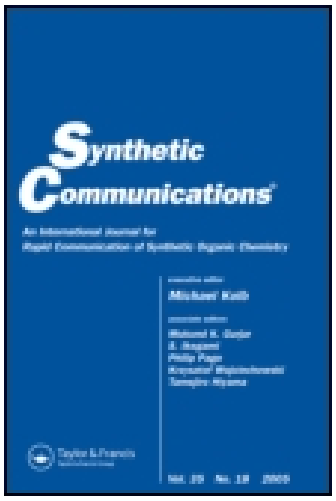

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Efficient and Novel Synthesis of N-Aryl-N′-ethoxycarbonylthiourea and Arene-bis-ethoxycarbonylthiourea Derivatives Catalyzed by TMEDA

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Efficient and Novel Synthesis of *N*-Aryl-*N*′-ethoxycarbonylthiourea and Arene-*bis*-ethoxycarbonylthiourea Derivatives Catalyzed by TMEDA

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ABSTRACT

A series of *N*-aryl-*N*′-ethoxycarbonyl thioureas and arene-*bis*-ethoxycarbonylthiourea derivatives have been synthesized in good to excellent yields under the TMEDA catalyzed conditions at room temperature.

Key Words: Ethyl chloroformate; Thiocyanate; Catalysts; TMEDA.

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INTRODUCTION

N-Aryl-*N*′-ethoxycarbonyl thioureas have attracted much attention due to their strong coordination ability,[1] for example, many *N*-substituted-*N*′-ethoxycarbonyl thioureas are commercially utilized as the collector for copper sulfides and precious metals.[2] Moreover, *N*-aryl-*N*′-ethoxycarbonyl thioureas exhibit high antibacterial activity.[3] It is also an important intermediate for synthesis of heterocyclic compounds.[4] In view of these and as a part of our work of the synthesis, biological activity, and coordination behavior of thiourea derivatives,[5] herein we report an efficient method for synthesis *N*-aryl-*N*′-ethoxycarbonyl thioureas (**4a–1**) and arene-*bis*-ethoxycarbonylthiourea derivatives (**5a–e**) catalyzed by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) under mild conditions.

The common methods for the preparation of these compounds are via the reaction of ethoxycarbonylthiocyanate (**3**) with corresponding aromatic amines or arene diamines.[6] Obviously, the compound **3** is the key intermediate for **4** and **5**. As early as 1908, Dixon and Taylor [7] repoted that potassium thiocyanate (**2**) reacted with ethyl chloroformate (**1**) in acetone solutions to give the compound **3**, but this method gives **3** in very low yield and ethoxycarbonylthiocyanate as by-product.[8] Hence it is not a good method for preparation **3**. In our earlier work, we reported that acyl isothiocyanate could be synthesized in high yield by the reaction of benzoyl chloride with potassium thiocyanate under solid–liquid phase-transfer catalytic conditions,[5b] however, we have not obtained the compound **3** in high yield using similar method.

Recently, Sano et al.[9] reported that TMEDA could promote the acylation of alcohols with benzoyl chloride. Kunz and Bechtolsheimor[10] reported that pyridine could catalyze the reaction between 2-(triphenylphosphonio)ethyl chloroformate and alcohols. In view of these, we think TMEDA and other amine such as pyridine also can catalyze the reaction between **1** and **2** by enhancing reactivity of **1**. In order to select the best reaction condition and the best catalyst for synthesis **3**, we carried out a series of experiments. At first, we estimated the reactivity of the model reaction (Sch. 1) between **1** (10 mmol) and **2** (12 mmol) with catalytic amount of TMEDA (0.1 mmol) at room temperature in different solvents. Since the compound **3** is an oily product, we did not separate it and added the aniline (10 mmol) slowly to the reaction mixture with continuous stirring at room temperature for 5 hr (Table 1). From these data, we concluded that ethyl acetate is the appropriate solvent for this reaction.

