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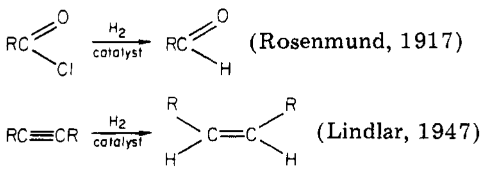
Metallic Palladium, the Actual Catalyst in Lindlar and Rosenmund Reductions?

Summary: We provide evidence 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.

Sir: The hydrogenation of alkynes to *cis*-alkenes (Lindlar reduction) and the catalytic hydrogenolysis of acid chlorides to aldehydes (Rosenmund reduction) are well-known textbook examples of reactions with "selectively poisoned" catalysts (Scheme I).[1] The partial hydrogenation of alkynes to give *cis*-alkenes, an important reaction in natural product synthesis, is usually achieved by heterogeneous hydrogenation with "poisoned" Lindlar catalysts. There has been considerable effort in the past to replace this "mythical" catalyst by homogeneous methods. Thus, Li in THF,[2] Na with BF_3 in diglyme,[3] diisobutylaluminum hydride and methyllithium,[4] chloroborane in ether,[5] $PdCl_2$ and H_2 in DMF,[6] $LiAlH_4$ and $TiCl_4$,[7] $Rh(NBD)(PPhMe_2)_3$,[8] and CuI[9] can be used to hydrogenate alkynes to give *cis*-alkenes. None of these methods, however, has replaced the Lindlar catalyst, which is used in the total synthesis of leukotrienes,[10] prostaglandins,[11] carbohydrates,[12] and various other natural products.[13]

The Lindlar catalyst and its modifications generally consist of deactivated palladium supported on $BaCO_3$ or $CaCO_3$, although Pd/C has also been used.[14] Historically, Lindlar catalysts are poisoned by lead acetate, with quinoline as additional cataylst poison.[15] Successful reactions with untreated catalysts have also been reported.[16] In a very recent paper Dev describes the effects of using various transition-metal chlorides to modify Lindlar catalysts. Dev finds that the $MnCl_2$-modified catalyst is the most selective for alkyne hydrogenation to alkenes;[17] however, no data concerning the stereoselectivity (cis/trans ratio) of the $MnCl_2$-poisoned catalyst were reported.

Scheme I



The Rosenmund reduction[18] catalyst is palladium supported on barium sulfate poisoned by sodium acetate,[19] *N,N*-dimethylaniline,[20] thiourea,[21] thiophene,[21] dibenzothiophene,[21] ethyldiisopropyl amine,[22] or, most commonly, quinoline (with and without sulfur).[23] While the Rosenmund reduction has long been replaced by more practical homogeneous procedures with metal hydrides, the secret of the selective catalyst deactivation has never been uncovered. The very similar preparation procedures suggest that the Rosenmund catalysts are related to Lindlar catalysts; although the literature, surprisingly, does not draw any comparison.

The broad range of poisons used to cause identical or similar modifications of the catalytic activity of supported palladium to give either Lindlar or Rosenmund catalysts is suggestive that the poisons are not involved in the catalytic process but rather change the surface of the catalyst. The generally accepted rationale for the effect of catalyst poisoning suggests that the "poison" blocks the most active catalyst sites and thus prevents undesired further reactions. However, as described below, we find that the poisons do not block certain active sites but rather act to rearrange the palladium structure in a very drastic way.

We find that untreated, commercial palladium foil catalyzes the hydrogenation of alkynes to *cis*-alkenes with high selectivity. The following test reactions were carried out in the presence of 6 cm^2 of palladium foil (see Table I). 5-Decyne is converted to *cis*-5-decene with no trans byproduct detectable. Diphenylacetylene as well gives pure *cis*-stilbene. Even dimethyl acetylenedicarboxylate, hydrogenated at 100 °C for 160 h, resulted in dimethyl maleate (cis/trans ratio 30:1).

