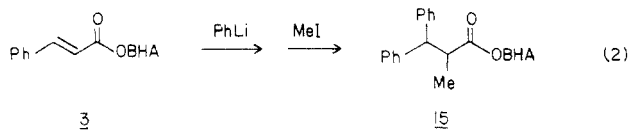
quenched with a proton source (MeOH), give high yields of saturated BHA esters **2**.[11] As in the case of BHT ester enolates,[8] the enolates resulting from additions to **1** are unstable at temperatures above approximately −20 °C but may be intercepted by electrophiles below −20 °C as illustrated in eq 2. where phenyllithium addition to **3** (−78 °C, 11 min) followed by alkylation with MeI (5 equiv, 5 min at −78 °C, 5 min at −20 °C) gave α-methylated ester **15** in 88% yield. Both BHA and BHT ester enolates have previously been shown to be highly useful in stereoselective aldol condensations[8,10] and the decomposition of BHT ester enolates in the presence of alkyllithium reagents has been shown to give ketones, presumably through additions to intermediate ketenes.[8]

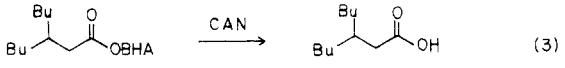


(2)

3 **15**

Our success with nucleophiles not normally successfully employed as Gilman reagents through their copper derivatives (entries 4 and 5) is noteworthy. Thus far our only unsuccessful addition with an alkyllithium reagent has been in the case of *tert*-butyllithium where complex products were obtained with both BHA and BHT esters. Interestingly, Grignard reagents appear not to undergo these additions: no reaction was observed with **3** and *n*-BuMgCl at temperatures up to −10 °C.

While both BHT and BHA esters are extremely resistant to hydrolysis,[10] BHT esters (and presumably BHA esters as well) may be reduced to primary alcohols with $LiAlH_4$ and BHA esters, upon oxidation with ceric ammonium nitrate (CAN), give corresponding carboxylic acids.[10] An example of the CAN oxidation of an addition product (**13**), is shown in eq 3 where the corresponding carboxylic acid (**16**) was obtained in 90% yield.[12]



(3)

13 **16**

In summary, sterically protected unsaturated esters containing the 2,6-di-*tert*-butylphenyl moiety appear to be exceptionally good Michael acceptors for a wide range of lithium reagents.

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(11) In a typical procedure 160 mg (0.47 mmol) of **12** (prepared in 71% yield from 2-heptenoyl chloride) in 4 mL of THF was treated with stirring at −78 °C with 0.37 mL (0.58 mmol) of 1.55 M *n*-BuLi in hexane over 0.5 min. The yellow solution was stirred for 7 min and then quenched by the addition of 100 μL of MeOH. After solvent removal in vacuo and treatment of the residue with CH_2Cl_2–H_2O, the oil obtained from the dried (Na_2SO_4) organic phase gave after PTLC (silica gel, 1:1 CH_2Cl_2–CCl_4) and vacuum drying 182 mg (95%) of **13**. An analytical sample was obtained after bulb-to-bulb distillation (210 °C (air), 0.05 mm); Anal. C, H.

(12) In a manner similar to that previously described,[10] 208 mg (0.51 mmol) of **13** in 2 mL of acetonitrile was treated under vigorous stirring with 1.0 mL (1.2 mmol) of 1.2 M ceric ammonium nitrate solution. After 50 min 300 mg of mannitol was added with continued stirring for 2 min followed by the addition of 1 mL of water and further stirring for 1 min. The mixture was poured into 15 mL of H_2O, made acidic by the addition of 2 mL of 4 N HCl and then twice extracted with 15 mL of Et_2O. The combined extracts were washed twice with 0.5 N NaOH (10 mL) and the combined aqueous layers were extracted with Et_2O. Acidification of the aqueous layer gave upon extraction with pentane (2 × 10 mL) an oil which after bulb-to-bulb distillation (150 °C (air), 0.05 mm) gave 86 mg (90%) of **16**; Anal. C, H. 2,6-Di-*tert*-butylquinone was recovered from the ethereal extracts.

