

Regio- and Stereo-selectivity in Uncatalysed and Catalysed Diels–Alder Reactions of Allenic Esters with Furan and 2-Methylfuran

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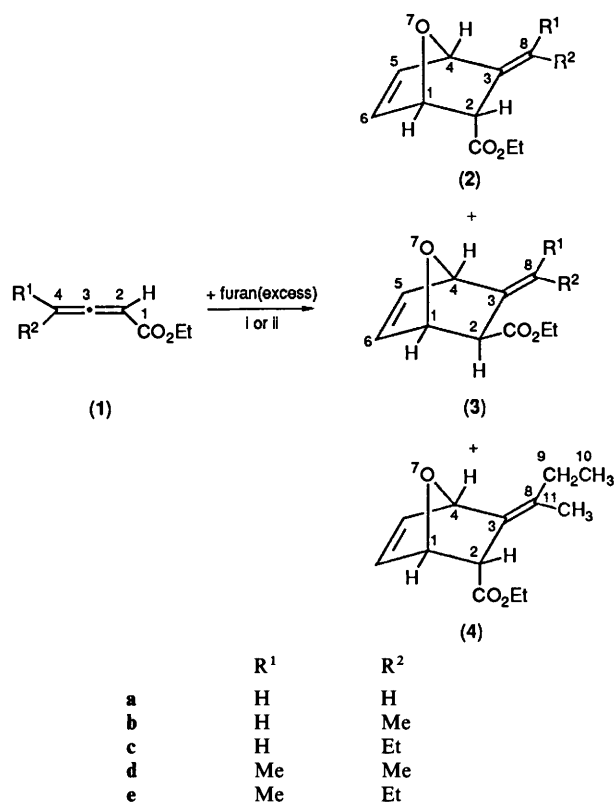
Complete regio- and stereo-selectivity in both uncatalysed and catalysed† Diels–Alder additions of furan to the allenic esters (**1a–e**), and of 2-methylfuran to the allenic esters (**1b, c**) has been determined through detailed ¹H and ¹³C NMR spectral investigations. Eu(fod)₃ and Pr(fod)₃ have been found to be very useful mild Lewis acid catalysts for these cycloadditions; several mol % of these reagents significantly enhance the selectivity and yield of these reactions without adversely affecting the fragile functionalities. A rationalization of the observed regio- and stereoselectivity and reactivity profile, based on the stereoelectronic factors operating in the transition states is given.

Although some activated allenes have recently been involved in the synthesis of natural products *via* Diels–Alder reactions,¹ synthetic and mechanistic studies involving allenes as dienophiles have attracted much less attention than studies on corresponding vinylic and acetylenic dienophiles. This is in spite of the fact that [2 + 4]cycloadditions of allenes offer a convenient route to easily functionalisable cyclic systems, with an alkylidene moiety, which can subsequently serve as important building blocks in the synthesis of natural products.^{1,2} The reason for this restricted use of allenes as dienophiles is their low dienophilicity and their tendency to undergo excessive polymerization under drastic conditions.^{1,3}

The present studies have thus been performed with a view to unravelling the complete regio- and stereoselectivity of Diels–Alder reactions involving allenic esters as dienophiles and as well as probing the catalytic conditions required in order to enhance the yields and selectivity of these additions. We have recently reported⁴ the use of lanthanide NMR shift reagents [Eu(fod)₃ and Pr(fod)₃] as catalysts in the enhancement of the yield and stereoselectivity of the Diels–Alder additions of cyclopentadiene to some allenic esters. Herein, we report on uncatalysed and Eu(fod)₃/Pr(fod)₃ catalysed additions of furan to the allenic esters ethyl buta-2,3-dienoate (**1a**), ethyl penta-2,3-dienoate (**1b**), ethyl hexa-2,3-dienoate (**1c**), ethyl 4-methylpenta-2,3-dienoate (**1d**) and ethyl 4-methylhexa-2,3-dienoate (**1e**), and of 2-methylfuran to the allenic esters (**1b, c**). Eu(fod)₃ and Pr(fod)₃ (recently recognized as mild Lewis acid catalysts⁵) have been found to be useful catalysts for Diels–Alder additions involving allenic esters, and they significantly enhance the stereoselectivity and yield of these reactions with much reduced reaction times (at room temperature). In addition to their powerful catalytic effect (several mol % of these reagents are sufficient) they have the advantage of being unreactive towards labile functionalities.‡ The regio- and stereochemical determinations are based on ¹H NMR chemical shifts, vicinal and long-range ¹H couplings, ¹H NOE measurements and ¹³C NMR chemical shifts.

Results and Discussion

Thermal addition of furan to the allenic esters (**1a–e**) was carried out by refluxing a solution of allenic ester with excess of furan (at 40 °C) for varying periods. The corresponding catalysed additions were carried out by leaving a mixture of allenic ester, furan (excess) and Eu(fod)₃ or Pr(fod)₃ (*ca.* 1 mol %) at room temperature for 12–60 h. Chromatographic separation of the mixtures (preparative layer chromatography, column chroma-



Scheme 1. Reagents and conditions: i, reflux, 40 °C; ii, room temperature in the presence of 1 mol % Eu(fod)₃ or Pr(fod)₃.

tography or by using a chromatotron-2) afforded various 2-*endo*-/*exo*-ethoxycarbonyl-3-(*E/Z*)-alkylidene-7-oxabicyclo-[2.2.1]hept-5-enes (**2**)–(**4**) (Scheme 1) along with some unchanged allenic esters. The reaction conditions, reaction times, overall yields and product ratios are summarised in Table 1.

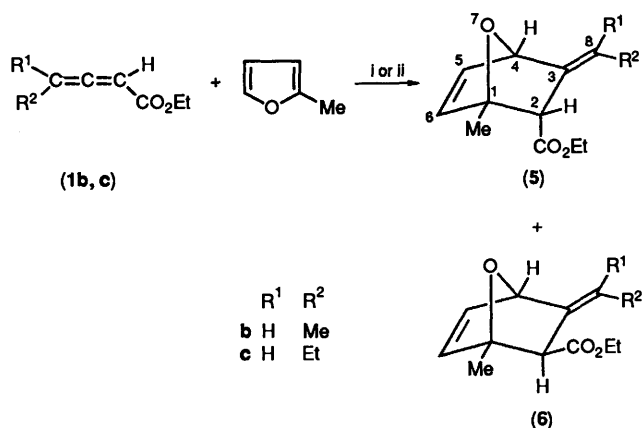
† Lanthanide NMR shift reagents Eu(fod)₃ and Pr(fod)₃.

