, and the analyses suggest that both the derivatives of the polyhydric primary alcohols and thalious hydroxide crystallise together. It is important to make clear that these analytical inexactitudes are due, not to the difficulty of determining the metal or of determining carbon or hydrogen in its presence, but, as explained below, to the reactive nature of the components of the molecule of which it now forms a part. Inspection of the analytical results given below and in the earlier numbers of this series will show that: (1) Carbon and hydrogen estimations are not interfered with by the presence of thallium. (2) Thalious salts of organic acids analyse well: occasional high hydrogen values suggest the presence of water of crystallisation. (3) The hydrogen values for chelate thalious compounds are usually good, but irregular carbon figures suggest the presence of thalious salts resulting from hydrolysis. (4) The percentages found for all three elements in chelate compounds of dialkylthallium are usually very good. This is associated with considerable stability. Like platinum catalyst poisons after Maxted has rendered them harmless (*J.*, 1940, 252), all the electronic shells round all the constituent atoms have been completed, and they no longer attract or are attracted by other molecules as much as those in which this is not the case. This is *mutatis mutandis* the Cambridge conception of the survival of the unattractive (Thomson, *Phil. Mag.*, 1921, **41**, 530) and their stability clearly marks the end-points of the reactions leading to their formation. This is, however, not so well marked with the thalious derivatives of the sugars. The sugars are easily oxidised, and univalent thallium is not only easily reduced to the metal but is also easily oxidised to the trivalent state, and is thus an oxygen carrier. Any thalious derivative of the sugars is thus liable to change, and it may change, if care be not taken, under the conditions of preparation. This instability makes them difficult to analyse as accurately as might be wished, but it also makes them useful synthetic agents.

EXPERIMENTAL.

Thalious Derivatives of Hydroxy-acids.—On adding *n*-thalious or -potassium hydroxide to *n*-solutions of tartaric or mesotartaric acid, the precipitation of the acid salt followed by the formation of the normal salt, which dissolves, follows the same course with both alkalis up to the point of neutrality (phenolphthalein). Here the resemblance ends. The first drop of thalious hydroxide in excess leads to precipitation of tetrathallium tartrate (Part II) or of *tetrathallium mesotartrate*, heavy white compact crystals, sparingly soluble and slowly darkened by light [Found: Tl (by titration), 42.41. $C_4H_2O_6Tl_4$ requires Tl, 41.14%].

A few analyses of known thalious tartrates and salts of other carbon acids are here given to illustrate the accuracy to be expected:

	Found.			Calc.		
	C, %.	H, %.	Tl, %.	C, %.	H, %.	Tl, %.
Thalious hydrogen mesotartrate, $C_4H_5O_6Tl$	13.9	1.7	—	13.6	1.4	—
Thalious tartrate, $C_4H_4O_6Tl_2$	8.9	0.85	73.2	8.6	0.7	73.4
Tetrathallium tartrate, $C_4H_2O_6Tl_4$	5.06	0.4	42.65 * 84.6 †	5.0	0.2	42.4 * 84.9 †
Thalious carbonate, Tl_2CO_3 :						
(commercial sample)	2.76	0.24	87.3	2.51	0	87.2
(recrystallised)	2.78	0.19	—	—	—	—
Thalious formate, CHO_2Tl	4.9	0.8	82.15	4.8	0.4	81.95
Thalious fumarate }	9.3	0.56	77.9	9.2	0.4	78.2
Thalious maleate } $C_2H_2O_4Tl_2$	9.4	0.4	77.8			
Thalious succinate, $C_4H_4O_4Tl_2$	9.2	0.85	77.6	9.16	0.76	77.9

* By titration.

† As iodide.

Although these results conform to the usually accepted standards of accuracy, it will be seen that where the molecular weights of normal and tetrathallium tartrates, for instance, are 556.8 and 963.6 respectively, they are inadequate to indicate the presence or absence of small quantities of water of crystallisation, probably influencing, as mentioned above, the course of alkylations. It may be mentioned in this connection that thallium hydrogen *d*-tartrate is described in the literature as anhydrous, while the *mesotartrate* is said to crystallise as a hemihydrate. In alkaline solution the behaviour of the metal resembles that of lead and antimony. The resemblance between tetrathallium and a double tartrate of thallium and antimony has already been pointed out in Part II (p. 2369), and comparison may also be made with a basic lead tartrate $Pb_2C_4H_2O_8 \cdot H_2O$ (Beilstein's "Handbuch", Vol. 3, p. 501).

