

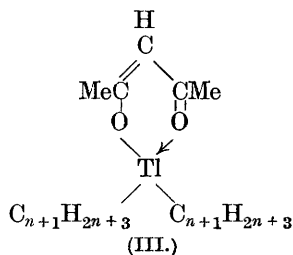
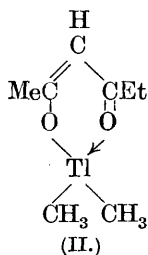
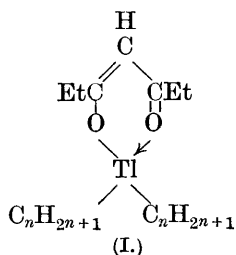
386. *Applications of Thallium Compounds in Organic Chemistry. Part VII. Chelate Rings.**

By R. C. MENZIES and E. R. WILTSHIRE.

THE scope of this and of the succeeding papers may be defined by recalling that the probable cyclic structure of acetylacetone in its platinous compounds was indicated by Werner (*Ber.*, 1901, **34**, 2586), and that Morgan (J., 1914, **105**, 193) pointed out the possible analogy of this and similar cyclic structures to the benzene ring, later (J., 1920, **117**, 1457) coining for them the adjective "chelate." Sidgwick and Callow (J., 1924, **125**, 527; Sidgwick, J., 1925, **127**, 907) summarised a series of papers indicating the existence of similar ring structures in many ortho-substituted benzene derivatives, β -diketones, and β -keto-esters. Confirmatory evidence is provided by Bawn (this vol., p. 1189), who showed that the bands characteristic of hydroxyl groups are missing from the infra-red spectra of enolised acetylacetone and other similar tautomeric substances. This ring formation, satisfying residual or co-ordinate affinity within the molecule, has, as one consequence, the result that less work is necessary to separate molecules in which it occurs from each other than in the case of isomeric substances in which ring structure is not possible. This is shown by the lower b. p.'s and greater solubility in organic solvents of substances of the former type. The most stable compounds of this type, the derivatives of polyvalent metals with acetylacetone and similar substances, contain two or more rings attached to each metallic atom. Compounds containing only one chelate ring are, as a rule, unstable, the ring structure easily reverting to the open enolic form (cf. Sidgwick and Brewer, J., 1925, 2379), and there is a sharp contrast between the properties of the compounds of the alkali metals with acetylacetone and those of, e.g., beryllium and copper, the stability of which, shown by their volatility, is ascribed by Morgan to their symmetry (*loc. cit.*, p. 190). Interest therefore attaches to the chelate derivatives of trimethylplatinum and of dialkylthallium, all of which are stable, crystalline solids. They contain only one chelate ring attached to each metallic

* See also Menzies, Sidgwick, Cutcliffe, and Fox, J., 1928, 1288.

atom; the molecules are unsymmetrical, but they are frequently volatile. The acetylacetones of thallium, and of dimethyl-, diethyl-, dipropyl-, and dibutyl-thallium, present a graduated series of which the thallos compound approaches, but does not reach, in instability sodium or potassium acetylacetone, whilst dibutylthallium acetylacetone in its greater stability and insolubility in water resembles the acetylacetones of copper or beryllium. Dibutyl- and dipropylthallium acetylacetones may be precipitated from dilute aqueous solutions of the hydroxides by addition of acetylacetone, but the diethyl-, dimethyl-, and thallos compounds only from concentrated aqueous solutions. The thallium in all these compounds may be estimated by titration with sulphuric acid, in presence of methyl-red; the last two compounds are titrated rapidly by adding the acid to the solid substances, the diethyl compound more slowly, whilst reaction between solid dipropylthallium acetylacetone and aqueous acid at room temperature takes days. This difference in the rate of titration is probably due to difference in solubility in water, for all these substances, and also the corresponding similarly graduated thallium and dialkylthallium propionylacetones and dipropionylmethanes, can be rapidly and accurately titrated if first dissolved in 80% ethyl alcohol. Inspection of the m. p.'s shows that in passing from the thallos to the dimethylthallium compounds there is a considerable rise in m. p., followed by a gradual fall on passing to the higher dialkylthallium derivatives. As far as we know, all chelate dimethylthallium compounds have higher m. p.'s than the corresponding diethylthallium compounds, the non-alkylated derivatives often melting lower than either. The well-known so-called anomalous higher melting points of methyl esters (Malkin, *Nature*, 1931, 127, 126) thus find a parallel among these organometallic compounds. The replacement of methyl by ethyl groups attached to carbon has a greater effect on the m. p. than the replacement of ethyl by methyl groups attached to thallium, for dimethyl-, diethyl-, and dipropylthallium dipropionylmethanes (I) have each, in turn, lower m. p.'s than the respectively isomeric diethyl-, dipropyl-, and dibutylthallium acetylacetones (III).



