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Polymer-Anchored Cobalt Tetraarylporphyrin Catalysts for the Conversion of Quadricyclane to Norbornadiene¹

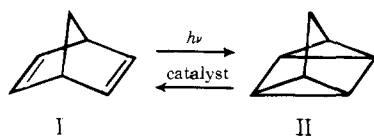
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Methods are described for the preparation of carboxamide- and sulfonamide-linked polystyrene-anchored cobalt(II) tetraarylporphyrins containing 0.28 to 0.44% cobalt, which are highly active catalysts for the conversion of quadricyclane to norbornadiene. These cobalt catalysts gradually lose some of their activity upon repeated recycling. This loss in catalytic activity apparently arises from partial oxidation, since the loss of catalytic activity can be partially restored by treatment with a strong reducing agent such as titanium(III). The apparent activities of these catalysts are increased if the catalyst is finely powdered, thereby suggesting diffusion limitation of the catalytic activity. Applications are discussed of these catalysts in a proposed solar energy storage system based on the reversible valence isomerization of norbornadiene to quadricyclane.

The photosensitized conversion of norbornadiene (I) to quadricyclane (II) coupled with the transition metal complex catalyzed reversion of quadricyclane to norbornadiene presents a promising system for solar energy storage.²⁻⁴ Both components I and II are liquids, with norbornadiene being



readily available and relatively inexpensive. Quantitative conversion of quadricyclane to norbornadiene produces 1.15×10^6 J/L.⁵ Quadricyclane is stable indefinitely under ambient conditions but can be rapidly converted to norbornadiene in the presence of appropriate catalysts.^{6,7}

Since 1975 at the University of Georgia we have been studying appropriate sensitizers and catalysts for a model solar energy storage system based on this reversible valence isomerization of norbornadiene (I) to quadricyclane (II). In this connection we are studying both sensitizers and catalysts immobilized on macroreticular polystyrene beads. In an actual solar energy system based on this principle such isolation of the sensitizer is an attractive option, but similar isolation of the catalyst is mandatory in order to keep the active catalyst away from the photochemical reactor where the conversion of norbornadiene (I) to quadricyclane (II) is taking place.

Previous papers from this laboratory have discussed research directed toward the development of new sensitizer structures,^{4,8,9} or toward the immobilization of sensitizers on polystyrene beads.² This paper discusses the preparation of

an immobilized catalyst for the conversion of quadricyclane (II) to norbornadiene (I).

An ideal catalyst for the conversion of quadricyclane (II) to norbornadiene (I) in a solar energy storage system should meet several requirements: (1) the active species should not be leached by the hydrocarbon reaction mixture; (2) it should not produce undesirable side reactions such as polymerization or dimerization; (3) it should be sufficiently active to evolve heat rapidly upon contact with quadricyclane. Cobalt(II) tetraarylporphyrins^{10,11} covalently bonded to macroreticular polystyrene¹² were chosen as the most likely candidates for a catalyst to meet these criteria. In this work we have developed new methods for anchoring cobalt tetraarylporphyrins to polystyrene through carboxamide and sulfonamide linkages. Such a procedure has allowed us to obtain routinely polystyrene-anchored cobalt(II) tetraarylporphyrins containing 0.3 to 0.5% cobalt.

Results and Discussion

Syntheses of the Catalysts (Figure 1). Macroreticular polystyrene beads cross-linked with 20% divinylbenzene (Dow XFS 4022) were nitrated with nitric acid in acetic anhydride at room temperature.¹³ The reaction proceeded at a moderate rate allowing control of the extent of the reaction by varying the time (see Experimental Section). Reduction of the resulting nitropolystyrene with stannous chloride in hydrochloric acid-acetic acid gave essentially complete conversion of the pendant nitro groups to amino groups. The completeness of the reduction was conveniently checked by noting the disappearance of the nitro infrared absorptions at 1521 and 1349 cm^{-1} while the presence of amino groups in the reduced

