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HYDROGENATION OF ALKYNES WITH A PALLADIUM ANCHORED POLYSTYRENE CATALYST

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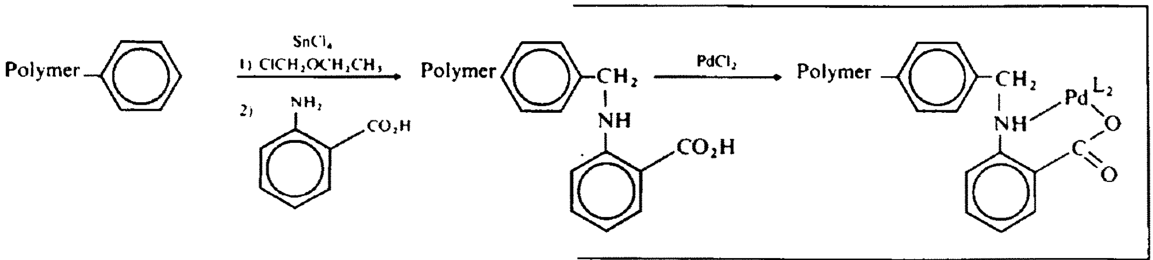
Abstract—Treating chloromethylated polystyrene beads with anthranilic acid and then palladium chloride gives a material capable of catalyzing the cis-hydrogenation of alkynes. Hydrogenation of phenylacetylene (10 mmol) with 0.017 g-atom (based on Pd) of catalyst at room temperature and 30 psig for 7.3 h resulted in 82 % styrene and 14 % ethylbenzene. Methylphenylacetylene was converted to cis-1-phenylpropene (60 %) and n-propylbenzene (17 %). Several other alkynes were also converted to cis alkenes. The catalyst is less selective than the Lindlar catalyst, but is air stable and stores well.

While the hydrogenation of olefins with polymer-bound analoges of homogeneous catalysts has received considerable attention, there are but few reports of alkyne hydrogenation using this type of catalyst.[2] During a recent hydrogenation study of a Pd(II) polymer-bound catalyst it was observed that whereas dienes were readily reduced, alkenes were saturated but slowly.[3] This discriminating property of the Pd(II) catalyst recommended a study of alkyne hydrogenation; we wished to determine if hydrogenation would cease at the alkene stage and whether the addition of hydrogen would be stereoselective. Herein are reported the results of this study.

RESULTS

The support for anchoring the catalyst is somewhat unusual, considering other investigations with polymer-bound catalysts, in that the polystyrene is highly crosslinked. The beads in this study have been Rohm and Haas XAD-4 (>50 % crosslinking with divinylbenzene, exact degree proprietary). The underivatized beads have a very high surface area (725 m^2/g), 35 % of the phenyl groups are at the surface, and the beads are described as macroreticular.[6]

The beads are derivatized by the reaction sequence of chloromethylation, alkylation of anthranilic acid, and coordination of Pd(II). Previous studies have demonstrated that the catalyst is concentrated at the surface of the beads and that certainly the bulk of the palladium is in the 2+ oxidation state.[7]



Using this catalyst the partial hydrogenations of several alkynes have been performed under very mild conditions. Results are summarized in the Table.

DISCUSSION

The data indicate that the conversion of alkynes to cis-alkenes is highly stereoselective. The catalyst demonstrates fair specificity with respect to termination at the alkene stage, though it is not as selective as the Lindlar catalyst. Reaction times vary considerably and it is apparent that the presence of an alcoholic functional group, a reasonably good coordinating group, slows the hydrogenation. Deactivated alkynes, exemplified by dimethylacethylenedicarboxylate, are hydrogenated at a rate comparable to other, non-deactivated alkynes. There was no evidence of dehydration of 4-phenyl-3-butyn-2-ol.

