Stereochemical studies of other systems are in progress.

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Stereochemical Aspects of the Intramolecular Diels–Alder Reactions of Methyl Deca-2,7,9-trienoates. 2. Lewis Acid Catalysis

Summary: The Lewis acid catalyzed intramolecular Diels–Alder reactions of all-trans trienes **1** and **2** afford exclusively the trans-fused cycloadducts; in contrast, mixtures of cis- and trans-fused cycloadducts are obtained from the catalyzed cyclizations of trienes **3** and **4**, the cis dienophile isomers of **1** and **2**.

Sir: We have studied the intramolecular Diels–Alder reactions of a series of methyl deca-2,7(*E*),9-trienoates and have found that the thermal cyclizations of these trienes preferentially afford trans-perhydroindene cycloadducts independent of dienophile stereochemistry.[1] The selectivity for the trans-fused product ranges from 60:40 in the least favorable case to a maximum of 83:17. Hopeful that the selectivity of these cyclizations could be altered or improved by Lewis acid catalysis,[2] we have initiated studies on this problem. We are pleased to report herein that the Diels–Alder reactons of trienes **1**–**4**[1] are subject to catalysis and that *in the presence of Lewis acids all-trans trienes 1 and 2 afford exclusively the corresponding trans-fused cycloadducts.*

Previous attempts to catalyze intramolecular Diels–Alder reactions have met with limited success. Prior to this study, only three examples of catalyzed intramolecular Diels–Alder reactions had been reported.[3,4] The rate accelerations observed in these cases have been only modest, and changes in product selectivity of the type frequently encountered in catalyzed bimolecular Diels–Alder reactions[2] were unknown. The results reported in Table I for **1** and **2** represent the first significant examples of both phenomena in an intramolecular Diels–Alder reaction. Whereas the thermal cyclizations require temperatures of at least 150 °C for a practical rate of cyclization, the catalyzed reactions are conveniently performed at temperatures below 50 °C—*in most cases at room temperature*—depending on the Lewis acid employed. These two reactions are also highly stereoselective, as noted above.

Typically, these cyclizations were performed by adding a Lewis acid to a solution of triene in CCl_4 or CH_2Cl_2 under an inert atmosphere, except for the reactions catalyzed by menthoxyaluminum dichloride[5] which were performed in a toluene–CH_2Cl_2 cosolvent mixture.[6] In most cases, stoichiometric quantities of Lewis acid were required for complete cyclization. The progress of the reactions was monitored by TLC or ^1H NMR spectroscopy. When complete as judged by these analytical methods, the reactions were worked up by aqueous extraction, and the cyclization products were then isolated by standard techniques.

The yield of cyclization product depends on the choice and amount of Lewis acid used, as triene polymerization competes with cyclization in nearly all of the examples reported in Table I. This problem is most serious with triene **4** and when $BF_3{\cdot}Et_2O$, $TiCl_4$, or $SnCl_4$ is used as catalyst. Polymerization is also a problem with $AlCl_3$ and $EtAlCl_2$,[7] two of the more efficient Lewis acids used in this study, but is minimized by limiting the amount of these reagents employed (entries 3, 4, 6, 7, 14, 15). Best results were obtained with **1** with $AlCl_3$, $EtAlCl_2$, Et_2AlCl, or menthoxyaluminum dichloride, and these reagents were therefore the only Lewis acids studied with **2**–**4**. Although acceptable yields of cycloadducts from **2** and **3** were obtained using $AlCl_3$, we favor use of $EtAlCl_2$, Et_2AlCl, or menthoxyaluminum dichloride because of their mildness and ease of handling.[8]

In contrast to the excellent selectivity and good yields of product realized with **1** and **2**,[9] the catalyzed cyclizations of cis trienes **3** and **4** are not improved relative to the thermal reactions either in terms of product yield or in terms of a significant change in product selectivity. The moderate change in selectivity realized with **4** and the lack of a change with **3** imply that increased secondary orbital control resulting from an interaction between the ester carbonyl and the Lewis acid,[10] which presumably accounts for the increased selectivity with **1** and **2**,[2] is insufficient to overcome the transition-state preference for the trans-fused product noted in the thermal cyclizations.[1,11]

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(1) Roush, W. R.; Ko, A. I.; Gillis, H. R. *J. Org. Chem.*, preceding paper in this issue, and references cited therein.

(2) Lewis acid catalysis is very effective in improving the selectivity of bimolecular Diels–Alder reactions; see: Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976; pp 161–165; Houk, K. N.; Strozier, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 4046; Houk, K. N. *Acc. Chem. Res.* **1975**, *11*, 361 and references therein.

(3) (a) Wenkert, E.; Naemura, K. *Synth. Commun.* **1973**, *3*, 447. (b) DeClercq, P. J.; Van Royen, L. A. *Ibid.* **1979**, *9*, 771. (c) Mukaiyama, T.; Tsuji, T.; Iwasawa, N. *Chem. Lett.* **1979**, 697. See also: Mukaiyama, T.; Iwasawa, N.; Tsuji, T.; Narasaka, K. *Ibid.* **1979**, 1175.

(4) Unsuccessful attempts have also been reported: (a) Parker, K. A.; Adamchuk, M. R. *Tetrahedron Lett.* **1978**, 1689; (b) Evans, A. J. Ph.D. Thesis, University of Minnesota, 1975.

