γ-Allenyl Allyl Benzothiazole Sulfonyl Anions Undergo *cis*-Selective (Sylvestre) Julia Olefinations

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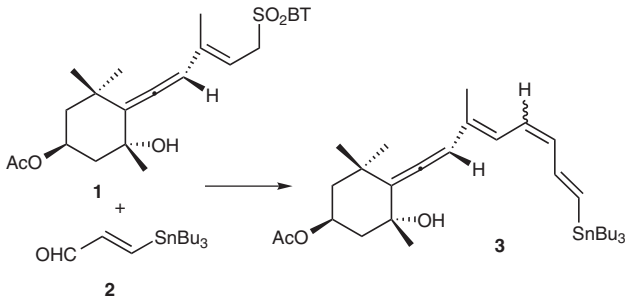
Abstract: γ-Allenyl allyl benzothiazolyl sulfones **8** and *ent*-**8** provided allenyl trienes and polyenes with *cis*-selectivities ranging from 71:29 to 100:0 upon condensation (NaHMDS, THF, –78 °C to 25 ºC) with a variety of unsaturated aldehydes.

Key words: Julia olefination, stereoselectivity, allenes, polyenes

The one-pot (Sylvestre) Julia olefination,[1] first reported in 1991 by Sylvestre Julia and coworkers,[2] is a variant of the classical (Marc) Julia[3] connective olefination reaction that uses heteroaryl (the original benzothiazole-2-yl,[2] BT, and the more recently reported 1-phenyl-1*H*-tetrazol-5-yl, PT;[4a] 1-*tert*-butyl-1*H*-tetrazol-5-yl, TBT[4b] and pyridin-2-yl, PYR[4c,d]) instead of arylsulfones. The intermediate β-alkoxysulfones in these heterocyclic analogues experience a Smiles rearrangement via a spirocyclic intermediate resulting in the transfer of the heterocycle from S to O to yield a sulfinate salt. Spontaneous elimination of SO_2 and lithium benzothiazolone (or the like) yields the alkene product. The (Sylvestre) Julia reaction thus circumvents the (recommended) isolation of the β-alkoxy arylsulfone intermediates, as well as their subsequent treatment with an acylating agent and a one-electron reductant, of the classical version. It is precisely the intermediacy of a radical species (of alkyl or vinyl nature when using SmI_2/HMPA[5] or Na/Hg,[6] respectively) what determines the high *trans*-stereoselectivity of the (Marc) Julia olefination.[7] On the other hand, being frequently substrate-dependent and further influenced by reactions conditions, predictions on the stereochemical outcome of the Sylvestre Julia (or Julia–Kocienski) olefination are problematic. Trends are nevertheless emerging. *Trans*-stereoselectivities are generally obtained for allyl BT- and benzyl BT-sulfones reacting with (branched) aldehydes.[2] Reversible addition–retroaddition (fragmentation) processes of the β-alkoxy BT-sulfone into resonance-stabilized α-metallated BT-sulfone and aldehyde as well as loss of lithium benzothiazolone to afford zwitterionic intermediates have been proposed to mechanistically justify the *E*-geometry of the formed olefin.[1] In the absence of the extra resonance stabilizing effect, as in alkyl BT-sulfones, *cis*/*trans* ratios favoring the former are obtained, which likely reflect the (kinetic) β-alkoxysulfone diastereomeric *syn*/*anti* ratios.[2] Notwithstanding the general trends, many exceptions to these predictions have been reported.[1]

It was recognized in a recent review article[1] that the combination of β,γ-unsaturated α-metallated sulfones and α,β-unsaturated aldehydes has been seldom exploited in synthesis of trienes (and higher polyenes) despite its convergent nature. Only the carotenoid field has witnessed the extension of the seminal studies reported by Kocienski et al. on the synthesis of the triene fragment of rapamycin.[8] Our group disclosed the preparation of a pentaenyl bisstannane for symmetrical carotenoid construction,[9] and Katsumura's group described the synthesis of the entire polyene system[10] of the carotenoid butenolide peridinin using in both cases BT-sulfone condensation reactions. In our approach to the latter compound,[11] we prepared allenyl triene **3** by coupling of **1** and **2**. As in the above cases and in keeping with other recent reports on trienes,[12] the major product had the *Z*-geometry (Scheme 1).



