373. *Application of Thallium Compounds in Organic Chemistry. Part X. Influence of Change of Substituent on the Properties of Chelate Rings.*
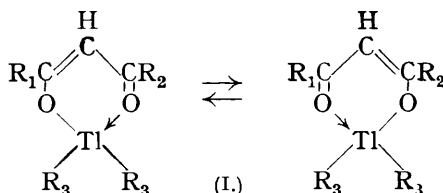
By R. C. MENZIES and A. R. P. WALKER.

IN Part VII * (J., 1932, 2604) it was recalled that ring structure due to co-ordination within the molecule was first indicated by Werner, the name " chelation " being later introduced by Morgan, and that additional evidence for ring closure of this type was

* 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.

published by Sidgwick and his co-workers (J., 1924, **125**, 527; 1925, **127**, 907). Morgan also (J., 1914, **105**, 193) pointed out the possible analogy with the benzene ring of the metallic compounds of β-diketones and β-keto-esters. It is admitted that the evidence for the rings is circumstantial. The conception is, however, a convenient hypothesis, which accounts for the facts. The observations recorded in Parts VII, VIII, and IX and in this paper are therefore discussed from the standpoint of changes in properties conditioned by changes of substituents attached to chelate rings. The thallium and dialkylthallium (and trimethylplatinum) derivatives of β-diketones and β-ketonic esters have only one ring system attached to each metallic atom, and consequently present simpler cases than do the better known derivatives of the multivalent metals.

For acetylacetones, $R_1 = R_2 = Me$.
„ propionylacetones, $R_1 = Me$, $R_2 = Et$.
„ dipropionylmethanes, $R_1 = R_2 = Et$.

$$\underset{R_3 \quad R_3 \qquad (I.)}{\overset{H}{\underset{Tl}{\underset{O \qquad O}{R_1C \diagup \diagdown CR_2}}}} \rightleftharpoons \underset{R_3 \quad R_3}{\overset{H}{\underset{Tl}{\underset{O \qquad O}{R_1C \diagup \diagdown CR_2}}}}$$

The general formula is represented by (I). No mixed dialkylthallium compounds are known, as is indicated by both alkyl groups attached to thallium being denoted by R_3; the thallous compounds may be regarded as obtained by removal of both R_3 groups from the metal. The changes conditioned by replacement of dimethylthallium by trimethylplatinum are described in Part IX.

Either R_1 or R_2 or both may be replaced by other groups, not necessarily the same. Attempts to prepare derivatives in which the median hydrogen atom is substituted have been unsuccessful. Methylacetylacetone and ethyl methylacetoacetate both gave very unstable dialkylthallium derivatives.

In all the compounds of the type under discussion there are, as shown in (I), two equally probable positions of the bonding electrons; stability is thus associated with the possibility of resonance, an association not available on Sugden's first formula (J., 1929, 316) involving attachment of the metal to the two oxygen atoms by singlet linkages.

In (I) every atom has the effective atomic number (E.A.N.) of an inert gas. In the non-alkylated thallous chelate compounds this is no longer true for the metal, and their lower stability (Part VI, p. 2241) may be partly due to this; but that protection of the metal by inert attached groups is also a factor, follows from the gradation in properties in the dialkylthallium compounds as the size of the alkyl group is increased (cf. Part VII, p. 2605).

Much of the chemistry of thallous and dialkylthallium derivatives can be explained by the consideration that the electron grouping of 81 atoms round the thallium nucleus may either lose one electron, forming a positively charged ion of E.A.N. 80, or gain five electrons, as in (I), with completion of the stable E.A.N. 86. The familiar thallous ion formed in the former case has the same E.A.N. as the neutral mercury atom, and, as pointed out by Lowry (J., 1928, 1765), these are related in the same way as is the molecule of methane to the ammonium ion (and also, it may be added, as is the atom of argon to the potassium ion), " so that a molecule in the one series becomes an ion in the other." The three ions form salts which resemble one another closely and are all typical polar compounds, usually soluble in water, insoluble in organic solvents, and non-volatile. The compounds formed by the thallium atom after it has gained five electrons are different : they are soluble in organic solvents and frequently volatile, behaving as typical non-polar compounds. The physical properties of these two types of compound are thus dissimilar, but, owing to the size of the atom and the distance of the electrons involved from the central controlling force, the energy changes in passing from one type to the other are small. This is well illustrated in Part V (p. 1573), where it is shown that on shaking 337 g. of thallous hydroxide with successive portions of 100 c.c. of absolute alcohol at 20°, the temperature never exceeded 25°, a 76% yield of thallous ethoxide being obtained (for its structure, see Sidgwick and Sutton, J., 1930, 1470). The reverse reaction proceeds readily,