‡ In the initial few experiments, anhydrous AlCl₃ was used as catalyst, when acceleration of the reaction was observed. Messy reaction mixtures with much intractable materials resulted and the isolation of adducts was found to be extremely difficult.

Table 1. Reaction conditions, reaction times, overall yields^a and product ratios for the addition of furan to allenic esters (1a–e).

Allenic ester	Reaction conditions ^b	Reaction time	Yield (%)	Product ratio		
				(2)	(3)	(4)
(1a)	Uncatalysed	72 h	50	62	38	—
	Catalysed ^c	12 h	80	80	20	—
(1b)	Uncatalysed	7 days	40	75	25	0
	Catalysed	12 h	70	only	0	0
(1c)	Uncatalysed	7 days	34	78	22	0
	Catalysed	20 h	75	89	11	0
(1d)	Uncatalysed	16 days	22	90	10	—
	Catalysed	48 h	63	only	0	—
(1e)	Uncatalysed	16 days	22	67	0	33
	Catalysed	60 h	40	75	0	25

^a Based on amount of allenic ester consumed in reaction. ^b Uncatalysed, 40 °C; catalysed, room temp. ^c Catalysed by 1.0 mol % of Eu(fod)₃ or Pr(fod)₃.



Scheme 2. Reagents and conditions: i, benzene reflux; ii, room temperature in the presence of 1 mol % Eu(fod)₃ or Pr(fod)₃.

The distinction between the 2-*endo*-ethoxycarbonyl [(2) and (4e)] and 2-*exo*-ethoxycarbonyl adducts (3) rests on (a) the coupling constant ³J_{1,2}, the value of which varied from 5.0–4 Hz in the case of the 2-*endo*-ethoxycarbonyl adducts (Table 2) to ca. 0 in the case of adducts with the ethoxycarbonyl group *exo*-oriented⁶ and (b) on δ_{2-H} which was, as anticipated,⁶ shifted upfield by 0.60–0.65 ppm in the *exo*-adducts. These assignments are supported⁷ by the observed downfield shift of δ_C for C-1 and C-3 and in particular for C-6, and by the upfield shift of δ_C for C-4 in going from *endo*-(2a–c) to the corresponding *exo*-ethoxycarbonyl adducts (3a–c), Table 3.

The assigned geometry (E) at the exocyclic double bond (in the absence of corresponding Z isomers) for adducts (2b, c) and (3b, c) was suggested by ¹³C NMR studies, i.e., in going from the *endo* adduct (2a) to the *endo* adducts (2b, c), the C-2 resonance records an upfield shift of 2.1–2.3 ppm, whereas the C-4 resonance is shifted slightly downfield (0.6–0.7 ppm, Table 3), thereby signifying^{4,7,8} that in adducts (2b, c) the alkyl groups (at C-8) are *cis* to C-2. Similar conclusions can be drawn by a comparison of δ_C for C-2 and C-4 in *exo*-adduct (3a) with the shifts for the corresponding carbon atoms in *exo*-adducts (3b, c).

The above geometric assignments have been further

confirmed by ¹H NOE measurements on compounds (2b, c) and (3b, c). Thus irradiation of 8-Me in adducts (2b) and (3b) produced, respectively, a 23.17 and 17.11% enhancement of the integrated intensity of the 2-H resonance, whereas the 4-H resonance was suppressed (Table 4), thereby establishing a *cis* relationship between 8-Me and 2-H in both (adducts (2b) and (3b)). Similarly, a *cis* relationship between 4-H and 8-H, and a *trans* relationship between 2-H and 8-H, in adducts (2b) and (3b), is established by irradiation of the 8-H resonance and monitoring of the 2-H and 4-H resonances (Table 4). Identical conclusions regarding the geometric assignments in (2c) and (3c) can be drawn from ¹H NOE measurements (Table 4).

The geometric assignments in the case of the *endo* adducts (E)-(2e) and (Z)-(4e) are based on the homoallylic couplings involving 2-H and 8-Me and 8-CH₂ group hydrogen atoms. These are based on the premise that *transoid* homoallylic couplings are always greater than the *cisoid* homoallylic couplings;⁹ thus, ⁵J_{2,8-Me} has a greater value (1.46 Hz) in (E)-(2e) than in (Z)-(4e) (1.08 Hz) (Table 2). The ¹³C NMR data [obtained from a mixture of structures (2e) and (4e)] is compatible with these geometric assignments.

The results of uncatalysed and catalysed Diels–Alder addition of 2-methylfuran to the allenic esters (1b, c) (Scheme 2) are summarized in Table 5. The ¹H and ¹³C NMR data obtained for compounds (5) and (6) are given in Tables 6 and 7. The position assigned to 1-Me in the adducts (5b, c) and (6b, c) is based on: (a) an absence of geminal coupling for 2-H in the case of *endo* adducts (5b, c)*; (b) the absence of the geminal coupling to be expected between a 1-H and 6-H; (c) the observation that the C-4 resonance in the ¹³C NMR spectrum of (5, c) and (6b, c) has almost the same chemical shift value as in the case of the corresponding adducts of furan, (2b, c) and (3b, c); and (d) the downfield shift of the C-2 resonance (4–5 ppm) in compounds (5b, c) and (6b, c), as compared to its value in compounds (2b, c) and (3b, c), respectively i.e., the effect of a β-methyl group.⁷ The geometry (E) at the exocyclic double bond in compound (5b, c) and (6b, c) has been assigned by analogy with the presently obtained stereochemistry for the corresponding adducts of furan (2b, c) and (3b, c); it is inferred from a comparison of the ¹³C NMR chemical shift value of C-4 in *endo* adducts (5b, c) and *exo* adducts (6b, c) with the C-4 chemical shift value, respectively, in *endo* adducts (2a–c) and *exo* adducts (3a–c). The rest of the structural and stereochemical assignments have been achieved as for the adducts of furan.

Based on the results obtained it can be concluded that: (a) In Diels–Alder reactions involving the allenic esters (1a–e), complete [2 + 4] periselectivity, even under catalytic conditions, is obtained, and only the C(2)–C(3) π-bond of the allenic esters is involved in cycloadditions.

* The *endo*-ethoxycarbonyl adducts are characterized⁶ by, *inter alia*, the observance of the 2-H resonance at low field as compared with δ_C for 2-H in the *exo*-adducts (6b, c).