Our results are especially remarkable for two reasons: (1) Conventional Lindlar hydrogenations use supported catalysts with surface areas much larger than 100 m^2/g, whereas our palladium foil has a surface area of only 6 cm^2. The conversion achieved (turnover frequency = 4 (molecules/(surface atom × second))) is even more surprising, when we consider that such turnover frequencies larger than 1 have only been observed under ultrahigh vacuum conditions with extremely clean surfaces.[24]

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Table I. Reduction of Alkynes with Palladium Foil

alkyne	rxn time, h	temp	cnvn, %	alkene, % cis	alkene, % trans	alkane, %	solvent
BuC≡CH	24	RT[a]	64	100		0	hexane
PhC≡CPh	13	RT[a]	26	96	0	4	
BuC≡CBu	4	68 °C	27	100	0	0	
$Me_2OCC≡CCO_2Me$	90	100 °C	67	97	3	0	

[a] RT, room temperature.

(2) Lindlar reductions are very rarely completely selective. The observed cis/trans ratio commonly varies between 10 and 30, and often the reaction must be carefully monitored and stopped in order to achieve the desired cis excess. The high selectivity achieved with the foil is therefore very unusual and certainly worth further study to pursue other practical applications. The palladium foil is not as readily deactivated as are supported catalysts and may be used indefinitely. We are presently engaged in the development of a more practical modification of this foil method in order to provide a reliable synthetic method for cis hydrogenation of alkynes.

Our results suggest that the actual catalytic species in the Lindlar catalysts is the metallic palladium and the poison serves only to modify the surface structure of the catalyst. In fact, the above-described studies evolved as a consequence of the following experiments that justify the concept of surface reordering.

During a hydrodenitrogenation study[25] we observe that a palladium on silica catalyst loses all its hydrogenolysis activity after contact with indole (which is structurally related to the Rosenmund and Lindlar poison quinoline). During this treatment the surface area of the catalyst reduces from 395 m^2/g to 195 m^2/g (N_2–BET method). Considering the high surface area of the pure support (235 m^2/g), these data indicate that the catalyst has lost almost all of its palladium surface. Combustion analysis of the deactivated catalyst[26] does not reveal a significant presence of carbon, and the traces of nitrogen detected are not consistent with adsorbed indole.[27] This deactivated catalyst did, however, produce *cis*-5-decene from 5-decyne and propanal from propionyl chloride, thus acting as both a "Lindlar" and a "Rosenmund" catalyst.

We also find that palladium black, after contact with triethylamine and D_2O at 150 °C for 20 h in a batch reactor, is completely rearranged to metallic palladium.[28] The scanning electron micrographs[29] demonstrate the observed change: Figure 1 shows the untreated palladium black[30] 500× and 25 000× magnification and Figure 2 shows the same palladium after contact with the amine. Clearly, the metal has completely changed its structure and is converted to metallic particles of low surface area.

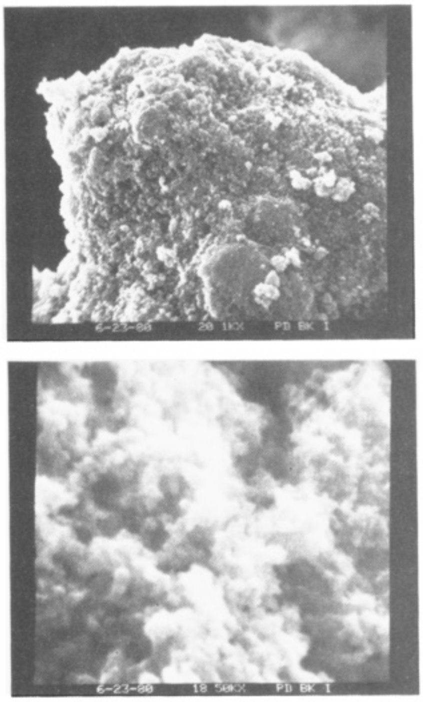

Figure 1. Palladium black at magnification 500× (top) and 25 000× (bottom).[29]

