5-((3-BROMOALLYL)SULFONYL)-1H-TETRAZOLES
FOR BROMODIENE SYNTHESIS†

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† Dedicated to Professor Kiyoshi Tomioka on the occasion of his 70th birthday

Abstract – Reagents for one-step construction of conjugated bromodienes from aldehydes are described. Various 1-alkyl- and 1-aryl-tetrazoyl bromoallylic sulfones were synthesized and evaluated in bromodiene synthesis. 1-Alkyl-tetrazoyl sulfones selectively afforded (1E,3Z)-bromodienes, while 1-aryl-tetrazoyl sulfones resulted in low selectivity.

Conjugated bromodienes are useful building blocks in organic synthesis. Transition metal-catalyzed cross-coupling reactions with bromodienes provide reliable stereoselective access to conjugated polyenes. In addition, several marine natural products bear a conjugated bromodiene unit. Consequently, various reagents and synthetic protocols to provide bromodienes are reported, such as stereoselective reduction/hydrogenolysis of gem-dibromoalkenes, bromo-decarboxylation of α,β,γ,δ-unsaturated carboxylic acids, cross-coupling reaction of 1,2-dihaloethylene with alkenylmetal reagents, bromomethylation of α,β-unsaturated aldehydes, ring-opening reaction of halocyclobutenes, and others. These reactions are synthetically useful, but at least two steps are generally required because the carbon elongation process and transformation into bromodienes are often performed separately. For example, Takai olefination followed by cross-coupling, and Seyferth–Gilbert homologation followed by hydrostannylation and NBS treatment, were performed to access bromodienes from aldehydes. In terms of step-economy, a one-step direct introduction of the bromodiene unit starting from aldehydes is ideal, especially when the starting aldehydes are precious intermediates in multi-step synthesis. To address this issue, Yamada and coworkers utilized diethyl 3-bromo-2-propenylphosphonate in their synthesis of...
aglycon of aurisides A and B. The reactivity of the Honor–Wadsworth–Emmons reagent, however, was moderate and bromodiene was obtained in low yield. For our ongoing synthetic studies on related marine natural products, we required a new reactive reagent to efficiently provide the bromodiene unit. Here we describe our studies to elucidate the utility of 1-alkyl- and 1-aryl-tetrazoyl bromoallylic sulfones in bromodiene synthesis via Julia olefination. The substituent at the tetrazole ring affected both the $E/Z$ selectivity and reactivity.

Because tetrazoyl allylic sulfones are reported to be highly reactive Julia reagents for introducing diene units, we envisioned the use of a bromoallylic variant in this study. We first synthesized various 1-aryl- and 1-alkyl-tetrazoyl bromoallylic sulfones to explore substituent effects on the reactivity and selectivity (Scheme 1). Mercaptotetrazoles reacted with alcohol under Mitsunobu conditions to afford stannylsulfide in 82%-89% yield. The tributylstannyl group was almost quantitatively transformed into bromosulfide by treatment with NBS, and oxidation of bromosulfide was accomplished by ammonium molybdate and hydrogen peroxide to give bromoallylic sulfones. Oxidation of with a bulky substituent, either a $t$-butyl or adamantyl group, resulted in low yield, while sterically less hindered gave bromoallylic sulfone in 75% yield.

