

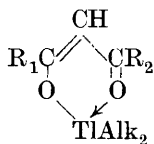
412. *Applications of Thallium Compounds in Organic Chemistry. Part VIII. Molecular Association of Dialkylthallium Chelate Compounds.*

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It is convenient to regard the dialkylthallium derivatives of β -diketones and β -ketonic esters as having the attached general structure. Differentiation in position between the organic radicals

R_1 and R_2 is immaterial, as the ring structure is probably symmetrical (Morgan, J., 1914, 105, 193).

The dimethyl- and the diethyl-thallium derivatives obtained by substituting different organic radicals at R_1 and R_2 form, respectively, two parallel series which are very similar in chemical properties. They can all be prepared by a general method and exhibit the behaviour characteristic of chelate compounds.



In benzene solution they are associated, and the degree of association depends to a marked extent both on the nature of the groups R_1 and R_2 and, to a smaller extent, on the alkyl groups attached to the thallium atom. On the graphs shown, the degrees of association in dry benzene, determined cryoscopically, are plotted against the simple molecular concentration (weight of solute per 100 g. of solvent divided by the simple molecular weight). The compounds studied were the dimethyl- and the diethyl-thallium derivatives of ethyl acetoacetate, methyl acetoacetate, propionylacetone, ethyl benzoylacetate, benzoylacetone, dipropionylmethane, and dibenzoylmethane. (Dimethylthalli)propionylacetone and both the acetylacetones were, however, too sparingly soluble for their molecular weights to be determined by this method.

The association at first increases slightly with concentration, but in most cases an approximately constant value is reached below a molecular concentration of 0.01 g.-mol./100 g. of benzene, and this serves as a convenient concentration for comparison.

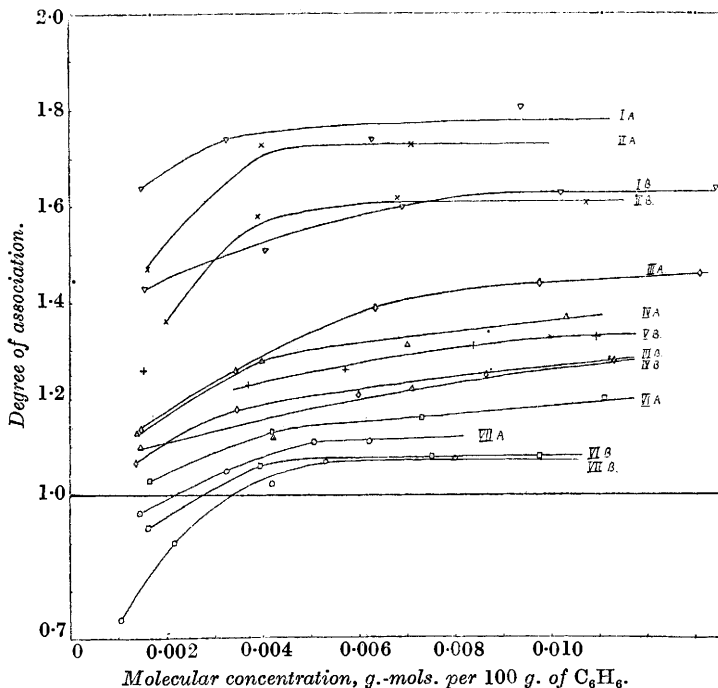
Influence of Groups R_1 and R_2 attached to the Chelate Ring.—In both the dimethyl- and the diethyl-thallium series of derivatives the association is very small when R_1 and R_2 are the same hydrocarbon radical, as in the compounds of dipropionylmethane ($R_1 = R_2 = C_2H_5$) and dibenzoylmethane ($R_1 = R_2 = C_6H_5$). When R_1 is changed to CH_3 , as in the propionylacetone ($R_1 = CH_3$; $R_2 = C_2H_5$) and benzoylacetone ($R_1 = CH_3$; $R_2 = C_6H_5$) derivatives, the association is increased. Another increase in association resulting from a similar change is seen by comparing the derivatives of ethyl benzoylacetate ($R_1 = C_6H_5$; $R_2 = O \cdot C_2H_5$) and ethyl acetoacetate ($R_1 = CH_3$; $R_2 = O \cdot C_2H_5$), the latter being more associated.

An increase in association is also observed when an oxygen atom is introduced into R_1 or R_2 , ethyl (diethylthalli)acetoacetate ($R_1 = CH_3$; $R_2 = O \cdot C_2H_5$) being considerably more associated than (diethylthalli)propionylacetone ($R_1 = CH_3$; $R_2 = C_2H_5$). Moreover, the derivatives of ethyl and methyl acetoacetate, in which R_1 is a methyl group and R_2 an alkoxy-group, are the most highly associated of all the compounds studied. (The methyl ester, however, is slightly less associated than the ethyl indicating that

substituting a methyl for an ethyl group in this position has not the same effect.)

Summarising, it can be said that the dimethylthallium derivatives investigated form a well-defined series in which the association decreases in the order given above. In the diethylthallium derivatives the association decreases in the same order, but the separation

FIG. 1.



