**Figure 1.** A perspective representation of the structure of angasiol.

electronegative atoms (61.61, 36.54), two –CHBr– groups (65.31 and 51.53 as determined by single-frequency proton decoupling), two methine carbon atoms (63.52, 35.83), eight methylene carbon atoms (51.36, 50.00, 39.79, 38.13, 32.83, 31.96, 31.63, 30.33), and three methyl groups (32.61, attached to a carbon atom bearing an electronegative substituent, 22.66, and 21.20). The $^1$H NMR spectrum suggested that each proton on a bromine-bearing carbon atom was vicinal to a methylene with diastereotopic hydrogen atoms: 1.03 (s, 3 H), 1.24 (s, 3 H), 1.47 (s, 3 H), 1.2–2.5 (m, 18 H), 3.93 (d of d, $J$ = 4.5, 8 Hz, 1 H), and 4.14 (d of d, $J$ = 6.5, 11 Hz, 1 H).

Single crystals of angasiol suitable for data collection were obtained from acetone–hexane. The X-ray precession photographs displayed orthorhombic symmetry with systematically extinct reflections: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; and $00l$, $l = 2n + 1$, which conformed uniquely to the noncentrosymmetric space group $P2_12_12_1$. Least-squares refinement of 15 reflections between the angular range $3.4 \leq 2\theta \leq 17.2°$ yielded the lattice parameters $a$ = 9.441 (3), $b$ = 9.529 (2), and $c$ = 23.683 (9) Å, which for $z$ = 4 gives $\rho_{calcd}$ = 1.49 g/cm$^3$ ($\rho_{obsd}$ = 1.46 g/cm$^3$ by flotation in toluene–carbon tetrachloride). Diffraction intensities were measured using graphite monochromated Mo $K_\alpha$ radiation on a Syntex PĪ autodiffractometer operating in the $2\theta–\theta$ mode. Of 2841 reflections examined ($2\theta \leq 55°$) 2176 unique reflections were accepted with $|F_o| > 0$. Corrections were made for Lorentz, polarization, and absorption ($\mu$ = 38 cm$^{-1}$) effects.[10]

The structure was solved by standard heavy-atom techniques.[11] A comparison was made of the two configurational isomers with isotropic temperature factors for carbon and oxygen and anisotropic temperature factors for bromine using anomalous scattering factors for Br.[12] Standard residuals at convergence for the two enantiomers were $R$ = 0.1582 and 0.1562, respectively, and the weighted residuals $R_w$ = $(\sum_w(|F_o| - |F_c|)^2/\sum_w|F_o|^2)^{1/2}$ of 0.1240 and 0.1227, respectively, where $w$ = $1/\sigma_{F_o}^2$. Statistical significance of $R_w$-factor ratio at 0.995 significance level indicated the second enantiomer to be correct. Conformational and absolute configurational aspects of the angasiol molecule are presented in Figure 1. The seven chiral centers are C-1 ($S$), C-4 ($R$), C-5 ($S$), C-6 ($S$), C-9 ($S$), C-13 ($S$), and C-16 ($S$).

Refinement was unsuccessful when carbon and oxygen atoms were allowed to vary anisotropically. A certain degree of disorder is present and is most apparent in the large temperature factor for C-7. Results from attempts to refine alternate positions for C-7, C-12, C-14, C-18, and O-13 were inconclusive, terminating any further attempts toward anisotropic refinement. After hydrogen atoms were placed at calculated positions 1.0 Å from their respective carbon atoms, full-matrix least-squares refinement converged to final crystallographic residuals $R$ = 0.074 and $R_w$ = 0.072 for 875 reflections restricted to sin $\theta/\lambda$ < 0.45 and $F_o$ > $1.0\sigma_{F_o}$.

**Supplementary Material Available.** Figures 2 and 3 showing bond angles and bond lengths, Tables I and II of atomic positional and thermal parameters of angasiol, and procedures for the isolation of angasiol (5 pages). Ordering information is given on any current masthead page.

