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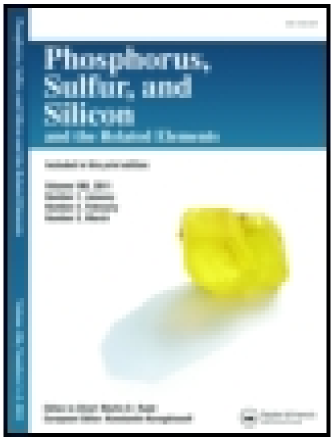

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AN EFFICIENT SYNTHESIS OF POLYMETHYLENE-BIS-AROYL THIOUREA DERIVATIVES UNDER THE CONDITION OF PHASE-TRANSFER CATALYSIS

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AN EFFICIENT SYNTHESIS OF POLYMETHYLENE-BIS-AROYL THIOUREA DERIVATIVES UNDER THE CONDITION OF PHASE-TRANSFER CATALYSIS

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Reaction of polymethylene diamine with aroyl chloride and ammonium thiocyanate under the condition of solid–liquid phase-transfer catalysis using polyethylene glycol-400 (PEG-400) as the catalyst yielded polymethylene-bis-aroyl thiourea derivatives ***3a–q*** *in good-to-excellent yield. The products have been characterized by analytical and spectral (IR and* H^1 *NMR) data.*

Keywords: PEG-400; Phase transfer catalysis; polymethylene-bis-aroyl thiourea; synthesis

INTRODUCTION

A number of 1,3-disubstituted thiourea derivatives are associated with various kinds of biological activities. Some thioureas have been found to be useful as herbicides, insecticides, and plant-growth regulators.[1] In view of these observations and in continuation of our earlier work on the synthesis and biological activity of thiourea derivatives,[2–5] we now report a convenient and efficient method for the preparation of polymethylene-bis-aroyl thiourea derivatives under the condition of solid–liquid phase-transfer catalysis using polyethylene glycol-400 (PEG-400) as phase-transfer catalyst.

Aroyl chloride (**1**) obtained by the reaction of aromatic acid with thionyl chloride was treated with ammonium thiocyanate under the

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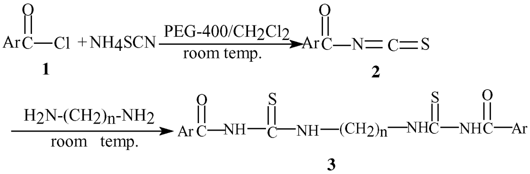
condition of solid–liquid phase-transfer catalysis using 3% PEG-400 as the catalyst to give the corresponding aroyl isothiocyanate (**2**). Without isolation, compound **2** was treated with polymethylene diamine to afford polymethylene-bis-aroyl thiourea derivatives (**3**) in good-to-excellent yield (Scheme 1).

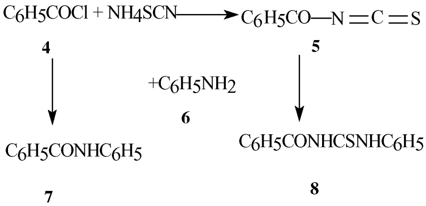


SCHEME 1

RESULTS AND DISCUSSION

Acyl isothiocyanates have been prepared under liquid–liquid phase-transfer catalysis using tetrabutylammonium bromide as the catalyst, which after isolation reacted with aniline to give the corresponding thiourea derivatives.[6] However, in the presence of water, hydrolysis of the aroyl chloride may occur, and the yield of the acyl isothiocyanate is decreased. Parekh has reported that acyl chloride reacts with different phenylthioureas to yield N^1-acyl-N^3-arylthioureas, but long reaction times and high temperature are required.[7] Jirman[8] has also reported that substituted benzoyl chloride reacts with N^1-acetyl-N^3-arylthioureas to give the corresponding acylthiourea derivatives; however, long reaction times, high temperature, and the preparation of N^1-acetyl-N^3-arylthioureas are required. Other methods[9] for preparation of acylthioureas have also been reported, but none of them was completely satisfactory for our purpose. Consequently, we have conducted our reaction under solid–liquid phase-transfer catalysis conditions using PEG-400 as the catalyst. It was found that the acyl chloride was quantitatively converted to the corresponding acyl isothiocyanate. This intermediate was then treated with polymethylene diamines to give the thiourea derivatives **3** in high yield.

