Preparation of 1-Hydroxy-8-(methylthio)naphthalene (5b) and 1-Hydroxy-2-(methylthio)naphthalene (6b). The dianion of **4** (2 mmol), generated as shown in the general procedure, was quenched with dimethyl disulfide (1 mL), dissolved in 1.5 mL of THP, and then stirred for 30 min. Standard extractive workup (ether) yielded a crude oily material, which was purified by chromatography on a short-path silica gel column (CH_2Cl_2–hexane) and then separated on preparative silica gel plates (CH_2Cl_2–hexane, 2:5), thus furnishing **5b**, **6b**, and **7b** in 50%, 19%, and 1% yield, respectively.

5b: yellow oil; bp 120 °C (10^{-3} mmHg); IR (film) 3380, 2930, 1565, 1255, 820, 760 cm^{-1}; ^1H NMR δ 7.84–7.00 (m, 7 H), 2.48 (s, 3 H); EIMS, *m/e* (relative abundance) 190 (M^+, 100), 175 (52), 147 (49), 115 (19), 102 (13), 69 (12). Anal. Calcd for $C_{11}H_{10}OS$: C, 69.44; H, 5.29. Found: C, 69.85; H, 5.20.

6b: yellow oil; bp 70 °C (10^{-3} mmHg); IR (film) 3380, 2920, 1565, 1380, 1260, 1070, 880, 800 cm^{-1}; ^1H NMR δ 8.18 (m, 1 H, H8), 7.80–7.20 (m, 6 H), 2.33 (s, 3 H); EIMS, *m/e* (relative abundance) 190 (M^+, 100), 175 (69), 147 (32), 115 (24), 102 (15), 69 (17), 63 (20). Anal. Calcd for $C_{11}H_{10}OS$: C, 69.44; H, 5.29. Found: C, 69.24; H, 5.19.

Attempted Preparation of 1-Hydroxy-8-methylnaphthalene (5c) and 1-Hydroxy-2-methylnaphthalene (6c). 1-Naphthol (**4**) (2 mmol) was first treated with *t*-BuLi as illustrated in the general procedure and then quenched with methyl iodide (1.84 g) dissolved in THP (3 mL). The usual extractive workup (ethyl acetate) furnished an unseparable mixture, which was shown (GC/MS) to contain two monomethyl derivatives and one dimethyl derivative, as well as starting material in a 2:10:1:7 ratio.

Preparation of 5-(Methylthio)-1,4-naphthoquinone (8b). A methanolic solution (9 mL) of **5b** (0.21 g) was added all at once to 10 mL of a buffered solution (pH 6) of Fremy's salt (0.6 g). The mixture was vigorously stirred for 15 min and then extracted with ethyl acetate (7 × 25 mL). The extracts were washed with brine and water and then dried over anhydrous Na_2SO_4. Removal of the solvent furnished crude **8b**, which gave crystals from methanol (89% yield): mp 200–201 °C; IR (KBr) 1655, 1640, 1600, 1565, 1325, 1285, 1135, 1075, 770 cm^{-1}; ^1H NMR δ 7.95–7.60 (m, 3 H), 6.95 (d, J = 10.2 Hz, 1 H), 6.92 (d, J = 10.2 Hz, 1 H), 2.51 (s, 3 H); EIMS, *m/e* (relative abundance) 204 (M^+, 60), 190 (34), 189 (76), 187 (34), 171 (19), 147 (14), 115 (29), 89 (17), 75 (29), 45 (17), 44 (100). Anal. Calcd for $C_{11}H_8O_2$: C, 64.69; H, 3.95; S, 15.69. Found: C, 64.58; H, 4.12; S, 15.86.

Preparation of 2-(Methylthio)-1,4-naphthoquinone (9b). A cooled (0 °C) solution of **6b** (0.105 g) in methanol (5 mL) was treated with 20 mL of a buffered solution of Fremy's salt (2.5 g), as above. The solution was left to stir for 60 min and then worked up as usual. The organic extracts (ethyl acetate), once washed with brine and water, were evaporated in vacuo, thus yielding 0.855 g (70%) of **9b**, which sublimed at 98 °C (10^{-3} mmHg): mp 185–186 °C (benzene–ethanol) (lit.[20] mp 185–186 °C); IR (KBr) 1660, 1635, 1580, 1545, 1290, 1290, 1120, 1090, 1070, 1020, 860, 800, 775 cm^{-1}; ^1H NMR δ 8.16–8.03 (m, 4 H), 6.57 (s, 1 H)8 2.38 (s, 3 H); EIMS, *m/e* (relative abundance) 204 (M^+, 100), 203 (31), 189 (80), 176 (31), 147 (12), 143 (13), 133 (18), 104 (29), 89 (40), 76 (65), 50 (45).

