Tetrahedron: Asymmetry Vol. 2, No. 12, pp. 1283-1294, 1991
Printed in Great Britain

0957-4166/91 $3.00+.00
Pergamon Press plc

THE EFFECT OF ALUMINA ON THE DIELS-ALDER REACTIONS OF CYCLOPENTADIENE WITH MENTHYL ACRYLATE AND DIMENTHYL FUMARATE.

George W. Kabalka*, Richard M. Pagni*, Satinder Bains, George Hondrogiannis, Miechelle Plesco,
Robert Kurt, Danielle Cox, and James Green

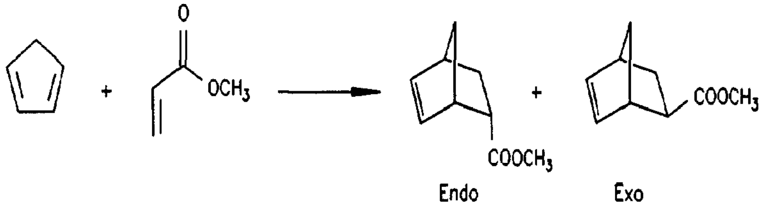
Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600 U.S.A.

(*Received* 1 *October* 1991)

Abstract: Alumina catalyzes the Diels-Alder reactions of cyclopentadiene with optically active menthyl acrylate and dimenthyl fumarate. Significant diastereoselectivity is observed in each case.

INTRODUCTION

The Diels-Alder reaction, or 4 + 2 cycloaddition reaction, continues to attract a great deal of attention because of its importance in the theory of organic reactions[1] and organic synthesis.[2] The reaction is perhaps the best method for the creation of six-membered rings and up to four new stereogenic centers are formed stereospecifically. With appropriate reactants, high regio- and endo-exo selectivity is observed. When the reaction is run in the presence of Lewis acids, the reaction rate is increased[3] and endo-exo selectivity is enhanced significantly (eq. 1).[4]

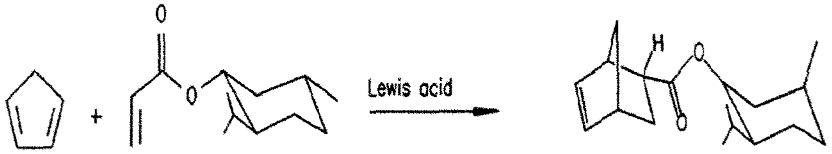


(1)

	Endo		Exo
No Catalyst	7·3	:	1
AlCl$_3$	99	:	1

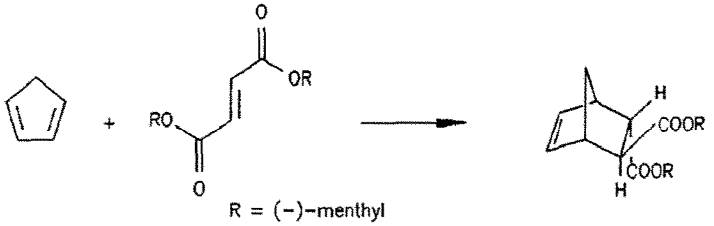
If an optically active dienophile such as (-)-menthyl acrylate is treated with cyclopentadiene in the presence of a Lewis acid, significant diastereomeric excesses are found in the products. For example, reactions of cyclopentadiene with (-)-menthyl acrylate in the presence of SnCl$_4$ in toluene at 4-8°[5] or

$AlCl_3{\cdot}Et_2O$ in CH_2Cl_2 at -70°[6] yielded predominantly the endo esters with a diastereomeric excess of 41% and 70%, respectively (eq. 2). In the absence of the Lewis acid, only 8% diastereomeric excess was found in the endo adduct.[5,6] Oppolzer *et al.* also reported enhanced endo-exo selectivity and diastereoselectivity of the endo esters using a variety of Lewis acids.[7] Corey and his students improved the diastereoselectivity of this reaction even more by using an optically active catalyst.[8] Even the reaction of cyclopentadiene with achiral methyl acrylate yielded a large enantiomeric excess in the endo ester when catalyzed by optically active Lewis acids.[8,9]



(2)

Similar trends were also observed in the reaction of (-)-dimenthyl fumarate with cyclopentadiene (eq. 3) and other dienes, i.e., low product diastereoselectivity in the absence of catalyst and high diastereoselectivity in its presence.[10]

