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Lithiation of 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole

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A B S T R A C T

The reaction of lithiation of 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole with in position 5 of the thiazole ring and double lithiation with t-butyllithium (t-BuLi) in positions 2 and 5 lithium diisopropylamide (LDA) are investigated. When lithiated and dilithiated thiazoles were treated with different electrophiles, a number of trifunctional 1,3-thiazoles were obtained with high yields.

1. Introduction

Natural and synthetic derivatives of 1,3-thiazole have diverse biological activity and play a significant role in the processes of life, which stimulates a steady interest in research in the synthesis of new derivatives of this type. 1,3-Thiazole derivatives exhibit the activities of selective enzyme inhibitors,[1-4] sigma receptors,[5,6] adenosine receptors[7,8] antagonists, and new T-type calcium channel blockers.[9] The actual task today is to obtain polyfunctional 1,3-thiazoles, which are suitable for further modification in order to synthesize the libraries of thiazole derivatives for screening and searching for pharmacologically promising compounds. One of the methods of such products synthesis calls for metalation reagents giving with 1,3-thiazoles organometallic derivatives, which are converted into functionalized 1,3-thiazoles when treated by electrophiles.

The object of the present study is metalation of 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole **1**.[10] The following reagents are known to apply for metalation of 2-bromo-1,3-thiazoles: LDA,[11-14] TMPMgCl·LiCl,[15] $TMP_2Zn·2MgCl_2·2LiCl$,[15-18] TMP_2Zn.[19] In all cases, the metalation takes place in position 5 of the 1,3-thiazole ring.

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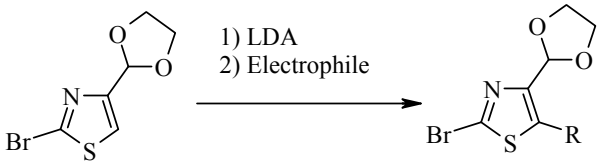
We showed earlier[20] that lithiation of 1,3-thiazole **1** with *n*-butyllithium occurs at position 2. Under the action of DMF on the formed lithium derivative, 4-(1,3-dioxolan-2-yl)-1,3-thiazole-2-carbaldehyde is formed.

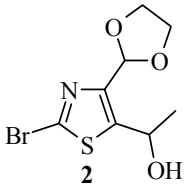
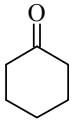
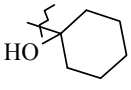
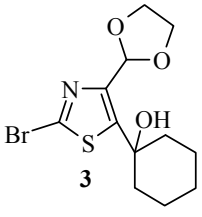
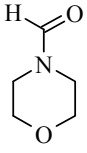
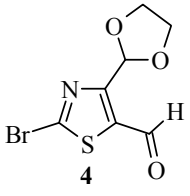
2. Results and discussion

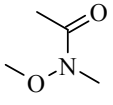
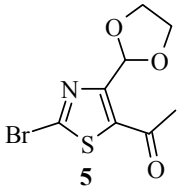
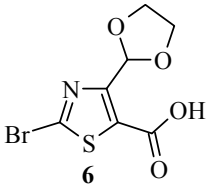
To introduce the functional groups in position 5 of 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole **1**, we carried out its lithiation with LDA in tetrahydrofuran at -70 ° C. Interaction of the lithiated thiazole with acetaldehyde yields 1-[2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazol-5-yl]ethan-1-ol **2 (**Table 1, Entry 1**)**, analogously with cyclohexanone, 1-[2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazol-5-yl]cyclohexan-1-ol **3 (**Table 1, Entry 2**)** was obtained. For the introduction of an aldehyde group, morpholin-4-carbaldehyde was used, and N-methoxy-N-methylacetamide was used to introduce an acetyl group, which led to 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole-5-carbaldehyde **4 (**Table 1, Entry 3**)** and 1-[2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazol-5-yl]ethan-1-one **5 (**Table 1, Entry 4**).** When using CO_2 as an electrophile, 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole-5-carboxylic acid **6 (**Table 1, Entry 5**)** was obtained. Some examples of the displacement of substituents in 1,3-thiazole under the action of metallating reagents were reported including Halogen Dance Reaction in the presence of LDA. [21-23] To confirm the structure of compounds (**2-6**) and to study a possibility of the Halogen Dance Reaction, we performed lithiation of 1,3-thiazole **1** in the above conditions using water as the electrophile. As a result, we obtained the starting compound **1** with a quantitative yield. This result is indicative of the absence of the halogen dance under lithiation of 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole **1** with LDA.