Scheme 1 *Reagents and conditions*: NaHDMS, THF, –78 °C; then **2**, –78 °C to 25 °C; 70% of a 75:25 *Z*/*E*-**3** mixture.

This finding led to question whether this stereochemical outcome was general for polyenes. We wish to report the general finding that γ-allenyl allyl sulfones indeed afford *cis*-polyenes upon reaction with unsaturated aldehydes. In addition, we correct our assignment of the geometry of symmetrical 1,ω-bis(tributylstannyl)-1,3,5,7,9-decapentaene (**16**) obtained by the same method and previously reported as *trans*.[9]

The γ-allenyl allyl BT-sulfone **8** and its enantiomer *ent*-**8** were prepared, pairwise along the sequence described in Scheme 2, by Stille cross-coupling[13] of bromoallenes **7** with stannylated allyl BT-sulfone **11**.[14] We have demonstrated that Stille cross-coupling reaction conditions induce an *anti*-selective S_N2' displacement by palladium on

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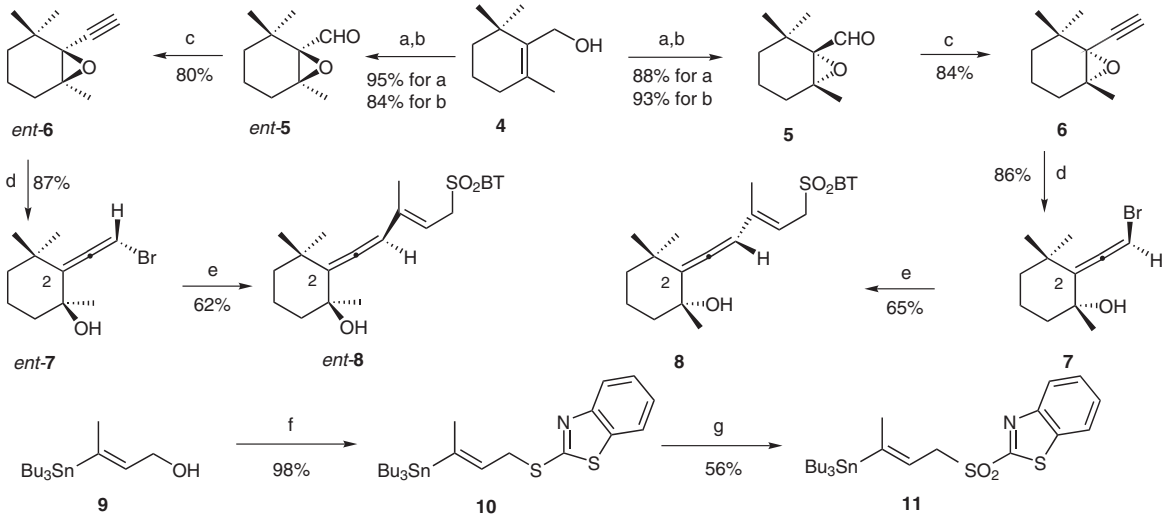


Scheme 2 γ-Allenyl allyl benzothiazolyl sulfone synthesis. *Reagents and conditions*: a. D-(–)-DET or L-(+)-DET, Ti(O*i*-Pr)$_4$, *t*-BuOOH, CH_2Cl_2, –20 °C, 12 h; b. DMSO, $(COCl)_2$, –60 °C, 15 min, then Et_3N, 10 min; c. LDA, $TMSCHN_2$, THF, –78 °C, 1 h; then 25 °C, 2 h; d. HBr, CuBr, NH_4Br, Et_2O, –10 °C, 2.5 min; e. **11**, $PdCl_2(PhCN)_2$, *i*-Pr_2NEt, DMF–THF, 45 °C, 2 h; f. BTSH, DIAD, PPh_3, THF, 0 °C to 25 °C, 30 min; g. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 35% H_2O_2, EtOH, 25 °C, 2.5 h.

