The X-ray diffraction study of **1** and **11** is in progress. We are currently studying various physical and chemical properties of **1** and **11**.[15]

Acknowledgment. We thank Y. H. Law for measuring the accurate masses for all new compounds. This work was partially supported by a Messrs. Ho Tim & Ho Yin Research Grant administered by the Chinese University of Hong Kong.

(15) The less descriptive IUPAC names for **1**, **6**, and **11** are 5,8:13,16-diethenodibenzocyclododecene, 9,10-didehydro-5,8:11,14-diethenobenzocyclododecene, and 5,8:15,18-diethenobenzonaphthocyclododecene, respectively.

Transition-State Conformations of a Lewis Acid Catalyzed Diels–Alder Reaction. The Low-Temperature Cycloaddition of 1-(1-Oxo-2-propenyl)-2-(3-isopropenyl-4-methyl-3-pentenyl)benzene

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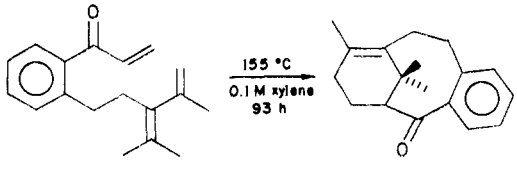
An analysis of various transition-state conformations is the organic chemists modus operandi for predicting product outcome and evaluating the relative merits of competing reaction pathways. This is particularly true in intramolecular Diels–Alder chemistry where issues of regio- and stereochemistry are determined by subtle conformational factors.[1] Unfortunately it is often impossible to relate the transition-state analysis to the resultant product molecules since under normal conditions the conformational isomer populations do not remain under kinetic control.

We report in this paper a rather unique opportunity to probe the relationship between transition-state conformation and product outcome in a Lewis acid catalyzed intramolecular Diels–Alder reaction. Our results establish that the relative stability of the conformational isomers of the product are amplified slightly in the transition states that lead to them.

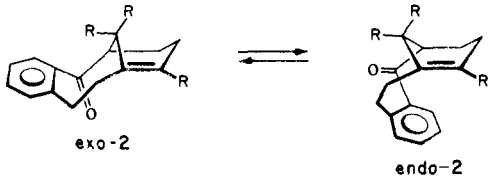
The thermal cycloaddition of trienone **1** (toluene, 155 °C, 0.1 M xylene, 93 h) affords a single cycloadduct in 70–80% isolated yield.[2] The gross structure of the tricyclo[9.3.1.0^{3,8}]pentadecane



1 2

ring system was established by a combination of ^{1}H and ^{13}C NMR spectroscopy.

Force-field calculations[3] and molecular models reveal two plausible low-energy conformations of the cycloadduct, *endo*- and *exo*-**2**. At room temperature, the rate of interconversion of the



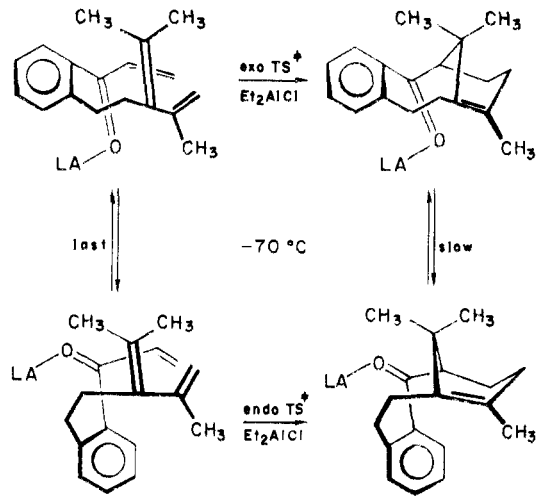
exo-2 endo-2

(1) For recent reviews, see: (a) Taber, D. F., "Intramolecular Diels–Alder and Ene Reactions": Springer-Verlag, Berlin, 1984. (b) Ciganik, E. *Org. React.* **1984**, *32*, 1. (c) Fallis, A. *Can. J. Chem.* **1984**, *62*, 183.

(2) Shea, K. J.; Davis, P. D., *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 419; *Angew. Chem., Suppl.* **1983**, 564.