In order to compare the catalytic effect of TMEDA, we examined the similar reaction with different amines as catalysts, as well as, PEG-400 as a solid–liquid phase-transfer catalyst (Table 2). From these data, we can find the TMEDA is the best catalyst for this reaction. Finally, we explored the

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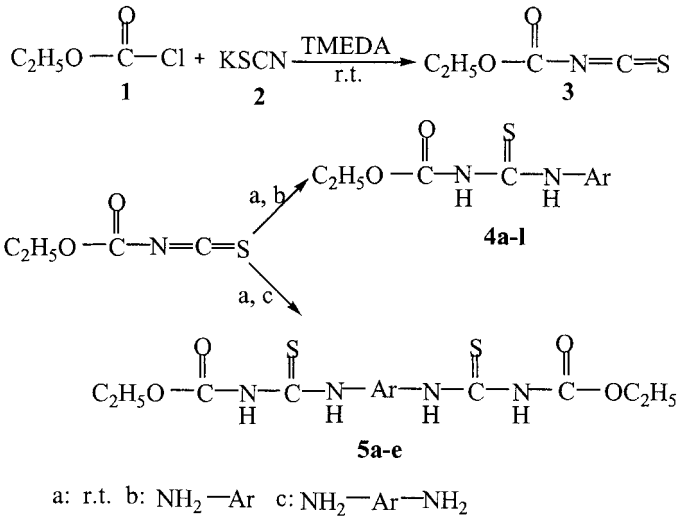

Scheme 1.

general validity of the present methodology; different ethoxycarbonylthioureas **4a–1** and **5a–e** were synthesized in excellent yields (Table 3).

The details of the reaction mechanism are not clear at present but Sano et al.[9] supposed that a benzoyl chloride–TMEDA complex plays a significant role to enhance the reactivity of benzoyl chloride. Additionally, Kunz and Bechtolsheimer[10] reported that the 2-(triphenylphosphonio)ethyl chloroformate–pyridine complex is the key intermediate to enhance the reactivity of 2-(triphenylphosphonio)ethyl chloroformate. Therefore, we think the formation of ethyl chloroformate–TMEDA complex (Sch. 2) is the key step of the catalytic procedure.

In brief, TMEDA is an excellent catalyst for the synthesis of this kind of isothiocyanate and thiourea. The use of TMEDA as the catalyst has many

Table 1. Yields of **4a** in different solvents.

Entry	Solvents	Yields of **4a** (%)
1	Acetone (8 mL)	54
2	CH_2Cl_2 (8 mL)	56
3	Ethyl acetate (8 mL)	96
4	Ethyl acetate (20 mL)	68

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Table 2. Yields of **4a** under the different catalysts catalyzed.

Entry	Catalysts[a]	Yields of **4a** (%)
1	TPA[b]	60
2	TAA[c]	80
3	Pyridine	76
4	TMEDA	96
5	PEG-400[d]	42
6	PEG-400 + TAA	68
7	PEG-400 + Pyridine	45
8	PEG-400 + TMEDA	74

[a]The use of each catalyst is 0.1 mmol.
[b]Tripropyl amine.
[c]Triamyl amine.
[d]Polyethylene glycol-400.

advantages such as excellent yields, high efficiency (10 mmol ethyl chloroformate only need 0.1 mmol TMEDA), mild reaction conditions (all reactions are performed at room temperature), and simple operation. For these reasons, this methodology represents an important improvement for the preparation of this kind of products.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded in KBr on a Nicolet NEXUS 670 FT-IR spectrophotometer and ^{1}H-NMR spectra on a FT-80A instrument using TMS as internal reference. Elemental analysis was determined on PE-2400 CHN instrument.

Typical Procedure for Preparation of 4a–1 and 5a–e

The synthesis of **4a–1** and **5a–e** were carried out by adding powdered **2** (12 mmol), to an ethyl acetate solution of **1** (10 mmol) and TMEDA (0.1 mmol). The reaction mixture was stirred at room temperature for 5 hr. Then the aromatic amine (10 mmol) (to give **4a–1**) or arene diamine (5 mmol) (to give **5a–e**) was slowly added to the reaction mixture with constant stirring. The reaction mixture was stirred at room temperature for 5 hr again. After evaporate the solvent in vacuum, the products were obtained from washing the precipitation with 10 mL 75% ethanol three times and

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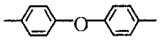
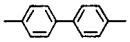
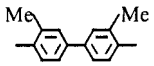
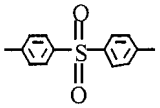
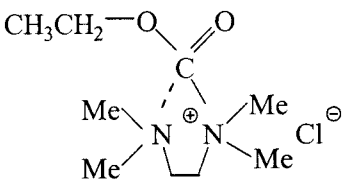
Table 3. Compounds **4a–1** and **5a–e** prepared.