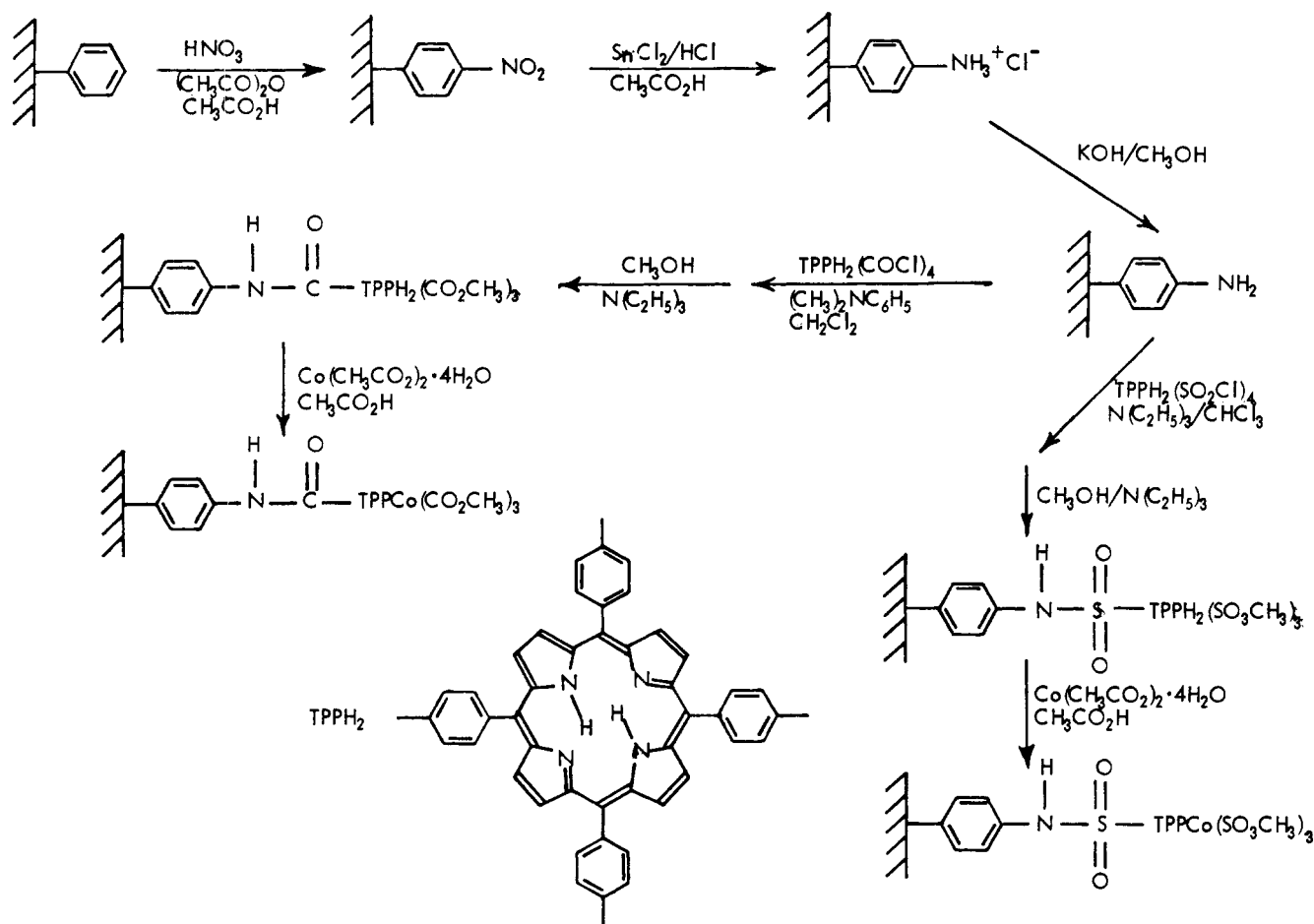


Figure 1. General outline of the schemes for the syntheses of the polystyrene-anchored cobalt(II) tetraarylporphyrins.

product was confirmed by the appearance of an infrared absorption at $\sim 2400\text{ cm}^{-1}$ due to $\text{RNH}_3^+\text{Cl}^-$.

Triethylammonium and sodium (*p*-sulfonatophenyl)porphyrin were prepared from ammonium (*p*-sulfonatophenyl)porphyrin¹⁴ by metathesis with triethylamine and cation exchange, respectively. Treatment of either salt with thionyl chloride provided tetrakis[*p*-(chlorosulfonyl)phenyl]porphyrin which, except for complete removal of excess thionyl chloride, was used for the synthesis without further purification.

Addition of aminopolystyrene to a solution of tetrakis[*p*-(chlorosulfonyl)phenyl]porphyrin and triethylamine in either chloroform, dichloromethane, or tetrahydrofuran gave, after an extended reaction period, a blue-black polymer presumed to have the free base porphyrin attached to the polystyrene backbone through a sulfonamide linkage. Treatment with a mixture of methanol and triethylamine allowed the methanolysis of unreacted chlorosulfonyl groups. In all cases an extraneous precipitate, generally in small quantity, was observed after the reaction of the aminopolystyrene with the tetrakis[*p*-(chlorosulfonyl)phenyl]porphyrin; this precipitate disappeared during isolation of the product. Tetrahydrofuran appeared to be a rather poor solvent for this reaction since in all cases rather large amounts of this precipitate remained at the end of the reaction and occasionally the reaction failed.

An analogous series of reactions starting from tetrakis(*p*-carboxyphenyl)porphyrin was used to produce a carboxamide-linked polystyrene-bound porphyrin. *N,N*-Dimethylaniline was the preferred base of the coupling of the aminopolystyrene with the tetrakis[*p*-(chloroformyl)phenyl]porphyrin since addition of triethylamine to the carbonyl chloride rapidly produced a precipitate of unknown composition.

A description of the reaction conditions for the preparation

of each batch of the polystyrene-anchored cobalt(II) tetraarylporphyrin catalysts is given in Table I.

The cobalt was incorporated into the polystyrene-anchored tetraarylporphyrins using cobalt(II) acetate in boiling acetic acid under nitrogen. The cobalt-containing catalysts are stable to air when dry.

The visible spectrum of the aminated polystyrene is essentially featureless between 350 and 800 nm. The sulfonamide-linked free base porphyrin polymer showed absorptions at 427, 526, 556, 598, and 654 nm with the 427-nm peak being by far the most intense. After cobalt incorporation, spectra of both carboxamide-linked and sulfonamide-linked porphyrin polymers showed two strong absorptions at 425 and 435 nm with the 425-nm peak being somewhat the less intense of the two and generally appearing as a shoulder on the 435-nm peak. A weaker absorption at 540 to 550 nm is the only detectable feature at longer wavelength, indicating essentially complete cobalt incorporation into the porphyrin.

Spectral changes produced by oxidation and reduction were examined for a single batch of polymer (2B-1). Treatment of the sulfonamide-linked cobalt porphyrin polymer with either methanolic Ti(III) or methanolic Cr(II) reduced the relative intensity of the 425-nm peak when compared to the 435-nm peak, while treatment with dilute hydrogen peroxide in methanol slightly increased the relative intensity of the 425-nm peak. The peak at 425 nm may thus be ascribed to the Co(III) porphyrin and the peak at 435 nm to the Co(II) porphyrin. As prepared, the catalyst contains both cobalt oxidation states.

Activities and Stabilities of the Polystyrene-Anchored Cobalt(II) Tetraarylporphyrins as Catalysts. Treatment of 0.1 g of the polystyrene-anchored cobalt(II) tetraarylporphyrin with 1 to 2 mL of quadricyclane results in the rapid

Table I. Preparation of the Polystyrene-Anchored Cobalt(II) Tetraarylporphyrin Catalysts

catalyst batch no.	conversion of the porphyrin to the acid chloride		polymer anchoring of the acid chloride				reaction		anal. (%) after metal incorporation
	materials	time h	aminopolystyrene used batch	amount, g	solvent (mL)	base (mL)	temp, °C	time, h	
1A-1	2.61 g H ₂ TPP(CO ₂ H) ₄ , 20 mL SOCl ₂ , 20 mL C ₆ H ₅	2	1A	9.26	THF (100)	Et ₃ N (10)	65	12	0.44 Co; 1.43 N
2A-1	3.01 g [Et ₃ NH] ₄ H ₂ TPP(SO ₃) ₄ , 40 mL SOCl ₂ , 20 mL CHCl ₃	3	2A	5.02	CHCl ₃ (150)	Et ₃ N (10)	25	18	0.45 Co; 1.30 N; 0.95 S
2A-2	0.515 g [Et ₃ NH] ₄ H ₂ TPP(SO ₃) ₄ , 40 mL SOCl ₂ , 20 mL CHCl ₃	3	2A	5.00	CHCl ₃ (150)	Et ₃ N (10)	25	18	0.34 Co
2B-1	0.510 g [Et ₃ NH] ₄ H ₂ TPP(SO ₃) ₄ , 40 mL SOCl ₂ , 20 mL CHCl ₃	3	2B	5.02	CHCl ₃ (150)	Et ₃ N (10)	25	18	0.31 Co
2B-2	3.064 g [Et ₃ NH] ₄ H ₂ TPP(SO ₃) ₄ , 40 mL SOCl ₂ , 20 mL CHCl ₃	3	2B	4.14	CHCl ₃ (150)	Et ₃ N (10)	25	18	0.28 Co; 1.24 N; 0.88 S
2B-3	1.46 g H ₂ TPP(CO ₂ H) ₄ , 50 mL SOCl ₂ , 5 mL C ₅ H ₅ N	3	2B	3.05	CH ₂ Cl ₂ (70)	PhNMe ₂ (10)	25	18	0.45 Co
2B-4	0.493 g Na ₄ H ₂ TPP(SO ₃) ₄ , 40 mL SOCl ₂ , 5 mL C ₅ H ₅ N	4	2B	2.00	CH ₂ Cl ₂ (60)	Et ₃ N (10)	25	18	0.48 Co; 1.31 N; 0.70 S