Table 2. Chemical shifts (δ_{H} (ppm) and coupling constants (J /Hz) in adducts (2), (3), and (4e).

Compound	1-H	2-H	4-H	5-H	6-H	8-H	-CO ₂ CH ₂ -	CO ₂ CH ₂ CH ₃	Others
(2a)	5.22, br d $J_{1,2}$ 5.00	3.57, m $J_{1,2}$ 5.00	5.05, br s	6.43, br s (2 H)		5.12, br d $J \approx 2.50$	4.10, q J 7.12	1.25, t J 7.12	—
(3a)	5.34, br s $J_{1,2} \approx 0$	2.95, br s $J_{1,2} \approx 0$	5.14, br s	6.49 δ A, dd $J_{\text{A,B}}$ 5.50 $J_{4,5}$ 2.00	6.48 δ B, dd $J_{\text{A,B}}$ 5.50 $J_{6,1}$ 1.75	5.22, brd $J \approx 1.75$	4.22, sp q, $J = 7.12$ J_{gem} 1.15	1.25, dist. t $J = 7.12$	—
(2b)	5.24, br d $J_{1,2}$ 4.65	3.56, m $J_{1,2}$ 4.65 $^4J_{2,8}$ 1.95 $^5J_{2,9}$ 0.98	5.01, br s	6.47 δ A, dd $J_{\text{A,B}}$ 5.80 $J_{4,5}$ 1.69	6.28 δ B, dd $J_{\text{A,B}}$ 5.80 $J_{6,1}$ 1.60	5.66, sq q J 6.98 $^4J_{2,8}$ 1.95	4.12, q J 7.10	1.24, t J 7.10	1.62, sp d, 3 H, 9-H ^a J 6.06 $^5J_{2,9}$ 0.98
(3b)	5.25, br s $J_{1,2} \approx 0$	2.96, br s	5.02, br s	6.51 δ A, dd $J_{\text{A,B}}$ 5.60 $J_{4,5}$ 1.69	6.34 δ B, dd $J_{\text{A,B}}$ 5.60 $J_{6,1}$ 1.49	5.62, sq q J 6.90 $^4J_{2,8}$ 1.60	4.22, q J 7.08	1.28, t J 7.08	1.64, sp d, 3 H, J 6.90 $^5J_{2,9}$ 0.77
(2c)	5.22, br d $J_{1,2}$ 4.39	3.60, m $J_{1,2}$ 4.39 $^4J_{2,8}$ 1.60 $^5J_{2,9}$ 0.95	5.04, br s	6.47 δ A, dd $J_{\text{A,B}}$ 6.20 $J_{4,5}$ 1.71	6.28 δ B, dd $J_{\text{A,B}}$ 6.20 $J_{6,1}$ 1.46	5.58, sp t J 7.08 $^4J_{2,8}$ 1.60	4.10, q J 7.10	1.24, t J 7.10	1.98, br qn, 2 H, 9-H, J 7.08 $^5J_{2,9}$ 0.95 0.96, t, 3 H 10-H, J 7.08
(3c)	5.24, br s $J_{1,2} \approx 0$	2.96, br s	5.04, br s	6.47 δ A, dd $J_{\text{A,B}}$ 6.20 $J_{4,5}$ 1.79	6.20 δ B, dd $J_{\text{A,B}}$ 6.20 $J_{6,1}$ 1.46	5.60, sp t J 6.96 $^4J_{2,8}$ 0.99	4.28, q J 7.08	1.27, t J 7.08	2.02, m, 2 H, 9-H J 6.96, J 7.22, $^5J_{2,9} \approx 0.9$ 0.96, t, 3 H, 10-H, J 7.22
(2d)	5.22, br d $J_{1,2}$ 4.20	3.57, m $J_{1,2}$ 4.20	5.34, br s	6.44 δ A, dd $J_{\text{A,B}}$ 6.00 $J_{4,5}$ 1.79	6.36 δ B, dd $J_{\text{A,B}}$ 6.00 $J_{6,1}$ 1.56	—	4.12, q J 7.08	1.26, t J 7.08	1.78, d, 3 H, 10-H $^5J_{2,10}$ 1.45 (C ₂ - <i>trans</i>) 1.62, d, 3 H, 9-H $^5J_{2,9}$ 1.04 (C ₂ - <i>cis</i>)
(3d)	5.20, br s $J_{1,2} \approx 0$	2.79, br s $J_{1,2} \approx 0$	5.36, br s	6.50 δ A, dd $J_{\text{A,B}}$ 5.60 $J_{4,5}$ 1.50	6.33 δ B, dd $J_{\text{A,B}}$ 5.60 $J_{6,1}$ 2.00	—	4.20, q J 7.10	1.27, t J 7.10	1.80, br s, 3 H, 9-H 1.60, br s, 3 H, 10-H
(2) + (4e) (<i>E/Z</i> mixture)	5.21, br d $J_{1,2} \approx 4.54$	3.59, m $J_{1,2} \approx 4.54$	5.32, br s	6.51 (2e) δ A, dd $J_{\text{A,B}}$ 5.60 $J_{4,5}$ 1.65 6.49 (4e) δ A, dd $J_{\text{A,B}}$ 5.60 $J_{4,5}$ 1.60	6.29 (4e) δ B, dd $J_{\text{A,B}}$ 5.60 $J_{6,1}$ 1.46 6.25 (2e) δ B, dd $J_{\text{A,B}}$ 5.60 $J_{6,1}$ 1.48	— —	4.11, br q J 7.08	1.25, t J 7.08	2.20–1.80 m, 9-H, (2e), (4e) $^5J_{2,9} \approx 0.9$ (2e) $^5J_{2,9} \approx 1.20$ (4e) 1.75, d, 3 H, 11-H (2e) $^5J_{2,11}$ 1.46 1.59, d, 3 H, 11-H (4e) $^5J_{2,11}$ 1.08 0.96 and 0.92, ts 10-H, J 7.60

^a 9-, 10-, and 11-H refer to hydrogen atoms on C-9, C-10, and C-11, respectively (see Schemes).

(b) The dienophilicity of allenic esters falls along the series (1a) \longrightarrow (1e).

(c) The endoselectivity of furan addition to the above allenic esters improves along the series (1a) \longrightarrow (1e): addition to allenic ester (1e) yields only *endo* adducts. However, for uncatalysed addition of 2-methylfuran to allenic esters (1b, c) both *endo* and *exo* adducts are obtained in almost equal amounts.

