Diels–Alder Addition of Cyclopentadiene to Allenic Esters: Catalysis by Lanthanide Complexes

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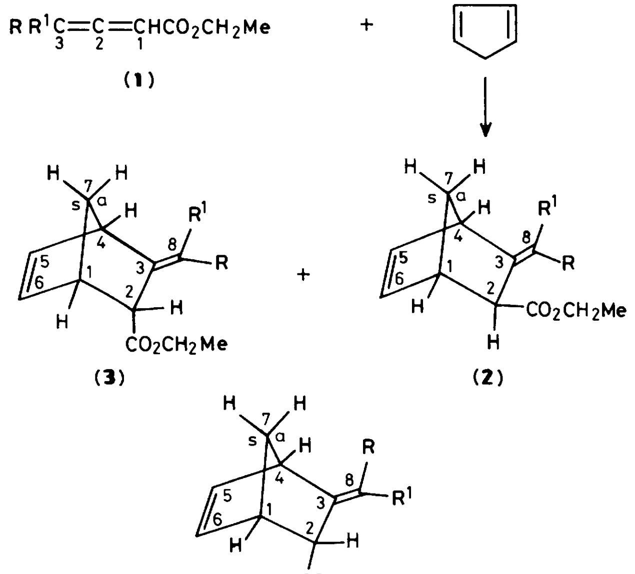
Stereoselectivity and yields are markedly enhanced for Diels–Alder additions involving cyclopentadiene and allenic esters (**1a—c**), on catalysis by lanthanide complexes, Eu(fod)$_3$ and Pr(fod)$_3$.

In general, the use of allenes as synthons in cycloadditions is restricted on account of their low dienophilicity and tendency to undergo excessive polymerisation under forcing conditions.[1] In this communication, we report cycloaddition reactions involving cyclopentadiene and three allenic esters *i.e.*, ethyl penta-2,3-dienoate (**1a**), ethyl hexa-2,3-dienoate (**1b**), and ethyl 4-methylpenta-2,3-dienoate (**1c**), with and without catalysis[2] by Eu(fod)$_3$ and Pr(fod)$_3$.† Under catalytic conditions, a marked improvement in stereoselectivity and yields of the cycloadducts is observed.

In an uncatalysed reaction, 4 mM of the allenic ester‡ was refluxed with 2.5—3.0 equiv. of cyclopentadiene in 50 ml of dry benzene. In the catalysed reaction, 1.0 mole% of Eu(fod)$_3$ or Pr(fod)$_3$ was added to the reaction mixture (both catalysts gave identical results) and left at room temperature. The products were separated using Chromatotron-2 (silica gel PF254 Merck, 2 mm, benzene–hexane 1 : 1, 5 ml/min.) or by column chromatography (silica gel, 60—120 mesh, petroleum ether–benzene 9 : 1), and were characterised by mass, ^{1}H n.m.r. (with extensive homodecoupling experiments), and ^{13}C n.m.r. (COM decoupled and SFORD)§ spectroscopy, and comparison of spectral data with that of known bicyclo[2.2.1]heptene systems.[3] The results are presented in Table 1.

The distinction between 2-*endo* and 2-*exo* configurations of the adducts is based on the value of vicinal coupling constant, $^3J_{1,2}$ and the C$_2$–H chemical shift.[3a,b] The assignments are further supported by the observation of long range coupling, $^4J_{2,7s}$ (*ca.* 1.8 Hz), in the case of *exo*-adducts (**2a—c**) (due to W relationship),[3a,4] and the downfield shift of C$_3$, C$_1$, and in particular, C$_6$, and the upfield shift of C$_4$, on going from *endo* (**3a,b,c**) to the corresponding *exo*-adducts (**2a,b,c**).[3a,5] The assigned stereochemistry at the *exo*-cyclic double bond in (**2a,b**), (**3a,b**) and (**4a,b**) is based on: i, comparison of allylic and, in particular, homoallylic couplings involving C$_2$–H and C$_8$–H, and C$_2$–H and C$_8$–alkyl groups, respectively, in pairs of the *endo*-adducts (**3a, 4a** and **3b, 4b**); here, a high value of homoallylic coupling supports the *trans*-arrangement between C$_2$–H and C$_8$–alkyl groups;[3a,4] ii, comparison[5,6] of δ C$_2$ and C$_4$ in (**3a,b**), (**4a,b**) with corresponding values in the *endo*-adduct (**3d**) (R = R^1 = H, C$_2$ at δ 49.5 and C$_4$ at δ 51.1)¶; and iii, comparison[5,6] of δ C$_2$ and δ C$_4$ in (**2a,b**) with corresponding values in the *exo*-adduct (**2d**) (R = R^1 = H, C$_2$ at δ 48.6 and C$_4$ at δ 50.0).¶



(**1—4**) **a**; R = Me ; R^1 = H
b; R = MeCH$_2$; R^1 = H
c; R = R^1 = Me

Table 1.

