reaction was run in a three-neck flask with a sealed stirrer and a condenser protected with a $CaCl_2$ tube. The excess sodium was destroyed with 37% H_2SO_4. The benzene layer was separated from the aqueous layer, extracted with four 50-mL portions of 20% Na_2CO_3 solution, washed with two 50-mL portions of H_2O, and dried over anhydrous Na_2SO_4. The filtered benzene solution was evaporated under reduced pressure. The resulting yellow slurry was heated to boiling in 150 mL of acetone, filtered, and allowed to cool, and placed in the refrigerator. Crystals formed. After standing 3 or 4 days, the crystals were collected, 8.1 g (16%). A pure sample from 2-ethoxyethanol melted at 181–182 °C; exact mass calcd for $C_{30}H_{24}O$ m/e 400.1821, found m/e 400.1826. Anal. Calcd for $C_{30}H_{24}O$: C, 89.96; H, 6.04. Found: C, 89.70; H, 5.85.

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Registry No. Ia, 38462-79-2; chalcone, 94-41-7.

Endo Selectivity of Allenic Esters in Diels–Alder Additions to Cyclopentadiene. The Effect of Added Aluminum Trichloride and an Approach to Dehydrosantalene Analogues[1]

Z. M. Ismail and H. M. R Hoffmann*

Institut für Organische Chemie der Universität Hannover, Schneiderberg 1B, D-3000 Hannover, Federal Republic of Germany

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In contrast to the massive research effort that has gone into the study of Diels–Alder reactions with acrylic and acetylenic esters, surprisingly little use has been made of allenic esters as dienophiles.[2] Occassionally, the literature has also been confusing with respect to configurational assignments.[2c] In the course of some model experiments for the synthesis of santalenes, we have investigated Diels–Alder additions of cyclopentadiene to a number of allenic esters. Our results are summarized in Table I.

The endo and exo configurations of the cycloadducts were assigned by ^1H NMR and GC retention times. For instance, the endo 2-H proton (R = H) in exo adduct **1x** appeared as a multiplet centered at 2.83 ppm, i.e., 0.63 ppm upfield from the exo 2-H proton in endo adduct **1n** (anisotropic shielding by the 5,6 double bond in **1x**). Consistently, the *endo*-methoxy signal in endo adducts **3bn** appeared upfield from the signal of the exo epimer **3bx**. On GC (glass capillary column) the endo epimers **2bn**, **3bn**, and **4n** had longer retention times than the corresponding exo epimers. An elegant chemical proof of configurations **3an** and **3ax** has been described by Barnett and McKenna.[2f]

Clearly, the α-alkylated allenic esters **3b** and **4** as well as allenic acid **3a**[2f,g] violate the Alder endo rule, formation of the exo adduct being preferred. This behavior is reminiscent of the special position held by dienophiles of the methacrylic ester type, which also favor exo addition (exo with respect to the ester grouping).[3] The decreased endo selectivity of methacrylic ester has recently been ascribed to decreased reactivity of the dienophile.[3a]

Addition of $AlCl_3$ to esters **2b** and **3b** increased the reaction rate, the reaction temperature being lowered from that of boiling benzene to room temperature. Simultaneously, the proportion of endo adduct increased: for **2b** from an endo/exo ratio of 64:36 to 86:14. For the less reactive dienophile **3b**, the validity of the endo rule was restored: from an endo/exo ratio of 40:60 in the uncatalyzed reaction to 76:24 in the presence of $AlCl_3$. Since the reactivity and endo selectivity of allenic esters with long α side chains R (cf. **4** and **5**) are comparatively poor, the sequential introduction of the alkyl group R, as described by Bertrand,[2k] may be used if R is to be exo.

In summary, endo selectivity of allenic dienophiles appears to depend on reactivity. While Lewis acids have been used successfully in many Diels–Alder reactions[3,4] as well as ene reactions,[5] their utility for activating allenic esters seems to have been overlooked.[2] As with more conventional dienophiles, Lewis acid catalysis lowers the reaction temperature and increases the yield and endo selectivity.

Experimental Section

Preparation of Allenic Esters. 2,3-Butadienoic acid (**1**) was prepared according to Jones et al.[2a] Its ethyl ester (**2b**) was obtained conveniently via the modified Wittig reaction as described by Hansen.[6] 2-Alkyl-2,3-butadienoic esters **3b** and **4** were prepared by the method of Taylor, Robey, and McKillop.[7] The procedure may be exemplified by the synthesis of **5** which was previously unknown.