(d) 2-Methylfuran is a much more reactive diene than furan. It adds regioselectively to allenic esters (1b, c) to yield only *ortho* Diels–Alder adducts.

(e) The dienes show complete π -facial selectivity in their

approach to the C(2)–C(3) π -bond, leading to only *E*-geometry at the exocyclic double bond in the adducts; the *Z* isomer- (minor) is obtained only from addition of furan to allenic ester (1e).

(f) Catalysis of these reactions by Eu(fod)₃ and Pr(fod)₃ greatly improves the yields, *endo* selectivity, and to some extent, π -facial selectivity. The catalysed reactions are cleaner and require short reaction times, even at room temperature.

Though allenes are known to undergo facile [2 + 2] cycloadditions,^{1j,3b} the preference shown for the $\pi_s^4 + \pi_s^2$ mode of addition in reactions of allenic systems with 1,3-dienes has been taken^{1j,10} as evidence against the concerted

Table 3. Chemical shift (δ_c /ppm) values for various carbon atoms in Diels–Alder adducts (2)–(4).^a An asterisk * indicates a tentative assignment only.

Adduct	C-1	C-2	C-3	C-4	C-5	C-6	C-8	CO ₂	CO ₂ CH ₂	CO ₂ CH ₂ CH ₃	8-R
(2a)	79.8	48.8	143.2	83.1 ^b	135.3*	135.2*	107.0	170.8	60.8	13.5	
(3a)	81.1	47.9	143.8	81.7	135.1	136.2	107.7	173.6	60.7	13.8	
(2b)	80.0	46.7	134.6	83.7	135.1	133.0	118.1	170.0	60.4	13.8	15.3
(3b)	81.7	46.6	135.0	82.5	134.3	137.2	118.7	172.2	60.5	14.1	15.2
(2c)	80.1	46.9	133.1	83.8	135.3	133.1	125.5	170.2	60.5	14.0	23.7, 13.0
(3c)	81.9*	46.6	133.4	82.5*	134.0	137.0	125.9	172.7	60.9	14.1	23.6, 13.5
(2d) ^c	80.4	47.7	125.9	80.9	134.8	132.7	128.3	170.8	60.5	14.1	22.4, 21.1

^a A mixture of compounds (2e) and (4e) gave the following resonances in the ¹³C NMR spectrum in which the minor peaks (m) may be attributed to the minor component (4e): δ 80.9, 80.7, 80.4 (C-1 and C-4), 127.8, 124.3, 123.8 (quaternary carbons C-3 and C-8), 134.8, 133.8(m), 132.7, 132.5(m) (C-5 and C-6), 60.6 (–CO₂CH₂–), 47.4 and 47.2(m) (C-2), 28.9 and 29.1(m) (8-CH₂), 18.5(m), 17.8 (8-CH₃), 14.1 (CO₂CH₂CH₃), 11.4 (8-CH₂CH₃) and 171.2 (–CO₂–). ^b The down-field signal among the two resonances for the oxygen-bridged carbon atoms (C-1 and C-4) is assigned to C-4, this being the carbon atom α to two olefinic carbon atoms. ^c The ¹³C NMR spectrum of the corresponding *exo* adduct (3d) could not be obtained.

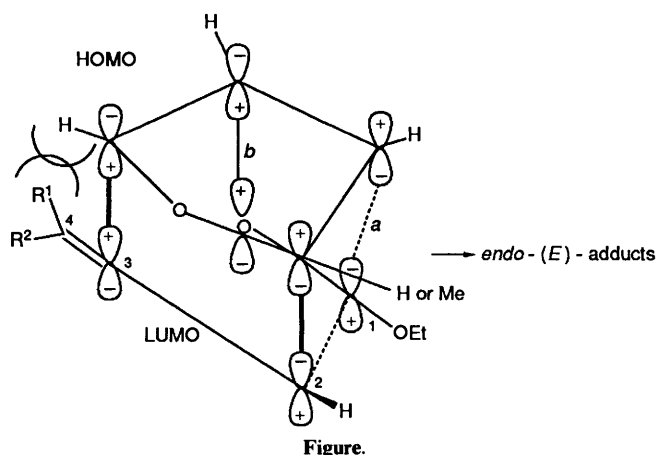
Table 4. ¹H NOE (% enhancement) values in compounds (2b, c) and (3b, c).

Compound	Signal irradiated	Signals monitored	
		2-H	4-H
(2b)	9-H	23.12	–5.6
	8-H	0	10.0
(3b)	9-H	17.11	–5.0
	8-H	0	9.11
(2c)	9-H	17.0	–3.6
	8-H	–3.0	15.0
(3c)	9-H	16.0	–5.0
	8-H	–1.5	17.0

Table 5. Reaction conditions, reaction time, overall yields and product ratio for addition of 2-methylfuran to allenic esters (1b, c).

Allenic ester	Reaction condition	Reaction time/h	Yield ^a (%)	Adduct ratio	
				(4)	(5)
(1b)	Uncatalysed ^b	4	70	52	48
	Catalysed ^c	2	80	70	30
(1c)	Uncatalysed ^b	4	72	50	50
	Catalysed ^c	2	80	74	26

^a Based on quantity of allenic ester consumed in reaction. ^b Benzene reflux. ^c Room temperature; catalysed by 1 mol % Eu(fod)₃ or Pr(fod)₃.

**Figure.**

mechanism for [2 + 2] cycloadditions and cyclodimerizations of allenes. The loss of dienophilicity in going from allenic ester (1a) to (1e) is attributable to substitution of allenic hydrogens by alkyl groups [in esters (1b–e)] which increases the energy of the LUMO of the C(1)–C(2) π -bond,¹¹ thereby affecting the donor-acceptor complementarities for the Diels–Alder reactions of first-type (normal Diels–Alder reactions).¹² The loss of reactivity in the case of dialkylallenes (1d, e) could also be partly due to steric reasons *i.e.* the alkyl groups blocking the approach of the diene molecule (see the Figure).