Dithallium glycolate. Glycollic acid was neutralised by thallose hydroxide solution, and a further equal volume was then added. Compact colourless crystals of *dithallium glycolate* slowly separated, resembling, but more soluble than, tetrathallium tartrates, and like them, darkened by light [Found: Tl (by titration), 42.1. $C_2H_2O_3Tl_2$ requires Tl, 42.4%].

From a solution of glycollic acid accurately neutralised with thallose hydroxide (phenolphthalein) were obtained on evaporation needles of the very soluble normal salt described by Fahlberg (*J. pr. Chem.*, 1873, 7, 339). From a solution of lactic acid neutralised with thallose hydroxide a colourless syrup was obtained on evaporation, which did not crystallise; but on evaporating a solution to which twice the amount of hydroxide necessary for neutralisation had been added, as above, *dithallium lactate* slowly separated on nucleation with a sample obtained by rapid evaporation in a test-tube, in large, highly refracting, colourless crystals [Found: C, 7.6, 7.8; H, 0.91, 1.03; Tl (by titration), 39.4. $C_3H_4O_3Tl_2$ requires C, 7.25; H, 0.8; Tl, 41.15. $C_3H_4O_3Tl_2 \cdot H_2O$ requires C, 7.0; H, 1.2; Tl, 39.7%].

The above basic salts are all colourless. Yellow hexathallium gluconate was described in Part III (p. 189). Saccharic acid also gives a substance approximating in composition to hexathallium saccharate, the way to which lies through *thallium hydrogen saccharate*, now described.

Crude brown potassium hydrogen saccharate (19 g.) was dissolved in water and partly neutralised with thallose hydroxide. The dark brown liquid was then boiled with animal charcoal, and considerable excess of thallose hydroxide added to the almost colourless filtrate. The solution was then made slightly acid with acetic acid, and again boiled with animal charcoal, filtered hot, and cooled. Crude thallium hydrogen saccharate (14.8 g.) separated, which probably contained a little potassium, as the titration value corresponded to 101.3% of thallium hydrogen saccharate. After recrystallation from hot water, however, 2.126 g. required 5.11 c.c. of *N*-thallose hydroxide (calc., 5.14 c.c.), indicating 99.4% purity (Found: C, 18.3; H, 2.3. $C_6H_8O_8Tl$ requires C, 17.4; H, 2.2%). The neutral solution obtained by titration gave a glass on evaporation to dryness, thus resembling the normal lactate and also recalling Hirst and Purves's attempt to prepare normal thallium *xylotrimethoxyglutaric acid* (*J.*, 1923, 123, 1358). The syrup was then redissolved, and on the addition of four further equivalents of thallose hydroxide an amorphous yellow precipitate came down, more being obtained by adding alcohol to the filtrate. These on titration showed 52.24% and 50.74% of thallium, respectively. Hexathallium saccharate should contain 85.74% of thallium of which two-thirds or 57.16% should be titratable. It is possible that, on the lines indicated in Part III for the similar yellow hexathallium compounds of gluconic acid and of sorbitol, better analytical results could be obtained. But it is already evident that again the close resemblance between thallose and potassium salts in neutral or acid solutions persists. On making the solution alkaline with thallose hydroxide, more sparingly soluble substances are formed. From hydroxy-acids containing 2, 3, and 4 carbon atoms, these are colourless. From acids and alcohols containing 6 carbon atoms they are yellow. As will be seen below, this yellow colour already appears in the derivatives of ethylene glycol and of glycerol. (Solid $TlOH$ is also yellow.)

Normal *thallose mucate* is easily prepared by neutralising the acid. It is sparingly soluble but can be crystallised from hot water. Its analysis is a good example of the general rule that the more sparingly soluble an organic thallium salt is the better does it analyse (Found: C, 11.8; H, 1.35. $C_6H_8O_8Tl_2$ requires C, 11.7; H, 1.3%).

