References and Notes

(1) Kinetics of Halogenation of Olefins and Acetylenes. 6. For part 5 in this series, see ref 3.

(2) Taken in part from the Ph.D. Dissertation of S. DeYoung, Bryn Mawr College, May 1976.

(3) S. J. Ehrlich and E. Berliner, *J. Am. Chem. Soc.*, **100,** 1525 (1978).

(4) P. W. Robertson, N. T. Clare, K. J. McNaught, and G. W. Paul, *J. Chem. Soc.*, 335 (1937); I. K. Walker and P. W. Robertson, *ibid.*, 1515 (1939).

(5) The rate constants k_2 are in $M^{-1}\ s^{-1}$ and k_3 in $M^{-2}\ s^{-1}$.

(6) S. DeYoung, S. Ehrlich, and E. Berliner, *J. Am. Chem. Soc.*, **99,** 290 (1977).

(7) J. E. Dubois and F. Garnier, *Tetrahedron Lett.*, 3961 (1965); R. E. Buckles and J. P. Yuk, *J. Am. Chem. Soc.*, **75,** 5048 (1953); G. A. Olah and T. R. Hockswender, Jr., *ibid.*, **96,** 3574 (1974), and references cited therein; M. F. Ruasse and J. E. Dubois, *J. Org. Chem.*, **37,** 1770 (1972); C. G. Gebelein and G. D. Frederick, *ibid.*, **37,** 2211 (1972); G. MOdena, F. Rivetti, and U. Tonellato, *ibid.*, **43,** 1521 (1978).

(8) (a) J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, **91,** 1469 (1969); (b) **91,** 1477 (1969); (c) **91,** 1483 (1969).

(9) The product distribution in the presence of NaOAc is somewhat obscured by the fact that in these runs the NaBr concentration was also varied, and NaBr increases the amount of dibromide and therefore suppresses sodium acetate or solvent incorporation. See also ref 8b.

(10) D. S. Tarbell and P. D. Bartlett, *J. Am. Chem. Soc.*, **59,** 407 (1937).

(11) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", American Elsevier, New York, 1966, p 140.

(12) Reference 8. Also see A. Modro, G. Schmid, and K. Yates, *J. Org. Chem.*, **42,** 3673 (1977); K. Yates and R. S. McDonald, *ibid.*, **38,** 2465 (1973). In the more nucleophilic solvent methanol, more solvent incorporation occurs; see J. E. Dubois and J. R. Chretien, *J. Am. Chem. Soc.*, **100,** 3507 (1978).

(13) J. M. Agoff, M. C. Cabaleiro, and J. C. Podesta, *Chem. Ind.* (*London*), 305 (1974); J. M. Agoff and M. C. Cabaleiro, *Tetrahedron Lett.*, 3535 (1975); M. A. Wilson and P. D. Woodgate, *J. Chem. Soc.*, *Perkin Trans. 2,* 141 (1976).

(14) P. B. D. de la Mare and R. Bolton, ref 11, Chapter 7; K. Yates and W. V. Wright, *Tetrahedron Lett.*, 1927 (1965); R. E. Buckles, J. L. Miller, and R. J. Thurmaier, *J. Org. Chem.*, **32,** 888 (1967); G. A. Olah, R. D. Porter, C. L. Jeuell, and A. M. White, *J. Am. Chem. Soc.*, **94,** 2044 (1972).

(15) R. C. Fahey and H.-J. Schneider, *J. Am. Chem. Soc.*, **90,** 4429 (1968).

(16) G. H. Schmid, A. Modro, and K. Yates, *J. Org. Chem.*, **42,** 871 (1977); G. H. Schmid and T. T. Tidwell, *ibid.*, **43,** 460 (1978); G. H. Schmid, *ibid.*, **43,** 777 (1978).

(17) J. A. Pincock and K. Yates, *J. Am. Chem. Soc.*, **90,** 5643 (1968); *Can. J. Chem.*, **48,** 3332 (1970); also ref 3. In iodination: M. H. Wilson and E. Berliner, *J. Am. Chem. Soc.*, **93,** 208 (1971); E. Mauger and E. Berliner, *ibid.*, **94,** 194 (1972); V. L. Cunningham and E. Berliner, *J. Org. Chem.*, **39,** 3731 (1974). In hydrochlorination: R. C. Fahey and D. J. Lee, *J. Am. Chem. Soc.*, **90,** 2124 (1968); *ibid.*, **88,** 5555 (1966).

