Alkene Synthesis

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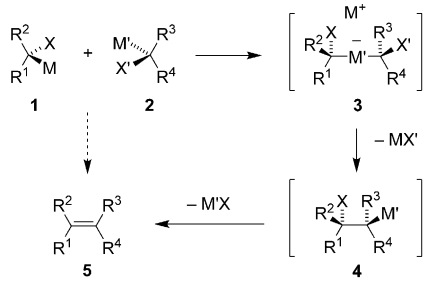
Stereospecific Synthesis of Alkenes by Eliminative Cross-Coupling of Enantioenriched sp^3-Hybridized Carbenoids

*Zhenhua Wu, Xun Sun, Kristin Potter, Yang Cao, Lev N. Zakharov, and Paul R. Blakemore**

Abstract: *1-Aryl-1,2-dialkylethenes were generated by a sequence of electrophilic substitution, 1,2-metalate rearrangement, and β-elimination initiated by the addition of enantioenriched α-(carbamoyloxy)alkylboronates to enantioenriched lithiated carbamates. The carbenoid stereochemical pairing [i.e., "like" = (S)+(S) or "unlike" = (S)+(R)] and the elimination mechanism (syn or anti), not substituent effects, determined the configuration of the trisubstituted alkene target. For example, (Z)-2,5-diphenyl-2-pentene was produced in 70 % yield with E/Z = 5:95 by a like combination of Li and B carbenoids and syn (thermal) elimination whereas the E isomer was obtained in the same yield with E/Z > 98:2 by an otherwise identical process involving an unlike stereochemical pairing. The concept elaborated overcomes an intrinsic limitation of traditional strategies for direct connective alkene synthesis, which cannot realize meaningful stereochemical bias unless the alkene substituents are strongly differentiated.*

The carbon–carbon double bond is of fundamental importance, and molecules containing some type of π_{CC} system are widespread and have broad utility. In general, carbon–carbon double bonds are stereogenic and/or decorated non-symmetrically, and so synthetic methods designed to access them should be capable of both stereo- and regiocontrol.[1] In spite of this fact, conventional direct methods for the preparation of alkenes, the most common class of compounds containing π_{CC} bonds, do not wholly address selectivity issues. For example, carbonyl olefination based approaches are regiospecific but good stereocontrol is dependent on the alkene substituents being adequately differentiated by steric or electronic factors.[2] As a consequence, excellent stereoselectivity is only guaranteed for 1,2-disubstituted alkene targets, and the stereocontrolled synthesis of tri- and tetrasubstituted examples remains a challenge.[3] When alkenes are prepared by alkyne elementometalation,[4] stereospecificity is achieved but regiocontrol is dependent on the substituents being again distinguished in some special way, and poor selectivity is anticipated for generic internal alkynes.[5] To overcome the limitations of existing strategies, a connective synthesis of alkenes was envisioned by eliminative cross-coupling of enantioenriched sp^3-hybridized carbenoids **1** and **2** (Scheme 1).[6] No biasing features are required within the substituents (R^1–R^4) to achieve fully controlled alkene formation with this concept. The process is trivially regiospecific, and stereochemical information encoded within the two carbenoid subunits is translated via a sequence of three stereospecific processes [electrophilic substitution (**1** + **2** → **3**), 1,2-metalate rearrangement (**3** → **4**), and β-elimination (**4** → **5**)] into any desired configuration of the target alkene **5**. Herein, the realization of this eliminative cross-coupling approach for the synthesis of a series of trisubstituted alkenes belonging to the styrene class is reported.[7]



- overall coupling outcome is intrinsically regiospecific and stereospecific
- *like* ('homochiral') or *unlike* ('heterochiral') pairing of **1** and **2** determines configuration of **5**
- role promiscuity between M/M' and X/X' is inconsequential, all four possible pathways (one illustrated) lead to the same alkene **5** if no change in fundamental mechanism
- in the absence of kinetic resolution, if e.r.(**1**)=*x*:1 and e.r.(**2**)=*y*:1 then d.r.(**5**)=(*xy*+1)/(*x*+*y*)

Scheme 1. Eliminative cross-coupling of enantioenriched carbenoids for the synthesis of alkenes.