Thallose Derivatives of Polyhydric Alcohols.—Sparingly soluble, of definite composition, yellow and darkened by light are *trithallium glycerol* and *tetrathallium erythritol*. A typical preparation is the following. Tetrathallium erythritol (51.1 g., 71.6%) crystallised after some hours' standing from a solution containing erythritol (9.3 g.), 6*N*-thallose formate (50 c.c.), 6*N*-sodium hydroxide (50 c.c.) and water (150 c.c.) (Found: C, 5.10; H, 0.76; Tl, 87.0. $C_4H_6O_4Tl_4$ requires C, 5.13; H, 0.65; Tl, 87.4%). The *glycerol* compound was prepared similarly (Found: C, 5.18; H, 0.70; Tl, 87.7. $C_3H_5O_3Tl_3$ requires C, 5.18; H, 0.72; Tl, 87.3%).

Thallium compounds of ethylene glycol. De Forcrand (*Compt. rend.*, 1923, 176, 20) described monothallium ethylene glycol prepared from thallose ethoxide and ethylene glycol as a beautiful precipitate closely resembling dehydrated uranium nitrate. He prepared the glycerol derivative, $C_3H_5(OH)_2OTl$, similarly but did not report analyses. Chablay (*Ann. Chim.*, 1917, 8, 185) prepared dithallium ethylene glycol from monosodium ethylene glycol and thallose nitrate, both dissolved in liquid ammonia. According to him, monothallium ethylene glycol is first formed, 2 mols. of which interact with formation of ethylene glycol and the disubstituted compound. Chablay noted that the compound is soluble in water and that the metal can be determined by titration. He also described a dithallium mannitol made in the same way. Several preparations have now been made of a yellow substance crystallising from weighed quantities of ethylene glycol dissolved in equivalent amounts of aqueous thallose hydroxide. From 2*N*-solutions yellow crystals were obtained, the mother-liquor from which was 0.92*N* at room temperature. Analyses indicated that they were a mixture of approximately 2 mols. of dithallium ethylene glycol with 1 mol. of thallose hydroxide [Found: C, 4.14, 4.00, 3.80; H, 0.95, 0.94, 0.85; Tl, 87.7, 88.7. Calc. for $C_2H_4O_2Tl_2$: C, 5.12; H, 0.86; Tl, 87.2. Calc. for $TlOH \cdot C_2H_4(OH)_2$: C, 0; H, 0.45; Tl, 92.3. Calc. for $2(C_2H_4O_2Tl_2) \cdot TlOH$: C, 4.17; H, 0.79; Tl, 88.9. Calc. for $2(C_2H_4O_2Tl_2) \cdot TlOH \cdot H_2O$: C, 4.11; H, 0.95; Tl, 87.5%].

Similar results were obtained with pentaerythritol. This alcohol (6 g.) was dissolved in water (20 c.c.) and filtered hot, and thallose ethoxide (44.6 g.; 1 equiv. for each hydroxyl group) was also dissolved in water (60 c.c.), boiled, and filtered hot; on being mixed, the solution became yellow, and, on cooling,

crystals having the appearance of those of thallos hydroxide separated. The whole was then boiled down to half bulk. On cooling, a heavy, yellow, sandy powder separated which adhered firmly to the sides of the flask. This was separated with some difficulty and filtered through a weighed Gooch crucible, washed with alcohol and ether, and dried in a vacuum over phosphoric oxide for 24 hours (Substance A; 18.65 g.) [Found : C, 4.67; H, 0.9; Tl 86.96. Calc. for $C_5H_9O_4Tl_4$: C, 6.32; H, 0.85; Tl, 86.1. Calc. for $C_5H_9O_4Tl_4 \cdot TiOH, H_2O$: C, 5.05; H, 0.93; Tl, 86.0%]. A further 8.5 g. were similarly obtained by adding alcohol to the filtrate (Substance B) [Found : C, 4.82; H, 0.93; Tl (titration), 86.09; Tl (iodide), 87.65%]. The substance obtained from ethylene glycol is thus slightly less soluble than thallos hydroxide, and that from pentaerythritol slightly more soluble. All three solubilities are of the same order, and both alcoholic derivatives appear to form mixed crystals with the hydroxide.