colourless liquid thallous ethoxide being quickly changed into yellow solid thallous hydroxide on shaking with cold water. This hydrolysis of thallous compounds of alcohols, phenols, and β-diketones by water, with regeneration of the parent substances and formation of alkaline thallous hydroxide, is so complete as to afford the most convenient means for the estimation of thallium in these compounds (Parts II and IV), and it was later shown (J., 1928, 1288) that similar derivatives of dimethyl- and diethyl-thallium were also easily hydrolysed by water with formation of the dialkylthallium hydroxide, and could be titrated in the same way. Solid dimethylthallium derivatives of β-diketones and ketonic esters do not become coloured on keeping in a glass container in daylight, they are easily volatilised, and their solutions in organic solvents can be evaporated almost to dryness without decomposition; in all three respects they are more stable than the corresponding thallous derivatives, but there is little obvious difference in their behaviour with water. Both dimethylthallium and thallous acetylacetones, for instance, dissolve in this solvent; in both solutions, the thallium may be accurately estimated by immediate titration, and the diketone is slowly hydrolysed with formation of acetic acid so that the titration value falls on standing. The rate of fall is more rapid in solutions of thallous acetylacetone, which stands between the corresponding sodium and dimethylthallium derivatives in this respect, but all three solutions give curves of the same type and of the same order, the differences in the rates being small.

As, however, the size of the alkyl groups attached to the metal is increased, solubility in water and rate of reaction with aqueous solutions are diminished, it being shown (Part VI) that solid dimethylthallium tetra-acetylethane dissolves in and reacts rapidly with standard sulphuric acid, a good end-point being obtained almost at once. Similar cold titration of diethylthallium tetra-acetylethane also gives a good end-point, but takes about an hour, constant shaking being necessary to effect solution. Dimethyl- and diethyl-thallium acetylacetones show the same difference in behaviour on titration, and reaction between solid di-*n*-propylthallium acetylacetone and aqueous acid at room temperature requires several days (Part VII).

That this increased resistance is a property of the individual molecule and is not merely due to the sparing solubility of the solid in water, as suggested in Part VII, is indicated by the volatility in steam from $0 \cdot 2N$-alkaline solution of a number of the compounds under discussion, as shown in Table I (for experimental details, see p. 1684). The distillate from

TABLE I.

Volatility of thallium derivatives in steam.

	Tl.	TlMe$_2$.	TlEt$_2$.	TlPr$^a_2$.	TlBu$^a_2$.
Acetylacetone	—	—	— (A)	+ (B)	+ (C)
Propionylacetone	—	—	—	M. p.	M. p.
Dipropionylmethane	—	+ (A) Very faint	M. p. (B)	M. p. (C)	M. p.

— = distillate contained no thallium or dialkylthallium ion (absence of yellow or white precipitate on addition of potassium iodide). + = distillate contained dialkylthallium ion in solution, but no solid chelate compound came over. M. p. = unchanged solid chelate compound was obtained in quantity sufficient for m.p. determinations, and in most cases for estimation of thallium by titration as well.

The three pairs of compounds marked A, B, and C, severally, are isomeric.

dilute acid solutions contained no thallium or dialkylthallium ions or derivatives. Under none of the observed conditions was the thallous ion or thallous compounds present in the distillate from the corresponding thallous compounds.

These results may be accounted for by the consideration that before hydrolysis can take place in alkaline solution, with formation of dialkylthallium hydroxide and the alkali-metal derivative of the diketone, approach of the hydroxyl ion to the metal and of the alkali-metal ion to the enolic oxygen is necessary. The probability of this necessary antecedent approach is progressively diminished as the sizes of the alkyl groups R_1, R_2, and R_3 are increased. Similar approach of the hydrogen ion present in acid solution to the enolic oxygen is facilitated by its smaller size and greater mobility.