Effect of Metal Loading and Triphenylphosphine on Product Selectivities in the Hydrogenation of Di-*tert*-butylacetylene and 3-Hexyne over Palladium/Alumina

Summary: The effect of triphenylphosphine and metal loading and/or dispersion on the product distributions from di-*tert*-butylacetylene indicates that the surface structure of the metal particles also may affect stereospecificities by promoting different catalytic mechanisms at different sites.

Sir: Recently, the claim was made "that the poisons used in the preparation of Lindlar and Rosenmund catalysts do not block active sites but act to rearrange the surface structure of the catalyst".[1] The authors cited the cis stereospecificity of the hydrogenation (26–76% conversion) of disubstituted alkynes on palladium foil and the physical change of palladium black when heated with diethylamine and D_2O at 150 °C for 20 h. However, the slowness of the hydrogenation, which is consistent with the small fraction of the palladium atoms which are exposed to the reactants, and the foil's lack of porous structure minimize the effect of diffusion in modifying the intrinsic selectivity of the surface reaction.[2-4] The quinoline used with a Lindlar catalyst lowers the rate of the surface reactions by competing with the alkyne for reactive sites and, because the strength of its adsorption on palladium falls between that of the alkyne and the product alkene, it almost excludes the latter from the surface even when the conversion of the alkyne to alkene is complete.[3,5-7]

We report evidence that the hydrogenation of alkynes on palladium occurs by at least two mechanisms at structurally differen surface sites. The reaction conditions were chosen to avoid diffusion-limited kinetics as judged from prior experiments with cyclohexene and norbornene and by the constancy of the turnover frequency for the hydrogenation of both 3-hexyne and di-*tert*-butylacetylene (DTBA) on 1% to 5% Pd/Al_2O_3 catalysts which also varied in dispersion.[8-12] On these catalysts the initial

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(4) Wheeler, A. *Adv. Catal.* **1951**, *3*, 249–327.
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(6) Steenhock, A.; van Wijngaarden, B. H.; Pabon, H. J. J. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 961–973.
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(8) Hawkins, J. A., Doctoral Dissertation, University of Arkansas, Fayetteville, AR 1983.
(9) The catalyst support was prepared from Catapal SB alumina (CONOCO) according to procedures in ref. 10. The 1–5% Pd/Al_2O_3 catalysts were prepared by impregnating the above alumina (≤325 mesh) with palladium chloride following procedures of Aben (ref 11). Reactions were performed at 30 °C in a small (30 mL) vortically stirred reactor using procedures similar to those described by Kung, Pellet, and Burwell (ref 10) to establish that reactants were free of poisons and that the rates of hydrogenation were free of diffusional limitations. Generally 10–50 mg of catalyst (1–5% Pd on alumina) and 0.1–0.3 mL of alkyne in 1–3 mL of cyclhexane were used.

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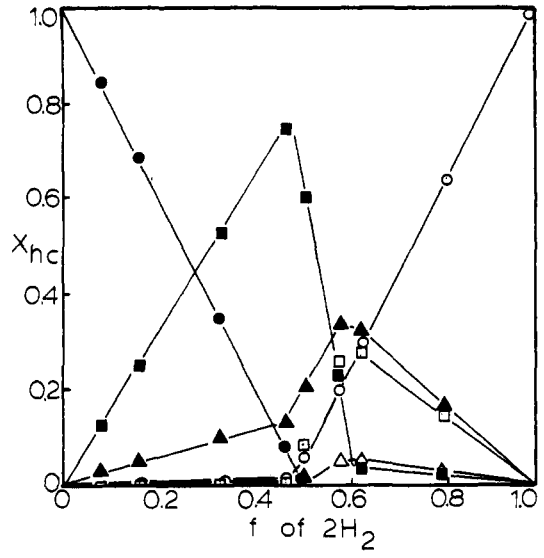

Figure 1. Product distribution from hydrogenation of 3-hexyne (2.2 mmol) over 20 mg of 5% Pd/Al_2O_3, $D = 0.18$: (●) 3-hexyne, (■) *cis*-3-hexene, (▲) *trans*-3-hexene; (▲) *cis*-2-hexene, (□) *trans*-2-hexene, (○) hexane.