In searching for the best conditions, the condensation of benzoyl chloride (**4**) with ammonium thiocyanate in methylene dichloride in the presence of a phase-transfer catalyst was studied at room temperature in detail. Instead of the isolation of the formed benzoyl isothiocyanate (**5**), the reaction mixture was quenched by the addition of aniline (**6**) after 1 h. The added **6** gives rise to the formation of N-phenyl benzamide (**7**) and N^1-benzoyl-N^3-Phenyl thiourea (**8**) from the starting benzoyl chloride 4 and the resulting benzoyl isothiocyanate (**5**), respectively (Scheme 2).



SCHEME 2

Without a phase-transfer catalyst, no reaction was observed and **4** was recovered as phenyl benzamide **7**. Among the catalysts studied, 18-crown-6 and tetrabutylammonium bromide led to good results; however, polyethylene glycol derivatives appeared as the best catalysts, and we used PEG-400 to perform the experiments described below. Other quatermary ammonium salts tested, 15-crown-5, DB-15-crown-5, and cyclodextrins such as α-, β-, and γ-CD are not effective. The results are summarized in Table I.

TABLE I Effect of Catalyst on the Yield of N^1-benzoyl-N^3-phenyl thiourea (**8**) and N-phenyl benzamide (**7**)

		Yield (%)	
Run	Catalyst	7^a	8^b
1	18-crown-6	0	85
2	15-crown-5	82	0
3	DB-15-crown-5	85	0
4	α-CD	83	0
5	β-CD	76	0
6	γ-CD	81	0
7	PEG-400	0	98
8	PEG-600	0	98
9	PEG-2000	0	96
10	PEG-6000	0	92
11	Bu_4NBr	0	91
12	$PhCH_2NBu_3Cl$	81	0
13	$PhCh_2NMe_3Cl$	90	0
14	$PhCh_2NMe_3NO_3$	82	0
15	Me_4NCl	83	0
16	no PTC	92	0

[a] m.p. of **7** is 162–163°C (Lit.[10] 163–164°C).
[b] m.p. of **8** is 146–148°C (Lit.[6] 148°C).

TABLE II Melting Points, Yields, and Elemental Analyses of Compounds **3a–q**

					Elemental analysis (%) found (calcd.)		
Product	Ar	n	m.p. (°C)	Yield (%)	C	N	N
3a	C_6H_5	2	214–216	92	55.90(55.96)	4.59(4.66)	14.28(14.51)
3b	C_6H_5	4	196–198	86	57.91(57.97)	5.47(5.31)	13.36(13.53)
3c	C_6H_5	6	176–178	82	59.86(59.73)	5.90(5.88)	12.39(12.27)
3d	2-ClC_6H_4	2	230–232	86	47.26(47.37)	3.61(3.51)	12.07(12.2)
3e	2-ClC_6H_4	4	178–180	83	54.34(54.54)	4.40(4.54)	11.80(11.57)
3f	2-ClC_6H_4	6	187–188	85	51.80(51.80)	4.65(4.76)	10.82(10.96)
3g	4-$NO_2C_6H_4$	2	218–220	95	45.62(45.62)	3.19(3.36)	17.43(17.6)
3h	4-$NO_2C_6H_4$	4	219–221	81	47.45(47.45)	3.82(3.97)	16.78(16.67)
3i	4-$NO_2C_6H_4$	6	167–168	83	49.75(49.75)	4.42(4.51)	15.92(15.7)
3j	4-$CH_3OC_6H_4$	2	238–240	88	53.72(53.72)	4.98(4.93)	12.67(12.75)
3k	4-$CH_3OC_6H_4$	4	218–220	90	55.43(55.43)	5.37(5.48)	11.67(11.81)
3l	4-$CH_3OC_6H_4$	6	210–212	93	57.59(57.59)	6.21(5.98)	11.10(11.1)
3m	2-Furoyl	2	227–228	87	45.93(45.89)	3.96(3.85)	15.27(15.29)
3n	2-Furoyl	4	204–205	85	48.86(48.71)	4.85(4.60)	14.50(14.2)
3o	2-Furoyl	6	>260	78	51.32(51.16)	5.41(5.25)	13.21(13.26)
3p	3-$NO_2C_6H_4$	2	215–216	80	45.51(45.38)	3.27(3.36)	17.58(17.6)
3q	3-$NO_2C_6H_4$	6	203–204	92	49.73(49.62)	4.47(4.51)	19.88(15.79)