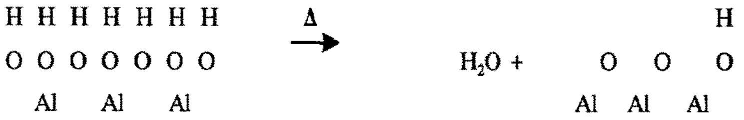


(3)

Much current effort is being devoted to finding unusual environments and conditions to effect the Diels-Alder reaction. These include: cycloadditions under pressure to accelerate the rates of sluggish reactions,[11] reactions in unusual solvents such as H_2O,[12] reactions catalyzed by enzymes[13] and antibodies,[14] and in heterogeneous media such as silica,[15] clays,[16] zeolites,[17] which may induce shape selectivity in the reactions, and alumina.[18]

Alumina is a particularly interesting environment in which to run the Diels-Alder reaction because, when the solid is activated, Lewis acid sites are created on its surface which should catalyze the reaction, alter endo-exo selectivity, and enhance diastereoselectivity in reactions involving optically active dienophiles. It is in fact this latter area which is the focus of the present paper.

Peri[19] and Knözinger and Ratnasamy[20] have proposed models which successfully explain many features of the surface of alumina. Simply put, the unactivated material has a top layer of OH groups above a layer of aluminum ions. When the solid is heated an acidic OH group donates a proton to an adjacent basic OH group to form H_2O which is driven from the surface (normal dehydration). This reaction partially exposes an aluminum ion on the surface which should function as a Lewis acid. Unfortunately, this picture is incomplete because the environment of the partially exposed aluminum ion, and thus its acidity, depends on the plane of the alumina crystallite exposed at the surface and also on the temperature range in which the aluminum ions become coordinatively unsaturated. If the (111) crystal face is exposed, for example, activation at ≤ 300° results in the loss of up to 50% of the OH groups (25% acidic, 25% basic), leaving behind 50% of unreacted, equivalent OH groups and 25% exposed aluminum ions (plus 25% oxide anions) which function as normal Lewis acids. Dehydration above 300° cannot occur between adjacent acidic and basic OH groups; it must occur between equivalent OH groups. This results in abnormal dehydration, creating defect sites which are fewer in number than normal acidic sites but catalytically more active. Activation at still higher temperatures creates additional catalytic sites having still different environments.



$$\begin{array}{ccccccc} H&H&H&H&H&H&H\\ O&O&O&O&O&O&O\\ &Al&&Al&&Al& \end{array} \xrightarrow{\Delta} H_2O + \begin{array}{ccc} &&H\\ O&O&O\\ Al&Al&Al \end{array} \qquad (4)$$

It is the purpose of the present paper to determine the effect these acidic sites have on the Diels-Alder reactions of cyclopentadiene with (-)-menthyl acrylate and (-)-dimenthyl fumarate. In addition to synthetically useful selectivities which may be obtained, the reactions may shed additional light on the nature and number of the acidic sites on the alumina surface.

RESULTS AND DISCUSSION

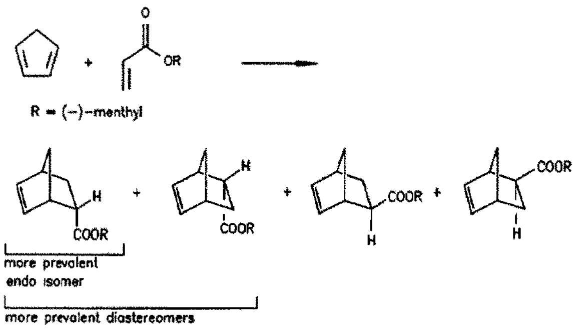
The Diels-Alder reactions were run on Brockmann neutral grade alumina (surface area - 155 m^2 g^{-1}) in the absence of solvent. All reactions were run at a total loading well below a coverage of a monolayer because experience has shown that the influence of the surface is lost when the reactions are run at greater than one monolayer surface coverage.[21] Further details about the reactions and product analyses may be found in the **EXPERIMENTAL SECTION.**

The reactions of cyclopentadiene and (-)-menthyl acrylate were run at temperatures ranging from +65° to -78° on alumina which had been activated at temperatures as high as 800°. Taking into account the fact that cyclopentadiene dimerizes on alumina, good material balances were obtained in all cases. Endo-exo selectivity and the diastereoselectivity of the more prevalent endo adducts were measured for every reaction. The results for reactions run on alumina activated for four hours are presented in Table 1, with the diastereoselectivities (as % diastereomeric excess) shown in parentheses.

