Tetrahedron Letters No.38, pp. 3341-3342, 1970. Pergamon Press. Printed in Great Britain.

# TRANSTHALLATION REACTIONS WITH AROMATIC COMPOUNDS[1]

A.V. Huygens, J. Wolters and E.C. Kooyman

Chemical Laboratories, P.O. Box 75, University of Leiden,The Netherlands

(Received in UK 29 June 1970; accepted for publication 17 July 1970)

The recent interest in organo-thallium chemistry[2-5] prompts us to report our results on transthallation investigations.

Following up the discovery and development of the transmercuration reaction[6-9] we have now found that transthallation can be also effected. For monosubstituted benzenes, the reaction can be represented by:

$$C_6H_5TlX_2 + C_6H_5Y \rightleftarrows YC_6H_4TlX_2 + C_6H_6 \qquad (1)$$

So far our work was limited to X = trifluoroacetate. Phenylthallium(III)di-trifluoroacetate reacts in an excess of benzene derivatives (Y = F, Cl, Br, J, $OCH_3$ etc.) to produce mixtures of isomeric aromatic thallium(III) compounds (Table I). Reaction temperatures of 70-90°C. and relatively long reaction times (100 - 2000 h) appeared to be required. Determination of the isomer patterns was accomplished by converting the aromatic thallium(III) compounds into the aromatic iodides[5], which were analyzed by comparison of glc retention times with those of authentic samples.

Isomer distributions for the halobenzene derivatives show significant changes with time. It is assumed that those after long reaction times refer to equilibria, as observed in our transmercurations[6-9]:

$$o'\text{-},m'\text{-},p'\text{-}YC_6H_4TlX_2 \overset{C_6H_5Y}{\rightleftarrows} o\text{-},m\text{-},p\text{-}YC_6H_4TlX_2 \qquad (2)$$

Presumably, equilibrium has been established in both runs with anisole.

The equilibrium patterns for the halobenzene derivatives are different from those resulting from the arylmercuryacetates in that much lower proportions of ortho-isomers are present, viz. 43, 12, 10 and 8% as compared with 86, 72, 65 and 51%. In both series, these percentages are decreasing with increasing size of the halogen. More detailed comments will be given later on. Kinetic and mechanistic studies of these novel reactions are in hand in this laboratory[10].

Table I

Transthallations of some benzene derivatives

| Reactants$^x$ | Temp. ($^oC$.) | Reaction time (h) | Conversion$^{xx}$ | Isomer distribution of $YC_6H_4TlX_2$ | | |
|---|---|---|---|---|---|---|
| | | | | %o | %m | %p |
| $C_6H_5Tl(OCOCF_3)_2$ + $C_6H_5OCH_3$ | 90 | 405 | 95 | 65 | 23 | 12 |
| | 90 | 1032 | > 99 | 65 | 23 | 12 |
| $C_6H_5Tl(OCOCF_3)_2$ + $C_6H_5F$ | 80 | 96 | 75 | 57 | 7 | 36 |
| | 80 | 866 | 95 | 45 | 23 | 32 |
| | 80 | 1250 | 95 | 43 | 25 | 32 |
| $C_6H_5Tl(OCOCF_3)_2$ + $C_6H_5Cl$ | 80 | 115 | 60 | 49 | 15 | 36 |
| | 80 | 885 | 95 | 13 | 52 | 35 |
| | 80 | 1053 | > 99 | 12 | 52 | 36 |
| | 80 | 1269 | > 99 | 12 | 55 | 33 |
| $C_6H_5Tl(OCOCF_3)_2$ + $C_6H_5Br$ | 80 | 115 | 80 | 47 | 19 | 34 |
| | 80 | 1053 | 95 | 12 | 53 | 35 |
| | 80 | 1269 | > 99 | 10 | 56 | 34 |
| | 80 | 1436 | > 99 | 10 | 54 | 36 |
| $C_6H_5Tl(OCOCF_3)_2$ + $C_6H_5J$ | 80 | 96 | -- | 35 | 33 | 32 |
| | 80 | 866 | -- | 9 | 63 | 28 |
| | 80 | 1250 | -- | 8 | 65 | 27 |

x Molar intake ratios 1 : 75 to 1 : 225 xx Percentage converted $C_6H_5TlX_2$

## REFERENCES

1. The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO)
2. E.C. Taylor, F. Kienzle, R.L. Robey, A. McKillop, J.Am.Chem.Soc. 92, 2175 (1970)
3. A.G. Lee, J. Organometal. Chem. 22, 537 (1970)
4. A. McKillop, J.S. Fowler, M.J. Zelesko, J.D. Hunt, E.C. Taylor and G. McGillivray, Tetrahedron Letters 29, 2423 (1969)
5. A. McKillop, J.S. Fowler, M.J. Zelesko, J.D. Hunt, E.C. Taylor and G. McGillivray, Tetrahedron Letters 29, 2427 (1969)
6. E.C. Kooyman, J. Wolters, J. Spierenburg and J. Reedijk, J. Organometal. Chem. 3, 487 (1965)
7. J. Wolters, Thesis Leiden 1965
8. J. Verwey, Thesis Leiden 1969
9. a. J. Spierenburg, Thesis Leiden 1970
   b. We are indebted to Dr. J. Spierenburg for his stimulating interest
10. A.V. Huygens, Thesis to be published