kcal/mol. (Note—the designations endo and exo in this context refer only to the conformations of **2** and to the transition states that lead to them.)

At temperatures above −40 °C the interconversion of *endo*- and *exo*-**2** is fast ($t_{1/2} \approx 4$ min); continued warming to room temperature returns the endo/exo ratio to its equilibrium value (89:11).

The energy difference between the two transition-state conformations is very similar to but slightly greater than the ground-state energy difference between the two conformations of the product. This slight amplification of the product energy differences in the transition state may be a result of a "tight" transition state for the Diels–Alder reaction, a conclusion that has been drawn from several activation volume studies of the Diels–Alder reaction.[9] Regardless of the origin of the differences, the experiment graphically demonstrates the parallel between the transition state and product stabilities in the Lewis acid catalyzed intramolecular Diels–Alder cycloaddition.

Acknowledgment. Financial support from the National Science Foundation, CHE 82-11041, is gratefully acknowledged.

Registry No. 1, 85371-26-2; **2**, 85371-19-3.

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[9] (a) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *20*, 779. (b) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407. (c) Grieger, R. A.; Eckert, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 7149.

Concurrent Catalytic Reduction/Stoichiometric Oxidation Using Oligomerically Ligated Catalysts and Polymer-Bound Reagents

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In this paper we describe procedures using macromolecular reagents which permit the simultaneous use of otherwise incompatible reagents and the recovery and separation of each individual reagent, catalyst, or reaction product. Numerous literature examples describe the advantageous use of the physiochemical properties of insoluble macromolecular reagents in synthetic, mechanistic, and catalytic studies.[1] Included among these examples are cases in which the insolubility of two separate polymeric reagents or catalysts is used to permit use of mutually self-destructive species.[2,3] Here we describe a different approach to separation of two mutually incompatible species in which the size of a soluble macromolecular reagent is used to keep a catalyst and reagent apart. Our strategy allows simultaneous reactions to be carried out with incompatible reagents or catalysts and allows separate recovery and isolation of each reagent, catalyst, or product. Specifically, we describe a rhodium hydrogenation catalyst ligated by diphenylphosphinated ethylene oligomers which can be used as a homogeneous catalyst to effect alkene reduction of a substrate which is at the same time being oxidized by an insoluble poly(vinylpyridine)-bound Cr(VI) oxidant.

Table I. Concurrent Catalytic Reduction/Stoichiometric Oxidation of Unsaturated Alcohols^{a}

substrate	time, h	temp, °C	product, % yield^{b}
3-cyclohexene-methanol	12	100	cyclohexanecarbox-aldehyde (80)
3-cyclohexenylphenyl-methanol	18	100	cyclohexyl phenyl ketone (>95)
	18	100	cyclohexyl phenyl ketone (>95)^{c}
	20	100	cyclohexyl phenyl ketone (30)^{d}
3-cyclohexenylphenyl-methanol	20	70/100^{e}	cyclohexyl phenyl ketone (85)^{d}
3-cyclohexenylphenyl-methanol^{f}	20	70/100^{e}	3-cyclohexenyl phenyl ketone (95)
10-undecen-1-ol	24/24	70/100^{e}	undecanal (88)
1-phenyl-10-undecen-1-ol	24	100	1-phenylundecan-1-one (95)
11-dodecen-2-ol	18	100	2-dodecanone (75)

^{a}Reaction conditions are described in the text. ^{b}Yields of product ketone were measured by gas chromatography. Ketones formed in <90% yield typically contained saturated alcohol as the major impurity due to incomplete oxidation. ^{c}Second cycle of catalyst that had already been exposed to PVPCC for 20 h. ^{d}Third cycle of reaction for catalyst that had already been exposed to PVPCC for 40 h. The low yield of saturated ketone in this case was accompanied by 70% of unsaturated ketone indicating that the catalyst's activity had substantially diminished. ^{e}The oxidation step was carried out at 70 °C and heating to 100 °C was delayed until the oxidation was complete. ^{f}ClRh(PPh_3)$_3$ was used as the hydrogenation catalyst. No hydrogenation activity was detected.