Dithallium trimethylene glycol (23 g.; 95.3%) was obtained as a light yellow precipitate on adding thallos ethoxide (25 g.) in ether to trimethylene glycol (3.8 g.). It was soluble in water but not in benzene [Found : C, 7.61; H, 1.50; Tl, 84.2. $C_3H_6O_2Tl_2$ requires C, 7.46; H, 1.25; Tl, 84.7%].

The thallos derivatives of the hexahydric alcohols resemble those of the di-, tri-, and tetra-hydric alcohols in being yellow and coloured more deeply by light. They differ from them in that they are precipitated instantly on mixing the respective solutions and in being amorphous.

From mixed 2N-solutions containing approximately 1 equiv. of thallos hydroxide for each hydroxyl group of inositol (m. p. 225°) a heavy yellow precipitate of *hexathallium inositol* was obtained [Found : Tl (titration), 87.36. $C_6H_8O_6Tl_6$ requires Tl, 87.6%. $C_6H_8O_6Tl_5$ requires Tl, 85.37%. $C_6H_8O_6Tl_4$ requires Tl, 82.11%]. On adding a slight excess of N-sodium hydroxide to the solution resulting from the above titration a similar yellow solid separated [Found : Tl (titration), 83.5%]. From N-solution the replacement of hydrogen by thallium is not so complete (Found, for precipitate from inositol and 1.1 equivs. of TiOH for each hydroxyl group : C, 5.62; H, 0.58; Tl, 85.75. $C_6H_8O_6Tl_6$ requires C, 5.614; H, 0.43; Tl, 87.6%. $C_6H_8O_6Tl_5$ requires C, 6.01; H, 0.58; Tl, 85.37%).

Inositol has no terminal groups which can be oxidised, and of 0.0298 equiv. of thallos hydroxide taken in this last experiment 0.0297 equiv. was accounted for by titration of the solid and of the mother-liquor. In a comparative experiment using glucose and working in the cold, 7.4% of the titratable thallium disappeared, having been neutralised by acid products of oxidation.

From mannitol and dulcitol and 1 equiv. of thallos hydroxide for each hydroxyl group in approximately 1.3N-solution, yellow derivatives were obtained containing 85.94 and 84.05% thallium respectively by titration ($C_6H_{10}O_6Tl_6$, $C_6H_9O_6Tl_5$, and $C_6H_{10}O_6Tl_4$ require respectively Tl, 87.45, 85.23, and 82.11%). The dulcitol compound is coloured brown by light : the inositol compound is turned black. Of the three, the mannitol compound is least changed in colour by light.

The above observations suggest that the thallos derivatives of secondary polyhydric alcohols tend to be less soluble than those of primary, that in the more sparingly soluble derivatives replacement of hydroxyl hydrogen by the metal occurs, but that in cases where the solubility is of the same order as that of the hydroxide addition of thallos hydroxide and of water also takes place. In addition to this, as pointed out on p. 1378, complete substitution of hydrogen by the metal does not always occur from aqueous solutions in more complicated molecules. The derivatives of sucrose, a disaccharide containing eight hydroxyl groups, of which three are primary, and of salicin, a phenolic glucoside containing five hydroxyl groups of which two are primary, are now discussed in the light of the above remarks.

(i) A typical preparation of the *thallos* derivative of sucrose is the following. Sucrose (8.8 g.) was dissolved in water (8 c.c.), cooled, and mixed with 1.275N-aqueous thallos hydroxide solution (68.5 c.c.), i.e., 5 equivs. per mol. of sucrose. After about 2 minutes the mixture became cloudy, and after an hour the white solid separating was filtered off at the pump and kept on a tile in a vacuum over sulphuric acid, taking 4 days to attain constant weight (22.5 g.) [Found : Tl (titration), 70.7; Tl (as iodide), 71.6. $C_{12}H_{18}O_{11}Tl_4$ requires Tl, 70.7%]. On drying, the solid turned yellow. A sample of thallos hydroxide placed in a dry tube at 100° turns black owing to formation of thallos oxide (Tl_2O), whilst the colour of the sucrose compound is unchanged by this treatment.