Methyl 2-Ethenylidene-6-methylhept-5-enoate (5). (i) 4-Methyl-3-pentenyl Iodide (6).[8] Cyclopropyldimethylmethanol (50 g, 0.5 mol) was dissolved in absolute ether (500 mL), and zinc iodide (160g, 0.5 mol) was added in portions with stirring. After 1 h at room temperature, the mixture was refluxed for 0.5 h and suction filtered. The filtrate was washed with water, dried (Na_2SO_4), and freed from ether to leave an oil which was distilled, giving 4-methyl-3-pentenyl iodide (100 g, ca. 95%). In our hands, the fragmentation with ZnI_2 proceeded more smoothly and gave fewer byproducts (GC) than the reaction with MgI_2.[8]

(ii) Alkylation of Acetoacetic Ester. Ethyl acetoacetate (5.25 g, 40 mmol) in 1,2-dimethoxyethane (25 mL) was treated with several portions of sodium hydride (50%; 1.90 g, 40 mmol). After

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(2) (a) Jones, E. R. H.; Mansfield, G. H.; Whiting, M. C. *J. Chem. Soc.* **1956**, 4080. (b) Kurtz, P.; Gold, H.; Dieselnkötter, H. *Justus Liebigs Ann. Chem.* **1959**, *624*, 1; (c) Agosta, W. C. *J. Am. Chem. Soc.* **1964**, *86*, 2638, footnotes 1 and 26. (d) Bertrand, M.; LeGras, J. *Bull. Soc. Chim. Fr.* **1967**, 4336. (e) Büchi, G.; Carlson, J. A. *J. Am. Chem. Soc.* **1968**, *90*, 5336. (f) Barnett, W. E., McKenna, J. C. *Tetrahedron Lett.* **1971**, 227. Barnett, W. E.; McKenna, J. C. *J. Chem. Soc. D* **1971**, 551. (g), Gream, G. E.; Pincombe, C. F. *Aust. J. Chem.* **1974**, *27*, 543. (h) Kozikowski, A. P.; Floyd, W. C.; Kuniak, M. P. *J. Chem. Soc., Chem. Commun.* **1977**, 582. (i) Kozikowski, A. P.; Kuniak, M. P. *J. Org. Chem.* **1978**, *43*, 2083. (k) Bertrand, M.; Monti, H.; Huong, K. C. *Tetrahedron Lett.* **1979**, 15. (l) Suzuki, T.; Kagaya, S.; Tomino, A.; Katsuo, U.; Kametani, T. *J. Chem. Soc., Perkin Trans 1*, **1980**, 2801.

(3) (a) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779 and references therein. (b) Carruthers, W. "Some Modern Methods of Organic Synthesis"; Cambridge University Press: Cambridge, England, 1978; Chapter 3. (c) Wollweber, H. "Diels-Alder-Reaktion"; Georg Thieme Verlag: Stuttgart, 1972.

(4) It is also interesting to note that the unusually reactive dienophile which is obtained by carboxylation of trichloroallenyllithium adds to cyclopentadiene to yield the endo epimer only: Köbrich, G.; Wagner, E. *Chem. Ber.* **1970**, *103*, 2515.

(5) (a) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426. (b) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556.

(6) Lang, R. W.; Hansen, H. J. *Helv. Chim. Acta* **1980**, *48*, 438.

(7) Taylor, E. C.; Robey, R. L.; McKillop, A. *J. Org. Chem.* **1972**, *37*, 2797. See also: Bestmann, H. J.; Hartung, H. *Chem. Ber.* **1966**, *99*, 1198.

(8) (a) McCormick, J. P.; Barton, D. L. *J. Chem. Soc., Chem. Commun.* **1975**, 303. (b) Julia, M.; Julia, S.; Guegan, R. *Bull. Soc. Chim. Fr.* **1960**, 1072.

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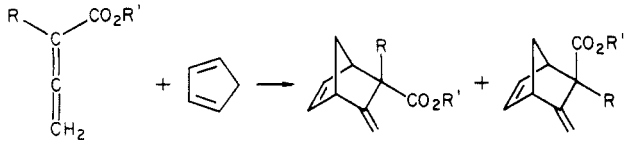
Table I. Endo/Exo Ratios for Diels-Alder Reactions of 2,3-Butadienoic Acid Derivatives (1–5) to Cyclopentadiene



dienophile endo exo

dienophile	R	R'	adduct endo	adduct exo	endo/exo ratio	reaction time, temp, and solvent	yield, %
1	H	H	1n	1x	68:32	12 h, 25 °C, Et_2O	86
2a	H	Me	2an	2ax	69:31[a]	reflux, benzene	85
2b	H	Et	2bn	2bx	64:36	6 h, 80 °C, benzene	90
2b + $AlCl_3$	H	Et			86:14	45 min, 25 °C, benzene	95
3a	Me	H	3an	3ax	40:60[b]		
3b	Me	Me	3bn	3bx	40:60	8 h, 80 °C, benzene	~80
3b + $AlCl_3$	Me	Me			76:24	45 min, 25 °C, benzene	90
4	n-C_5H_{11}	Me	4n	4x	40:60	12 h, 80 °C, benzene	50
5	$CH_2CH_2CH{=}CMe_2$	Me	5n	5x	48:52[c]	18 h, ~120 °C, toluene	50