Diphenylphosphinated ethylene oligomers to be used as ligands were prepared by anionic oligomerization of ethylene to a M_v of 1200 or greater.[4] Quenching the living oligomers so formed with chlorodiphenylphosphine produced polyethyldiphenylphosphine which was found to be insoluble at 25 °C but soluble to the extent of 1 g of phosphinated oligomer/10 mL of toluene at 100 °C.[5] In order to prepare the rhodium hydrogenation catalyst, 3 g of high-density polyethylene, 1 g of a polyethyldiphenylphosphine ligand (0.67 $-P(C_6H_5)_2/g$) and 0.70 g of freshly prepared $ClRh(C_2H_4)(P(C_6H_5)_3)_2$ (1 mmol) were dissolved in 25 mL of toluene at 100 °C. Cooling this solution entrapped the ethylene oligomer ligated rhodium catalyst.[6] Typically, the polyethylene powder so obtained contained 0.1 mmol of Rh catalyst/g of polymer. Dissolution of this catalyst in fresh solvent and ^{31}P NMR at 100 °C in xylene showed that the solution of Rh(I) catalyst contained a single broadened peak suggesting that no triphenylphosphine was present since triphenylphosphine would have given rise to a second different ^{31}P NMR absorption. The facile exchange of phosphine ligands at temperatures at which the catalyst and polymer are soluble has not allowed us to determine if all the oligomeric phosphine ligands are bound to Rh. However, the P/Rh ratio in these catalysts can be estimated to be in the range 2–3.[7]

Poly(vinylpyridine)-bound chromium(VI) oxidants such as poly(vinylpyridinium chlorochromate) (PVPCC) were previously described by Frechet.[8] In this work we used both commercially available reagents[9] and reagents made fresh from poly(vinylpyridine), HCl, and chromium trioxide.[8]

Concurrent catalytic alkene reduction/stoichiometric Cr(VI) alcohol oxidation reactions like eq 1 were successfully carried out

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[1] Pittman, C. U., Jr. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 8, pp 553–611. Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109–148. Mathur, N. C.; Narang, C. K.; Williams, R. E. "Polymers as Aids in Organic Chemistry"; Academic Press: New York, 1980. Hodge, P., Sherrington, D. C., Eds. "Polymer-Supported Reactions in Organic Synthesis"; Wiley: New York, 1980.

[2] Patchornik, A. *Nouv. J. Chim.* **1982**, *6*, 639–643.

[3] Pittman, C. U., Jr.; Smith, L. R. *J. Am. Chem. Soc.* **1975**, *97*, 1749–1754.

[4] Derivation of living polymers derived from alkyllithium-initiated oligomerization of ethylene is discussed in: Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1–90.

[5] Bergbreiter, D. E.; Blanton, J. R. *J. Chem. Soc., Chem. Commun.* **1985**, 337–338.

[6] Bergbreiter, D. E.; Chen, Z.; Hu, H.-P. *Macromolecules* **1984**, *17*, 2111–2116.

[7] Pignolet, L. H., Ed. "Homogeneous Catalysis with Metal Phosphine Complexes"; Plenum: New York, 1984.

[8] Frechet, J. M. J.; Darling, P.; Farrall, M. J. *J. Org. Chem.* **1981**, *46*, 1728–1730.

[9] PVPCC was obtained commercially from Fluka Chemical Corp., Hauppauge, NY.

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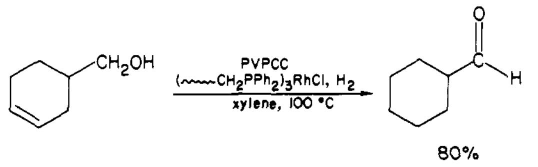

(1)

with a variety of primary and secondary unsaturated alcohols (Table I). The results of reactions like eq 1 coupled with the observation that Wilkinson's catalyst could not be used in similar chemistry (vide infra) show that the use of a soluble oligomeric ligand is sufficient to kinetically isolate two mutually destructive species.

