suggest that this conclusion is rather general.

Acknowledgment. Financial support from the National Science Foundation is gratefully acknowledged (CHE 7907588 and PRM 7919451). J.L.J. spent a 1981–82 sabbatical leave from CSULB in the Chemistry Department, University of California, Irvine, whose kind hospitality and intellectual stimulation were much appreciated.

Registry No. $PhCH[OCH_2C(CH_3)_3]_2$, 56377-78-7; $PhCH(OCH_2CH_3)_2$, 774-48-1; $PhCH(OCH_3)_2$, 1125-88-8; $PhCH(OCH_2CH_2OCH_3)_2$, 71412-83-4; $PhCH(OCH_2CH_2Cl)_2$, 59606-97-2; $PhCH(OCH_2CF_3)_2$, 87088-60-6; $PhCH(OCH_2CCl_3)_2$, 37150-43-9.

Palladium/Polystyrene Catalysts

David E. Bergbreiter,* Bushi Chen,[1] and Thomas J. Lynch

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received February 1, 1983

The reaction of reactive alkali metal organometallic derivatives of divinylbenzene-cross-linked polystyrene with solutions of dichloro(1,5-cyclooctadiene)palladium(II) to form palladium/polystyrene catalysts is described. Organometallic polymers used in these reactions include polystyryllithium, polystyrylbenzyllithium, polystyrylphenyl(trimethylsilyl)methyllithium and polystyrene-bound sodium anthracene. The palladium/polystyrene catalysts formed in these reactions were characterized by ESCA and electron microscopy, and their activity as hydrogenation catalysts was examined in various solvents and under various conditions of catalyst pretreatment. Comparisons of the catalytic activity of these catalysts to commercial Pd/C in the hydrogenation of various substrates are also made. Novel catalytic activity observed for these palladium/polystyrene catalysts includes some activity as decarbonylation catalysts in reactions with simple alkyl and aryl aldehydes and their use in place of tetrakis(triphenylphosphine)palladium(0) as a catalyst for the formation of tertiary allylamines from allyl esters and secondary amines. The interaction of functional groups such as organolithium and carboxylic acid groups attached to the polystyrene support with the active centers of the hydrogenation catalysts was also demonstrated by their effect on the activity of these hydrogenation catalysts.

Heterogeneous catalysts are often prepared as dispersions of metal crystallites on high surface area inorganic supports by impregnating the support with a solution of a metal salt, removing volatiles, and reducing the oxidized metal to elemental metal.[2] The resulting catalysts are useful in a wide variety of reactions in organic chemistry.[3] In order to avoid the relatively harsh conditions and metal agglomeration often produced by these procedures[4] and to explore the possibility of preparing more modifiable, more reactive, and/or more selective heterogeneous catalysts we have studied the use of reactive organometallic polymers and their reaction with palladium(II) salts as a route to palladium(0) catalysts. Our results described in this paper show that palladium/polystyrene catalysts can be prepared under mild conditions in this manner and that the resulting catalysts compare favorably with other conventional heterogeneous palladium catalysts.

The use of functionalized organic polymers to support catalysts is a topic of current interest especially as it concerns the support of otherwise homogeneous transition-metal complexes.[5] Such studies have included nearly every transition metal and have led to polymer-based catalysts for many different sorts of reactions. It is therefore not surprising that palladium catalysts, which are widely useful in organic chemistry,[6] have also received attention as candidates for attachment on organic polymers. Indeed, palladium species such as phosphine-ligated palladium(0) and phosphine-ligated palladium(II) complexes,[7] bipyridyl-ligated palladium(II),[8] and ionically bound palladium(II)[9] have all been successfully attached to functionalized divinylbenzene- (DVB) cross-linked polystyrene to give useful catalysts. Other novel heterogeneous palladium catalysts have also been prepared from potassium–graphite[10] or as colloidal dispersions in various types of organic polymer matrices.[11] This paper describes the preparation of highly dispersed palladium(0) catalysts by means of initial attachment or reduction of a homogeneous palladium(II) complex using reactive organoalkali metal derivatives of divinylbenzene-cross-linked polystyrene. As is described in detail below, the palladium/polystyrene species resulting from these procedures consist of small palladium(0) crystallites (ca. 20–40 Å in diameter) dispersed throughout DVB-cross-linked polystyrene beads

---

[1] A visiting scholar at Texas A&M from the Institute of Chemistry, Chinese Academy of Sciences, Beijing, People's Republic of China.

(2) Satterfield, C. N. "Heterogeneous Catalysis in Practice"; McGraw-Hill: New York, 1980.

(3) (a) Freifelder, M. "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary"; Wiley-Interscience: New York, 1978. (b) Rylander, P. N. "Organic Syntheses with Noble Metal Catalysts"; Academic Press: New York, 1973.

(4) Ruckenstein, E.; Dadyburjor, D. B. *J. Catal.* **1977**, *48*, 73–86. Jarrell, M. S.; Gates, B. C.; Nicholsen, E. D. *J. Am. Chem. Soc.* **1978**, *100*, 5727–5732.

(5) (a) Minkiewicz, J. V.; Milstein, D.; Lieto, J.; Gates, B. C.; Albright, R. L. *ACS Symp. Ser.* **1982**, *No. 192*, 9–29. (b) Ciardelli, F.; Braca, G.; Carlini, C.: Sbrana, G.; Valentini, G. *J. Mol. Catal.* **1982**, *14*, 1–17. (c) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109–148. (d) Whitehurst, D. D. *CHEMTECH* **1980**, 44–49.

(6) (a) Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. II. (b) Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer Verlag: Berlin, 1980. (c) Trost, B. M. *Pure Appl. Chem.* **1981**, *53*, 2357–2370.

(7) (a) Bruner, H.; Bailar, Jr., J. C. *Inorg. Chem.* **1973**, *12*, 1465–1469. (b) Pittman, C. U., Jr.; Ng, Q. *J. Organomet. Chem.* **1978**, *153*, 85–97. (c) King, R. B.; Hanes, R. M. *J. Org. Chem.* **1979**, *44*, 1092–1094. (d) Kaneda, K.; Kurosaki, H.; Terasawa, M.; Imanaka, T.; Teranishi, S. *Ibid.* **1981**, *46*, 2356–2362. (e) Trost, B. M.; Warner, R. W. *J. Am. Chem. Soc. 1982*, *104*, 6112–6114.

(8) (a) Card, R. J.; Neckers, D. C. *Inorg. Chem.* **1978**, *17*, 2345–2349. (b) Card, R. J.; Liesner, C. E.; Neckers, D. C. *J. Org. Chem.* **1979**, *44*, 1095–1098. (c) Drago, R. S.; Nyberg, E. D.; El A'mma, A. G. *Inorg. Chem.* **1981**, *20*, 2461–2466.

(9) Holy, N. L.; Shelton, S. R. *Tetrahedron* **1981**, *37*, 25–26.

(10) Savoia, D.; Thrombini, C.; Umani-Ronchi, A.; Verardo, G. *J. Chem. Soc., Chem. Commun.* **1981**, 540–541.

