This article was downloaded by: [University of Western Ontario] On: 11 November 2014, At: 12:43 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

A Facile Method to 1,4-Diacyl Semicarbazides: Syntheses of 1-Aryloxyacetyl-4-(4-Chlorobenzoyl)-Thiosemicarbazides and Semicarbazides

Xicun Wang $^{\rm a}$, Zheng Li $^{\rm a}$, Yuxia Da $^{\rm a}$ & Jichou Chen $^{\rm a}$

^a Department of Chemistry, Northwest Normal University, Lanzhou, Gansu, 730070, P.R. China Published online: 04 Dec 2007.

To cite this article: Xicun Wang , Zheng Li , Yuxia Da & Jichou Chen (2000) A Facile Method to 1,4-Diacyl Semicarbazides: Syntheses of 1-Aryloxyacetyl-4-(4-Chlorobenzoyl)-Thiosemicarbazides and Semicarbazides, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:18, 3405-3411, DOI: <u>10.1080/00397910008086980</u>

To link to this article: http://dx.doi.org/10.1080/00397910008086980

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no

representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

A FACILE METHOD TO 1,4-DIACYL SEMICARBAZIDES: SYNTHESES OF 1-ARYLOXYACETYL-4-(4-CHLOROBENZOYL)-THIOSEMICARBAZIDES AND SEMICARBAZIDES

Xicun Wang, Zheng Li^{*}, Yuxia Da and Jichou Chen

Department of Chemistry, Northwest Normal University, Lanzhou, Gansu, 730070, P.R.China

ABSTRACT: A facile method to diacyl semicarbazides is described. Reactions of 4-chlorobenzoyl chloride with ammonium thiocyanate first, then with aryloxyacetic acid hydrazides under phase transfer catalysis give 1-aryloxyacetyl-4-(4-chlorobenzoyl)-thiosemicarbazides (Ia-h). Compounds Ia-h on treatment with potassium iodate under reflux result in the formation of 1-aryloxyacetyl-4-(4-chlorobenzoyl)-semicarbazides (IIa-h) in excellent yields.

Substituted semicarbazides have attracted much attention due to their diverse biological, industrial and agricultural importance. These compounds can be used as herbicides¹, plant growth regulators² and color developers³.

^{*} To whom correspondence should be addressed

It has been proved that 1,4-diacyl thiosemicarbazides can be easily prepared via phase transfer catalysis on treatment acyl chlorides with ammonium thiocyanate and acid hydrazides^{4,5}. However, 1,4-diacyl semicarbazides have not been obtained by means of analogous routes using ammonium cyanate instead of ammonium thiocyanate because of the unstability of intermediate acyl isocyanates.

Here we wish to report a facile method for preparation of 1,4-diacyl semicarbazides using 1,4-diacyl thiosemicarbazides as starting materials and potassium iodate as reagent.

Reactions of 4-chlorobenzoyl chloride with ammonium thiocyanate first, then with aryloxyacetic acid hydrazides in the presence of polyethylene glycol-400 (PEG-400) at room temperature give 1-aryloxyacetyl-4-(4-chlorobenzoyl)thiosemicarbazides (Ia-h) in 85-93% yields. Further, compounds Ia-h on treatment with potassium iodate in the suspension of water under reflux afford 1aryloxyacetyl-4-(4-chlorobenzoyl)-semicarbazides (IIa-h) in 86-96% yields (Scheme).

It is observed that potassium iodate reacts spontaneously with diacyl thiosemicarbazides **Ia-h** leading to diacyl semicarbazides **IIa-h** in the all of cases studied. Moreover, these solid-liquid reactions can be easily taken place in the aqueous slurry under gentle reflux. The color change of aqueous solution from colorless to violet because of the release of iodine can conveniently indicate the

1,4-DIACYL SEMICARBAZIDES

progress of the reaction. All reactions studied can be completed within half an hour. The products can be readily separated only by filtration.

Scheme



EXPERIMENTAL SECTION

IR spectra were recorded using KBr pellets on an Alpha Centauri FTIR spectrophotometer and ¹H NMR spectra on a FT-80A instrument using (CD₃)₂SO as solvent and Me₄Si as internal standard. Elemental analyses were performed on a Carlo-Erba 1106 Elemental Analysis instrument. Melting points were observed in an open capillary tube and uncorrected. 4-chlorobenzoyl chloride⁶ and aryloxyacetic acid hydrazides⁷ were prepared according to literature procedures. Ammonium thiocyanate and PEG-400 were commercially available and used as received.