Table 1. Selectivities in the Reaction of (-)-Menthyl Acrylate with Cyclopentadiene.

	Endo:Exo Ratio (% Diastereomeric Excess)				
	Reaction Temperature				
Alumina Activation Temperature	-78°	-10°	0°	25°	65°
800°		(26.0)	3.2 (22.6)	1.6	1.2
600°				3.2	1.2
400°	15.2 (33.7)	4.9	9.0 (29.1)	8.5 (29.0)	8.1
Unactivated					4.3 (14.9)
Neat					2.4 (9.0)

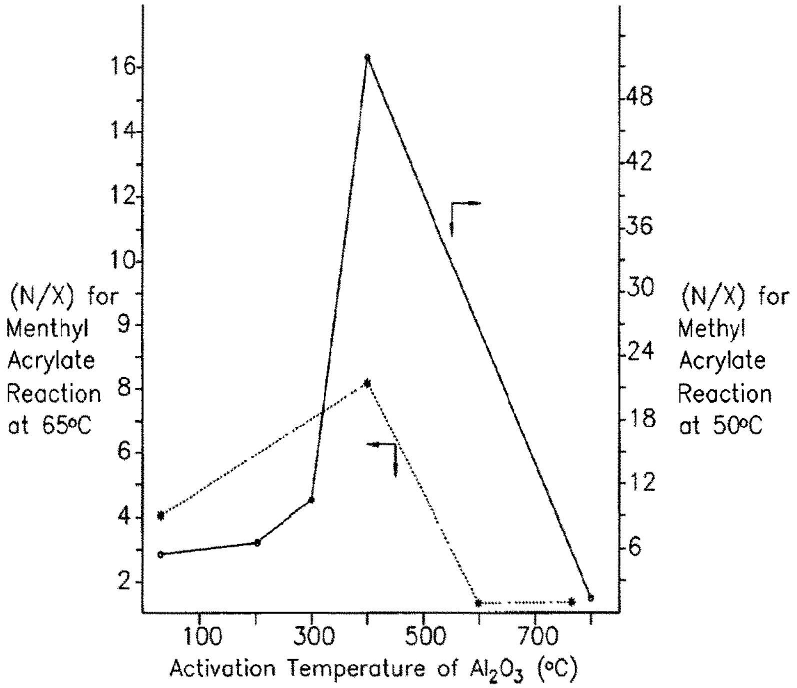
Note that endo-exo selectivity and diastereoselectivity are greater for reactions run on unactivated alumina than for reactions run neat. This pattern has been observed for every Diels-Alder reaction we have examined to date.[18c-e] As expected, selectivities increase on all activated aluminas as the reaction temperature is decreased. That the reactions on alumina are well behaved can be deduced by examining the endo-exo ratios (N/X) obtained on alumina activated at 400°. A plot of ln(N/X) versus T^{-1}(K) yields the straight line: $\ln(N/X) = (305 \pm 29)T^{-1} + (1.14 \pm 0.11)$ (correlation coefficient = 0.9866), from which one can derive $\Delta H^{\ddagger}_{N} - \Delta H^{\ddagger}_{X} = -(606 \pm 57)$ cal mol^{-1} and $\Delta S^{\ddagger}_{N} - \Delta S^{\ddagger}_{X} = (2.27 \pm 0.22)$ cal K^{-1} mol^{-1}, where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the activation parameters of the reactions forming the endo and exo products The temperature dependence of the diastereomeric excesses was also well behaved. For reactions run at temperatures between +65° and 0° on alumina activated for six hours (not shown in Table 1), the diastereomeric excesses yield the straight line: $\ln(d_1/d_2) = (167 \pm 33)T^{-1} + (0.031 \pm 0.016)$ (correlation coefficient = 0.9631), where d_1/d_2 is the ratio of the more prevalent endo diastereomer over the less prevalent one; from this equation one obtains $\Delta H^{\ddagger}(d_1) - \Delta H^{\ddagger}(d_2) = -(332 \pm 66)$ cal mol^{-1} and $\Delta S^{\ddagger}(d_1) - \Delta S^{\ddagger}(d_2) = (0.062 \pm 0.032)$ cal mol^{-1} K^{-1}. Extrapolation of the data to -78°, where the Diels-Alder reaction is very slow, yields $d_1/d_2 = 2.43$ and thus a diastereomeric excess of 42%, values similar to what has been observed in solution.