**Scheme 1.** Synthesis of bromoallylic sulfones
With various bromoallylic sulfones 5 in hand, we compared the reactivity and \( E/Z \) selectivity in a model reaction with decanal (6a). 1-Phenyltetrazoyl sulfone 5a gave bromodiene 7a in 72% yield with \((1E,3E)/(1E,3Z) = 52:48\) selectivity (Table 1, entry 1). Although Julia-Kocieński olefination using 1-phenyltetrazoyl sulfones without an allylic unit generally affords alkenes with high \( E \)-stereoselectivity, bromoallylic sulfone 5a resulted in poor regioselectivity. The observed moderate \( E/Z \) selectivity with 1-aryl-tetrazoyl bromoallylic sulfones is similar to that observed in other allylic sulfones.\(^{13}\) Aryl-sulfone 5b and 5c were used to investigate the electronic effects, but neither 5b nor 5c improved the \( E/Z \)-selectivity (entries 2, 3). Trials to improve \( E \)-selectivity using 5b failed. For example, the reaction using 5b in either DMF or DME/HMPA resulted in mixtures of all possible isomers with moderate yield.\(^{18}\) In contrast to 1-aryl-tetrazoyl sulfones 5a-5c, 1-alkyl-substituted sulfones 5d-5g afforded bromodiene 7a with good \( Z \)-selectivity (entries 4-7). Sterically hindered 5f with a \( t \)-butyl group and 5g with an adamantyl group showed perfect \( Z \)-selectivity \((E/Z = 2:>98)\), while bromodiene 7a was obtained in low yield (entry 6, 18%; entry 7, 25%). 1-iPr-tetrazoyl sulfone 5e exhibited good

### Table 1. Optimization of reaction conditions

<table>
<thead>
<tr>
<th>entry</th>
<th>( R ), 5</th>
<th>base</th>
<th>% yield(^a)</th>
<th>((1E,3E)/(1E,3Z))^{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph 5a</td>
<td>LiHMDS</td>
<td>72</td>
<td>52:48</td>
</tr>
<tr>
<td>2</td>
<td>( p )-MeO-C(_6)H(_4) 5b</td>
<td>LiHMDS</td>
<td>78</td>
<td>58:42</td>
</tr>
<tr>
<td>3</td>
<td>( p )-CF(_3)-C(_6)H(_4) 5c</td>
<td>LiHMDS</td>
<td>71</td>
<td>54:46</td>
</tr>
<tr>
<td>4</td>
<td>Me 5d</td>
<td>LiHMDS</td>
<td>59</td>
<td>11:89</td>
</tr>
<tr>
<td>5</td>
<td>iPr 5e</td>
<td>LiHMDS</td>
<td>65</td>
<td>6:94</td>
</tr>
<tr>
<td>6</td>
<td>'Bu 5f</td>
<td>LiHMDS</td>
<td>18</td>
<td>2:&gt;98</td>
</tr>
<tr>
<td>7</td>
<td>adamantyl 5g</td>
<td>LiHMDS</td>
<td>25</td>
<td>2:&gt;98</td>
</tr>
<tr>
<td>8</td>
<td>iPr 5e</td>
<td>NaHMDS</td>
<td>39</td>
<td>17:83</td>
</tr>
<tr>
<td>9</td>
<td>iPr 5e</td>
<td>KHMDS</td>
<td>5</td>
<td>38:62</td>
</tr>
</tbody>
</table>

\(^a\)Isolated yield. \(^b\) Determined by \(^1\)H NMR analysis.
reactivity as well as high Z-selectivity (entry 5, 65% yield, $E/Z = 6:94$). Other bases, such as NaHMDS and KHMDS, resulted in lower yield and selectivity, and LiHMDS gave the best results (entry 5 vs entries 8 and 9). The observed base effects were different from those of the related allylic sulfones without a bromide unit,\textsuperscript{13a,13c} while good Z-selectivity using 5e-5g is similar to that in previous studies.\textsuperscript{13a} Scope and limitations of aldehydes are summarized in Table 2. In the previous report of Julia olefination using allylic 1-phenyltetrazoyl sulfones without a bromide unit,\textsuperscript{13c} $\alpha$-branched aldehydes furnished conjugated dienes $E$-selectively. With sulfone 5e, however, moderate Z-selectivity was observed with $\alpha$-branched aldehydes 6c and 6d. Aryl aldehyde 6e also gave bromodiene 7e with good Z-selectivity, albeit in low yield.

