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Phase Transfer Catalyzed Synthesis of 1-Aryloxyacetyl-4-(5-aryl-2-furoyl)-thiosemicarbazide Derivatives

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PHASE TRANSFER CATALYZED SYNTHESIS OF 1-ARYLOXYACETYL-4-(5-ARYL-2-FUROYL)-THIOSEMICARBAZIDE DERIVATIVES

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ABSTRACT: Eleven new 1-aryloxyacetyl-4-(5-aryl-2-furoyl)thiosemicarbazides were prepared in good to excellent yield under the condition of solid-liquid phase transfer catalysis at room temperature.

A series of 1,4-disubstituted thiosemicarbazides and their related heterocyclic compounds are associated with various kinds of biological activities[1]. In continuation of our earlier work on the synthesis of plant-growth regulators[2-5],

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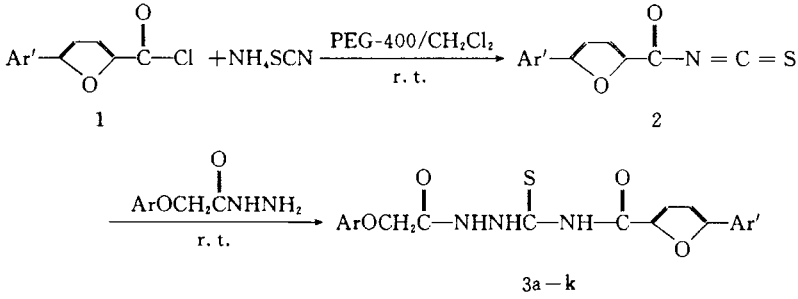
we report in this communication the preparation of some mew 1-aryloxyacetyl-4-(5-aryl-2-furoyl) thiosemicarbazides under the condition of solid-liquid phase transfer catalysis using polyethylene glycol-400 (PEG-400) as PTC.

We started the synthesis of the title compounds from 5-aryl-2-furoyl chloride (1), which is readily available by reaction of 5-aryl-2-furoic acid with thionyl chloride. Treatment of 1 with ammonium thiocyanate under the condition of solid-lipuid phase transfer catalysis using 3% PEG-400 as PTC gave 5-aryl-2-furoylisothiocyanate (2). This compound need not be isolated and reacted immediately with aryloxyacetic acid hydrazides affording the 1-aryloxyacetyl-4-(5-aryl-2-furoyl)thiosemicarbazides(3) in good to excellent yield. (Table 1).



Acyl isothiocyanates have been available under the liquid-liquid phase transfer catalysis using tetrabutylammonium bromide as PTC, however, in the presence of water, hydrolysis of the acyl chloride may occur, and the yield of the acyl isothiocyanate decreased[6]. Harrison has also reported that polymer-supported thiocyanate reacting with benzoyl chloride in benzene yielded benzoyl isothiocyanate, but the preparation of the polymer-supported reagent required long reaction times and vacuum conditions[7]. Therefore, the reaction was then

Table 1. Preparation of 1-aryloxyacetyl-4-(5-aryl-2-furoyl) thiosemicarbazides(3)

Product	Ar	Ar′	m. p. (℃)	Yield(%)※
3a	2-$CH_3C_6H_4$	3-$NO_2C_6H_4$	218. 5—219. 5	94
3b	4-$CH_3C_6H_4$	..	215—216	89
3c	2,4-$Cl_2C_6H_3$	..	228—229	88
3d	4-$CH_3OC_6H_4$	..	215—216. 5	90
3e	4-ClC_6H_4	..	206—207	95
3f	C_6H_5	..	191—192	93
3g	2-$CH_3C_6H_4$	4-$NO_2C_6H_4$	232—233	96
3h	4-$CH_3C_6H_4$	..	256—257	93
3i	C_6H_5	..	237—238	85
3j	4-$CH_3OC_6H_4$	..	289. 5—291	92
3k	4-ClC_6H_4	..	280—281	86

※ Yields of the isolated products were based on aryloxyacetic acid hydrazides.

operated under solid-liquid phase transfer catalysis condition using PEG-400 as catalyst. It was found that acyl chlorides were quanitatively converted to the corresponding acylisothiocyanates. These intermediates reacted with the aryloxyacetic acid hydrazides to give the title compounds 3 in high yield.

In summary, we described a facile and convenient method for the synthesis of 1, 4-disubstituted acylthiosemicarbazides 3 under solid-liquid phase transfer catalysis conditions. The advantages of the present method are manifold. First of all, the reaction conditions are remarkably mild; phase transfer catalyst PEG-400 is of low cost, relative nontoxicity[8], high stable and easy available; Campared with the reported method, this one is simple, high-yielding, has short reaction times and is applicable to industrial scale.