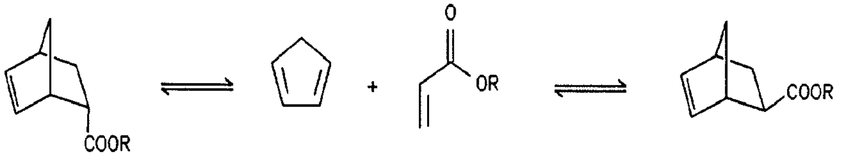
(5)

Although the data in Table 1 are incomplete, it is clear that both selectivities are markedly dependent on the activity of the alumina, increasing initially on going from unactivated alumina to alumina activated at 400° and then decreasing on alumina activated at higher temperatures. A plot of (N/X) versus alumina activation temperature for the reactions of (-)-menthyl acrylate[18d] and methyl acrylate[18c] with cyclopentadiene (Figure 1) reveals that both Diels-Alder reactions exhibit similar behavior, with maximum selectivity being obtained on 400°-alumina.

Figure 1. Selectivities in the Reactions of Methyl and Menthyl Acrylate with Cyclopentadiene



These trends in Figure 1 can be explained in terms of the Knözinger-Ratnasamy model of the surface of alumina and fundamental organic chemistry. Unactivated alumina, of course, has no acidic properties and the observed selectivities reflect the solvent-like properties of the surface. Berson has defined[22] a solvent parameter Ω which is equal to log(N/X) for the reaction of methyl acrylate and cyclopentadiene in the solvent of interest at 20°. This parameter correlates well with E_T values. Ω for unactivated alumina is larger than 0.763 because the model reaction was run at 65°, where log(N/X) = 0.763. The selectivity and thus Ω should be higher at 20°. Unactivated alumina thus has solvent-like properties similar to ethanol and acetic acid.[23] Activation of the solid exposes normal Lewis acid sites to the surface. The catalyzed Diels-Alder reaction on the activated alumina surface will compete with the uncatalyzed reaction, resulting in reaction selectivities being altered. Activation above 300° exposes a new type of acid site. These new sites are fewer in number than the acid sites originally exposed to the surface but are catalytically much more active, profoundly altering the endo-exo and diastereoselectivities. Based on the linearity of the ln(N/X) and $\ln(d_1/d_2)$ versus T^{-1} plots described earlier, the chemistry on 400°-alumina is dominated by a single type of catalytic site. Surprisingly, the selectivities decrease when the reactions are run on more highly activated alumina; presumably, these sites also catalyze the retro-Diels-Alder reaction. Experiments have shown that the retro-Diels-Alder reaction of the methyl acrylate-cyclopentadiene adducts[18c] is very slow on 400°-alumina but relatively fast on 800°-alumina at ambient temperatures. It is easy to show mathematically that both measured selectivities will be reduced by the reversibility of the Diels-Alder reaction,[21] being most prominent when the rates of the Diels-Alder and retro-Diels-Alder reactions are similar. Because there is current interest in using the retro-Diels-Alder reactions synthetically,[24] the highly activated alumina may yet prove to be a useful catalyst for this process.



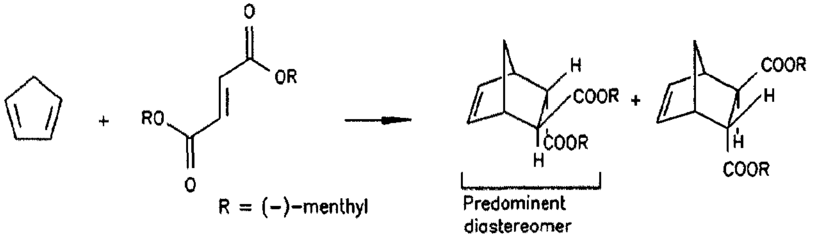
(6)

The Diels-Alder reactions of (-)-dimenthyl fumarate with cyclopentadiene were run at ambient temperature on alumina as described above; good material balances were obtained in all cases. Unlike the (-)-menthyl acrylate reactions where four diastereomers are generated, the (-)-dimenthyl fumarate reactions yield only a single pair of diastereomers. The results of the experiments on alumina and modified alumina, as well as in solution, are reported in Table 2.