In a typical procedure, 3 mmol of unsaturated alcohol was dissolved in 10 mL of xylene along with a 4-fold excess of PVPCC and 0.03 mmol of the rhodium catalyst dispersed in polyethylene. This reaction mixture was heated to 100 °C for 18 h under hydrogen. A fairly rapid uptake of hydrogen was observed followed by a slower oxidation of the alcohol group. Alternatively, the oxidation was first accomplished at 70 °C for 15 h after which time heating to 100 °C dissolved the polyethylene and oligomerically ligated rhodium catalyst. In either case, the product ketone was separated from the spent oxidant and the Rh(I) catalyst by first cooling the reaction mixture to precipitate the Rh(I) catalyst and then filtering the resulting suspension. The mixture of rhodium catalyst and spent chromium oxidant was then extracted with hot toluene in a jacketed Soxhlet apparatus for 8 h under nitrogen and the toluene solution was cooled to recover the rhodium catalyst as a polyethylene dispersion. The rhodium catalyst could then be reused in a subsequent reaction.[10] In practice, the same sample of the rhodium catalyst was usable for up to three cycles at 100 °C. After about 40 h of exposure to PVPCC at 100 °C, the oligomeric Rh(I) catalyst was no longer active. At 70 °C the catalyst retained its activity. Decarbonylation of aldehydes was not a significant problem in the experiments in Table I. However, formation of a rhodium carbonyl by aldehyde decarbonylation is likely to eventually lead to catalyst deactivation in cases where aldehydes are produced. A control experiment (Table I) showed that $ClRh(PPh_3)_3$ could not be used in place of the oligomerically ligated rhodium catalyst in either of the procedures described above. Addition of Wilkinson's catalyst to a solution of an unsaturated alcohol followed by heating to effect oxidation of the alcohol led to no hydrogen uptake. After the alcohol oxidation was complete, analysis of the solution in this case showed triphenylphosphine oxide had formed. Thus, the insoluble oxidant oxidized both the Rh(I) and the triphenylphosphine ligand.

In summary, soluble, nonpolar alkene oligomers can be used to kinetically isolate one soluble species from a second insoluble species. The successful demonstration that a Rh(I) catalyst and its oxidation-sensitive phosphine ligands survive in the same reactor as a Cr(VI) oxidant suggests that such isolation procedures should be generally useful. In addition, by using oligomeric ligands prepared from ethylene oligomers, we can use entrapment in polyethylene to recover the catalyst at the end of a reaction cycle.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Texas A&M Center for Energy and Mineral Resources for support of this research.

Registry No. PVPCC, 66212-21-3; $CH_2{=}CH(CH_2)_9OH$, 112-43-6; $CH_2{=}CH(CH_2)_8CH(Ph)OH$, 97135-06-3; $CH_2{=}CH(CH_2)_8CH(OH)CH_3$, 21951-49-5; $CH_3(CH_2)_9C(O)Ph$, 4433-30-1; $ClRh(PPh_3)_3$, 14694-95-2; 3-cyclohexene-1-methanol, 1679-51-2; (3-cyclohexen-1-yl)phenylmethanol, 831-13-0; cyclohexanecarboxaldehyde, 2043-61-0; cyclohexyl phenyl ketone, 712-50-5; 3-cyclohexen-1-yl phenyl ketone, 831-14-1; undecanal, 112-44-7; 2-dodecanone, 6175-49-1.

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(10) Analysis by ICP of the solid residue from filtrates from hydrogenations using similar catalysts and 1-octene show that <0.1% of the charged rhodium catalyst was lost to solution during recovery of a poly(ethyldiphenylphosphine)-ligated rhodium catalyst by entrapment in a polyethylene precipitate.

On the Structure of the Allyl Anion

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This paper compares the geometry of the allyl anion deduced from photoelectron spectroscopic measurements[1] with structures calculated at reliable ab initio levels.[2-5] The serious discrepancies indicate that the experimental values are unlikely to be correct.