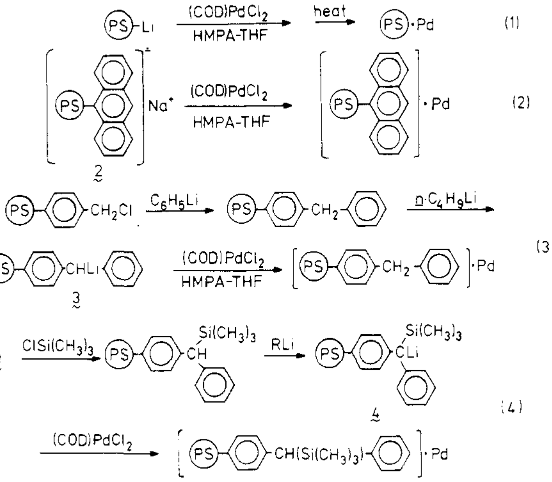
(11) (a) Hirai, H. *J. Macromol. Sci., Chem.* **1979**, *A13*, 633–649. (b) Coleman, D. R.; Royer, G. P. *J. Org. Chem.* **1980**, *45*, 2268–2269.

0022-3263/83/1948-4179$01.50/0 © 1983 American Chemical Society

and have useful and interesting properties in a variety of reactions.

Results and Discussion

We have used several different types of reactive organometallic derivatives of DVB-cross-linked polystyrene to prepare these palladium/polystyrene catalysts. Equations 1–4 describe these various procedures. Polystyryllithium and polystyrene-bound sodium anthracene used in eq 1 and 2, respectively, have both been described previously in the litereature.[12,13] Lithiated benzylpolystyrene (**3**) was prepared by treating chloromethylated polystyrene (1% divinylbenzene cross-linked) with phenyllithium to yield benzylpolystyrene, which was then in turn deprotonated with either *n*-butyllithium or phenyllithium to give **3**. [(Polystyrylphenyl)phenyl(trimethylsilyl)methyl]lithium (**4**) was prepared by reaction of **3** with chlorotrimethylsilane to form polystyrylphenyl(trimethylsilyl)methane which could then be deprotonated by an organolithium reagent to yield **4**. The polymeric lithium reagents **3** and **4** were highly colored red and purplish beads, respectively, and were stable for long periods of time as suspensions in ethereal solvents in the absence of air and moisture. These latter two organolithium polymeric reagents could be prepared with up to 0.87 and 0.75 mequiv of organolithium reagent per g of polymer, respectively, based on the amount of *n*-butyllithium consumed in forming these reagents or on an acid–base titration of the lithiated polymers.



Transformation of each of these reactive derivatives of polystyrene into palladium/polystyrene catalysts was accomplished by allowing the reactive polymers to react with either a solution or suspension of (1,5-cyclooctadienyl)palladium dichloride, (COD)PdCl$_2$, in tetrahydrofuran–hexamethylphosphoramide (THF–HMPA) or THF, respectively. The products of these reactions were always a greyish polymer when the reactions were carried out at room temperature. In the case of the reactions shown in eq 3, the initially formed product could be isolated as a light yellow polymer if the addition of the palladium(II) complex to the lithiated polystyrene was carried out at −78 °C. In all cases the resulting palladium/polystyrene beads were subjected to an extraction process with THF in a Soxhlet apparatus (temperature of ca. 65 °C). Palladium/polystyrene catalysts prepared in room temperature reactions showed only modest decreases in catalytic activity after 10 days of such an extraction process and were typically extracted for 5 days (cf. Table I) to remove non-polymer-bound species. Yellow palladium/polystyrene beads prepared at −78 °C according to eq 3 were typically extracted for 5 days as well. However, in the latter case, thermolysis and/or agglomerization of palladium species evidently occurred during the extraction process, and the bead's color changed from yellow to grey. Accompanying this color change was a significant increase in catalytic activity and observation by electron microscopy of the formation of palladium crystallites. Further extraction beyond 5 days produced no significant change in catalytic activity for these catalysts, although electron microscopy did show a slight increase in the size of the palladium crystallites (vide infra). The palladium catalysts prepared according to eq 1–3 were each characterized by electron microscopy (cf. data in Table II and pictures available as Figure 1 in Supplementary Material). Of the three types of palladium/polystyrene catalysts, PS–b–Pd (b = benzyl) was found to be the most uniform in terms of the size of its palladium crystallites (25 ± 5 Å), and it and PS–Pd were studied the most thoroughly as hydrogenation catalysts.

Table I. Changes in Relative Activity of Various Palladium/Polystyrene Hydrogenation Catalysts with Varying Extraction Treatments[a, b]

extraction time, days	PS-Pd	PS-anthracene-Pd[c]	PS-b-Pd[c]	PS-b-Pd[d]
0	0.38	0.07	0.10	1.00
1	0.84	0.33	0.52	*e*
2	1.00	0.71	0.62	*e*
3	0.89	0.90	0.72	0.78
4	*e*	1.00	0.84	*e*
5	0.84	*e*	1.00	0.93
8	*e*	*e*	0.92	0.78
10	0.56	0.83	0.86	0.85

[a] Relative initial rates for 1-octene hydrogenation at 25 °C and 1 atm pressure. The maximum rate for each catalyst was set equal to 1.00 in this table. Absolute values for these rates are given in Table II. [b] Extractions were carried out at ca. 65 °C using THF in a Soxhlet apparatus. [c] Catalyst prepared at −78 °C. [d] Catalyst prepared at room temperature. [e] Not measured.

The PS–Pd catalyst consisted primarily of palladium crystallites of similar size (25 ± 5 Å) but did contain some larger (ca. 70 Å) crystallites as well. the PS–anthracene–Pd catalyst was atypical in that all of the palladium on these polystyrene beads was deposited in the form of relatively large (60 Å and larger) crystallites at the edges of the beads even when eq 2 was carried out at −78 °C. The percentage loading of palladium on each of these palladium/polystyrene catalysts is given in Table II. Some changes in the palladium crystallite size of these palladium/polystyrene catalysts were noted by electron microscopy when these catalysts were heated for longer periods of time, but the resultant changes in size of the palladium crystallites were relatively small in the case of PS–Pd and PS–b–Pd (Table II). The activities of these catalysts were quite unform through repeated extractions or hydrogenation reactions (Tables I and II).

ESCA spectroscopy has also been used to characterize these palladium/polystyrene catalysts. The results of these experiments on PS–Pd and PS–b–Pd indicated $Pd_{3d_{3/2}}$ and $Pd_{3d_{5/2}}$ binding energies of 342.4 and 337.1 eV and 341.7 and 336.1 eV, respectively, which are more characteristic of palladium(0) (341.8 and 336.1 eV measured with Pd/C) than palladium(II) (343.8 and 338.5 eV measured with (COD)PdCl$_2$).[14]

---

(12) Burlitch, J. M.; Winterton, R. C. *J. Organomet. Chem.* **1978**, *159*, 299–316.

(13) Bergbreiter, D. E.; Killough, J. M. *J. Chem. Soc. Chem. Commun.* **1980**, 319–320.

