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Phase Transfer Catalyzed Synthesis of 1,6-Diaroyldithiohydrazodicarbonam Derivatives

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PHASE TRANSFER CATALYZED SYNTHESIS OF 1,6-DIAROYLDITHIOHYDRAZODICARBONAMIDE DERIVATIVES

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Abstract Reaction of hydrazine hydrate with aroyl chloride and ammonium thiocyanate under the condition of solid-liquid phase transfer catalysis using polyethylene glycol-600 (PEG-600) as the catalyst yielded 1,6-diaroyldithiohydrazodicarbonamides 3a — 3h in good to excellent yield.

A series of 1,3-disubstituted thiourea derivatives are associated with various kinds of biological activities, some of them have been used as herbicides, insecticides and plant-growth regulators[1]. However, preparation and bioactive studies of the thiurea derivatives of hydrazine have received limited attention. In view of these observation and in continuation of our earlier work on the synthesis and biological activity of thiourea derivatives[2-5], we report herein a convenient and efficient methods for the preparation of 1,6-diaroyldithiohydrazodicarbonamide derivatives under the condition of solid-liquid phase transfer catalysis using PEG-600 as the catalyst.

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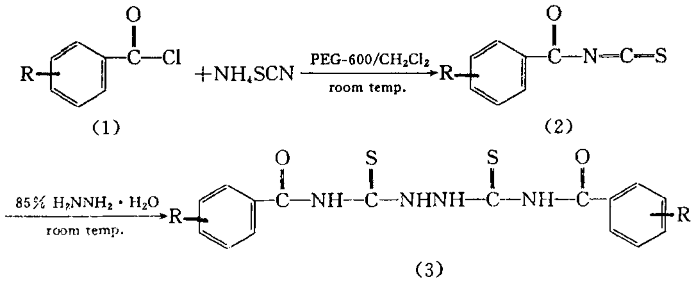
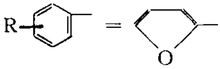
Aroyl chloride (1) obtained by the reaction of aromatic acid with thionyl chloride was treated with ammonium thiocyanate under the condition of solid-liquid phase transfer catalysis using 3% PEG-600 as the catalyst to give the corresponding aroyl isothiocyanate (2) in quantitative yield. Without separation of these intermediates and them reacted with 85% hydrazine hydrate to give 1,6-diaroyldithiohydrazodicarbonamide (3) in good to excellent yield(Scheme 1).



3	R	3	R
a	H	e	$3\text{-}NO_2$
b	2-Cl	f	2-I
c	$4\text{-}NO_2$	g	4-Br
d	$4\text{-}CH_3O$	h	

Scheme 1

Aroyl isothiocyanates are known to condense with amines, alcohols, amino-acids, hydrazine, phenols, and thiols[5], but the reactions of acyl isothiocyanates are complex, since addition to —N=C=S system and nucleophilic substitution at the carbonyl-carbon atom may compete with one another[6-8]. Hoggarth[8] has reported that benzoyl isothiocyanate reacts with hydrazine hydrate to give a mixture of 3-phenyl-1,2,4-triazole-5-thiol, 1,4-dibenzoylthiosemicarbazide and benzoyl hydrazide. We have found, however, that if 85% hydrazine hydrate was dropped into the solution of benzoyl isothiocyanate in methylene chloride, only 1,6-dibenzoyldithiohydrazodicarbonamide was formed, the formation of other compounds obtained by Hoggarth was not observed. It may be presumed that 4-benzoylthiosemicarbazide is formed first and then it reacts immediately with another molecular of benzoy isothiocyanate to give the corresponding 1, 6-dibenzoyldithiohydrazodicarbonamide (3a).

As a representative case the reaction of hydrazine hydrate with benzoyl chloride(la) and ammonium thiocyanate was carried out at room temperature under the condition of solid-liquid phase transfer catalysis using PEG-600 as the catalyst. The crude product obtained was recrystallized from DMF-EtOH-H_2O to obtained a pure compound, m. p. > 250℃. The IR (KBr) spectrum displayed absorptions at 3227cm^{-1}, 1674 cm^{-1}and 1163 cm^{-1}, which are assigned for NH, C=O and C=S functions respectively. The ^{1}H NMR (DMSO-d_6) spectrum revealed signals at δ14. 22 (s, 2H, NH, D_2O exchangeable), δ12. 12 (s, 2H, NH, D_2O exchangeable) and δ7. 52 — 8. 06 (m, 10H, arom.). Base on the foregoing spectral data, the compound was assigned 1,6-dibenzoyldithiohydrazodicarbonamide structure (3a).

In conclusion, this one-pot procedure is a facile and convenient method for the synthesis of 1, 6-diaroyldithiohydrazodicarbonamide derivatives under solid-liquid phase transfer catalysis conditions, with the advantages of mild conditions, simple operation, short reaction times and high yield. The catalyst PEG-600 is inexpensive, relatively nontoxic, highly stable and easily available.

Experimental Procedures

IR Spectra were recorded using KBr pellets on an Alpha Centauri FT-IR spectrophotometer and ^{1}H-NMR spectra on a FT-80A instrument, DMSO-d_6 was used as solvent and Me_4Si as internal standard. Elemental analyses were performed on a PE-2400 CHN instrument. Mps were observed in an open capillary tube and are uncorrected. Aroyl chloride was prepared in 85—96% yield by refluxing aromatic acid and an excess of thionyl chloride.

