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A NOVEL MOLECULAR RECOGNITION IN MONTMORILLONITE IN THE ARYLATION OF ACRYLATES**

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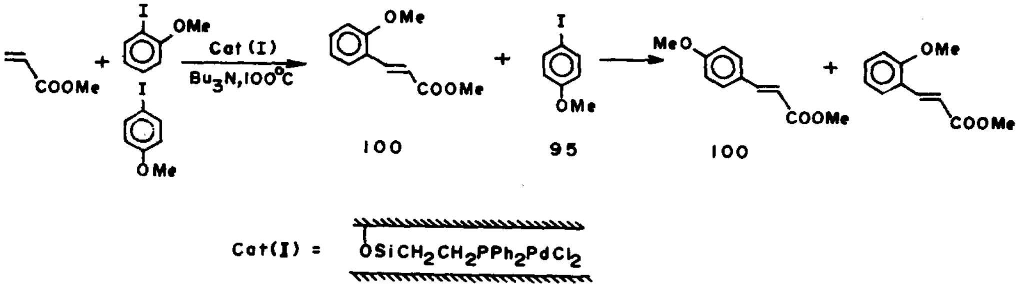
Summary *: A novel sequential and preferential substrate selectivity in arylation of acrylates with iodobenzenes by interlamellar montmorilloniteethylsilyldiphenylphosphinepalladium(II) chloride catalyst is reported for the first time.*

The search and preparation of new materials that can impart molecular recognition reminiscent of enzymatic selectivity is of current interest[1-9]. A recent example of preferential substrate selectivity[2] towards n-octane achieved by palladium-iron system in zeolites in competitive oxidation of cyclohexane and n-octane is comparable to that of enzymic selectivity. But rapid deactivation of the catalyst because of pore filling and destruction of the catalyst for recovery of entrapped product are the major problems encountered in this zeolites. We report here a novel sequential and preferential substrate selectivity in arylation of acrylates with iodobenzenes by interlamellar montmorilloniteethylsilyldiphenylphosphinepalladium(II) chloride catalyst (I)[10] (Pd/P is 1:1) (K10 montmorillonite, a class of smectite clay obtained from Fluka) for the first time (Scheme 1). In addition to this, high activity (566 mol h^{-1} ,mol^{-1})[11]

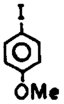
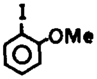
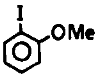
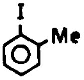
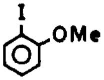
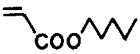
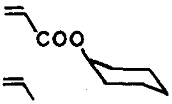
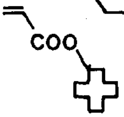


SCHEME-1

** IICT Communication No. : 2526.

TABLE -1

SEQUENTIAL & PREFERENTIAL SUBSTRATE SELECTIVE ARYLATION REACTIONS

Entry	Substrate S_1	Substrate S_2	Relative Rates of S_1 /S_2 in individual reaction	Ratio of S_1 : S_2 in competitive reaction [a]
Methylacrylate with Iodobenzenes				
1			4/1·33	100: <5
2			4/2	100: 16
3			2/1·33	100: <5[b]
4			4/2	100: 20
5			4/1·33	100: 15
6			4/4	100:60
Iodobenzene with acrylates				
7			4/4	100:50
8			4/2	100:40
9			4/1	100: 1[d]
10			4/1[c]	100: 1[d]

a: Ratio is at 100% Selective conversion of S_1 as analysed by GC b: Analysed by NMR c: Rate of reaction retarted and stopped subsequently d: Products of S_2 started after 100% formation of S_1 product.

of the catalyst (**I**) consistant quantitative trans-selectivity, rate and continuity of reaction for number of recycles are the notable features. No such trans-selectivity has been observed in analogous polymer bound and homogeneous catalytic systems[12].

Two sets of competitive arylation reactions (Table-1) were designed and performed using different iodobenzenes (10 mmols each) with methylacrylate (22 mmols) and graded sized acrylates (11 mmols each) with iodobenzene (24 mmols) in presence of tributylamine (25 mmols) and catalyst (**I**) 50 mg (0.017 mmols of Pd) at 100°C under nitrogen atmosphere. Preferential substrate selectivity was observed towards iodobenzene in presence of o,p-iodoanisoles (entry 1,2) or p-iodocumene (entry 6) and iodotoluenes (entry 4,5) in presence of corresponding iodoanisoles. Preferential, sequential and near quantitative discrimination of p-iodoanisole in favour of o-iodoanisole or iodobenzene is an unusual finding in these reactions (entry 1,3), similarly a trend for substrate selectivity which is seen in competitive arylation reaction between methylacrylate and n-pentylacrylate (entry 7) with iodobenzene culminated into absolute selectivity when n-pentylacrylate was replaced with cyclohexyl acrylate (entry 9) or cyclododecyl acrylate (entry 10). All the arylation reactions described in Table-1 conducted in homogeneous environment with palladium phosphine complex, no significant trend towards preferential substrate selectivity was observed.

The unimpressive preferential selectivity towards iodobenzene in presence of p-iodocumene and very impressive selectivity towards iodobenzene and o-iodoanisole in presence of p-iodoanisole which has almost same molecular dimension in space filling as p-iodocumene in arylation reaction indicate that some sort of attractive or repulsive forces from the support hydroxyls or basal oxygens of silicate layers with p-methoxy substituent of the substrate causes the prevention or destabilization of the transition states involved in the process coupled with imposition by restricted space availability. The support interaction also extends to the o-iodoanisole but not as extent as with p-substituted one which is evident in the preferential selectivities.

The successful use of montmorillonite for sequential molecular recognition opens up a new era in catalysis for direct use of mixture of substrates in the reactions, hence avoiding cumbersome process of separation of the mixtures especially of o- and p-isomers before use.

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