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**George R. Pettit,\* Cherry L. Herald**
**James J. Einck, Lawrence D. Vanell**
**Peter Brown, Devens Gust**

*Cancer Research Institute and*
*Department of Chemistry, Arizona State University*
*Tempe, Arizona 85281*

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## Versatile Polymer-Bound Hydrogenation Catalyst. Anthranilic Acid Anchored Palladium(II) Catalysis

*Summary:* Anchoring the bidentate ligand anthranilic acid to chloromethylated polystyrene beads, followed by refluxing with palladium chloride, has resulted in a catalyst effecting the hydrogenation of alkenes, dienes, and even benzene. The catalyst is air-stable and has a lifetime of at least 10 000 catalytic cycles per palladium atom.

*Sir:* In the search for active homogeneous hydrogenation catalysts, Pd(II) has assumed a very minor role because its complexes, in fact, demonstrate a very narrow range of activity. Terminal alkynes,[1] terminal alkenes,[2] conjugated alkenes,[3] and polyenes[4] provide the only published examples.

The area of polymer-bound catalysts is receiving intensive investigation because of the possibility of creating materials having the activity of soluble catalysts while at the same time permitting the ease of product separation inherent in heterogeneous catalysts. But here, too, Pd(II)–polymers have demonstrated only the ability to hydrogenate alkenes and polyenes.[5]

Earlier we reported that a catalyst of high activity can be prepared by anchoring anthranilic acid to chloromethylated polystyrene beads (Rohm and Haas, XAD-4), followed by complexation with rhodium.[6] We wish to report that a similar approach can be used to prepare a Pd(II) catalyst (eq 1).



$$\xrightarrow{PdCl_2} \quad \text{"Pd(II)"catalyst} \quad (1)$$
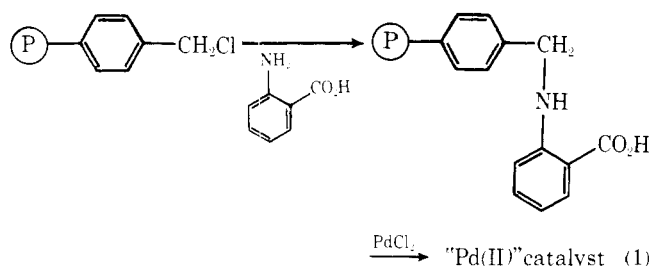
The catalyst is prepared by treating chloromethylated polystyrene beads (1.41 mequiv Cl/g) with a 50% molar excess of anthranilic acid in ethanol and warming (55 °C) for 36 h. After filtering and washing thoroughly with ethanol, 18 g of the beads were suspended in 500 mL of acetone and 0.43 g (2.46 mmol) of PdCl₂ and 5 mL of acetonitrile were added. The suspension was refluxed for 72 h under nitrogen, filtered, washed with acetone, and vacuum-dried; analysis (0.38% Pd, 0.39% N) indicated a 1:7 relationship between palladium and anthranilic acid.

Based on other Pd(II) catalysts[4,5] one would anticipate that monoolefins would hydrogenate slowly, at least in comparison with analogous rhodium catalysts. This has been verified by the conversion of 4-octyne to *cis*-4-octene and formation of cyclooctene from 1,3- and 1,5-cyclooctadienes (Table I). Unlike the homogeneous catalyst PdCl₂(PPh₃)₂, but similar to the Pd(II)–phosphine polymer,[5b] the rate of hydrogenation of a 1,3-diene was faster than that of a 1,5-diene.

The palladium catalyst is active, yet selective, in the conversion of 4-octyne to the cis olefin. If the cis alkene is left in contact with the catalyst for several days, isomerization to the trans configuration occurs.

There appear to be no reports of arene hydrogenation by either homogeneous or polymer-bound palladium(II) catalysts.[7] This catalyst, however, does hydrogenate benzene and is, therefore, the first to do so.

One of the problems observed with phosphine-anchored polymer catalysts is the sensitivity of the catalysts to oxidation.[8] No similar problems are observed with the anthranilic acid anchored polymers. The catalyst has been stored under air for long periods without decomposition and no precautions have been taken to remove oxygen from the substrates before hydrogenation.