[a] Reference 2k. [b] References 2f,g. [c] Endo epimer assumed to have the longer GC retention time on a glass capillary column.

evolution of hydrogen had ceased, the solution was heated to 90 °C, and homoallylic iodide **6** (10 g, 48 mmol) in 1,2-dimethoxyethane (25 mL) was added. After being refluxed for a further 20 h, the mixture was cooled and distributed between ether–water. The resulting organic phase was separated, dried ($MgSO_4$), and distilled, giving ethyl 2-acetyl-6-methylhept-5-enoate (7 g, 82%): 90-MHz ^1H NMR ($CDCl_3$) δ 1.26 (t, J = 7 Hz, 3 H, CH_2CH_3), 1.58 (s, 3 H, Me), 1.68 (s, 3 H, Me), 1.77–2.05 (m, 4 H), 2.22 (s, 3 H, COMe), 3.33–3.52 (m, 1 H), 4.18 (q, J = 7 Hz, 2 H, OCH_2), 4.94–5.2 (m, 1 H).

(iii) Preparation of the Pyrazolone. The ester (5.3 g, 25 mmol) in methanol was dropped into a solution of 80% hydrazine hydrate (1.6 g, 25 mmol) in methanol (30 mL) and stirred for 3 h at room temperature. The resulting white precipitate was filtered off and recrystallized from methanol: mp 218–220 °C; yield 3.5 g (83%); 90-MHz ^1H NMR (Me_2SO) δ 1.52 (s, 3 H), 1.63 (s, 3 H), 2.02 (s, 3 H), 2.16 (m, 4 H), 3.11–4.0 (br, 2 H), 5.11 (m, 1 H). Anal. Calcd for $C_{10}H_{16}N_2O$: C, 66.63; H, 8.95; N, 15.54. Found: C, 66.98; H, 9.23; N, 15.63.

(iv) Preparation of 5. A solution of thallium(III) nitrate (14 g, 36 mmol) in methanol (50 mL) was stirred into a suspension of 3 g (18 mmol) of the pyrazolone in methanol (25 mL) at room temperature. After 30 min the precipitated thallium salt was filtered off. The filtrate was poured onto water, extracted with $CHCl_3$, dried (Na_2SO_4), and distilled, giving **5**: 1.7 g (52%); IR ($CHCl_3$) 1708 (ester), 1930, 1960 cm^{-1} (allene); 90-MHz ^1H NMR (CCl_4) δ 1.59 (s, 3 H, Me), 1.67 (s, 3 H, Me), 2.0–2.24 (m, 4 H), 3.68 (s, 3 H, OMe), 4.88–5.22 (m, 3 H).

Cycloaddition Procedure. Commercial aluminum trichloride (Merck) (ca. 0.5–1 molar equiv with respect to **2b** and **3b**) was vigorously stirred into a solution of the allenic ester (9 mmol) over a period of 20 min, and cyclopentadiene (0.9 g, 1.5 equiv) was added. The reaction was followed by GC. After 45 min, ester **2b** could no longer be detected, and the reaction mixture was worked up by the usual procedure.

3-Methylenebicyclo[2.2.1]hept-5-ene-2-carboxylic acid (1n,x): 90-MHz ^1H NMR ($CDCl_3$) δ 1.33–2 (m, 4 H, 2 CH_2), 2.77–2.88 (dd, 1 H, *endo*-H), 3.16–3.33 (m, 4 H, bridgehead H's), 3.42–3.53 (dt, 1 H, *exo*-H), 5.0–5.22 (2 d, 4 H, 2 CH_2=), 6.18 (t, J = 2 Hz, 4 H, 2 CH=CH), 10.88–11.33 (br, 2 H, 2 CO_2H). The spectral properties of the ethyl esters **2bn,bx** have been described.[9]

Methyl 2-methyl-3-methylenebicyclo[2.2.1]hept-5-ene-2-carboxylate (3bn,bx) (uncatalyzed cycloaddition): 90-MHz ^1H NMR δ 1.24 (s, 3 H, *endo*-CH_3), 1.5 (s, 3 H, *exo*-CH_3), 1.58–1.70 (m, 2 CH_2), 2.85–3.33 (m, 4 H, bridgehead H's), 3.62 (s, 3 H, *endo*-OCH_3), 3.7 (s, 3 H, *exo*-OCH_3), 4.9–5.2 (m, 4 H, 2 CH_2=), 6.1–6.3 (m, 4 H, 2 CH=CH). The **3bn/3bx** ratio was 40:60 (^1H NMR, GC).