The unfavourable steric interaction (Figure) between the α -hydrogen atoms of furan and the R¹ and R² groups at C-4 is responsible for the π -facial selectivities observed; approach of the diene molecule from the less hindered *i.e.*, from the side of the smaller group leads to an *E*-geometry at the exocyclic double bond in adducts (2b, c) and (3b, c). In the case of structure (1e), in which R¹ and R² (Me and Et) are of comparable size the formation of the *Z* isomer (4e) also takes place. Such stereoselectivity was anticipated by Pasto and Heid in the addition of tetraphenylcyclopentadienone (TPCD) to mono- and dialkylallenes, but only the products resulting from decarbonylation of the initial adducts were isolated.^{11a} As reported by them^{11a} the above unfavourable steric interaction led to a change in site (π -bond) selectivity *i.e.*, addition of TPCD also occurred at the alkyl group bearing the allene π -bond, however, no such product, involving addition to the C(3)–C(4) π -bond has been obtained in the present studies. The π -facial selectivities exhibited by these cycloadditions also point towards their concerted nature (one-step addition).

Again, the unfavourable steric interaction shown in the transition state (Figure) may be one of the reasons for the observed regioselective addition of 2-methylfuran. Although the formation of *ortho* Diels–Alder adducts in the addition of 2-methylfuran to allenic esters is in accordance with theory^{12,13} and with simple considerations of π -electron polarisations in diene and dienophiles (in the present case), the Diels–Alder additions of 2-methylfuran to some activated vinylic dienophiles are known to give both regioisomers,¹⁴ *i.e.*, *meta* Diels–Alder adducts have also been obtained.

Endoselectivity in Diels–Alder reactions is still a subject of great interest and many explanations, including the 'principle of maximum accumulation of unsaturation in transition state',¹⁵ secondary-orbital interaction,^{12,16} steric interactions,¹⁷ dipole-dipole interactions¹⁸ and attractive van der Waals interactions¹⁹ have been offered. The kinetically controlled²⁰ formation of *endo* adducts in Diels–Alder reactions seems to be due to some secondary interactions which favour a compact transition state. Though secondary orbital interactions still remain the most plausible explanation (in spite of reservations expressed by some authors²¹), steric factors may play an

Table 6. Chemical shifts (δ_{H} /ppm) and coupling constants (J /Hz) for adducts (**5**) and (**6**).

Compound	1-Me	2-H	4-H	5-H	6-H	8-H	CO ₂ CH ₂	CO ₂ CH ₂ CH ₂	Others
(5b)	1.73, s	3.25, br s	4.94, sp s $J_{4,5}$ 1.70	6.48 δA , dd $J_{\text{A,B}}$ 5.60 $J_{4,5}$ 1.70	6.08 δB , dd $J_{\text{A,B}}$ 5.60	5.57, sp q J 7.08 $^4J_{2,8}$ 1.94	4.12, q J 7.10	1.25, t J 7.10	1.62, sp d, 3 H, 9-H J 7.08 $^5J_{2,9}$ 0.9
(6b)	2.1, s	2.96, br s	5.04, br s	6.44 δA , dd $J_{\text{A,B}}$ 5.60 $J_{4,5}$ 1.50	6.10 δB , dd $J_{\text{A,B}}$ 5.60	5.56, sp q J 7.30 $^4J_{2,8}$ 1.7	4.23, q J 7.10	1.29, t J 7.10	1.57, br d, 3 H, 9-H
(5c)	1.71, s	3.23, br s	4.89, sp s $J_{4,5}$ 1.5	6.45 δA , dd $J_{\text{A,B}}$ 5.60 $J_{4,5}$ 1.5	6.05 δB , dd $J_{\text{A,B}}$ 5.60	5.43, sp t J 7.0 $^4J_{2,8}$ 2.2	4.10, q J 7.08	1.24, t J 7.08	1.99, m, 2 H, 9-H J 7.0, 7.1 $^5J_{2,9}$ 0.95 0.95, t, 3 H, 10-H J 7.1
(6c)	1.95, s	2.96, br s	5.03, sp s $J_{4,5}$ 1.75	6.44 δA , dd $J_{\text{A,B}}$ 5.60 $J_{4,5}$ 1.5	6.12 δB , dd $J_{\text{A,B}}$ 5.60	5.47, sp t J 7.3 $^4J_{2,8}$ 2.0	4.22, q J 7.0	1.29, t J 7.10	1.91, m, 2 H, 9-H J 7.3, $^5J_{2,9} \approx 0.9$ 0.90, t, 3 H, 10-H J 7.3

^a See footnote a, Table 2.

Table 7. NMR chemical shift (δ_{C} /ppm) values for various carbon atoms in adducts (**5**) and (**6**).

Compound	C-1	C-2	C-3	C-4	C-5	C-8	-CO ₂	CO ₂ CH ₂	CO ₂ CH ₂ CH ₃	Others ^a
(5b)	88.5	52.3	138.0	83.5	135.5	117.1	170.5	60.5	14.1	18.2 (1-Me) 15.2 (C-9)
(6b)	88.8	50.6	138.4	82.0	137.0	117.1	171.4	60.5	14.3	16.1 (1-Me) 15.0 (C-9)
(5c)	88.5	52.4	136.3	83.6	135.6	124.5	170.7	60.5	14.0	23.5 (C-9) 18.2 (1-Me) 13.4 (C-10)
(6c)	88.9	50.6	136.8	82.1	137.0	124.4	171.7	60.7	14.3	23.4 (C-9) 16.0 (1-Me) 13.4 (C-10)

^a See footnote a, Table 2.

important role in certain cases.^{17,19} However, according to earlier postulations¹⁶ the interaction *a* (Figure) is the secondary orbital interaction which stabilizes an *endo* transition state, whereas Salem²² has found that this interaction *a* is not stabilizing (rather it is destabilizing), whereas the *b* interaction is the actual stabilizing interaction; the experimental findings of Cardenas²³ are in agreement with the postulations of Salem. In case of allenic esters (**1a–e**) the ¹H and ¹³C NMR (including ¹³C NMR relaxation time, T_1 , measurements), and UV spectral investigations²⁴ have revealed that there is a gradual change of preferred rotameric conformation of the ester function from *s-trans* in ester (**1a**) through (**1b–d**) to *s-cis* in structure (**1e**) and this parallels the *endo* selectivity observed for the addition of allenic esters to furan. However, in the case of 2-methylfuran addition to (**1b, c**) both *endo* and *exo* adducts are obtained in almost equal amounts. The excess formation of *exo* adduct in Diels–Alder addition of 2-methylfuran to some olefinic dienophiles has been reported in the literature^{14,25} and is attributed to the reversibility of these cycloadditions.^{14,25,26}