Preparation of 1-(Methylthio)anthrone (11) and 1-(Methylthio)-9,10-anthraquinone (12). Direct lithiation of commercial anthrone **10** (0.78 g, 4 mmol) was carried out as illustrated in the general procedure. The resulting paste was cooled to 0 °C and, subsequently, treated with dimethyl disulfide (0.75 g, 8 mmol). After 10 min the resulting mixture was worked up as usual. Column chromatography (silica gel, hexane–chloroform, 9:1) of the crude solid furnished 0.443 g of an easily oxidizable material, which on further chromatography provided 0.152 g of **11** and 0.100 g of **12**.

11: orange solid; mp 138–140 °C; IR (KBr) 1630, 1595, 1460, 1385, 1320, 1280, 930, 900, 810, 740, 710 cm^{-1}; ^1H NMR δ 2.46 (s, 3 H), 4.38 (s, 2 H), 7.10–7.60 (m, 6 H), 8.31 (m, 1 H, H8). An analytically pure sample of **11** could not be obtained.

12: orange solid; mp 196–8 °C; IR (KBr) 1660, 1560, 1410, 1330, 1310, 1260, 1230, 1155, 1130, 965, 950, 800 cm^{-1}; ^1H NMR (200 MHz) δ 2.53 (s, 3 H), 7.62 (dd, J = 8.2, 1.6 Hz, 1 H, H2), 7.70 (dd, J = 8.2, 7.2 Hz, 1 H, H3), 7.77 (ddd, J = 8.2, 7.2, 1.6 Hz, 1 H, H6), 7.79 (ddd, J = 8.2, 7.2, 1.6 Hz, 1 H, H7), 8.12 (dd, J = 7.2, 1.6 Hz, 1 H, H4), 8.24 ddd, J = 7.2, 1.6, 0.5 Hz, 1 H, H8), 8.32 (ddd, J = 7.2, 1.6, 0.5 Hz, 1 H, H5); EIMS, *m/e* (relative abundance) 254 (M^+, 54), 241 (6), 240 (15), 239 (100), 238 (9), 237 (45), 221 (14), 183 (5), 165 (7), 152 (7); exact mass calcd for $C_{15}H_{10}O_2S$ 254.0402 (M^+), found 254.0380.

(20) Fieser, L. F.; Brown, R. M. *J. Am. Chem. Soc.* **1949**, *71*, 3610.

Acknowledgment. This work was supported by a research grant from the CAICYT (Project 1073/84). We are particularly indebted to the University of Málaga (Department Organic Chemistry) and University of Santiago de Compostela (Department Organic Chemistry) for recording our 200-MHz ^1H NMR spectra. Thanks are also due to Dr. G. Tojo and J. M. Riego for obtaining HRMS.

Registry No. 1, 135-19-3; **2a**, 581-71-5; **2b**, 116130-48-4; **2c**, 17324-04-8; **3**, 483-55-6; **4**, 90-15-3; **4** (dimethyl deriv), 40529-54-2; **5a**, 35689-26-0; **5b**, 116130-50-8; **5c**, 32849-41-5; **6b**, 90033-53-7; **6c**, 7469-77-4; **7a**, 116130-49-5; **7b**, 116130-51-9; **8b**, 116130-52-0; **9b**, 26037-60-5; **10**, 90-44-8; **11**, 116130-53-1; **12**, 2687-50-5; 1,3-$(OH)_2C_6H_4$, 108-46-3.