Preparations carried out with 4 equivs. of the hydroxide to one of sucrose gave substances of similar appearance but of slightly lower thallium content. For instance, 284.6 g. (yield 71.7%) [Found : Tl (titration), 69.9; Tl (as iodide), 68.7%] were obtained from 117.4 g. of sucrose and 4 equivs. of 1.26N-thallos hydroxide. Higher proportions of the hydroxide did not give rise to a corresponding increase of the thallium content, for on treating sucrose with 8 equivs. followed by slow evaporation in a vacuum the first crop separating contained 71.2% of thallium, determined as iodide. The carbon percentages, however, were low and those for hydrogen high. A nearer approach to the observed percentages is afforded by the formula $(C_{12}H_{18}O_{11}Tl_3)_2 \cdot 3TiOH, H_2O$ or $(C_{12}H_{18}O_{11}Tl_4)_2 \cdot TiOH, 3H_2O$, both adding up to $C_{24}H_{36}O_{22}Tl_8$, which requires C, 11.13; H, 1.67; Tl, 71.5% (Found, for two typical samples : C, 11.14, 11.57; H, 1.98, 1.78; Tl, 70.7, 71.6%) and both similar to the results found for the derivatives of ethylene glycol and pentaerythritol.

It is of interest to compare these results with those of Mackenzie and Quin (*J.*, 1929, 951) and of Percival (*J.*, 1935, 648).

(ii) Salicin (3 g.) and thallium hydroxide crystals (9 g.; 3.9 equivs.) were dissolved separately in water, and the solutions mixed and heated; on cooling and addition of alcohol, 7.5 g. of a light yellow substance separated (Found : C, 17.27; H, 1.99; Tl, 64.2%). On evaporation of the solution in a vacuum desiccator, white crystals separated which turned yellow on drying (Found : C, 17.27; H, 1.92; Tl, 63.6%). The mother-liquor yielded a white precipitate on addition of alcohol. These also turned yellow on drying (Found : C, 16.67; H, 1.94; Tl, 63.2. $C_{12}H_{15}O_7Tl_3$ requires C, 17.4; H, 1.65; Tl, 68.4%. $C_{12}H_{15}O_7Tl_3 \cdot 2H_2O$ requires C, 16.73; H, 2.05; Tl, 65.8%).

Surgical cotton-wool (1.71 g., dried over phosphoric oxide. Found : C, 42.7; H, 6.18. Calc. for cellulose : C, 44.44; H, 6.18%) was placed in 1.52N-thallos hydroxide solution and left for 24 hours. The product was then washed repeatedly with alcohol, which converts excess thallos hydroxide into the ethoxide which then dissolves in the alcohol. The product was unchanged in appearance but became yellow on drying, when it weighed 8.24 g. [Found : C, 9.58; H, 1.41; Tl (titration), 73.1;

Tl (as iodide), 75.3%). In another experiment 4.35 g. of the same cotton-wool were boiled with 1.52N-thallos hydroxide for 15 minutes, washed with alcohol, and dried as before. The dried product weighed 17.36 g. [Found : C, 11.29; H, 1.67; Tl (titration), 63.5; Tl (as iodide), 72.4. Dithallium cellulose requires C, 12.66; H, 1.41; Tl, 71.86%. Trithallium cellulose requires C, 9.32; H, 0.91; Tl, 79.41%. ($C_6H_8O_5Tl_2$), $TlOH_2 \cdot 2H_2O$ requires C, 10.3; H, 1.52; Tl, 73.25%]. In view of the uncertain composition of the cotton-wool used, these results cannot be considered as more than indicating a possible point of departure with pure cellulose should this ever prove to be obtainable.