Table 1. Lithiation of 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole **1** with LDA.



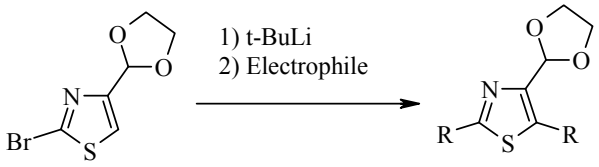
1 **2-6**

Entry	Electrophile	R	Products	Yield (%)
1			 **2**	92
2			 **3**	87
3			 **4**	85

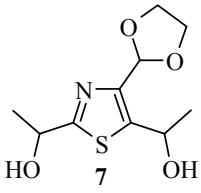
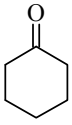
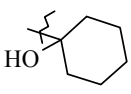
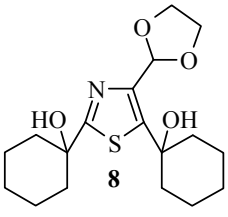
4			 **5**	83
5	CO_2		 **6**	93

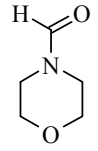
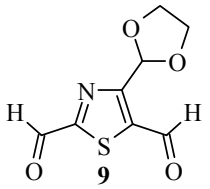
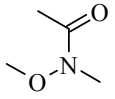
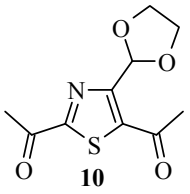
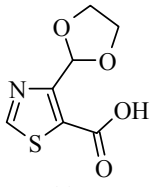
For the introduction of functional groups in positions 2 and 5 of 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole **1**, it was lithiated with *t*-butyllithium in tetrahydrofuran at -80 ° C. This case is the first example of simultaneous direct litiation and Br/Li exchange in the 1,3-thiazole ring. Interaction of the formed dilithium 1,3-thiazole derivative with acetaldehyde yielded 1,1'-[4-(1,3-dioxolan-2-yl)-1,3-thiazole-2,5-diyl]di(ethan-1-ol) **7 (**Table 2, Entry 1**)**, as well in the reaction with cyclohexanone, 1,1'-[4-(1,3-dioxolan-2-yl)-1,3-thiazole-2,5-diyl]di(cyclohexan-1-ol) **8 (**Table 2, Entry 2**)** was obtained. According to spectral data, alcohols **7** and **8** exist as diastereomer mixtures in the ratio 1: 1 (product **7**) and 7: 3 (product **8**). For the introduction of two aldehyde groups, morpholin-4-carbaldehyde was used, and N-methoxy-N-methylacetamide was used to introduce two acetyl groups, which led to dicarbonyl derivatives of thiazole: 4-(1,3-dioxolan-2-yl)-1,3-thiazole-2,5-dicarbaldehyde **9 (**Table 2, Entry 3**)** and 1,1'-[4-(1,3-dioxolan-2-yl)-1,3-thiazole-2,5-diyl]di(ethan-1-one) **10 (**Table 2, Entry 4**).** With CO_2 as an electrophile, unstable 4-(1,3-dioxolan-2-yl)-1,3-thiazole-2,5-dicarboxylic acid is formed, which decarboxylation leads to formation of 4-(1,3-dioxolan-2-yl)-1,3-thiazole-5-carboxylic acid **11 (**Table 2, Entry 5**)**.

Table 2. Lithiation of 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole **1** with *t*-BuLi.



1 **7-11**

Entry	Electrophile	R	Products	Yield (%)
1			 **7**	93
2			 **8**	87

3			 **9**	84
4			 **10**	84
5	CO_2		 **11**	74

3. Conclusion

It was shown that lithiation of 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole **1** with LDA proceeds in position 5 but its lithiation with *t*-butyllithium occurs simultaneously in positions 2 and 5. When resulting lithium derivatives were treated by electrophiles, a number of new trifunctionally substituted derivatives of 1,3-thiazole were obtained. The obtained compounds are low molecular weight synthones for creating new bioregulators.

