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Copper-mediated regioselective allylation and propargylation of 2-(alkylthio)oxazoles

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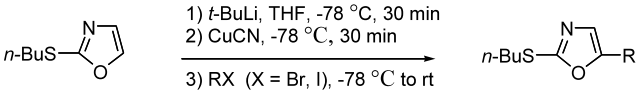
Abstract—Copper-mediated regioselective allylation and propargylation of 2-(*n*-butylthio)oxazole at the C5-position provided 2,5-disubstituted oxazoles in moderate to good yields. Subsequent removal of the *n*-butylthio group with deactivated W2-Raney nickel gave 5-substituted oxazoles.

Oxazole-triene antibiotics such as phthoxazolin, inthomycin, neooxazolomycin, oxazolomycin, diacetyloxazolomycin,[1] and bengazoles[2] are natural products which have 5-substituted oxazoles. In connection with our studies concerning the total synthesis of (±)-inthomycin C, a high yielding process for the synthesis of **5-subsituted** oxazoles is required.[3] It is known that the TosMIC method[4] and the alkynylation[5] of the 5-(bromomethyl)oxazole can prepare the oxazole fragment of neooxazolomycin and (±)-phthoxazolin A, respectively. However, these methods resulted in low overall yields because of the instability of the precursors. It had been shown that 2-(methylthio)oxazole could be deprotonated with *n*-BuLi in the presence of TMEDA in THF at −78°C, and the anion was subsequently reacted with carbonyl electrophiles such as aldehydes, ketones, acid chlorides and nitriles.[6] It is anticipated that this chemistry can be modified to prepare the 5-substituted oxazole fragment of inthomycin C using allylic or propargylic bromide.

Initially, 2-(methylthio)oxazole was deprotonated with *n*-BuLi in the presence of TMEDA in THF at −78°C[6] and the anion was subsequently reacted with allyl bromide; however, none of alkylated product was obtained after several trials. Further studies showed that *t*-BuLi (1.1 equivalents) alone effectively deprotonated the 2-(methylthio)oxazole at C5-position selectively at −78°C in 30 min. This lithiated oxazole can react with allyl or propargyl bromides in the presence of copper salts[7] to give regiospecific 5-substituted oxazoles. It was found that 2-(*n*-butylthio)oxazole, which was prepared by selective *S*-alkylation[6] of oxazole-2-thione[8] and 1-iodobutane, was less volatile and easier to prepare and handle than 2-(methylthio)oxazole (Scheme 1). As a result all subsequent studies were done on 2-(*n*-butylthio)oxazole.



Scheme 1.

Table 1 shows the results of the allylation, alkylation and propargylation of 2-(*n*-butylthio)oxazole as depicted in Scheme 1.[9] Allylation with allyl bromide proceeded in high yield (Table 1, entry 1). Alkylation with unprotected propargyl bromide gave a 2:1 mixture of acetylenic and allenic oxazoles (Table 1, entry 2). Similar product distribution was observed when substituted phenyl lithium reacted with propargyl chloride giving a similar amount of alkyne and allene.[10] The allenic product could be a result of an SN_2' process which could be prevented if the alkyne was protected with a trimethylsilyl group. In fact, only the acetylenic oxazole was formed in moderate yield (57%) when 3-bromo-1-(trimethylsilyl)propyne was used in place of propargyl bromide (Table 1, entry 3). However, a considerable amount of unreacted 2-(*n*-butylthio)oxazole was recovered (28%) under the conditions employed. It was found that the use of stoichiometric amount of

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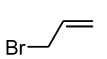
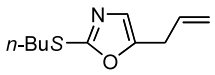
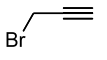
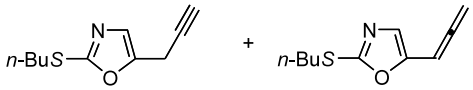
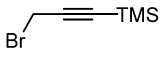
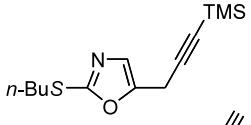
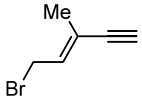
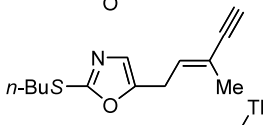
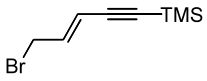
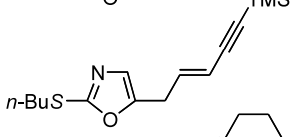
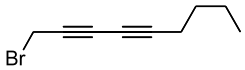
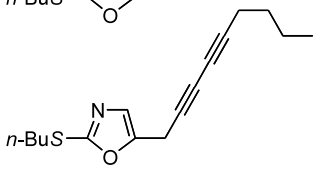
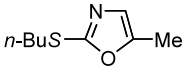
Table 1. C5-selective alkylation of 2-(*n*-butylthio)oxazole[a]