Other palladium complexes can also be used in place of (COD)$PdCl_2$ to form palladium/polystyrene catalysts. For example, palladium(II) acetate, dichlorobis(tri-*n*-butylphosphine)palladium(II), dichloro(norbornadiene)palladium(II), and dichlorobis(triphenylphosphine)palladium(II) have all been used in reactions with lithiated polystyrenes to form, after extraction for 1–5 days at 65 °C with tetrahydrofuran, palladium/polystyrene catalysts whose activity is essentially the same as the palladium/polystyrene catalysts derived from the procedures shown in eq 1–4 with (COD)$PdCl_2$ as the palladium precursor. Although the intermediates in the synthesis of these palladium/polystyrene catalysts were not characterized, analogies with homogeneous palladium(II) chemistry suggest that σ-bonded polystyrylpalladium complexes would form initially. Subsequent thermolysis of these organopalladium species on workup or during the extraction process would form palladium metal which could then diffuse in the polymer matrix to eventually form the observed palladium crystallites. decomposition of arylpalladium complexes or reduction of palladium(II) salts by alkali metal aromatic radical anions are both precedented reactions leading to palladium metal.[15] The cyclooctadiene complex of polystyrylpalladium(II) is likely to be especially thermally unstable based on literature attempts to prepare diene complexes of diphenylpalladium(II).[16] However, we have not determined at what stage cyclooctadiene is lost in the transformations shown overall in eq 1–4.

Catalytic Reactions Using Palladium/Polystyrene. The palladium/polystyrene catalysts prepared above were all active as alkene hydrogenation catalysts as expected. Table II compares each of these catalysts to commerical Pd/C catalysts in hydrogenation reactions of alkenes and alkynes. Of these polystyrene-supported catalysts, PS–anthracene–Pd was the least active and was not studied further. As was discussed above, palladium in this catalyst was the most aggregated and least uniform in its distribution in the polymer matrix. The other palladium/polystyrene catalysts, PS–Pd (eq 1), PS–b–Pd (eq 3), and PS–Sib–Pd (eq 4), were more active. PS–Sib–Pd and PS–b–Pd were generally comparable in activity in the hydrogenation reactions studied. Both PS–b–Pd and PS–Sib–Pd were comparable in activity to 10% Pd/C.

All of the hydrogenation reactins described in this paper were performed at 25 ± 0.2 °C and at atmospheric pressure. In a typical procedure, the apparatus containing the catalyst was evacuated and flushed with hydrogen four times and solvent was then added through a septum-capped sidearm. The reaction was then initiated by adding the substrate to the heterogeneous reaction mixture and stirring vigorously with a magnetic stirring bar. The hydrogenation rate was determined by observation of the changes in fluid level of a gas buret containing hydrogen.

The rates of heterogeneous reactions like those described here can be limited by both the intrinsic rate of the chemical reaction of interest or by physical phenomena such as diffusion of reactants to the catalyst surface. In some cases, reactor design or reaction conditions can determine which of these situations exist by facilitation of or inhibition of diffusion of the reactants to the active catalyst sites. We have endeavored to determine the relative importance of these various factors to the hydrogenation rates measured in Table II using the following experiments.

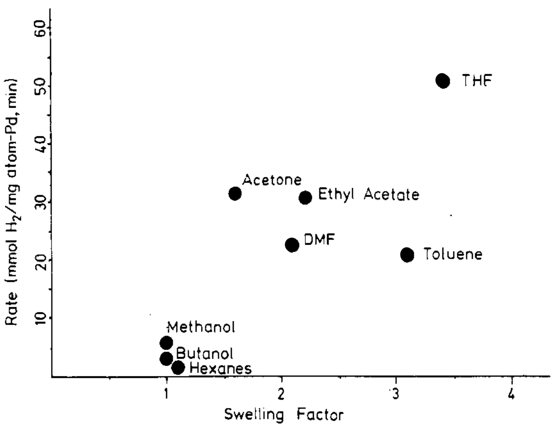


Figure 2. Relationship between hydrogenation rate for 1-octene hydrogenation in different solvents at 25 °C and at atmospheric pressure and the swelling factor for PS–b–Pd in the various solvents (defined as the volume of the catalyst beads after 4 h swelling in the presence of the indicated solvent divided by the volume of the catalyst beads before the addition of solvent).

First, the amount of the catalyst was doubled in some hydrogenation reactions of 1-octene using PS–Pd catalysis. As expected for a hydrogen-rich system, the hydrogenation rate doubled. This result suggests that the reaction is not limited by hydrogen diffusion into the solvent. Second, a vibromixer was used in place of a magnetic stirrer to provide agitation of the reaction mixture. The hydrogenation rates obtained with the vibromixer doubled with PS–anthracene–Pd and increased 40% with the 5% Pd/C catalyst relative to the rates measured using magnetic stirring. This suggests that diffusion of reactants from solution to the heterogeneous catalyst sites partly determines the observed rates. The rates in the following discussions and in Table II were all collected under identical conditions (see Experimental Section) so that the differences in rates observed primarily reflect the differences in activities of the particular polystyrene-based catalysts rather than the conditions under which the rates were determined.

The choice of solvent for these hydrogenation reactions is important for several reasons. First, hydrogenation reactions generally proceed best in more polar solvents.[17] However, since these palladium/polystyrene catalysts are dispersed on lightly DVB-cross-linked (1–3%) polymers, swelling of the polymer is an even more important criterion.[18] Figure 2 illustrates this for the PS–b–Pd catalyzed hydrogenation of 1-octene. Analogous effects were seen in studies using PS–Pd catalysts. Based on these studies, it is apparent that moderately polar solvents such as THF and ethyl acetate that can also swell the catalyst beads are best for this reaction. Less polar solvents such as toluene which are good swelling solvents for these polymers are reasonably good. Poor swelling solvents such as hexane or methanol are not useful regardless of their polarity. Our subsequent studies have used THF whenever possible as the solvent for reactions using these catalysts.

These palladium/polystyrene catalysts have a shelf life of over 1 year and can be reused repeatedly. After 75

---

(14) Two sets of peaks or broad peaks would have been expected if both palladium(II) and palladium(0) were present in these catalysts. Cf.: Duch, M. W. In "Catalysis in Organic Syntheses"; W. H. Jones, Ed., Academic Press: New York, 1980; pp 133–153.

(15) Maitlis, P. M.; Russell, M. J. H. In "Comprehensive Organometallic Chemistry"; Wilkinson, G.; Stone, F. G. A.; Abel, E. W. Eds.; Pergamon Press: Elmsford, NY, 1982, Vol. 6, pp 243–350.

(16) Calvin, G.; Coates, G. E. *J. Chem. Soc.* **1960**, 2008–2014. Rausch, M. D.; Tibbetts, F. E. *J. Organomet. Chem.* **1970**, *21*, 487–494.

(17) Cerveny, L.; Ruzicka, V. *Adv. Catal.* **1981**, *30*, 335–377.

(18) Swelling profoundly affects reactions using DVB-crosslinked polystyrene reagents that have <2% cross-linking. Cf.: Birr, C. "Aspects of the Merrifield Peptide Syntheses"; Springer-Verlag: Berlin, 1978.