(18) P. B. D. de la Mare, *Q. Rev. Chem. Soc.*, **3,** 126 (1949); P. B. D. de la Mare and R. Bolton, ref 14; R. C. Fahey, *Top. Stereochem.*, **3,** 237 (1968); R. E. Buckles, J. L. Miller, and R. J. Thurmaier, ref 14; J. E. Dubois and E. Bienvenue-Goetz, *Bull. Soc. Chim. Fr.*, 2086 (1968); J. E. Dubois and X. Q. Huynh, *Tetrahedron Lett.*, 3369 (1971); R. C. Fahey, M. T. Paine, and D. J. Lee, *J. Org. Chem.*, **39,** 1124 (1974).

(19) P. D. Bartlett and D. S. Tarbell, *J. Am. Chem. Soc.*, **58,** 466 (1936).

(20) E. Berliner and M. C. Beckett, *J. Am. Chem. Soc.*, **79,** 1425 (1957); R. P. Bell and E. N. Ramsden, *J. Chem. Soc.*, 161 (1958); R. P. Bell and T. Spencer, *ibid.*, 1156 (1959); R. P. Bell and D. J. Rawlinson, *ibid.*, 63 (1961).

(21) K. Nozaki and R. A. Ogg, Jr., *J. Am. Chem. Soc.*, **64,** 697, 704, 709 (1942).

(22) N. P. Kanyaev, *Zh. Obshch. Khim.*, **29,** 841 (1959).

(23) J. R. Atkinson and R. P. Bell, *J. Chem. Soc.*, 3260 (1963); R. P. Bell and M. Pring, *J. Chem. Soc. B,* 1119 (1966).

(24) P. B. D. de la Mare and R. Bolton, ref 14, p 121.

(25) J. E. Dubois, A. F. Hegarty, and E. D. Bergmann, *J. Org. Chem.*, **37,** 2218 (1972).

(26) R. C. Fahey, M. W. Monahan, and C. A. McPherson, *J. Am. Chem. Soc.*, **92,** 2810 (1970); R. C. Fahey and M. W. Monahan, *ibid.*, **92,** 2816 (1970); R. C. Fahey and C. A. McPherson, *ibid.*, **93,** 2445 (1971); R. C. Fahey, C. A. McPherson, and R. A. Smith, *ibid.*, **96,** 4534 (1974); D. J. Pasto, G. R. Meyer, and B. Lepeska, *ibid.*, **96,** 1858 (1974).

(27) P. B. D. de la Mare and R. D. Wilson, *J. Chem. Soc.*, *Perkin Trans. 2,* 2048, 2055, 2062 (1977).

(28) Rolston and Yates[8] observed that in the bromination of substituted styrenes $\rho_{Br_2} > \rho_{Br_3^-}$ (−4.21 and −2.02, respectively), which they interpret to be consistent with the lower electrophilicity of the tribromide ion *or* an Ad_E3 process, because less charge would be developed at C_α in either process. In the present case, a change of solvent from 75 to 50% aqueous acetic acid increases k_2 by a factor of 7.9 but k_3 by only 4.6, also indicating that less cationic charge is developed in the reaction corresponding to the second term in the rate equation.

(29) K. W. F. Kohlrausch and A. Pongratz, *Monatsh. Chem.*, **64,** 374 (1934).

(30) M. Reimer, *J. Am. Chem. Soc.*, **64,** 2510 (1942).

(31) A. Michael, *Chem. Ber.*, **34,** 3640 (1901).

(32) P. B. D. de la Mare and M. A. Wilson, *J. Chem. Soc.*, *Perkin Trans. 2,* 653 (1973).

(33) J. Read and A. C. P. Andrews, *J. Chem. Soc.*, **119,** 1774 (1921).

(34) We are greatly indebted to Professor P. B. D. de la Mare for supplying us with this sample.

(35) J. J. Sudborough and K. J. Thompson, *J. Chem. Soc.*, **83,** 666 (1903). This acid, conceivably formed by dehydration of one of the bromohydrins, was not found among the reaction products.