Table 2. Substrate scope of aldehydes

<table>
<thead>
<tr>
<th>entry</th>
<th>aldehyde 6: R</th>
<th>% yield of 7*</th>
<th>(1$E$,3$E$)/(1$E$,3$Z$)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6a</td>
<td>C$<em>8$H$</em>{17}$</td>
<td>7a 65</td>
</tr>
<tr>
<td>2</td>
<td>6b</td>
<td>Ph</td>
<td>7b 57</td>
</tr>
<tr>
<td>3</td>
<td>6c</td>
<td></td>
<td>7c 77</td>
</tr>
<tr>
<td>4</td>
<td>6d</td>
<td></td>
<td>7d 39</td>
</tr>
<tr>
<td>5</td>
<td>6e</td>
<td>Ph-Cl</td>
<td>7e 25</td>
</tr>
</tbody>
</table>

\*Isolated yield. \textsuperscript{b}Determined by $^1$H NMR analysis.

In summary, we synthesized a series of 1-alkyl- and 1-aryl-tetrazoyl bromoallylic sulfones and evaluated their $E$/Z-selectivity and reactivity. While 1-aryl-tetrazoyl sulfones gave bromodiene with modest $E$/Z-selectivity, 1-alkyl-tetrazoyl bromoallylic sulfones selectively provided (1$E$,3$Z$)-bromodienes.
Tuning of steric bulkiness was important, and 1-iPr-tetrazoyl sulfone exhibited good reactivity as well as high Z-selectivity. The reagent would be useful for the synthesis of natural products bearing the (1E,3Z)-bromodiene unit. Application of these reagents in a total synthesis is ongoing and will be reported in due course.

**EXPERIMENTAL**

**General.** Melting points were determined on a Yamato melting point apparatus model MP-21 and were uncorrected. Infrared (IR) spectra were recorded on JASCO FT/IR-5300 spectrophotometer and absorbance bands are reported in wavenumber (cm\(^{-1}\)). Proton nuclear magnetic resonance (\(^1\)H NMR) spectra, carbon nuclear magnetic resonance (\(^{13}\)C NMR) spectra and fluorine nuclear magnetic resonance (\(^{19}\)F NMR) spectra were recorded on JEOL JMN-ECP 400 (400 MHz), JEOL JMN-ECS 400 (400 MHz), JEOL JMN-ECX 400P (400 MHz), JEOL JMN-ECA 500 (500 MHz) spectrometers with tetramethylsilane in CDCl\(_3\) (\(\delta_H 0.00\)), hexafluorobenzene in CDCl\(_3\) (\(\delta_F -164.9\)), chloroform-\(d_1\) (\(\delta_H 7.26, \delta_C 77.0\)) or DMSO-\(d_6\) (\(\delta_H 2.50, \delta_C 39.5\)) as an internal standard. Coupling constants (\(J\)) are reported in hertz (Hz). Abbreviations of multiplicity are as follows: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sext, sextet; sept, septet; m, multiplet; br, broad. Data are presented as follows: chemical shift, multiplicity, coupling constants, integration and assignment. ESI (electrospray ionization) mass spectra were measured with Thermo Scientific Exactive spectrometer and EI (electro ionization) mass spectra were measured with JNM-T100GCV spectrometer. Flash column chromatography was carried out on Kanto silica gel 60 N (40–50 mesh). Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 F\(_{254}\) plates. Visualization was accomplished with ultraviolet light and anisaldehyde, followed by heating. Reagents and solvents were purified by standard means or used as received unless otherwise noted. The numbering of bromodienes is assigned from terminal brominated carbon atom.