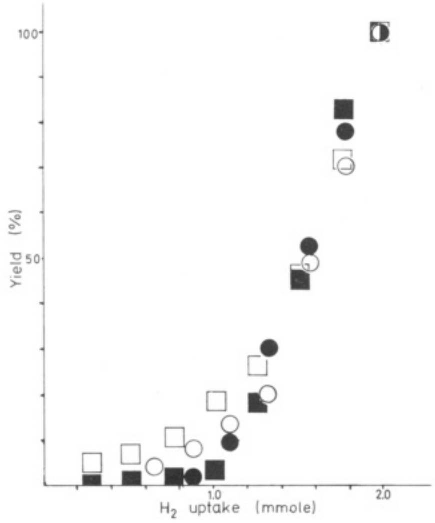


Figure 3. Comparison of PS–b–Pd and 1% Pd/C catalysts in hydrogenation of alkynes plotted as the yield of the fully hydrogenated alkyne (ethylbenzene or hexane) vs. the hydrogen uptake during the reaction. Hydrogenation of phenylacetylene by 1% Pd/C (□); hydrogenation of phenylacetylene by PS–b–Pd (■); hydrogenation of 3-hexyne by 1% Pd/C (○); and hydrogenation of 3-hexyne by PS–b–Pd (●). Catalyst/substrate ratios were 500:1 in all cases.

cycles of 1-octene hydrogenation, catalyst recovery, and catalyst drying, PS–b–Pd still had 50% of its original activity. At this point, the PS–b–Pd had a turnover number (mmol of 1-octene hydrogenated/mmol of palladium) exceeding 40 000. In a single batch reaction PS–Pd had a similarly high turnover number of 14 000 for a styrene hydrogenation reaction.

The selectivity of a heterogeneous catalyst is a useful way to evaluate a catalyst's reactivity and utility and to compare it to existing catalysts. In order to do this with these palladium/polystyrene catalysts, we have briefly examined the utility of these catalysts for the selective hydrogenation of alkynes to alkenes. These studies show that PS–Pd and PS–b–Pd are roughly comparable to several other recently reported heterogeneous palladium catalysts for selective alkyne hydrogenation with selectivities (defined as 100[% alkene]/[% alkene + % alkyne]) of 92% and 85%, respectively. The selectivity of these palladium/polystyrene catalysts derived from eq 3 is further illustrated by the data of Figure 3 in which yield of ethylbenzene or hexane is plotted vs. the uptake of hydrogen in hydrogenations of phenylacetylene or 3-hexyne by PS–b–Pd or 1% Pd/C. In both cases, there is a sharper break in the curve showing the yield of alkane with PS–b–Pd catalysis which corresponds to a higher selectivity with this palladium/polystyrene catalyst. These palladium/polystyrene catalysts are, however, apparently not as selective as other highly dispersed palladium(0) catalysts such as palladium/silica for the selective hydrogenation of an alkyne to an alkene.[19] As was true in several other reports of alkyne hydrogenation,[8b,20] these PS–Pd, PS–b–Pd, and PS–Sib–Pd catalysts were slower at hydrogenating some alkynes than the corresponding alkene while maintaining some selectivity (cf. $C_6H_5C_5H$ in Table II).

The initial rates of catalyzed hydrogenations of terminal alkenes listed in Table II often decreased after some of the alkene had been reduced. This was due to isomerization of the terminal alkene into an internal alkene that was, in turn, hydrogenated at a slower rate. This isomerization and slower hydrogenation of an internal alkene are typical of other palladium catalysts.[3,8] In the case of other catalysts such a 1% or 5% Pd/C, this isomerization is actually more pronounced. As a result, a polystyrene-supported catalysts such as PS–b–Pd is actually a measurably better catalyst for 1-hexene hydrogenation when one considers hydrogenation rates after 25% of the reaction rather than just initial rates as was done in Table II. Figure 4 illustrates this by providing a direct comparison of the efficacy of PS–b–Pd and 1% Pd/C in 1-hexene hydrogenation. The rate decrease seen in the curves for 1-hexene hydrogenation using 1% Pd/C catalysis are the result of isomerization of 1-hexene to 2- and 3-hexenes which hydrogenate at slower rates. Although isomerization can and does occur with the palladium/polystyrene catalysts, higher sustainable hydrogenation rates can be achieved with palladium/polystyrene catalysts in hydrogenation of terminal alkenes at comparable substrate/palladium levels than can be achieved with 1% Pd/C as is shown by the data in this figure.

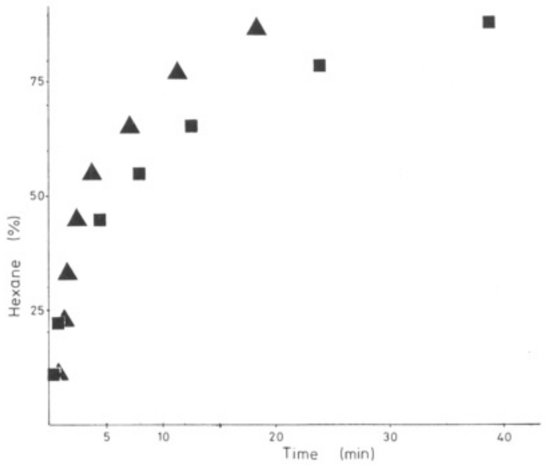
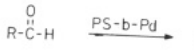


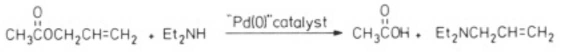
Figure 4. Comparison of hydrogenation rates through the course of complete hydrogenation of 1-hexene by 1% Pd/C (■) and PS–b–Pd (▲) showing the more rapid decrease in rate of hexene hydrogenation seen with 1% Pd/C as a hydrogenation catalyst as the reaction proceeded. Catalyst/substrate ratios were 500:1 in all cases.

Palladium is known to catalyze a variety of reactions other than hydrogenation of alkenes and alkynes and isomerization.[6] In the course of our studies we have therefore attempted a cursory survey of the possible utility of these palladium/polystyrene catalysts as alternatives to existing catalysts for some of these reactions. The results of these studies are discussed further below.

Decarbonylation of an aldehyde to yield a hydrocarbon is a synthetically useful reaction that can be accomplished with a number of transition-metal catalysts.[3b,21] We have found that these palladium/polystyrene catalysts are also useful in this transformation and that these polystyrene-supported catalysts are more active than Pd/C catalysts in carrying out this process (eq 5).



$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}H \xrightarrow{PS\text{-}b\text{-}Pd} R\text{-}H \qquad (5)$$



$$CH_3\overset{O}{\overset{\|}{C}}OCH_2CH{=}CH_2 + Et_2NH \xrightarrow{\text{"Pd(0)" catalyst}} CH_3\overset{O}{\overset{\|}{C}}OH + Et_2NCH_2CH{=}CH_2 \qquad (6)$$

---

[19] Carturan, G.; Gottardi, V. *J. Mol. Catal.* **1978**, *4*, 349–359.

[20] Carturan, G.; Facchin, G.; Cocco, G.; Enzo, S.; Navazio, G. *J. Catal.* **1982**, *76* 405–417.

[21] Hawthorne, J. O.; Wilt, M. H. *J. Org. Chem.* **1960**, *25*, 2215–2216.

