Aromatic Coupling of Arylthallium(III) Compounds by Palladium(II) Chloride

By SAKAE UEMURA*

(*Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan*)

and YOSHIHIRO IKEDA and KATSUHIKO ICHIKAWA

(*Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto, Japan*)

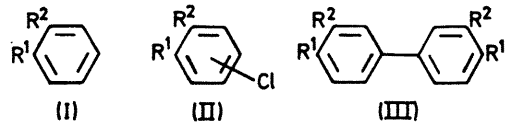
Summary In HOAc containing NaOAc arylthallium(III) compounds reacted with $PdCl_2$ to give mainly aromatic coupled products.

ORGANIC synthesis using metal–metal exchange is of current interest.[1] Recently, aromatic coupling by Hg^{II} [2] or Tl^{III}[3] salts in the presence of a Pd^{II} salt was reported in which aromatic mercuration or thallation followed by Hg–Pd or Tl–Pd exchange is thought to occur. In fact,[2] the reactions of *p,p'*-bitolylmercury with $Pd(OAc)_2$ and of tolylmercuric acetate with $PdCl_2$ gave *p,p'*-bitolyl and a mixture of bitolyl isomers, respectively. No reports about direct reaction of aromatic thallium(III) compounds with a Pd^{II} salt, however, can be found in the literature.

As part of a study of the reaction of aromatic thallium(III) compounds with metal halides,[4] we found that HOAc solutions of arylthallium(III) compounds, $RC_6H_4Tl(X)Y$, reacted with $PdCl_2$ and NaOAc on being heated under reflux for 5 h, to give biaryls in good yields (see Table). The biaryls were identified by g.c., i.r., and n.m.r. Small amounts of the corresponding hydrocarbons and chlorinated aromatics were obtained as by-products. The inorganic products were metallic Pd and a Tl^{I} salt.

The nature of X and Y has little effect on the yields of biaryls (Table), except in the case of X, Y = Ph, Cl. The yield of chlorobenzene is high when X and Y are both Cl. Although $PdCl_2$ alone is effective for biaryl synthesis, addition of NaOAc to the reaction mixture resulted in

increased yields of biaryls probably because of the formation of more effective Pd^{II} species, as has been shown in the case of oxidative coupling of aromatics[6] and olefins[7] by $PdCl_2$.



(I) (II) (III)

TABLE[a]

Arylthallium(III) compound (mmol)		$PdCl_2$ (mmol)	NaOAc (mmol)	Product yield (%) (I)[b]	(II)[b]	(III)[c]
				(R^1=R^2=H)		
$PhTl(OAc)ClO_4$[5]	10	5	10	trace	3	49
"	10	2·5	5	trace	1	59
"	10	1	2	trace	trace	75
"	20	10	—	trace	trace	35
$PhTlCl_2$	10	5	10	trace	30	39
$PhTl(OAc)_2$	3	1·5	3	trace	—	59
$PhTl(OCOCF_3)_2$	3	1·5	3	trace	—	44
Ph_2TlCl	3	3	3	trace	trace	12
				(R^1=Me, R^2=H)		
p-$MeC_6H_4Tl(OAc)ClO_4$	10	5	10	3	3	69
				(R^1=R^2=Me)		
m,p-$Me_2C_6H_3Tl(OAc)ClO_4$	10	5	10	2	trace	66
				(R^1=MeO, R^2=H)		
p-$OMeC_6H_4Tl(OAc)ClO_4$	10	5	10	26	4	70

[a] Solvent, HOAc 50 ml; 117°; 5h. [b] Based on arylthallium(III) compound. [c] Based on half the amount of starting arylthallium(III) compound.

(*Received, January 13th*, 1971; *Com.* 063.)

[1] P. M. Henry, *Tetrahedron Letters*, 1968, 2285; R. F. Heck, *J. Amer. Chem. Soc.*, 1968, **90**, 5518, 5526, 5531, 5538, 5546; *ibid.*, 1969, **91**, 6707.
[2] M. O. Unger and R. A. Fouty, *J. Org. Chem.*, 1969, **34**, 18.
[3] P. M. Henry, *J. Org. Chem.*, 1970, **35**, 3083.
[4] K. Ichikawa, Y. Ikeda, and S. Uemura, *Chem. Comm.*, 1971, 169.
[5] K. Ichikawa, S. Uemura, E. Uegaki, and T. Nakano, *Bull. Chem. Soc. Japan*, 1971, **44**, 545.
[6] R. van Helden and G. Verberg, *Rec. Trav. chim.*, 1965, **84**, 1263.
[7] S. Uemura, T. Okada, and K. Ichikawa, *J. Chem. Soc. Japan*, 1968, **89**, 692.