Epimerization and Stereoselectivity in the Diels–Alder Reaction of Monosubstituted Dienophiles

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Introduction

The Diels–Alder reaction between 1-substituted 1,3-butadiene and monosubstituted dienophiles can give two stereoisomers, endo and exo. Generally, the endo isomer is kinetically preferred and the exo isomer is thermodynamically more stable; however, exceptions to this generalization are known.[1] Epimerization is usually not observed under mild conditions for either the thermal or Lewis acid catalyzed reactions.[2-7] More vigorous reaction conditions in the presence of a strong base are needed to initiate conversion to the more stable exo stereoisomer.[2,3] In our investigation of the stereoselectivity in the Diels–Alder reaction between *trans*-1,3-pentadiene (piperylene) and acrolein, a rapid epimerization at room temperature was unexpectedly observed in the presence of a Lewis acid.[8] To understand the scope of this phenomenon, we initiated

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(3) Inukai, T.; Kojima, T. *J. Org. Chem.* **1967**, *32*, 869.
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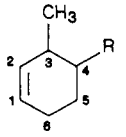
(7) (a) Overman, L. A.; Petty, C. B.; Ban, T.; Huang, G. T. *J. Am. Chem. Soc.* **1983**, *105*, 6335. (b) Overman, L. E.; Jessup, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 5179. The endo/exo ratios with acrolein and crotonaldehyde were observed to decrease with time.
(8) After completion of this study Rousch et al. reported substantial epimerization with an aldehyde substituent in a Lewis acid catalyzed intramolecular Diels–Alder reaction: (a) Rousch, W. R.; Esenfeld, A. P.; Warmus, J. S. *Tetrahedron Lett.* **1987**, *28*, 2447. (b) Rousch, W. R.; Riva, R. *J. Org. Chem.* **1988**, *53*, 710.

0022-3263/88/1953-5348$01.50/0

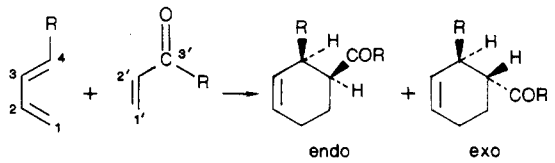
Table I. ^{13}C NMR Chemical Shifts (ppm) of the Stereoisomers



subst (R)	C-1	C-2	C-3	C-4	C-5	C-6	CH_3	R	ref
CHO-*endo*	126.6	132.0	29.9	50.6	18.7	24.4	17.0	204.2	*a*
CHO-*exo*	125.8	131.7	29.7	53.6	21.8	23.7	20.4	205.2	*a*
CHO-*endo*	126.5	131.8	29.7	50.5	18.5	24.3	16.9	204.0	*b*
CHO-*exo*	125.8	131.5	29.6	53.6	21.5	23.7	20.3	204.7	*b*
CHO (calcd)	126.5	131.7	31.5	53.8	21.3	24.4			*b*
$COOCH_3$-*endo*	126.0	132.0	31.3	43.2	19.6	25.1	16.5	174.8, 51.1	*a*
$COOCH_3$-*exo*	125.6	132.2	32.8	47.9	24.8	26.0	20.4	175.9, 51.4	*a*
$COOCH_3$-*endo*	125.8	131.7	31.1	43.5	19.4	24.9	16.5	175.0, 51.1	*b*
$COOCH_3$-*exo*	125.5	132.0	32.6	47.7	24.6	25.8	20.3	176.3, 51.4	*b*
$COOCH_3$ (calcd)	127.1	131.9	34.4	48.0	24.2	25.1			*b*
CN-*endo*	126.2	129.9	31.4	31.1	24.0	22.4	18.4	120.4	*a*
CN-*exo*	126.0	130.1	33.9	32.9	25.1	23.5	20.2	122.0	*a*
CN-*endo*	126.2	129.9	31.4	31.1	24.1	22.4	18.5	120.4	*b, c*
CN-*exo*	126.0	130.1	33.8	32.9	25.1	23.5	20.2	122.0	*b, c*
$COCH_3$-*endo*	126.2	132.0	31.0	51.3	25.2	28.3	16.1	209.7, 18.5	*a*
$COCH_3$-*exo*	125.3	132.5	31.6	55.4	25.0	28.8	20.3	210.9, 18.4	*a*

[a] This work. [b] Reference 13. [c] Reference 22.

a study, which is reported in this paper, of epimerization in both the thermal and Lewis acid catalyzed Diels–Alder reactions of monosubstituted dienophiles with *trans*-1,3-pentadiene.