The formation of symmetric alkenes by eliminative "dimerization" (i.e., homocoupling) of more reactive carbenoids is an often observed side reaction.[8] Hodgson and co-workers deliberately exploited this phenomenon to make 2-buten-1,4-diol derivatives by homocoupling of 1-lithiooxiranes and demonstrated that the *E*/*Z* ratio of the olefin product was dependent on the enantiopurity of the carbenoid, as anticipated.[9] The synthesis of non-symmetric alkenes by cross-coupling of racemic carbenoids has been occasionally explored; however, these approaches offer poor, or else not generalizable, stereoselectivity.[10] In a seminal effort that goes a long way to validate the premise of the above scheme, Matteson and co-workers described the cross-coupling of enantioenriched α-chloroalkylboronates and enantioenriched Still-type carbanions to afford stereodefined contiguous stereodiad motifs bearing vicinal boron and oxygen substituents [Eq. (1); MOM = methoxymethyl].[11] Elimination was not pursued; however, treatment of the β-oxyboronate

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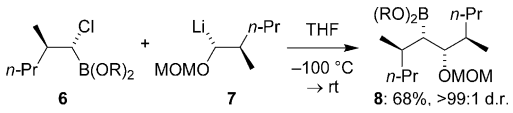
products with a basic nucleophile would be expected to induce *anti* β-elimination to yield alkenes.

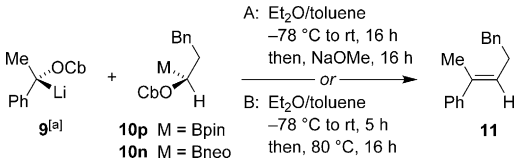


(1)

The first two steps of eliminative cross-coupling (**1** + **2** → **3** → **4**) resemble stereospecific reagent-controlled homologation (StReCH),[12] a process typically used for the iterative chain extension of boronic esters by sequential insertions of scalemic carbenoids into the C–B bond.[13] Studies by Aggarwal et al. have established that Hoppe-type lithiated carbamates are a robust class of carbenoids for StReCH.[14] Significantly, they demonstrated that fully substituted organolithium reagents derived from enantiopure secondary O-benzylic carbamates are capable of stereospecific insertion into boronic esters.[15] Given this precedent and wishing to eschew the targeting of easily made 1,2-disubstituted alkenes, we focused our experiments on the synthesis of 1-aryl-1,2-dialkylethenes, a class of styrenes that are difficult to prepare stereoselectively by traditional direct means.[16] To establish the basic parameters for this styrene synthesis, eliminative cross-coupling of lithiated carbamate **9** with α-carbamoyloxyboronates **10p** and **10n** to generate **11** was examined (Table 1).[17]

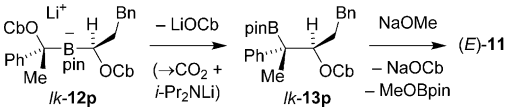
After optimizing reaction variables for an alkene synthesis involving an elimination stage triggered by exogenous alkoxide anion (method A), it was observed that coupling of (±)-**9** and (±)-**10p** showed little stereoselectivity (Table 1, entry 1). This is an ideal result because it reveals that *like* ("homochiral") and *unlike* ("heterochiral") stereochemical pairings of **9** and **10p** occur at similar rates. Eliminative cross-coupling using (±)-**9** and (*S*)-**10p** gave styrene **11** with *E*/*Z* ≈ 1:1 as expected (entry 2). Assuming that method A involves *anti* elimination, a *like* stereochemical pairing of scalemic samples of **9** and **10p** was selected to target (*E*)-**11** (entry 3). In the event, it was discovered that addition of (*S*)-**10p** (97% *ee*) to (*S*)-**9** (97% *ee*) at −78 °C followed by warming to room temperature gave pre-elimination adduct *lk*-**13p** (via ate complex *lk*-**12p**) as an essentially single regio-/diastereoisomer [Eq. (2)].[18]

Table 1: A model eliminative cross-coupling reaction.