Table 2. Selectivities in the Reaction of Cyclopentadiene with (-)-Dimenthyl Fumarate.

Reaction Conditions	Ratio of Diastereomers	Diastereomeric Excess
$AlCl_3/Et_2O$	2.24	38.3%
Neat	0.926	-3.84%
Unactivated Al_2O_3	1.32	13.8%
200°-Al_2O_3	1.40	16.8%
400°-Al_2O_3	1.43	17.7%
700°-Al_2O_3	1.51	20.3%
BBr_3/400°-Al_2O_3	1.46	18.7%
BBr_3/400°-Al_2O_3 with (-)-Menthol	1.77	27.8%

The $AlCl_3$-catalyzed reaction in ether, which gave a diastereomeric excess of 38.3%, with the (S,S)-diastereomer predominating, is a good standard by which to compare the surface reactions. By contrast the reaction run in the absence of solvent and catalyst gave a slight excess of the (R,R)-diastereomer. As seen in all previous cases, the selectivity was found to be higher on unactivated alumina than when compared to the reaction run neat. This again is a reflection of the solvent-like properties of the surface. When the reaction was run on alumina of increasing activity, there was a corresponding increase in the diastereoselectivity, although the highest selectivity does not compare to that observed in the $AlCl_3$/ether reaction.

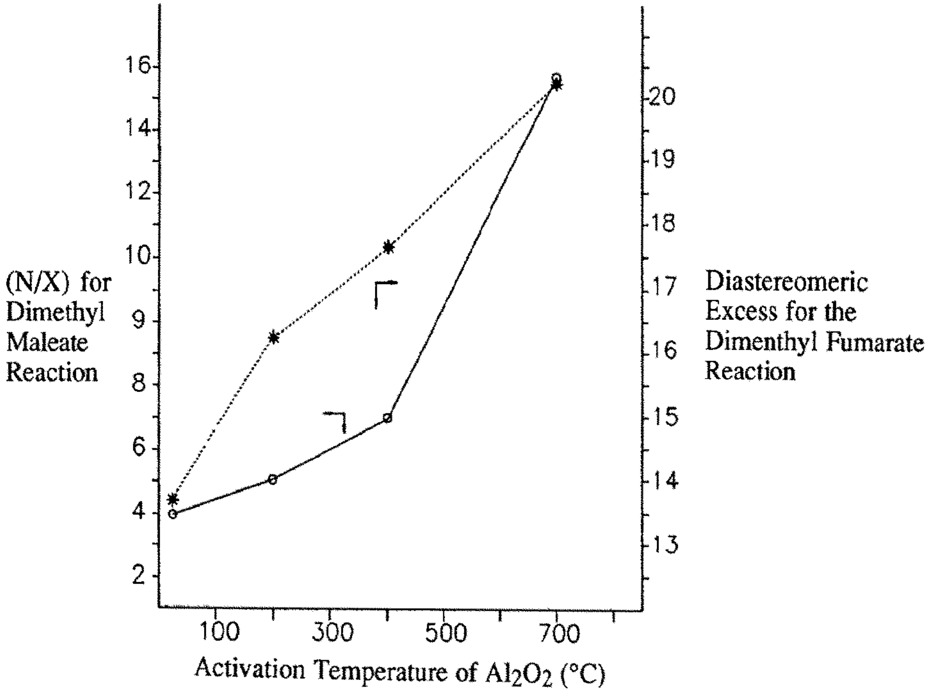


(7)

It is important to note that the observed trend in selectivity does not parallel the trends observed in the methyl acrylate and (-)-menthyl acrylate reactions. There is no initial rise and then a drop in the selectivity as was observed in the previous cases. There is a good correlation, however, to a related reaction: the cycloaddition of dimethyl maleate and cyclopentadiene to give endo and exo adducts (Figure