It is again evident from Table I that increase in size of the alkyl groups R_1 and R_2

leads to increased protection. Volatility in steam from alkaline solution is first shown in the acetylacetone and in the propionylacetone series by the di-*n*-propylthallium derivatives, and in the dipropionylmethane compounds by the dimethylthallium derivative.

The familiar increase in solubility in organic solvents as solubility in water and reactivity with aqueous solutions diminish is shown in Table II, in which are given the solubilities in *n*-hexane of the compounds under discussion. In Table III the m. p.'s are recorded * (in addition to these, the di-*n*-butylthallium *derivatives* of propionylacetone and dipropionylmethane had m. p. 72° and 41° respectively).

In all these compounds the interatomic forces are largely satisfied within the molecule. Increase in size of alkyl groups attached to the ring makes the molecules more self-contained. They are less easily attacked by other potentially reactive molecules or ions; in the absence of the latter each molecule is more easily separated from its neighbours.

TABLE II.

Solubilities in n-*hexane at* 27° (expressed as g. of substance in 100 g. of solution).

	Tl.	TlMe$_2$.	TlEt$_2$.	TlPr$^a_2$.	TlBu$^a_2$.
Acetylacetone	0·012	0·12	0·20 (A)	0·15 (B)	1·32 (C)
Propionylacetone	1·52	0·77	4·65	12·4	49·3 (at 18°)
Dipropionylmethane	41·1	14·5 (A)	17·0 (B)	21·7 (C)	very soluble

In passing from R_3 = Me to R_3 = Et (acetylacetone series), the solubility is increased 1·7 times, but when R_1 and R_2 are changed from Me to Et, it is increased 120 times. The other isomeric pairs show differences of the same order. Why changes in size of substituents attached to carbon should have so much greater influence is not obvious.

The derivatives of ethyl acetoacetate and of ethyl malonate may be regarded as formed by replacement respectively of one and both alkyl groups R_1 and R_2 by the ethoxy-group. In Parts VII and VIII it is shown that these replacements result in lower m. p.'s and increase in molecular association in benzene solution. These changes also condition greater solubility in organic solvents, and in the case of the thallous compounds, greater reactivity.

Ethyl thalloacetoacetate is less stable than thallous acetylacetone, but the thallium in both may be accurately estimated by titration; ethyl thallomalonate, of low m. p. and readily soluble in organic solvents, is also readily soluble in water but gives an almost neutral solution in which the metal cannot be titrated (compare ethyl sodiocyanoacetate; Thorpe and Young, J., 1900, **77**, 936).

EXPERIMENTAL.

Preparation of Propionylacetone and Dipropionylmethane.—The general method, for which the authors are indebted to Professor Sugden, was to take 1 mol. of methyl ethyl ketone, 6 mols. of ethyl acetate or propionate, and 1 atomic proportion of sodium.

Comparative action of sodium, potassium, and lithium. In three preparations of propionyl-acetone carried out as described, with sodium as the condensing agent, yields of 30·4, 38·8, and 39·7% of the copper salt were obtained. In two preparations using potassium, the yields were 21·3 and 19·4%. Two preparations using lithium, which also dissolved, gave no yield.

From methyl ethyl ketone and ethyl propionate, sodium being used, a 21·8% yield of the copper derivative of dipropionylmethane was obtained. From 110 g. of copper propionyl-acetone, 8·9 g. of propionylacetone (b. p. 65—68°/24 mm.) and 61·2 g. (b. p. 67—70°/24 mm.) were obtained, giving a total yield of 70·1 g., or 79·8%. From 128·3 g. of copper dipropionyl-methane, 89·7 g. (70%) were obtained.

11·1 G. of thallous dipropionylmethane (m. p. 68·5°. Found : Tl, by titration, 61·2. Calc. : 61·4%) crystallised from 23·2 g. of thallous ethoxide and 11·9 g. of dipropionylmethane in 100 c.c. of *n*-hexane cooled in ice and salt; a further 9·6 g., m. p. 68°, were obtained by boiling off part of the solvent and again cooling similarly; total, 21·5 g. (69·7%). Solutions of this substance in hexane rapidly become brown on keeping.

