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Glycerin as alternative solvent for the synthesis of Thiazoles

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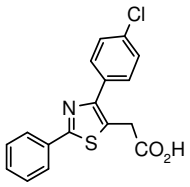
Abstract: A variety of α-bromoketones undergoes smooth condensation with thiourea/ thioamide compounds to afford the corresponding substituted thiazole derivatives in excellent yields. The condensation reactions were carried out in a recyclable reaction medium glycerin without using any catalyst. All the reactions were completed within 2 hours of reaction time at room temperature.

Keywords: Bromoketone; thiourea; urea; thiazole; catalyst-free; glycerin.

1. Introduction

Thiazole and its derivatives play a vital role in nature. For example, the thiazolium ring present in vitamin B_1 serves as an electron sink and its coenzyme form is important for the decarboxylation of α-keto acids. This heterocyclic system has found broad applications in drug development for the treatment of allergies, inflammation, hypertension, schizophrenia, bacterial and HIV infections.[1] A tetrahydrothiazole also appears in the skeleton of penicillin which is one of the first and most important broad spectrum antibiotics. Aminothiazoles are known to be ligands of estrogen receptors as well as a novel class of adenosine receptor antagonists.[2,3]



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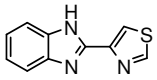

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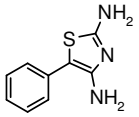

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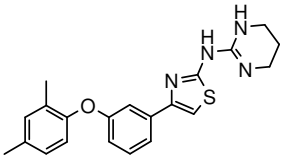

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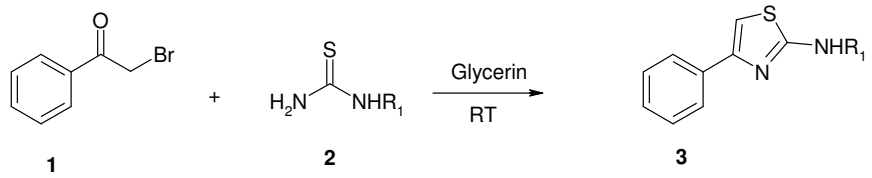
In view of the emerging importance of thiazoles and their derivatives, several methods for their synthesis were developed using various catalysts,[4-8] conditions[9-14] and strategies.[15-21] However, many of these reported methods suffer from drawbacks such as harsh reaction conditions, unsatisfactory yields, prolonged reaction time, tedious workup procedures and use of expensive catalysts. Therefore, the development of efficient and environmental friendly green chemical processes is a major challenge for chemists in organic synthesis.

Glycerin is main byproduct in biodiesel production and available plenty at low cost has gain importance in recent years as a reusable reaction medium for organic transformations.[22-29] As part of our ongoing program to develop a novel methodologies [30-34] using alternative protocols, herein we report, a simple and efficient process for the synthesis of triazole derivatives under catalyst-free conditions using glycerin as recyclable reaction medium.

2. Results and discussion

In a typical experiment, an equimolar amount of 2-bromo-1-phenylethanone (**1**) and thiourea (**2a**) were reacted in glycerin at room temperature to afford the corresponding product, 4-phenyl thiazol-2-amine (**3a**). The reaction was completed within 1 hour and the product was obtained in excellent yields. The reaction was carried out without using any catalyst.