Acknowledgements

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4. Experimental

^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on Bruker Avance DRX 500 spectrometer in DMSO-d_6 solution with TMS as an internal standard. The IR spectra were recorded on a Vertex 70 spectrometer from KBr pellets. Melting points were measured with a Büchi melting point apparatus and are uncorrected. Elemental analysis was carried out in the Analytical Laboratory of Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine. The chromatomass spectra were recorded on an Agilent 1100 Series high performance liquid chromatograph equipped with a diode matrix with an Agilent LC\MS mass selective detector allowing a fast switching the ionization modes positive/negative. The reaction progress was monitored by the TLC method on Silica gel 60 F_{254} Merck.

2-Bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole **1** were prepared as descriubed in the literature.[10]

Procedure A. Lithiation of 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole with lithium diisopropylamide (LDA).

A solution of LDA was prepared as follows: to diisopropylamine (2.4 g; 23.7 mmol) in anhydrous THF (25 mL) at -30 ºC was added 8.1 mL of *n*-BuLi (2.5 M solution in hexane, 20.3 mmol) under Ar. After stirring at -10 ºC for 10 min, the reaction mixture was cooled at -70 ºC. To the LDA solution was added dropwise a solution of 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole **1** (4.0 g, 16.9 mmol) in anhydrous THF (25 mL), and the mixture was stirred at -60 ºC for 1 h.

1-[2-Bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazol-5-yl]ethan-1-ol (2). A solution of acetaldehyde (1.87 g, 42.5 mmol) in anhydrous THF (5 mL) was added dropwise to a mixture (**A**) at –70°C over 10 min. The reaction mixture temperature was adjusted to –20°C in 0.5 h. After addition of water (30 mL) dropwise, the mixture was stirred during 2 h at 20–25°C. The organic layer was separated, the aqueous layer was extracted with ethyl acetate, and combined organic extracts were dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by chromatography (10:l CH_2Cl_2/EtOAc) gave **2** (4.37g, 92%) as a yellow oil.

IR (KBr, cm^{-1}): 3372, 2973, 2891, 1429, 1110, 1027, 994, 943. ^{1}H NMR, δ: 1.35 (3H, d, J 6.6 Hz, CH_3), 3.93 (2H, m, OCH_2CH_2O), 4.06 (2H, m, OCH_2CH_2O), 5.24 (1H, m, CHOH),5.90 (1H, s, O-CH-O), 6.04 (1H, s, OH). ^{13}C NMR, δ: 26.5, 62.0, 64.8, 64.9, 98.0, 132.8, 145.7, 151.0. MS: 281 $[M]^+$. Anal. calcd for $C_8H_{10}BrNO_3S$: C, 34.30; H, 3.60; Br, 28.52; N, 5.00; S, 11.45. Found: C, 34.37; H, 3.57; Br, 28.46; N, 4.94; S, 11.41.

1-[2-Bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazol-5-yl]cyclohexan-1-ol (3). A solution of cyclohexanone (2.83 g, 28.8 mmol) in anhydrous THF (5 mL) was added dropwise to a mixture (**A**) at –70°C over 10 min. The reaction mixture temperature was adjusted to –20°C in 0.5 h. After addition of water (30 mL) dropwise, the mixture was stirred during 2 h at 20–25°C. The organic layer was separated; the aqueous layer was extracted with ethyl acetate, and combined organic extracts were dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by chromatography (CH_2Cl_2) gave **3** (4.93g, 87%) as a white crystals, mp 111-113 ^{0}C.

IR (KBr, cm^{-1}):3398, 2936, 2898, 1433, 1354, 1170, 1123, 1024, 975, 929, 906. ^{1}H NMR, δ: 1.15-1.95 (10H, m, C_6H_{10}), 3.94 (2H, m, OCH_2CH_2O), 4.09 (2H, m, OCH_2CH_2O), 5.85 (1H, s, O-CH-O), 6.28 (1H, s, OH). ^{13}C NMR, δ: 21.3, 24.4, 38.9, 65.0, 70.7, 97.0, 131.7, 146.7, 154.6. MS: 335 $[M]^+$. Anal. calcd for $C_{12}H_{16}BrNO_3S$: C, 43.12; H, 4.83; Br, 23.91; N, 4.19; S, 9.59. Found: C, 43.18; H, 4.86; Br, 23.99; N, 4.25; S, 9.51.