Entry	Electrophile	Product	Isolated Yield (%)
1			96
2			90[b]
3			57, 94,[c] 83[d]
4			47
5			53
6			57
7	MeI		59

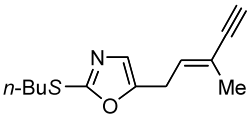
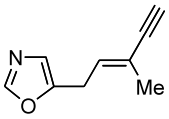
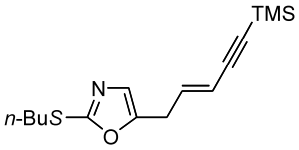
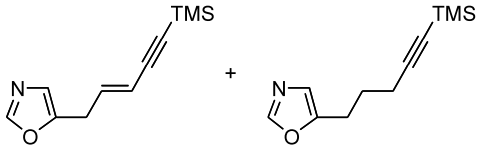
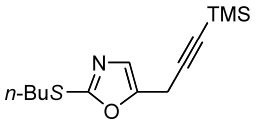
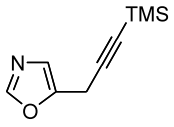
[a] 2-(*n*-Butylthio)oxazole (1 equivalent), *t*-BuLi (1.1 equivalents), CuCN (0.2 equivalents), and electrophile (2 equivalents).
[b] Alkyne:allene is 2:1.
[c] CuCN·2LiCl (1 equivalent).
[d] $CuBr{\cdot}SMe_2$ (1 equivalent).

solubilized copper sources such as $CuBr{\cdot}SMe_2$ and CuCN·2LiCl gave much higher yields than with CuCN (Table 1, entry 3). Bromo-enynes (Table 1, entries 4 and 5) and bromo-diyne (Table 1, entry 6) also produced regiospecifically 5-alkylated product. Methyl iodide was also a suitable electrophile (Table 1, entry 7).

Next, the desulfurization of *n*-butylthio group was investigated.[9] The oxazole products in entries 3, 4 and 5 were chosen to be desulfurized because they most resembled the left-hand fragment of the oxazole triene antibiotics. The desulfurization reagent was deactivated W2-Raney nickel,[11] chosen because W2-Raney nickel is a neutral type and should be milder than its acidic or basic forms. It needs to be deactivated in refluxing ethanol, acetone or a combination of these two solvents prior to use to reduce the amount of hydrogen content in order to prevent the hydrogenation of the double and triple bonds.[12] The desulfurization was first attempted at room temperature, but there was no reaction at all. The reaction was run at higher temperatures and it was found that the desulfurization took place in refluxing ethanol or ethanol/acetone. An enyne with an unprotected alkyne decomposed under these conditions (Table 2, entry 1). When an enyne-oxazole with a silyl-protected terminal alkyne was used, a separable mixture of enyne and acetylenic oxazole favoring the latter was obtained (Table 2, entry 2). When Raney nickel was deactivated further, a mixture of products was still obtained, albeit with a longer reaction time, but the major product was the desired enyne oxazole. A silyl-protected acetylenic oxazole desulfurized cleanly in high yield (Table 2, entry 3). 5-(3-Trimethylsilyl-prop-2-ynyl)-oxazole and (*E*)-5-(5-trimethylsilyl-pent-2-en-4-ynyl)-oxazole could be further elaborated to either electrophilic or nucleophilic cross-coupling partners for the completion of inthomycin C or other oxazole-triene antibiotics.

In conclusion, copper salts such as CuCN, $CuBr{\cdot}SMe_2$ and CuCN·2LiCl were demonstrated to mediate the regioselective allylation, alkylation and propargylation of the lithium anion of 2-(*n*-butylthio)oxazole providing 2,5-disubstituted oxazoles in moderate to good yields. The *n*-butylthio group was removed with deactivated W2-Raney nickel in a presence of sensitive enyne and alkyne to produce 5-substituted oxazoles.