Modest (77%, 60 h) yields of simple hydrocarbons such as undecane were obtained from aliphatic aldehydes such as dodecanal while no undecane was obtained under similar conditions using 1% Pd/C as a catalyst. Aryl aldehydes were decarbonylated with both catalysts, with the yields depending on the type of substituents on the aromatic aldehyde. In general PS–b–Pd catalyzed decarbonylations were faster and proceeded in higher yield than similar 1% Pd/C catalyzed reactions (Table III in the supplementary material provides some specific comparisons). Aldehydes having other functional groups such as 2-hexenal underwent reactions other than decarbonylation. Unlike the hydrogenation reactions discussed above, attempts to recycle these palladium catalysts were unsuccessful in the case of the dodecanal decarbonylation. When additional aldehyde was added to spent catalyst no undecane was formed. Instead a high-boiling compound was observed by GC. Analysis by GC–MS indicated that this product was the aldol product of this aldehyde (*m*/*e* 350). Thus, while PS–b–Pd is able to successfully decarbonylate several types of aldehydes and does so faster and with higher yields than Pd/C, other aldehydes or recycling the original catalyst results in formation of byproducts other than the desired decarbonylation products. In addition, the reactions were rather slow even with the PS–b–Pd catalyst.

Nucleophilic substitution of allylic esters and ethers is another common reaction catalyzed by palladium species, usually in homogeneous systems with tetrakis(triphenylphosphine)palladium(0) (**5**) catalysis (eq 6).[6] Since the palladium/polystyrene catalysts we have described in this paper consist of relatively highly dispersed palladium(0), we have examined their applicability to this type of allyl transfer reaction. The results of these initial studies are listed in Table IV and show that PS–Sib–Pd is an effective catalyst for formation of tertiary allylamines from allyl esters and allyl ethers and secondary amines. Although 1% Pd/C can be used in some cases to carry out similar transformations, the yields are less with 1% Pd/C and the reaction times are substantially longer. While other heterogeneous palladium catalysts have been reported which can function in place of homogeneous catalysts like **5**,[8] such reports have most commonly used polymer-bound phospine complexes of palladium(0) rather than palladium(0) deposited on some support.[22] Not surprisingly, homogeneous palladium(0) catalysts known to be effective as allylic substitution catalysts are much more effective in this reaction than palladium/polystyrene. For example, tetrakis(triphenylphosphine)palladium is approximately 5000 times more active than palladium/polystyrene under comparable conditions. In large part this reflects the fact that all of the palladium atoms in the homogeneous catalyst are active while a heterogeneous palladium crystallite can only have a fraction of its palladium atoms accessible to homogeneous reagents. In spite of the considerable difference in rates seen for this heterogeneous palladium/polystyrene catalyst and $((C_6H_5)_3P)_4Pd$, the durability, ease of handing, and experimental simplicity achieved with the heterogeneous catalysts make them potentially useful in such reactions. The heterogeneous catalysts have been recycled up to ten times with no decrease in activity and typically are stored in air (the phosphine ligated homogeneous catalyst is, in contrast, subject to ready air oxidation). The heterogeneous catalysts do, however, require elevated temperature (65 °C) and longer reaction times to compensate for their decreased activity.

These allyl transfer reactions catalyzed by palladium/polystyrene appear to be quite general reactions. Other secondary amines used successfully with allyl acetate include allylphenylamine, piperidine, and *N*-methylaniline. Primary amines such as aniline undergo competitive reaction at the acetoxy carbonyl carbon leading to allyl alcohol and acetanilide in addition to disubstitution (formation of diallylphenylamine in addition to the monosubstitution product, allylphenylamine). Primary amines are thus not useful nucleophiles in this reaction. Other nucleophiles have also been examined. Acetylacetone, diethyl malonate, and ethyl acetoacetate also undergo palladium/polystyrene-catalyzed substitution on allyl acetate. However, these carbon nucleophiles appear to be much less reactive in these palladium/polystyrene-catalyzed reactions and give conversions of only 30% in 2 days at 65 °C in THF. No nucleophilic substitution is seen with carbon nucleophiles and 1% Pd/C. Further studies are presently under way to determine the mechanism of these reactions and to increase their synthetic utility.

A unique advantage of using an organic polymer like polystyrene to support these palladium(0) catalysts is that we can potentially study a variety of unusual support–catalyst interactions. DVB-cross-linked polystyrene of the type used in this work is a flexible polymer that is known to permit various sites on the polymer matrix to interact through conformational changes in the polymer backbone.[23] This phenomenon and the ability to use a wide variety of organic reactions to functionalize the polystyrene backbone of these palladium/polystyrene catalysts mean that very different types of support–catalyst interactions can be studied. This is shown by the data in Table V (available as supplementary material), which shows that functional groups elsewhere on the polystyrene evidently can interact with the active catalyst sites. In the examples studied, the effects of carboxylic acid groups, organolithium reagents, and alkali metal aromatic radical anions have all been surveyed. Hydrogenation rates were lower in every case when functionalized polystyrenes were used. In cases where the other functional group was an organometallic reagent, we were able to successfully restore the catalyst's original activity by quenching the organometallic species with methanol.

In summary, the reaction of lithiated DVB-cross-linked polystyrenes with soluble palladium(II) salts is a viable way to prepare heterogeneous palladium catalysts dispersed in a polystyrene matrix. The catalysts prepared in this fashion have useful activity in a variety of reactions and provide further opportunities to study novel support–catalyst interactions.

Experimental Section

General Methods. The macroporous polystyrene beads used to prepare lithiated polystyrene in this study were 3% DVB-cross-linked, 20–50 mesh, and obtainable from Aldrich Chemical Co. 1% DVB-cross-linked chloromethylated polystyrene (Merrifield's resin) was obtained from Sigma Chemical Co. Ethereal and hydrocarbon solvents were distilled from suspensions or solutions of sodium benzophenone. Tetramethylethylenediamine (TMEDA) was dried by first refluxing it over calcium hydride and then distilling it. Reagent grade alkynes and alkenes were used as received. Purification of alkenes or alkynes by column chromatography or distillation before use did not result in any changes in hydrogenation rates. Palladium on carbon catalysts were obtained from Oxy-Catalysts, Inc., West Chester, PA, and

---

[22] Heterogeneous but reactive forms of palladium(0) whose reactivity is similar to $((C_6H_5)_3P)_4Pd$ are known. Cf.: Savoia, D.; Trombini, C.; Umani-Ronchi, A.; Verardo, G. *J. Chem. Soc., Chem. Commun.* 1981, 541–542 and references therein.

[23] For a discussion of site–site interactions in various polystyrenes cf.: Chang, Y. H.; Ford, W. T. *J. Org. Chem.* 1981, *46*, 5364–5371.