Entry	Li carb.	B carb.	Pairing	Method	Target	Yield [%]	*E*/*Z*
1	(±)-**9**	(±)-**10p**	intrinsic	A[b]	(*E*+*Z*)-**11**	80	54:46
2	(±)-**9**	(*S*)-**10p**	*like*/*unlike*	A[b]	(*E*+*Z*)-**11**	70	56:44
3	(*S*)-**9**	(*S*)-**10p**	*like*	A[b]	(*E*)-**11**	69	98:2
4	(*R*)-**9**	(*S*)-**10p**	*unlike*	A[b]	(*Z*)-**11**	72	6:94
5	(*S*)-**9**	(*S*)-**10n**	*like*	A	(*E*)-**11**	69	>98:2
6	(*R*)-**9**	(*S*)-**10n**	*unlike*	A	(*Z*)-**11**	65	52:48
7	(*S*)-**9**	(*S*)-**10n**	*like*	B	(*Z*)-**11**	70	5:95
8	(*R*)-**9**	(*S*)-**10n**	*unlike*	B	(*E*)-**11**	70	>98:2

[a] Generated by lithiation using *s*-BuLi or *t*-BuLi, Et_2O, −78 °C, 20 min. [b] Reaction conducted in Et_2O solvent only. Bneo = B[$OCH_2(CMe_2)CH_2O$], Bpin = B[$O(CMe_2)_2O$], CbO = *i*-Pr_2NCO_2.

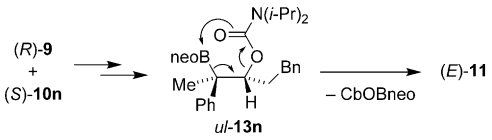


(2)

Treatment of *lk*-**13p** with NaOMe induced *anti* elimination to give (*E*)-**11** in good overall yield and with a level of stereoselectivity commensurate with statistical considerations.[19] To conclude this proof-of-concept study, the *unlike* stereochemical pairing of **9** and **10p** was studied next under essentially identical conditions (entry 4). The thermodynamically less stable alkene isomer (*Z*)-**11** was obtained in comparable yield and with stereoselectivity only slightly lower than that previously observed.

In an effort to improve the yield, a neopentylglycol boronate (**10n**)[20] was examined as a sterically less encumbered alternative to the pinacol boronic ester used above (**10p**). The *like* stereochemical pairing of **9** and **10n** proved satisfactory to access (*E*)-**11** (entry 5), but the *unlike* combination anticipated to target (*Z*)-**11** instead gave a mixture of alkene isomers favoring (*E*)-**11** (entry 6). Upon closer scrutiny, spectroscopic analysis of the reaction mixture revealed that a significant quantity of (*E*)-**11** was present before the alkoxide addition stage. In this case, spontaneous *syn* elimination of the pre-elimination adduct *ul*-**13n** by a bora-Wittig mechanism[2,21] competed with the usual alkoxide-mediated *anti* elimination pathway [Eq. (3)].[22] The fact that neopentylglycol boronates allow for *syn* elimination was deliberately exploited by simply omitting alkoxide addition and heating the reaction mixture (toluene, 80 °C) following ate complex rearrangement (method B). In this manner, (*Z*)-**11** was now successfully obtained from (*S*)-**10n** by pairing it in a *like* fashion with (*S*)-**9** (entry 7). (*E*)-**11** was similarly targeted from (*S*)-**10n** by *unlike* stereochemical pairing with (*R*)-**9** (entry 8). Thermolytic *syn* elimination from pinacol boronate pre-elimination adducts *lk*-**13p** and *ul*-**13p** was too sluggish at 80 °C to be practically useful.

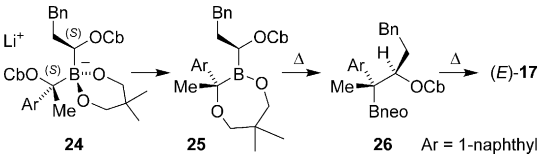
At this juncture, two viable eliminative cross-coupling methods for the stereospecific synthesis of styrene **11** had been identified, and we sought to determine the limit of these approaches for the preparation of other 1-aryl-1,2-dialkylethenes (Table 2). All alkenes were separately targeted in both *E* and *Z* configurations, and for each isomer, outcome data for the coupling method that gave the best result among those evaluated are illustrated. In general, the *E* isomers were best accessed by *like* pairings and *anti*