The basic thallos compounds described above are to be classified as salts, for they are, in the main, insoluble in non-hydrolytic solvents and soluble in water; they are also likely to char on heating without melting (cf. Sidgwick and Brewer, *J.*, 1925, 127, 2379). Thallos methoxide is intermediate. The thallos derivatives of the other normal primary alcohols have definite m. p.s and are more soluble in organic solvents than in water. The basic salts described, however, do resemble many chelate compounds in being stable to alkalis. This property is shared by acetals, and, as was described in Part X, several of the dialkylthallium derivatives of β -diketones are volatile in steam from alkaline solutions. This took place much more easily with the derivatives of dipropionylmethane than with those of acetylacetone. Further, beryllium dipropionylmethane (see below) is volatile in steam in the presence of a little ammonia while beryllium acetylacetone is not. It is not clear whether these facts are really connected.

Beryllium dipropionylmethane is readily made by heating beryllia with the diketone in benzene until the distillate is clear, filtering the residue from excess of beryllia, distilling off the benzene, and finally distilling the residue in a water-pump vacuum; m. p. 63° (Found : C, 62.5; H, 8.46. Found, after distillation in steam, and drying : C, 61.9; H, 8.4. $C_{14}H_{22}O_4Be$ requires C, 63.8; H, 8.4%). It closely resembles beryllium acetylacetone, but is inconveniently soluble in ether, and is better recrystallised from ligroin. On boiling with water containing a little ammonia it distills with the steam essentially unchanged. This does not happen with beryllium acetylacetone.

Action of Air, Light, and Moisture on Thallos Derivatives of Cotton-wool, Salicin, and Sucrose. (Adapted from a report by E. R. WILTSHIRE.)—The observation that the yellow colour of these compounds either appeared on or was intensified by drying led to an examination of the effect of exposing them to a moist atmosphere. Light caused darkening of the first compound. The experiments were therefore carried out by leaving the substances over water in closed vessels in the dark. In each case the yellow colour was gradually lost. As many of the dialkylthallium derivatives are lighter in colour than the corresponding derivatives of the non-alkylated metal, it is reasonable to suppose that this loss of colour is due to the attachment of water to the metal. The precipitate, for example, obtained by passing hydrogen sulphide through a solution of a thallos salt is black, but a white precipitate is obtained from dialkylthallous salts. No information, however, as to the existence of definite hydrates could be obtained from the increase of weight, as the absorption of water appeared to continue indefinitely. After one month the three derivatives gained 44, 58, and 18%, respectively.

A similar experiment was then carried out with a thallium derivative of more definite composition. Thallos fumarate gained the equivalent of 1 mol. of water after 50 days and of 2 mols. after three months. Diethylthallium fumarate gained 3% in 22 days, 1 mol. of water corresponding to 2.4%. In Part II it was shown that thallos 2-methylpyridine-3 : 4 : 6-tricarboxylate gained the equivalent of 1 mol. of water in 6 days, after which the weight became constant.

Exposure of thallium derivatives to a moist atmosphere. In each case, a weighed amount of the substance was placed on a watch-glass in a receptacle containing water in the dark :

A.	Thallium cellulose.	Thallium salicin.	Thallium sucrose.
Original wt., g.	0.823	0.517	1.967
Increase after 1 month, g.	0.366	0.302	0.358
" " 1 month, %	44.47	58.4	18.2

The colour in each case gradually disappeared, and finally darkening began to take place. None of the substances came to constant weight.

B.	Thallos fumarate.		Diethylthallium fumarate.	
	G.	%.	G.	%.
Original weight	6.617	—	0.599	—
Increase in wt. after 20 days	0.144	2.2	0.017	3.0
" " " 50 " 	0.219	3.3	—	—
" " " 3 months	0.452	5.8	—	—
Calc. for addition of 1 mol. of H_2O	—	3.45	—	2.4

Constant weight was not obtained, but in each case exposure to the atmosphere quickly caused reversion to the original weight.

Dimethyl- (Found : C, 16.32; H, 2.46. Calc. for $C_8H_{14}O_4Tl_2$: C, 16.46; H, 2.42%) and diethylthallium fumarates (Found : C, 22.58; H, 3.37. Calc. for $C_{12}H_{22}O_4Tl_2$: C, 22.6; H, 3.48%) were prepared respectively in 52 and 56% yields by double decomposition between thallos fumarate and the dialkylthallium iodide in boiling water.