2-Bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole-5-carbaldehyde (4). A solution of morpholine-4-carbaldehyde (2.93 g, 25.4 mmol) in anhydrous THF (5 mL) was added dropwise to a mixture (**A**) at –70°C over 10 min. The reaction mixture temperature was adjusted to –20°C in 0.5 h. . After addition of acetic acid (6 mL) in water (30 mL) dropwise, the mixture was stirred during 2 h at 20–25°C. The organic layer was separated; the aqueous layer was extracted with ethyl acetate, and combined organic extracts were dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by chromatography (CH_2Cl_2) gave **4** (3.8g, 85%) as a yellow crystals, mp 110-112ºC.

IR (KBr, cm^{-1}): 2961, 2891, 1664, 1412, 1306, 1115, 1036, 944. ^{1}H NMR, δ: 4.02 (2H, m, OCH_2CH_2O), 4.14 (2H, m, OCH_2CH_2O), 6.31 (1H, s, O-CH-O), 10.21 (1H, s, CHO). ^{13}C NMR, δ: 65.7, 98.3, 140.8, 144.2, 159.4, 183.9. MS: 265 $[M]^+$. Anal. calcd for $C_7H_6BrNO_3S$: C, 31.84; H, 2.29; Br, 30.26; N, 5.30; S, 12.14. Found: C, 31.95; H, 2.27; Br, 30.14; N, 5.34; S, 12.19.

1-[2-Bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazol-5-yl]ethan-1-one (5). A solution of *N*-methoxy-*N*-methylacetamide (2.97 g, 28.8 mmol) in anhydrous THF (5 mL) was added dropwise to a mixture (**A**) at –70°C over 10 min and stirred at room temperature overnight. The reaction mixture was poured into aqueous saturated NH_4Cl solution (100 mL), and stirred for 2 h.The organic layer was separated; the aqueous layer was extracted with ethyl acetate, and combined organic extracts were dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by chromatography (CH_2Cl_2) gave **5** (3.91g, 83%) as a white crystals, mp 88-89 ^{0}C.

IR (KBr, cm^{-1}): 2968, 2892, 1674, 1391, 1285, 1229, 1119, 1033, 938, 807. ^{1}H NMR, δ: 2.56 (3H, s, CH_3), 4.00 (2H, m, OCH_2CH_2O), 4.13 (2H, m, OCH_2CH_2O), 6.45 (1H, s, O-CH-O). ^{13}C NMR, δ: 30.9, 65.2, 96.4, 139.2, 140.0, 156.4, 189.7. MS: 279 $[M]^+$. Anal. calcd for $C_8H_8BrNO_3S$: C, 34.55; H, 2.90; Br, 28.73; N, 5.04; S, 11.53. Found: C, 34.59; H, 2.83; Br, 28.82; N, 5.01; S, 11.65.

2-Bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole-5-carboxylic acid (6). The mixture (**A**) was treated with excess of gaseous CO_2 and stirred at -60 ºC for 1 h, the reaction mixture was allowed to warm to 0 ºC. Next, hydrochloric acid (5 mL) in water (30 mL) was added dropwise. The organic layer was separated; the aqueous layer was extracted with ethyl acetate, and combined organic extracts were dried over sodium sulfate. The solvent was removed under reduced pressure. Yield 4.4 g (93%), yellow crystals, mp 156-157ºC.

IR (KBr, cm^{-1}): 2973, 2882, 1693, 1540, 1400, 1313, 1274, 1115, 1038, 989. ^{1}H NMR, δ: 3.97 (2H, m, OCH_2CH_2O), 4.15 (2H, m, OCH_2CH_2O), 6.60 (1H, s, O-CH-O), 12.50 (1H, bs, COOH). ^{13}C NMR, δ: 65.7, 96.0, 132.2, 140.6, 158.5, 161.3. MS: 281 $[M]^+$. Anal. calcd for $C_7H_6BrNO_4S$: C, 30.02; H, 2.16; Br, 28.53; N, 5.00; S, 11.45. Found: C, 30.11; H, 2.12; Br, 28.59; N, 4.97; S, 11.51.