(36) T. W. Abbott and D. Althousen in "Organic Syntheses", Collect. Vol. 2, A. H. Blatt, Ed., Wiley, New York, 1943, p 270. The procedure for the bromination of the *ethyl* ester was followed.

(37) C. Lieberman, *Chem. Ber.*, **24,** 1101 (1891).

(38) S. Bagchee, K. N. Gaind, and J. N. Ray, *J. Chem. Soc.*, 657 (1938).

Polymer-Anchored Palladium(II) Complexes as Catalysts for the Conversion of Quadricyclane to Norbornadiene

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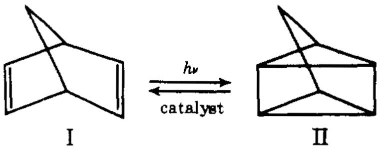
Reaction of diphenylphosphinated macroreticular polystyrene with $(CH_3CN)_2PdCl_2$ gives a polymer-supported palladium(II) chloride which is an active catalyst for the conversion of quadricyclane to norbornadiene. However, the activity of this catalyst is less by factors of 2–85 than that of the soluble catalyst $[(C_6H_5)_3P]_2PdCl_2$. The new polymer-supported palladium catalyst, like previously reported polymer-supported catalysts for this reaction, loses some of its activity upon repeated recycling.

A promising system for the storage of solar energy is based on the photosensitized conversion of norbornadiene (I) to quadricyclane (II) as the energy-storage step followed by the catalyzed exothermic reversion of quadricyclane to norbornadiene as the energy-release step.[2–4] Ideal catalysts for this reversion reaction must meet stringent criteria including long-term stability as well as the ability to effect rapid quantitative conversion with no side reactions. In addition, in an actual energy storage device based on this principle, the catalyst must be immobilized to prevent dispersion of the catalyst throughout the system.



I II

Several catalyst systems are known which catalyze the conversion of quadricyclane (II) to norbornadiene (I). These include soluble complexes of rhodium(I),[5] nickel(II),[6] cobalt(II),[6] iron(II),[6] and palladium(II)[5,7] and the soluble metal dithiolenes[8] $[(CF_3)_2C_2S_2]_2Ni$ and $[(CF_3)_2C_2S_2]_3Mo$. However, most of these complexes do not lend themselves readily to immobilization onto an insoluble polymer. Thus the most

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common immobilization method for transition-metal compounds involves binding to polymeric phosphine ligands,[9] but most of the metal complexes cited above lose their catalytic activities in the presence of phosphines.

One class of active catalysts for the conversion of quadricyclane to norbornadiene which is adapted to a non-phosphine route of immobilization includes the metal porphyrins.[6,10] Polystyrene-anchored cobalt(II) porphyrins were shown to be active catalysts in previous work from this laboratory.[11] However, a major difficulty of these catalysts is their sensitivity toward deactivation through oxidation of cobalt(II) to cobalt(III). A similar potential risk of oxidation of palladium(0) to palladium(II) also exists in the polystyrene-anchored palladium(0) bipyridine complexes recently reported by Card and Neckers.[12]

The objective of the work described in this paper was the development of an immobilized catalyst for the conversion of quadricyclane (II) to norbornadiene (I) which would not be sensitive toward oxidation. Palladium(II) complexes were attractive candidates for such a catalyst since they are not particularly sensitive toward oxidation and were known to be active catalysts for the conversion of quadricyclane to norbornadiene.[5,7] In this work we used a polymeric palladium(II) tertiary phosphine complex because of the easy availability of polymeric phosphine ligands. Even though phosphine palladium(II) complexes had not been reported to be catalysts for the conversion of quadricyclane to norbornadiene, these complexes were known to be effective for similar ring opening reactions.[13]

Results and Discussion

The polymer-anchored phosphinepalladium(II) chloride catalysts were prepared by stirring diphenylphosphinated macroreticular polystyrene beads[14] with palladium(II) chloride in acetonitrile solution. The resulting lemon yellow beads were active catalysts for the conversion of quadricyclane (II) to norbornadiene (I). Two independent samples of beads prepared by this general method gave the following elemental analyses: Polymer A: Pd, 0.70; P, 0.28; Cl, 0.39. Polymer B: Pd, 1.36; P, 0.97; Cl, 1.08; N, 0.026. These analytical data are insufficient to define an exact structure for this polymer. However, the absence of significant amounts of coordinated acetonitrile is indicated by both the low nitrogen analysis and the absence of nitrile bands in the infrared spectra of the polymers. Polymer B has a considerably higher phosphine loading on the polystyrene but a smaller percentage of palladium-complexed phosphines.