(5) Hayakawa, Y.; Fueno, T.; Furukawa, J. *J. Polym. Sci.* **1967**, *5*, 2099. Racemic menthoxyaluminum dichloride was used throughout this study. The chiral catalyst has been previously applied to bimolecular Diels–Alder reactions: Hashimoto, S.-I.; Korneshima, N.; Koga, K. *J. Chem. Soc., Chem. Commun.* **1979**, 437.

(6) The $AlCl_3$-catalyzed cyclizations of **1** and **3** performed in toluene give poor results, owing to Friedel–Crafts reaction with the solvent.

(7) $EtAlCl_2$ has previously been used as a catalyst for ene reactions: Snider, B. B.; Rodini, D. J.; Conn, R. S. E.; Sealfon, S. *J. Am. Chem. Soc.* **1979**, *101*, 5283.

(8) $EtAlCl_2$ and Et_2AlCl are commercially available as 25% solutions in either hexane (Alfa) or toluene (Aldrich). Menthoxyaluminum dichloride is conveniently prepared in situ from menthol and $EtAlCl_2$ (toluene).

(9) The lower yields of **7** from **2** are in part a consequence of the volatility of this compound.

(10) Evidence that such complexation occurs is provided by the observation that the ^1H NMR signals for the methoxyl groups and C(3) H of **1**–**4** are shifted in the presence of 1.0 equiv of $EtAlCl_2$. Invariably, the methoxyl signal is shifted upfield, whereas the resonance for C(3) H is shifted downfield.

(11) Control experiments established that mixtures of **5** and **6**, **7** and **8**, **9** and **10**, and **11** and **12** are stable toward $EtAlCl_2$ under the conditions reported in Table I. Thus, it is unlikely that the product ratios reported for other Lewis acids reflect selective decomposition of the cis-fused cycloadducts.

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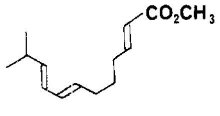
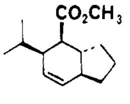
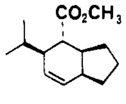
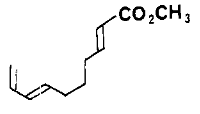
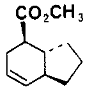
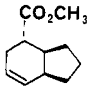
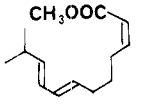
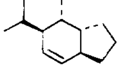
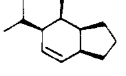
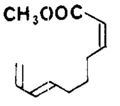
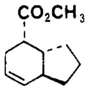
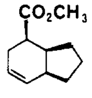
Table I

entry	substr[a]	catalyst (equiv)	conditions	yield,[b] %	products and ratios[c]
	 1				 5  6
1		-	150 °C, 40 h	72	72:28[d]
2		menthyl-OAlCl$_2$ (1.4)	23 °C, 48 h	79-83	100:0[d]
3		EtAlCl$_2$ (0.9)	23 °C, 18 h	70	100:0[d]
4		(1.1)	23 °C, 12 h	47	100:0[e]
5		Et$_2$AlCl (1.0)	23 °C, 48 h	77	100:0[e,g]
6		AlCl$_3$ (0.1)	23 °C, 18 h	75-84	100:0[d]
7		(0.5)	23 °C, 7 h	55	100:0[e]
8		BF$_3$·Et$_2$O (1.5)	50 °C, 46 h	52	100:0[e]
9		TiCl$_4$ (0.2)	50 °C, 10 h	47	100:0[e]
10		(1.6)	23 °C, 1 h	23	100:0[e]
11		SnCl$_4$ (1.0)	50 °C, 24 h	42	100:0[e]
	 2				 7  8
12		-	150 °C, 24 h	65	60:40[d,f]
13		menthyl-OAlCl$_2$ (1.0)	23 °C, 48 h	72	100:0[d,f]
14		EtAlCl$_2$ (0.9)	23 °C, 36 h	60	100:0[e]
15		(1.1)	23 °C, 48 h	34	100:0[d,f]
16		Et$_2$AlCl (0.9)	23 °C, 43 h	50	100:0[e]
17		AlCl$_3$ (0.1)	50 °C, 10 h	50	100:0[d,f]
	 3				 9  10
18		-	180 °C, 6 h	75	67:33[f]
19		EtAlCl$_2$ (0.9)	23 °C, 40 h	59	63:37[f]
20		AlCl$_3$ (0.1)	50 °C, 18 h	48	68:32[f]
	 4				 11  12
21		-	180 °C, 5 h	75	65:35[f]
22		EtAlCl$_2$ (1.0)	23 °C, 40 h	27	52:48[f]
23		menthyl-OAlCl$_2$ (1.0)	23 °C, 72 h	20	56:44[f]

[a] The thermal chemistry of 1-4 is described in ref 1. [b] The yield of isolated (chromatographed) product. [c] Ratio of trans-fused to cis-fused cycloadduct. [d] Product ratio determined by 250-MHz NMR analysis under conditions with resolution greater than a 60:1 signal to noise ratio. Less than 2% of the cis-fused isomer could go undetected under these conditions. [e] Product ratio determined by NMR analysis at either 60 or 90 MHz. As much as 5% of the cis-fused product could go undetected by this method. [f] Product ratio determined by GC analysis (10-ft column, 4% SE-30/Chromosorb G). [g] 10% of unchanged 1 was also recovered.

We are continuing to study the catalyzed cyclizations of 3 and 4 with hope that improved conditions or catalysts can be found. At the present time, however, the great potential of Lewis acid catalyzed cyclizations appears restricted to all-trans trienes for which the transition-state preference for the trans-fused product and secondary orbital control reinforce one another. Applications of this method to more highly functionalized trienes are in progress, as are studies of absolute stereochemical induction.

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