

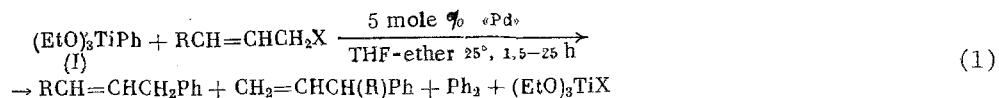
CROSS-COUPLING REACTION OF PHENYLTRIETHOXYTITANIUM WITH
ALLYL HALIDES CATALYZED BY PALLADIUM COMPLEXES

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Cross-coupling reactions of organometallic compounds with allyl halides catalyzed by palladium complexes have been reported for derivatives of magnesium [1], zinc, aluminum, zirconium [2], tin, and copper [3].

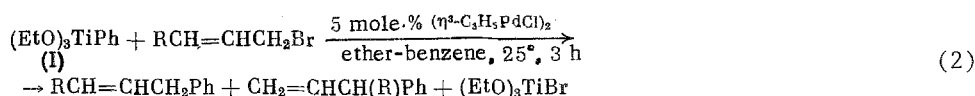
We have found that phenyltriethoxytitanium (I) which is readily prepared in situ by the reaction of $(\text{EtO})_3\text{TiCl}$ with PhLi or with PhMgBr in ether reacts with allyl halides ($\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$ (II), $\text{CH}_2=\text{CHCH}_2\text{Br}$ (III), $\text{MeCH}=\text{CHCH}_2\text{Br}$ (IV), and $\text{PhCH}=\text{CHCH}_2\text{Br}$ (V)) under mild conditions in 1:1 THF-ether at 25°C in the presence of 5 mole % bis(π -allylpalladium chloride) (VI) or tetrakis(triphenylphosphine)palladium (VII):



The starting halides, catalyst, reaction time, products, and product yield are: (II), (VI), 1.5 h, $\text{PhCH}_2\text{CH}=\text{CH}_2$ (100%), (III); (VI), 3 h, $\text{PhCH}_2\text{CH}=\text{CH}_2$ (100%); (IV), (VI), 4 h, $\text{MeCH}=\text{CHCH}_2\text{Ph}$ (50%), $\text{CH}_2=\text{CHCH}(\text{Me})\text{Ph}$ (10%), Ph_2 (40%); (IV), (VII), 20 h, $\text{MeCH}=\text{CHCH}_2\text{Ph}$ (53%), $\text{CH}_2=\text{CHCH}(\text{Me})\text{Ph}$ (46%); (V), (VI), 25 h, $\text{PhCH}=\text{CHCH}_2\text{Ph}$ (52%), Ph_2 (46%).

Under these conditions, (I) does not react with allyl halides in the absence of the palladium catalyst.

The replacement of THF by DMF and DMSO in the reaction of (I) with (IV) catalyzed by (VI) leads to an increase in the yield of Ph_2 and decrease in the yield of the allyldemetallation products. The use of 1:1 ether-benzene as the solvent, on the other hand, completely suppresses the formation of Ph_2 .



$\text{R} = \text{MeCH}=\text{CHCH}_2$ and $\text{PhCH}=\text{CHCH}_2$.

The starting bromides, products, and product yields are: (IV), $\text{MeCH}=\text{CHCH}_2\text{Ph}$ (77%), $\text{CH}_2=\text{CHCH}(\text{Me})\text{Ph}$ (18%); (V), $\text{PhCH}=\text{CHCH}_2\text{Ph}$ (98%).

LITERATURE CITED

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