It is generally accepted that endo stereoselectivity originates from secondary orbital interactions between the nonbonding π-orbitals of the diene (C-3) and the dienophile (C-3′).[9,10] Recently, Houk et al.[11] and Fox et al.[12] have suggested that steric effects are the major factor that controls the stereoselectivity in the Diels–Alder reactions of cyclopentadiene and its analogues and that secondary orbital effects, if present, are small. To further define the roles of steric effects and secondary orbital interactions, we have compared the stereoselectivity in the Diels–Alder reactions of *trans*-1,3-pentadiene and cyclopentadiene with monosubstituted dienophiles. The steric effects will be similar in both the endo and exo modes of additions for *trans*-1,3-pentadiene while greater steric repulsion is expected in the exo addition for cyclopentadiene because of the methylene group. Frontier molecular orbital theory is employed to predict the effect of the secondary orbital interactions.

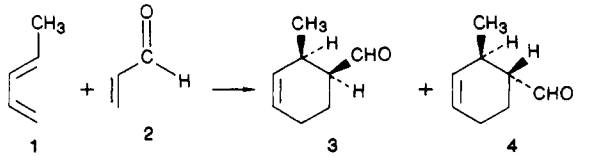
Results

The Diels–Alder reaction between *trans*-1,3-pentadiene (**1**) and acrolein (**2**) was carried out at room temperature. Two major products were detected by ^1H NMR analysis of the adduct mixture and were assigned as the endo **3** and exo **4** adducts. This assignment was confirmed by ^{13}C NMR analysis of the adducts, which were in excellent agreement with previously reported spectra (Table I).[13] Two sets of doublets that corresponded to the aldehyde protons of the adducts were observed in the ^1H NMR spectrum of the adduct mixture and an endo/exo ratio of 85:15 was obtained by integration of the peaks, after 6 days of reaction at room temperature. An equilibrium endo/exo ratio of 63:37 was obtained after 30 days of reaction at room temperature. When the reaction was carried out at 60 °C, endo/exo ratios of 82:18 by ^1H NMR and 92:8 by ^{13}C NMR analyses were obtained after 2 days,[14] and the equilibrium ratio of 63:37 was obtained in only 4 days via ^1H NMR spectroscopy.

Table II. Effect of GC Column Temperature on the Endo/Exo Ratio of the Reaction between *trans*-1,3-Pentadiene and Acrolein

column temp,[a] °C	*endo*-**3**/*exo*-**4**	column temp,[a] °C	*endo*-**3**/*exo*-**4**
60	84:16	120	81:19
80	83:17	140	78:22
100	82:18	160	75:25

[a] A 0.125-in. glass column that was packed with 10% OV-210, Chromosorb W-HP 80/100 was used.



The boron trifluoride catalyzed reaction of **1** and **2** was carried out at −78 °C in methylene chloride. The equilibrium endo/exo ratio of 63:37 was obtained in 25 min. When an equimolar amount of BF_3–etherate was added to the thermal adduct mixture (85:15 ratio) at room temperature, the same equilibrium ratio was also obtained in 25 min.

The effects of Lewis acid catalysis and temperature on the stereoisomer ratio suggest that commonly employed

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(12) Fox, M. A.; Cardona, R.; Kiwiet, N. J. *J. Org. Chem.* **1987**, *52*, 1469.
(13) Nakagawa, K.; Sawai, M.; Ishii, Y.; Ogawa, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2487.
(14) The discrepancy between the ^1H NMR and ^{13}C NMR integrations in this case may be due to nuclear Overhauser effect and/or differences in relaxation times of the carbons in the ^{13}C NMR analysis.