**General Procedure for Julia Olefination**

To a stirred solution of isopropylsulfone 5e (0.33 mmol) in DME (1.3 mL) was added LiHMDS (0.315 mL, 0.315 mmol, 1.0 M THF solution) at –78 °C (dry ice/acetone bath). After stirring for 5 min, aldehyde 6 (0.30 mmol) in DME (1.5 mL) was added to the solution dropwisely and rinsed 2 times with DME (1.0 mL, 0.5 mL). The whole mixture was stirred at this temperature for 2 h, and then warmed to room temperature gradually by removing dry ice and stirred for 20 h. The reaction mixture was quenched with H\(_2\)O (2 mL) and the whole mixture was extracted with EtOAc. The organic layer was washed with H\(_2\)O and brine, and dried over anhydrous Na\(_2\)SO\(_4\). Filtration and evaporation in vacuo furnished crude product, which was purified by flash column chromatography (silica gel, eluent: hexane only) to afford bromodiene.
(1E,3Z)-1-Bromotrideca-1,3-diene (7a)
18–78% yield ((1E,3E)/(1E,3Z) = 52:48–2:>98). Colorless oil; Rf 0.77 (hexane only); IR (neat) 2925, 1574, 1465, 929, 799 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.88 (t, \(J = 6.8\) Hz, 3H, CH\(_2\)CH\(_2\)CH\(_3\)), 1.27 (m, 12H, twelve of CHCH\(_2\)(CH\(_2\))\(_7\)CH\(_3\)), 1.35–1.41 (m, 2H, two of CHCH\(_2\)(CH\(_2\))\(_7\)CH\(_3\)), 2.13 (td, \(J = 7.5, 1.2\) Hz, 2H, CHCH\(_2\)CH\(_3\)), 5.49 (dt, \(J = 10.9, 7.5\) Hz, 1H, CHCHCH\(_2\)), 5.90 (dd, \(J = 11.2, 10.9\) Hz, 1H, CHCHCHCH\(_2\)), 6.27 (d, \(J = 13.8\) Hz, 1H, BrCHCH), 6.99 (ddd, \(J = 13.8, 11.2, 1.2\) Hz, 1H, BrCHCHCH); 13C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.1 (CH\(_3\)), 22.7 (CH\(_2\)), 27.9 (CH\(_2\)), 29.2 (CH\(_2\)), 29.3 (CH\(_2\)), 29.4 (CH\(_2\)), 29.5 (CH\(_2\)), 29.6 (CH\(_2\)), 31.9 (CH\(_2\)), 108.6 (CH), 125.6 (CH), 133.2 (CH), 133.9 (CH); EI-HRMS \(m/z\) calcd for C\(_{13}\)H\(_{23}\)Br (M)+ 258.09831, found 258.09938. 1H NMR and 13C NMR spectra of pure (1E,3Z)- isomer obtained from the reaction with adamantyl sulfone 5g are provided in Supporting Information.

((1E,3Z)-1-Bromohexa-1,3-dien-6-yl)benzene (7b)
57% yield ((1E,3E)/(1E,3Z) = 6:94). Colorless oil; Rf 0.38 (hexane only); IR (neat) 3062, 3042, 2925, 2856, 1573, 1496, 1453, 930, 801, 745, 698 cm\(^{-1}\); 1H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.48 (dtd, \(J = 7.6, 7.4, 1.2\) Hz, 2H, CHCH\(_2\)Ar), 2.72 (t, \(J = 7.4\) Hz, 2H, CH\(_2\)CH\(_2\)Ar), 5.53 (dt, \(J = 10.8, 7.6\) Hz, 0.94H, CHCH\(_2\) of (1E,3Z)-isomer), 5.77 (dt, \(J = 15.1, 7.0\) Hz, 0.06H, CHCH\(_2\) of (1E,3E)-isomer), 5.90–6.03 (m, 1H, CHCHCH\(_2\)), 6.20 (d, \(J = 13.4\) Hz, 0.06H, BrCHCH of (1E,3E)-isomer), 6.23 (d, \(J = 13.4\) Hz, 0.94H, BrCHCH of (1E,3Z)-isomer), 6.68 (dd, \(J = 13.4, 10.6\) Hz, 0.06H, BrCHCH of (1E,3E)-isomer), 6.95 (ddd, \(J = 13.4, 11.6, 1.2\) Hz, 0.94H, BrCHCH of (1E,3Z)-isomer); 13C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 29.6 (CH\(_2\) of (1E,3Z)-isomer), 34.3 (CH\(_2\) of (1E,3E)-isomer), 35.3 (CH\(_2\) of (1E,3E)-isomer), 35.5 (CH\(_2\) of (1E,3Z)-isomer), 106.6 (CH of (1E,3E)-isomer), 109.2 (CH of (1E,3Z)-isomer), 125.9 (CH of (1E,3E)-isomer), 126.0 (CH of (1E,3E)-isomer), 126.3 (CH of (1E,3Z)-isomer), 128.1 (CH of (1E,3E)-isomer), 128.3 (CH of (1E,3Z)-isomer), 128.4 (CH of (1E,3Z)-isomer), 128.6 (CH of (1E,3E)-isomer), 132.2 (CH of (1E,3Z)-isomer), 132.9 (CH of (1E,3E)-isomer), 135.1 (CH of (1E,3E)-isomer), 137.5 (CH of (1E,3E)-isomer), 141.2 (C of (1E,3Z)-isomer), 141.3 (C of (1E,3E)-isomer); EI-HRMS \(m/z\) calcd for C\(_{12}\)H\(_{13}\)Br (M)+ 236.02006, found 236.01997.