Procedure B. Lithiation of 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole with *t*-BuLi.

A solution of *t*-BuLi (1.7 M solution in pentane, 54.4 mmol) under Ar was added dropwise to a solution of of 2-bromo-4-(1,3-dioxolan-2-yl)-1,3-thiazole **1** (4.0 g, 16.9 mmol) in anhydrous THF (100 mL) at –80°C over 10 min. The mixture was stirred during 30 min at –80°C.

1,1'-[4-(1,3-Dioxolan-2-yl)-1,3-thiazole-2,5-diyl]di(ethan-1-ol) (7). A solution of acetaldehyde (2.99 g, 67.9 mmol) in anhydrous THF (5 mL) was added dropwise to a mixture (**B**) at –80 °C over 10 min. The reaction mixture temperature was adjusted to –20°C in 0.5 h. After addition of water (30 mL) dropwise, the mixture was stirred during 2 h at 20–25°C. The organic layer was separated; the aqueous layer was extracted with ethyl acetate, and combined organic extracts were dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by chromatography (EtOAc) gave **7** (3.87g, 93%) as a yellow oil.

IR (KBr, cm^{-1}): 3375, 2983, 2894, 1422, 1121, 1021, 996, 948. ^{1}H NMR, δ: 1.35 (3H, d, *J* 6.0 Hz, CH_3), 1.40 (3H, m, CH_3), 3.91 (2H, m, OCH_2CH_2O), 4.06 (2H, m, OCH_2CH_2O), 4.83 (1H, m, C<u>H</u>OH), 5.23 (1H, m, C<u>H</u>OH), 5.68 (1H, d, *J* 3.3 Hz, OH), 5.87 (1H, s, O-CH-O), 6.01 (1H, d, *J* 4.2 Hz, OH). ^{13}C NMR, δ: 24.0, 24.2, 26.8, 26.9, 61.7, 61.7, 64.6, 66.7, 66.8, 98.8, 98.9, 144.8, 145.3, 145.4, 174.7, 174.8. MS: 246 $[M]^+$. Anal. calcd for $C_{10}H_{15}NO_4S$: C, 48.97; H, 6.16; N, 5.71; S, 13.07. Found: C, 49.08; H, 6.11; N, 5.80; S, 13.14.

1,1'-[4-(1,3-Dioxolan-2-yl)-1,3-thiazole-2,5-diyl]di(cyclohexan-1-ol) (8). A solution of cyclohexanone (6.15 g, 62.7 mmol) in anhydrous THF (10 mL) was added dropwise to a mixture (**B**) at –80°C over 10 min. The reaction mixture temperature was adjusted to –20°C in 0.5 h. After addition of water (30 mL) dropwise, the mixture was stirred during 2 h at 20–25°C.The organic layer was separated; the aqueous layer was extracted with ethyl acetate, and combined organic extracts were dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by chromatography (4:l CH_2Cl_2/EtOAc) gave **8** (5.2 g, 87%) as a white crystals, mp 96-97^{0}C.

IR (KBr, cm^{-1}): 3396, 2941, 2854, 1679, 1476, 1446, 1137, 1113, 965. ^{1}H NMR, δ: 1.13-1.95 (20H, m, $2C_6H_{10}$), 3.91 (2H, m, OCH_2CH_2O), 4.13 (2H, m, OCH_2CH_2O), 5.39 (1H, bs, OH), 5.62 (1H, bs, OH), 6.43 (1H, s, O-CH-O). ^{13}C NMR, δ: 21.4, 21.5, 24.8, 25.0, 37.6, 64.6, 70.0, 72.9, 97.9, 146.7, 147.5, 177.0. MS: 354 $[M]^+$. Anal. calcd for $C_{18}H_{27}NO_4S$: C, 61.16; H, 7.70; N, 3.96; S, 9.07. Found: C, 61.28; H, 7.65; N, 3.99; S, 9.13.