Table III. Stereoselectivity[a] and Epimerization in the Diels–Alder Reaction of Monosubstituted Dienophiles

	trans-1,3-pentadiene				
	endo/exo		epimerization: eqlb time of isomers		cyclopentadiene: endo/exo
dienophile	GC	NMR	25 °C	60 °C	
acrolein–Lewis acid	*b*		25 min		
methyl vinyl ketone–Lewis acid	95:5 (25 °C)[c]		5 days		
methyl acrylate–Lewis acid	95:5 (25 °C)[d]		>6 days		95:5 (0 °C)[e]
acryloyl chloride					91:9 (35 °C)[f]
acrolein	84:16 (60 °C)[g]	85:15 (25 °C)[g,h] 82:18 (60 °C)[g,h] 92:8 (60 °C)[g,i]	30 days	4 days	80:20 (25 °C)[j,k]
methyl vinyl ketone	88:12 (60 °C)[g]	83:17 (60 °C)[g,i]		not detected	82:18 (35 °C)[f]
methyl acrylate	59:41 (60 °C)[g] 57:43 (25 °C)[d]	59:41 (60 °C)[g,i]		not detected	74:26 (35 °C)[f] 70.5:29.5 (100 °C)[l]
acrylonitrile	56:44 (60 °C)[g]			not detected	55:45 (100 °C)[l]

[a] Reaction temperature is given in parentheses. The endo/exo ratio usually decreases as the reaction temperature is increased. [b] Kinetically controlled ratio could not be determined because of rapid epimerization. [c] Reference 21. [d] Reference 3. [e] Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16. [f] Reference 6. [g] This work. [h] ^{1}H NMR analysis. [i] ^{13}C NMR analysis. [j] Reference 20. [k] Other studies[4,6] have reported ratios of 75:25 and 70.5:29.5; however, the percentage of the endo isomer is probably higher because epimerization can occur under the analysis conditions that were employed. [l] Reference 4.

Table IV. Effect of Lewis Acid Catalysis on the Endo/Exo Ratio of the Reaction between *trans*-1,3-Pentadiene and Methyl Vinyl Ketone at 25 °C

time after BF_3 addition to adduct mixture	endo/exo[a]	time after BF_3 addition to adduct mixture	endo/exo[a]
0	88:12	2 days	55:45
1 h	85:15	5 days	30:70
1 day	71:29	7 days	30:70

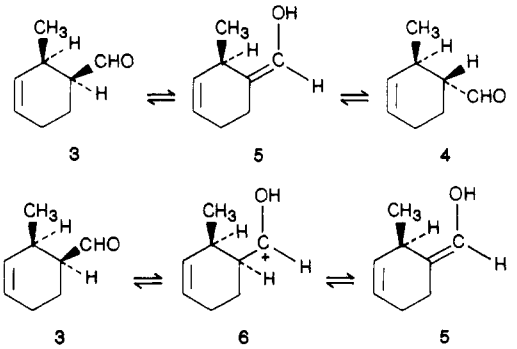
[a] Determined by GC analysis at 60 °C column temperature.

separation techniques such as column chromatography and gas chromatography (GC) may alter the endo/exo.[15] This concern was confirmed by GC analysis of the adduct mixture **3**/**4** at various column temperatures. The endo/exo ratio was shifted toward the exo isomer as the column temperature was increased; for example, the ratio was 84:16 at a column temperature of 60 °C and 75:25 at a column temperature of 160 °C (Table II). Furthermore, the lower endo/exo ratio in the GC analysis versus ^{13}C NMR analysis suggest that epimerization may already be occurring at the 60 °C column temperature.

The reactions of methyl vinyl ketone, methyl acrylate, and acrylonitrile with *trans*-1,3-pentadiene were investigated in a similar manner (Table III). Epimerization was not observed in the thermal reactions; however, the addition of BF_3–etherate solution to the adduct mixtures initiated epimerization in the cases of methyl vinyl ketone and methyl acrylate. The equilibrium endo/exo ratio was reached in 5 days at room temperature for the methyl vinyl ketone (Table IV). The adducts of methyl acrylate did not reach equilibrium after 6 days; however, the ratio did change in favor of the exo adduct.

Discussion

Epimerization is known to proceed through a keto–enol equilibrium **3** ⇌ **5** ⇌ **4**, which needs a liable α-hydrogen.[1] This α-hydrogen is present in all of the reactions. The propensity of an adduct to undergo epimerization can be related to the formation of the ionic structure **6** under acidic conditions.[16] Thus, a Lewis acid will shift the equilibrium toward **6** and thereby enhance epimerization. The ability of the methyl and methoxy groups to retard epimerization can be attributed to shift of the keto–enol equilibrium toward the keto structure. For example, the enol contents of acetaldehyde, acetone, and ethyl acetate are 0.001%, 0.000 000 6%, and not detected, respectively.[1]