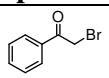
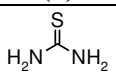
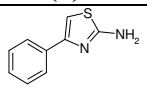
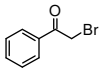
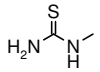
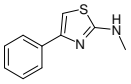
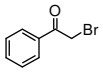
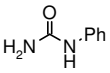
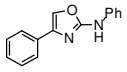
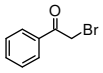
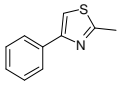
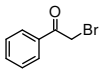
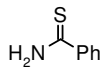
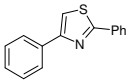
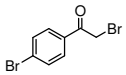
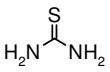
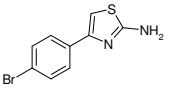
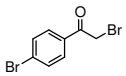
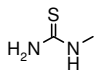
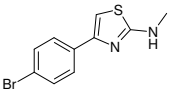
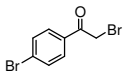
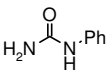
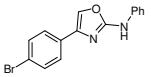
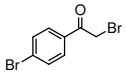
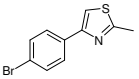
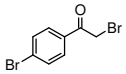
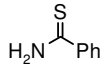
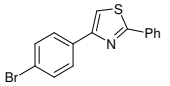
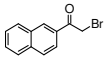
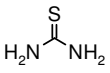
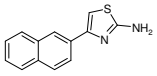
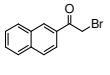
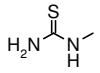
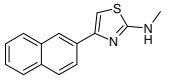
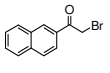
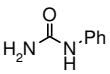
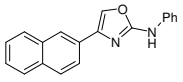
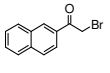


Scheme 1. Synthesis of thiazoles

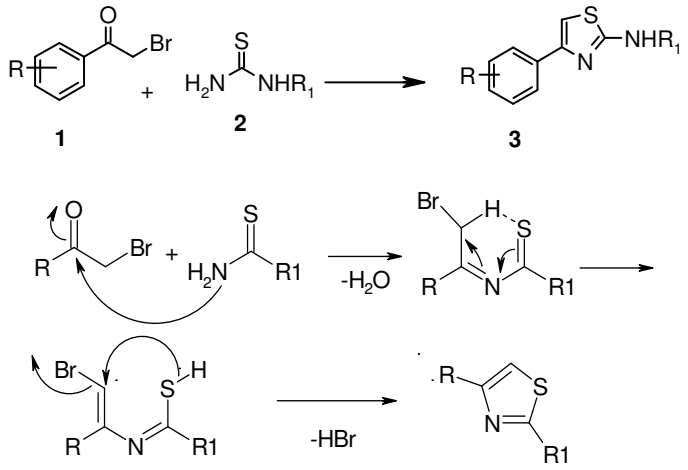
In a similar manner, 2-bromo-1-phenylethanone (**1**) was reacted smoothly with 1-methyl thiourea (**2b**), 1-phenyl thiourea (**2c**), thioacetamide (**2d**) and thiobenzamide (**2e**) successfully. Encouraged by the results obtained with the above experiments, we have extended this methodology to various bromo carbonyl compounds, as well as different substituted thiourea compounds.

In another typical experiment, 2-bromo-1-(naphthalen-2-yl)-ethanone was treated with thiourea in glycerin at room temperature to afford the corresponding derivative, 4-(naph thalene-2-yl)-thiazol-2-amine (**3k**) in excellent yields and the reaction was completed within 1 hour. This reaction was successfully applied to various substituted thiourea compounds such as 1-methyl thiourea (**2l**), 1-phenylthiourea (**2m**), thioacetamide (**2n**) and thiobenzamide (**2o**) with excellent yields. In general, all the reactions were carried out using glycerin as recyclable reaction medium and without using any catalyst. All the reactions carried out at room temperature. After completion of reaction, the reactants were extracted with ethyl acetate and the glycerin was used for further reactions without any problem. All the reactions were completed within 2.5 hours of reaction time and with excellent yields and the details were clearly mentioned in the table 1.

Table 1. Efficient synthesis of thiazoles in Glycerin under catalyst-free conditions.

Entry	Bromo compound (1)	Thiurea (2)	Product (3) [a]	Reaction Time (h)	Yield (%) [b]
a				1.0	92
b				1.5	90
c				1.0	92
d				2.0	89
e				1.0	90
f				1.0	92
g				1.5	89
h				1.5	91
i				2.0	87
j				1.5	90
k				1.0	91
l				2.0	87
m				1.5	90
n				2.5	86
o				2.0	87

[a]All the products were characterized by spectroscopy data.
[b]Yields were isolated and unoptilized.



