mg (0.10 mmol) of $Pd(OAc)_2$, 1.4 mL (10 mmol) of triethylamine, and 4 mL of acetonitrile. The tube was then flushed with argon, capped, and placed in the steam bath and stirred at 100 °C for 3.5 h. At the end of this time GLC analysis showed that all of the halide had reacted. The reaction tube was filled with a solid. The solid was filtered and washed with CH_3CN. Recrystallization from a large volume of benzene gave a 55% yield (1.56 g) of light tan needles: mp 275–278 °C.

Quinoline from Acrolein Dimethyl Acetal. In a heavy-walled Pyrex tube equipped with a stirring bar were placed 2.19 g (10 mmol) of 2-iodoaniline, 1.25 g (12.5 mmol) of acrolein dimethyl acetal, 22.4 mg (0.10 mmol) of $Pd(OAc)_2$, 1.4 mL (10 mmol) of triethylamine, and 4 mL of acetonitrile. The tube was flushed with argon and capped. It was then placed in the steam bath and stirred at 100 °C for 72 h. At this time GLC analysis showed that all of the halide had reacted. The products were isolated by evaporating the acetonitrile under reduced pressure and treating the residue with 10% HCl. An ether extraction of the acidic solution removed the 2-quinolone. Evaporation of the ether gave a 32% yield of product: mp 161–162 °C. The acidic solution was then basified with $NaHCO_3$ and extracted with ether. Evaporation of the ether and distillation, bp 115–117 °C (0.25 mm), gave quinoline in 53% yield.

Methyl 1,3-Dihydrobenzo[*c*]furan-1-ylacetate. In a heavy-walled Pyrex tube were placed 1.87 g (10 mmol) of *o*-bromobenzyl alcohol, 1.12 mL (12.5 mmol) of methyl acrylate, 22.4 mg (0.10 mmol) of $Pd(OAc)_2$, 60.8 mg (0.20 mmol) of tri-*o*-tolylphosphine, and 5 mL of triethylamine. The tube was flushed with argon, capped, and placed in a steam bath for 72 h. At this time the reaction mixture was filtered to remove amine salt. The salt was washed with ether and the filtrate was diluted with water. The ether layer was separated, dried over $MgSO_4$, filtered, and concentrated. Distillation of the residual oil afforded the product in 68% yield: bp 115 °C (2 mm).

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Registry No.—3-Phenylhexane, 4468-42-2; acrolein dimethyl acetal, 6044-68-4; methyl 1,3-dihydrobenzo[*c*]furan-1-ylacetate, 66416-76-0.

Supplementary Material Available: Table III with physical properties and spectra of the products prepared (2 pages). Ordering information is given on any current masthead page.

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[Poly(styryl)bipyridine]palladium(0)-Catalyzed Isomerization of Quadricyclene[1]

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The isomerization of quadricyclene is catalyzed by [poly(styryl)bipyridine]palladium(0). The rate of isomerization increases with increased metal loading and with increased amounts of added catalyst, but decreases with increasing concentration of quadricyclene. Significantly decreased activity is observed on reuse of the catalyst, due in part to leaching of the metal. However, on a gram to gram basis, [poly(styryl)bipyridine]palladium(0) is ~30 times as active as 10% Pd/C. Even after two cycles, the recovered catalyst is as active as Pd/C.

The photochemical synthesis of quadricyclene from norbornadiene was first reported by Hammond, Turro, and Fischer in 1961.[2] In spite of a strain energy of ~80 kcal/mol[3] quadricyclene is thermally stable, the half life for rearrangement to norbornadiene being greater than 14 h at 140 °C.[2] However, this rearrangement is efficiently homogeneously catalyzed by a number of transition metal ions at or even below room temperature.[4]

For several reasons the interconversion of norbornadiene and quadricyclene has attracted attention as a model system for solar energy storage and utilization. Both isomerizations can be conducted efficiently under conditions where only very minor amounts of side products are produced. Quadricyclene has a high volumetric storage capacity[3b] and norbornadiene is readily available at relatively low cost.