TABLE III Spectral Data for Compounds **3a–q**

Product	IR (KBr) cm^{-1}	^{1}H NMR (δ) ppm
3a	3420, 3232 (NH); 1665 (CO) and 1154 (CS)	3.98 (t, 4H, CH$_2$); 7.36–7.98 (m, 10H, C6H5); 10.95 (s, 2H, NH); 11.31 (S, 2H, NH).
3b	3418, 3221 (NH); 1670 (CO) and 1151 (CS)	1.70 (t, 4H, CH2); 3.68 (t, 4H, CH2); 7.45–7.92 (m, 10H, C6H5); 10.91 (s, 2H, NH); 11.02 (s, 2H, NH).
3c	3238 (NH); 1667 (CO) and 1151 (CS)	1.45 (t, 4H, CH2); 1.65 (t, 4H, CH2); 3.60 (t, 4H, CH2); 7.45–7.93 (m, 10H, C6H5); 10.89 (s, 2H, NH); 11.01 (s, 2H, NH).
3d	3169 (NH); 1693 (CO) and 1182 (CS)	3.98 (t, 4H, CH2); 7.47–7.54 (m, 8H, C6H5); 10.71 (s, 2H, NH); 11.35 (s, 2H, NH).
3e	3245 (NH); 1691 (CO) and 1178 (CS)	1.71 (t, 4H, CH2); 3.67 (t, 4H, CH2); 7.47–7.96 (m, 8H, C6H5); 10.96 (s, 2H, NH); 11.07 (s, 2H, NH).
3f	3320 (NH); 1694 (CO) and 1180 (CS)	1.43 (t, 4H, CH2); 1.65 (t, 4H, CH2); 3.57 (t, 4H, CH2); 7.48–7.98 (m, 8H, C6H5); 10.72 (s, 2H, NH); 11.73 (s, 2H, NH).
3g	3223 (NH); 1690 (CO) and 1170 (CS)	3.96 (t, 4H,CH2); 7.46–7.58 (m, 8H,C6H5); 10.81 (s, 2H, NH); 11.37 (s, 2H, NH).
3h	3213 (NH); 1691 (CO) and 1173 (CS)	1.07 (t, 4H, CH2); 3.68 (t, 4H, CH2); 7.48–7.98 (m, 8H, C6H5); 10.98 (s, 2H, NH); 11.09 (s, 2H, NH).
3i	3220, 1690 (NH); 1690 (CO) and 1172 (CS)	1.43 (t, 4H, CH2); 1.65 (t, 4H, CH2); 3.62 (t, 4H, CH2); 7.45–7.98 (m, 8H, C6H5); 10.85 (s, 2H, NH); 11.77 (s, 2H, NH).
3j	3342, 3265 (NH); 1660 (CO) and 1172 (CS)	3.63 (t, 6H, CH3); 3.82 (t, 4H, CH2); 6.96–7.98 (m, 8H, C6H5); 10.90 (s, 2H, NH); 11.03 (s, 2H, NH).
3k	3403, 3221 (NH); 1668 (CO) and 1165 (CS)	1.69 (t, 4H, CH2); 3.63 (, 6H, CH3); 3.84; 6.96–7.97 (m, 8H, C6H5); 10.90 (s, 2H, NH); 11.03 (s, 2H, NH).
3l	3296, 3220 (NH); 1655 (CO) and 1158 (CS)	1.50 (t, 4H, CH2); 1.60 (t, 4H, CH2); 3.60 (t, 4H, CH2); 3.80 (S, 6H, CH3); 6.9–7.95 (m, 8H, C6H5); 10.95 (s, 2H, NH); 11.03 (s, 2H, NH).
3m	3406, 3219 (NH); 1673 (CO) and 1154 (CS)	3.96 (t, 4H, CH2); 6.72–7.87 (m, 6H, furan3, 4,5-H); 10.91 (s, 2H, NH); 11.77 (s, 2H, NH).
3n	3317, 3262 (NH); 1675 (CO) and 1162 (CS)	1.68 (t, 4H, CH2); 3.82 (t, 4H, CH2); 6.90–7.85 (m, 6H, furan3, 4,5-H); 10.93 (s, 2H, NH); 11.53 (s, 2H, NH).
3o	3326, 3217 (NH); 1688 (CO) and 1175 (CS)	1.46 (t, 4H, CH2); 1.62 (t, 4H, CH2); 3.58 (t, 4H, CH2); 6.54–7.79 (m, 6H, furan3, 4,5-H); 10.81 (s, 2H, NH); 11.72 (s, 2H, NH)
3p	3291, 3211 (NH); 1685 (CO) and 1158 (CS)	3.92 (t, 4H, CH2); 7.58–8.52 (m, 8H, C6H5); 10.80 (s, 2H, NH); 11.31 (s, 2H, NH).
3q	3359, 3218 (NH); 1673 (CO) and 1159 (CS)	1.43 (t, 4H, CH2); 1.64 (t, 4H, CH2); 3.65 (t, 4H, CH2); 7.66–8.70 (m, 8H, C6H5); 10.74 (s, 2H, NH); 11.72 (s, 2H, NH).