Scheme 2. Probable reaction mechanism

The reaction may proceed via initial formation of an imine followed by sulfur or oxygen insertion resulting in the formation of 2-aminothiozole derivatives as shown in the scheme 2.

3. Conclusion

In summary, we have demonstrated a simple and novel methodology for the synthesis of thiazole derivatives by the coupling of 2-bromo ketones and thiourea compounds. The present method offers significant advantages such as no catalyst, mild reaction conditions, high conversions, short reaction times, cleaner reaction profiles, excellent yields and recyclability of the solvent.

4. Experimental

General Methods. Melting points were recorded on Buchi R-535 apparatus. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using KBr disk. ^{1}HNMR-Spectra were recorded on Gemini-200 spectrometer in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV.

General procedure. A mixture of 2-bromo carbonyl compound (2 mmol) and thiourea (2 mmol) was stirred in glycerin (2 mL) at room temperature. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction as indicated by TLC, ethyl acetate (2x10 mL) was added and stirred well. The ethyl acetate layer was separated by simple decantation. The ethyl acetate extract was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude compound was purified by column chromatography using silica gel 60-120 mesh. All the pure products were identified by their spectroscopy data.

Spectral data for all the compounds:

4-Phenylthiazol-2-amine (**3a**). White solid. Mp.134-136 ^{0}C (Lit.[Ref.13] 150-151 ^{0}C). IR (KBr): υ 3434, 3253, 3155, 2924, 2855, 1599, 1520, 1482, 1440 1336, 1216, 1071, 910, 846, 773 cm.$^{-1}$; ^{1}H NMR ($CDCl_3$): δ 4.97 (brs, 2H), 6.69 (s, 1H), 7.25-7.39 (m, 3H), 7.70-7.75 (m, 2H).; EIMS *m/z* (%): 177 (m^{+1}100), 149 (10), 134 (90), 104 (15), 89 (30), 77 (15), 63 (10), 42 (15).

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***N*-Methyl-4-phenylthiazol-2-amine** (**3b**). Yellow solid. Mp.118-120 ^{0}C (Lit.[Ref.14]138 ^{0}C). IR (KBr): υ 3221, 3115, 3001, 2922, 1586, 1481, 1402, 1329, 1155, 1055, 919, 841, 775, 671 cm.$^{-1}$; ^{1}H NMR ($CDCl_3$): δ 2.99 (s, 3H), 6.40 (brs, 1H), 6.62 (s, 1H), 7.22-7.40 (m, 3H), 7.74 (d, 2H, *J* = 6.6 Hz).; EIMS *m/z* (%). 190 (m^+ 35), 162 (30), 134 (90), 121 (10), 102 (25), 89 (22), 77 (20), 65 (20), 47 (100).

***N*-4-Diphenyloxazol-2-amine** (**3c**). Yellow solid. Mp.110-112 ^{0}C. IR (KBr): υ 3186, 2923, 2853, 1564, 1498, 1461, 1424, 1309, 1067, 915, 842, 749, 695 cm.$^{-1}$; ^{1}HNMR ($CDCl_3$): δ 6.75 (s, 1H), 6.99-7.08 (m, 1H), 7.25-7.40 (m, 8H), 7.77 (d, 2H, *J* = 6.8 Hz).;
EIMS *m/z* (%): 253 (m^{+1} 100), 190 (10), 142 (10), 102 (10), 98 (10), 60 (10).

2-Methyl-4-phenylthiazole (**3d**). White solid. Mp. 66-68 ^{0}C (Lit.[Ref.9] 67-68 ^{0}C). IR (KBr): υ 3423, 3103, 3058, 2924, 2853, 1597, 1496, 1322, 1265, 1168, 1023, 976, 849, 740, 672 cm.$^{-1}$; ^{1}H N MR ($CDCl_3$): δ 2.80 (s, 3H), 7.24-7.40 (m, 4H), 7.84 (d, 2H, *J* = 7.0 Hz).; EIMS *m/z* (%): 175 (m^+ 75), 149 (10), 134 (100), 108 (10), 89 (25), 63 (10), 45 (10).