The only other published account of the hydrogenation of several alkynes using a polymer-bound catalyst was in a recent paper by Neckers and associates.[2a] For our catalyst the hydrogenation is more selectively terminated at the olefin stage. Furthermore, there is evidence that the Neckers catalyst may actually be Pd(O). ESCA evidence for our catalyst has established that at least the bulk of the metal remains in the 2+ oxidation state, and recent studies of methyl sorbate hydrogenation revealed that a portion of the catalyst deliberately reduced to Pd(O) gave a significantly different product distribution than that of the Pd(II) catalyst.[8] While this does not unequivocally prove that Pd(O) is not a factor, it does indicate that the status of the palladium is significantly different than in the Neckers catalyst.

While our catalyst is not as selective as the Lindlar catalyst[9] it does have two characteristics which may render it useful for some applications. Unlike the Lindlar catalyst it is air-stable and may be stored indefinitely at room temperature without apparent

Table 1. Hydrogenation of alkynes at 25 and 30 psig

Alkyne (mmol)	Catalyst (g-atom Pd)	Time (h)	Solvent	Products (%)
Phenylacetylene (10)	0.017	7.3	95 % Ethanol	Phenylacetylene (4) Styrene (82) Ethylbenzene (14)
Methylphenylacetylene (4)	0.008	19.6	Ethyl ether	Methylphenylacetylene (23) cis-1-Phenylpropene (60) n-propylbenzene (17)
4-Octyne (27)	0.008	2.4	None	4-Octyne (16) cis-4-Octene (80) Octane (4)
Dimethylacetylene dicarboxylate (5.9)	0.017	18.0	Ethyl ether	Dimethylacetylene-dicarboxylate (17) Dimethylmaleate (84) Dimethylsuccinate (4)
Propargyl alcohol[a](40)	0.34	15.0	None	Propargyl alcohol (5) Allyl alcohol (90) n-Propyl alcohol (5)
4-Phenyl-3-butyn-2-ol (13.6)	0.017	36.0	Ethyl ether	4-Phenyl-3-butyn-2-ol (5) 4-Phenyl-cis-3-buten-2-ol (90) 4-Phenyl-2-butanol (5)
1,7-Octadiyne (38)	0.017	36.0	None	1,7-Octadiyne (60) 1,7-Octadiene (20) Octane (20)

[a] Hydrogenated at 800 psig.

loss of activity. Furthermore, activities from one batch to another are quite similar and correlate most closely with the palladium analysis.

EXPERIMENTAL

Catalyst preparation. The beads were washed prior to chloromethylation, using the scheme described by Frechet.[4] Washing eliminates the problem of bead fragmentation. The beads were chloromethylated for 30 min according to the procedure of Pepper *et al.*[5] Anal: Cl, 1.32 % (0.37 mequiv/g). Anthranilic acid was anchored to the beads by treating 176 g of the chloromethylated beads with 88 g of recrystallized anthranilic acid and refluxing 21 h in 95 % ethanol. The beads were filtered and washed thoroughly with ethanol. Anal: Cl, 0.60 % (0.17 mequiv/g); N, 0.46 % (0.33 mequiv/g). To 18.0 g of the anthranilic acid anchored beads was added 200 ml of acetone, 0.43 g of $PdCl_2$ and 2.0 ml of acetonitrile. The suspension was refluxed under nitrogen for 71 h, then filtered, washed with acetone and air-dried 20 h. Analysis: Pd, 2.05 % (0.19 mequiv/g); N, 0.38 % (0.27 mequiv/g); Cl, 0.71 % (0.20 mequiv/g)

Hydrogenation procedure. Low-pressure hydrogenations were carried out in a standard apparatus (Parr Instrument Co., Model 3911). In a typical run a 300 ml reactor was charged with alkyne and catalyst (and solvent) and the system was selaed, purged three times with hydrogen, then pressurized to 30 psig. All hydrogenations were performed at room temp. Samples were removed periodically through a capillary tube and analyzed for completeness by glc. Propargyl alcohol did not hydrogenate at 30 psig, so it was hydrogenated at 800 psig in an Aminco Shaking Assembly (No. 44-13106).

General. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee, USA. Hydrogenation products were analyzed by GLC (10 % Carbowax, 1/4 in × 6 ft), ^{1}H-NMR, and IR.

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