A related aspect of these additions is the high dienic reactivity of 2-methylfuran; reaction of 2-methylfuran with esters (**1b, c**) was much faster and gave adducts in high yield (*ca.* 70%) as compared to reactions of furan with (**1b, c**) (Tables 1 and 5). Very high yields of cycloadducts (up to 100%) in additions involving 2-methylfuran as diene have been reported, whereas furan has been recognized as a particularly weak diene,^{14b,27} Dewar has attributed²⁵ the effect of an otherwise weakly

perturbing methyl substituent (in going from furan to 2-methylfuran) to the involvement of highly unsymmetrical (polar) transition states in these additions (non-synchronous additions); the polar nature of these additions can also be related to the decreased selectivity of these additions.²⁸

Catalysis of these reactions with Eu(fod)₃ and Pr(fod)₃ has not only increased the yields but also the stereoselectivity (*endo* selectivity and π -facial selectivity). This violation of reactivity-selectivity principles has been attributed, in terms of an FMO approach,^{16d,29} to complexation between a Lewis acid and the polar group of a dienophile; the increased reactivity is therefore related to a decrease in the energy of the LUMO dienophile, whereas the increased *endo* selectivity is explained by an increase in the dienophile LUMO coefficient at the centre involved in secondary orbital interaction. However, the role of the centre suggested for involvement in stabilising secondary orbital interaction, according to this approach,^{16,29} has been disputed.^{22,23} According to Epiotis,^{12d,13a,c,28} for non-ionic (semi polar) reactions, increased interaction (on catalysis) between fundamental and charge-transfer configuration leads to a decrease in the potential barrier of the reaction with no advancement of the transition state along the reaction coordinate, leading to increased reactivity and selectivity; his postulation has been supported by Branchadell *et al.*³⁰ However, it must be mentioned that the role of conformational changes in catalysed Diels–Alder reactions was not ruled out by Houk,^{29b} and Branchadell *et al.* have also found³⁰ that a

significant difference in the energy of the transition states, for *endo* and *exo* adduct formation is only obtained when calculations are based on the *s-cis* conformation of the dienophile.

Experimental

IR spectra were recorded on Unicam SP-1200 and Nicolet-5DX Fourier transform IR spectrophotometers. Mass spectra were obtained on a JEOL-JMS-D-300 mass spectrometer. Microanalyses were carried out on a Perkin-Elmer 240C elemental analyser. NMR spectra were recorded on a JEOL-JNM-FX-100 (99.55 MHz for ^1H and 24.99 MHz for ^{13}C) NMR spectrometer, using CDCl_3 as solvent and TMS as internal standard. ^1H NOE measurements were carried out, using standard JEOL procedures, on degassed sample solutions. The optimum power level of the irradiating frequency was selected and both spectra, with and without NOE (using GATED decoupling), were obtained under identical acquisition conditions. The ^1H T_1 values required for setting the acquisition parameters were determined by FTIR experiments. The values obtained for the integrals were corrected for Normalized Gain Factor (NGF).

Furan and 2-methylfuran were procured from E. Merck and were distilled before use. Allenic esters (**1a–e**) were prepared according to the method of Lang and Hansen³¹ and were characterized spectroscopically.²⁴ $\text{Eu}(\text{fod})_3$ and $\text{Pr}(\text{fod})_3$ were procured from Merck Sharp and Dhome, Canada. All b.p.s are uncorrected. Data for the esters (**1a–e**): (**1a**), yield 50%; b.p. 50 °C/15 mmHg (lit.,³² 44 °C/13 mmHg); $\nu_{\text{max}}(\text{film})$ 1965, 1942, and 1720 cm^{-1} ; (**1b**), yield 70%; b.p. 68 °C/10 mmHg (lit.,^{31a} 75 °C/14 mmHg); $\nu_{\text{max}}(\text{film})$ 1958 and 1725 cm^{-1} ; (**1c**), yield 60%; b.p. 66 °C/10 mmHg; $\nu_{\text{max}}(\text{film})$ 1950 and 1720 cm^{-1} ; (**1d**), yield 50%; b.p. 67 °C/10 mmHg; $\nu_{\text{max}}(\text{film})$ 1960 and 1720 cm^{-1} ; and (**1e**), yield 40%; b.p. 67 °C/10 mmHg; $\nu_{\text{max}}(\text{film})$ 1955 and 1720 cm^{-1} .

Thermal Addition of Furan to Ethyl Buta-2,3-dienoate (1a).—Freshly distilled allenic ester (**1a**) (300 mg) was mixed with freshly distilled furan (10 ml, excess) in a 25 ml round-bottom flask provided with an efficient condenser and CaCl_2 moisture-guard tube. The mixture was refluxed slowly (temperature-regulated water bath, 40 °C) and the progress of the reaction was monitored using TLC; a fresh quantity of furan was added to compensate for losses during reflux. After 72 h excess furan was allowed to evaporate and the residue, following preparative layer chromatography (20 × 20 cm, silica gel G coated, 2 mm, plates, developed in benzene and components extracted with CHCl_3) afforded adducts (**2a**) (140 mg), (**3a**) (85 mg) and some unchanged (**1a**) (20 mg, identified spectroscopically). Compound (**2a**), gummy material, pure on TLC (R_f 0.65, CHCl_3) (Found: C, 66.50; H, 6.71. $\text{C}_{10}\text{H}_{12}\text{O}_3$ requires C, 66.66; H, 6.66%); $\nu_{\text{max}}(\text{CCl}_4)$ 1730, 1580(w), 1460, 1370, 1320, 1260, 1040, 1020, 840, and 800 cm^{-1} ; m/z 180 (5, M^+), 151, 150, 135, 112, 97, 85, 83, 71, 69, 68, and 57 (100). Compound (**3a**), thick oil, pure by TLC (R_f 0.40, CHCl_3) (Found: C, 66.5; H, 6.6. $\text{C}_{10}\text{H}_{12}\text{O}_3$ requires C, 66.66; H, 6.66); $\nu_{\text{max}}(\text{CCl}_4)$ 1730, 1600(w), 1440, 1380, 1330, 1250, 1180, 1140, 910, and 890 cm^{-1} ; m/z 180 (15, M^+), 165, 151 (95), 135, 123, 108, 107, 91, 79, 71, 69, 68, and 28 (100).