Table II. Comparative Rates of Hydrogenation of Alkenes and Alkynes Using Various Heterogeneous Palladium Catalysts[a]

	rate,[b] mmol H_2/mmol Pd, min				
substrate	1% Pd/C	PS-Pd[c]	PS-b-Pd[d]	PS-Sib-Pd[e]	PS-anthracene-Pd[f]
1-octene	79.6	48.7	62.9	79.1	2.4
cyclohexene	44.5	6.7	41.6	45.1	*g*
cyclooctene	4.8	0.7	1.2	*g*	*g*
2-methyl-2-butene	10.7	0.8	3.9	*g*	*g*
mesityl oxide	28.5	4.2	8.0	*g*	*g*
phenylacetylene	66.6 (112.5)[h]	50.7	76.7 (83.3)[h]	68.2 (161.9)[h]	*g*
diphenylacetylene	161.9 (67.2)[h]	105 (59.0)[h]	83.8 (38.3)[h]	146.9 (81.0)[h]	*g*
1-octyne	95.2	47.5	64.8	101.8	

[a] Hydrogenation rates were measured for reactions run at 25 ± 0.2 °C at 1 atm in 10 mL of THF on ca. 2 mmol substrate using ca. 5×10^{-3} mmol of Pd in the form of the indicated catalyst. [b] Rates reported are initial rates measured within the first 5 min of the reaction. In some cases isomerization or formation of alkene (from an alkyne) led to a much slower rate during the reaction. [c] Catalyst prepared according to eq 1 containing 1.3% Pd and palladium crystallites of ca. 25 ± 5 Å diameter on crushed polystyrene beads. Heating this catalyst for 24 h at 120 °C decreased its activity as a hydrogenation catalyst for 1-octene by 40% and increased the size of the palladium crystallites to ca. 30 ± 5 Å. [d] Catalyst prepared according to eq 3 containing 1.5% Pd and palladium crystallites of ca. 25 ± 5 Å diameter. After 10 days of extraction with THF, the palladium crystallites were ca. 33 ± 5 Å in diameter and the hydrogenation rate for 1-octene decreased by 14%. [e] Catalyst prepared according to eq 4 containing 0.5% Pd. [f] Catalyst prepared according to eq 2 containing 6.1% Pd and palladium crystallites of ca. 90 Å diameter. [g] This rate was not measured. [h] This rate is that measured after 1 equiv of H_2 had been consumed.

Table IV. Catalytic Formation of Allyl Amines Using Heterogeneous Palladium(0) Catalysts[a]

starting materials						1% Pd/C		PS-Sib-Pd	
allyl compd	amine	product	solvent	temp, °C	substrate/ palladium, mol/mol	time, h	yield, %	time, h	yield, %[b]
$CH_2{=}CHCH_2OCOCH_3$	$HN(C_2H_5)_2$	$CH_2{=}CHCH_2N(C_2H_5)_2$	neat	65	2000	50	2.0	50	92.0
$CH_2{=}CHCH_2OCOCH_3$	$HN(C_2H_5)_2$	$CH_2{=}CHCH_2N(C_2H_5)_2$	$CH_3C_6H_5$	65	100	24	23.8	14	84.0
$CH_2{=}CHCH_2OCOCH_3$	$H\overline{N(CH_2)_4CH}_2$	$CH_2{=}CHCH_2\overline{N(CH_2)_4CH}_2$	neat	80	2000	10	33.7	5	72.6
$CH_2{=}CHCH_2OCOCH_3$	$HN(CH_3)C_6H_5$	$CH_2{=}CHCH_2\overline{N(CH_3)C}_6H_5$	neat	80	2000	24	3.6	16	57.0
$CH_2{=}CHCH_2OC_6H_5$	$H\overline{N(CH_2)_4CH}_2$	$CH_2{=}CHCH_2\overline{N(CH_2)_4CH}_2$	neat	100	2000	24	3.0	19	68.1
$CH_2{=}CHCH_2OH$	$H\overline{N(CH_2)_4CH}_2$	$CH_2{=}CHCH_2\overline{N(CH_2)_4CH}_2$	neat	100	2000			18	5.0
$CH_2{=}CHCH_2OSi(CH_3)_3$	$H\overline{N(CH_2)_4CH}_2$	$CH_2{=}CHCH_2\overline{N(CH_2)_4CH}_2$	neat	100	2000			2	1.0
$CH_2{=}CHCH_2OCF(CF_3)_2$	$HN(C_2H_5)_2$	$CH_2{=}CHCH_2N(C_2H_5)_2$	neat	65	2000			11	58.1
$CH_2{=}CHCH_2OCF(CF_3)_2$	$HN(C_2H_5)_2$	$CH_2{=}CHCH_2N(C_2H_5)_2$	$CH_3C_6H_5$	65	300	48	53.6	1	57.0
$CH_2{=}CHCH_2OCF(CF_3)_2$	$H\overline{N(CH_2)_4CH}_2$	$CH_2{=}CHCH_2\overline{N(CH_2)_4CH}_2$	THF	65	300	14	83.1	2	96.4
$CH_2{=}CHCH_2OCF(CF_3)_2$	$H\overline{NCH_2CH_2OCH_2CH}_2$	$CH_2{=}CHCH_2\overline{NCH_2CH_2OCH_2CH}_2$	THF	65	300	48	67.8	10	80.2
$CH_2{=}CHCH_2OCF(CF_3)_2$	$HN(CH_3)C_6H_5$	$CH_2{=}CHCH_2N(CH_3)C_6H_5$	THF	65	300	24	2.0	6	63.5
$CH_2{=}CHCH_2OCH_2CH_2CH_3$	$H\overline{N(CH_2)_4CH}_2$	$CH_2{=}CHCH_2\overline{N(CH_2)_4CH}_2$	THF	65	300			24	1.0

[a] Reactions were carried out under the conditions listed in the table and the products were characterized by GC and ^1H NMR comparison with authentic allylamines. [b] Yields were determined by GC.

Aldrich Chemical Co. Elemental analyses were performed by Gailbraith Labs, Knoxville, TN. Palladium analyses for the palladium/polystyrene catalysts agreed with those obtained by combustion of these palladium/polystyrene catalysts and analysis of the residual palladium spectrophotometrically.[25] Other chemicals used were purchased commerically as reagent grade materials. Manipulations of air- or water-sensitive materials were performed by using standard procedures.[26]

Polystyryllithium (PS–Li). Polystyryllithium was prepared from macroporous polystyrene and *n*-BuLi and TMEDA according to a literature procedure.[24] The resulting lithiated polymer was washed twice with pentane and once with THF to remove nonpolymeric organometallic reagents and then was immediately used for preparation of a palladium catalyst.

Sodium Polystyrylanthracene (PS–anthracene$\cdot^-$Na$^+$). A THF (200 mL) suspension of 25 g of brominated polystyrene (Aldrich Chemical Co., 34% bromine) in a 500-mL round-bottomed flask was cooled to −78 °C, and *n*-BuLi (95 mL, 147 mmol) was added by syringe. The resulting mixture was shaken for 4 h, at which point the resulting lithiated polymer was washed twice with THF by forced siphon with a cannula. A THF solution (350 mL) of anthrone (24 g, 124 mmol) was added to the washed PS–Li at room temperature using a cannula and the mixture was shaken overnight. The product polymer was then collected in a Büchner funnel, washed three times with 100-mL portions of acetone, and dried. PS–anthracene was then prepared from this intermediate polymer by refluxing a suspension of this polymer in 350 mL of toluene containing 1.25 g of *p*-toluenesulfonic acid. After 24 h, no more water was collected in the Dean–Stark receiver connected to this apparatus and the anthracene-containing polymer was isolated by filtration followed by acetone washing and drying in vacuo. Addition of an excess of a THF solution of sodium naphthalene to this polymer produced dark, almost black, polymer beads of polymeric radical anion which were washed free of soluble impurities by forced siphon with three portions of clean THF.