Frontier molecular orbital theory[17] has been used successfully in accounting for reactivity,[18] regioselectivity,[19] and stereoselectivity[10] in the Diels–Alder reaction. In the application of the theoretical approach to stereoselectivity, the secondary orbital interactions between the carbonyl carbon of the dienophile and the secondary carbons of the diene are assumed to control the stereoselectivity. Thus, stereoselectivity is predicted to increase when (1) the secondary orbital coefficients increase and/or (2) the energy gap between the diene HOMO and the dienophile LUMO decreases for the normal Diels–Alder reaction. For a series of structurally similar dienophiles, the following substituent effect is predicted from these generalizations and the LUMO's of the dienophiles (Table V): $CHO{-}BF_3 > COCl > CHO \simeq COCH_3 > COOCH_3 > CN$. Consideration of closed-shell repulsion[17] via π-electron densities (Table V) does not change this order. This substituent effect, which is based on secondary orbital interactions, is generally followed in the reactions of *trans*-1,3-pentadiene and cyclopentadiene (Table III). The only exceptions are two studies,[4,6] which reported the same stereoselectivity for acrolein and methyl acrylate. This deviation

(15) Pfeuffer, L.; Pindur, U. *Helv. Chim. Acta* **1987**, *70*, 1419. The diene component of a Diels–Alder reaction was observed to easily equilibrate towards the thermodynamically stable isomer upon contact with silica gel.
(16) Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1.
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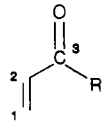
Table V. CNDO/2 Lowest Unoccupied Molecular Orbitals and π-Electron Densities of Various Dienophiles from the Transition-State Geometry[a]



dienophile	LUMO coefficients C-1	LUMO coefficients C-2	LUMO coefficients C-3	LUMO energy, eV	π-electron density C-1	π-electron density C-2	π-electron density C-3
acrolein–BF_3	0.604	−0.376	−0.539	0.55 (0.43)[b]	0.884	1.048	0.741
acryloyl chloride	0.580	−0.347	−0.458	1.19	0.917	1.032	0.837
acrolein	0.623	−0.427	−0.437	2.13 (2.60)[b]	0.950	1.010	0.849
methyl vinyl ketone	0.606	−0.423	−0.430	2.21	0.959	1.007	0.842
methyl acrylate	0.647	−0.461	−0.408	2.29 (2.91)[b]	0.933	1.028	0.819
acrylonitrile	0.671	−0.558	−0.262	2.93 (2.86)[b]	0.984	1.003	0.960

[a] A bond length of 1.40 Å was used for the carbon–carbon double bond. See: Townshend, R. E.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 2190 and ref 17. The relative trends in the LUMO energies and coefficients are the same for both the transition-state geometry and the ground-state geometry. [b] LUMO energies from ab initio calculations: Kahn, S. D.; Pau, C. F.; Overman, L. E.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7381.

from theory may be due to epimerization of the acrolein adducts under reaction conditions and/or the GC separation conditions that were employed. In the most recent study of the reaction between cyclopentadiene and acrolein, a higher endo/exo ratio of 80:20 was found when the reaction mixture was analyzed by NMR.[20] Also, Rousch et al.[8] observed a substituent effect, CHO > $COCH_3$ > $COOCH_3$ > CONRR, on the stereoselectivity of the intramolecular Diels–Alder reaction that is consistent with the theory.

The stereoselectivities in the reactions of *trans*-1,3-pentadiene and cyclopentadiene were surprisingly similar. If steric repulsion in the exo addition to the cyclopentadiene is the major controlling factor, then higher stereoselectivity in the reactions of cyclopentadiene would be expected because both the steric effects and the secondary orbital interactions favor the endo addition. The only dienophile for which this phenomenon appears to be present is methyl acrylate, and even in this case the relative substituent effect via the secondary orbital interactions is still followed.

In conclusion, the stereochemistry in the Diels–Alder reactions of *trans*-1,3-pentadiene with monosubstituted dienophiles is accounted for by secondary orbital effects and not by steric effects.

