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AROMATIC SUBSTITUTION OF OLEFIN. V

REACTION OF PHENYL-SUBSTITUTED ETHYLENES WITH BENZENE(1)

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In previous papers,(2) we reported a novel substitution reaction in which styrene undergoes 'phenylation' on a beta-C atom of styrene with benzene in the presence of palladium(II) salts such as palladium(II) acetate or palladium(II) chloride with sodium acetate, yielding stilbene derivatives in excellent yields. This is the first example of substitution reaction between olefins and aromatic compounds resulting aromatic-substituted olefins. Therefore, it is of interest to expand this reaction to both other olefins and aromatic compounds.

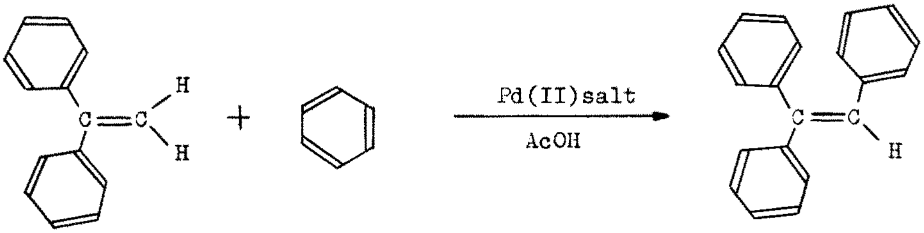
We wish to report the substitution reactions of 1,1-diphenylethylene, *trans*-stilbene and triphenylethylene with benzene in the presence of palladium(II) salts. The experimental results are summarized in Table I.
It has become clear that phenyl-substituted ethylene such as diphenylethylene, *trans*-stilbene or triphenylethylene can react with benzene, yielding the corresponding phenyl-substituted ethylenes in both $Pd(OAc)_2$ and $PdCl_2$-NaOAc systems. As is shown in Table I, the yield decreases with the increasing number of the phenyl groups on starting olefin in both systems. This can be attributed to the steric hindrance of phenyl groups. When two systems of palladium(II) salts is compared with respect to the yield, $Pd(OAc)_2$ system is better than $PdCl_2$-NaOAc system, suggesting that even in the latter system, $Pd(OAc)_2$ is formed through the abstraction of Cl^- on palladium(II) by Na^+.

Further, it is of interest to point out that the phenylation reaction takes place step by step in this condition. For example, though 1,1-diphenylethylene

Table I. Reaction of Phenyl-substituted Ethylenes with Benzene

Olefin	Product	Yield, %[a]	
		$Pd(OAc)_2^b$	$PdCl_2^b$-NaOAc
1,1-Diphenylethylene	Triphenylethylene	72	45
trans-Stilbene	Triphenylethylene	28	20
Triphenylethylene	Tetraphenylethylene	13	trace

[a] The yield is based on starting olefin.
[b] An equal mol. equiv. to olefin was used.



has two hydrogen atoms which can be substituted by benzene, only one hydrogen atom suffers aromatic substitution, affording triphenylethylene and no further substituted olefin is formed. Similarly _trans_-stilbene affords triphenylethylene, the mono-substituted one.

The following procedure is representative. In a mixture of 2.88 g (0.016 mole) of 1,1-diphenylethylene,(3) 40 ml of acetic acid and 170 ml of dry benzene, was dissolved 3.50 g (0.016 mole) of palladium(II) acetate. The solution was stirred for 8 hr at reflux temperature. There was an immediate precipitate of palladium metal (sometimes palladium mirror was formed on the wall). The resulting mixture was treated with 10% aq. solution, washed with water and the organic layer was separated, dried over sodium sulfate. After the evaporation of the solvent, the residue was subjected to column chromatography of alumina (140 g). There were obtained 2.95 g (72% yield) of triphenylethylene, mp 67.5-68.5° (lit.(4) mp 67-68°) and 0.33 g of 1,1,4,4-tetraphenylbutadiene.(5) These products exhibited IR and NMR spectra in accordance with their structures.

Further works of this reaction are now proceeding with mechanistic investigations in order to expand possible applications to the synthetic organic chemistry, and details will be described in a full paper.

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