these bromoallenes, followed by a [1,3]-metallotropic shift before transmetallation with the stannanes to finally afford the corresponding substituted vinylallenes with inversion of configuration.[11]

The synthesis of sulfone **11** started with alkenylstannane **9**,[15] which was converted into sulfide **10** using the Mitsunobu variant[16] (BTSH, PPh_3, DIAD, 0 – 25 °C, 98%). Oxidation of **10** with a peroxymolybdate(VI)[17] reagent in the presence of H_2O_2 [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 35% H_2O_2, EtOH, 25 °C, 56%] delivered **11**. Enantiopure bromoallenes **7** and *ent*-**7** were in turn acquired by the regio- and stereoselective displacement (S_N2' *anti*) of alkynyl oxiranes **6** under Chemla's[18] conditions (48% HBr, CuBr, NH_4Br, Et_2O, –10 °C, 2.5 h). Alkynyl oxiranes **6** and *ent*-**6** were traced back to the Sharpless asymmetric epoxidation[19] of β-cyclogeraniol **4**[20] by a modification (use of stoichiometric quantities) of the reported procedure,[21] oxidation of the epoxyalcohols to **5** (Swern conditions)[22] and Colvin rearrangement[23] of the vinylcarbenes obtained upon treatment of aldehydes **5** with the anion of trimethylsilyldiazomethane (Scheme 2). The enantiomeric purity of the bromoallenes was assessed by chiral HPLC [Chiralcel OD-H, 5 μm, 0.46 × 15 cm, 97.5:2.5 hexane–EtOH, 0.15 mL/min; $t_{R(1S,2aS)} = 20.15$ min; $t_{R(1R,2aR)} = 21.14$ min], and ee values of 99% were measured for each enantiomer. We surmise that the high enantioselectivity was preserved along the sequence from that enforced by the reagent in the SAE of **4**.

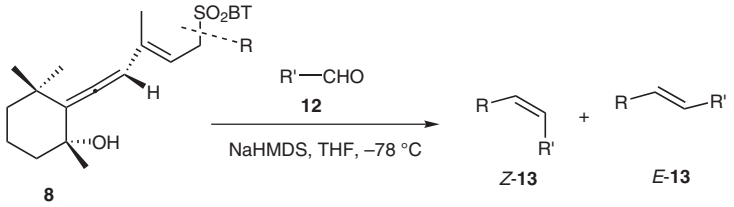
The anions of γ-allenyl allyl BT-sulfones **8** were generated with NaHMDS in THF at –78 °C, as optimized for carotenoid synthesis.[11] Aldehydes **12a**–**g**[24] were added at –78 °C, and the temperature was raised to 25 °C before quenching. Purification by chromatography after work-up afforded the allenyl trienes (or polyenes) **13** in the yields and isomer ratio at the newly formed double bond listed in Table 1. Reactions and purifications were carried out in light-protected glassware to minimize isomerizations.

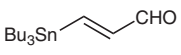
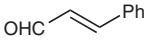
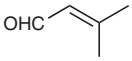
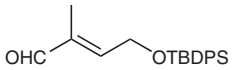
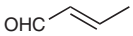
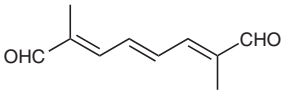
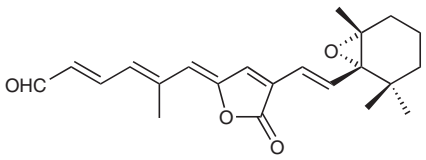
Regardless of the aldehyde structure, the stereoselectivity is good to excellent and favors the *Z*-isomer. Entries 1–5 include a variety of α,β-unsaturated aldehydes **12**[24] which afforded allenyl trienes with *Z*/*E* ratios ranging from 71:29 (**13d**) to 92:8 (**13c**). Assignment of the geometries relied on the values of proton coupling constants (i.e., for the newly formed double bond of **13b** *Z*: J = 10.4 Hz; *E*: J = 14.1 Hz) and were further confirmed by NOE studies. Crotonaldehyde **12e**, on the other hand, provided an intractable mixture of products, perhaps due to the special lability of the allenyl triene formed. The polyenyl aldehydes **12f** and **12g** afforded single products of *Z* geometries. Control of aldehyde reactivity in symmetrical octadienal **12f** could be made possible by the use of 1.1 mol equivalents of **12f**. Allenyl pentaenal **13f**[25] (65%) was accompanied by a small amount (10%) of the symmetrical carotenoid, the product of two-fold Julia condensation. Lastly, the entire C37-norcarotenoid skeleton of the carotenoid butenolides, such as peridinin, could be prepared stereoselectively (only the *Z*-isomer was obtained) using aldehyde **12g**.[26]