2,4-Diphenylthiazole (**3e**). White solid. Mp.118-120 ^{0}C (Lit.[Ref.13] 91-92 ^{0}C). IR (KBr): υ 3447, 3114, 2924, 2855, 1505, 1466, 1392, 1233, 1102, 1050, 974, 851, 762, 687 cm.$^{-1}$; ^{1}HNMR ($CDCl_3$): δ 7.41-7.48 (m, 6H), 7.51 (d, 2H, *J* = 10.5 Hz), 7.86 (d, 2H, *J* = 10.5 Hz), 7.99-8.05 (m, 1H).; EIMS *m/z* (%): 238 (m^{+1} 100), 134 (55), 103 (15), 90 (30).

4-(4-Bromophenyl)-Thiazol-2-amine (**3f**). Brown solid. Mp.164-166 ^{0}C (Lit.[Ref.6] 176-177 ^{0}C). IR (KBr): υ 3426, 3280, 3108, 2925, 1532, 1468, 1391, 1334, 1067, 1035, 1004, 822, 727, 669 cm.$^{-1}$;^{1}H NMR ($CDCl_3$): δ 4.96 (brs, 2H, NH_2), 6.70 (s, 1H), 7.47 (d, 2H, *J* = 8.0 Hz), 7.62 (d, 2H, *J* = 8.0 Hz).; EIMS *m/z* (%): 257 (m^{+2} 100), 255 (m^+ 90), 225 (10), 149 (10).

4-(4-Bromophenyl)-*N*-Methylthiazol-2-amine (**3g**). Yellow solid. Mp. 138-140 ^{0}C.; IR (KBr): υ 3259, 3109, 2924, 1574, 1450, 1392, 1104, 1048, 827, 723, 665 cm.$^{-1}$; ^{1}H NMR ($CDCl_3$): δ 3.00 (s, 3H), 5.75 (brs, 1H), 6.67 (s, 1H), 7.47 (d, 2H, *J* = 8.0 Hz), 7.64 (d, 2H, *J* = 8.0 Hz).; EIMS *m/z* (%). 271 (m^{+2} 100), 269 (m^+ 90), 220 (10), 115 (10), 91 (10).

4-(4-Bromophenyl)-*N*-Phenyloxazol-2-amine (**3h**). Yellow solid. Mp. 112-114 ^{0}C.; IR (KBr): υ 3250, 3186, 2923, 2853, 1564, 1498, 1461, 1424, 1309, 1067, 915, 842, 749, 695 cm.$^{-1}$; ^{1}H NMR ($CDCl_3$): δ 6.76 (s, 1H), 7.02-7.12 (m, 1H), 6.37 (d, 4H, *J* = 7.0 Hz), 7.43-7.55 (m, 2H), 7.61-7.64 (m, 2H).

4-(4-Bromophenyl)-2-Methylthiazole (**3i**). White solid. Mp. 130-132 ^{0}C (Lit.[Ref.8] 127 ^{0}C). IR (KBr): υ 3113, 2921, 1504, 1462, 1397, 1170, 1065, 980, 848, 742, 658 cm.$^{-1}$; ^{1}H NMR ($CDCl_3$): δ 2.79 (s, 3H), 7.27 (s, 1H), 7.51 (d, 2H, *J* = 7.0 Hz), 7.75 (d, 2H, *J* = 7.0 Hz).; EIMS *m/z* (%): 257 (m^{+2} 100), 255 (m^{+1} 97), 231 (10), 178 (10), 102 (10), 91 (10), 77 (10).