generation of heat. Within 15 to 60 s the liquid begins to boil vigorously. After 5 min, more than 99% conversion of quadricyclane to norbornadiene had occurred based on gas chromatographic analysis of the liquid. Clearly these polystyrene-anchored cobalt(II) tetraarylporphyrins meet the requirement of rapid generation of heat with quadricyclane required for the energy release step of the solar energy storage system.

A more detailed analysis was undertaken of the kinetics of the conversion of quadricyclane to norbornadiene catalyzed by these polystyrene-anchored cobalt(II) tetraarylporphyrins. The disappearance of quadricyclane, initially 0.1 M, in benzene at 30 ± 0.2 °C was monitored by gas chromatography with 0.025 M of *p*-xylene as an internal standard. A first-order plot of ln [quadricyclane] vs. time gave a straight line within experimental error. In addition, a linear least-squares treatment of the data as a first-order reaction gave observed rate constants (k_0) with σ_{k_0}/k_0 less than 2% over four to six half-lives. There was thus ample justification for treating the kinetics of these systems as first order in quadricyclane.

The standard activities (designated as k_w in Table II) for each batch of catalyst were obtained as the first-order rate constant normalized to 1 g of catalyst in 1 L of solution. The standard activities listed in Table II were obtained from experiments with 0.1 g of catalyst in 10 mL of solution and represent the means of at least four determinations made on the first run of fresh catalyst.

The activities of both carboxamide-linked and all five sulfonamide-linked catalyst batches are quite similar with k_w varying only from 0.88×10^{-4} to $2.42 \times 10^{-4} \text{ s}^{-1} (\text{g/L})^{-1}$ while the activity based on cobalt content (k_m in Table II) varies from 1.8 to $3.9 \text{ s}^{-1} (\text{mol/L})^{-1}$. No correlation of catalytic activity with cobalt content is immediately apparent. This lack of correlation probably arises from variations in the ratio of Co(II) to Co(III) among the various batches. Analytical data

Table II. Standard Activities of the Polystyrene-Anchored Cobalt(II) Tetraarylporphyrin Catalysts for the Conversion of Quadricyclane to Norbornadiene

batch ^a	link-age ^b	% Co	mol of Co × 10 ⁵ /g	$k_w \times 10^4, \text{ s}^{-1} (\text{g/L})^{-1}$	$k_m, \text{ s}^{-1} (\text{mol/L})^{-1}$
1A-1	C	0.44	7.5	2.42 (0.23) ^c	3.2 (0.31) ^c
2A-1	S	0.45	7.6	1.95 (0.19)	2.6 (0.25)
2A-2	S	0.34	5.8	2.15 (0.11)	3.7 (0.20)
2B-1	S	0.31	5.3	2.07 (0.13)	3.9 (0.25)
2B-2	S	0.28	4.8	0.88 (0.052)	1.8 (0.11)
2B-3	C	0.45	7.6	1.37 (0.11)	1.8 (0.15)
2B-4	S	0.48	8.2	1.73 (0.13)	2.1 (0.16)

^a The batch numbers refer to the preparations in Table I. ^b C = carboxamide linked; S = sulfonamide linked. ^c The figures in parentheses in these columns refer to standard deviations obtained from four or more runs.

also suggest some nonporphyrin, and thus inactive,¹⁰ cobalt is present. Thus the S/Co ratios for batches 2A-1 and 2B-4 are 3.9 and 2.7, respectively, whereas a minimum of 4 is expected from the parent cobalt tetrakis(sulfonatophenyl)porphine.

The retention of the catalytic activity of batch 1A-1 after repeated use was examined (Table III). A single charge of this catalyst was repeatedly treated with new batches of 1.0 M quadricyclane in mixed xylenes. The disappearance of quadricyclane vs. an internal benzene standard was monitored by gas chromatography. A good correlation was observed of the decrease in catalytic activity with the total volume of the solution to which the catalyst was exposed. More specifically, a linear least-squares plot of k_w vs. V_T (total volume of quadricyclane solutions) gives a slope of $-1.35 \times 10^{-6} \text{ s}^{-1} (\text{g/L})^{-1} \text{ mL}^{-1}$ with an extrapolated V_T intercept of 127 mL corresponding to an average turnover number, based on cobalt content, in excess of 15 000.

A 0.107-g charge of catalyst batch 2A-1 was examined extensively for loss of activity upon repeated recycling using 0.1 M quadricyclane in benzene (Table IV). The loss in activity is clearly not as regular as that with 1 M quadricyclane (Table III) but is definitely present. Treatment of catalyst, partially deactivated through repeated use, with solutions of titanium(III) in organic solvents^{15,16} restored some of the lost catalytic activity but never returned the catalytic activity to that of the fresh catalyst. Treatment of the deactivated catalyst with the stronger reducing agent potassium benzophenone ketyl also partially restored the catalytic activity but concurrently produced a green species. The ability of reducing agents such as titanium(III) and potassium benzophenone ketyl to restore partially the loss of activity upon repeated use of these polystyrene-anchored cobalt(II) tetraarylporphyrin

Table III. Recycling Studies on the Carboxamide-Linked Polystyrene-Anchored Cobalt(II) Tetraarylporphyrin Catalyst for the Conversion of Quadricyclane to Norbornadiene^a

run no.	$k_w \times 10^4, \text{ s}^{-1} (\text{g/L})^{-1}$	$V_T, \text{ mL}^c$
1	1.58 (0.015) ^b	10.2
2	1.46 (0.0073)	20.1
3	1.30 (0.0090)	30.2
4	1.16 (0.0065)	40.3
5	0.903 (0.0068)	61.1

^a These runs used 0.1096 g of batch 1A-1 of the carboxamide-linked polystyrene-anchored cobalt(II) porphyrin and 1.0 M quadricyclane in mixed xylenes. ^b The figures in parentheses in this column represent the errors in the first-order kinetic plots, volumes of solutions, and initial weights of the catalyst but do not include variation in temperature (±0.2 °C) or physical loss of catalyst. ^c These figures represent the total volume of solution to which the catalyst was exposed including that for the listed run.