The Dialkylthallium Tartrates.—These can be prepared by neutralising tartaric acid with aqueous solutions of the dialkylthallium hydroxides. 4.196 G. of tartaric acid are theoretically required to neutralise 235 c.c. of 0.238N-diethylthallium hydroxide : the weight required lay between 4.1 and 4.19 g. The solution was filtered and evaporated to small bulk on the water-bath. The compound is very soluble in water. On concentration, four crops were obtained : (1) 3.1 g., (2) 6.95 g. on concentrating the aqueous solution. On adding methyl alcohol to the filtrate from crop (2), 3.7 g. were obtained

(crop 3), and finally 2.5 g. on evaporating to dryness (crop 4). Crops 2 and 3 were analysed (Found, respectively: C, 22.4, 19.2; H, 3.17, 3.35. Calc. for $C_{12}H_{24}O_6Tl_2$: C, 21.58; H, 3.63%).

Treatment of diethylthallium tartrate with methyl iodide. 2.63 G. of the tartrate were refluxed with methyl iodide for 17 hours; on removal of the methyl iodide, extraction with ether, filtration, and evaporation of the ether, 0.48 g. of syrup was obtained together with 2.9 g. of colourless diethylthallium iodide, corresponding to 58.3% of thallium in the diethylthallium tartrate taken (Calc.: Tl, 61.3%). As this was evidence that the methylation did proceed, the preparation was then repeated with 11.7 g. of the tartrate. A syrup was obtained which was distilled in a water-pump vacuum; the distillate solidified on nucleation with an authentic sample of dimethyl tartrate (Found: C, 40.85; H, 5.72. Calc.: C, 40.45; H, 5.52%).

Dipropylthallium tartrate. This can be prepared from normal thallos tartrate and dipropylthallium bromide by boiling them together with water. The *substance* (Found: C, 27.13; H, 4.42. $C_{16}H_{32}O_6Tl_2$ requires C, 26.34; H, 4.42%) is very soluble both in water and in benzene. Probably connected with this is the fact that on evaporating an aqueous solution on a water-bath, crystallation first begins on the surface of the solution. This also takes place with solutions of diethylthallium tartrate. This surface crystallisation is also characteristic of the dialkylthallium halides, and in their case takes place in a very regular pattern (*Nature*, 1931, 907). The floating crystals are probably visible examples of McBain's ionic micelles.

Attempts to prepare tetrakis-dimethyl- and -diethyl-thallium tartrates by heating tetrathallium tartrate with the respective dialkylthallium halide resulted in the formation of the trisdialkylthallium tartrates only; the incomplete substitution which appears in the thallos compounds of more complicated substances now occurs in the simple tartaric acid molecule, the effective size of the metal having been increased and its strength as an alkali reduced by alkylation.

Treatment of tetrathallium tartrate with dimethylthallium bromide. 4.82 G. (1 equiv.) of the tartrate were boiled with 6.3 g. (4 equivs.) of the bromide. The solution was cooled, filtered from thallos bromide, and concentrated to small bulk. 0.16 G. of sparingly soluble substance, probably unreacted bromide, was filtered off, and then on adding alcohol 2.4 g. of a white precipitate of *trisdimethylthallium tartrate* were obtained [Found (titration): Tl, 22.8. $C_{10}H_{21}O_6Tl_3$ requires Tl (titration), 24.0%]. Another portion, washed with alcohol and acetone and dried in a vacuum, contained Tl, 23.4% (by titration).

Treatment of tetrathallium tartrate with diethylthallium iodide. 12 G. of the tartrate were heated in water with excess of the iodide. Two crops were obtained, containing severally Tl, 20.75, 23.16% (by titration). On addition of potassium iodide to a solution, diethylthallium iodide was recovered corresponding to 66.64% of thallium [*trisdiethylthallium tartrate*, $C_{16}H_{32}O_6Tl_3$, requires Tl (total), 65.63; Tl (by titration), 21.88%].

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