2). In both reactions displayed in Figure 2, the selectivity increases steadily as the activity of the solid is increased. The drop in selectivity observed in the methyl acrylate and menthyl acrylate reactions is due to the reversibility of the Diels-Alder reaction on the more highly activated alumina. This suggests that the Diels-Alder reactions of dimethyl maleate and dimenthyl fumarate with cyclopentadiene on alumina are not reversible. This is not the case, however. Previous work[18c] has shown that the two dimethyl maleate/cyclopentadiene and one dimenthyl fumarate/cyclopentadiene adducts do undergo the retro-Diels-Alder reaction on 700°-alumina. This further suggests to us that, although rate data are not available, the rate of the Diels-Alder reaction is much faster than the retro-Diels-Alder reaction in the (-)-dimenthyl fumarate case. This would reduce any loss in the diastereomeric excess. Furthermore, it follows from this analysis that the Lewis acid sites generated on the highly activated alumina also give even higher selectivities in the Diels-Alder reaction than sites generated on 400°-alumina. Any loss of selectivity on the highly activated alumina must then be due to how effectively the retro-Diels-Alder reaction competes with the Diels-Alder reaction. Why it is effective for the monoesters but not the diesters is presently not clear.

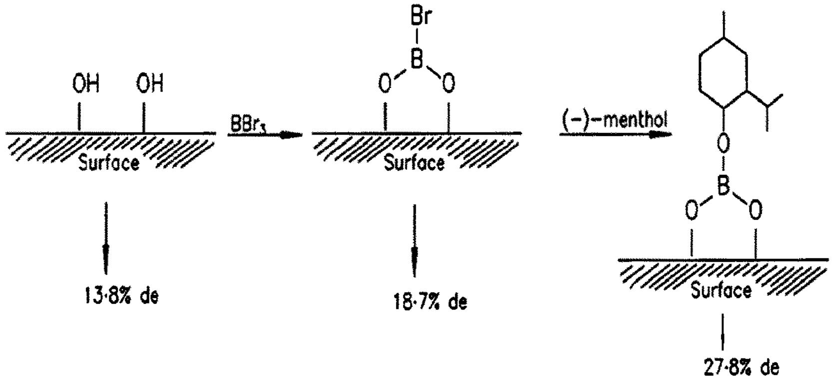
Figure 2. Selectivities in the Reactions of Dimethyl Maleate and Dimenthyl Fumarate with Cyclopentadiene



Although certain Lewis acid sites on alumina yield selectivities in the Diels-Alder reaction which are comparable to or even higher than those observed in solution, the sites simultaneously catalyze reactions which reduce selectivity. In addition, strongly basic sites are also generated on the surface, which catalyze reactions such as epimerizations;[18c] this complicates the situation. As several types of different acid sites may co-exist on the surface, each catalyzing the Diels-Alder reaction in its own way, quantitative assessment of the chemistry may be impossible.

An alternate approach, which may alleviate many of these problems, is to use the neutral alumina as a support for a chemisorbed Lewis acid of known strength. This modified alumina would possess no strongly basic sites, but would possess a single type of Lewis acid. A solid Lewis acid would also have the advantage of being easily disposed of when the reaction is complete which is certainly not the case for Lewis acids in solution. The results below suggest that this approach has merit.

When 1 mmol of BBr_3 is adsorbed onto 1 g of unactivated alumina, the resulting solid gives a higher diastereoselectivity for the (-)-dimenthyl fumarate reaction than does unactivated alumina itself (Table 2). Preliminary analysis of this solid suggests that two of the three bromines of BBr_3 are displaced by reaction with surface OH groups and one remains attached. This suggests that the Lewis acid site on the modified alumina could be made chiral by displacing the third bromine with an optically active alkoxide. This in fact was accomplished by treating the modified alumina with 1 equivalent of (-)-menthol. When the Diels-Alder reaction was performed on the twice-modified alumina, the diastereomeric excess went up by 50%. However, reaction of dimethyl fumarate with cyclopentadiene on the chiral solid yielded an adduct with 0% enantiomeric excess.



(8)

Although the chemistry described above infers a great deal about the nature of acid sites on alumina, are the reactions synthetically useful? The answer to this question depends on what is most desirable in the reaction. For the menthyl acrylate reactions, endo selectivity is higher (at -78°) than observed previously in solution, but the best diastereoselectivity observed in the endo products is somewhat less than observed in solution. For the dimenthyl fumarate reactions, since the reactions were all run at ambient temperature, the results do not compare favorably to those obtained at -78° in solution.[10] Better results should be obtained for the surface reactions when run at -78°. The BBr_3-modified aluminas clearly show promise as catalysts which enhance diastereoselectivity in the Diels-Alder reaction.