Table IV. Studies on the Regeneration of Recycled Catalyst Using Reducing Agents^a

run/operation	$k_w \times 10^4, \text{s}^{-1} (\text{g/L})^{-1}$
1	2.59 (0.042) ^b
2	1.84 (0.047)
3	1.44 (0.019)
4	1.29 (0.013)
5	1.39 (0.012)
6	1.31 (0.011)
Reduction with Titanium(III) Solution A1 ^c (5 mL for 30 min)	
7	1.67 (0.022)
8	1.56 (0.013)
Reduction with Titanium(III) Solution A2 ^c (5 mL for 30 min)	
9	1.71 (0.012)
10	1.55 (0.012)
11	1.46 (0.0090)
12	1.39 (0.0079)
13	1.37 (0.0082)
14	1.34 (0.0099)
15 ^d	0.69 (0.0037)
16 ^d	0.50 (0.0081)
17	0.53 (0.0075)
Reduction with Titanium(III) Solution A2 ^c (10 mL for 45 min) ^e	
18	0.73 (0.0090)
Reduction with Titanium(III) Solution B ^c (5 mL for 1 h)	
19	0.83 (0.0086)
Reduction with Titanium(III) Solution B ^c	
20	0.98 (0.019)
21	0.87 (0.0097)
Reduction with Potassium Benzophenone Ketyl in Tetrahydrofuran	
22	1.07 (0.020)
23	1.04 (0.012)

^a These runs were performed in the indicated sequence using 0.107 g of sulfonamide-linked polystyrene-supported cobalt(II) porphyrin from batch 2A-1 (Table I). Except where indicated 10 mL of 0.1 M quadricyclane in benzene was used. ^b The figures in parentheses in this column represent the error in the first-order kinetics plots, volumes of reaction solutions, and initial weight of the catalyst. Variations in temperature ($\pm 0.2^\circ\text{C}$) and physical loss of catalyst on workup are not included. ^c Details are given in the Experimental Section for the preparations of these titanium(III) solutions by the reductions of methanolic titanium tetrachloride with metallic tin or zinc under various conditions. ^d These runs were made using neat quadricyclane rather than 10 mL of 0.1 M quadricyclane in benzene. ^e Initially 5 mL of the red-brown titanium(III) solution A2 was added to the catalyst. When this was decolorized after 15 min, the remaining 5 mL was added and the mixture stirred for another 30 min.

catalysts suggests that this loss of catalytic activity arises from oxidation of the cobalt(II) porphyrin to the corresponding cobalt(III) porphyrin. The nature of the oxidant is uncertain.

Spectral changes associated with deactivation were examined using a 0.12-g charge of catalyst from batch 2B-1. Treatment with 25 mL of neat quadricyclane resulted in 80% loss of the original activity. A spectrum of the deactivated catalyst revealed the 425-nm peak [Co(III)] to be more intense than the 435-nm peak [Co(II)]; this was an inversion in relative intensity of the two peaks from the fresh catalyst.

The fairly high activity per gram of the polymer-bound cobalt(II) tetraarylporphyrin catalyst, the rather low activity of this catalyst based on metal content compared to that observed in homogeneous systems,¹¹ and the rather great variances in activity obtained for various charges of the same batch of catalyst all suggest that the catalytic activity is limited by diffusion. Since the 0.1-g charge of catalyst used in this

Table V. Activities of Pulverized Samples of the Sulfonamide-Linked Polystyrene-Anchored Cobalt(II) Tetraphenylporphyrin Catalyst for the Conversion of Quadricyclane to Norbornadiene^a

run no.	catalyst wt, mg	vol of soln, mL	$k_0 \times 10^4, \text{s}^{-1}$	$k_w \times 10^4, \text{s}^{-1} (\text{g/L})^{-1}$	$w/v, \text{g/L}^c$
1	6.97	10.50	3.63 (0.078) ^b	5.48 (0.12) ^b	0.66
2	7.56	9.80	4.68 (0.063)	6.07 (0.82)	0.77
3	10.13	10.00	7.29 (0.26)	7.20 (0.27)	1.01
4	15.65	9.96	16.14 (0.26)	10.27 (0.17)	1.57

^a Catalyst batch 2A-1. ^b The figures in parentheses in these columns represent the errors but do not include temperature deviation ($\pm 0.2^\circ\text{C}$). ^c w/v = ratio of the weight of catalyst to the volume of the solution.

study contains relatively few beads (200 to 400 beads estimated), a nonrepresentative distribution of particle sizes might be present in some of these charges. In the presence of such effects, catalyst charges with an excess in small beads would give a greater rate than those with an excess of large beads.

The reduction of the apparent catalytic activity by diffusion was demonstrated by observation of the rates of reaction with several samples of catalyst batch 2A-1 which had been ground to a fine power (Table V). In all experiments with powdered beads, the normalized rate constant (k_w) was greater than the largest k_w for whole beads ($2.59 \times 10^{-4} \text{s}^{-1} (\text{g/L})^{-1}$).

The experiments with ground catalyst also provide some insight into the source of deactivation of the catalyst. If the activity is first order in polymer bound catalyst, and there is a constant concentration of a species in the quadricyclane solution which reacts with the catalyst to give an inactive material, then a plot of k_0 vs. w/V should be linear with a positive w/V intercept, where k_0 is the observed rate constant for the disappearance of quadricyclane, w is the weight of catalyst, and V is the volume of reaction solution. Precisely this behavior is observed: a plot of k_0 vs. w/V gives a straight line with a slope of $1.39 \pm 0.094 \times 10^{-3} \text{s}^{-1} (\text{g/L})^{-1}$ and a w/V intercept of $0.44 \pm 0.045 \text{g/L}$. Additionally, deactivation is indicated by the first-order kinetic plots where a decrease in the apparent rate constant was observed very early in the reaction; the reaction is first order over the final 80% in all cases. Neither complexation with quadricyclane or norbornadiene nor an irreversible side reaction with either material is consistent with the significantly nonzero w/V intercept. Inhibition by norbornadiene could conceivably give a system which would mimic first-order kinetics at high percent conversion, i.e., when the norbornadiene concentration is relatively constant; however, this inhibition is inconsistent with the cumulative deactivation observed with whole beads. Any reaction of quadricyclane with the catalyst leading to catalyst degradation should give poor first-order kinetics over a substantial portion of the reaction; half of the deactivation should occur after the first half-life, while in fact, deactivation is complete within the first half-life. The most consistent explanation is that the observed deactivation arises from interaction of the catalyst with some trace component of the reaction mixture.