One of the most reasonable designs for this type of solar energy utilization involves conducting the two isomerizations in separate chambers. This would require the development of heterogeneous catalysts, at least for the isomerization of quadricyclene to norbornadiene, but probably for the photochemical process as well. Some work in development of polymer bound catalysts for the photochemistry[9] and the isomerization of quadricyclene[10] has been reported. In the latter case, King has found that a polystyrene anchored phosphinepalladium(II) chloride catalyst was ca. 1000 times less active than the soluble $((C_6H_5)_3P)_2PdCl_2$. Moreover, extensive loss of catalytic activity was observed after several cycles of use.[10] King also reported the use of a polymer bound cobalt porphyin system which was more active than the palladium system, but which was subject to deactivation through oxidation.

We have recently reported the preparation of poly(styryl)-bipyridine.[11] This material holds promise as a polymer support for the preparation of a large number of heterogeneous transition metal catalysts.[1,12] We have examined the use of a variety of transition metal complexes of poly(styryl)bipyridine as catalysts for the quadricyclene to norbornadiene isomerization. We report the results of that work here.

Results and Discussion

Several transition metal complexes of poly(styryl)bipyridine were tested as catalysts for the isomerization of quadricyclene to norbornadiene. These included complexes of silver, nickel, cobalt, and palladium. The only complex of poly(styryl)bipyridine which was an effective catalyst involved Pd(0). Interestingly, [poly(styryl)bipyridine]palladium(II) acetate showed no catalytic activity.

The preparation of [poly(styryl)bipyridine]palladium(0),

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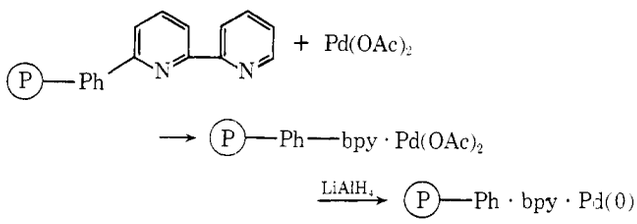
Table I. Rate of Isomerization of Quadricyclene[a]

no.	wt of catalyst, mg	% Pd[b]	cycle of catalyst	quantity of quadricyclene, g	T_{50},[c] min	no. of runs
1	100	7.59	1st	1.1	40 ± 2	3
2	100	7.17	1st	1.1	130	1
3	200	7.59	1st	1.1	12 ± 2	2
4	200	(7.59)	2nd	1.1	240 ± 100	2
5	200	(7.59)	3rd	1.1	380 ± 20	2
6	200	(7.59)	4th	1.1	450	2
7	200	2.03	1st	0.35	7	1
8	200	2.03	1st	0.75	56	1
9	200	2.03	1st	1.15	240	1
10	200	2.03	1st	1.7	500	1

[a] In all reactions, quadricyclene was added by syringe to 10 mL of dry toluene. An aliquot was removed for analysis by GLC. The catalyst was then added to the stirred solution. [b] Determined by elemental analysis (Spang Microanalytical Lab). [c] Time required for the amount of quadricyclene to decrease to half its original value.

illustrated below, involves the lithium aluminum hydride reduction of [poly(styryl)bipyridine]palladium(II) acetate.[12] Quadricyclene was prepared according to the procedure of



Smith[13] and distilled over potassium before use.

In a typical reaction, 1.1 g of the quadricyclene was added to 10 mL of toluene (distilled over sodium and stored over 4A molecular sieves) at room temperature. A given amount of [poly(styryl)bipyridine]palladium(0) was added to the stirred solution and the progress of the isomerization was followed by GLC using a 2 m × 0.25 in. column packed with 10% tris(cyanoethoxy)propene over Chromosorb W at 90 °C.

The reaction does not follow simple first-order kinetics. The most convenient way of presenting the data is in terms of the time required for the reaction to consume 50% of the original quadricyclene (T_{50}). (This is not to be confused with the half-life of the reaction as progressively longer periods of time are required for each depletion of starting material to 50% of the preceding value.) The data are presented in Table I.

Several conclusions are apparent. First, the rate of isomerization increases with increasing metal loading. The rate of isomerization also increases with increasing amount of catalyst used. Third, the rate of isomerization greatly decreases on reuse of catalyst. Interestingly, even during the third use, the catalyst is as active as an equal weight of fresh 100% palladium on carbon (T_{50} = 350 min under the same conditions).