Table 2. Deactivated W2-Raney nickel in desulfurization

Entry	Electrophile	Product	Isolated Yield (%)
1			Decomposition
2			60[a]
3			94

[a] The ratio of enyne:alkyne was 1:2 if W2-Raney nickel was deactivated in refluxing EtOH:acetone (1:1) for 1 h, then thiooxazole was added and the reaction was refluxed for 1 h. The ratio of enyne:alkyne was 3:1 if W2-Raney nickel was deactivated in acetone for 12 h, then thiooxazole was added and the reaction was refluxed for 7.5 h.

Acknowledgements

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9. **Sample procedure:** To a solution of 2-(*n*-butylthio)oxazole (3 mmol) in THF (5 mL) was added freshly titrated *t*-BuLi (3.3 mmol, 1.1 equivalents) dropwise at −78°C. After stirring for 30 min, this anion solution was transferred via a cannula into a cold (−78°C) suspension of dried CuCN (0.6 mmol, 0.2 equivalent) in THF (10 mL) or $CuBr{\cdot}SMe_2$ (3 mmol) in THF (10 mL) or a solution $CuCN{\cdot}2LiCl$ (3 mmol) prepared by mixing CuCN (3 mmol) and LiCl (6 mmol, 2 equivalents) in THF (10 mL) at rt. After stirring for another 30 min, the electrophile (6 mmol, 2 equivalents) was added into this mixture via syringe. The cold bath was removed and the reaction was stirred at room temperature for 2 h. Then, the reaction was quenched with saturated ammonium chloride solution and the product was extracted with diethyl ether. The organic layer was washed with brine and dried over $MgSO_4$. After filtering off $MgSO_4$, the solvent was removed under reduced pressure. The product was purified by column chromatography on silica gel.
2-Butylthio-5-(allyl)oxazole. Column chromatography on silica gel using 95:5 hexanes:EtOAc afforded a yellow oil (96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 1H), 5.90 (ddt, 1H, J=17.0, 10.1, 6.6 Hz), 5.21 (dq, 1H, J=10.4, 1.4 Hz), 5.17 (m, 1H), 3.39 (dq, 2H, J=6.6, 1.4 Hz), 3.13 (t, 2H, J=7.1 Hz), 1.77–1.67 (m, 2H), 1.44 (sext, 2H, J=7.4 Hz), 0.94 (t, 3H, J=7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 151.9, 132.3, 124.0, 117.8, 32.2, 31.5, 30.1, 21.7, 13.5; IR (KBr) cm^{-1}: 3122, 3084, 2960, 2932, 2873, 1643, 1495, 1152, 1110, 978, 920, 823, 751, 691; HRMS (EI, 70 eV) for $C_{10}H_{15}NOS$ [M^+] calcd 197.0874, found 197.0883.
2-Butylthio-5-(prop-2-ynyl)oxazole. Column chromatography on silica gel using 95:5 hexanes:Et_2O afforded a yellow oil (60% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89 (s, 1H), 3.59 (m, 2H), 3.15 (t, 2H, J=7.3 Hz), 2.16 (t, 1H, J=2.9 Hz), 1.73 (quint, 2H, J=7.7 Hz), 1.46

(sext, 2H, $J=7.3$ Hz), 0.94 (t, 3H, $J=7.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 148.0, 124.7, 77.3, 70.5, 32.2, 31.4, 21.7, 16.4, 13.5; IR (KBr) cm^{-1}: 3302, 2961, 2932, 2873, 1654, 1610, 1493, 1151, 1108, 985, 827; HRMS (EI, 70 eV) for $C_{10}H_{13}NOS$ [M^+] calcd 195.0718, found 195.0726. **2-Butylthio-5-(prop-1,2-dienyl)oxazole.** Column chromatography on silica gel using 95:5 hexanes:Et_2O afforded a yellow oil (30% Yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.09 (t, 1H, $J=6.9$ Hz), 5.24 (d, 1H, $J=6.9$ Hz), 5.22 (d, 1H, $J=6.9$ Hz), 3.15 (t, 2H, $J=7.4$ Hz), 1.75 (quint, 2H, $J=7.1$ Hz), 1.44 (sext, 2H, $J=7.4$ Hz), 0.94 (t, 3H, $J=7.1$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.0, 160.2, 146.1, 124.9, 81.8, 80.0, 32.2, 31.5, 21.7, 13.5; IR (KBr) cm^{-1}: 3125, 2960, 2933, 2873, 1944, 1669, 1535, 1487, 1319, 1216, 1161, 1115, 1098, 968, 857, 753; HRMS (EI, 70 eV) for $C_{10}H_{13}NOS$ [M^+] calcd 195.0718, found 195.0721.

