

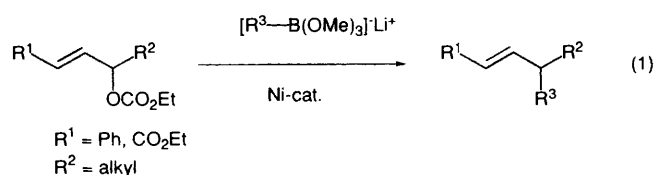
## Regioselectivity in the nickel-catalysed coupling of cyclic carbonates of but-3-ene-1,2-diols with organoborates

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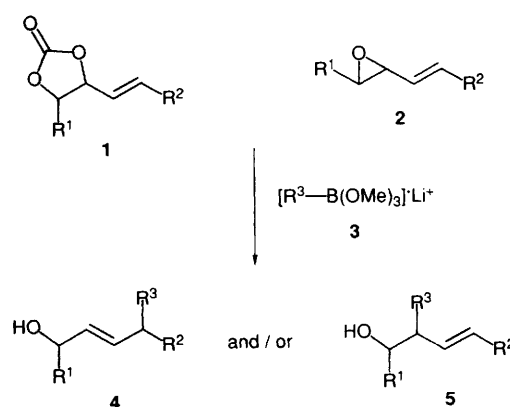
The regioselectivity of nickel-catalysed coupling of but-3-ene-1,2-diol cyclic carbonates **1** and organoborates **3** is examined, in which an ester or olefin directs the coupling site to afford conjugated products.

Palladium-catalysed coupling of buta-1,3-diene monoepoxides with 'hard' organometallics such as organo-mercurials,<sup>1</sup> -boranes,<sup>2</sup> and -stannanes<sup>3</sup> has been obtained with a certain degree of regioselectivity.<sup>4</sup> Because vinylic epoxides as such are reactive compounds, stable synthetic equivalents are of value for their preparation and purification, especially for application to the synthesis of complicated natural products. Previously we reported<sup>5</sup> the nickel-catalysed reaction of allylic carbonates and organoborates, in which non-stabilized 'hard' species of organoborates transfer to the allylic position regioselectively [eqn. (1)]. The reaction conditions have to be almost neutral

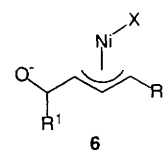


to be compatible with the ester group in the carbonate. We selected cyclic carbonates of but-3-ene-1,2-diols **1** as synthetic equivalents of buta-1,3-diene monoepoxides **2** (Scheme 1). By analogy with the palladium-catalysed coupling reaction of but-3-ene-1,2-diol derivatives and soft nucleophiles,<sup>6</sup> and that of buta-1,3-diene monoepoxides with soft<sup>7</sup> or hard<sup>1-3,8</sup> nucleophiles,  $\eta^3$ -allylnickel intermediates such as **6**<sup>9</sup> would be formed and the alkoxy-bearing substituent in **6** might influence the reactivity and regioselectivity. In the palladium-catalysed reaction of buta-1,3-diene monoepoxides, hard nucleophiles attack the allylic position distal to the alkoxy-bearing substituent producing allylic alcohols **4**. Herein, we report that the nickel-catalysed coupling of **1** with **3** shows different regiochemistry and that high selectivity arises from substrates possessing an ester or olefin substituent on the  $\eta^3$ -allylic system of **6**.

For comparison, a control reaction was carried out using carbonate **7** with furylborate **3a** (R<sup>3</sup> = 2-furyl) or phenylborate **3b** (R<sup>3</sup> = Ph) in the presence of 10 mol% of [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] or [NiCl<sub>2</sub>(dppf)] [dppf = 1,1'-bis(diphenylphosphino)ferrocene],<sup>10</sup> respectively, in tetrahydrofuran (THF) at 60 °C (Table 1, entry 1). Regioisomers **8** and **9** were produced in ratios of 35–65:65–35. The choice of ligand (PPh<sub>3</sub>, dppf) had little effect on the product ratios. These results in hand, *syn*- and *anti*-**10**, **13**, **15** and **17**, which were prepared from the corresponding 1,2-diols (triphosgene, C<sub>5</sub>H<sub>5</sub>N, CH<sub>2</sub>Cl<sub>2</sub>),<sup>11</sup> were submitted to the reaction with furylborate **3a** (Table 1, entries 2–6). In the case of *syn*- and *anti*-**10**, mixtures of the regioisomers **11** and **12** were obtained in quite similar ratios irrespective of the stereochemistry of the carbonate **10**. The ratios of **11/12** were



Scheme 1

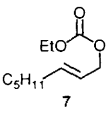
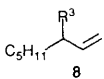
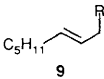
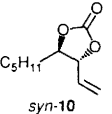
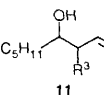
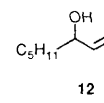
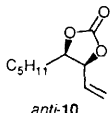
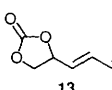
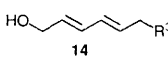
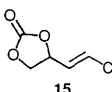
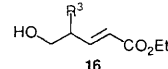
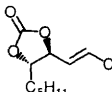
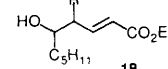
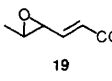
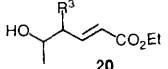
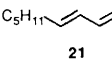
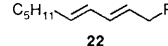
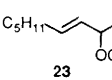
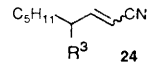


higher than those of entry 1. The reactions of carbonates **13**, **15**, **17** to furnish **14**, **16**, **18**, respectively, regioselectively in high yields, were perhaps surprising. In addition it was unexpected that the choice of ligand had no effect on the regiochemistry. These results are consistent with the formation of an  $\eta^3$ -allylnickel intermediate of type **6**. Subsequent reductive elimination of **6** (R<sup>2</sup> = CO<sub>2</sub>Et) afforded  $\alpha,\beta$ -unsaturated esters **16** and **18**, while migration of the  $\eta^3$ -allylic unit of **6** (R<sup>2</sup> = CH=CH<sub>2</sub>) to the terminal site followed by reductive elimination produced conjugated diene **14**. In other words the regioselectivity stemmed from a strong and ligand-independent tendency to form conjugation with a pre-existing ester or olefin in the reductive elimination step: the alkoxy-bearing substituent did not have any additional influence on the regiochemistry, but just acted as a more bulky substituent than a simple alkyl one (entries 1–3).