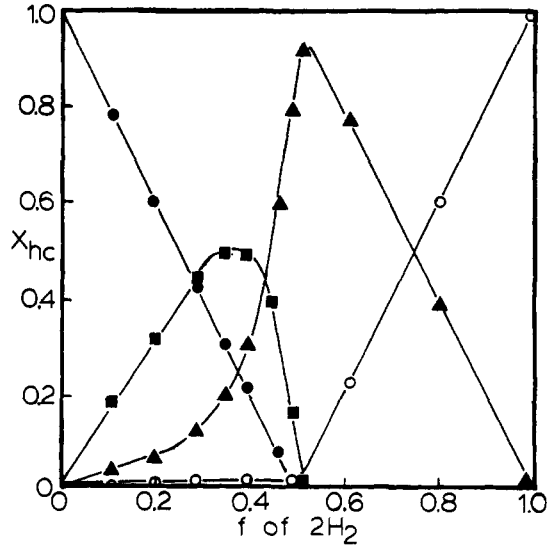

Figure 2. Product distribution from the hydrogenation of di-*tert*-butylacetylene (1.3 mmol) over 15 mg of 5% Pd/Al_2O_3, $D = 0.06$: (●) di-*tert*-butylacetylene, (■) *cis*-di-*tert*-butylethylene, (▲) *trans*-di-*tert*-butylethylene, (○) 2,2,5,5-tetramethylhexane.

product distributions showed a small trend toward increasing cis selectivity with increasing dispersion (3-hexyne, 80–84%; DTBA, 75–84%); however, the plots of composition vs. conversion for DTBA deviated from linearity at an earlier stage than did plots for 3-hexyne (Figures 1 and 2).[13] In competition with cyclohexene, 3-hexyne gave an improved cis selectivity (cis 88%, trans 11%, ane 1%) and DTBA also gave linear plots to about 80% conversion and less than 0.5% of the alkane although the initial cis selectivities were essentially unchanged. The most selective reduction of DTBA to *cis*-DTBE occurred over a lightly loaded catalyst (0.16% Pd/Al_2O_3; dispersion, 0.6) prepared

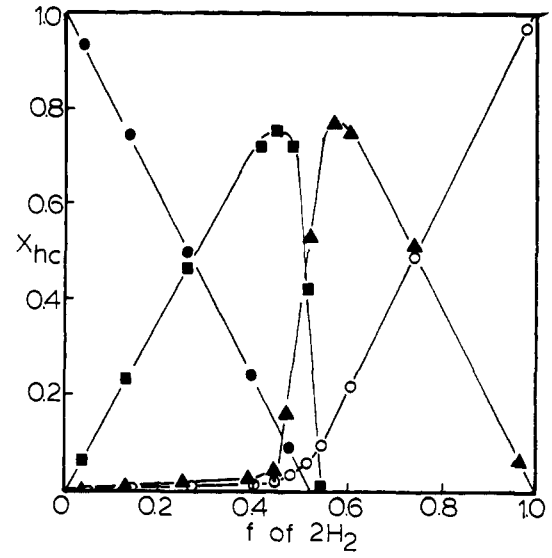

Figure 3. Product distribution from the hydrogenation of di-*tert*-butylacetylene (0.55 mmol) over 26 mg of 0.16% Pd/Al_2O_3, $D = 0.5$. Symbols as in Figure 2.

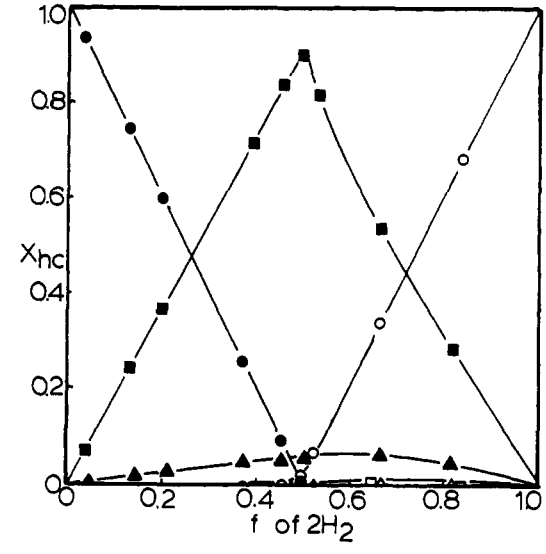

Figure 4. Product distribution from the triphenylphosphine-poisoned hydrogenation of 3-hexyne (0.9 mmol) over 30 mg of 5% Pd/Al_2O_3, $D = 0.18$; $PPh_3/Pd_s = 2.0$. Symbols as in Figure 1.