Entry	Ar	Products	Yields (%)
1	C_6H_5	**4a**	96
2	4-$CH_3C_6H_4$	**4b**	97
3	4-$CH_3COC_6H_4$	**4c**	85
4	4-ClC_6H_4	**4d**	86
5	2,4,6-triClC_6H_2	**4e**	81
6	3-BrC_6H_4	**4f**	83
7	2,4,6-triBrC_6H_2	**4g**	84
8	4-FC_6H_4	**4h**	80
9	1-Naphthyl	**4i**	95
10	4-$CH_3OC_6H_4$	**4j**	87
11		**4k**	75
12		**4l**	82
13		**5a**	87
14		**5b**	98
15		**5c**	97
16		**5d**	72
17		**5e**	94

15 mL H_2O three times. If necessary, recrystallization **4a–1** from ethanol and **5a–e** from DMF–EtOH–H_2O gave the pure product.

***N*-Phenyl-*N′*-ethoxycarbonylthiourea (4a).** Yield 96%, m.p. 125–126°C. IR (KBr): $\nu = 3416$ (NH), 3220 (NH), 1712 (C═O), 1596, 1534, 1449 (C═C), 1237 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 11.48$ (s, 1H, NH), 8.29 (s, 1H,



Scheme 2.

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NH), 7.50 (m, 5H, ArH), 4.361 (q, 2H, CH_2), 1.368, (t, 3H, CH_3). Anal. Cacld. for $C_{10}H_{12}N_2O_2S$: C, 53.55; H, 5.39; N, 12.49. Found (%): C, 53.55; H, 5.40; N, 12.54.

***N*-(4-Methylphenyl)-*N′*-ethoxycarbonylthiourea (4b).** Yield 97%, m.p. 149–150°C. IR (KBr): $\nu = 3421$ (NH), 3241 (NH), 1712 (C═O), 1529 (C═C), 1237 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 11.38$ (s, 1H, NH), 8.33 (s, 1H, NH), 7.45 (q, 4H, ArH), 4.34 (q, 2H, CH_2), 2.37 (s, 3H, CH_3), 1.36, (t, 3H, CH_3). Anal. Cacld. for $C_{11}H_{14}N_2O_2S$: C, 55.44; H, 5.92; N, 11.76. Found: C, 55.47; H, 5.90; N, 11.75.

***N*-Acetylphenyl-*N′*-ethoxycarbonylthiourea (4c).** Yield 85%, m.p. 177–178°C. IR (KBr): $\nu = 3174$ (NH), 3061 (NH), 1728, 1681 (C═O), 1618, 1598, 1537 (C═C), 1249 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 11.76$ (s, 1H, NH), 8.43 (s, 1H, NH), 7.96 (q, 4H, ArH), 4.35 (q, 2H, CH_2) 2.61 (s, 3H, CH_3), 1.36 (t, 3H, CH_3). Anal. Cacld. for $C_{12}H_{14}N_2O_2S$: C, 55.44; H, 5.92; N, 11.76. Found: C, 54.04; H, 5.87; N, 10.80.

***N*-(4-Chlorophenyl)-*N′*-ethoxycarbonylthiourea (4d).** Yield 86%, m.p. 120–122°C. IR (KBr): $\nu = 3424$ (NH), 3259 (NH), 1725 (C═O), 1592, 1554, 1527 (C═C), 1249 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 11.48$ (s, 1H, NH), 8.29 (s, 1H, NH), 7.50 (q, 4H, ArH), 4.35 (q, 2H, CH_2) 1.36, (t, 3H, CH_3). Anal. Cacld. for $C_{10}H_{11}N_2O_2SCl$: C, 46.42; H, 4.29; N, 10.83. Found: C, 46.27; H, 4.64; N, 10.54.

***N*-(2,4,6-Trichlorophenyl)-*N′*-ethoxycarbonylthiourea (4e).** Yield 81%, m.p. 177–178°C. IR (KBr): $\nu = 3432$ (NH), 3194 (NH), 1728 (C═O), 1554, 1514 (C═C), 1242 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 10.92$ (s, 1H, NH), 8.55 (s, 1H, NH), 7.45 (s, 2H, ArH), 4.369 (q, 2H, CH_2) 1.371 (t, 3H, CH_3). Anal. Cacld. for $C_{10}H_{19}N_2O_2SCl_3$: C, 36.57; H, 3.00; N, 9.24. Found: C, 36.66; H, 2.77; N, 9.24.