A first crop of 20·3 g. of *thallous propionylacetone*, m. p. 86° (decomp.) (Found : Tl, by

---

* From these solubilities and melting points, " the nominal heats of solution " (Sidgwick and Taylor, J., 1922, **121**, 1857) have been calculated. It is hoped to publish these later, together with those calculated from determinations now in progress of solubilities at other temperatures.

titration, 63·5. $C_6H_9O_2Tl$ requires Tl, 64·37%), was similarly obtained from 21·3 g. of thallous ethoxide and 9·94 g. (2% excess) of propionylacetone (yield 79·3%). From the mother-liquor cooled in solid carbon dioxide and ether, only 0·2 g. more was obtained, a striking indication of the great decrease in solubility conditioned by substituting methyl for ethyl in the chelate ring. The sample used for solubility determination, obtained by cooling a benzene–hexane solution in ether and carbon dioxide, had m. p. 89° (Found : Tl, by titration, 64·8%).

Di-n-propylthallium Propionylacetone (I; $R_1 = Me$, $R_2 = Et$, $R_3 = Pr^a$).—30 G. of di-*n*-propylthallium chloride were refluxed with 23 g. of thallous ethoxide in 250 c.c. of absolute alcohol, until the solution gave with potassium iodide a white precipitate of di-*n*-propylthallium iodide, uncontaminated by yellow thallous iodide. To attain this end, it was necessary to filter the solution from precipitated thallous chloride, and heat it with a further 2·5 g. of the organo-metallic chloride.

365 C.c. of solution were obtained, which were estimated by titration to contain 22·6 g. of di-*n*-propylthallium ethoxide. After addition of 7·8 g. of propionylacetone, the solution was evaporated to dryness. The resulting brown solid was dissolved in ligroin (charcoal) and filtered hot. The brown colour was not removed by two treatments with animal charcoal. The product was again evaporated to dryness on a water-bath, dissolved in pentane, and cooled to − 80° in solid carbon dioxide–ether. More was recovered from the mother-liquor; m. p. (after a final recrystallisation from light petroleum) 108° (Found, by titration : Tl, 48·62. $C_{12}H_{23}O_2Tl$ requires Tl, 48·97%). Yield 11·5 g.

12·3 G. of *di-n-butylthallium propionylacetone* (I; $R_1 = Me$, $R_2 = Et$, $R_3 = Bu^a$) were similarly prepared from 295 c.c. of 0·268N-di-*n*-butylthallium ethoxide in ethyl alcohol and a slight excess (theory 9·01 g.) of propionylacetone. The solution became brown, as before, and on cooling a hexane solution of the crude brown substance in ether and solid carbon dioxide, a brown solid separated. Almost colourless material was later obtained by cooling the hexane solution in ice and salt; m. p. 72·0° (Found : Tl, 46·87. $C_{14}H_{27}O_2Tl$ requires Tl, 47·04%).

Di-n-butylthallium Dipropionylmethane (I; $R_1 = R_2 = Et$, $R_3 = Bu^a$).—From 5·6 g. of dipropionylmethane and 110 c.c. of 0·398N-di-*n*-butylthallium ethoxide were obtained 19·9 g., m. p. 41°, of *di-n-butylthallium dipropionylmethane*; it was slightly brown, but was so soluble at ordinary temperatures in hexane that it could only be recrystallised by cooling in ether and solid carbon dioxide (Found : C, 39·9, 39·66; H, 6·63, 6·43; Tl, 45·7, 45·65. $C_{15}H_{29}O_2Tl$ requires C, 40·39; H, 6·56; Tl, 45·85%).

Determinations of Solubilities of Thallium Chelate Compounds in n-*Hexane at* 27°.—The solubilities were determined by mechanically shaking mixtures of the compounds and *n*-hexane (Carless, Capel, and Leonard; b. p. 68·6—68·8°/755 mm.) in glass vessels immersed in a tank of water at 27°. To serve as a check upon the results thus obtained, mixtures were also allowed to attain equilibrium in an air-incubator, kept at 27°, the vessels being hand-shaken at regular intervals.