2-Butylthio-5-(3-trimethylsilyl-prop-2-ynyl)oxazole. Column chromatography on silica gel using 95:5 hexanes:Et_2O afforded a yellow oil (57% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (distorted t, 1H, $J=1.2$ Hz), 3.62 (distorted d, 2H, $J=1.2$ Hz), 31.5 (t, 2H, $J=7.3$ Hz), 1.74 (quint, 2H, $J=7.3$ Hz), 1.47 (sext, 2H, $J=7.3$ Hz), 0.95 (t, 3H, $J=7.3$ Hz) 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 148.5, 124.8, 99.2, 87.2, 32.3, 31.5, 21.7, 17.8, 13.5, –0.2; IR (KBr) cm^{-1}: 3127, 2961, 2933, 2874, 2184, 1610, 1533, 1495, 1465, 1251, 1151, 1109, 1034, 977, 844, 761; HRMS (CI with ammonia) for $C_{13}H_{22}NOSSi$ [M+H]$^+$ calcd 268.1191, found 268.1186.

2-Butylthio-5-(3-methyl-pent-2-en-4-ynyl)oxazole. Column chromatography on silica gel using 95:5 hexanes:Et_2O afforded a yellow oil (47% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.72 (m, 1H), 6.01 (t of m, 1H), 3.42 (d, 2H, $J=7.6$ Hz), 3.13 (t, 2H, $J=7.6$ Hz), 2.84 (s, 1H), 1.87 (q, 3H, $J=0.7$ Hz), 1.72 (quint, 2H, $J=7.1$ Hz), 1.45 (sext, 2H, $J=7.6$ Hz), 0.94 (t, 3H, $J=7.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 151.0, 132.0, 123.9, 120.1, 85.7, 75.0, 32.2, 31.5, 25.0, 21.8, 17.2, 13.5; NOE (400 MHz, $CDCl_3$) the allylic hydrogens enhanced when the methyl group was irradiated that confirmed the *E*-configuration of the double bond; IR (KBr) cm^{-1}: 3294, 2959, 2931, 2873, 2096, 1605, 1494, 1465, 1379, 1217, 1149, 1109, 980, 873, 823; HRMS (EI, 70 eV) for $C_{13}H_{17}NOS$ [M^+] calcd 235.1031, found 235.1022.

(*E*) 2-Butylthio-5-(5-trimethylsilyl-pent-2-en-4-ynyl)-oxazole. Column chromatography on silica gel using 95:5 hexanes:EtOAc afforded a light yellow solid (53% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.71 (t, 1H, $J=1.1$ Hz), 6.16 (dt, 1H, $J=15.8$, 7.0 Hz), 5.60 (dt, 1H, $J=1.5$, 16.1 Hz), 3.39 (dt, 2H, $J=1.1$, 7.0 Hz), 3.08 (t, 2H, $J=7.3$ Hz), 1.71–1.63 (m, 2H), 1.46–1.36 (m, 2H), 0.89 (t, 3H, $J=7.3$ Hz) 0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 150.5, 138.4, 124.5, 112.9, 102.8, 94.9, 32.3, 31.5, 29.1, 21.7, 13.5, –0.17; IR (neat) cm^{-1}: 2960, 2932, 2874, 2172, 2127, 1605, 1493, 1465, 1418, 1249, 1148, 1110, 1078, 955; HRMS (EI, 70 eV) for $C_{15}H_{23}NOSSi$ [M^+] calcd 293.1270, found 293.1262.