EXPERIMENTAL SECTION

Activated Alumina. This was prepared according to the literature procedure.[26]

Reaction of Cyclopentadiene with (-)-Menthyl Acrylate. The following is representative of the procedure. To 7.40 mmol of (-)-menthyl acrylate[27] at 0° was added with stirring, 31.6 g of alumina and then 9.4 mmol of cyclopentadiene. The reaction flask was heated (oil bath) to 65° and stirred for 15 h. After cooling, the mixture was extracted with acetone, filtered through Celite, and concentrated *in vacuo* to afford 1.64 g (80%) of an 81:19 endo:exo mixture (GC) of esters. This mixture was dissolved in ether and added to $LiAlH_4$ (230 mg, 6.06 mmol) in 80 mL ether at 25°. The reaction was quenched with sat. aq. Na_2SO_4, dried ($MgSO_4$), and concentrated *in vacuo* to afford a mixture of *endo-* and *exo-*bicyclo(2.2.1)hept-5-en-2-methanols (92%). The isomeric alcohols were separated by prep GC (on a 30% Carbowax 20M on 60-80 mesh Chromosorb W column) at 190°.[5] Optical rotations of the endo alcohol were measured in 95% ethanol.

Reaction of Cyclopentadiene with (-)-Dimenthyl Fumarate. The following is representative of the procedure. To a 250-mL round bottom flask containing 47.3 g of alumina was added a solution of (-)-dimenthyl fumarate (3.93 g, 10 mmol) in 50 mL of ether. After removing the ether *in vacuo*, cyclopentadiene (1.0 mL, 12 mmol) was added dropwise after which the reaction was stirred for 20 h at RT. Extraction with methanol and concentration *in vacuo* afforded the Diels-Alder adducts (90%). The mixture of esters (4.02 g, 8.77 mmol) was saponified in refluxing 70% methanolic KOH (6 h). The solvent was removed *in vacuo* leaving a solid mass which was dissolved in water. The aq. solution was extracted with ether to remove menthol and then acidified with conc. HCl. The acidified, aqueous mixture was extracted several times with ether. The combined ether extracts were washed with water, dried and the ether removed *in vacuo*, yielding 2.00 g of the diacid. The diacid was then re-esterified with CH_2N_2 in ether. The resulting dimethyl ester was purified by flash chromatography and analyzed for enantiomeric excess by ^1H nmr in $CDCl_3$ using the chiral shift reagent tris[3-(heptafluorpropylhydroxymethylene)-(+)-camphorato]europium (III).

Synthesis of BBr_3/Aluminas. Hexane (50 mL) was added under N_2 to a 60 g sample of Al_2O_3, which had previously been activated at 400°, in a 250-mL round bottomed flask with side arm and stir bar. After cooling to 0°, 60 mmol of BBr_3 (1 molar solution) in hexane was added through a double-ended 18 guage needle. HBr gas is released during this operation. After stirring for 30 min, the liquid phase was removed *in vacuo*, leaving behind a free flowing powder.

To 33 g of the above solid contained in an argon flushed 500-mL round bottomed flask, fitted with septum inlet and stir bar, was added dry hexane (33 mL) via a double-ended needle. After cooling in ice, a solution of 5.17 g (0.033 mol) of (-)-menthol in 33 mL of dry hexane was added under argon with stirring over 10 min. Some gas evolution (negative for acidity and halide) was observed during the first half of the addition. After an additional 20 min, the solution was separated from the alumina by filtration through a fritted funnel under Ar. The resulting solid was washed three times under Ar with 30 mL aliquots of dry hexane and then dried *in vacuo*.

Acknowledgment: This work was supported by the National Science Foundation, Research Corporation, and the Department of Energy. MP, RK and DC thank the University of Tennessee Science Alliance Center for Excellence for support.