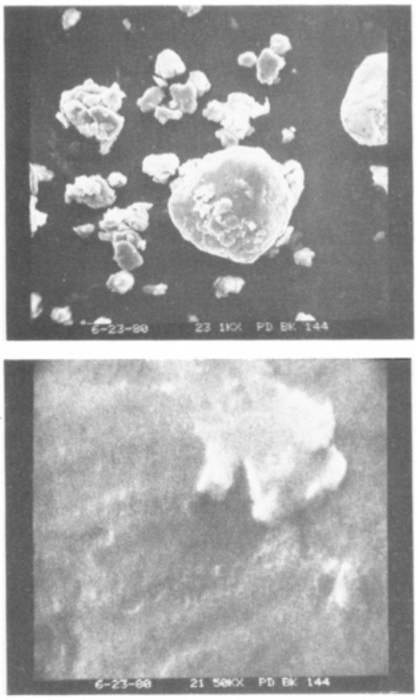

Figure 2. Palladium black after contact with triethylamine at 150 °C, magnification 500× (top) and 25 000× (bottom).[29]

In addition to these observations, we have recently presented evidence that amines (e.g., quinoline) react with palladium black to form labile palladium–hydride species.[28] Moreover, it is well-known that high surface area palladium reversibly "dissolves" large quantities of hydrogen with

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(24) Calculated from data given in: Somorjai, G. A. "Chemistry in Two Dimensions: Surfaces"; Cornell University Press: Ithaca, NY, 1981; pp 445–446.

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(26) Values obtained from combustion analysis of the deactivated palladium catalyst: 0.34% C, 0.04% H, and 0.02% N.

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(29) The pictures were taken with a Cambridge Mark IIA SEM. The resolution at 10^5 magnification allows the detection of particles with sizes of 300 Å.

(30) Purchased from Strem Chemicals and used as is.

great facility, through formation of labile palladium hydrides.[31] It is our contention that these hydrides in decomposing change the metal crystallite morphology to reduce surface area.

These observations strongly support our hypothesis that the poisons used to deactivate palladium catalysts do not block active sites but act to rearrange the surface structure of the palladium.

That the catalyst poisons are not involved in the actual reductions is also supported by the observed transformation of benzoyl chloride (429 mg) to benzaldehyde with ultrapure palladium powder[32] (29 mg) at 0 °C (7% conversion after 16 h). The same, untreated palladium powder also catalyzes the transformation of 5-decyne (10 mL) to *cis*-5-decene (after 22 h, complete conversion to 70% *cis*-, 8% *trans*-5-decene, 12% decane, and 10% unidentified isomers was obtained).

However, the "Lindlar"-active palladium foil showed no activity for the conversion of benzoyl chloride to benzaldehyde under various conditions. This experiment demonstrates that despite similar catalyst preparation procedures, the two reactions are catalyzed by different active sites; the active site for semihydrogenation being the "metallic" palladium, the nature of the active site for acid chloride hydrogenolysis is not identified yet. A detailed investigation with defined palladium surfaces is actively being pursued.[33]

Acknowledgment. W.F.M. thanks the College of Chemistry at Berkeley and the Research Corporation for their support. R.M.L. and Y.S. thank the National Science Foundation and the Army Research Office for support through NSF Chem. Eng. Grant No. 82-19541 and ARO contract no. DAAG29-81-k-0086.

Registry No. BuC≡CH, 693-02-7; PhC≡CPh, 501-65-5; BuC≡CBu, 1942-46-7; Me$_2$OCC≡CCO$_2$Me, 762-42-5; BuCH=CH$_2$, 592-41-6; (*Z*)-PhCH=CHPh, 645-49-8; (*Z*)-BuCH=CHBu, 7433-78-5; (*Z*) Me$_2$OCCH=CHCO$_2$Me, 624-48-6; palladium, 7440-05-3; triethylamine, 121-44-8; benzoyl chloride, 98-88-4; benzaldehyde, 100-52-7.

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[32] Purchased from Thiocol, 0.25–0.55 μm, purity 99.95%.

[33] W.F.M., work in progress.