General procedure for the preparation of compounds Ia-h

To a solution of 4-chlorobenzoyl chloride (0.53 g, 3 mmol) in 15 mL of methylene dichloride, ammonium thiocyanate (0.34 g, 4.5 mmol) and

Table 1 Physical data of compounds Ia-h and IIa-h										
		m.p.	Yield	Found(Calcd.) (%)						
Compd.	Ar	(°C)	(%)		H	Ν				
_		231-232	90	52.91	3.93	11.71				
Ia	C ₆ H ₅			(52.82)	(3.88)	(11.55)				
Ib		242-243	92	54.31	4.32	11.21				
	2-CH ₃ C ₆ H ₄			(54.04)	(4.27)	(11.12)				
Ic		207-208	89	54.12	4.29	11.24				
	3-CH ₃ C ₆ H ₄			(54.04)	(4.27)	(11.12)				
		180-181	93	54.26	4.38	11.36				
Id	4-CH ₃ C ₆ H ₄			(54.04)	(4.27)	(11.12)				
Ie		221-222	87	52.01	3.96	10.75				
	4-CH ₃ OC ₆ H ₄			(51.84)	(4.08)	(10.67)				
		251-252	86	47.20	3.19	13.93				
R	$2-O_2NC_6H_4$			(47.00)	(3.21)	(13.72)				
-		243-244	91	48.58	3.15	10.69				
Ig	4-CIC ₆ H ₄			(48.35)	(3.30)	(10.57)				
Ih		211-212	85	58.31	4.09	10.27				
	2-Naphtnyl			(58.04)	(3.90)	(10.15)				
IIa	C ₆ H ₅	209-210	96	55.41	4.11	12.17				
				(55.26)	(4.06)	(12.08)				
IIb	2-CH₃C ₆ H₄	239-240	91	56.80	4.58	11. 8 0				
				(56.53)	(4.47)	(11.63)				
		187-188	92	56.69	4.49	11.78				
ЦС	3-CH3C6H4			(56.53)	(4.47)	(11.63)				
		218-219	89	56.72	4.51	11.79				
Шđ	4-UH3U6H4			(56.53)	(4.47)	(11.63)				
IIe	4-CH₃OC ₆ H₄	174-175	86	54.29	4.31	11.29				
				(54.05)	(4.27)	(11.12)				
Пf	2-O2NC6H4	234-235	88	49.19	3.40	14.39				
				(48.93)	(3.34)	(14.27)				
Пg	4-ClC₅H₄	174-175	89	50.41	3.50	11.12				
				(50.28)	(3.43)	(10.99)				
IIh	2-Naphthyl	179-180	90	60.50	4.07	10.61				
				(60.38)	(4.05)	(10.56)				