(3) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

Scheme I



two conformational isomers is slow on the NMR time scale; thus, at 250 MHz, the ^{1}H NMR consists of a superimposition of the spectra of *endo*- and *exo*-**2**.

Analysis of the spectra utilizing NOE and saturation transfer NMR spectroscopy permitted unambiguous assignment of the two isomers.[4] Our results can be summarized as follows: at 25 °C *endo*-**2** is the major conformational isomer in solution (*endo*-**2**/*exo*-**2** = 89:11), the free energy difference calculated from the experimentally observed ratios is $\Delta\Delta G°_{25\,°C}$ = 1.24 ± 0.15 kcal/mol. The equilibrium ratio was found to be insensitive to temperature over a 75-deg range (45 to −30 °C).[5] Variable-temperature NMR revealed the barrier height separating the two conformational isomers is quite high; analysis of site exchange of two methyl resonances (Me_{16} and Me_{18}) yields an average single point free energy barrier $\Delta G^‡$ = 16.5 ± 0.1 kcal/mol.[4]

We have also reported that type II intramolecular Diels–Alder cycloadditions are amenable to Lewis acid catalysis.[6] Trienone **1** is particularly responsive to catalysis by diethylaluminum chloride. For example, after 1 h in the presence of 0.3 equiv of Et_2AlCl in CD_2Cl_2 at −70 °C, trienone **1** gives cycloadduct **2** in 90% isolated yield.

The low-temperature reaction conditions provide a rare opportunity to establish the *conformational selectivity* of the Lewis acid catalyzed intramolecular Diels–Alder reaction. Scheme I summarizes the various competing reactions involved in the experiment.

At −70 °C interconversion of the conformational isomers of **1** is fast.[7] Interconversion of the conformational isomers of cycloadduct **2**, however, is slow.[8] Based upon the experimentally measured free energy of activation we estimate $t_{1/2} \approx 6$ h at −70 °C.

Under the Lewis acid catalyzed reaction conditions the ratio *endo*-**2**/*exo*-**2** represents the *kinetically controlled* rate of *conformational isomer formation*, thus k_{endo}/k_{exo} = 70 (−70 °C), from which the difference in free energy of activation for the two competing reactions can be computed, $\Delta\Delta G^‡_{-70°C}$ = 1.70 ± 0.02

(4) Shea, K. J.; Gilman, J. W. *Tetrahedron Lett.* **1984**, *24*, 2451.

(5) The variation in the ratio of *endo*-**2**/*exo*-**2** between 25 and −40 °C falls within the experimental uncertainty of the integrated peak intensities (4%). At room temperature this ratio is not influenced by the presence 0.3 equiv of diethylaluminum chloride.

(6) Shea, K. J.; Gilman, J. W. *Tetrahedron Lett.* **1983**, *24*, 657.

(7) (a) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801. (b) Naito, I.; Kinoshita, A.; Yonemitsu, T., *Bull. Chem. Soc. Jpn.* **1976**, *49*, 339. (c) Lister, D. G. "Internal Rotation and Inversion": Academic Press: London, 1978; p 162.

(8) The conformational integrity of **2** at −70 °C in the presence of Lewis acids was established in the following manner. A single crystal of pure *endo*-**2** was dissolved at −100 °C in CD_2Cl_2, warmed to −70 °C, and then treated with 0.3 equiv of Et_2AlCl. *exo*-**2** could not be detected after 1 h (*endo*-**2**/*exo*-**2** > 250:1 at −70 °C). Upon warming the equilibrium ratio of the two conformations was readily achieved.

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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.

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

(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	cyclohexanecarboxaldehyde (80)
3-cyclohexenylphenylmethanol	18	100	cyclohexyl phenyl ketone (>95)
	18	100	cyclohexyl phenyl ketone (>95)[c]
	20	100	cyclohexyl phenyl ketone (30)[d]
3-cyclohexenylphenylmethanol	20	70/100[e]	cyclohexyl phenyl ketone (85)[d]
3-cyclohexenylphenylmethanol[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

(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.

0002-7863/85/1507-4792$01.50/0