General Procedure for the preparation of 1,6-diaroyldithiohydrazodicarbonamides

Powdered ammonium thiocyanate (15mmol), aroyl chloride (10mmol), PEG-600 (0. 27g, 3% with respect to ammonium thiocyanate) and methylene dichloride (25ml) were placed in a dried round-bottomed flask containing a magnetic stirrer bar and stirred at room temperature for 1h, then a solution of 85% hydrazine hydrate (5 mmol) in *dichloromethane* (10ml) was added dropwise over 30 min, and the mixture was stirred for 1h. The corresponding 1,6-diaroyldithiohydrazodicarbonamide (3) precipitates immediatly. The product is filtered, washed with water to remove inorganic salts, dried and recystallized from DMF-EtOH-H_2O to give the title compounds (3).

1, 6-**Dibenzoyldithiohydrazodicarbonamide** (3a). 76%, m. p. > 250℃. IR (KBr): ν3227, 1674, 1163cm^{-1}. ^{1}H NMR(DMSO−d_6): δ14. 22(s, 2H, NH), 12. 12 (s, 2H, NH), 7. 52−8. 06(m, 10H, ArH)ppm. Anal. Calcd. for $C_{16}H_{14}N_4O_2S_2$: C, 53. 63; H, 3. 91; N, 15. 64. Found: C, 53. 54; H, 3. 67; N, 15. 41.

1, 6-**Di (2-chlorobenzoyl) dithiohydrazodicarbonamide** (3b). 68%, m. p. > 250℃. IR(KBr): ν3234, 1685, 1161cm^{-1}. ^{1}H NMR(DMSO−d_6): δ13. 97(s, 2H, NH), 12. 60 (s, 2H, NH), 7. 46 − 7. 75 (m, 8H, ArH). And. Calcd. for $C_{16}H_{12}Cl_2N_4O_2S_2$: C, 44. 96; H, 2. 81; N, 13. 11. Found: C, 44. 95; H, 2. 73; N. 13. 07.

1, 6-**Di (4-nitrobenzoyl) dithiohydrazodicarbonamide** (3c). 96%, m. p. > 250℃. IR(KBr): ν3200, 1684, 1168 cm^{-1}. ^{1}H NMR(DMSO-d_6): δ13. 10(s, 2H, NH), 10. 60 (s, 2H, NH). 7. 02 − 7. 96 (m, 8H, ArH). Anal. Calcd. for $C_{16}H_{12}N_6O_6S_2$: C, 42. 85; H, 2. 68; N, 18. 75. Found: C, 42. 85; H, 2. 45; N, 18. 64.

1, 6-**Di (4-methoxybenzoyl) dithiohydrazodicarbonamide** (3d). 82%, m. p. > 250℃. IR(KBr): ν3275, 1659, 1171 cm^{-1}. ^{1}H NMR(DMSO-d_6): δ14. 25(s, 2H, NH), 11. 90(s, 2H, NH), 7. 01 − 7. 99(m, 8H, ArH), 3. 65(s, 6H, CH_3). Anal. Calcd. for $C_{18}H_{18}N_4O_4S_2$: C, 51. 67; H, 4. 31; N, 13. 40. Found: C, 51. 56; H, 4. 19; N, 13. 67.

1, 6-Di (3-nitrodenzoyl) dithiohydrazodicarbonamide (3e). 85%, m. p. > 252℃. IR(KBr): ν3228, 1675, 1173cm^{-1}. ^{1}H NMR(DMSO-d_6): δ13. 82 (s, 2H, NH), 11. 96 (s, 2H, NH), 7. 06 — 7. 98 (m, 8H, ArH). Anal. Calcd. for $C_{14}H_{12}N_6O_6S_2$: C, 42. 85; H, 2. 68; N, 18. 75. Found: C, 42. 86; H, 2. 58; N, 18. 59.

1, 6-Di (2-iodobenzoyl) dithiohydrazodicarbonamide (3f). 78%, m. p. > 258℃. IR(KBr): ν3227, 1688, 1163cm^{-1}. ^{1}H NMR(DMSO-d_6): δ13. 98 (s, 2H, NH). 12. 61 (s, 2H, NH), 7. 28 — 7. 76 (m, 8H, ArH). Anal. Calcd. for $C_{16}H_{12}I_2N_4O_2S_2$: C, 31. 49; H, 1. 98; N, 9. 18. Found: C, 31. 52; H, 1. 83; N, 9. 34.

1, 6-Di (4-bromobenzoyl) dithiohydrazodicarbonamide (3g). 86%, m. p. > 257℃. IR(KBr): ν3231, 1668, 1172cm^{-1}. ^{1}H NMR(DMSO-d_6): δ14. 01 (s, 2H, NH), 11. 95 (s, 2H, NH), 7. 35 — 7. 98 (m, 8H, ArH). Anal. Calcd. for $C_{16}H_{12}Br_2N_4O_2S_2$: C, 37. 23; H, 2. 34; N, 10. 85. Found: C, 37. 46; H, 2. 37; N, 10. 68.

1, 6-Di(2-furoyl)dithiohydrazodicarbonamide (3h). 89%, m. p. >254℃. IR (KBr): ν3318, 1673, 1158cm^{-1}. ^{1}H NMR(DMSO-d_6): δ13. 97(s, 2H, NH), 11. 98 (s, 2H, NH). 6. 72—6. 77(m, 2H, f_4-C-H), 7. 83—7. 88(m, 4H, f_3-and f_5-C-H). Anal. Cálcd. for $C_{12}H_{10}N_4O_4S_2$: C, 42. 59; H, 2. 98; N, 16. 56. Found: C, 42. 63; H, 3. 00; N, 16. 62.

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