The decrease in rate is accompanied by some leaching of the metal. After four cycles, the amount of palladium decreased from 7.59 to 6.82%. Comparison of the data from runs 6 and 9 suggests that this leaching is not sufficient, in itself, to account for the decreased activity on reuse of the catalyst.

There was no significant difference in activity when the catalyst was isolated before the second use as compared to when a second portion of quadricyclene was added to the original solution. The reaction solution itself, after removal of the catalyst by filtration, does not catalyze isomerization; therefore, any leached metal must be in an inactive form.

The reaction is not effected by the presence of oxygen or acetophenone, a typical photosensitizer. No differences in reaction rate were observed when the reaction was carried out under nitrogen instead of in the atmosphere. The addition of 5% acetophenone (relative to the amount of quadricyclene) at the beginning of the catalytic isomerization did not result in a significant rate change. Only acetophenone and norbornadiene were observed by NMR and GLC after 48 h. These results suggest that it may be possible to construct a solar energy system which involves a homogeneous photosensitizer.

Comparison of the data from runs 7–10 demonstrates a significant rate decrease as the original concentration (and total amount) of quadricyclene is increased. Since this observation may be connected with the mode of catalyst inactivation, several additional experiments were carried out.

First, pretreatment of the catalyst with norbornadiene decreases the activity. In one example, 100 mg of [poly(styryl)bipyridine]palladium(0) (0.02 mequiv of Pd) was stirred in a toluene solution of norbornadiene for >2 h. The polymer was isolated by filtration, thoroughly washed, and then used to catalyze the quadricyclene isomerization. The T_{50} observed for this process was >15 h, substantially longer than the T_{50} = 380 ± 40 min observed for fresh catalyst under otherwise identical conditions. Three of the more probable explanations for the deactivation of the catalyst under these conditions include: oxidation of the Pd(0) to an inactive Pd(II) state; irreversible poisoning of the catalyst by some impurity not removed in the purification of the norbornadiene; or, some inactivation caused by interaction of the catalyst with norbornadiene.

To evaluate the possibility of catalyst poisons, a toluene solution of quadricyclene was stirred in the presence of [poly(styryl)bipyridine]nickel(II) chloride for 2 h before the introduction of the [poly(styryl)bipyridine]palladium(0). The reaction rate was nearly identical to that in the absence of the nickel compound. This result suggests that the presence of small amounts of catalyst poisons in the reaction solution is unlikely. Any strongly complexing poison would be expected to complex to nickel approximately as well as to palladium. Removal of any of the poison in this manner should result in a rate increase. This was not observed.

Used catalyst was treated with lithium aluminum hydride and then reused. This should reactivate the catalyst if oxidation were an important process. Unfortunately, the catalyst is not reactivated in this manner. In one example, 100 mg of [poly(styryl)bipyridine]palladium(0) (0.02 mequiv of Pd) was used in a standard isomerization procedure with T_{50} = 38 ± 40 min. This material was treated with 0.5 molar equiv of $LiAlH_4$ in tetrahydrofuran and, after appropriate workup, was reused as catalyst. This time a T_{50} > 22 h was observed. Thus, reversible oxidation to palladium(II) is not responsible for catalyst deactivation.

The most reasonable mechanism of catalyst inactivation involves the interaction of palladium(0) with norbornadiene

in some apparently irreversible manner, although the possibility of the presence of a very selective poison has not been rigorously excluded.

Experimental Section

Unless otherwise indicated, all elemental analyses were performed by Spang Microanalytical Laboratory. Infrared spectra were obtained on a Perkin-Elmer 337 grating infrared spectrophotometer and nuclear magnetic resonance spectra on either a Varian Associates CFT-20 or A-60 NMR spectrophotometer.