Experimental Section

Analytical Methods. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were obtained on a Perkin-Elmer Model 621 spectrometer with grating optics. Ultraviolet and visible spectra were obtained on a Cary Model 15 spectrophotometer.

Gas chromatography was performed with a Varian series 2700 instrument with a flame ionization detector and on column injection. A 10 ft \times 1/8 in. stainless steel column packed with 5% SF-96 1% Apiezon N on 60-80 mesh Chromosorb W/AW-DMCS was employed.

The flow rate of the nitrogen carrier gas was set at 60 mL/min. The column was normally conditioned at 200 °C for 12 h prior to use. Treatment with sulfur in carbon disulfide with the column and injector at 120 °C followed by baking out for 2 h at 200 °C decreased the column isomerization of quadricyclane, particularly in cases where undiluted reaction mixtures were analyzed.

Samples of reaction mixtures were normally diluted in pentane or carbon disulfide (1 to 5% v/v) and analyzed using an injector temperature of 90 °C and a column temperature of 70 °C. Peak area ratios of quadricyclane to internal standard generally gave a (standard deviation)/(value) ratio of less than 1% for three analyses of the same sample. Occasionally it was necessary to analyze the undiluted reaction mixture; a column temperature of 90 °C was employed to speed the analysis at the expense of a small loss in precision.

Visible spectra of polymer bound species were obtained as follows: A sample of polymer was ground to a fine powder in a small ball mill and mixed (1 to 10% by weight) with silica gel (60–200 mesh). This mixture was added to a 1.00-mm path-length cell containing benzene and the spectrum recorded vs. a cell containing silica gel–benzene. Values of λ_{\max} are reasonably reproducible (± 3 nm); however, the observed value of absorbance is somewhat dependent on sample preparation with respect to both polymer particle size and sample homogeneity within the cell. Absorbance is not linearly related to the fraction of polymer in the polymer–silica gel mixture. The relative absorbance of two peaks is roughly comparable among several polymer–silica gel compositions and among the different preparations of the same polymer.

Materials. Thionyl chloride (Baker, practical) was fractionally distilled through a 0.8 × 20 cm Vigreux column. The initial and final 20% of the distillate were both discarded. The retained material was stirred with 5% by volume of triphenyl phosphite for 30 min and distilled through a similar Vigreux column. The very pale yellow to clear fractions were collected and stored in the dark in a brown bottle until use.

Triethylamine and pyridine were stirred with calcium hydride for 12 h and then distilled directly under nitrogen immediately before use. Pyrrole was dried over potassium hydroxide pellets under nitrogen for 24 h and then distilled under reduced pressure into a –78 °C cooled receiver. It was stored under nitrogen until used. Benzaldehyde was distilled immediately before use discarding the initial fraction containing water.

Solvents Used in Syntheses. Propionic acid was dried over P₄O₁₀ for at least 6 h and distilled under reduced pressure. Chloroform and dichloromethane were washed twice with 98% sulfuric acid, once with water, twice with 10% aqueous sodium bicarbonate, and once with water; they were then dried over sodium sulfate followed by calcium chloride and then distilled from P₄O₁₀ under dry nitrogen and stored in the dark under nitrogen. Benzene and tetrahydrofuran were pre-dried over calcium hydride, distilled under nitrogen from potassium benzophenone ketyl, and stored under nitrogen. Methanol was distilled from magnesium methoxide under nitrogen and stored under nitrogen.

Solvents Used in Kinetic Studies. Benzene was distilled through a 2 × 100 cm column packed with glass beads. The fractions containing less than 0.1% extraneous components and free from toluene by gas chromatographic analysis were washed repeatedly with 98% sulfuric acid until the acid was not discolored. They were then washed successively with water, 10% aqueous sodium bicarbonate, and water. The resulting material was dried over potassium hydroxide, distilled successively from P₄O₁₀ and potassium benzophenone ketyl, and stored under nitrogen.

p-Xylene was recrystallized repeatedly from methanol at –78 °C until less than 0.01% toluene was present by gas chromatographic analysis. After two water washes the material was repeatedly washed with 98% sulfuric acid until the acid remained colorless. During these acid washings the temperature of the mixture was kept below 20 °C. The xylene was next washed successively with water, 10% aqueous sodium bicarbonate, and water, dried over potassium hydroxide, and finally distilled over P₄O₁₀.

Mixed xylenes were washed with sulfuric acid and purified further by a procedure similar to that used for *p*-xylene.

Tetraphenylporphine and Tetrakis(*p*-carboxyphenyl)porphine. *meso*-Tetraphenylporphine (TPPH₂) and *meso*-tetrakis(*p*-carboxyphenyl)porphine (H₂TPP(CO₂H)₄) were prepared by the method of Adler and co-workers.¹⁷ Porphines prepared in this manner are known to contain several percent of the corresponding chlorins. However, the presence of this impurity seemed unlikely to interfere with subsequent uses of the materials.

Absorption spectrum of TPPH₂ in benzene:^{18,19} 419 (470), 484 (3.9), 513 (19), 545 (7.9), 590 (5.4), 646 (4.4). Absorption spectrum of

H₂TPP(CO₂H)₄ in pyridine:¹⁴ 423 (418), 486 (3.7), 518 (18), 554 (8.7), 596 (5.4), 653 (4.2).

Ammonium Tetrakis(*p*-sulfonatophenyl)porphine. Ammonium *meso*-tetrakis(*p*-sulfonatophenyl)porphine [(NH₄)₄H₂TPP(SO₃)₄] was prepared by the procedure of Fleischer and co-workers¹⁴ with the following modification: The sulfuric acid reaction mixture, containing the sulfonated porphine diacid, was poured onto three volumes of crushed ice. The resulting solution was slowly added to ice-cold, concentrated, aqueous ammonia. Sufficient ammonia was present to keep the solution blue at all times. Ammonia and water were removed on a rotary evaporator until precipitation occurred. The mixture was filtered. The recovered solid was dried and powdered. The solid was Soxhlet extracted with methanol with further purification following the method of ref 14. Anal. Calcd for (NH₄)₄H₂TPP(SO₃)₄·9H₂O [C₄₄H₆₀O₂₁N₈S₄]: C, 45.4; H, 5.2; N, 9.6; S, 11.1. Found: C, 47.4; H, 5.3; N, 9.8; S, 11.3. Mole ratio N/S: calculated 2.0, found 1.99. Absorption spectrum in deaerated H₂O: 414 (164), 517 (16), 565 (6.6), 583 (6.4), 640 (3.9).