(3)

elimination (method A) using neopentylglycol (neo) or pinacol (pin) boronates whereas *like* pairings and *syn* elimination (method B) as applied to neopentylglycol boronates were typically superior for the synthesis of *Z* isomers. When *syn* elimination was desired, it was found that an aqueous work-up to remove basic species (which may trigger *anti* elimination) prior to thermolysis led to improved stereoselectivity. An acceptable level of stereocontrol was possible for a majority of alkene targets, and in all cases, it was possible to selectively synthesize the *E* or the *Z* isomer. The coupling efficiency diminished as the steric demand of the substituents surrounding the double bond increased (**11**, **18**, **19**, and **23**) but it was impressive that highly strained *Z* alkenes could be targeted successfully (e.g., **17** and **23**), even in those cases where the olefin was exocyclic to a benzofused bicyclic scaffold (**20**, **21**, and **22**).[23]

Anomalous behavior observed during attempts to secure α-vinyl naphthalene **17** necessitated the development of a new method (C) to achieve stereoselectivity. Uniquely in this case, and possibly owing to heightened steric hindrance caused by the α-naphthyl substituent, O atom migration competed with the canonical mechanism for 1,2-metalate rearrangement, and stereocontrol was forfeit. Addition of $MgBr_2{\cdot}OEt_2$ after ate complex formation facilitated clean formation of the borinate product of O atom migration (**25**), which was transformed stereospecifically into the olefin, presumably via boronate **26**, upon heating [Eq. (4)]. Double inversion of stereochemistry at the benzylic carbon atom originating from the lithiated carbamate accounts for the generation of the *E* alkene from a *like* carbenoid pairing and a *syn* elimination pathway (and similarly, a *Z* alkene from an *unlike* pairing).



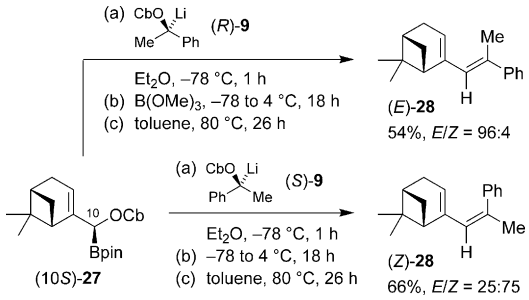
(4)

Table 2: Synthesis of *E*- and *Z*-configured 1-aryl-1,2-dialkylethenes by eliminative cross-coupling.[a]

Li carb. / B carb.				
best (*E*) mtd[a] yield, *E*/*Z*	**11** *neo•like•A*[b] 69%, >98:2	**14** *neo•like•A* 37%, >98:2	**15** *neo•like•A* 67%, 97:03
best (*Z*) mtd[a] yield, *E*/*Z*	**11** *neo•like•B*[b] 70%, 05:95	**14** *neo•like•B* 48%, 07:93	**15** *neo•like•B* 43%, <2:98
16 *neo•like•A* 45%, >98:2	**17** *neo•like•C* 51%, 90:10	**18** *pin•like•A* 60%, 90:10	**19** *neo•unlike•B* 42%, >98:2
16 *neo•like•B* 54%, 09:91	**17** *neo•unlike•C* 50%, 07:93	**18** *pin•unlike•A* 59%, 33:67	**19** *neo•like•B* 26%, 19:81
20 *pin•like•A* 50%, >98:2	**21** *pin•like•A* 40%, >98:2	**22** *neo•like•A* 46%, 92:08	**23** *neo•like•A* 11%, 97:03
20 *pin•unlike•A* 25%, 14:86	**21** *neo•like•B* 82%, 20:80	**22** *neo•like•B* 46%, 12:88	**23** *neo•like•B* 19%, 14:86

[a] Optimal method for targeting the *E* (top) or *Z* (bottom) isomer indicated by: boronate type (pin or neo)·stereochemical pairing (*like* or *unlike*)·method (see Table 1 for methods A and B; method C: Et_2O/toluene, −78 °C, 1 h; then $MgBr_2{\cdot}OEt_2$, −78 °C to RT, 16 h, workup; then toluene, 80 °C, 16 h). [b] Data for **11** recapitulated from Table 1 (entries 5 and 7). In a majority of examples, the enantiopurity of the carbenoid components was ≥96% *ee*. See the Supporting Information for specific details of individual reactions.