REFERENCES AND NOTES

1. Woodward, R. B.; Hoffmann, R. *Conservation of Orbital Symmetry*; Academic Press: New York, 1970.
2. Finguelli, F.; Taticchi, A. *Dienes in the Diels-Alder Reaction*; Wiley Interscience: New York, 1990.
3. Dailey, W. P.; Forman, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 2762.
4. Isaacs, N. S. *Physical Organic Chemistry*; Longman/Wiley: New York, 1987; p. 705.
5. Farmer, R. F.; Hamer, J. *J. Org. Chem.* **1966**, *31*, 2418.
6. Sauer, J.; Kredel, J. *Angew. Chem. Int. Ed. Eng.* **1965**, *4*, 989.
7. Oppolzer, W.; Kurth, M; Reichlin, D; Moffatt, F. *Tetrahedron Lett.* **1981**, 2545.
8. Corey, E. J.; Imwiukelried, R.; Pikul, S.; Xiang, Y. B. *J. Am. Chem. Soc.* **1989**, *111*, 5493.
9. Ketter, A.; Glahsl, G.; Herrmann, R. *J. Chem. Res. (S)* **1990**, 278.
10. Furuta, K.; Iwanaga, K.; Yamamoto, H. *Tetrahedron Lett.* **1986**, 4507.
11. a) Le Noble, W. J. *Organic High Pressure Chemistry*; Elsevier: Amsterdam, 1988; p. 143. b) Zhulin, V. M.; Kabotyanakaya, E. B.; Kel'tseva, M. V.; Bogdanov, U. S.; Korenhkov, Y. D. *J. Org. Chem.* **1991**, , 2404.
12. Breslow, R. *Acc. Chem. Res.* **1991**, *24*, 159.
13. Rao, K. R.; Srinivasan, T. N.; Bhanumathi, N. *Tetrahedron Lett.* **1990**, 5959.
14. Braisted, A. C.; Schultz, P. G. *J. Am. Chem. Soc.* **1990**, *112*, 7430.
15. a) Veselovsky, V. V.; Gybin, A. S.; Lozanova, A. V.; Moiseenkov, A. M.; Smit, W. A.; Caple. R.

Tetrahedron Lett. **1988**, 175. b) Conrads, M.; Mattay, J.; Ransink, J. *Chem. Ber.* **1989**, *122*, 2207.

16. a) Laszlo, P.; Lucchetti, J. *Tetrahedron Lett.* **1984**, 2147. b) Laszlo, P.; Moison, H. *Chem. Lett.* **1989**, 1031. c) Collet, C.; Laszlo, P. *Tetrahedron Lett.* **1991**, 2905.
17. Narayana Murthy, Y. V. S.; Pillai, C. N. *Synth. Commun.* **1991**, *21*, 783.
18. a) Baumann, R.; Parlar, H. *Angew. Chem. Int. Ed. Eng.* **1981**, *20*, 1014. b) Koreeda, M.; Ricca, D. J.; Luengo, J. I. *J. Org. Chem.* **1988**, *53*, 5586. c) Hondrogiannis, G.; Pagni, R. M.; Kabalka, G. W.; Anosike, P.; Kurt, R. *Tetrahedron Lett.* **1990**, 5433. d) Hondrogiannis, G.; Pagni, R. M.; Kabalka, G. W.; Kurt, R.; Cox, D. *Tetrahedron Lett.* **1991**, 2303. e) Bains, S.; Pagni, R. M.; Kabalka, G. W. *Tetrahedron Lett.* in press.
19. Peri, J. B. *J. Phys. Chem.* **1965**, *69*, 220.
20. a)Knözinger, H.; Ratnasamy, *Catal. Rev. Sci. Eng.* **1978**, *17*, 31. b) Knözinger, H. in *Catalysis by Acids and Bases*; Imelik, B.; *et al.* editors; Elsevier: Amsterdam, 1985; p. 111.
21. Unpublished results.
22. Berson, J.; Hamlet, Z.; Mueller, W. A.; *J. Am. Chem. Soc.* **1962**, *84*, 297.
23. Braum, R.; Sauer, J. *Chem. Ber.* **1986**, *119*, 1269.
24. a) Marchand, A. P.; Vidyasagar, V. *J. Org. Chem.* **1988**, *53*, 4412. b) Grieco, P.; Abood, N. *J. Org. Chem.* **1989**, *54*, 6008; *Chem. Commun.* **1990**, 410.
25. The reaction in toluene in the absence of catalyst yielded a 2% diastereomeric excess with the (S,S)-isomer in excess.[10]
26. Gaetano, K.; Pagni, R. M.; Kabalka, G. W.; Bridwell, P; Walsh, E.; True, J.; Underwood, M. *J. Org. Chem.* **1985**, *50*, 499.
27. Oppolzer, W.; Chapius, C.; Dupuis, D.; Guo, M. *Helv. Chim. Acta* **1985**, *68*, 2100.

DEDICATION

Dedicated to Professor Herbert C. Brown on the occasion of his 80th birthday.