Triethylammonium Tetrakis(*p*-sulfonatophenyl)porphine. A mixture of 5.0 g (4.3 mmol) of (NH₄)₄H₂TPP(SO₃)₄, 10 mL of triethylamine, and 500 mL of methanol was boiled under reflux for 30 min with stirring. Solvent was removed completely on a rotary evaporator at ~25 °C (25 mm). The resulting solid was dried for 12 h at ~25 °C (0.1 mm). The powdered solid was Soxhlet extracted into 125 mL of absolute ethanol containing 0.5 mL of triethylamine. Filtration of the contents of the pot followed by drying of the precipitate at 25 °C (0.1 mm) gave 4.1 g of a purple powder. Additional product (1.2 g) was obtained by evaporation of the filtrate followed by Soxhlet extraction of the recovered solid into a 1:5 ethanol–isopropyl alcohol mixture and recovery as above. The total yield of triethylammonium tetrakis(*p*-sulfonatophenyl)porphine [(Et₃NH)₄H₂TPP(SO₃)₄] was 5.3 g (87%). Anal. Calcd for (Et₃NH)₄H₂TPP(SO₃)₄·4H₂O [C₆₈H₉₈O₁₆N₈S₁₆]: C, 57.9; H, 7.0; N, 7.9; S, 9.1. Found: C, 58.1; H, 7.0; N, 8.0; S, 9.3. Mole ratio N/S: calculated 2.0, found 1.96. Absorption spectrum in deaerated H₂O: 414 (499), 518 (16.), 555 (6.8), 583 (6.5), 640 (4.3).

Sodium Tetrakis(*p*-sulfonatophenyl)porphine. A solution of (Et₃NH)₄H₂TPP(SO₃)₄ (5.11 g, 3.8 mmol) in deionized water was passed through a column containing 450 g of Amberlite IR 120H cation exchange resin in sodium form. A sample of the eluate upon treatment with aqueous sodium hydroxide gave no odor of triethylamine. The eluate was evaporated to dryness on a rotary evaporator and the residue dried at 25 °C (0.1 mm). The crude product was purified by two successive cycles of Soxhlet extraction into dry methanol followed by precipitation with benzene to give, after drying at 25 °C (0.1 mm) for 12 h, gray purple solid sodium tetrakis(*p*-sulfonatophenyl)porphine, [Na₄H₂TPP(SO₃)₄]. Anal. Calcd for Na₄H₂TPP(SO₃)₄·10H₂O [C₄₄H₄₆O₂₂N₄S₄Na₄]: C, 43.9; H, 3.9; N, 4.7; S, 10.7. Found: C, 45.2; H, 3.7; N, 4.7; S, 10.6. Mole ratio N/S: calculated 1.0, found 1.02. Absorption spectrum in deaerated H₂O:¹⁴ 413 (532), 518 (16), 554 (6.6), 582 (6.4), 638 (3.6).

Preparation and Purification of Quadricyclane.^{10,20} A Hanovia 450 W medium-pressure mercury arc housed in a Pyrex immersion well equipped with a nitrogen purge, dry ice condenser, and magnetic stirrer was charged with a mixture of 300 mL of redistilled norbornadiene, 10 mL of acetophenone, and sufficient pentane (~700 mL) to fill the apparatus. Photolysis with a continuous slow nitrogen purge gave 99% conversion in 3 days. The reaction mixture was distilled through a 2 × 100 cm column packed with glass beads. Vacuum was applied to maintain the pot temperature below 80 °C. A 150-mL bright-yellow fraction containing 0.5% norbornadiene was collected. Neither further distillation nor treatment with alumina, silica gel, Norit, or LiAlH₄ decolorized this fraction. However, treatment with potassium metal under nitrogen at 75 °C for 6 h followed by quantitative vacuum distillation into a receiver cooled to –78 °C gave a colorless product. The quadricyclane thus obtained was stored under nitrogen at –10 °C. Gas chromatographic analysis of this quadricyclane indicated 99.4% purity. The major impurity (~0.5%) was norbornadiene. Several components with longer retention times than quadricyclane were minor impurities ($\leq 0.1\%$ total).

Preparation of Aminopolystyrene. Batch 1A. A suspension of 31.76 g (0.305 mol as styrene) of macroreticular polystyrene (Dow XFS 4022) in 122 mL of acetic anhydride was treated at 5 °C with a solution of 9.5 mL (9.4 g of HNO₃, 0.15 mol) of 70% nitric acid in 27 mL of acetic acid. The resulting mixture was stirred for 30 min at 5 °C and then for 4.5 h at room temperature. The reaction mixture was filtered on a frit and the polymer washed with the following solutions in the indicated sequence: (1) twice with acetic acid; (2) successively with tetrahydrofuran–acetic acid mixtures in proportions 1:10, 1:5, 2:3, 1:1, 3:2, 5:1 and 10:1; (3) twice with pure tetrahydrofuran; (4) successively

with methanol-tetrahydrofuran mixtures in the proportions 1:10, 1:5, 2:3, 1:1, 3:2, 5:1, and 10:1; (5) successively with methanol-water mixtures in the proportions 10:1, 5:1, and 1:1; (6) twice with 1:1 methanol-water; (7) three times with sodium bicarbonate in 1:1 methanol-water; (8) twice with 1:1 methanol-water; (9) successively with methanol-water mixtures in proportions 3:2, 5:1, and 10:1; (10) three times with pure methanol. The resulting polymer was air dried until free flowing and finally dried at 25 °C (0.1 mm) for 12 h. The resulting pale yellow-orange nitropolystyrene exhibited strong infrared bands (1% in KBr) at 1521 and 1349 cm^{-1} not present in the original polystyrene indicative of aromatic nitro groups. Elemental analysis on this polymer gave 1.83% nitrogen indicating 14% nitration of the benzene rings in the polystyrene.