2-Butylthio-5-(nona-2,4-diynyl)oxazole. Column chromatography on silica gel using 98:2 hexanes:Et_2O afforded a light yellow oil (57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (d, 1H, $J=1.1$ Hz), 3.09 (t, 2H, $J=7.0$ Hz), 2.22 (t, 2H, $J=7.0$ Hz), 1.71–1.64 (m, 2H), 1.49–1.34 (m, 8H), 0.89 (overlapped t, 3H, $J=7.3$ Hz), 0.86 (overlapped t, 3H, $J=7.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 147.7, 125.1, 79.6, 69.6, 67.5, 64.8, 32.4, 31.7, 30.4, 22.1, 22.0, 19.0, 17.3, 13.74, 13.69; IR (neat) cm^{-1}: 2959, 2932, 2872, 2262, 1608, 1492, 1465, 1149, 1109, 981; HRMS (EI, 70 eV) for $C_{16}H_{21}NOS$ [M^+] calcd 275.1343, found 275.1346.

2-Butylthio-5-(methyl)oxazole. Column chromatography on silica gel using 95:5 hexanes:Et_2O afforded a yellow oil (59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (q, 1H, $J=1.1$ Hz), 3.13 (t, 2H, $J=7.3$ Hz), 2.28 (d, 3H, $J=1.1$ Hz), 1.72 (quint, 2H, $J=7.3$ Hz), 1.43 (sext, 2H, $J=7.7$ Hz), 0.94 (t, 3H, $J=7.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 150.1, 123.9, 32.2, 31.5, 21.7, 13.5, 10.9; IR (KBr) cm^{-1}: 3122, 2960, 2929, 2873, 1614, 1497, 1450, 1284, 1215, 1152, 1109, 1009, 954, 818, 691; HRMS (EI, 70 eV) for $C_8H_{13}NOS$ [M^+] calcd 171.0719, found 171.0723.

Desulfurization: W2-Raney nickel (0.2 g) was deactivated by heating in refluxing EtOH:acetone (1:1, 10 mL) for 1 h. Then 2-butylthio-5-(prop-2-ynyl)oxazole (40 mg) was added in and the solution was refluxed until TLC (90:10 Hex:EtOAc) indicated that the reaction was complete (3 h). The reaction mixture was then passed through a pad of celite. The celite cake was washed with Et_2O and acetone. The solvent was removed under reduced pressure and the crude oil was purified by flash column chromatography on silica gel using 90:10 hexanes:EtOAc to afford a colorless oil (37 mg, 94% yield). **5-(3-Trimethylsilyl-prop-2-ynyl)oxazole.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (s, 1H), 6.91 (s, 1H), 3.62 (s, 2H), 0.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 147.6, 123.3, 99.0, 87.3, 17.6, –0.19; IR (neat) cm^{-1}: 2960, 2900, 2184, 1602, 1510, 1250, 1098, 1031, 964, 843; HRMS (EI, 70 eV) for $C_{12}H_{11}NO_2S$ [M^+] calcd 179.0764, found 179.0771.

(*E*)-5-(5-Trimethylsilyl-pent-2-en-4-ynyl)oxazole. Column chromatography on silica gel using 95:5 hexanes:acetone afforded a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 6.79 (s, 1H), 6.20 (dt, 1H, $J=15.7$, 7.0 Hz), 5.58 (dt, 1H, $J=15.7$, 1.8 Hz), 3.45 (dt, 2H, $J=6.6$, 1.1 Hz), 0.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 149.5, 138.3, 123.0, 113.0, 102.7, 94.4, 29.0, –0.17; IR (neat) cm^{-1}: 3583, 3124, 2959, 2900, 2172, 2126, 1599, 1510, 1422, 1249, 1100, 1077, 953, 842, 759; HRMS (CI with NH_3) for $C_{11}H_{16}NOSi$ [M+H]$^+$ calcd 206.1001, found 206.1001. **5-(5-Trimethylsilyl-pent-4-ynyl)oxazole.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 6.75 (s, 1H), 2.74 (distorted t, 2H, $J=7.3$ Hz), 2.25 (t, 2H, $J=7.3$ Hz), 2.82 (quint, 2H, $J=7.0$ Hz), 0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 150.1, 122.3, 105.9, 85.6, 26.4, 24.3, 19.2, 0.10; IR (neat) cm^{-1}: 3583 (sharp s), 3123 (sharp s), 2958, 2175, 1646, 1511, 1455, 1433, 1249, 1100, 842; HRMS (CI with NH_3) for $C_{11}H_{18}NOSi$ [M+H]$^+$ calcd 208.1158, found 208.1154.

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