***p*-Polystyrylbenzyllithium (PS–b–Pd) (3).** Chloromethylated polystyrene (100 g, 1.04 mequiv of CH_2Cl/g of polymer) was weighed into a 1-L flame-dried round-bottomed flask. THF (700 mL) was added followed by 150 mL of 1.6 N phenyllithium in benzene–ether solution. The flask was shaken overnight after which time the polymer developed a deep red color. The reaction was quenched with 400 mL of methanol to yield benzylated polystyrene, which was then isolated by filtration and extracted for 12 h with refluxing toluene and dried. Portions of this benzylated polystyrene (e.g., 2.0 g) were then suspended in ether (10 mL) and treated with *n*-BuLi (1.6 mL of a 1.8 N solution) to regenerate the lithiated polymer **3** as needed.

[Phenyl(trimethylsilyl)(polystyrylphenyl)methyl]lithium (PS–Sib–Li) (4). Addition of excess chlorotrimethylsilane to a suspension of **3** in benzene–ether at −78 °C followed by shaking for 24 h at room temperature led to a trimethylsilylated benzylpolystyrene which could be deprotonated by *n*-BuLi or phenyllithium to give **4** in the form of purplish beads. The lithiated polymer **4** prepared in this fashion was used directly to make PS–Sib–Pd.

Analysis of Lithiated Polymers. Analysis of PS–Li followed reported procedures.[27] The amounts of organolithium reagent on polymers **3** and **4** were estimated by measuring the amount of *n*-BuLi (or phenyllithium) consumed in formation of **3** and **4** and comparing this number to the amount of starting *n*-BuLi. Polymers **3** and **4** could also be quenched with alcohol, and the amount of base on the polymer could than be determined by unexceptional titrimetric procedures.

Dichloro(1,5-cyclooctadiene)palladium(II). (COD)$PdCl_2$ was prepared by a literature procedure.[28]

Preparation of Polymeric Palladium Catalysts. A THF (10 mL) suspension of an organometallic polymer (e.g., PS–Li, 3.00 g) and a THF–HMPA (30 mL) solution of (COD)$PdCl_2$ (2.1 mmol) were combined and shaken for 24 h at room temperature. The metal-exchanged polymer was then washed with THf for 5 days in a Soxhlet extractor and dried in vacuo. PS–Pd catalysts were crushed in a Spex Industries Mixer/Mill, Model 5100. The other palladium/polystyrene catalysts were used without this crushing operation.

Hydrogenations. Typically, hydrogenations were performed by weighing the catalyst (e.g., 0.100 g) into a flame-dried 50-mL round-bottomed flask with a side arm. The flask was attached to the apparatus and then evacuated and filled with H_2 four times. The solvent (10 mL) was added and magnetically stirred to equilibrate the temperature to 25.0 ± 0.2 °C in a constant temperature bath. The level of the dibutylphthalate (leveling fluid) in the buret was recorded and the substrate to be reduced was injected with a syringe as the timer was started. The time and buret readings were recorded at convenient intervals and the data could be plotted as time vs. mmol of H_2. Rates were calculated from the slopes of the initial linear segments of these plots or directly from the data. All hydrogenation rates are reported as mmol of hydrogen consumed per min per mmol of palladium (H_2 mmol/min, mmol Pd).

Decarbonylations. Dodecanal, *p*-methoxybenzaldehyde, *p*-chlorobenzaldehyde, and 2-hexenal were each (0.589 mmol) combined with either 1% Pd/C (0.1864 g, 0.0174 mmol of Pd) or PS–b–Pd (0.0878 g, 0.0174 mmol of Pd) and 4 mL of toluene in a 20-mL round-bottomed flask fitted with a reflux condensor and mineral oil bubbler. The apparatus was flushed with argon then stirred and heated to reflux. Aliquots (2 μL) were intermittently removed with a 10-μL syringe and analyzed by gas chromatography using the internal standard method.

Electron Micrographs. A Hitachi electron microscope, Model HU-11E-1, was used by Randy Scott of the Electron Microscope Center of Texas A&M University to obtained electron micrographs of the polymeric catalysts. Samples were prepared by embedding the catalyst beads in unpolymerized Araldite–epoxy media following Mollenhauer's method.[29] Sections of beads were cut with a diamond knife and supported on copper mesh. Average crystallite diameters were measured from the electron micrographs under a light microscope (12 ×) that had a graduated eye piece.

ESCA Spectra. ESCA spectra were obtained on a Hewlett-Packard 5950A spectrometer. Samples were prepared by crushing the polymeric palladium catalysts, the palladium(II) complex, or the Pd/C catalyst (e.g., 30 mg each) with an equal weight of graphite for 3 min. The powdered sample was bound to the assembled sample holder by pressing the sample onto the double-sided tape with a plastic spatula. The double-sided tape also held the sample cover to the base of the holder.

Allylic Substitution Reactions. The following are representative procedures. A mixture of 2 mL of allyl acetate (19 mmol), 3.7 mL of piperidine (38 mmol), and 0.2 g (0.0095 mmol) of PS–Sib–Pd were added to a 50-mL round-bottomed flask equipped with a magnetic stirrer. This mixture was then heated at the appropriate temperature under nitrogen and analyzed periodically by GC. The allylamine product was characterized by GC and by ^1H NMR spectroscopy. Reactions using a solvent other than the amine were typically carried out on a 2–5-mmol scale using 5–10 mL of solvent in a directly analogous manner.

Acknowledgment. Support of this research by the Office of Naval Research and the Texas A&M Center for Energy and Mineral Resources is gratefully acknowledged. The assistance of Wayne Scott in carrying out some of the decarbonylation experiments is also gratefully acknowledged.

Registry No. $CH_2{=}CHCH_2OCOCH_3$, 591-87-7; $CH_2{=}CHCH_2OC_6H_5$, 1746-13-0; $CH_2{=}CHCH_2OH$, 107-18-6; $CH_2{=}CHCH_2OSi(CH_3)_3$, 18146-00-4; $CH_2{=}CHCH_2OCF(CF_3)_2$, 15242-17-8; $CH_2{=}CHCH_2OCH_2CH_2CH_3$, 1471-03-0; $HN(C_2H_5)_2$, 109-89-7; $HN(CH_2)_4CH_2$, 110-89-4; $HN(CH_3)C_6H_5$, 100-61-8; $HNCH_2CH_2OCH_2CH_2$, 110-91-8; $CH_2{=}CHCH_2NCH_2CH_2CH_2OCH_2CH_2$, 696-57-1; $CH_2{=}CHCH_2N(C_2H_5)_2$, 5666-17-1; $CH_2{=}CHCH_2$

---

(24) Grubbs, R. H.; Su, S. H. *J. Organomet. Chem.* **1976**, *122*, 151–157.

(25) Ayres, G. H.; Alsop, J. H., III. *Anal. Chem.* **1959**, *31*, 1135–1138.

(26) Brown, H. C. "Organic Syntheses via Boranes"; Wiley: New York, 1975; Chapter 9.

(27) Bergbreiter, D. E.; Killough, J. M. *Macromolecules* **1980**, *13*, 187–189.

(28) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 3413–3416.

(29) Mollenhauer, H. H. *Stain Technol.* **1964**, *39*, 111–114.