The nitropolystyrene was reduced to aminopolystyrene using stannous chloride. A mixture of 20.0 g (0.0261 mol of nitro groups), 80 mL of acetic acid, and a solution of 22.0 g (0.11 mol) of stannous chloride dihydrate in 24 mL of concentrated hydrochloric acid was degassed and then stirred for 48 h at room temperature. The mixture was filtered on a frit; the polymer was stirred with a 1:4 mixture of concentrated hydrochloric acid and acetic acid for 30 min and the liquid was removed by filtration. The HCl-acetic acid wash was repeated four additional times. The polymer was then slurried with 20 mL of a 1:4 concentrated hydrochloric acid-acetic acid mixture. Tetrahydrofuran was added to the stirred slurry in increments of 5, 5, 10, 10, 10, 20, 20, 20, 30, 30, and 40 mL at 5-min intervals. The liquid was removed by filtration and the polymer was washed twice with tetrahydrofuran and once with methanol. The resulting polymer was air dried until free flowing and then dried under vacuum at 25 °C (0.1 mm) for 18 h.

The pale yellow polymer exhibited an infrared band (2% in KBr) at 2400 cm^{-1} indicating the presence of amine hydrochloride but still exhibited the nitro bands at 1521 and 1349 cm^{-1} indicating incomplete reduction of the aromatic nitro groups. Elemental analysis indicated 1.56% nitrogen and 2.04% chlorine corresponding to 1.1 mmol of nitrogen and 0.57 mmol of chlorine per g indicating a minimum of 52% reduction of the nitro groups.

Study on the Rate of Nitration of Polystyrene. A 20.1-g sample of macroreticular polystyrene beads (0.193 mol as styrene) was nitrated using 77 mL of acetic anhydride, 6.1 mL (6.05 g, 0.096 mol) of 70% nitric acid, and 17 mL of acetic acid in a procedure identical to that used for batch 1A above. Samples (2.0 g) were withdrawn after 1, 2, 4, and 4.75 h of reaction and subjected to purification using the procedure given above for the batch 1A nitration. Nitrogen analyses of the resulting nitropolystyrenes gave the following results: 1-h sample, 0.72% N (5.5% ring nitration); 2-h sample, 1.08% N (8.3% ring nitration); 4-h sample, 1.66% N (13.0% ring nitration).

Batch 2A. This procedure eliminated the extensive workup of the nitropolystyrene used in batch 1A; instead the nitropolystyrene was reduced immediately after sufficient washing to remove unreacted nitric acid.

The initial nitration proceeded in a manner completely analogous of that of batch 1A using 50.07 g of the macroreticular polystyrene (Dow XFS 4022, 0.48 mol as styrene), 190 mL of acetic anhydride, 15 mL of 70% nitric acid, and 42 mL of acetic acid. After a total of 5 h of stirring this mixture, the reaction mixture was filtered on a frit. The resulting polymer was stirred five times for 15 min each with portions of acetic acid. The still wet polymer was stirred at 40 °C for 3 days with 200 mL of acetic acid and a solution of 55 g (0.275 mol) of stannous chloride dihydrate in 60 mL of concentrated hydrochloric acid. The resulting aminopolystyrene was washed successively with the following liquids: (1) five times for 15 min each time with a 3:10 mixture of concentrated hydrochloric acid and acetic acid; (2) three times with 3:5:5 hydrochloric acid-tetrahydrofuran-methanol; and (3) twice with methanol. The resulting polymer was dried at 25 °C (0.1 mm) for 24 h. The infrared spectrum of the resulting pale yellow aminopolystyrene exhibited a broad amine hydrochloride band at $\sim 2400 \text{ cm}^{-1}$ and only very weak nitro bands at 1521 and 1349 cm^{-1} . Elemental analyses indicated 0.95% nitrogen and 2.30% chlorine corresponding to 0.68 mmol of nitrogen and 0.65 mmol of chlorine per g of polymer indicating 96% reduction of the nitro groups to amino groups.

Batch 2B. A portion of polymer batch 2A (19.98 g) was reduced by a procedure similar to that used for batch 1A using 100 mL of acetic acid, 41.2 g of stannous dichloride dihydrate, and 50 mL of concentrated hydrochloric acid with a reaction time of 14 h. The infrared spectrum of the resulting polymer was essentially unchanged from that of batch 2A.

Preparation of the Polystyrene-Anchored Cobalt(II) Tetraarylporphyrin Catalysts (Table I). Seven batches of polystyrene-anchored cobalt(II) tetraarylporphyrin were used in this study. The specific quantities of materials and solvents employed in

the preparation of each batch are given in Table I. The procedure reported is that used for batch 2B-4 and is representative of that used for the other batches.

A 2.0-g (1.3 mmol of NH_2) sample of batch 2B of aminopolystyrene hydrochloride was converted to the free amine by washing twice for 20 min each with 20-mL portions of 10% methanolic potassium hydroxide. The resulting polymer was washed five times with methanol and then twice with dichloromethane. It was dried first in air and then at 60 °C (0.1 mm) for 4 h.

A mixture of 0.49 g (0.48 mmol) of $\text{Na}_4\text{H}_2\text{TPP}(\text{SO}_3)_4 \cdot 10\text{H}_2\text{O}$, 4 mL of pyridine, and 40 mL of thionyl chloride was boiled for 4 h under reflux after allowing the original gas evolution to subside. All volatile materials were removed at 25 °C (0.1 mm). The resulting solid was dried at 25 °C (0.1 mm) for 1 h, slurried with dichloromethane which was removed under vacuum, and then dried at 25 °C (0.1 mm) for 6 h to remove completely the thionyl chloride and give the green to purple sulfonyl chloride. The crude sulfonyl chloride was stirred for 5 min with a mixture of 10 mL of triethylamine and 60 mL of dichloromethane. The free amine form of the aminopolystyrene prepared as outlined above was added to this mixture which was then stirred for 18 h at room temperature under a dry atmosphere. The resulting mixture was filtered giving a blue polymer and an extraneous blue precipitate of unknown composition. The polymer and such precipitate that could not be avoided were quickly transferred to a dried extraction thimble and then Soxhlet extracted under nitrogen with dichloromethane until the washes were pale red. The polymer was removed and stirred with 100 mL of methanol and 5 mL of triethylamine for 15 min, removed by filtration on a frit, washed with methanol until the washings were colorless, and dried at $\sim 25 \text{ }^\circ\text{C}$ (0.1 mm) for 1 h. The polymer was Soxhlet extracted with dichloromethane under nitrogen until the washings were clear and dried under vacuum for 12 h. A blue-purple polymer was obtained.