Finally, in a foray to gauge the potential of eliminative carbenoid cross-coupling for the synthesis of more complex alkenes, conversion of (+)-α-pinene-derived boronate (10*S*)-**27**[24] into the precursor of a known chiral pentadienyl anionic ligand [conjugated diene (*E*)-**28**][25] was explored (Scheme 2). Separate transformations targeting both the *E* and *Z* isomers of diene **28** proceeded in good yield, and it was notable that *syn* elimination was achievable from a pinacol boronate, presumably because of the doubly activated (allylic/benzylic)



Scheme 2. Stereoselective synthesis of a conjugated diene from an (+)-α-pinene-derived boronate.

nature of the relevant pre-elimination adducts in this case. Synthesis of (*E*)-**28** benefitted from the addition of trimethylborate as a nucleophile scavenger after ate complex formation [without $B(OMe)_3$: 39% yield, $E/Z = 97:3$]; however, the presence of this additive was detrimental when (*Z*)-**28** was targeted [with $B(OMe)_3$: 49% yield, $E/Z = 35:65$].

In summary, we have demonstrated that eliminative cross-coupling of enantioenriched carbenoids is a viable strategy for

the stereospecific assembly of alkenes. The double bond configuration is programmed by carbenoid stereochemical pairing (*like* or *unlike*) and the type of elimination (*syn* or *anti*). Thus, by contrast to traditional methods for alkene synthesis that rely on substituent effects for stereocontrol, the advocated approach is in principle applicable to the stereoselective synthesis of essentially any type of stereogenic alkene, no matter how subtle, or otherwise, the features distinguishing the stereoisomers. Herein, the concept was established for trisubstituted alkenes of the styrene class, and it remains to be extended to other important types of olefins, including tetrasubstituted derivatives. Studies along these lines, and conceptually related work directed at the synthesis of allenes and higher cumulenes, are ongoing and will be the subject of future reports.

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Keywords: alkenes · carbenoids · metalate rearrangements · organometallic reagents · stereoablation

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[17] Lithiated carbamates were generated essentially as previously described by Aggarwal et al. (Ref. [15a]), beginning with catalytic enantioselective reduction of prochiral ketones using Noyori transfer hydrogenation. α-Carbamoyloxy boronates were made by (−)-sparteine/*s*-BuLi mediated lithiation–borylation of the appropriate *O*-alkyl *N*,*N*-diisopropyl carbamates according to the method of Hoppe et al.; see: E. Beckmann, V. Desai, D. Hoppe, *Synlett* **2004**, 2275–2280.
[18] In this case, the putative ate complex *lk*-**12p** rearranged with selective loss of the benzylic OCb nucleofuge; however, it should be noted that such regioselectivity is not generally required for successful eliminative cross-coupling because both possible regioisomers would converge to the same alkene. The relative stereochemistry of *lk*-**13n** produced in an analogous manner was proven by oxidative deborylation (NaOOH) followed by cyclization (NaH, DMF, 100 °C) to give the corresponding epoxide, which was analyzed by ^{1}H NMR spectroscopy (NOESY). See the Supporting Information for details.
[19] Given that both carbenoids in this case had 66:1 e.r. (97% *ee*) the anticipated stereoselectivity for alkene formation would be $E/Z = (66^2+1)/(66+66) \approx 33{:}1$ (i.e., 97:3). See Scheme 1 for the general formula.
[20] X-ray diffraction analysis of (*S*)-**10n** confirmed its gross structure and absolute stereochemistry. This α-carbamoyloxy boronate was observed to exist (in the solid state) in cyclic form with the carbonyl group O atom coordinated to a quaternized B atom. CCDC 1491635 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
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[22] *syn* Elimination from *ul*-**13n** is more rapid than from its epimer *lk*-**13n** because for the latter, the two largest substituents (Ph and $BnCH_2$) eclipse one another in the necessary reactive conformation. Facile spontaneous *syn* elimination from adducts such as *ul*-**13n** (leading to *E* alkenes) means that *Z* alkenes should not be targeted from neopentylglycol boronates using *unlike* pairings and *anti* elimination.
[23] Eliminative dimerization of the lithiated carbamate was not a significant side reaction except for the α-lithioindanyl carbamate leading to alkene **20** (see the Supporting Information). The

root cause of low yields is as yet unclear, and we speculate that occurrences of poor stereoselectivity are due to competition between *syn* and *anti* elimination pathways.

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