((1E,3Z)-1-Bromobuta-1,3-dien-4-yl)cyclohexane (7c)
77% yield ((1E,3E)/(1E,3Z) = 16:84). Colorless oil; Rf 0.76 (hexane only); IR (neat) 2925, 2849, 1574, 1447, 930, 801, 755 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.05–1.13 (m, 2H, one of C\(_2\)’-C\(_6\)’-CH\(_2\)), 1.15–1.22 (m, 1H, one of C\(_4\)’-CH\(_2\)), 1.27–1.35 (m, 3H, one of C\(_3\)’-CH\(_2\)), one of C\(_4\)’-CH\(_2\) and one of C\(_5\)’-CH\(_2\)), 1.62–1.75 (m, 4H, one of C\(_2\)’-CH\(_2\), one of C\(_3\)’-CH\(_2\), one of C\(_5\)’-CH\(_2\) and one of C\(_6\)’-CH\(_2\)).
1.95–2.01 (m, 0.16H, C1'-CH of (1E,3E)-isomer), 2.34–2.42 (m, 0.84H, C1'-CH of (1E,3Z)-isomer), 5.34 (dd, J = 10.9, 10.3 Hz, 0.84H, CHCHCy of (1E,3Z)-isomer), 5.68 (dd, J = 15.5, 6.9 Hz, 0.16H, CHCHCy of (1E,3E)-isomer), 5.80 (dd, J = 11.8, 10.9 Hz, 0.84H, CHCHCHCy of (1E,3Z)-isomer), 5.92 (dd, J = 15.5, 10.9 Hz, 0.16H, CHCHCHCy of (1E,3E)-isomer), 6.18 (d, J = 13.5 Hz, 0.16H, BrCHCH of (1E,3E)-isomer), 6.27 (d, J = 12.6 Hz, 0.84H, BrCHCH of (1E,3Z)-isomer), 6.66 (dd, J = 13.5, 10.9 Hz, 0.16H, BrCHCHCH of (1E,3E)-isomer), 7.00 (dd, J = 12.6, 11.8 Hz, 0.84H, BrCHCH of (1E,3Z)-isomer); EI-HRMS m/z calcd for C_{10}H_{15}Br (M)+ 214.03571, found 214.03490.