In view of these results, we re-examined the reaction of stannylated dienal **14** and dienyl BT-sulfone **15**.[9] Under the same general conditions, the symmetrical 1,ω-bis(tributylstannyl)-1,3,5,7,9-decapentaene (**16**) of *Z*-geometry[12] was obtained as single product (Scheme 3).[27]

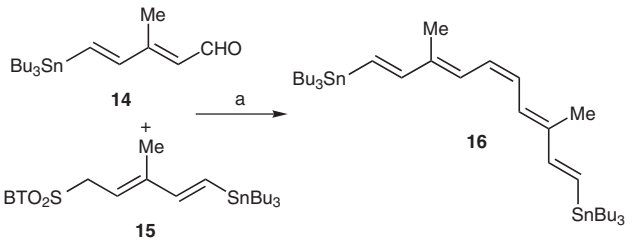
The *Z*>*E* stereoselectivity in the connective olefination reaction of allenyl allyl BT-sulfones and unsaturated aldehydes to afford polyenes appears, therefore, to be general. If the Julia reaction is to rival other double-bond forming processes (Wittig and Horner–Wadsworth–Emmons condensations), then substrates and/or reaction conditions must be found that afford predictable and stereocomple-

Table 1 Yields (%) and *Z*/*E* Isomer Ratio for the (Sylvestre) Julia Olefination of **8** and *ent*-**8** with Aldehydes **12a–g**



Entry	BT-sulfone	R′CHO	Polyene	Yield (%)	*Z*:*E* ratio[a]
1	**8**	 **12a**	**13a**	82	86:14
2	**8**	 **12b**	**13b**	83	78:22
3	**8**	 **12c**	**13c**	86	92:8
4	*ent*-**8**	 **12d**	**13d**	78	71:29
5	*ent*-**8**	 **12e**	**13e**	Decomposition	–
6	*ent*-**8**	 **12f**	**13f**[25]	65[b]	100:0
7	**8**	 **12g**	**13g**[26]	63	100:0

[a] Determined by integration of the ^{1}H NMR spectra of the reaction mixtures, which were separated by HPLC (preparative Nova-Pak, HR Silica, 1.9 × 30 cm, 6 μm; 95:5 hexane–EtOAc; flow rate: 3.5 mL/min).
[b] Yield of **13f**. The bis-olefination polyene (10%) was also obtained.



Scheme 3 *Reagents and conditions*: a) NaHMDS, THF, –78 °C; then **15**, –78 °C to 25 °C, 12 h; 83%.

mentary outcomes. In this regard, at least for trienes, reversal (*E*>*Z*) of the stereoselectivity shown here[12] has been reported to result from the condensation of alkyl BT-sulfones and dienals (cf. rapamycin[8] and tiacynomicin synthesis[28]).

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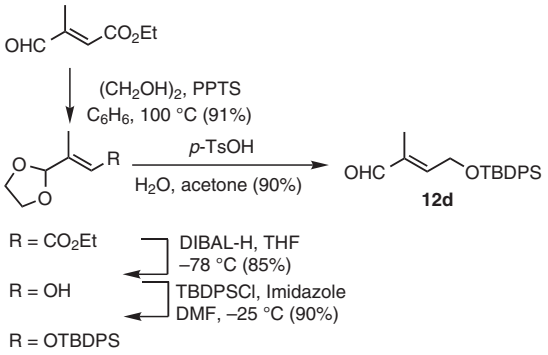
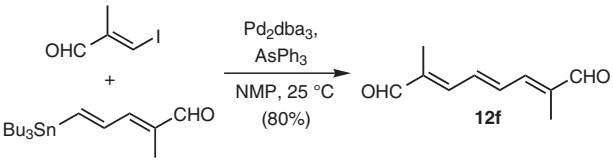