$\text{Eu}(\text{fod})_3$ Catalysed Addition of Furan to Compound (1a).—To ethyl buta-2,3-dienoate (**1a**) (200 mg) was added freshly distilled furan (10 ml, excess) and $\text{Eu}(\text{fod})_3$ (1.0 mol %). The reaction mixture was kept at room temperature for 12 h, after which excess furan was allowed to evaporate. The residue, following preparative layer chromatography (plates developed with benzene and components extracted with CH_2Cl_2) gave

compound (**2a**) (205 mg) and (**3a**) (52 mg); no unchanged ester (**1a**) was isolated.

$\text{Pr}(\text{fod})_3$ Catalysed Addition of Furan to Compound (1a).—To a solution of ethyl buta-2,3-dienoate (100 mg) in furan (10 ml) was added $\text{Pr}(\text{fod})_3$ (1.0 mol %) and the mixture was kept at room temperature for 12 h. Preparative layer chromatographic separation of the crude mixture, gave compounds (**2a**) (100 mg) and (**3a**) (30 mg).

Thermal Addition of Furan to Ethyl Penta-2,3-dienoate (1b).—The allenic ester (**1b**) (400 mg) was treated with furan (10 ml) in a manner as described above for the thermal addition of furan to ester (**1a**). After 7 days excess furan was allowed to evaporate and the residue, on separation by PLC (plates developed with benzene and components extracted with CHCl_3 , and further purified by filtration through silica gel, 60–120 mesh, column) gave compounds (**2b**) (160 mg), (**3b**) (54 mg) and unchanged (**1b**) (50 mg, identified through IR spectroscopy). Compound (**2b**), gummy material, purely TLC (R_f 0.6, CHCl_3) (Found: C, 67.95; H, 7.25. $\text{C}_{11}\text{H}_{14}\text{O}_3$ requires C, 68.04; H, 7.22%); $\nu_{\text{max}}(\text{CCl}_4)$ 1725, 1585(w), 1450, 1370, 1320, 1250, 1170, 1120, 1070, 1010, and 900 cm^{-1} ; m/z 194 (4, M^+), 166, 165, 149, 148, 133, 126, 125, 111, 105, 97, 93, 77, 69, 68, 53, and 28 (100). Compound (**3b**), gummy material; R_f 0.4, CHCl_3 (Found: C, 67.9; H, 7.3. $\text{C}_{11}\text{H}_{14}\text{O}_3$ requires C, 68.04; H, 7.22%); $\nu_{\text{max}}(\text{CCl}_4)$ 1730, 1610(w), 1435, 1375, 1325, 1280, 1135, 1060, and 1000 cm^{-1} ; m/z 194 (5, M^+), 166, 165, 151, 149, 121, 91, 85, 77, 69, 68, 57, and 28 (100).

$\text{Eu}(\text{fod})_3$ Catalysed Addition of Furan to Compound (1b).—To ethyl penta-2,3-dienoate (**1b**) (100 mg) was added freshly distilled furan (10 ml, excess) and $\text{Eu}(\text{fod})_3$ (1.0 mol %) and the mixture was kept at room temperature for 12 h, after which time the mixture was chromatographed over silica gel G coated PLC plates (developed with benzene and components extracted with CH_2Cl_2). A single component (**2b**) (90 mg) was thus obtained together with unreacted compound (**1b**) (16 mg, characterized spectroscopically).

$\text{Pr}(\text{fod})_3$ Catalysed Addition of Furan to Compound (1b).—To a solution of compound (**1b**) (50 mg) and freshly distilled furan (10 ml, excess) was added $\text{Pr}(\text{fod})_3$ (1.0 mol %) and the reaction mixture was kept at room temperature and worked-up as described above for the $\text{Eu}(\text{fod})_3$ catalysed addition, to give compound (**2b**) as a single component (43 mg) and a trace amount of unchanged compound (**1b**).

Thermal Addition of Furan to Ethyl Hexa-2,3-dienoate (1c).—Freshly distilled compound (**1c**) (400 mg) was treated with excess freshly distilled furan, as described above, for 7 days. Separation (PLC) of the crude reaction product (PLC plates developed in benzene; components extracted with CHCl_3 ; further purification by filtration through a silica gel column, 60–120 mesh) gave compounds (**2c**) (145 mg), (**3c**) (40 mg) and unchanged (**1c**) (ca. 35 mg). Compounds (**2c**), gummy material, pure by TLC (R_f 0.55, CHCl_3) (Found: C, 69.03; H, 7.5. $\text{C}_{12}\text{H}_{16}\text{O}_3$ requires C, 69.23; H, 7.69%); $\nu_{\text{max}}(\text{CCl}_4)$ 1725, 1600(w), 1460, 1360, 1320, 1290, 1250, 1100, 1060, and 960 cm^{-1} ; m/z 208 (6, M^+), 180, 179, 149, 140, 107, 105, 97, 91, 85, 68, 65, and 28 (100). Compound (**3c**), gummy material, R_f 0.45, CHCl_3 ; $\nu_{\text{max}}(\text{CCl}_4)$ 1730, 1610(w), 1480, 1370, 1320, 1290, 1260, 1150, 1090, 1010, and 900 cm^{-1} ; m/z 208 (15, M^+), 179, 163, 148, 145, 135, 109, 107, 91, 87, 85, 81, 74, 69, 55, and 28 (100).

$\text{Eu}(\text{fod})_3$ Catalysed Addition of Furan to Compound (1c).—To ethyl hexa-2,3-dienoate (**1c**) (140 mg) was added furan (10 ml, excess) and $\text{Eu}(\text{fod})_3$ (1.0 mol %) and the mixture was kept at

room temperature for 20–22 h. The mixture gave, on separation by PLC (as above), compounds (2c) (120 mg), (3c) (15 mg) and unchanged (1c) (20 mg).

Almost similar results were obtained with Pr(fod)₃ as catalyst (under identical conditions).