In the first case (Table III), the mixtures were introduced into doubly stoppered, glass vessels, and allowed to warm in the thermostat. The shaking device accommodated three bottles at a time; these were clamped by means of wing nuts into a carrier, fixed to a horizontal axis. The axis rotated through the arc of a circle in a vertical plane, the mean position during shaking being when the vessels were horizontal. The rate of shaking was 40 times per minute, thus ensuring adequate mixing. This was continued for 8 hours, and then the vessels were clamped vertically for an hour to allow the undissolved solute to settle completely. 5—8 G. of solution were withdrawn by means of a weighed pyknometer, weighed, and pipetted into small tared Pyrex flasks, the pyknometer being well rinsed with hot alcohol or hexane. The flasks were put in a vacuum desiccator, which contained both paraffin wax and calcium chloride. When the desiccator was evacuated 2 or 3 times per day, the solvent normally took 2 or 3 days to dry off, the last drying being completed in another desiccator, until constant weight was attained. The m. p. of the solid was always taken, and if the amount sufficed, the solid was titrated against 0·1N-acid, methyl-red being used as indicator, to determine the percentage of thallium. The solubilities, *S*, are recorded in g./100 g. of solution.

Starting from room temperature, saturation was always attained within 8—9 hours, for no increase in solubility occurred after further prolonged shaking. When the determinations were carried out by using the air-oven (Table IV), the mixtures were occasionally heated to 40°, and then kept in the incubator till equilibrium was reached at 27°; in general, 2 days were essential. For instance, the solubility of diethylthallium propionylacetone at 27° after 6 hours and after 2 days was 5·1 and 4·6%, whereas that of dimethylthallium dipropionylmethane at 26° was 17·8 and 13·1% after 7 hours and 2 days respectively.

TABLE III.

Details of solubility determinations in n-hexane.

Compound.				M. p. after	Solution,	Solute,		
R_1.	R_2.	R_3.	M. p.	recovery.	g.	g.	S.	Mean.
Me	Me	—	160·5°	150°	6·437	0·0008	0·012	0·012
					7·371	0·0009	0·012	
Me	Et	—	89—90	79	6·400	0·0992	1·55	1·52
					7·008	0·1058	1·50	
Et	Et	—	70	—	9·8757	4·0605	41·1	
Me	Me	Me	213·5	212·5	6·570	0·0073	0·11	0·12
					7·192	0·0085	0·12	
					7·380	0·0076	0·10	
					6·795	0·0083	0·12	
					6·007	0·0072	0·12	
					7·012	0·0085	0·12	
Me	Et	Me	161	159·5	7·249	0·0560	0·77	0·77
					6·813	0·0483	0·71*	
					7·317	0·0562	0·77	
					7·801	0·0601	0·77	
Et	Et	Me	120	118	7·765	1·1055	14·3	14·5
					6·045	0·9130	15·1	
					7·002	0·9863	14·1	
					6·503	0·9432	14·5	
Me	Me	Et	200·5	199	6·589	0·0121	0·18	0·20
					5·767	0·0125	0·21	
					7·396	0·0150	0·20	
					6·877	0·0149	0·22	
					6·846	0·0133	0·19	
Me	Et	Et	146·5	143	6·801	0·2835	4·16 †	4·65
					7·807	0·3646	4·67	
					8·099	0·3730	4·61	
					6·196	0·2911	4·69	
					6·020	0·2799	4·65	
Et	Et	Et	115	112·5	5·632	0·9910	17·7	17·0
					8·337	1·3822	16·6	
					4·022	0·6831	17·0	
					7·511	1·2621	16·8	
Me	Me	Pr^a	180	178—180·5	6·555	0·0093	0·14	0·15
					6·840	0·0112	0·16	
					6·883	0·0105	0·15	
					7·400	0·0112	0·15	
					7·027	0·0109	0·16	
					6·569	0·0094	0·14	
					7·113	0·0113	0·16	
					6·005	0·0091	0·15	
Me	Et	Pr^a	108	105·5—106·5	6·516	0·8175	12·6	12·4
					7·739	0·9320	12·1	
					7·140	0·8781	12·3	
					5·631	0·7096	12·5	
Et	Et	Pr^a	88·5	87	8·069	1·7470	21·6	21·7
					7·502	1·6361	21·8	
					6·102	1·3173	21·6	
Me	Me	Bu^a	137·5	136	7·870	0·1035	1·32	1·32
					7·728	0·0993	1·29	
					7·444	0·1023	1·37	
					7·155	0·0939	1·31	
					7·011	0·0924	1·32	

* At 24°. † At 25°.

