# 7. *Applications of Thallium Compounds in Organic Chemistry. Part IX. Changes observed on replacing Dialkylthallium by Trimethylplatinum in Chelate Rings.*

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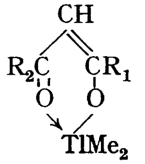
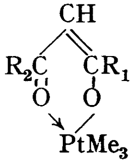
In Parts VII and VIII (J., 1932, 2604, 2734) the properties of chelate compounds of β-diketones and β-ketonic esters with dialkylthallium have been discussed. The changes observed on replacing dimethylthallium (I) by trimethylplatinum (II) in chelate rings are now described.

(I.)





(II.)

The chelate derivatives of trimethylplatinum with acetylacetone, dipropionylmethane, and ethyl acetoacetate are white crystalline substances soluble in organic solvents. They resemble the corresponding dialkylthallium compounds in being volatile, but differ from the lower members in being insoluble in water.

The acetylacetone derivative and that of dipropionylmethane decompose without melting at 200° and 190° respectively, the benzoylacetone compound at 187°, and ethyl (trimethylplatini)acetoacetate melts with blackening and evolution of gas when placed suddenly, in a tube sealed at both ends, into a bath at 200°. The corresponding dimethylthallium compounds melt at 214°, 121°, 128°, and 128° respectively. With these may be compared the low melting point, 9—10°, of diethylgold acetylacetone (Gibson and Simonsen, J., 1930, 2535).

In the table the molecular associations of the trimethylplatinum derivatives of dipropionylmethane and of ethyl acetoacetate in freezing benzene are compared with those of their dimethylthallium derivatives (*loc. cit.*, p. 2739).

| | Trimethylplatinum. | | | Dimethylthallium. | | |
|---|---|---|---|---|---|---|
| | Mol. conc. | Mol. wt. | Association. | Mol. conc. | Mol. wt. | Association. |
| Dipropionylmethane | 0·00171 | 703·3 | 1·914 | 0·00165 | 374 | 1·03 |
| | 0·00434 | 740·6 | 2·016 | 0·00418 | 407 | 1·13 |
| | 0·00685 | 734·5 | 1·999 | 0·00728 | 421 | 1·16 |
| | 0·00975 | 756·0 | 2·057 | 0·0111 | 434 | 1·20 |
| Ethyl acetoacetate | 0·00162 | 848 | 2·30 | 0·00150 | 595 | 1·64 |
| | 0·00316 | 805 | 2·18 | 0·00324 | 634 | 1·74 |
| | | | | 0·00622 | 634 | 1·74 |
| | | | | 0·00932 | 658 | 1·81 |

It is evident that the forces holding the molecules together are much greater in the platinum compounds than in the thallium compounds. The unimolecular formulæ for the trimethylplatinum compounds in question indicate for the metal an effective atomic number of 84, or 2 less than that of the next inert gas (cf. Sidgwick, J., 1923, **123**, 725), and also a covalency of 5. The stable double molecular weights just described may be explained as due to co-ordination between the platinum of one molecule and an oxygen in its neighbour (cf. Sidgwick and Sutton, J., 1930, 1472), increasing the effective atomic number to 86 and the co-ordination number of the metal to 6. They thus afford yet another example of the familiar stability of 6-covalent compounds of quadrivalent platinum, but also serve to throw into better relief the variable covalency of thallium discussed in Part VIII.

## EXPERIMENTAL.

The method used to prepare the trimethylplatinum derivatives of dipropionylmethane, of ethyl acetoacetate, and of benzoylacetone was similar to that described by Menzies (J., **1928**, 565) for the prep. of trimethylplatinum acetylacetone. The thallous salts were not isolated, but the $PtMe_3I$ was added to a solution of TlOEt and the diketone.

The reaction goes quite readily with dipropionylmethane and with ethyl acetoacetate, but more slowly with benzoylacetone. It is never, however, so rapid nor so complete as with the Tl compounds. $PtMe_3I$ in slight excess, TlOEt, and the diketone or ketonic ester are best heated under reflux with boiling $C_6H_6$, the mixtures evaporated to dryness, and the residue extracted with ligroin or hexane, from which the trimethylplatinum derivative readily separates on cooling.

The separation of TlI from a solution of $PtMe_3I$ and TlOEt in $C_6H_6$ also takes place very slowly; indeed, the reaction does not appear to go to completion. Undue heating of the solution causes darkening and thus it is unprofitable to attempt to isolate a solution of $PtMe_3(OEt)$ as is done in the prep. of dialkylthallium derivatives.

The trimethylplatinum compounds described are all chelate compounds (being sol. in org. solvents), and when carefully heated in a tube they sublime, giving a Pt mirror in the same way as the acetylacetone compound.

*Ethyl (trimethylplatini)acetoacetate*, hexagonal plates from $Et_2O$ (Found : C, 29·4, 29·7; H, 4·9, 5·1; Pt, 52·45. $C_9H_{18}O_3Pt$ requires C, 29·2; H, 4·9; Pt, 52·8%).

*Trimethylplatinum dipropionylmethane*, thick needles from hexane (Found : C, 32·9, 32·7; H, 5·55, 5·3; Pt, 51·5, 52·8. $C_{10}H_{20}O_2Pt$ requires C, 32·7; H, 5·5; Pt, 53·1%).

*Trimethylplatinum benzoylacetone* was obtained neither in purity nor in amount sufficient for molecular-weight determinations. The analytical figures indicate, however, that a crude sample was obtained. It is described as giving additional evidence that chelate derivatives of trimethylplatinum remain solid at temp. above the m. p.'s of the corresponding dimethylthallium derivatives. It is sol. in $C_6H_6$, from which it separates in irregular cryst. lumps, very sparingly sol. in ligroin, and readily sol. in MeOH, from which it crystallises in long prisms, often radiating from a centre (Found : C, 39·5, 39·1; H, 4·6, 4·6; Pt, 46·6. $C_{13}H_{18}O_2Pt$ requires C, 38·9; H, 4·5; Pt, 48·6%).

The combustions were carried out by Dr. Ing. A. Schoeller, the Pt estimations by covering the substance with I in a crucible, adding a little $CHCl_3$, and carefully heating the mixture finally to redness as described by Pope and Peachey (J., **1909**, **95**, 572).

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