With the above results in hand, we have prepared seventeen polymethylene-bis-aroyl thioureas by the reaction of polymethylene diamines with aroyl chloride and ammonium thiocyanate under the condition of solid–liquid phase-transfer catalysis in the presence of catalytic amounts of PEG-400. The results obtained are reported in Table II.

In summary, this is a facile and convenient method for the synthesis of polymethylene-bis-aroyl thiourea derivatives under solid–liquid phase-transfer catalysis conditions, with the advantages of mild conditions, simple operation, short reaction times, and high yield over the reported method. The catalyst PEG-400 is inexpensive, relatively nontoxic, highly stable, and easily available.

EXPERIMENTAL

General

All melting points were determined in open capillary tubes and are uncorrected.

IR spectra were recorded using KBr pellets on an Alpha Centauri Fourier transform infrared (FT IR) Spectrophotometer and ^{1}H NMR spectra on Bruker AC-80 instrument, DMSO-d_6 was used as the solvent and TMS as internal standard. The chemical shifts are expressed as δ. Elemental analyses were performed with a PE-2400 CHN instrument.

General Procedure for the Preparation of Polymethylene-bis-aroyl Thioureas (3)

Powdered ammonium thiocyanate (1.14 g, 15 mmol), aroyl chloride (1.41 g, 10 mmol), PEG-400 (0.18 g, 3% with respect to ammonium thiocyanate) and methylene dichloride (25 ml) were placed in a dried round-bottomed flask containing a magnetic stirrer bar and stirred at room temperature for 1 h. Then a solution of polymethylene diamine (4.5 mmol) in methylene dichloride (10 ml) was added dropwise over 0.5 h, and the mixture was stirred for 1 h. The corresponding polymethylene-bis-aroyl thiourea (**3**) precipitated immediately. The product was filtered, washed with water to remove inorganic salts, dried, and recrystallized from DMF-EtOH-H_2O to give the title compounds (**3**).

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