Journal of Organometallic Chemistry, 99 (1975) C8—C10

Preliminary communication

REACTIONS OF ORGANOTHALLIUM COMPOUNDS WITH OLEFINS

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(Received August 8th, 1975)

Summary

Arylthallium compounds react with olefins in the presence of Li_2PdCl_4, the overall reaction being the replacement of an olefinic hydrogen by the aryl group.

Recent work has shown that organomercury compounds react with olefins in the presence of palladous salts, the overall reaction being the replacement of an olefinic hydrogen by the organic group originally linked to mercury [1]. Organopalladium compounds were postulated as intermediates.

We wish to report some preliminary studies of the reactions of organothallium compounds with olefins in the presence of Li_2PdCl_4 in methanol. The overall reaction scheme is:

$$ArTlX_2 \text{ (or } Ar_2TlX) + RCH{=}CHR' \xrightarrow{Li_2PdCl_4} ArC(R){=}CHR' + (HPdX)$$

(Ar = Phenyl, *p*-Tolyl, Mesityl; R = H, Phenyl; R′ = CO_2CH_3, H; X = $OCOCF_3$, $OCOCH_3$, Cl, CN)

Our results show that reasonable yields of products are obtained, except when organothallium cyanides are used as starting materials (see Table 1). The reaction, therefore, provides a convenient procedure for introducing an aryl group into an olefin, since the arylthallium compounds are readily prepared [2]. The palladous salt need be present only in catalytic quantities if cupric chloride is also present in order to re-oxidise the palladium, although higher yields are obtained if an equimolar quantity is used.

The preliminary results suggest that the reaction may have a high degree of stereospecificity; GLC analysis of the styrene/phenylthallium *cis*-trifluoroacetate system showed that no *cis*-stilbene was formed, and for the other reactions, only the *trans* isomer was obtained. In several reactions using phenylthallium compounds, biphenyl was detected as a side product. This was not unexpected, since arylthallium compounds are known to give biaryls in the presence of palladium salts [3].

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TABLE 1

THE REACTION OF ORGANOTHALLIUM COMPOUNDS WITH OLEFINS IN THE PRESENCE OF Li_2PdCl_4

Organothallium compound $ArTlX_2$ or Ar_2TlX	Olefin $RCH{=}CHR'$		Reaction time (days)	% yield of product $ArC(R){=}CHR'$
	R	R′		
$PhTl\ (OCOCF_3)_2$	H	CO_2CH_3	3	88[a,b]
$PhTl\ (OCOCF_3)_2$	H	CO_2CH_3	2	24[b], 22[c]
$PhTl\ (OCOCF_3)_2$	H	CO_2CH_3	3	27[b]
$PhTl\ (OCOCF_3)_2$	Ph	H	3	30[c]
$PhTlCl_2$	H	CO_2CH_3	3	76[b]
$PhTlCl_2$	Ph	H	3	75[c]
$PhTl\ (CN)_2$	H	CO_2CH_3	2	0
$Ph_2TlOCOCH_3$	H	CO_2CH_3	2	61[b], 45[c]
Ph_2TlCl	H	CO_2CH_3	3	62[b], 60[c]
Ph_2TlCl	Ph	H	2	41[c]
Ph_2TlCN	H	CO_2CH_3	2	<1[b]
p-Tol $Tl(OCOCF_3)_2$	H	CO_2CH_3	3	42[c]
(p-Tol)$_2$Tl $OCOCH_3$	H	CO_2CH_3	3	54[c]
(p-Tol)$_2$TlCl	H	CO_2CH_3	2	32[c]
Mesityl$Tl(OCOCF_3)_2$	H	CO_2CH_3	3	57[c]

[a] This reaction was carried out using an equimolar quantity of Li_2PdCl_4. In all other reactions, only a catalytic quantity of palladium salt was used. [b] Yield by GLC. [c] Isolated yield..

In a typical reaction using a catalytic quantity of palladous salt, equimolar quantities of the arylthallium compound, cupric chloride and the olefin, were dissolved in anhydrous methanol and a 0.01 molar equivalent of Li_2PdCl_4 (prepared by dissolving equivalent amounts of anhydrous lithium chloride and palladous chloride in anhydrous methanol) was immediately added. The mixture was stirred for two to three days at room temperature, and then heated under reflux for one hour. Ether was then added, and the mixture filtered. The filtrate was washed with water, and the dried ethereal solution was either analysed by GLC, or the product isolated by removing the solvent at reduced pressure. Higher yields of product can probably be obtained by increasing the amount of catalyst used.

It is assumed that a key step in the process is a transmetallation resulting in the formation of an organopalladium compound, which then adds to the olefin; an elimination then occurs, producing HPdX and the desired product. Hydrogen replacement at the less substituted carbon atoms occurs. Analogous reactions have been postulated for palladium/mercury systems [1], and an example of palladium/thallium exchange involving an alkylthallium compound has been reported [4].

In addition to the above olefin systems, two acetylenic systems were also examined. Methylpropiolate was treated with phenylthallium bis(trifluoroacetate), and phenylacetylene was treated with either phenylthallium chloride. Our preliminary studies indicated that methyl phenylpropiolate and diphenylacetylene were not formed in these reactions. In this respect, the thallium systems differ from analogous reactions using mercury compounds, where Heck [5] has reported the formation of diphenylacetylene from phenylacetylene.

Acknowledgement

The award of an SRC Studentship (to TS) is gratefully acknowledged.

References

1 R.F. Heck, J. Amer. Chem. Soc., 90 (1968) 5525.
2 A. McKillop and E.C. Taylor, Advan. Organometal. Chem., 11 (1973) 147.
3 S. Uemura, Y. Ikeda and K. Ichikawa, Chem. Commun., (1971) 390.
4 S. Uemura, K. Zushi, M. Okano and K. Ichikawa, Chem. Commun., (1972) 234.
5 R.F. Heck, Chem. Abstr., 79 (1973) 917525.