Thermal Addition of Furan to Ethyl 4-Methylpenta-2,3-dienoate (1d).—Compound (1d) (500 mg) was treated with excess furan (10 ml) for 16 days, under similar conditions as described above for uncatalysed additions. Separation (PLC) of the crude mixture (plates developed with benzene; components extracted with CHCl₃; further purification by filtration through a silica gel column) afforded compounds (2d) (106 mg), (3d) (12 mg) and (1d) (140 mg, identified spectroscopically). Compounds (2d), pale coloured semi-solid, *R*_f 0.6, CHCl₃ (Found: C, 69.0; H, 7.7. C₁₂H₁₆O₃ requires C, 69.23; H, 7.69); *v*_{max}(CCl₄) 1 730, 1 610(w), 1 540, 1 460, 1 280, 1 210, 1 160, and 1 090 cm⁻¹; *m/z* 208 (20, *M*⁺), 192, 191, 179, 166, 164, 163, 140, 91, 68, 44, and 28 (100). Compound (3d), gummy material, *R*_f 0.45, CHCl₃; *v*_{max}(CCl₄) 1 730, 1 620(w), 1 560, 1 440, 1 375, 1 280, 1 100, 1 080, and 865 cm⁻¹; *m/z* 208 (25, *M*⁺), 192, 179, 163, 91, 69, 68, and 28 (100).

Eu(fod)₃ Catalysed Addition of Furan to Compound (1d).—To ethyl 4-methylpenta-2,3-dienoate (140 mg) was added an excess of freshly distilled furan (10 ml) and Eu(fod)₃ (1.0 mol %) and the mixture was kept at room temperature for 48 h. The crude material, following PLC separation, gave a single product identified as compound (2d) (75 mg) and unchanged (1d) (60 mg).

Identical results were obtained with Pr(fod)₃ as catalyst.

Thermal Addition of Furan to Ethyl 4-Methylhexa-2,3-dienoate (1e).—Freshly distilled ester (1e) (500 mg) was mixed with furan (10 ml, excess) and refluxed for 16 days using the set up as described above for similar reactions. The crude residue remaining after evaporation of furan was separated by PLC (as above) to give a single component (110 mg) and unchanged ester (1e) (150 mg, characterized by TLC and IR spectroscopy). The major component gave a single spot on TLC (*R*_f 0.6, CHCl₃; *R*_f 0.45, C₆H₆). It was found to be 2:1 mixture of compounds (2e) and (4e) (based on ¹H NMR spectroscopy) (Found: C, 69.9; H, 8.25. C₁₃H₁₈O₃ requires C, 70.27; H, 8.12%); *v*_{max}(CCl₄) 1 730, 1 620(w), 1 590, 1 550, 1 460, 1 360, 1 260, 1 040, 1 015, and 970 cm⁻¹; *m/z* 222 (20, *M*⁺), 207, 193, 177, 154, 145, 69, 68, 55, and 28 (100).

Eu(fod)₃ Catalysed Addition of Furan to Compound (1e).—To a solution of ester (1e) (200 mg) in furan (10 ml) was added Eu(fod)₃ (1.0 mol %) and the mixture was kept at room temperature for 60 h. The residue was filtered through a silica gel (60–120 mesh) column (hexane–benzene, 1:1) to remove high molecular weight materials. After removal of solvent (under reduced pressure) the oily residue was dissolved in CH₂Cl₂ (2 ml) and placed on a chromatotron-2(silicagel PF 254 Merck, 2 mm). Elution with hexane–ethyl acetate (98:2; 5 ml min⁻¹) gave a single component (115 mg). This was found to be a mixture (3:1) of compounds (2e) and (4e) (by integration of the ¹H NMR signals due to 8-Me).

Thermal Addition of 2-Methylfuran to Ethyl Penta-2,3-dienoate (1b).—To ethyl penta-2,3-dienoate (126 mg) was added 2-methylfuran (1 ml, excess) and benzene (10 ml) and the mixture was refluxed for 4 h. The mixture was then concentrated and chromatographed over silica gel G coated PLC plates using benzene as solvent. The components were extracted with CH₂Cl₂ to afford two major products, compounds (5b) (76 mg) and (6b) (70 mg). Compound (5b), pale coloured oil, *R*_f 0.60, CHCl₃; *v*_{max}(CCl₄) 1 730, 1 580(w), 1 450, 1 380, 1 320, and

1 260 cm⁻¹; *m/z* 208 (2, *M*⁺), 194, 193, 180, 179, 165, 147, 134, 133, 126, 106, 82, 81, and 28 (100). Compound (6b), a pale-coloured semi-solid, *R*_f 0.42, CHCl₃; *v*_{max}(CCl₄) 1 720, 1 590(w), 1 460, 1 380, 1 310, and 1 250 cm⁻¹; *m/z* 208 (5, *M*⁺), 193, 180, 179, 163, 147, 133, 119, 107, 106, 105, 83, 81, and 28 (100).

Eu(fod)₃ Catalysed Addition of 2-Methylfuran to Compound (1b).—A mixture of ethyl penta-2,3-dienoate (200 mg), 2-methylfuran (1 ml) and Eu(fod)₃ (1.0 mol %) was kept at room temperature for 2 h. The mixture was chromatographed over silica gel (PLC, benzene) and the components were extracted with CH₂Cl₂ to afford compounds (5b) (180 mg) and (6b) 84 mg; their identity was established spectroscopically.

Thermal Addition of 2-Methylfuran to Ethyl Hexa-2,3-dienoate (1c).—To ethyl hexa-2,3-dienoate (140 mg) was added 2-methylfuran (1 ml, excess) and the mixture was refluxed in benzene (15 ml) for 4 h. The mixture was then concentrated and chromatographed over silica gel G coated PLC plates (benzene as mobile phase, components extracted with CH₂Cl₂). Two major products, compounds (5c) (81 mg) and (6c) (80 mg) were obtained. Compound (5c), pale-coloured thick oil, *R*_f 0.58, CHCl₃; *v*_{max}(CCl₄) 1 730, 1 580(w), 1 440, 1 380, 1 320, 1 280, and 1 240 cm⁻¹; *m/z* 222 (5, *M*⁺), 207, 194, 193, 177, 161, 147, 126, 120, and 119 (100). Compound (6c), pale-coloured viscous oil; *R*_f 0.58, CHCl₃; *v*_{max}(CCl₄) 1 720, 1 575(w), 1 460, 1 370, 1 315, and 1 250 cm⁻¹; *m/z* 222 (20, *M*⁺), 207, 194, 193, 177, 161, 147, 135, 133, 121, 120, 119, 105, 94, and 83 (100).

Eu(fod)₃ Catalysed Addition of 2-Methylfuran to Compound (1c).—In a parallel experiment, a mixture of compound (1c) (140 mg), 2-methylfuran (excess, 1 ml), and Eu(fod)₃ (1 mol %) was kept at room temperature for ca. 2 h, and after the usual work-up (as for the previous case), compound (5c) (131 mg) and (6c) (46 mg), identified spectroscopically, were obtained as the major products.

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