Polymer Bound Bipyridine (1). Polystyrene–2% divinylbenzene copolymer beads (50 g, ca. 0.4 mol of phenyl residues), 6 mL (0.1 mol) of bromine, and 1 g of ferric chloride were added to 500 mL of chloroform and the resulting red solution was stirred at room temperature for 48 h. Aqueous sodium bisulfite was carefully added to the solution until nearly all of the unreacted bromine was converted to bromide. The supernatant aqueous layer was periodically decanted off and discarded. The resulting chloroform suspension was filtered through fritted glass. The polymer was washed extensively with benzene, acetone, water, hexane, and ether. The pale yellow polymer was dried in a vacuum oven at ca. 60 °C for 6–8 h.

The brominated polymer (8 g, ca. 0.02 mol of bromophenyl residues) was added to 100 mL of dry THF in a three-neck 500-mL round-bottom flask fitted with a condensor, nitrogen inlet, and rubber septum. The system was purged with nitrogen and maintained under a positive nitrogen pressure. The solution was cooled to 0 °C and *n*-butyllithium (20 mL of a 2.2 M solution in hexane, 0.044 mol) was added via syringe to yield a pinkish solution. The solution was allowed to stir at 0 °C for 45 min and was then allowed to warm to room temperature. After stirring for 1 h at room temperature, bipyridine (7.5 g, 0.048 mol) was added as a solid. An immediate color change from red-brown to dark purple was observed. The solution was brought to reflux and maintained at reflux for 3 h. The reaction solution was allowed to cool to room temperature and air was bubbled through the solution until the entire solution had become golden yellow. The resulting polymer was separated by filtration through fritted glass and was thoroughly washed with THF, benzene, and ethyl acetate.

The infrared spectra (KBr pellet) has been presented elsewhere.[12]

Polymer Bound (Bipyridine)palladium(II) Acetate (2). Palladium acetate (1 mmol, 0.22 g) was dissolved in 50 mL of THF and a 100-mL round-bottom flask. Polymer **1** (1 g) was added, the flask was stoppered, and the solution was stirred at room temperature overnight. The resulting polymer was isolated by filtration through fritted glass and thoroughly washed with THF, benzene, and ethyl acetate in repeated cycles until at least three complete cycles were color free.

The presence of the acetate ligands is evident from the IR spectrum which includes bands at 1560 and 1545 cm^{-1}.[14]

Reduction of [Poly(styryl)bipyridine]palladium Acetate. Lithium aluminum hydride (76 mg, 2 mmol) was added to 50 mL of dry tetrahydrofuran. Polymer **2** (1 g) was added and the resulting solution was stirred for 2 h. The black polymer was isolated by filtration through fritted glass and washed thoroughly with ethyl acetate, tetrahydrofuran, dilute acetic acid, and aqueous sodium bicarbonate. The IR spectrum of the product was similar to that of **2** except for the loss of the bands at 1560 and 1545 cm^{-1}. The amount of palladium incorporation was determined by elemental analysis.

Quadricyclene. Quadricyclene was prepared by the method of Smith[13] and was refluxed over potassium for several hours and then distilled over potassium before use. This method resulted in receipt of a mixture containing ca. 10% norbornadiene and ca. 90% quadricyclene determined by GLC analysis.

Isomerization of Quadricyclene. In a typical procedure 1.1 g of quadricyclene was added to 10 mL of dry toluene (distilled over sodium). The reaction solution was stirred and an aliquot was removed for examination by GLC. This involved use of a 2 m × 0.25 in. column packed with 10% tris(cyanoethoxy)propane on Chromosorb W at 90 °C in an H.P. 5710 A gas chromatograph with flame ionization detector. This allowed clean separation of norbornadiene, quadricyclene, and toluene. The relative amounts of norbornadiene and quadricyclene were determined by disk integration.

[Poly(styryl)bipyridine]palladium(0) (200 mg) was added to the stirred reaction mixture. Aliquots were taken periodically (usually 25-min intervals) and analyzed by GLC. The reaction was clean and no other products were observed. The data from this and other runs are presented in Table I.

Two other runs were carried out under conditions nearly identical to those described above. In one case the reaction was conducted under nitrogen; in the other case, 5 mol % acetophenone was added to the initial reaction mixture. No change in kinetic behavior was observed in either case.

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Registry No.—Poly(styrene)divinylbenzene copolymer, 9003-70-7; 2,2′-bipyridine, 366-18-7; palladium, 7440-05-3; quadricyclene, 278-06-8.

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