	Table 2 Spectral data of compounds Ia-n and IIa-n								
Compd	IR (KBr, \vee , cm ⁻¹)		'H NMR (DMSO-d ₆ , δ ,ppm)						
Compa.	N-H	C=0	C=S	N-H	Ar	CH ₂	CH3		
Ia	3301	1702	1165	12.06(s,1H)	7.07-7.89	4.68			
	3241	1685		11. 76(s,1H)	(m,9H)	(s,2H)			
				11.01 (s,1H)					
Ib	3277	1681	1170	12.53(s,1H)	6.99-8.13	4.71	2.27		
	3174	1672		11.72(s,1H)	(m,8H)	(s,2H)	(s,3H)		
				10.99(s,1H)					
Ic	3280	1680	1166	12.56(s,1H)	7.08-8.16	4.69	2.25		
	3169	1671		11. 78(s,1H)	(m,8H)	(s,2H)	(s,3H)		
				10.91(s,1H)					
Id	3278	1683	1173	12.58(s,1H)	7.11-8.14	4.72	2.26		
	3182	1670		11.76(s,1H)	(m,8H)	(s,2H)	(s,3H)		
				10.98(s,1H)	_				
Ie	3281	1685	1172	12.59(s,1H)	7.12-8.15	4.73	3.40		
	3176	1674		11.75(s,1H)	(m,8H)	(s,2H)	(s,3H)		
				11.03(s,1H)					
If	3248	1688	1168	12.73(s,1H)	7.16-8.23	4.80			
	3157	1669		11.82(s,1H)	(m,8H)	(s,2H)			
				11.05(s,1H)					
Ig	3271	1681	1171	12.66(s,1H)	7.11-8.32	4.78			
	3168	1665		11.81(s,1H)	(m,8H)	(s,2H)			
				11.09(s,1H)					
Ih	3267	1689	1178	12.61(s,1H)	7.10-8.32	4.72			
	3218	1667		11.76(s,1H)	(m,11H)	(s,2H)			
				10.96(s,1H)					
Пя	3218	1713		11.82(s,1H)	7.02-8.21	4.76			
	3098	1628		10.91(s,2H)	(m,9H)	(s,2H)			
Пр	3220	1717		11.84(s,1H)	6.91 -8 .18	4.75	2.22		
	3152	1629		10. 88(s,2H)	(m,8H)	(s,2H)	(s,3H)		
Пc	3246	1708		11.90(s,1H)	7.10-8.09	4.72	2.24		
	3181	1630		10. 79(s,2H)	(m,8H)	(s,2H)	(s,3H)		
Πd	3257	1701		11.79(s,1H)	7.08-8.11	4.74	2.21		
	3177	1628		10.91(s,2H)	(m,8H)	(s,2H)	(s,3H)		
Ile	3242	1698		11.86(s,1H)	6.97-8.15	4.76	3.39		
	3074	1630		10. 83(s,2H) .	(m,8H)	(s,2H)	(s,3H)		
Πſ	3200	1687		11.85(s,1H)	6. 89-8 .23	4.78			
	3075	1623		10.92(s,2H)	(m,8H)	(s,2H)			
Πg	3237	1703		11. 87(s,1H)	7.01-8.13	4.71			
	3143	1631		10.79(s,2H)	(m,8H)	(s,2H)			
IIh	3242	1713		11.84(s,1H)	7.23-8.08	4.76			
	3057	1622		11.08(s,2H)	(m,11H)	(s,2H)			

Table 2 Spectral data of compounds Ia-h and IIa-h

polyethylene glycol-400 (0.04 g, 0.1 mmol) were added. The mixture was stirred for 1 h at room temperature. Then an aryloxyacetic acid hydrazide (2.95 mmol) was added and the reaction mixture was stirred for another 0.5 h at room temperature. To the resulting mixture, water (10 mL) was added so that the inorganic salts were dissolved, then the slurry was filtered, the solid was washed with water (3×5 mL) and recrystallized from DMF-EtOH-H₂O, and the product was given. The physical and spectral data of compounds Ia-h are shown in Table 1 and Table 2.

General procedure for the preparation of compounds IIa-h

A suspension of compound I (0.5 mmol) and potassium iodate (0.16 g, 0.75 mmol) in 30 mL of water was refluxed for 0.5 h. The resulting mixture was filtered, the solid was washed with water (3×5 mL) and recrystallized from DMF-EtOH-H₂O, then the product was given. The physical and spectral data of compounds **Ha-h** are shown in Table 1 and Table 2.

Acknowledgement: The authors thank the Natural Science Foundation of Gansu Province for the financial support of this work.

REFERENCES

- 1. Cross, B., US 4,026,697, 1977. (Chem. Abstr., 87: 84700).
- 2. Kirkpatrick, J.L. and Patel, N.R., US 4,272,279, 1981. (Chem. Abstr., 95:

115273).

- Katsumata, T.; Nakamura, T.; Takeuchi, K.; Morita, K.; Naruse, H. and Makuta, T., JP 10 62,9937, 1998. (Chem. Abstr., 128: 250644).
- 4. Wei, T.B.; Chen, J.C.; Wang, X.C. and Zhang, Y.M., J. Chem. Research (s), 1995, 138.
- Wang, X.C.; Wei, T.B.; Chen, J.C.; Borisova, E.Y.; Cherkashin, M.I. and Tolstikov, G.A., *Zh. Org. Khim.*, 1996, 32(3), 472. (Chem. Abstr., *125*: 300565).
- 6. Berliner, J.P. and Richter, S.B., US 3, 306, 726, 1967. (Chem. Abstr., 67: 81941).
- 7. Husain, M.I. and Amir, M., J. Indian Chem. Soc., 1986, 63, 317.

(Received in the USA 11 December 1999)