Experimental Section

^1H NMR and ^{13}C NMR spectra were taken on a JEOL FX90 multinuclear fourier transform NMR instrument. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and coupling constants in cycles per second (hertz). NMR signals are designated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. GC analysis were carried out on a Hewlett-Packard 7620A research chromatograph that was equipped with a flame-ionization detector and a glass column (6-ft length, 0.125-in. o.d., 10% OV-210, Chromosorb W-HP 80/100).

The reactions of methyl vinyl ketone, methyl acrylate, and acrylonitrile were carried out by the same general procedure that is given for acrolein. The reaction times at 60 °C were varied to obtain 80% addition of the reactants by GC analysis. The structural assignments of the adducts were confirmed by ^{13}C NMR analysis, and the integration of the C-4 peak was used to establish the endo/exo ratio by ^{13}C NMR analysis. The ^{13}C NMR spectra of the adducts were in excellent agreement with previously reported spectra (Table I). The reactions of the various dienophiles with *trans*-1,3-pentadiene have been previously studied: acrolein,[13] methyl vinyl ketone,[21] methyl acrylate,[3,13] and acrylonitrile.[13,22]

Reaction of *trans*-1,3-Pentadiene and Acrolein. Acrolein (0.009 mol) and *trans*-1,3-pentadiene (0.007 mol) were added to 1 mL of cyclohexane and 20 mg of hydroquinone and sealed in a glass tube with a septum. The mixture was heated at 60 °C for 96 h. The progress of the reaction was monitored by GC analysis until the reaction was 80% complete. The unreacted acrolein and the solvent were removed from the reaction mixture under reduced pressure. The mixture was diluted with ether, washed with water, dried with $MgSO_4$, filtered, and then concentrated. Analysis of the adduct mixture by ^1H NMR spectroscopy gave the endo/exo ratio of 63:37. The endo/exo ratio was 85:15 by ^1H NMR analysis when the reaction was carried out at room temperature for six days.

The Lewis acid catalyzed reaction was carried out by adding 0.5 mL of BF_3–etherate to 10% acrolein in methylene chloride at −78 °C (1:1 molar ratio of acrolein and BF_3). The *trans*-1,3-pentadiene was added, and the reaction was followed by GC analysis. Twenty seconds after the addition of diene, the isomer ratio was 88:12. The reaction was complete after 25 min, and the final endo/exo ratio was 63:37. The reaction mixture was filtered and diluted with ether, washed with a saturated solution of $NaHCO_3$ and then with water, dried over $MgSO_4$, and filtered again, and the solvent was removed. ^1H NMR analysis of the adduct mixture also gave an endo/exo ratio of 63:37.

Another experiment was carried out by adding an equimolar amount of BF_3–etherate to the isolated adduct mixture of the thermal reaction (85:15 ratio) at room temperature. The equilibrium ratio 63:37 was reached in 25 min.

^1H NMR ($CDCl_3$) of **3**: δ 9.74 (d, 1 Hz, 1 H, aldehyde), 5.65 (d, 2 Hz, 2 H, alkene), 2.5–2.7 (m, 2 H, methine), 2.0–2.1 (m, 2 H, methylene), 1.7–1.9 (m, 2 H, methylene), 0.96 (d, 7 Hz, 3 H, methyl).

^1H NMR ($CDCl_3$) of **4**: δ 9.65 (d, 2 Hz, 1 H, aldehyde), 5.65 (d, 2 Hz, 2 H, alkene), 2.5–2.7 (m, 2 H, methine), 2.0–2.1 (m, 2 H, methylene), 1.7–1.9 (m, 2 H, methylene), 1.03 (d, 6 Hz, 3 H, methyl).

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Registry No. 1, 2004-70-8; 2, 107-02-8; 3, 873-30-3; 4, 766-48-3; methyl vinyl ketone, 78-94-4; methyl acrylate, 96-33-3; acrylonitrile, 107-13-1; *cis*-methyl 2-methyl-3-cyclohexene-1-carboxylate, 22973-22-4; *trans*-methyl 2-methyl-3-cyclohexene-1-carboxylate, 7605-51-8; *cis*-2-methyl-3-cyclohexene-1-carbonitrile, 57278-90-7; *trans*-2-methyl-3-cyclohexene-1-carbonitrile, 57278-89-4; acryloyl chloride, 814-68-6; acrolein–boron trifluoride, 105456-06-2.

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