4-(4-Bromophenyl)-2-Phenylthiazole (**3j**). White solid. Mp. 122-124 ^{0}C (Lit.[Ref.29] 135 ^{0}C). IR (KBr): υ 3114, 2924, 2855, 1505, 1466, 1392, 1233, 1102, 1050, 974, 851, 762 cm.$^{-1}$;^{1}H NMR ($CDCl_3$): δ 7.40-7.50 (m, 5H) 7.55 (d, 2H, *J* = 7.0 Hz), 7.87 (d, 2H, *J* = 7.0 Hz), 8.02 (d, 1H, *J* = 7.0 Hz).;EIMS *m/z* (%): 318 (m^{+2} 50), 316 (m^+ 48), 237 (100), 225 (10), 133 (48).

4-(Naphthalen-2-yl)-Thiazol-2-amine (**3k**). Brown solid. Mp. 140-142 ^{0}C (Lit.[Ref.6] 150-151 & Lit.[Ref.7] 135 ^{0}C). IR (KBr): υ 3436, 3169, 3057, 2927, 1530, 1392, 1220, 1111, 1038, 857, 749, 706 cm.$^{-1}$; ^{1}H NMR ($CDCl_3$): δ 5.05 (brs, 2H), 6.82 (s, 1H), 7.40-7.48 (m, 2H), 7.78-7.88 (m, 4H), 8.28 (s, 1H).; EIMS *m/z* (%): 227 (m^{+1} 100), 115 (10).

***N*-Methyl-4-(naphthalen-2-yl)-thiazol-2-amine** (**3l**). Light yellow solid. Mp.116-118 ^{0}C (Lit.[Ref.15]123-124 ^{0}C). IR (KBr): υ 3244, 3114, 3052, 2918, 1584, 1449, 1399, 1127, 1050, 949, 862,

741 cm.$^{-1}$; ^{1}H NMR ($CDCl_3$): δ 3.00 (s, 3H), 6.45 (brs, 1H, NH), 6.80 (s, 1H), 7.39-7.48 (m, 2H), 7.74-7.86 (m, 4H), 8.27 (s, 1H).; EIMS *m/z* (%): 241 (m^{+1} 100), 122 (10), 98 (10).

4-(Naphthalen-2yl)-*N*-Phenyloxazol-2-amine (**3m**). Dark yellow solid. Mp. 140-142 ^{0}C (Lit. [Ref.20]149-150 ^{0}C). IR (KBr): υ 3424, 3106, 3052, 2925, 1595, 1468, 1241, 1053, 984, 831, 758, 684 cm.$^{-1}$; ^{1}H NMR ($CDCl_3$): δ 7.40-7.50 (m, 5H), 7.56 (s, 1H), 7.75-7.90 (m, 3H), 8.00-8.12 (m, 4H), 8.50 (brs, 1H, NH).; EIMS *m/z* (%): 303 (m^{+1} 80), 283 (20), 130 (10), 121 (15), 102 (85), 88 (20), 79 (10), 74 (50), 60 (100).

2-Methyl-4-(naphthalene-2-yl)-thiazole (**3n**). Brown solid. Mp. 80-82 ^{0}C. ^{1}H NMR ($CDCl_3$): δ 2.80 (s, 3H), 7.38-7.49 (m, 3H), 7.75-7.95 (m, 4H), 8.40 (s, 1H).; EIMS *m/z* (%): 226 (m^{+1} 100), 205 (10), 180 (10), 149 (15), 123 (10), 115 (10), 102 (10).

4-(Naphthalen-2yl)-2-Phenylthiazole (**3o**). White solid. Mp. 120-122 ^{0}C.^{1}HNMR ($CDCl_3$): δ 7.40-7.50 (m, 6H), 7.55 (s, 3H), 7.78-7.90 (m, 1H), 8.00-8.12 (m, 2H), 8.50 (brs, 1H, NH).; EIMS *m/z* (%); 310 (M+Na, 75), 288 (M^{+} 100), 230 (20), 204 (10), 171 (25), 125 (40), 107 (20), 99 (10), 89 (15), 71 (10).

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