Evaluation of the longevity of the catalyst was performed in the following manner. Using a 4.0 g sample (0.38% Pd) of the palladium catalyst, 150 mL of undistilled 1,3-cyclooctene was hydrogenated at 50 psig and room temperature for 1 h. Analysis demonstrated that 64% of the diene remained and the balance of the material was cyclooctene (35%) and the cyclooctane (1%). On the average this represented approximately 3700 cycles per palladium atom. The filtered and acetone-washed catalyst was then used to hydrogenate 150 mL of unpurified, U.S.P. corn oil. After 14 h at 500 psig and 80 °C the corn oil was 48% hydrogenated, representing another 5000–6000 catalytic cycles per palladium atom. Analysis of the catalyst indicated the palladium content (0.27%) to be somewhat reduced compared to the original catalyst (0.38% Pd). Repetition of the hydrogenation of 1,3-cyclooctadiene revealed that the catalyst had retained 10% of its original activity. The lifetime of the catalyst would be considered modest in comparison with several phosphine-anchored polymers.

The major deactivation mechanism, in view of the modest loss of metal, does not appear to be metal elution but is, perhaps, a consequence of changes in the beads. That alterations in the catalyst are occurring is indicated by the observation that upon hydrogenation of 1,3-COD the cyclooctene/cyclooctane ratio dropped from 35:1 to 6:1, comparing the initial and highly used catalysts. There is also a shift in the carbonyl absorption (IR) from 1674 to 1727 cm⁻¹ for these two catalyst samples, a shift consistent with a conversion from carboxylate

**Table I. Hydrogenation with Pd(II)–Polymer**

| substance | mmol | mmol catalyst | time, h | pressure, psig | temp, °C | products | cycles/ atom-h |
|---|---|---|---|---|---|---|---|
| cyclohexene | 200 | 0.026 | 16 | 400 | 80 | cyclohexane (60) | 290 |
| 1,3-cyclooctadiene | 40 | 0.0050 | 0.75 | 50 | room | cyclooctane (1) cyclooctene (52) | 5800 |
| 1,3-cyclooctadiene | 40 | 0.050 | 48 | 50 | room | cyclooctane (30) cyclooctene (70) | |
| 1,5-cyclooctadiene | 40 | 0.0050 | 0.75 | 50 | room | cyclooctane (trace) cyclooctene (25) 1,3-cyclooctadiene (6) | 2700 |
| 4-octyne | 35 | 0.0064 | 4 | 50 | room | octane (7) *cis*-4-octene (90) | 1400 |
| cinnamaldehyde | 160 | 0.064 | 1 | 400 | 85 | 3-phenylpropanal (30) 3-phenyl-1-propanol (30) | |
| cinnamyl alcohol | 160 | 0.025 | 16 | 400 | 100 | 3-phenyl-1-propanol (100) | 400 |
| corn oil (138 g) | | 0.125 | 14 | 500 | 80 | 48% hydrogenation | |
| soybean oil methyl ester (8 g) | | 0.041 | 1 | 300 | 80 | 60% hydrogenation | |
| benzene | 200 | 0.125 | 16 | 600 | 100 | cyclohexane (19) | 20 |
| benzene | 100 | 0.400 | 24 | 600 | 100 | cyclohexane (83) | |
| *p*-xylene | 160 | 0.050 | 30 | 800 | 100 | 1% hydrogenation | 1 |

to the free acid.

Bailar[5b] established that the oxidation state of the palladium in phosphine-anchored XAD-4 beads was 2+ by treating the polymer with ethanolic cyanide to remove the Pd(II). We have utilized this technique on our anthranilic acid anchored beads and find that 90% of the palladium is removed from once-used beads (virtually the same degree of removal observed by Bailar). Furthermore, the beads displayed only 1% of their original hydrogenation activity after treatment.

Additional evidence for Pd(II) was gained by XPS studies. The $3d_{3/2}$ and $3d_{5/2}$ levels of palladium metal are reported to be at 340.9 and 335.7 eV, respectively.[9] Several Pd(II) complexes (no amine complexes were included in the study) have binding energies of 341.9–344.4 and 336.6–339.6 eV, respectively, for these levels.[9a] Peaks occur at 342.3 and 337.0 eV in the unused catalyst and at 342.0 and 336.5 eV in a once-used (for 1,3-COD hydrogenation) catalyst; these energies are clearly in agreement with those expected for Pd(II).

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**Norman L. Holy**

*Department of Chemistry*
*Western Kentucky University*
*Bowling Green, Kentucky 42101*