EXPERIMENT

Equipment. IR spectra were recorded with an Alpha Centauri FT－IR spectra photometer (using KBr pellets). ^{1}H-NMR spectra were recorded on FT-80A instrument, DMSO-d_6 was used as solvent and TMS as internal stardard. Elemental analysis were performed by a Carlo Erba 1106 Elemental Analysis instrument. Melting points were determined with a XT4 melting Point Determinator and were uncorrected.

Reagents. Ammonium thiocyanate, dichloromethane and PEG-400 were commercial products of highest reagent grade and used as received. 5-Aryl-2-furoyl chlorides 1 were prepared by refluxing 5-aryl-2-furoic acids[9] and an excess of thionyl chloride ,according to a previously reported procedure[10]. The known aryloxyacetic acid hydrazides were obtained by the procedure of Husain and Amir[11], with one modification in that potassium iodide was used as the catalyst.

General procedure. Powdered ammonium thiocyanate(4.5mmol),5-aryl-2-furoyl chloride (1, 3mmol), 0.054g PEG-400 (3% with respect to ammonium thiocyanate) and 15mL of dichloromethane were placed in a dried round-bottomed flask containing a magnetic stirrer bar and stirred at room temperature for 1h, then, the aryloxyacetic acid hydrazide (2.9mmol) was added, and the mixture were stirred for 0.5h. The corresponding thiosemicarbazide precipitates immediately. The product is filtered, washed with water to remove inorganic salts,dried and crystallized from DMF-EtOH-H_2O to give products(3).

3a:IR(KBr) 3299,3235,3130,2918,1668,1699,1548,1346,1251,1174 and 1033 cm^{-1};^{1}H-NMR(DMSO-d_6) δ 2.27(S,3H,CH_3),4.81(S,2H,CH_2),6.78(d,1H,

f_4-C－H), 7. 13－8. 02(m, 9H, Ar－H and f_3-C－H), 10. 93(s, 1H, NNHCS), 11. 73(s, 1H, CONHN), 12. 52(br, 1H, CONHCS); Anal. Calcd. for $C_{21}H_{18}N_4O_6S$: C, 55. 50; H, 3. 99; N, 12. 33. Fund: C, 55. 32; H, 3. 73; N, 12. 47.

3b: IR(KBr) 3334, 3267, 3117, 2916, 1670, 1702, 1550, 1335, 1257, 1163 and 1030 cm^{-1}; [1] H-NMR(DMSC-d_6) δ 2. 29(s, 3H, CH_3), 4. 88(s, 2H, CH_2), 7. 05－8. 13 (m, 9H, Ar－H and f_3-C－H), 6. 81(d, 1H, f_4-C－H), 10. 91(s, 1H, NNHCS), 11. 75(s, 1H, CONHN), 12, 58(br, 1H, CONHCS); Anal. Calcd. for $C_{21}H_{18}N_4O_6S$: C, 55. 50; H, 3. 99; N, 12. 33. Found: C, 55. 41; H, 3. 85; N, 12. 52.

3c: IR (KBr) 3274, 3206, 2916, 1666, 1673, 1526, 1346, 1250, 1163 and 1047 cm^{-1}; [1] H-NMR(DMSO-d_6) δ 5. 11(s, 2H, CH_2), 6. 96(d, 1H, f_4-C－H), 7. 03－8. 32 (m, 8H, Ar-H and f_3-C－H), 11. 05 (s, 1H, NNHCS), 11. 80 (s, 1H, CONHN), 12. 73(br, 1H, CONHCS); Anal. Calcd. for $C_{20}H_{14}Cl_2N_4O_6S$: C, 47. 16; H, 2. 77; N, 11. 00. Found: C, 47. 42; H, 2. 81; N, 10. 85.

3d: IR(KBr) 3329, 3266, 3174, 2919, 1667, 1679, 1545, 1345, 1247, 1155 and 1033 cm^{-1}; [1] H-NMR(DMSO-d_6) δ 3. 51(s, 3H, CH_3O), 4. 82(s, 2H, CH_2), 6. 97(d, 1H, f_4-C－H), 7. 15－8. 1(m, 9H, Ar－H and f_3-C－H), 10. 97(s, 1H, NNHCS), 11. 65 (s, 1H, CONHN), 12. 68(br, 1H, CONHCS); Anal. Calcd. for $C_{21}H_{18}N_4O_7S$: C, 53. 61; H, 3. 86; N, 11. 91. Found: C, 53. 84; H, 3. 73; N, 11. 67.