***N*-(3-Bromophenyl)-*N′*-ethoxycarbonylthiourea (4f).** Yield 83%, m.p. 97–98°C. IR (KBr): $\nu = 3415$ (NH), 3179 (NH), 1711 (C═O), 1589, 1531, 1472 (C═C), 1237 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 11.52$ (s, 1H, NH), 8.28 (s, 1H, NH), 7.48 (m, 4H, ArH), 4.358 (q, 2H, CH_2) 1.370 (t, 3H, CH_3). Anal. Cacld. for $C_{10}H_{11}N_2O_2SBr$: C, 39.62; H, 3.66; N, 9.24. Found: C, 39.55; H, 3.90; N, 9.24.

***N*-(2,4,6-Tribromophenyl)-*N′*-ethoxycarbonylthiourea (4g).** Yield 84%, m.p. 196–198°C. IR (KBr): $\nu = 3430$ (NH), 3175 (NH), 1724 (C═O), 1514, 1442 (C═C), 1247 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 10.95$ (s, 1H, NH), 8.65 (s, 1H, NH), 7.80 (s, 2H, ArH), 4.37 (q, 2H, CH_2) 1.37 (t, 3H, CH_3). Anal. Cacld. for $C_{10}H_9N_2O_2SBr_3$: C, 26.06; H, 1.97; N, 6.08. Found: C, 26.07; H, 1.96; N, 6.11.

***N*-(4-Fluorophenyl)-*N′*-ethoxycarbonylthiourea (4h).** Yield 90%, m.p. 187–188°C. IR (KBr): $\nu = 3424$ (NH), 33168 (NH), 1726 (C═O), 1565, 1533, 1511 (C═C), 1252 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 11.38$

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(s, 1H, NH), 8.26 (s, 1H, NH), 7.50 (m, 4H, ArH), 4.36 (q, 2H, CH_2), 1.37 (t, 3H, CH_3). Anal. Cacld. for $C_{10}H_{11}N_2O_2SF$: C, 49.57; H, 4.58; N, 11.56. Found: C, 49.49; H, 4.58; N, 11.76.

***N*-(1-Naphthyl)-*N′*-ethoxycarbonylthiourea (4i).** Yield 95%, m.p. 106–108°C. IR (KBr): $\nu = 3426$ (NH), 3259 (NH), 1720 (C═O), 1597, 1521, 1478 (C═C), 1241 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 11.65$ (s, 1H, NH), 8.50 (s, 1H, NH), 7.64 (m, 7H, ArH), 4.39 (q, 2H, CH_2) 1.39 (t, 3H, CH_3). Anal. Cacld. for $C_{14}H_{14}N_2O_2S$: C, 61.29; H, 5.14; N, 10.21. Found: C, 61.51; H, 5.20; N, 10.27.

***N*-(4-Methoxyphenyl)-*N′*-ethoxycarbonylthiourea (4j).** Yield 87%, m.p. 137–138°C. IR (KBr): $\nu = 3431$ (NH), 3132 (NH), 1724 (C═O), 1564, 1538, 1492 (C═C), 1258 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 11.29$ (s, 1H, NH), 8.26 (s, 1H, NH), 7.28 (m, 4H, ArH), 4.34 (q, 2H, CH_2), 3.83 (s, 3H, CH_3) 1.36 (t, 3H, CH_3). Anal. Cacld. for $C_{11}H_{14}N_2O_2S$: C, 51.95; H, 5.55; N, 11.02. Found: C, 51.93; H, 5.49; N, 11.06.

***N*-(3-Pyridyl)-*N′*-ethoxycarbonylthiourea (4k).** Yield 75%, m.p. 167–168°C. IR (KBr): $\nu = 3408$ (NH), 3185 (NH), 1710 (C═O), 1555, 1533, 1479 (C═C, C═N), 1249 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 11.60$ (s, 1H, NH), 8.92 (s, 1H, NH), 8.50 (m, 2H, N═C–H), 8.25 (m, 1H, ArH), 7.40 (q, 1H, ArH), 4.37 (q, 2H, CH_2), 3.37 (s, 3H, CH_3) 1.36 (t, 3H, CH_3). Anal. Cacld. for $C_9H_{11}N_3O_2S$: C, 47.99; H, 4.92; N, 18.65. Found: C, 47.60; H, 5.07; N, 18.56.