(1E,3Z)-1-Bromo-5,5-dimethylhexa-1,3-diene (7d)
39% yield ((1E,3E)/(1E,3Z) = 21:79). Colorless oil; R_f 0.74 (hexane only); IR (neat) 2959, 2927, 1363, 1211, 980, 929, 770 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.07 (s, 1.9H, C(CH\(_3\))\(_3\) of (1E,3E)-isomer), 1.21 (s, 7.1H, C(CH\(_3\))\(_3\) of (1E,3Z)-isomer), 5.48 (d, J = 12.0 Hz, 0.79H, CHCH of (1E,3Z)-isomer), 5.75–5.81 (m, 1H, CHCHCH of (1E,3Z)-isomer and CHCH of (1E,3E)-isomer), 5.93 (dd, J = 15.5, 10.3 Hz, 0.21H, CHCHCH of (1E,3E)-isomer), 6.23–6.28 (m, 1H, BrCHCH), 6.71 (dd, J = 13.2, 10.3 Hz, 0.21H, BrCHCHCH of (1E,3E)-isomer), 7.27 (dddd, J = 13.2, 12.0, 1.2 Hz, 0.79H, BrCHCHCH of (1E,3Z)-isomer); \(^1\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 29.2 (CH\(_3\) of (1E,3E)-isomer), 31.3 (CH\(_3\) of (1E,3Z)-isomer), 106.0 (CH of (1E,3E)-isomer), 109.2 (CH of (1E,3Z)-isomer), 122.6 (CH of (1E,3E)-isomer), 123.8 (CH of (1E,3Z)-isomer), 133.4 (CH of (1E,3Z)-isomer), 137.7 (CH of (1E,3E)-isomer), 139.5 (CH of (1E,3Z)-isomer), 142.1 (CH of (1E,3E)-isomer); EI-HRMS m/z calcd for C\(_8\)H\(_{13}\)Br (M)+ 188.02006, found 188.01924.

1-((1E,3Z)-1-Bromobuta-1,3-dien-4-yl)-4-chlorobenzene (7e)
25% yield ((1E,3E)/(1E,3Z) = 7:93). Colorless oil; R_f 0.53 (hexane only); IR (neat) 1490, 1093, 934, 848, 798 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 6.17 (dd, J = 11.5, 11.5 Hz, 0.93H, CHCHCHAr of (1E,3Z)-isomer), 6.25–6.47 (m, 1H, CHCHCHAr), 6.51–6.54 (m, 1H, BrCHCH), 6.64 (dd, J = 15.5, 10.9 Hz, 0.07H, CHCHCHAr of (1E,3E)-isomer), 6.86 (dd, J = 13.2, 10.9 Hz, 0.07H, BrCHCHCH of (1E,3E)-isomer), 7.14 (dddd, J = 13.7, 12.0, 1.2 Hz, 0.93H, BrCHCHCH of (1E,3Z)-isomer), 7.21–7.24 (m, 2H, ArH), 7.90–7.35 (m, 2H, ArH); \(^1\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 109.6 (CH of (1E,3E)-isomer), 112.4
(CH of (1E,3Z)-isomer), 126.6 (CH of (1E,3E)-isomer), 127.5 (CH of (1E,3Z)-isomer), 127.6 (CH of (1E,3E)-isomer), 128.6 (CH of (1E,3Z)-isomer), 128.9 (CH of (1E,3E)-isomer), 130.1 (CH of (1E,3Z)-isomer), 131.9 (CH of (1E,3Z)-isomer), 133.3 (C of (1E,3Z)-isomer), 133.5 (CH of (1E,3Z)-isomer), 135.1 (CH of (1E,3Z)-isomer), 137.4 (C of (1E,3E)-isomer); EI-HRMS m/z calcd for C_{10}H_8BrCl (M)^+ 241.94979, found 241.94923.

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**REFERENCES AND NOTES**


14. Mercaptotetrazoles, **1b**, **1c**, **1e**, **1f** and **1g**, were prepared in 55–98% yield from commercially available isothiocyanates and sodium azide by following the literature procedures. For details, see Supporting Information; (a) H. W. Altland, *J. Org. Chem.*, 1976, **41**, 3395; (b) H. Quast and L. Bieber, *Chem. Ber.*, 1981, **114**, 3253; (c) C. Aïssa, *J. Org. Chem.*, 2006, **71**, 360.


18. The reaction with **5b** in DMF: 31% yield, **1E,3E/1E,3Z/1Z,3E/1Z,3Z** = 7:45:28:20; in DME/HMPA: 47% yield, **1E,3E/1E,3Z/1Z,3E/1Z,3Z** = 8:74:5:13.