In a recent paper, Oakes and Ellison (OE) reported the photodetachment spectra of the allyl anion, $CH_2CHCH_2^-$, and of two deuterated species, $CH_2CDCH_2^-$ and $CD_2CDCD_2^-$.[1] The electron affinity of the parent ion (EA = 8.25 ± 0.5 kcal/mol) was lower than that of an earlier investigation (EA = 12.7 ± 1.2 kcal/mol)[6] but agreed (when combined with other known thermochemical values) with the proton affinity (PA = 391 ± 1) determined both by flowing afterglow methods[5] and by our earlier MP2/4-31+G//4-31+G calculations (see below).[2] However, analysis of the photoelectron spectra led OE to propose that the CCC angle in the allyl anion is 140 ± 4° and that the C–C bond lengths (r_0) are 1.505 Å for the parent anion and 1.555 and 1.612 Å for the deuterated species, respectively. All of these geometrical parameters appear to be much too large, as does the suggested substantial increase of 0.107 Å in the C–C bond lengths in going from $C_3H_5^-$ to $C_3D_5^-$. The Born–Oppenheimer potential energy surface is independent of isotopic substitution. While averages over the zero-point motions on this surface can vary, these differences generally are very small.[7]

Hückel theory makes a simple prediction.[8] Since the π HOMO of the allyl anion is nonbonding, the extent of occupation of this MO should not influence the C–C bond lengths significantly. The C–C bond orders in the allyl cation, the allyl radical, and the allyl anion are all 1.5, just as in benzene. To a first approximation, the C–C bond lengths in all four species should be very similar. This is exactly what has been indicated by earlier work[4,5] and is found by high-level calculations (summarized in Table I). We

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(1) Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 7734–7741.

(2) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609–5612 and supplementary material. This was the first allyl anion calculation that employed full geometry optimization with an adequate (diffuse-function augmented) basis set. Also see: Schleyer, P. v. R.; Chandrasekhar, J.; Kos, A. J.; Clark, T.; Spitznagel, G. W. *J. Chem. Soc., Chem. Commun.* **1981**, *46*, 1693–1699.

(3) Full geometry optimizations without diffuse orbital-augmented basis sets: Boche, G.; Buckl, K.; Martens, D.; Schneider, D. R.; Wagner, H.-U. *Chem. Ber.* **1979**, *112*, 2961–2996. Cremoschi, P.; Morosi, G.; Simonetta, M. *J. Mol. Struct.* **1981**, *85*, 397–400. Pross, A.; DeFrees, D. J.; Levi, B. A.;Pollock, S. K.; Radom, L.; Hehre, W. J. *J. Org. Chem.* **1981**, *46*, 1693–1699. Also see ref 5.

(4) Earlier, pioneering calculations on the allyl anion were not carried out with full geometry optimizations; e.g.: (a) Peyerimhoff, S. O.; Buenker, R. J. *J. Chem. Phys.* **1969**. (b) Boerth, D. W.; Streitwieser, A. *J. Am. Chem. Soc.* **1978**, *100*, 750. (c) For calculations on the methylallyl anion, radical, and cation, see: Schleyer, P. v. R.; Dill, J. D.; Pople, J. A.; Hehre, W. J. *Tetrahedron* **1977**, *33*, 2497–2501. (d) Also see: Elliott, R. J.; Richards, W. G. *J. Mol. Struct.* **1982**, *87*, 211–216 for MNDO geometries.

(5) McKay et al. (McKay, G. I.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Can. J. Chem.* **1978**, *56*, 131–140) give $\Delta H_f{}^\circ{}_{298}$(allyl anion) = 29.0 ± 0.8 kcal/mol; the value OE deduced (29.5 ± 0.9 kcal/mol)[1] is in good agreement. From $\Delta H_f{}^\circ{}_{298}$(allyl radical) = 39.1 ± 1.5 kcal/mol recommended by McMillen et al. (McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532), EA_{298}(allyl) = 9.8 ± 2.4 kcal/mol.

(6) Zimmerman, D. H.; Brauman, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 3565–3568.

(7) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L. Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. L.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619–721.

(8) Heilbronner, E.; Bock, H. "Das HMO-Modell und seine Anwendung"; Verlag Chemie: Weinheim, 1968. Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemists"; Wiley-Interscience: New York, 1961. For similar reasons, the CCC angle in the allyl cation is decreased over the values in the allyl radical or in propene (Table I).