Tetrahedron Letters, Vol.31, No.10, pp 1495-1496, 1990
Printed in Great Britain

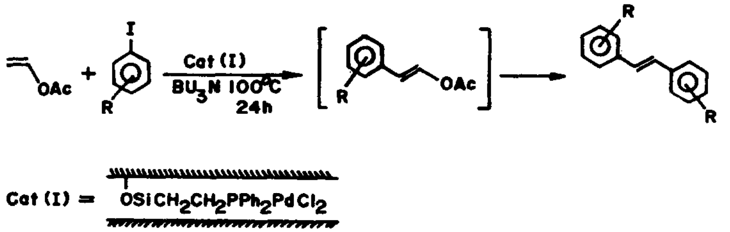
0040-4039/90 $3.00 + .00
Pergamon Press plc

A NOVEL SINGLE POT REACTION FOR SUBSTITUTION AND CROSS-COUPLING OF VINYLACETATE TO TRANS-STILBENES BY INTERLAMELLAR MONTMORILLONITE PALLADIUM CATALYST**

B.M. Choudary* and M. Ravichandra Sarma
Inorganic & Physical Chemistry Division
Indian Institute of Chemical Technology, Hyderabad 500 007, India

Abstract : Synthesis of trans-stilbenes on substitution and cross-coupling of vinylacetate by Interlamellar montmorillonite ethyl silyldiphenylphosphinepalladium(II)chloride catalyst is described.

Heck type arylation of various substituted alkenes leading to monoarylated alkene derivatives have been extensively studied[1]. However, a few reactions involving arylation of vinylacetates to stilbenes with negligible to poor yields are reported. Recent attention has been focussed on the cross-coupling of Alkenylalkoxysilanes[2] by aryl and alkenyl halides and Alkenyl Triflates[3] by derivatives of phosphoric acid with excellent yields. We report in this letter a single pot reaction for substitution and cross-coupling of vinyl acetate forming trans-stilbene in very good yields by interlamellar montmorilloniteethylsilyldiphenylphosphinepalladium(II)chloride catalyst (I)[4] for the first time (Scheme 1).



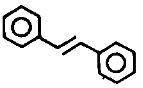
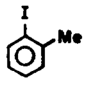
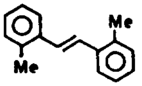
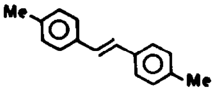
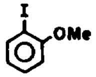
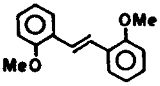
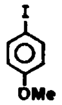
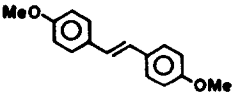
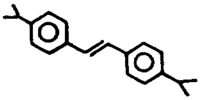
R = o-OMe, p-OMe, o-Me, p-Me & Isopropyl

SCHEME 1

Vinylacetate (25 mmols in excess) was reacted with Iodobenzene (20 mmols) in presence of n-tributylamine (25 mmols) and catalyst (I), 50 mg (0.017 mmols of Pd) at 100°C under nitrogen atmosphere for 24 hrs under vigorous stirring. The work-up was done by neutralising excess base by washing with 5N HCl and the ether extract washed with brine solution which on concentration and recrystallization in ethanol gave trans-stilbene (1.5 g) yielding 85% based on iodobenzene consumed. When this arylation reaction was extended to substituted iodobenzenes excellent yields of symmetrical trans-stilbenes have been obtained as described in Table-1.

** IICT Communication No. 2526

TABLE 1. SUBSTITUTION & CROSS-COUPLING REACTIONS OF VINYLACETATE BY CAT (I)

ENTRY	REACTANT	PRODUCT[a]	ISOLATED YIELD(%)
1			85
2			80
3			83
4			80
5			82
6			81

a: ALL THE PRODUCTS WERE CHARACTERISED BY NMR & MASS

The product analysis of GC/MS for the arylation of vinylacetate indicated that simultaneous formation of trans-stilbene and phenylvinylacetate with the domination of later, which on prolonged reaction all the monoarylated product was cross-coupled with unreacted Iodobenzene to form trans-stilbene. The arylation reaction conducted on methylacrylate/substituted acrylates gave exclusively monoarylated acrylate and no coupling product was observed[5].

The reaction conducted under homogeneous environment under identical reaction conditions catalysed by $Pd(PPh_3)_2Cl_2$ gave negligible yields of trans-stilbene. The reaction provides an evidence for the cross-coupling of phenylvinylacetate into trans-stilbene facilitated by montmorillonite support. The support induced palladium catalysed reaction a novel example, represents a significant achievement in the area of catalysis. In conclusion, this simple and convenient synthesis of trans-stilbene, useful intermediates for 3-arylisoquinolines, protoberberines etc.[6] in a single pot reaction offers an advantageous route.

Acknowledgement : We thank Department of Atomic Energy, India for financial support to (MRS).

References

1. (a) R.F. Heck, "Palladium Reagents in organic synthesis", Academic Press, New York (1985).
   (b) R.A. Abramovitch, D.H.R. Barton and J.P. Finet, Tetrahedron, 44, 3039 (1988).
2. Kohei Tamao, Kenj, Koboyashi & Yoshihiko Ito, Tetrahedron Lett. 30, 6051 (1989).
3. Dennis A. Hat and Jiim Erb, Tetrahedron Lett. 30, 5393 (1989).
4. For synthesis of catalyst see Ref. B.M. Choudary, K. Mukkanti and Y.V. Subba Rao, J. Mol. Cat. 48, 151 (1988).
5. B.M. Choudary, M. Ravichandra Sarma and K. Koteswara Rao (Results communicated).
6. B.J. Brisdon and P. Nair, Tetrahedron, 37, 173 (1981).

(Received in UK 4 January 1990)