3e: IR (KBr) 3328, 3237, 2917, 1668, 1675, 1554, 1345, 1251, 1174 and 1038 cm^{-1}; [1] H-NMR(DMSO-d_6) δ 5. 10(s, 2H, CH_2). 6. 88(d, 1H, f_4-C－H), 7. 13－8. 32 (m, 9H, Ar－H and f_3-C－H), 11. 01 (s, 1H, NNHCS), 11. 74 (s, 1H, CONHN), 12. 68(br, 1H, CONHCS); Anal. Calcd. for $C_{20}H_{15}ClN_4O_6S$: C, 50. 69; H, 3. 19; N, 11. 82. Found: C, 50. 73; H, 3. 08; N, 11. 81.

3f: IR(KBr) 3310, 3225, 3172, 2926, 1671, 1685, 1543, 1350, 1245, 1176 and 1031 cm^{-1}; ^{1}H-NMR(DMSO-d_6) δ 5.10(s, 2H, CH_2), 6.73(d, 1H, f_4-C—H), 7.28—8.15(m, 10H, Ar—H and f_3-C—H), 11.03(s, 1H, NNHCS), 11.71(s, 1H, CONHN), 12.83(br, 1H, CONHCS); Anal. Calcd. for $C_{20}H_{16}N_4O_6S$: C, 54.54; H, 3.66; N, 12.72. Found: C, 54.33; H, 3.81; N, 12.76.

3g: IR(KBr) 3345, 3237, 3173, 2921, 1668, 1674, 1550, 1347, 1246, 1168 and 1038 cm^{-1}; ^{1}H-NMR(DMSO-d_6) δ 2.29(s, 3H, CH_3), 4.85(s, 2H, CH_2), 6.81(d, 1H, f_4-C—H), 7.08—8.12(m, 9H, Ar—H and f_3-C—H), 10.97(s, 1H, NNHCS), 11.68(s, 1H, CONHN), 12.63(br, 1H, CONHCS); Anal. Calcd. for $C_{21}H_{18}N_4O_6S$: C, 55.50; H, 3.99; N, 12.33, Found: C, 55.62; H, 3.91; N, 12.28.

3h: IR(KBr) 3286, 3176, 2917, 1668, 1672, 1554, 1345, 1251, 1179 and 1030 cm^{-1}; ^{1}H-NMR(DMSO-d_6) δ 2.27(s, 3H, CH_3), 4.83(s, 2H, CH_2), 6.79(d, 1H, f_4-C—H), 7.15—8.13(m, 9H, Ar—H and f_3-C—H), 11.01(s, 1H, NNHCS), 11.73(s, 1H, CONHN), 12.68(br, 1H, CONHCS); Anal. Calcd. for $C_{21}H_{18}N_4O_6S$: C, 55.50; H, 3.99; N, 12.33. Found: C, 55.62; H, 3.85; N, 12.41.

3i: IR(KBr) 3343, 3217, 2920, 1668, 1673, 1545, 1347, 1250, 1169 and 1033 cm^{-1}; ^{1}H-NMR(DMSO-d_6) δ 4.96(s, 2H, CH_2), 6.79(d, 1H, f_4-C—H), 7.13—8.22(m, 10H, Ar—H and f_3-C—H), 10.98(s, 1H, NNHCS), 11.68(s, 1H, CONHN), 12.74(br, 1H, CONHCS); Anal. Calcd. for $C_{20}H_{16}N_4O_6S$: C, 54.54; H, 3.66; N, 12.72. Found: C, 54.62; H, 3.48; N, 12.71.

3j: IR(KBr) 3343, 3215, 3169, 2920, 1668, 1674, 1544, 1351, 1255, 1164 and 1030 cm^{-1}; ^{1}H-NMR(DMSO-d_6) δ 3.47(s, 3H, CH_3O), 4.85(s, 2H, CH_2), 6.89(d, 1H, f_4-C—H), 7.06—8.17(m, 9H, Ar—H and f_3-C—H), 10.97(s, 1H, NNHCS),

11.68(s,1H,CONHN),12.71(br,1H,CONHCS);Anal. Calcd. for $C_{21}H_{18}N_4O_7S$: C,53.61;H,3.86;N,11.91. Found:C,53.72;H,3.83;N,11.85.

3k:IR(KBr) 3345,3267,3172,2921,1666,1675,1544,1351,1247,1167 and 1032 cm^{-1};[1] H-NMR(DMSO-d_6) δ 5.08(s,2H,CH_2),6.93(d,1H,f_4-C—H),7.15—8.26(m,9H,Ar—H and f_3-C—H),11.07(s,1H,NNHCS),11.69(s,1H,CONHN),12.73(br,1H,CONHCS);Anal. Calcd. for $C_{20}H_{15}ClN_4O_6S$:C,50.69;H,3.19;N,11.82. Found:C,50.81;H,3.05;N,11.79.

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