Dialkyl compounds. The acetylacetones underwent slight decomposition during the solubility determinations, the solids recovered from solution darkening during melting. The original substances melted without darkening. The propionylacetones were little affected, the m. p. never being more than 4° below that of the pure substance : this was also the case with the dipropionylmethanes, except that the recovered dipropylthallium compound darkened slightly on melting. The thallous compounds were less stable (see Table III), and had darkened on recovery, especially the very soluble dipropionylmethane derivative.

TABLE IV.

Results obtained by using air-incubator as thermostat.

Compound.			Solution, g.	Solute, g.	S.	Remarks.
R_1.	R_2.	R_3.				
Me	Me	—	20·401	0·0030	0·015	} 27·5° in incubator.
			25·062	0·0042	0·017	
			6·031	0·0009	0·015	
Me	Et	—	5·437	0·0924	1·70	In incubator.
Me	Me	Me	7·391	0·0082	0·11	} Warmed to 40° and left for 2 days. Temp. 27°.
			5·011	0·0066	0·13	
Me	Et	Me	7·700	0·0647	0·84	} Warmed to 40° and left for 2 days. Temp. 28·5°.
			6·335	0·0531	0·84	
Et	Et	Me	7·203	1·2801	17·8	8 Hrs., oven at 26·5°.
			6·291	0·8250	13·1	24 ,, ,,
Me	Me	Et	6·370	0·0128	0·20	} Warmed to 40° and left for 2 days. Temp. 26·5°.
			6·402	0·0114	0·18	
Me	Et	Et	6·802	0·2835	4·17	2 Days, oven at 25°.
			5·021	0·2579	5·10	6 Hrs., ,, 25°.
			4·987	0·2287	4·60	24 ,, ,, ,,
Et	Et	Et	4·004	0·7203	18·0	2 Days, ,, 27·5°
Me	Me	Pr^a	7·036	0·0107	0·15	} Warmed to 40° and left for 2 days. Oven at 27·5°.
			6·895	0·0108	0·16	
Me	Et	Pr^a	7·786	0·8273	10·6	} Warmed to 40°. Oven at 25·5°.
			7·863	0·8345	10·6	
Et	Et	Pr^a	5·652	1·2321	21·8	2 Days, oven at 27°.
Me	Me	Bu^a	5·421	0·0650	1·21	Incubator at 26·5°.

Volatility of Dialkylthallium Chelate Compounds in Steam.—A little di-*n*-propylthallium acetylacetone (m. p. 181°) was placed in a distilling flask with water and a few drops of 2N-sodium hydroxide. The water was then boiled. No solid distilled over, but the distillate gave slowly a white precipitate of di-*n*-propylthallium iodide on addition of potassium iodide. 0·5 G. of di-*n*-propylthallium dipropionylmethane was then boiled with water, the solid melted, and part of the oil distilled over and solidified in the condenser; m. p., after recrystallisation from hexane, 86—88° (*vice* 89°). The solid recovered, however, was only a small part of that taken, and both undistilled aqueous solution and aqueous distillate after filtration gave abundant precipitates with potassium iodide.

In further experiments, 1 g. of each of di-*n*-butylthallium dipropionylmethane (i), di-*n*-propylthallium dipropionylmethane (ii), and di-*n*-propylthallium propionylacetone (iii) was slowly boiled with 50 c.c. of 0·2N-sodium hydroxide solution. In each case part of the substance was recovered unchanged from the distillate and from the inside of the condenser.

(i) M. p. 40° (*vice* 41°) (Found : Tl, by titration, 44·8. Calc. : 45·8%).
(ii) M. p. 87° (*vice* 89°) (Found : Tl, by titration, 48·4. Calc. : 48·9%).
(iii) M. p. 105° (*vice* 107°) (Found : Tl, by titration, 49·8. Calc. : 50·66%).