The rates of the conversion of quadricyclane (II) to norbornadiene (I) catalyzed by these polymers were measured at 30 °C in benzene or xylene solution using vapor-phase chromatography to analyze the reaction mixtures. The resulting kinetics were analyzed as pseudo-first-order reactions since only the quadricyclane concentration changes in the course of the experiment. The pseudo-first-order rate constants k_w were obtained from a linear least-squares plot of ln [quadricyclane] vs. reaction time in seconds and normalized to 1 g of catalyst in 1 L of solution. These k_w were converted to normalized rate constants based on metal content k_m by the equation:

$$k_m = k_w V/E$$

where V is the volume of the solution in liters and E represents the equivalents of palladium used per run based on the elemental analyses of the polymer quoted above.

Representative kinetic data obtained in this manner are summarized in Table I. These data include runs obtained by successively recycling the same batch of catalyst in different reactions. Before such recycling the polymer was washed three times with fresh solvent.

Table I. Kinetic Data for the Conversion of Quadricyclane to Norbornadiene by Palladium(II) Chloride Catalysts

catalyst	K_w, s^{-1} (g/L)$^{-1}$	K_m, s^{-1} (g atom Pd/L)$^{-1}$
(A) $[(C_6H_5)_3P]_2PdCl_2$[a]	1.2×10^{-2}	80
(B) polymer A (0.70 % Pd)		
fresh[b]	2.0×10^{-4}	0.30
first 9 data points	3.1×10^{-4}	0.47
last 9 data points	1.3×10^{-4}	0.20
1st recycle	1.5×10^{-4}	0.23
2nd recycle	1.6×10^{-4}	0.24
3rd recycle	0.41×10^{-4}	0.062
4th recycle	0.18×10^{-4}	0.028
fresh catalyst after norbornadiene equilibration	1.4×10^{-4}	0.21
fresh catalyst[c]	2.9×10^{-4}	0.44
(C) polymer B (1.36 % Pd)		
fresh[c]	9.4×10^{-4}	0.63
1st recycle	3.6×10^{-4}	0.24
2nd recycle	1.9×10^{-4}	0.13
3rd recycle	1.0×10^{-4}	0.07

[a] 0.5 M quadricyclane, 6.2×10^{-5} M Pd, benzene solvent. [b] 1.0 M quadricyclane, mixed xylenes as solvent. [c] 1.0 M quadricyclane, benzene solvent.

Recycling studies on the conversion of quadricyclane (II) to norbornadiene (I) using polymer A indicate that the initial activity of the fresh catalyst decreases slightly on the first recycle but that this slightly lowered activity is maintained in the second recycle. However, extensive losses of catalytic activity were found to occur during the third and fourth recycles.

When a portion of fresh polymer A was preequilibrated with a solution of norbornadiene (I) and then used as a catalyst for the conversion of quadricyclane to norbornadiene, the observed rate constant (Table I) was found to match most closely that of the untreated palladium catalyst after the first recycle. Thus exposure to norbornadiene has an inhibiting effect on polymer A. This could arise either from formation of a norbornadiene–palladium complex with reduced catalytic activity but still bound to the polymer or to metal leaching by displacement of the polymeric phosphine ligands by norbornadiene with formation of a soluble palladium complex.

If the first and last portions of the data from the kinetic study on fresh polymer A (Table I) are analyzed separately, a change is observed in the apparent rate constant during the course of the run. The initial value for the rate constant is high but this decreases to a value matching that observed for the first recycle by the end of the run. This eliminates metal leaching from the support as the cause of the catalyst deactivation, since a rate increase during the course of a run would be expected if this were the case.

The cause of the drastic rate decreases during the third and fourth recycles of polymer A is unclear. Possibly upon repeated recycling oxygen or peroxides oxidize some of the polymer-anchored phosphorus atoms to phosphine oxide units, which can lead to metal leaching from the polymer, and this becomes an important factor after the catalyst is recycled several times.

