# Switching of the Reaction Pathway for Allenecarboxylate Intramolecular Cycloaddition

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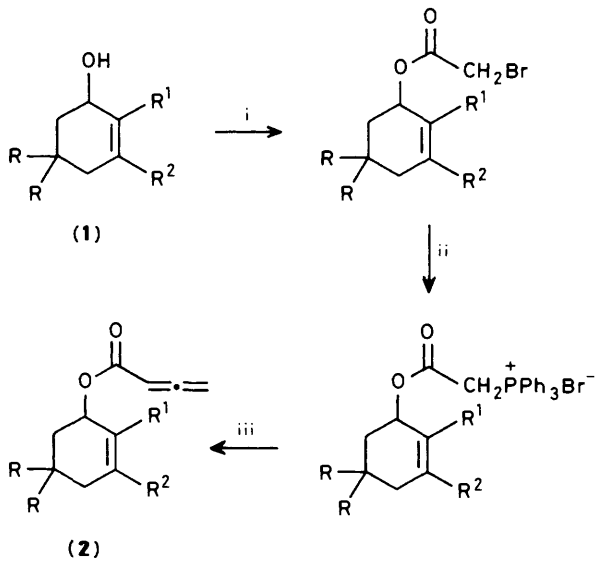
The [4 + 2] and [2 + 2] intramolecular cycloadditions to allenecarboxylates are strongly affected by conformational differences of the substrates in the transition state.

Incorporation of an ester linkage into a chain often has an adverse effect on the intramolecular Diels–Alder reaction.[1]

Recently, Heathcock and Hecker reported that intramolecular Diels–Alder reactions of crotonate esters were unsuccessful and would necessitate modification of the ester linkage.[2] As part of our research on intramolecular cycloadditions,[3] we report an intramolecular Diels–Alder reaction using an allenecarboxylate for the construction of a tricyclic six-membered lactone.

The allenecarboxylates (**2**)† were prepared from readily available alcohols (**1**) in three steps (Scheme 1). A solution of the allenecarboxylate (**2a**) in *o*-xylene was heated at 145 °C for 9 h. After removal of the solvent, the residue was purified by column chromatography on silica gel with hexane–ethyl acetate (4 : 1) as eluant to afford the [4 + 2] cycloadduct (**3a**)† [76%; m.p. 104—105 °C; $^1$H n.m.r., ($CDCl_3$) δ 5.83 (m, 1H, olefinic), 5.36 (m, 1H, olefinic), 4.64 (m, 1H, CHO), 3.0 (m, 1H, CH), 2.6—1.6 (m, 10H, $CH_2$); i.r. 1690 $cm^{-1}$ (δ-lactone)]. Similar treatment of (**2b**) afforded the [4 + 2] cycloadduct (**3b**)‡ (66%; m.p. 82—84 °C). These results were

