Formation of Chlorobenzene by the Reaction of Phenylthallium(III) Compounds with Copper Chloride

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Summary The reaction of phenylthallium(III) compounds with $CuCl_2$ and CuCl in AcOH, MeCN, and tetrahydrofuran gives mainly chlorobenzene.

REACTIONS of organometallic compounds with metal salts are of current interest.[1] In the case of aromatic thallium compounds, it was reported recently that arylthallium bis(trifluoroacetate) reacts with lead tetra-acetate to form the aryl acetate and with potassium cyanide (under u.v. irradiation) to form the aryl cyanide.[2]

We report that thallium attached to an aromatic ring PhTlXY (I) can be replaced by chlorine by treatment with $CuCl_2$ or CuCl in AcOH, MeCN containing LiCl and tetrahydrofuran.

$$\mathrm{PhTlXY} \xrightarrow[\text{or CuCl}]{\mathrm{CuCl_2}} \mathrm{PhCl}$$

(I) a; X = OAc, Y = ClO_4†
b; X = Y = Cl
c; X = Ph, Y = Cl
d; X = Y = OAc
e; X = Y = CF_3CO_2

AcOH solutions of phenylthallium(III) compounds and copper salts were kept at various temperatures for various reaction periods. The main organic product was chlorobenzene which was identified by g.c., i.r., and n.m.r. spectroscopy. Small amounts of benzene and biphenyl were also obtained. The results are shown in the Table.

The nature of X and Y has little effect on the yields of

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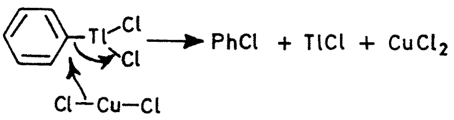
† Prepared by the reaction of aromatic substrates with thallium(III) acetate in AcOH containing $HClO_4$.[5]

chlorobenzene, except in the case X = Y = OAc (Id). Both $CuCl_2$ and CuCl were effective, but $Cu(OAC)_2$ was inactive even in the presence of LiCl. The effective reagent, therefore, appears to be the copper chlorides and not Cl^-. Addition of NaOAc to the reaction mixture resulted in a decreased yield of chlorobenzene and an increased yield of biphenyl, showing that the nature of the reaction had changed probably because of the formation of $(CuClOAc)_2$.[3] In AcOH solution, $PhTl(OAc)(ClO_4)$ did not react with the copper salts at 70°, while a 20% yield of chlorobenzene was obtained at 67° in tetrahydrofuran. This shows that the solvent has an important effect on the reaction.

Phenylthallium(III) compound (10 mmol)	Copper salt (mmol)	Solvent (50 ml)	Reaction temp (°)	Reaction time (h)	Products (yield, %)[a] Benzene	Chlorobenzene	Biphenyl
	$CuCl_2\cdot 2H_2O$						
$PhTl(OAc)(ClO_4)$ (Ia)	10	AcOH	117	1	4	56	trace
,,	10	,,	117	5	4	59	2
,,	10	,,	117	10	2	59	trace
,,	20	,,	117	5	2	60	trace
,,	10	,,[b]	117	5	3	12	9
,,	10	,,[c]	117	5	1	53	trace
,,	10	MeCN[d]	84	5	2	28	3
,,	10	THF	67	5	—	20	22
	CuCl						
,,[e]	20	AcOH	117	5	4	42	trace
	$Cu(OAc)_2$						
[e]	20	,,	117	5	13	—	2
,,	—	,,	117	5	24	—	trace
	$CuCl_2\cdot 2H_2O$						
$PhTlCl_2$ (Ib)	10	,,	117	5	2	67	trace
,,	1	MeCN[d]	84	20	2	32	21
Ph_2TlCl (Ic)	10	AcOH	117	5	10	45	trace
$PhTl(OAc)_2$ (Id)	10	AcOH	117	5	19	16	4
$PhTl(CF_3CO_2)_2$ (Ie)	10	,,	117	5	5	30	trace

[a] Based on phenylthallium(III) compound; [b] NaOAc (10 mmol) added; [c] LiCl (40 mmol) added; [d] LiCl (10 mmol) added; [e] 20 mmol; [f] LiCl (20 mmol) added.



Although the elucidation of the *detailed* mechanism requires further experiment, it is clear that the presen reaction is different from that reported by McKillop *et al.*,[2] ($ArTlI_2 \rightarrow ArI$), since $PhTlCl_2$ (Ib) remained unchanged even after a prolonged reaction period. An S_N2-type substitution of aliphatic thallium(III) salts with halide ion[4] is not applicable to the present case. Formation of an aromatic copper compound by metal exchange organo-thallium and copper salt also appears unlikely, since the yields of biphenyl to be expected from that intermediate were not obtained.

A four-centre reaction is the most plausible explanation of the results. The fact that greater amounts of PhCl were formed than of $CuCl_2$ consumed in the reaction of $PhTlCl_2$ (Ib) supports this mechanism.

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