Recycling studies on polymer B indicate that this catalyst is almost twice as active as polymer A during the initial run but that this activity is rapidly lost on recycling. Insufficient information is available to explain this rapid loss of activity for polymer B upon recycling.

Comparison of the rate constants for polymer B and the analogous soluble complex $[(C_6H_5)_3P]_2PdCl_2$ (Table I) shows that the soluble complex is more than 100 times as active as polymer B. A major cause of this rate difference is likely to be the slower diffusion of the quadricyclane to the catalyst sites inside the polymer matrix. Similarly large rate decreases (factors of 2 to 85) were observed with polystyrene-anchored $(R_3P)_3Rh(CO)H$ relative to analogous soluble monomeric rhodium(I) catalysts when these catalysts are used in hydroformylation reactions.[15]

It is also instructive to compare the relative activities of the new polymer-supported palladium(II) catalysts for the conversion of quadricyclane (II) to norbornadiene (I) with the previously reported polymer-supported catalysts for this reaction. A fresh batch of the polystyrylbipyridinepalladium(0) catalyst containing 7.59% palladium was reported to have a half-reaction time of 40 min[12] which is, within experimental error, essentially identical to the observed half-reaction time for our new polystyrene-anchored phosphine palladium(II) catalyst containing only 0.70% palladium. Thus our new polymer-supported palladium(II) catalysts are considerably more efficient on a metal content basis than the recently reported[12] polymer-supported palladium(0) catalyst. Even more striking is the reported[12] complete lack of catalytic activity of a polystyrene-anchored bipyridinepalladium(II) acetate catalyst compared with the considerable activity of the polystyrene-anchored phosphine palladium(II) chloride catalysts reported here. Thus the complement of ligands around the palladium(II) in these polymer-supported catalysts is very critical in affecting their catalytic activities for the conversion of norbornadiene to quadricyclane.

The new polymer-supported palladium(II) catalysts reported in this paper are considerably less active on a metal content basis than the previously reported[11] polymer-supported cobalt(II) tetraarylporphyrin catalysts. For the cobalt catalysts the rate constants k_m fall in the range 1.8 to 3.9 s^{-1} (g atom/L)$^{-1}$ depending upon the precise conditions used, whereas for the palladium catalysts reported here (Table I) the corresponding rate constants k_m are 0.63 s^{-1} (g atom/L)$^{-1}$ or lower. For this reason and because of the higher cost of palladium relative to cobalt, the polystyrene-supported phosphinepalladium(II) chloride catalysts are considerably less promising than the polystyrene-supported tetraarylporphyrincobalt(II) catalysts for use in a practical solar energy storage system based on the norbornadiene–quadricyclane interconversion. We have therefore discontinued further development of the polymer-supported palladium(II) catalysts reported here.

Experimental Section

All reaction solvents were distilled under a nitrogen atmosphere from an appropriate drying agent before use (metallic potassium for tetrahydrofuran and cyclohexane and calcium hydride for benzene and xylene). Microanalyses on the polymers were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Diphenylphosphinated Polystyrene. A 50-mL flask fitted with a septum and magnetic stirrer and connected to a positive pressure nitrogen system was charged successively with 7 mL (5.4 g, 47 mmol) of *N,N,N′,N′*-tetramethylethylenediamine, 10 mL of aromatic-free cyclohexane, and 15 mL of 1.6 M *n*-butyllithium solution (24 mmol). The resulting mixture was heated at 50 °C for 15 min and then cooled to room temperature. It was then added with a syringe to a flask containing 15 g of macroreticular polystyrene beads (Dow No. 4022, 20 to 50 mesh) and 100 mL of aromatic-free cyclohexane. The resulting mixture was heated with stirring at 50 °C for 2 h under a nitrogen atmosphere. After cooling to room temperature the cyclohexane solution was removed with a syringe. The lithiated beads were then washed with six 25-mL portions of aromatic-free cyclohexane with all transfers made through a septum using a syringe. The beads were then washed once with 50 mL of tetrahydrofuran before being suspended in another 50 mL of tetrahydrofuran. This suspension was treated slowly with 8.0 g (36.3 mmol) of freshly distilled $(C_6H_5)_2PCl$ in 25 mL of tetrahydrofuran. Some evolution of heat was observed at this point. After addition was complete, the slurry was allowed to stir overnight. The next day 10 mL of methanol was added to the slurry to destroy any excess lithated sites. Up to this point the lithiated beads must contact only inert atmospheres and dry oxygen-free solvents to prevent loss of the lithiated sites and introduction of phenolic functionalities. The beads were then recovered on a filter and washed by stirring overnight successively in 200 mL each of methanol, 1:1 methanol–tetrahydrofuran, and pure tetrahydrofuran. The beads were then vacuum dried.

