

TRANSTHALLATION REACTIONS WITH AROMATIC COMPOUNDS¹

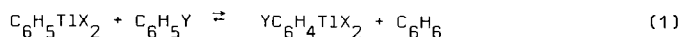
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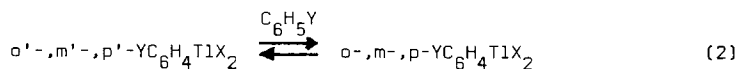
The recent interest in organo-thallium chemistry²⁻⁵ prompts us to report our results on transthallation investigations.

Following up the discovery and development of the transmercuration reaction⁶⁻⁹ we have now found that transthallation can be also effected. For monosubstituted benzenes, the reaction can be represented by:



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, OCH₃ 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 iodides⁵, 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 transmercuration⁶⁻⁹:



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 laboratory¹⁰.

Table I
Transthallations of some benzene derivatives

Reactants ^x	Temp. (°C.)	Reaction time (h)	Conversion ^{xx}	Isomer distribution of $\text{YC}_6\text{H}_4\text{TiX}_2$		
				%o	%m	%p
$\text{C}_6\text{H}_5\text{Ti}(\text{OCOCF}_3)_2 + \text{C}_6\text{H}_5\text{OCH}_3$	90	405	95	65	23	12
	90	1032	> 99	65	23	12
$\text{C}_6\text{H}_5\text{Ti}(\text{OCOCF}_3)_2 + \text{C}_6\text{H}_5\text{F}$	80	96	75	57	7	36
	80	866	95	45	23	32
	80	1250	95	43	25	32
$\text{C}_6\text{H}_5\text{Ti}(\text{OCOCF}_3)_2 + \text{C}_6\text{H}_5\text{Cl}$	80	115	60	49	15	36
	80	885	95	13	52	35
	80	1053	> 99	12	52	36
	80	1269	> 99	12	55	33
$\text{C}_6\text{H}_5\text{Ti}(\text{OCOCF}_3)_2 + \text{C}_6\text{H}_5\text{Br}$	80	115	80	47	19	34
	80	1053	95	12	53	35
	80	1269	> 99	10	56	34
	80	1436	> 99	10	54	36
$\text{C}_6\text{H}_5\text{Ti}(\text{OCOCF}_3)_2 + \text{C}_6\text{H}_5\text{I}$	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 $\text{C}_6\text{H}_5\text{TiX}_2$

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