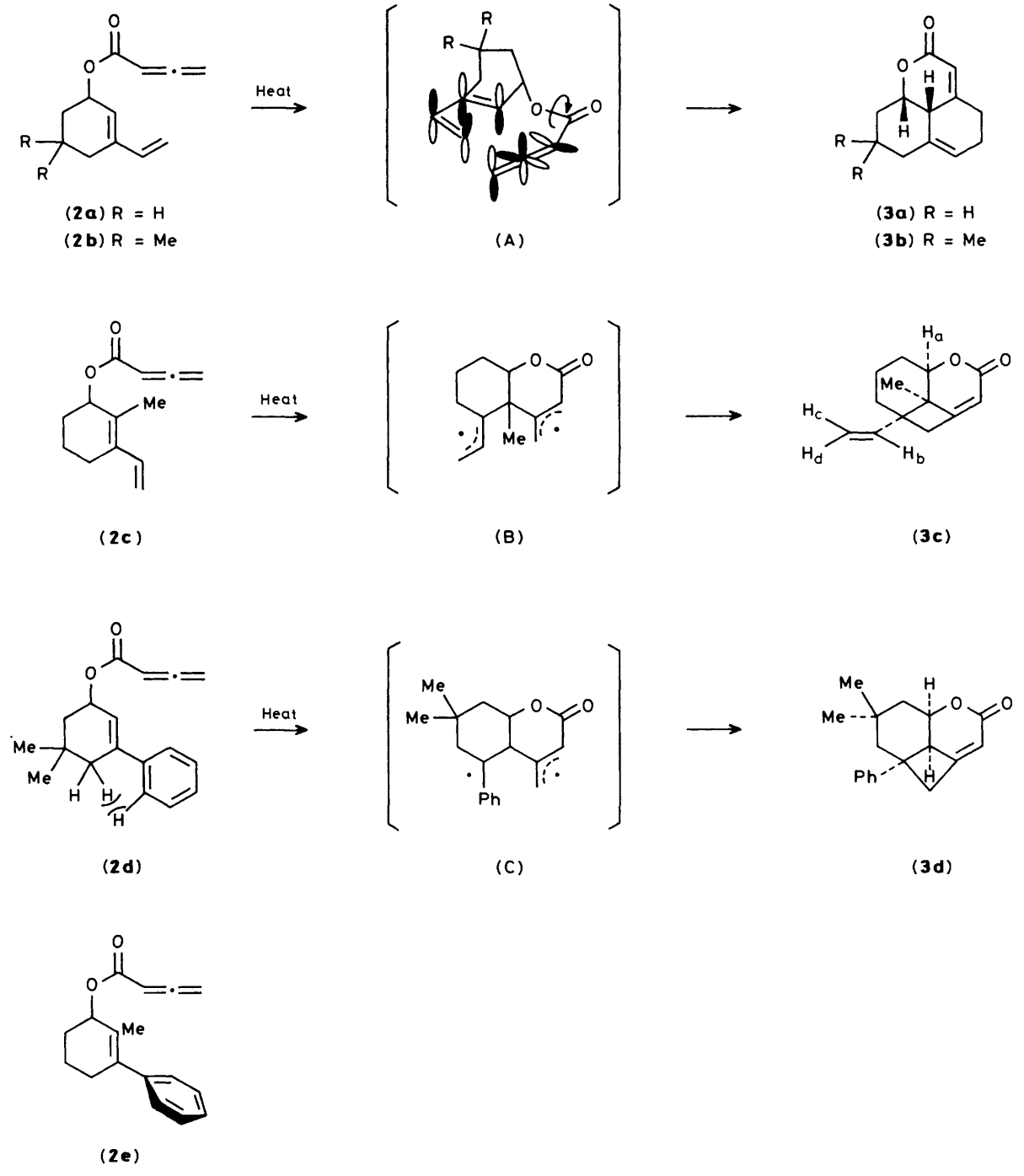



R, $R^1$: H or Me
$R^2$: Vinyl or phenyl

**Scheme 1.** *Reagents and conditions:* i, $BrCH_2COBr$–$Et_3N$ in $CH_2Cl_2$, −15 °C; ii, $PPh_3$ in benzene, room temperature; iii, $2Et_3N$, $CH_3COCl$ in $CH_2Cl_2$, room temperature.

† All new compounds gave satisfactory analytical and spectral data.

‡ $^1$H N.m.r., ($CDCl_3$): (**3b**) δ 5.83 (m, 1H, olefinic), 5.43 (m, 1H, olefinic), 4.76 (m, 1H, CHO), 3.12 (m, 1H, CH), 2.6—1.5 (m, 8H, $CH_2$), 1.0 (s, 3H, Me), 0.9 (s, 3H, Me); i.r. 1705 $cm^{-1}$ (δ-lactone). (**3d**) δ 7.29 (m, 5H), 5.86 (m, 1H, olefinic), 4.98 (m, 1H, CHO), 3.89 (dd, *J* 8, 2 Hz, 1H, CH), 3.01 (m, 2H, $CH_2$), 2.36—1.25 (m, 4H, $CH_2$), 0.92 (s, 3H, Me), 0.58 (s, 3H, Me); i.r., 1720 $cm^{-1}$ (δ-lactone).




Scheme 2

consistent with our expectation that the ester group is mostly in the s-*trans* form rather than the s-*cis* form in transition state (A), which should favour the Diels–Alder reaction (Scheme 2). However, thermal treatment of (**2c**) afforded the cycloadduct (**3c**)† [24%; m.p. 95—96 °C; $^1$H n.m.r., δ 5.98 (dd, *J* 16, 10 Hz, 1H, olefinic), 5.8 (m, 1H, olefinic), 5.18 (dd, *J* 10, 2 Hz, 1H, olefinic), 5.04 (dd, *J* 16, 2 Hz, 1H, olefinic), 4.26 (dd, *J* 10, 7 Hz, 1H, CHO), 3.27 (dd, *J* 15, 3 Hz, 1H, geminal $CH_2$), 2.49 (d, *J* 15 Hz, 1H, geminal $CH_2$), 2.4—1.0 (br., 6H, $CH_2$), 1.28 (s, 3H, Me); i.r., 1705 cm$^{-1}$ (δ-lactone)]. These spectral features were consistent with the [2 + 2] cycloadduct. The stereochemistry of (**3c**) was assigned by a nuclear Overhauser enhancement, indicating a *cis* relationship between the methyl group at δ 1.28 and $H_a$(25%), $H_b$(15%), $H_c$(5%), and $H_d$(5%). The [2 + 2] cycloadduct (**3d**)‡ obtained from thermal treatment of (**2d**) was obtained as an oil (64%). From Dreiding models it appears that the most favourable mode of cyclisation for the formation of the [2 + 2] cycloadducts (**3c**) and (**3d**) occurs when the cyclohexene ring defines an approximate boat or half chair conformation in the transition state due to the steric inhibition of the methyl or phenyl group. In both cases, one possibility is that a non-synchronous cyclisation of the diradical intermediates (B) and (C) is occurring.[4] When an *o*-xylene solution of (**2e**) was

heated under more drastic conditions, the starting material was recovered together with a small amount of intractable products. The transition state conformation required for this cycloaddition is clearly too sterically hindered for the reaction to proceed.

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