Preparation of the Polystyrene-Anchored Phosphinepalladium(II) Chloride Catalysts. A mixture of 0.5 g (2.8 mmol) of palladium(II) chloride and 10 mL of acetonitrile was stirred overnight to form yellow $(CH_3CN)_2PdCl_2$. This solution was treated with 50 mL of benzene and 10 g of diphenylphosphinated polystyrene. The resulting slurry was stirred for 2 days under nitrogen. The beads were recovered on a filter and washed by stirring overnight in 100 mL of benzene. After vacuum drying the beads were analyzed and used for the catalytic studies.

Kinetic Studies on the Polystyrene-Anchored Phosphinepalladium(II) Chloride Catalysts. To a 10-mL flask fitted with a septum and magnetic stirrer was added approximately 0.1 g of the desired catalyst. The flask was then allowed to equilibrate in a 30 °C (±0.1 °C) water bath. In a separate flask 10.0 mL of a benzene or xylene solution which was 1.0 M in quadricyclane and 0.5 M in an internal standard (*p*-xylene or benzene) was equilibrated in the same water bath. After equilibration was complete the benzene solution was transferred to the flask containing the catalyst. Ten-microliter aliquots were removed periodically from the reaction solution, diluted to 0.2 mL in pentane, and analyzed by vapor-phase chromatography on a Varian Series 2700 chromatograph with flame ionization detection. Separations were carried out on a 6 ft × 1/8 in. stainless steel column packed with 7.8% SF-96 Apiezon N on 60–80 mesh Chromosorb W. Quantitative data were obtained using internal standard calculation techniques from a Varian CDC-111 or Perkin-Elmer Model 1 digital integrator. The rate constants were calculated using equations generated by a linear least-squares computer program.

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Registry No.—Quadricyclane, 278-06-8; bis(triphenylphosphine)palladium(II) chloride, 13965-03-2; palladium(II) chloride bis(acetonitrile), 14592-56-4; diphenylphosphinous chloride, 1079-66-9.

References and Notes

(1) Postdoctoral research associate, 1976–1977.
(2) R. R. Hautala, J. Little, and E. M. Sweet, *Sol. Energy*, **19**, 503 (1977).
(3) C. Kutal, D. P. Schwendiman, and P. Grutsch, *Sol. Energy*, **19**, 651 (1977).
(4) D. P. Schwendiman and C. Kutal, *J. Am. Chem. Soc.*, **99**, 5677 (1977).
(5) H. Hogeveen and H. C. Volger, *J. Am. Chem. Soc.*, **89**, 2486 (1967).
(6) J. Manassen, *J. Catal.*, **18**, 38 (1970).
(7) P. G. Gassman and D. S. Patton, *J. Am. Chem. Soc.*, **90**, 7276 (1968).
(8) R. B. King and S. Ikai, *J. Mol. Catal.*, **4**, 361 (1978).
(9) R. H. Grubbs, *CHEMTECH*, 512 (1977).
(10) H. D. Wilson and R. G. Rinker, *J. Catal.*, **42**, 268 (1976).
(11) R. B. King and E. M. Sweet, *J. Org. Chem.*, **44**, 385 (1979).
(12) R. J. Card and D. C. Neckers, *J. Org. Chem.*, **43**, 2958 (1978).
(13) W. G. Dauben and A. Kielbania, Jr., *J. Am. Chem. Soc.*, **94**, 3669 (1972).
(14) D. C. Evans, M. H. George, and J. A. Barrie, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 247 (1947).
(15) C. U. Pittman, Jr., and R. M. Hanes, *J. Am. Chem. Soc.*, **98**, 5402 (1976).