Dimethylthallium deriv. of		Diethylthallium deriv. of	
▽	IA. Ethyl acetoacetate.	IB.	Ethyl acetoacetate.
×	IIA. Methyl acetoacetate.	II B.	Methyl acetoacetate.
◇	IIIA. Ethyl benzoylacetate.	III B.	Ethyl benzoylacetate.
△	IVA. Benzoylacetone.	IV B.	Benzoylacetone.
+		V B.	Propionylacetone.
□	VIA. Dipropionylmethane.	VI B.	Dipropionylmethane.
○	VIIA. Dibenzoylmethane.	VII B.	Dibenzoylmethane.

between the curves representing successive members is in several instances much smaller. Moreover, preliminary experiments with several dipropyl- and dibutyl-thallium derivatives indicate that in these cases the order is slightly different, probably owing to the effect of the groups R₁ and R₂ being modified as the size of the alkyl groups attached to the thallium is increased.

Influence of the Alkyl Groups attached to the Thallium Atom.—In

every case investigated, the dimethylthallium derivative exhibits a slightly greater association than the corresponding diethylthallium derivative at the specified molecular concentration. Thus, again, the effect of substituting methyl for ethyl groups in the molecule has been to cause an increase in association. Until, however, the effect of other alkyl groups attached to the thallium has been investigated, it cannot be decided whether this increase is due to any marked difference between the methyl and the ethyl group, or is merely part of a general gradation encountered as higher groups are substituted, as is the case with the m. p.'s (Menzies and Wiltshire, this vol., p. 2605). The preliminary experiments referred to above suggest that there is not the same gradation.

SUMMARY AND DISCUSSION.

The series of dimethyl- and diethyl-thallium chelate derivatives studied show an association in freezing benzene varying approximately between 1 and 2. The alkyl groups attached to the thallium atom have a small but definite effect on the association, but the most important factor is the constitution of the parent diketone or ketonic ester. In general, those compounds containing a methyl or alkoxy-group as a side chain in the chelate ring are more highly associated than those containing ethyl or phenyl groups in the same position.

Sidgwick and Sutton (J., 1930, 1468) observed that ethyl thallicoacetate has a double molecular weight in boiling benzene, and accounted for the association by assuming that the octet of electrons around the thallium atom is thereby completed either by a double bond between two thallium atoms or by co-ordinate links between the thallium of one molecule and an oxygen of another.

In the compounds under consideration, the thallium has, in the unimolecular formula, an effective atomic number of 86 (as has lead in its stable tetra-alkyls; cf. Berry and Lowry, J., 1928, 1765), and its electronic octet is completed. The molecular association now described was consequently unexpected. The thallium atom, however, is certainly concerned in this association, as it does not occur in its absence, ethyl acetoacetate, for instance, being unassociated in freezing benzene (Auwers, *Z. physikal. Chem.*, 1894, **15**, 34).

Now, trivalent thallium in its halogen compounds exhibits valencies of 5 and 6 as well as of 4 (Meyer, *Z. anorg. Chem.*, 1900, **24**, 321; *Ber.*, 1902, **35**, 1319; Renz, *Ber.*, 1902, **35**, 1111), compounds of all three types, $M(\text{TLX}_4)$, $M_2(\text{TLX}_5)$, and $M_3(\text{TLX}_6)$, being described, the thallium having effective atomic numbers of 86, 88, and 90; so the facts recorded in this paper may be accounted for by the assumption that, although the unimolecular form of

chelate dialkylthallium compounds, containing an electronic group of 8, is very stable, yet there is also a less strong tendency for the number to be increased above 8. If this be admitted, the association of these compounds is explicable as a reversible co-ordination between an oxygen atom in one molecule and the thallium in its neighbour, the greater association observed in the derivatives of the ketonic esters being due to the probability of the necessary antecedent approach between molecules containing three oxygen atoms being greater than in the case of the derivatives of the diketones which contain only two. The substitution of the smaller methyl for the ethyl or the phenyl group, either in the positions R_1 and R_2 or on the thallium atom, may increase the probability of co-ordination by allowing the atoms taking part to approach closer together.

In addition, the molecules are unsymmetrical, and if they have a dipole moment, the association may also be due to electrostatic attraction between similar molecules oriented in opposite directions. The greater association of dimethyl thallium compounds may then be a consequence of the forces involved acting through smaller distances than those separating the diethylthallium compounds. Any inverse law of attraction between molecules otherwise similar involves—once they are in contact—an increase of force with diminution in size.

These two causes are not incompatible and may well act together.

EXPERIMENTAL.

The f. p.'s were determined in an ordinary Beckmann apparatus, the C_6H_6 being dried by distillation over P_2O_5 after having been freed from S by successive treatments with $TlOEt$, followed by alk. $KMnO_4$ aq. By calibration with $C_{10}H_8$, the f. p. const. was determined as 52.5.