EXPERIMENTAL.

These compounds, of which thallos acetylacetonone (Kurowski, *Ber.*, 1910, **43**, 1078) and dimethyl- and diethyl-thallium acetylacetones (Menzies, Sidgwick, Cutcliffe, and Fox, *J.*, 1928, 1288) are already known, were all made from TIOEt or from the dialkylthallium ethoxides. About 1300 g. of TIOEt were made in a few hours from $\text{H}\cdot\text{CO}_2\text{Tl}$ (see *J.*, 1930, 1571), and the derivatives rapidly crystallised on mixing equiv. amounts of it with the diketone in light petroleum. Solutions of the dialkylthallium ethoxide in C_6H_6 were prepared by double decomp. of the respective dialkylthallium halides and TIOEt in C_6H_6 solution, and standardised with 0.2N- H_2SO_4 aq. (methyl-red). Dipropionylmethane was prepared from ethyl propionate and COMeEt (Fischer and Bartholomäus, *Ber.*, 1912, **45**, 1983), and propionylacetone similarly from EtOAc and COMeEt. Weighed amounts of the diketones were then added to the calc. vols. of the standardised solutions, and after removal of the C_6H_6 on a water-bath, the crude dry product was recrystallised from hexane or light petroleum. All these compounds separate from hexane in long silky needles, except dimethylthallium propionylacetone (II) and dipropionylmethane, which form compact prisms. All the alkylated Tl compounds described in this paper can be sublimed in air by careful heating in a test-tube. Their m. p.'s and analytical data are given in the following tables. The C and H contents of all org. Tl compounds may be estimated by

M. p.'s and Tl contents (by titration).

	M. p.	Tl, %.		C, %.		H, %.	
		Found.	Calc.	Found.	Calc.	Found.	Calc.
1. Thallos acetylacetonone	161°	67.06	67.34	19.76	19.77	2.43	2.33
2. Dimethylthallium acetylacetonone	214—215	61.21	61.3	25.00	25.20	3.9	3.9
3. Diethylthallium acetylacetonone	200	56.7	56.5	30.7	29.9	5.0	4.7
4. Dipropylthallium acetylacetonone, $\text{C}_{11}\text{H}_{21}\text{O}_2\text{Tl}$	181	52.62	52.5	{ 33.75 } { 34.08 }	33.89	{ 5.48 } { 5.63 }	5.43
5. Dibutylthallium acetylacetonone, $\text{C}_{13}\text{H}_{25}\text{O}_2\text{Tl}$	138—139	49.43	48.96	{ 37.36 } { 37.51 }	37.36	{ 5.92 } { 6.04 }	6.04
6. Thallos dipropionylmethane, $\text{C}_7\text{H}_{11}\text{O}_2\text{Tl}$	70	62.0	61.7	{ 25.11 } { 25.11 }	25.34	{ 3.32 } { 3.44 }	3.35
7. Dimethylthallium dipropionylmethane, $\text{C}_9\text{H}_{17}\text{O}_2\text{Tl}$	121	57.3	56.5	{ 29.72 } { 29.87 }	29.9	{ 4.45 } { 4.77 }	4.7
8. Diethylthallium dipropionylmethane, $\text{C}_{11}\text{H}_{21}\text{O}_2\text{Tl}$	116	52.3	52.5	{ 33.86 } { 33.85 }	33.89	{ 5.56 } { 5.58 }	5.43
9. Dipropylthallium dipropionylmethane, $\text{C}_{13}\text{H}_{25}\text{O}_2\text{Tl}$	89	49.35	48.96	{ 37.39 } { 37.17 }	37.36	{ 5.98 } { 5.90 }	6.04
10. Dimethylthallium propionylacetone, $\text{C}_9\text{H}_{15}\text{O}_2\text{Tl}$	162	60.1	58.81	{ 28.03 } { 27.73 }	27.64	{ 4.71 } { 4.43 }	4.35
11. Diethylthallium propionylacetone, $\text{C}_{11}\text{H}_{19}\text{O}_2\text{Tl}$	147	53.99	54.4	{ 31.51 } { 31.83 }	31.96	{ 5.11 } { 5.31 }	5.11

3 and 7, 4 and 8, 5 and 9 are respectively isomeric.

combustion in the usual way (Kuhlman, *Annalen*, 1863, **126**, 76). The combustions of Nos. 4–11 were carried out by Dr. Ing. A. Schoeller.

The authors thank the Colston Research Society for a grant.

THE UNIVERSITY, BRISTOL.

[Received, July 30th, 1932.]