The reaction of the epoxide **19** with **3a** also produced the  $\gamma$ -furyl substituted compound **20** regioselectively (entry 7), thus indicating the formation of the same type of  $\eta^3$ -allylnickel intermediate **6** (R<sup>2</sup> = CO<sub>2</sub>Et; R<sup>1</sup> = Me).

The regiochemistry was further examined using carbonates **21** and **23** (entries 8, 9). Conjugated products **22** and **24** were obtained as the sole products in high yields, respectively (*cf.* entry 1).<sup>12</sup> These results add further examples to this selectivity trend. We are continuing to explore the synthetic utility and mechanism of the reaction described herein.

**Table 1** Regioselectivity of the nickel-catalysed coupling reaction of the carbonates and epoxide with borates **3**<sup>a</sup>

Entry	Carbonate	R <sup>3</sup> of <b>3</b>	Ligand	Product, ratio <sup>b,c</sup>	Total yield (%) <sup>d</sup>
1				 <b>8</b>  <b>9</b>	
		2-furyl	PPh <sub>3</sub>	35:65	82
		2-furyl	dppf	40:60	87
		Ph	PPh <sub>3</sub>	60:40	88 <sup>e</sup>
		Ph	dppf	65:35	80 <sup>e</sup>
2				 <b>11</b>  <b>12</b>	
		2-furyl	PPh <sub>3</sub>	45 (40:60):55	78
		2-furyl	dppf	75 (65:35):25	68
3				<b>11</b> <b>12</b>	
		2-furyl	PPh <sub>3</sub>	45 (40:60):55	76
		2-furyl	dppf	75 (30:70):25	91
4				 <b>14</b>	
		2-furyl	PPh <sub>3</sub>	HO:R <sup>3</sup> = 76	76
		2-furyl	dppf	75 (30:70):25	81
5				 <b>16</b>	
		2-furyl	PPh <sub>3</sub>		56
		2-furyl	dppf		62
6				 <b>18</b>	
		2-furyl	PPh <sub>3</sub>	(60:40)	61
		2-furyl	dppf	(60:40)	67
7				 <b>20</b>	
		2-furyl	PPh <sub>3</sub>	(55:45)	66
		2-furyl	dppf	(60:40)	76
8				 <b>22</b>	
		2-furyl	PPh <sub>3</sub>		91
		2-furyl	dppf		69
9				 <b>24</b>	
		2-furyl	PPh <sub>3</sub>	(75:25)	97
		2-furyl	dppf	(65:35)	98

<sup>a</sup> Reactions were carried out in THF at 60 °C for 4 h. <sup>b</sup> The ratios of isomers were determined by <sup>1</sup>H NMR (300 MHz). <sup>c</sup> Given in parentheses are diastereoisomeric ratios for the homoallylic alcohols (entries 2, 3, 6 and 7), and *trans*:*cis* isomer of **24** (entry 9). <sup>d</sup> Isolated yields after column chromatography. <sup>e</sup> Based on recovered carbonate.

### Experimental

#### General procedure for the coupling reaction

To an ice-cold solution of furan (74 mg, 1.1 mmol) in dry THF (3 cm<sup>3</sup>) was added an ethereal solution of MeLi (1.35 mol dm<sup>-3</sup>; 0.60 cm<sup>3</sup>, 0.81 mmol) dropwise under a nitrogen atmosphere. The solution was stirred for 2 h at 0 °C and then B(OMe)<sub>3</sub>

(112 mg, 1.08 mmol) was added to it. After 15 min, the cooling bath was removed, and the cyclic carbonate **15** (50 mg, 0.27 mmol) and [NiCl<sub>2</sub>(dppf)] (18 mg, 0.027 mmol) were added successively. The dark green solution was heated to 60 °C and stirred for 4 h, during which time the solution became dark brown. After the solution had been cooled, saturated aqueous NaHCO<sub>3</sub> (15 cm<sup>3</sup>) was added to it and the mixture was

extracted with AcOEt ( $3 \times 15 \text{ cm}^3$ ). The combined organic solutions were dried over  $\text{MgSO}_4$  and concentrated under reduced pressure to leave a residual dark oil, which was purified by column chromatography ( $1.7 \times 10 \text{ cm}$ ; silica gel, 11 g) to afford the coupled compound **16** (35 mg, 62%),  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $J/\text{Hz}$ ) 7.38 (1 H, d,  $J$  1.0), 7.02 (1 H, dd,  $J$  7.5 and 16), 6.34 (1 H, dd,  $J$  1.0 and 2.5), 6.18 (1 H, d,  $J$  2.5), 5.93 (1 H, d,  $J$  16), 4.19 (2 H, q,  $J$  7.5), 3.95 (1 H, dd,  $J$  6.0 and 10), 3.90 (1 H, dd,  $J$  6.0 and 10), 3.81 (1 H, dt,  $J$  7.5 and 6.0) and 1.29 (3 H, t,  $J$  7.5).

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