Methyl 2-*n*-pentyl-3-methylenebicyclo[2.2.1]hept-5-ene-2-carboxylate (4n,x): 90-MHz ^1H NMR ($CDCl_3$) δ 0.77–1.04 (m, 6 H, 2 CH_3), 1.04–1.52 (m, 16 H, 8 CH_2) 1.52–1.76 (m, 4 H, 2 bridge CH_2's), 3.0–3.36 (m, 4 H, bridgehead H's), 3.62 (s, 3 H, *endo*-OCH_3), 3.71 (s, 3 H, *exo*-OCH_3), 5.08 (d, 4 H, 2 CH_2=), 6.0–6.27 (m, 4 H, 2 CH=CH); IR ($CHCl_3$) 1710 cm^{-1}. For **4n**: GC/MS (t_R = 35.2 min), m/e (relative intensity) 234 (M^+, 19), 175 (23), 170 (34), 160 (34), 146 (34), 145 (36), 132 (42), 131 (29), 119 (45), 117 (100), 115 (30), 105 (34), 103 (46), 99 (39), 94 (48), 92 (47), 79 (21), 77 (43), 66 (97). For **4x**: GC/MS (t_R = 34.4 min) m/e (relative intensity) 234 (M^+, 34), 175 (29), 146 (36), 145 (39), 132 (46), 131 (34), 119 (34), 117 (97), 115 (29), 105 (36), 94 (46), 92 (24), 77 (34), 66 (100).

Methyl 3-Methylene-2-(4-methyl-3-pentenyl)bicyclo-[2.2.1]hept-5-ene-2-carboxylate (5n,x). For 5n: GC/MS (t_R = 31.6 min); mass spectrum, m/e (relative intensity) 246 (M^+, 13), 231 (7), 215 (15), 214 (11), 203 (10), 190 (13), 187 (37), 180 (100), 177 (21), 165 (42), 158 (48), 148 (99), 133 (76), 121 (52), 120 (56), 117 (51), 105 (72), 91 (52), 82 (13), 79 (43), 66 (99), 59 (18). **For 5x**: GC/MS (t_R = 31.4 min); mass spectrum, m/e (relative intensity) 246 (M^+, 16), 231 (4), 215 (11), 214 (16), 203 (9), 190 (26), 187 (19), 180 (100), 177 (16), 165 (29), 158 (44), 148 (93), 133 (31), 121 (29), 120 (24), 117 (26), 105 (44), 91 (34), 82 (21), 79 (24), 66 (49), 59 (16). Two additional $C_{16}H_{22}O_2$ isomers (GC/MS m/e 246 (M^+)) of unknown structure were also detected in ca. 20% yield.

Registry No. 1, 5732-10-5; **1n**, 24657-50-9; **1x**, 67903-38-2; **2a**, 18913-35-4; **2an**, 66241-97-2; **2ax**, 77965-89-0; **2b**, 14369-81-4; **2bn**, 77965-90-3; **2bx**, 78018-39-0; **3a**, 18913-36-5; **3an**, 52558-07-3; **3ax**, 32763-66-9; **3b**, 18913-37-6; **3bn**, 77965-91-4; **3bx**, 77965-92-5; **4**, 35895-74-0; **4n**, 77965-93-6; **4x**, 77965-94-7; **5**, 77965-95-8; **5n**, 77965-96-9; **5x**, 77965-97-0; **6**, 43161-11-1; cyclopentadiene, 542-92-7; cyclopropyldimethylmethanol, 930-39-2; ethyl acetoacetate, 141-97-9; ethyl 2-acetyl-6-methylhept-5-enoate, 42809-53-0; 5-methyl-4-(4-methylpent-3-enyl)-2,4-dihydro-3*H*-pyrazol-3-one, 77965-98-1.

(9) Hoffmann, H. M. R.; Ismail, Z. M.; Weber, A. *Tetrahedron Lett.* 1981, 22, 1953.

Internal Nucleophilic Termination in Mercuric Ion Initiated Diene Cyclizations

Thomas R. Hoye,* Andrew J. Caruso, and Mark J. Kurth[1]

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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Recent interest in the internal trapping by an appropriately placed nucleophilic functional group of a carbo-

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