Cobalt was incorporated by stirring the polystyrene-anchored porphyrin base (1.6 g) with 5.2 g of cobalt(II) acetate tetrahydrate in 60 mL of acetic acid for 2 h under nitrogen at the boiling point.²¹ Occasionally a precipitate formed; if this interfered with stirring, small amounts of deaerated water were added until this precipitate dissolved. After being cooled under nitrogen, the mixture was filtered in air. The polymer was washed successively with water, methanol, and acetone, air dried until free flowing, and dried at $\sim 25 \text{ }^\circ\text{C}$ (0.1 mm) for 2 h. The polymer was then Soxhlet extracted with tetrahydrofuran under nitrogen for 6 h, air dried, and vacuum dried for 12 h to give a dark maroon product.

Studies on the Activities, Recycling, and Regeneration of the Polystyrene-Anchored Cobalt(II) Tetraarylporphyrin Catalysts (Tables II, III, IV, and V). Approximately 0.1 g of polymer-bound cobalt(II) tetraarylporphyrin was accurately weighed into a 25-mL round-bottom flask fitted with a serum cap adapter; the flask was equipped with a magnetic stirring bar, gas inlet adapter, and serum cap. The system was subjected to three cycles of evacuation and re-filling with nitrogen; thereafter a nitrogen atmosphere was maintained. During the reaction the flask was partially immersed in a water bath maintained at $30 \pm 0.2 \text{ }^\circ\text{C}$. At no time was either the serum cap or the gas inlet adapter below the water level of the bath.

Approximately 10 mL of the quadricyclane solution in benzene or xylene (purified by treatment with either potassium metal for at least 6 h or LiAlH_4 for at least 24 h) was introduced by a syringe and the timing begun. The recorded quantity of solution was obtained from the weight difference of the syringe before and after injection. Samples of the reaction solution (20 μL) were withdrawn and diluted into 0.2 mL of pentane or carbon disulfide for the gas chromatographic analysis. The initial sample was taken at 60 s with subsequent samples at 200- to 500-s intervals. Normally eight samples were taken over three to seven half-lives but occasionally as few as six samples were used.

The recycling studies (Tables III and IV) were conducted in a similar manner. At the end of the reaction period, the solvent was withdrawn through a flat tipped needle into a syringe and the catalyst washed three times for 15 min per wash with fresh, oxygen-free benzene. The catalyst was dried under a stream of nitrogen at 30 °C for 1 h before using it for the next catalytic run.

For the studies on the regeneration of the catalyst with reducing agents the following titanium(III) solutions were prepared and used where indicated in Table IV.

Titanium(III) Solution A1: Solvent was removed under vacuum from a mixture of 4 mL of titanium tetrachloride and 30 mL of methanol. The resulting paste was dissolved in 80 mL of tetrahydrofuran and stirred for 12 h with 5 g of tin metal to give a red-brown solution.

Titanium(III) Solution A2: A mixture of 4 mL of titanium tet-

racchloride, 5 g of tin metal, and 50 mL of methanol was stirred for 1 h to give a blue solution. This solution was evacuated at 25 °C (0.1 mm) for 1 min to remove excess hydrogen chloride.

Titanium(III) Solution B: Titanium tetrachloride (4 mL) was added to 20 mL of benzene followed by 10 mL of methanol. After 10 min 50 mL of tetrahydrofuran and excess zinc metal were added and the mixture stirred for 4 h at room temperature to give a maroon solution.

Aliquots of each of these titanium(III) solutions gave brilliant blue-purple solutions with deoxygenated water indicating the presence of titanium(III). The deep purple potassium benzophenone ketyl solution used for the regeneration study in Table IV was obtained by stirring a solution of 1.0 g of benzophenone in 50 mL of tetrahydrofuran with excess potassium metal for 24 h.

Stoichiometric reduction of all Ti(IV) was assumed since an excess of reducing agent was present in the reduction solution preparation.

Summary

Cobalt(II) tetraarylporphyrins supported through carboxamide and sulfonamide linkages on aminated macroreticular polystyrene beads cross-linked with divinylbenzene provide an active and inexpensive catalyst for the valence isomerization of quadricyclane (II) to norbornadiene (I). The presence of unreacted pendant amino groups causes some difficulties in the analysis of the system both because of lack of a direct method for determining the porphyrin nitrogen and by providing a possible coordination site for nonporphyrin cobalt. In a practical system these difficulties appear acceptable in view of the simplicity of preparation of the catalyst.

These polystyrene-bound cobalt(II) tetraarylporphyrin catalysts exhibit fair stability in use. Catalyst deactivation appears to be caused by reaction with some extraneous component in the quadricyclane. We have not identified the component. Activity of the catalyst may be partially restored by treatment with mild reducing agents, e.g., Ti(III). Coupled with the visible spectral observation that the Co(III)/Co(II) ratio of the catalyst increases upon deactivation, this reactivation by reducing agents implies that the operative deacti-

vation-reaction involves interconversion between Co(II) and Co(III). In a closed system, this mode of deactivation would presumably be limited to the first cycle.

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Registry No.—TPPH₂, 917-23-7; H₂TPP(CO₂H)₄, 14609-54-2; (NH₄)₄H₂TPP(SO₃)₄, 68438-24-4; (Et₃NH)₄H₂TPP(SO₃)₄, 68438-25-5; Na₄H₂TPP(SO₃)₄, 39050-26-5; quadricyclane, 278-06-8; norbornadiene, 121-46-0; polystyrene, 9003-53-6; Co(II), 22541-53-3; Ti(II), 22541-75-9.

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New Versatile Syntheses of 2-Substituted-2-amino Acid and 2,3-Dehydro-2-amino Acid Derivatives¹

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2-Substituted-2-amino acid derivatives were synthesized in high yields by reaction of 2-acetoxy-2-amino acid derivatives, which are synthetic potential intermediates, with various nucleophiles under basic conditions. Furthermore, the reaction of the 2-acetoxyamino acid derivatives with a nonnucleophilic base led to the synthesis of 2,3-dehydro-2-amino acid derivatives in excellent yields. In addition, the reaction in the presence of Lewis acid was carried out to afford the 2-substituted amino acid derivatives.

The synthesis of biologically active amino acids and their related compounds is one of the most attractive subjects in amino acid chemistry. In particular, syntheses of 2- or 3-substituted-2-amino acids and 2,3-dehydroamino acids have received increasing attention for preparation of pharmaceuticals such as antimicrobial agents. To synthesize such amino acids, we have selected two reactive species derived from the

parent 2-amino acids which can be called an "anionic amino acid synthon" and a "cationic amino acid synthon". We have already reported useful syntheses² using isonitriles as anionic synthons of physiologically important amino acids such as 2-alkylamino acids,³ 2-C-acylamino acids,⁴ and 3-hydroxy-amino acids.⁵ In the present work, a synthetic method using the cationic synthon will be described.