$\overline{N(CH_2)_4C}H_2$, 14446-67-4; $CH_2{=}CHCH_2N(CH_3)C_6H_5$, 6628-07-5; *n*-BuLi, 109-72-8; 1-octene, 111-66-0; cyclohexene, 110-83-8; cyclooctene, 931-88-4; 2-methyl-2-butene, 513-35-9; mesityl oxide, 141-79-7; phenylacetylene, 536-74-3; diphenylacetylene, 501-65-5; 1-octyne, 629-05-0; dodecanal, 112-54-9; *p*-methoxybenzaldehyde, 123-11-5; *p*-chlorobenzaldehyde, 104-88-1; 2-hexanal, 505-57-7; anthrone, 90-44-8; phenyllithium, 591-51-5; chlorotrimethylsilane, 75-77-4.

Supplementary Material Available: Electron micrographs showing the PS–Pd, PS–b–Pd, and PS–anthracene–Pd catalysts (Figure 1), a tabular comparison of the yields and reaction times for decarbonylation of aldehydes by PS–b–Pd, and 1% Pd/C (Table III), and a tabular summary of the effect of functional groups on polystyrene on hydrogenation of 1-octene by palladium/polystyrene catalysts (Table V) (3 pages). Ordering information is given on any current masthead page.

Dienes as Possible Intermediates in the Catalytic Hydrogenation of Aromatic Hydrocarbons. 1. Dienes Derived from 1,4-Di-*tert*-butylbenzene and a Rhodium Catalyst[1]

James F. Outlaw, Jr., James Ray Cozort, Nissim Garti, and Samuel Siegel*

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701

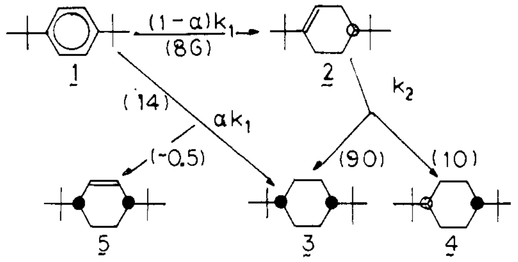
Received September 3, 1982

The evolution of the products upon hydrogenating three diene derivatives of 1,4-di-*tert*-butylbenzene (1) is compared with the formation of 1,4-di-*tert*-butylcyclohexene (2) and *cis*- and *trans*-1,4-di-*tert*-butylcyclohexane (3 and 4) from 1 on an alumina-supported rhodium catalyst to determine which diene (or dienes), upon adsorption on the catalyst, best represents the structure of the intermediate formed in the rate-determining surface reaction of 1. Of the dienes 1,4-di-*tert*-butyl-1,4-cyclohexadiene (6), 1,4-di-*tert*-butyl-1,3-cyclohexadiene (7), and 2,5-di-*tert*-butyl-1,3-cyclohexadiene (8), the last exhibits best the properties expected if it forms the same adsorbed intermediate as does 1 at the same hydrogen pressure. Unlike the arene, however, the dienes do not yield the cis-saturated isomer 3 as an initial product at low hydrogen pressures. Instead, *cis*-3,6-di-*tert*-butylcyclohexene (5) is formed along with ene 2 and arene 1; the dienes tend to exclude the cycloalkenes from the catalyst, their effectiveness increasing in the order 6 < 7 < 8. The result indicates that at low pressures little of arene 1 (less than 5%) is transformed directly to *cis*-1,4-di-*tert*-butylcyclohexane (3); instead enes 2 and 5 are produced initially, and because the concentration of the intermediate adsorbed dienes remains low during the hydrogenation of the arene, cis ene 5 is rapidly converted to 3 in the presence of the arene. At high hydrogen pressures, the cis ane 3 is an initial hydrogenation product of the dienes as it is of 1.

Introduction

Stereochemistry has furnished useful probes into the mechanism of catalytic hydrogenation.[2,3] Comparison between the stereochemistry of the hydrogenation (over reduced platinum oxide) of the xylenes and the derived dimethylcyclohexenes indicated that the *trans*-dimethylcyclohexanes, which are formed from the xylenes, result from the addition of hydrogen to desorbed cyclohexene intermediates.[4] Such intermediates are detected easily if ruthenium or rhodium catalysts are used.[5–7] Particularly large amounts of substituted cyclohexenes are produced from arenes with bulky substituents, for example, 1,2- and 1,4-di-*tert*-butylbenzene or 2-*tert*-butylbenzoic acid; the trans products appear only after the intermediates begin to be reduced.[8]

Scheme I. Simplified Kinetic Scheme for the Formation of Alkene Intermediates in the Hydrogenation of 1,4-Di-*tert*-butylbenzene (1)[12]



The kinetics of hydrogenation of aromatic hydrocarbons indicates that dienic structures are formed in the rate-controlling surface reaction.[9] Although, in principle, dienes may desorb from the catalyst, the reported isolation of a cyclohexadiene from the catalytic hydrogenation of an aromatic hydrocarbon has not been confirmed.[10,11] The orientation of the addition of hydrogen to an absorbed substituted arene, however, may be directed by the relative position and character of the substituents. And although dienes may not desorb from the catalyst, the dienic structure formed in the rate-controlling step may deter-

---

(1) (a) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, TX, April 1973. (b) Taken from the Ph.D. dissertations of James Outlaw, Jr., University of Arkansas (1971) and of James Ray Cozort, University of Arkansas (1975). (c) This research was supported by grants from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgement is hereby made to the donors of the said fund.

(2) Siegel, S. *Adv. Catal.* **1966**, *16*, 123–177.

(3) Burwell, R. L., Jr. *Intra-Sci. Chem. Rep.* **1972**, *6*, 135–149.

(4) Siegel, S.; Smith, G. V.; Dmuchovsky, B.; Dubbel, D.; Halpern, W. *J. Am. Chem. Soc.* **1962**, *84*, 3136–3139.

(5) Hartog, F.; Zwietering, P. *J. Catal.* **1963**, *2*, 79–81.

(6) Siegel, S.; Ku, V. *Proc. Int. Congr. Catal., 3rd, 1964* **1965**, pp 1199–1209.

(7) Weitkamp, A. W. *Adv. Catal.* **1968**, *18*, 1–110.

(8) (a) Van Bekkum, H. *Proc. Int. Congr. Catal., 3rd, 1964* **1965**, p 1208. (b) Van de Graaf, B.; Van Bekkum, H.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas*, **1968**, *87*, 777–785. (c) Ban Bekkum, H.; Buurmans, H. M. A.; Van Minnen-Pathuis, G.; Wepster, B. M. *Ibid.* **1969**, *88*, 779–794.

(9) Madden, W. F.; Kemball, C. *J. Chem. Soc.* **1961**, 302–308.

(10) Cram, D. S.; Allinger, M. L. *J. Am. Chem. Soc.* **1955**, *77*, 6289–6294.

(11) The diene isolated by Cram and Allinger (ref 10) from the hydrogenation of [2.2]paracyclophane is one of three isomers that are formed. None appear to have the 1,4-cyclohexadienic structure proposed by Cram and Allinger. Unpublished research in this laboratory by R. L. Yates, D. L. Wharry, N. Garti, S.-T. Lin, and S. Siegel.

0022-3263/83/1948-4186$01.50/0 © 1983 American Chemical Society