Scheme 4



Scheme 5

(25) Data for **13f**: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.45 (s, 1 H, CHO), 6.98 (dd, *J* = 14.4, 11.8 Hz, 1 H, H_{15}), 6.95 (d, *J* = 11.9 Hz, 1 H, $H_{14'}$), 6.68 (dd, *J* = 14.4, 11.7 Hz, 1 H, $H_{15'}$), 6.59 (d, *J* = 12.1 Hz, 1 H, H_{10}), 6.38 (t, *J* = 12.0 Hz, 1 H, H_{11}), 6.33 (d, *J* = 12.1 Hz, 1 H, H_{14}), 6.11 (s, 1 H, H_8), 5.95 (d, *J* = 11.9 Hz, 1 H, H_{12}), 2.13 (s, 3 H, C_{13}-CH3), 1.90–1.80 (m, 1 H, H_3), 1.87 (s, 3 H, $C_{13'}$-CH_3), 1.85 (s, 3 H, C_9-CH_3), 1.80–1.70 (m, 1 H, H_2 or H_4), 1.60–1.50 (m, 3 H, H_2 + H_3 + H_4), 1.40–1.30 (m, 1 H, H_2 or H_4), 1.32 (s, 3 H, C_5-CH_3), 1.27 (s, 3 H, C_1-CH_3), 1.04 (s, 3 H, C_1-CH_3) ppm. MS (EI$^+$): *m/z* (%) = 367 (27) [M$^+$ + 1], 366 (100) [M$^+$], 322 (35), 281 (41), 202 (28), 157 (36), 111 (37), 109 (32), 99 (27), 97 (60), 95 (27), 85 (61), 83 (62), 81 (30), 71 (80), 69 (85). HRMS (EI$^+$): *m/z* calcd for $C_{25}H_{34}O_2$: 366.2559; found: 366.2555. FT-IR (NaCl): ν = 3600–3400 (br, OH), 2960 (s, C-H), 2923 (s, C-H), 2853 (m, C-H), 1930 (w, C=C=C), 1731 (s, C=O), 1662 (s), 1552 (m), 1261 (s) cm^{-1}. UV (MeOH): λ_{max} = 294, 416 nm (Figure 1).

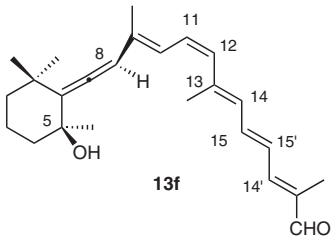


Figure 1

(26) Data for **13g**: ^{1}H NMR [600 MHz, $(CD_3)_2CO$]: δ = 7.50 (s, 1 H, H_{10}), 7.17 (d, *J* = 15.6 Hz, 1 H, H_7), 7.10 (t, *J* = 12.8 Hz, 1 H, $H_{15'}$), 6.76 (t, *J* = 12.3 Hz, 1 H, H_{15}), 6.70–6.60 (m, 2 H, $H_{10'}$ + H_{14}), 6.47 (t, *J* = 10.4 Hz, 1 H, $H_{11'}$), 6.42 (d, *J* = 15.6 Hz, 1 H, H_8), 6.22 (t, *J* = 11.5 Hz, 1 H, $H_{14'}$), 6.18 (s, 1 H, $H_{8'}$), 6.00 (s, 1 H, H_{12}), 3.54 (s, 1 H, OH), 2.21 (d, *J* = 6.0 Hz, 3 H, C_{13}-CH_3), 2.00 (m, 1 H, $H_{3'}$), 1.89 (s, 3 H, $C_{9'}$-CH_3), 1.90–1.80 (m, 2 H, $H_{4'}$ + H_4), 1.60–1.50 (m, 1 H, $H_{2'}$), 1.50–1.30 (m, 7 H, $H_{3'}$ + $H_{2'}$ + $H_{4'}$ + H_2 + 2 H_3 + H_4), 1.36 (s, 3 H, $C_{1'}$-CH_3), 1.28 (s, 3 H, $C_{5'}$-CH_3), 1.16 (s, 3 H, C_1-CH_3), 1.13