4-(1,3-Dioxolan-2-yl)-1,3-thiazole-2,5-dicarbaldehyde (9). A solution of morpholine-4-carbaldehyde (6.83 g, 59.3 mmol) in anhydrous THF (10 mL) was added dropwise to a mixture (**B**) at –80°C over 10 min. The reaction mixture temperature was adjusted to –20°C in 0.5 h. After addition of acetic acid (9 mL) in water (50 mL) dropwise, the mixture was stirred during 2 h at 20–25°C. The organic layer was separated; the aqueous layer was extracted with ethyl acetate, and combined organic extracts were dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by chromatography (4:l CH_2Cl_2/EtOAc) gave **9** (3.03 g, 84%) as a yellow crystals, mp 69-70ºC.

IR (KBr, cm^{-1}): 2902, 1696, 1670, 1450, 1292, 1192, 1106, 772. ^{1}H NMR, δ: 4.06 (2H, m, OCH_2CH_2O), 4.20 (2H, m, OCH_2CH_2O), 6.24 (1H, s, OCHO), 9.96 (1H, s, CHO), 10.42 (1H, s, CHO). ^{13}C NMR, δ: 65.7, 99.8, 141.4, 159.6, 168.5, 183.7, 183.8. MS: 214 $[M]^+$. Anal. calcd for $C_8H_7NO_4S$: C, 45.07; H, 3.31; N, 6.57; S, 15.04. Found: C, 45.21; H, 3.37; N, 6.49; S, 14.97.

1,1'-[4-(1,3-Dioxolan-2-yl)-1,3-thiazole-2,5-diyl]di(ethan-1-one) 10.

A solution of *N*-methoxy-*N*-methylacetamide (6.46 g, 62.6 mmol) in anhydrous THF (10 mL) was added dropwise to a mixture (**B**) at –80°C over 10 min and stirred at room temperature overnight. The reaction mixture was poured into aqueous saturated NH_4Cl solution (100 mL), and stirred for 2 h.The organic layer was separated; the aqueous layer was extracted with ethyl acetate, and combined organic extracts were dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by chromatography (CH_2Cl_2) gave **10** (3.45g, 84%) as a white crystals, mp 67-68^{0}C.

IR (KBr, cm^{-1}): 2962, 2889, 1693, 1450, 1370, 1273, 1230, 1103, 1057, 943. ^{1}H NMR, δ: 2.64 (3H, s, CH_3), 2.65 (3H, s, CH_3),4.03 (2H, m, OCH_2CH_2O), 4.20 (2H, m, OCH_2CH_2O), 6.50 (1H, s, O-CH-O). ^{13}C NMR, δ: 25.6, 31.2, 65.1, 96.9, 139.6, 157.6, 166.8, 191.2, 191.61. MS: 242 $[M]^+$. Anal. calcd for $C_{10}H_{11}NO_4S$: C, 49.78; H, 4.60; N, 5.81; S, 13.29. Found: C, 49.79; H, 4.63; N, 5.79; S, 13.33.

4-(1,3-Dioxolan-2-yl)-1,3-thiazole-5-carboxylic acid (11). The mixture (**B**) was treated with excess of gaseous CO_2 and stirred at -60 ^{o}C for 1 h, the reaction mixture was allowed to warm to 0 ^{o}C. Next, hydrochloric acid (5,5 mL) in water (30 mL) was added dropwise. The organic layer was separated; the aqueous layer was extracted with ethyl acetate, and combined organic extracts were dried over sodium sulfate. The solvent was removed under reduced pressure. Yield 2.52 g (74%), white crystals, mp 145-147 ^{o}C.

IR (KBr, cm^{-1}): 2898, 2471, 1705, 1550, 1410, 1330, 1268, 1110, 955. ^{1}H NMR, δ: 3.97 (2H, m, OCH_2CH_2O), 4.17 (2H, m, OCH_2CH_2O), 6.70 (1H, s, O-CH-O), 9.20 (1H, s, C^2-$H_{thiazol}$), 13.66 (1H, bs, COOH). ^{13}C NMR, δ: 65.1, 96.1, 127.6, 158.0, 158.8, 162.1. MS: 202 $[M]^+$. Anal. calcd for $C_7H_7NO_4S$: C, 41.79; H, 3.51; N, 6.96; S, 15.94. Found: C, 41.82; H, 3.49; N, 6.98; S, 15.89.

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