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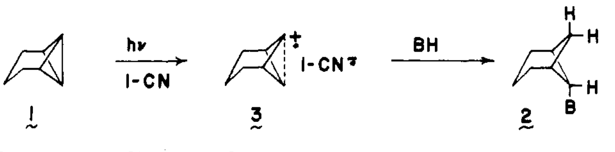
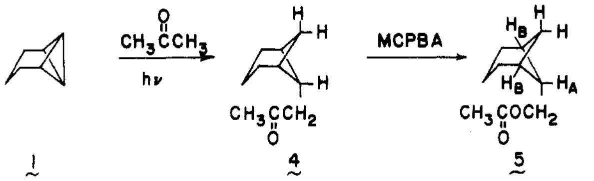
Photoinduced Additions to Carbon-Carbon σ Bonds. Addition of Acetone, Acetonitrile, and Ethyl Acetate to Bicyclo[1.1.0]butanes

Summary: Acetone, acetonitrile, and ethyl acetate have been photochemically added across the C1–C7 σ bond of tricyclo[4.1.0.0^{2,7}]heptane. This photoinitiated radical chain reaction was shown to occur in an anti-Markovnikov manner.

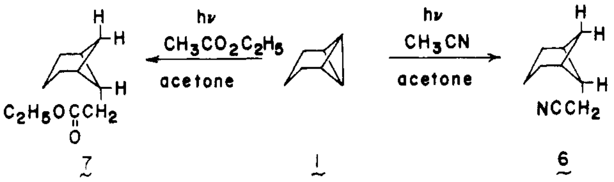
Sir: Recently, we presented evidence for the addition of nucleophiles across carbon–carbon σ bonds under conditions where photoexcited sensitizers first removed an electron from the carbon–carbon σ bond to produce a cation radical–anion radical pair.[1,2] In this manner, tricyclo[4.1.0.0^{2,7}]heptane (**1**) was readily converted into **2** via the intermediacy of the cation radical **3**, which was generated through electron transfer to excited-state 1-cyanonaphthalene (1-CN). This proceeded in high yield, where B was hydroxyl, methoxyl, and cyano. We now report on the photoinitiated addition of acetone, acetonitrile, and ethyl acetate across strained carbon–carbon σ bonds.



When a solution of 0.74 g of **1** in 41 mL of acetone was irradiated for 5.5 h in a Pyrex vessel under argon in a Rayonet photochemical reactor equipped with 16 300-nm lamps, 0.42 g (35% yield) of a pure, colorless liquid was obtained after distillation:[3] bp 100–103 °C (12 mm); ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.53–2.42 (3 H, m), 2.33–2.27 (2 H, m), 2.13 (3 H, s), 1.88–1.60 (6 H, m), 1.60–1.50 (2 H, m); ^{13}C NMR (CDCl$_3$) δ 208.78 (s), 41.50 (t), 37.45 (d), 36.01 (d), 30.04 (q), 27.99 (t), 22.78 (t), 13.88 (t); IR (neat) 2930, 2865, 1715, 1355, 1175, 1150 cm^{-1}. The spectral data indicated that acetone had added across the C1–C7 bond of the bicyclo[1.1.0]butyl moiety of **1** to give either **4** or its epimer. In order to establish the stereochemistry of the addition, **4** was treated with *m*-chloroperbenzoic acid to give an 84% yield of **5**. Examination of **5** by ^{1}H NMR at 300 MHz in the presence of a lanthanide shift reagent showed H$_A$ to be a pentet, which collapsed to a triplet ($J_{H_A-H_B}$ = 6.0 Hz) when the methylene protons adjacent to the acetoxyl group were decoupled. The observed coupling constant between H$_A$ and H$_B$ established the stereochemistry of the addition as shown in **4**.[1,2,4]



Under similar photochemical conditions, a 0.2 M solution of **1** in acetonitrile containing 0.2% acetone (v/v) was irradiated for 100 h, with an amount of acetone equivalent to 0.2% of the solution being added every 20 h. Workup by chromatography on silica gel gave a 42% isolated yield of **6**.[5] Irradiation of **1** in ethyl acetate containing 0.2% acetone for 120 h, with an amount of acetone equivalent to 0.2% of the solution being added at 20-h intervals, gave



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[5] In addition, a small amount (0.4–0.6%) of **4** was obtained in this reaction.

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