by impregnating the alumina support with bis(η^3-allyl)-palladium (Figure 3).[14] This result, as well as the effect of cyclohexene on the product selectivities, suggests that intraparticle diffusion affects the results when the more heavily loaded catalysts (1–5%) are used. Kung, Pellet, and Burwell have attributed the increase in the competitive reactivity of DTBA relative to cis-DTBE with an increase in the dispersion of platinum on alumina to the greater sticking probability of DTBA relative to its olefinic competitor at edges and steps compared to close-packed planes of the metal surface[10] and to the expectation that the proportion of atoms at edges and steps increases with dispersion.[15]

Triphenylphosphine was examined as a catalyst poison because it is reversibly adsorbed on palladium[16] under the conditions used in this study and because of the possibility that it may be adsorbed differentially by structurally different surface sites.[17] A ratio of triphenylphosphine

(10) Kung, H. H.; Pellet, R. J.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 5603–5611.
(11) Aben, P. C. *J. Catal.* **1968**, *10*, 224–229.
(12) Dispersion, *D*, is the percent of the total metal atoms which are at the surface and was determined by hydrogen–oxygen titrations according to Benson, J. E.; Hwang, H. S.; Boudart, M. *J. Catal.* **1973**, *30*, 146–153.
(13) Compare with Kung, H. H.; Burwell, R. L., Jr. *J. Catal.* **1980**, *63*, 11–24.
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(16) Fugii, Y.; Bailar, J. C. *J. Catal.* **1978**, *52*, 342–345.

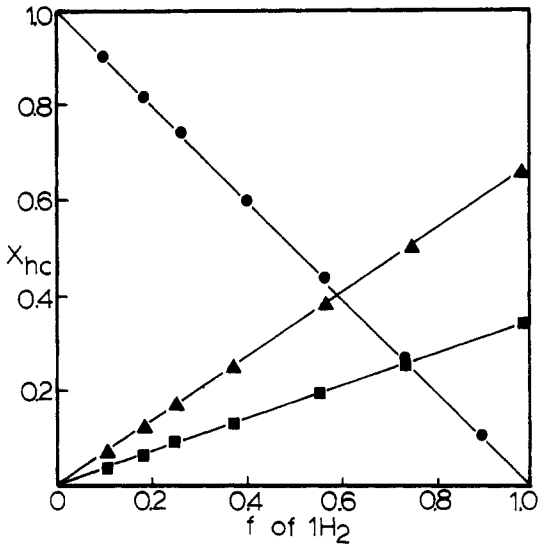

Figure 5. Product distribution from the triphenylphosphine-poisoned hydrogenation of di-*tert*-butylacetylene (0.26 mmol) over 27 mg of 5% Pd/Al_2O_3, $D = 0.18$; $PPh_3/Pd_s = 1.0$. Symbols as in Figure 2.

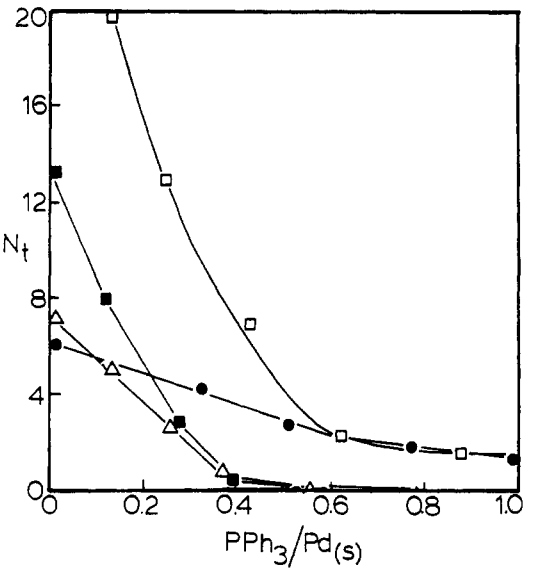

Figure 6. Effect of PPh_3/Pd_s ratio on the turnover frequency, N_t, molecules (surface atom)$^{-1}$ s^{-1} at 30 °C and 0.85 atm H_2: (□) norbornene, (■) di-*tert*-butylacetylene, (●) 3-hexyne, and (▲) cyclohexene.