In cases (i) and (ii) there was left in the flask after distillation a brown globule which did not crystallise on cooling or on nucleation, but in case (ii), on solution in hexane and evaporation of the solvent, brown crystals were left, m. p. 87°.

This volatility in steam is shown by the chelate compounds in the presence of added alkali, to a much smaller extent in its absence, but not in the presence of acid, as the following experiments show.

1 G. of di-*n*-propylthallium iodide was treated with an equivalent of thallous ethoxide (0·6 g.) in 50 c.c. of water, and distilled; the distillate was free from thallium. Phenolphthalein was then added, together with propionic acid in amount insufficient to make the reaction acid; on redistillation, the distillate was still free from thallium. This was also the case on adding more propionic acid until the reaction became acid. A few drops of dipropionylmethane were then added to the acid solution and the mixture again distilled; the distillate was again free from thallium, but on making the mixture again alkaline, and again adding more of the diketone and distilling, the distillate gave a copious white precipitate of di-*n*-propylthallium iodide with potassium iodide. No solid separated in the condenser.

It thus appears that neither di-*n*-propylthallium hydroxide nor propionate can be volatilised in steam, and further, that the chelate compound does not volatilise from acid solution.

Diethylthallium compounds show the same behaviour. A few c.c. of diethylthallium ethoxide in alcoholic solution were evaporated to dryness on a water-bath. The brown solid, probably impure carbonate, was boiled in a distilling flask with water; the distillate gave no precipitate with potassium iodide. A little dipropionylmethane was then added, and the distillation continued; a crystalline solid then separated in the condenser; m. p. 114°, mixed m. p. with pure diethylthallium dipropionylmethane (m. p. 116°), 113°.

The volatility of these compounds when steam-distilled from neutral solution is very much less than in alkaline solution. 1 G. of each of the following compounds was distilled with 50 c.c. of distilled water in the customary manner : di-*n*-butylthallium propionylacetone, di-*n*-propylthallium propionylacetone, and di-*n*-propylthallium dipropionylmethane. In no case did any solid separate in the condenser. The distillates (20 c.c.) each gave a white precipitate with potassium iodide, the intensity being greatest with the last compound and least with the first. After addition of 5 c.c. of 2*N*-sodium hydroxide and 10 c.c. of distilled water, the distillations were continued. The amounts volatilised were greater, but were in the same ratio as before. In each case, the compounds solidified in the condenser and were found by m. p. determinations to be unchanged chelate compounds.

Quantitative experiments with 1 g. of di-*n*-propylthallium dipropionylmethane indicate that its volatility is less when distilled with (*a*) 50 c.c. of 2*N*-sodium hydroxide than with (*b*) 50 c.c. of 2*N*-ammonia under identical conditions for the same time.

In (*a*), 0·7 g. solidified in condenser, and in (*b*), 0·85 g. Potassium iodide solution was added to both the distillates and to the residual liquids in the distilling flask. The intensity of the white precipitates indicated that in the distilling flask the residual chelate compound was least with (*b*), also that more thallium came over from this solution.

Similar experiments with the thallous compounds of acetylacetone, propionylacetone, and dipropionylmethane, and with trimethylplatinum dipropionylmethane, all gave negative results.

Dimethylthallium acetylacetone resembles the sodium and the thallous derivative in being soluble in water; all three solutions are alkaline, so it is probable that, in part at least, the chelate ring is broken in aqueous solution, and that this contains free acetylacetone together with hydroxyl ions and ions of the base. The amount of acid required to neutralise these three solutions decreases with time, probably owing to hydrolysis of the acetylacetone with formation of acetic acid. This happens most rapidly with aqueous solutions of sodium acetylacetone, and most slowly with dimethylthallium acetylacetone, which agrees with the known relative strengths of the three bases (see Hein and Meininger, *Z. anorg. Chem.*, 1925, **145**, 95; Ostwald, *J. pr. Chem.*, 1886, **33**, 356; 1887, **35**, 121). The differences in the rates, however, are not great. The results now described indicate that the preliminary rupture of the chelate ring, to whatever cause it may be due, is progressively inhibited by increase in the number of carbon atoms attached to it, and also by increase in the surrounding hydroxyl-ion concentration.