Allenic ester	Conditions (temp.)	Reaction time/h	% Yield	Product ratio (**2**:**3**:**4**)
(**1a**)	Uncatalysed (benzene, reflux)	14	38	25 : 67 : 8
	Catalysed (r.t.)	4	79	15 : 85
(**1b**)	Uncatalysed (benzene, reflux)	14	32	23 : 69 : 8
	Catalysed (r.t.)	4	84	14 : 86
(**1c**)	Uncatalysed (benzene, reflux)	10		No reaction (tlc)
	Catalysed (r.t.)	6	60	10 : 90

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† fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate.

‡ The esters (**1a—c**) were prepared according to literature method; R. P. Gandhi, M. P. S. Ishar, and A. Wali, *Tetrahedron Lett.*, 1987, 6679.

§ *Selected spectroscopic data*: (n.m.r. spectra were recorded at 99.55 MHz for ^{1}H and 24.99 MHz for ^{13}C nuclei in CDCl$_3$; *J* values are in Hz): (**2a**) ν_{max} (CCl$_4$): 1725 (CO$_2$–); ^{1}H n.m.r. δ 5.54 (sp q, 1H, C$_8$–H, $J_{8,C(8)-Me}$ 6.80, $J_{2,8}$ 2.46), 2.84 (br s, 1H, C$_2$–H), 2.01 (br d, 1H, C$_{(7)}$–H$_{anti}$), 1.62—1.48 (m, 1H, C$_7$–H$_{syn}$, $J_{7a,7s}$ 8.40, $J_{2,7s}$ 1.85), 1.54 (sp d, 3H, C$_8$–Me, $J_{2,C(8)-Me}$ 0.97); ^{13}C n.m.r. δ 173.6 (CO$_2$–), 140.5 (C$_3$), 137.6 (C$_6$), 135.2, 116.5, 60.4, 50.1 (C$_4$), 47.7, 47.1 (C$_1$, C$_2$), 46.8 (C$_7$), 15.0, 13.8; mass (*m/z*): 192(30) (M^+), 119(100). (**3a**) ν_{max} (CCl$_4$): 1730 (CO$_2$–); ^{1}H n.m.r. δ 5.25 (sp q, 1H, C$_8$–H, $J_{8,C(8)-Me}$ 6.84, $J_{2,8}$ 1.85), 3.39 (m, 1H, C$_2$–H, $J_{1,2}$ 3.75), 1.64 (br d, 1H, C$_7$–H$_{anti}$, $J_{7a,7s}$ 8.59), 1.53 (sp d, 3H, C$_8$–Me, $J_{2,C(8)-Me}$ 0.97), 1.45 (br d, 1H, C$_7$–H$_{syn}$); ^{13}C n.m.r. δ 171.9 (CO$_2$–), 139.4 (C$_3$), 135.4, 132.7 (C$_6$), 115.9, 59.7, 51.6 (C$_4$), 49.7 (C$_7$), 47.1 (C$_2$), 46.4 (C$_1$), 15.2, 13.8; mass (*m/z*): 192(5) (M^+), 28(100). (**4a**) ν_{max} (CCl$_4$): 1725 (CO$_2$–); ^{1}H n.m.r. δ 5.41 (sp q, 1H, C$_8$–H, $J_{8,C(8)-Me}$ 7.10, $J_{2,8}$ 1.49), 3.30 (br d, 1H, C$_2$–H, $J_{1,2}$ 3.75), 1.66 (sp d, 3H, C$_8$–Me, $J_{2,C(8)-Me}$ 2.04); ^{13}C n.m.r. δ 172.5 (CO$_2$–), 139.7, 134.4, 132.9 (C$_6$), 116.3, 60.1, 49.3 (C$_7$), 48.6, 48.3 (C$_2$, C$_4$), 46.7 (C$_1$), 15.5, 14.0; mass (*m/z*): 192 (24) (M^+), 28 (100). Similar data were obtained for (**2b, c**), (**3b, c**), and (**4b**).

¶ Data for (**2d**) and (**3d**), unpublished results from this laboratory.

In the above uncatalysed reactions, preferred formation of the *Z* isomers of both *exo*- and *endo*-adducts (**2a,b** and **3a,b**) takes place, the *E* isomers (**4a,b**) being produced to a lesser extent.|| Under Eu(fod)$_3$ and Pr(fod)$_3$ catalysis, however, the formation of *E* isomers is totally suppressed while *endo*-selectivities and the overall yield of the adducts are markedly enhanced. In addition, the latter reactions require lower temperatures and shorter reaction times.

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|| The formation of three 1:1 adducts in the uncatalysed reaction involving each of the allenic esters, (**1a**) and (**1b**), was confirmed by g.c.m.s. studies done on a Jeol JMS-D300 instrument (SE-30, 3 mm × 3 m, 120—250 °C, 10 °C/min., helium 1.4 kg/cm^2); the retention times obtained (min) were (**2a**) 3.5; (**3a**) 3.0; (**4a**) 2.7; (**2b**) 3.5; (**3b**) 3.2; (**4b**) 3.0. Other recognisable peaks in the chromatogram corresponded to cyclopentadiene, dicyclopentadiene, the esters (**1a,1b**) and their dimers (mass).

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