(PPh_3) to surface palladium atoms (Pd_s) of 2.0 slowed the rate of reduction of 3-hexyne, virtually eliminated the formation of hexane until all the alkyne had disappeared, and after the alkyne was consumed the isomerization of *cis*- to *trans*-3-hexene was much slower than its conversion to hexane (compare Figures 1 and 4). Futher increases in the ratio, PPh_3/Pd_s, causes a further reduction in the rate and, because under these conditions the rate is approximately first order in 3-hexyne, the reduction becomes very slow before all of the alkyne has been converted.[18]

Triphenylphosphine lowers the rate of hydrogenation of DTBA and increases the initial proportion of the trans isomer at the expense of the cis isomer and alkane. With ratios of PPh_3/Pd_s of about 0.5, *trans*-di-*tert*-butylethylene (trans-DTBE) is the principal initial product although the phosphine inhibits the further reactions of *cis*-DTBE (Figure 5).

We believe that the effect of triphenylphosphine on the stereochemistry of hydrogenating DTBA indicates that the reduction proceeds by different mechanisms at two types of sites at which the competitive reactivities of alkynes and alkenes also differ.[19] At one type of site the process involves a stereoelectronically controlled formation of the cis isomer whereas at the other, either stereoisomer and perhaps the alkane may be formed as initial products.[13] Presumably on the unpoisoned catalysts, the product of turnover frequency and fraction of reactive sites which yield cis must be greater than the corresponding product of turnover frequency and fraction of reactive sites which are not stereospecific. Triphenylphosphine excludes DTBA from the stereospecific sites more effectively than it does 3-hexyne (Figure 6).

The difference in reaction mechanisms appears analogous to the difference represented by mononuclear rhodium complexes which yield only *cis*-alkenes as initial products and the recently described dinuclear rhodium hydride complex $[(\mu\text{-H})Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2]_2$, which yields the trans isomer although, in principle, cis as well as trans isomers can be formed.[20-22] We presume that the structures of the surface sites are related to the structure of these homogeneous catalysts.

The effect of triphenylphosphine on the hydrogenation of 3-hexyne is like the effect of quinoline in that neither base completely excludes this alkyne from the cis stereospecific sites but is more tightly bound than is the *cis*-alkene. It also lowers the rate and therefore the effect of intraparticle diffusion on selectivity. Triphenylphosphine prevents reaction of DTBA at these sites but not at the sites at which both *cis*- and *trans*-alkenes are formed directly. This can be understood if the alkyne acts as a monodentate ligand at a monoatomic site but may act as a bidentate ligand at the binuclear site whereas the phosphine functions as a monodentate ligand at either site. Presumably, the stereospecificity of 3-hexyne could be altered by a monodentate Lewis base which is bound to a palladium atom more strongly than is PPh_3.

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(17) Siegel, S.; Outlaw, J.; Garti, N. *J. Catal.* **1978**, *52*, 102–115.
(18) For example with 42 mg of catalyst (1% Pd, $D = 0.45$; 1.8×10^{-6} mol Pd_s), 4.7×10^{-5} mol PPh_3, and 2.2×10^{-3} mol 3-hexyne the initial turnover frequency was 0.16 ± 0.03, dropped to 0.08 ± 0.2 at 50% conversions, and the reaction was terminated at 8.7 h; 7.5% of the alkyne was unconverted and the remainder was *cis*-3-hexene together with less than 0.1% of either the trans isomer or hexane.
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(22) See also: Yoshida, T.; Youngs, W. J.; Sakaeda, T.; Ueda, T.; Otsuka, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6273–6278.

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