***N*-(2-Thiazolyl)-*N′*-ethoxycarbonylthiourea (4I).** Yield 82%, m.p. 166–167°C. IR (KBr): $\nu = 3434$ (NH), 3169 (NH), 1725 (C═O), 1568, 1510 (C═C, C═N), 1244 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 9.71$ (s, 1H, NH), 8.35 (s, 1H, NH), 7.28 (m, 2H, ArH), 4.39 (q, 2H, CH_2), 1.37 (t, 3H, CH_3). Anal. Cacld. for $C_7H_9N_3O_2S_2$: C, 36.35; H, 3.92; N, 18.17. Found: C, 36.55; H, 3.68; N, 18.39.

1,4-Phenylene-*bis*-ethoxycarbonylthiourea (5a). Yield 88%, m.p. 210–211°C. IR (KBr): $\nu = 3428$ (NH), 3188 (NH), 1717 (C═O), 1590, 1522 (C═C), 1233 (C═S) cm^{-1}. ^{1}H-NMR (DMSO-d_6): $\delta_H = 11.62$ (s, 2H, NH), 10.86 (s, 2H, NH), 7.58 (s, 4H, ArH), 4.24 (q, 4H, CH_2), 1.27 (t, 6H, CH_3). Anal. Cacld. for $C_{14}H_{18}N_4O_4S_2$: C, 45.39; H, 4.90; N, 15.12. Found: C, 45.23; H, 5.06; N, 15.25.

4,4′-(*bis*-Ethoxycarbonylthioureido)-diphenyloxide (5b). Yield 98%, m.p. 187–188°C. IR (KBr): $\nu = 3414$ (NH), 3263 (NH), 1711 (C═O), 1569, 1530, 1499 (C═C), 1282 (Ar–O–Ar), 1234 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 11.42$ (s, 2H, NH), 8.31 (s, 2H, NH), 8.31 (s, 2H, NH), 7.28 (m, 8H, ArH), 4.35 (q, 4H, CH_2), 1.39 (t, 6H, CH_3). Anal. Cacld. for $C_{20}H_{22}N_4O_5S_2$: C, 51.93; H, 4.79; N, 12.11. Found: C, 52.07; H, 4.96; N, 12.17.

4,4′-(*bis*-Ethoxycarbonylthioureido)-diphenyl (5c). Yield 97%, m.p. > 280°C. IR (KBr): $\nu = 3425$ (NH), 3172 (NH), 1718 (C═O), 1602, 1532, 1497 (C═C), 1239 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 11.69$

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(s, 2H, NH), 10.93 (s, 2H, NH), 7.62 (m, 8H, ArH), 4.27 (q, 4H, CH_2), 1.29 (t, 6H, CH_3). Anal. Cacld. for $C_{20}H_{22}N_4O_4S_2$: C, 53.79; H, 4.97; N, 12.55. Found: C, 53.94; H, 5.11; N, 12.66.

4,4′-(*bis*-Ethoxycarbonylthioureido)-(3,3′-*bis*-methyl)diphenyl (5d). Yield 72%, m.p. $> 280^{\circ}$C. IR (KBr): $\nu = 3424$ (NH), 3165 (NH), 1715 (C═O), 1531, 1443 (C═C), 1246 (C═S) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 11.31$ (s, 2H, NH), 10.44 (s, 2H, NH), 7.50 (q, 6H, ArH), 4.26 (q, 4H, CH_2), 2.27 (s, 6H, CH_3), 1.28 (t, 6H, CH_3). Anal. Cacld. for $C_{22}H_{26}N_4O_4S_2$: C, 55.68; H, 5.54; N, 11.80. Found: C, 55.68; H, 5.67; N, 11.98.

4,4′-(*bis*-Ethoxycarbonylthioureido)-diphenylsulfone (5e). Yield 94%, m.p. $> 193-194^{\circ}$C. IR (KBr): $\nu = 3412$ (NH), 3179 (NH), 1731 (C═O), 1591, 1531, 1497 (C═C), 1229 (C═S), 1149(O═S═O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta_H = 11.90$ (s, 2H, NH), 10.43 (s, 2H, NH), 7.83 (s, 8H, ArH), 4.23 (q, 4H, CH_2), 1.24 (t, 6H, CH_3). Anal. Cacld. for $C_{20}H_{22}N_4O_6S_3$: C, 47.06; H, 4.43; N, 10.97. Found: C, 47.14; H, 4.62; N, 11.08.

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