(s, 3 H, C_5-CH_3), 1.10–1.00 (m, 1 H, H_2), 1.01 (s, 3 H, $C_{1'}$-CH_3), 0.91 (s, 3 H, C_1-CH_3) ppm. ^{13}C NMR [100 MHz, $(CD_3)_2CO$]: δ = 204.4 (s, $C_{7'}$), 170.2 (s, C=O), 149.1 (s, C_{11}), 139.8 (d, C_{14}), 138.7 (d, C_{10}), 137.9 (s, $C_{9'}$), 135.7 (s, C_{13}), 135.3 (d, C_7), 134.1 (d, $C_{15'}$), 131.5 (d, C_{15}), 130.4 (d, $C_{12'}$), 129.6 (d, $C_{11'}$), 126.5 (s, C_9), 124.4 (d, $C_{10'}$), 123.6 (d, C_8), 121.3 (s, $C_{6'}$), 120.5 (d, C_{12}), 104.4 (d, $C_{8'}$), 72.7 (s, C_6), 71.7 (s, $C_{5'}$), 67.3 (s, C_5), 42.6 (t, $C_{4'}$), 42.4 (t, $C_{2'}$), 37.5 (t, C_2), 36.2 (s, $C_{1'}$), 35.3 (s, C_1), 33.6 (q, $C_{1'}$-CH_3), 32.6 (q, $C_{5'}$-CH_3), 31.7 (t, C_4), 30.2 (q, $C_{1'}$-CH_3), 27.4 (q, C_1-CH_3), 27.1 (q, C_1-CH_3), 22.0 (q, C_5-CH_3), 20.0 (t, $C_{3'}$), 18.7 (t, C_3), 16.5 (q, C_{13}-CH_3), 15.2 (q, $C_{9'}$-CH_3) ppm. MS (FAB$^+$): *m/z* (%) = 558 (10) [M^+ + 2], 557 (11) [M^+ + 1], 556 (85) [M^+], 540 (12), 539 (26), 394 (15), 393 (26), 322 (27), 307 (29), 289 (20), 241 (12), 165 (27). HRMS (FAB$^+$): *m/z* calcd for $C_{37}H_{49}O_4$: 557.3631; found: 557.3613. FT-IR (NaCl): ν = 3600–3400 (br, OH), 2961 (s, C-H), 2923 (s, C-H), 2849 (m, C-H), 1926 (w, C=C=C), 1749 (s, C=O), 1521 (w), 1449 (w) cm^{-1} (Figure 2).

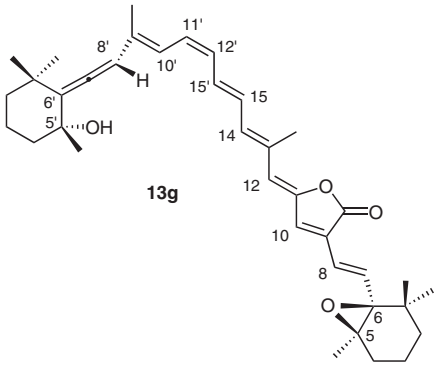


Figure 2

(27) Determined by 2D HMQC-TOCSY. Although the geometry of 1,ω-bis(tributylstannyl)-1,3,5,7,9-decapentaene (**16**) reported by our group was in error (ref.[9]), the structures of the final carotenoids β,β-carotene and (3*R*,3′*R*)-zeaxanthin obtained by Stille coupling of **16** with the corresponding trienyliodides are correct. Isomerization takes place at the carotenoid stage by the action of palladium, since reagent **16** is stable to the Stille coupling reaction conditions.

(28) Smith, A. B. III; Wan, Z. *J. Org. Chem.* **2000**, *65*, 3738.