The general method used to prepare these compounds was to act on the β -diketone or ketonic ester with the requisite dialkylthallium ethoxide (for details, see Menzies and Wiltshire, *loc. cit.*; Menzies, Sidgwick, Cutcliffe, and Fox, J., 1928, 1288). The compounds themselves were purified by repeated crystn. from *n*-hexane or pure dry ether. The Tl was determined by titration with 0.2N- H_2SO_4 and methyl-red.

The new compounds are described below, the others in the two papers referred to above.

Methyl (dimethylthalli)acetoacetate, m. p. 184° (Found: C, 24.1, 24.2; H, 3.6, 3.8; Tl, 58.8. $C_7H_{13}O_3Tl$ requires C, 24.0; H, 3.75; Tl, 58.4%), small colourless prisms from Et_2O . In this and the following prepn. the dialkylthallium methoxide was used instead of the corresponding ethoxide, so that there should be no possibility of methyl groups being replaced by ethyl.

Methyl (diethylthalli)acetoacetate, m. p. 127° (Found: C, 28.8, 28.7; H, 4.5, 4.6; Tl, 54.4. $C_9H_{17}O_3Tl$ requires C, 28.6; H, 4.5; Tl, 54.1%), crystallised from Et_2O in large, flat, colourless prisms.

Ethyl (dimethylthalli)benzoylacetate, m. p. 133° (Found: C, 36.8, 36.9; H, 4.1, 4.1; Tl, 48.1. $C_{13}H_{17}O_3Tl$ requires C, 36.7; H, 4.0; Tl, 48.0%),

	TlMe ₂ compound.			TlEt ₂ compound.		
	Mol. conc.	Mol. wt.	Associ- ation.	Mol. conc.	Mol. wt.	Associ- ation.
Ethyl aceto- acetate	0-00150	595	1-64	0-00156	561	1-43
	0-00324	634	1-74	0-00403	592	1-51
	0-00622	634	1-74	0-00689	627	1-60
	0-00932	658	1-81	0-0102	637	1-63
				0-0135	643	1-64
Methyl aceto- acetate	0-00159	513	1-47	0-00202	512	1-36
	0-00403	606	1-73	0-00389	594	1-58
	0-00715	605	1-73	0-00681	612	1-62
				0-0107	608	1-61
				0-0134	617	1-64
Propionyl- acetone	Too sparingly soluble.			0-00156	472	1-26
				0-00369	463	1-23
				0-00571	475	1-26
				0-00836	494	1-31
				0-0109	500	1-33
Ethyl benzoyl- acetate	0-00152	484	1-14	0-00137	487	1-07
	0-00345	536	1-26	0-00347	534	1-18
	0-00635	591	1-39	0-00599	549	1-21
	0-00974	613	1-44	0-00866	568	1-25
	0-0131	622	1-46	0-0113	580	1-28
Benzoylacetone	0-00138	448	1-13	0-00147	467	1-10
	0-00397	506	1-28	0-00422	476	1-12
	0-00699	518	1-31	0-00707	515	1-22
	0-0103	544	1-37	0-0112	541	1-28
Dipropionyl- methane	0-00165	374	1-03	0-00163	363	0-93
	0-00418	407	1-13	0-00396	411	1-06
	0-00728	421	1-16	0-00750	419	1-08
	0-0111	434	1-20	0-00975	423	1-08
Dibenzoyl- methane	0-00145	437	0-96	0-00105	359	0-74
	0-00323	482	1-05	0-00216	437	0-90
	0-00503	510	1-11	0-00422	494	1-02
	0-00621	506	1-11	0-00528	517	1-07
				0-00796	523	1-08

crystallised from *n*-hexane in light yellow prisms. The ethyl benzoylacetate (Claisen, *Annalen*, 1896, **291**, 70) was obtained from benzoyl chloride and ethyl acetoacetate as a light yellow oil (Found : C, 69.0, 68.9; H, 6.3, 6.3. Calc. : C, 68.7; H, 6.3%). It is possible that in both cases the colour is due to a trace of impurity.

Ethyl (diethylthalli)benzoylacetate, m. p. 95° (Found : C, 40.0, 39.8; H, 4.9, 4.7; Tl, 45.5. C₁₅H₂₁O₃Tl requires C, 39.7; H, 4.7; Tl, 45.1%), separated in colourless crystals when its hexane solution was cooled in ice.

(Dimethylthalli)dibenzoylmethane, m. p. 173—175° (Found : C, 44.5, 44.7; H, 3.8, 3.8; Tl, 45.2. C₁₇H₁₇O₂Tl requires C, 44.6; H, 3.7; Tl, 44.7%), and *(diethylthalli)dibenzoylmethane*, m. p. 112° (Found : C, 47.0; H, 4.4; Tl, 42.4. C₁₉H₂₁O₂Tl requires C, 47.0; H, 4.3; Tl, 42.1%), both crystallised from hexane or ether in large yellow prisms.

The m. p.'s of the TlMe₂ derivatives, being in each case higher than those of the TlEt₂ ones, thus conform to the gradation pointed out before (Menzies and Wiltshire, *loc. cit.*).

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