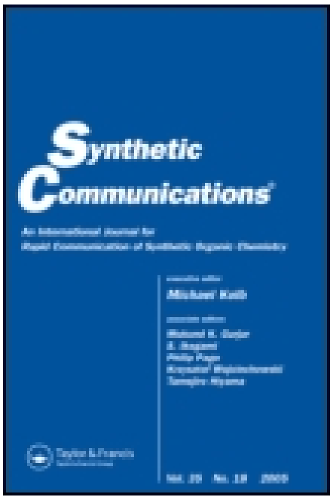
This article was downloaded by: [Washington University in St Louis]
On: 23 December 2014, At: 07:56
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Iodobenzene Diacetate Mediated Solid-State Synthesis of Heterocyclyl-1,3,4-oxadiazoles

V. S. Rao [a] & K. V. G. Chandra Sekhar [a]
[a] Chemistry Group , Birla Institute of Technology and Science , Pilani, 333 031, Rajasthan, India

Published online: 17 Aug 2006.

To cite this article: V. S. Rao & K. V. G. Chandra Sekhar (2004) Iodobenzene Diacetate Mediated Solid-State Synthesis of Heterocyclyl-1,3,4-oxadiazoles, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 34:12, 2153-2157, DOI: 10.1081/SCC-120038493

To link to this article: http://dx.doi.org/10.1081/SCC-120038493

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

SYNTHETIC COMMUNICATIONS®
Vol. 34, No. 12, pp. 2153–2157, 2004

Iodobenzene Diacetate Mediated Solid-State Synthesis of Heterocyclyl-1,3,4-oxadiazoles

V. S. Rao[*] and K. V. G. Chandra Sekhar

Chemistry Group, Birla Institute of Technology and Science,
Pilani, Rajasthan, India

ABSTRACT

A simple and efficient method has been developed for the oxidation of various heterocyclyl acylhydrazones **3** with iodobenzene diacetate (IBD) to heterocyclyl-1,3,4-oxadiazoles **4** in solid state. The reaction took place at room temperature within few minutes. The products were isolated by simple aqueous work-up in good yields.

Key Words: Iodobenzene diacetate; 1,3,4,-Oxadiazoles; Heterocyclyl acylhydrazones; Solid state synthesis.

INTRODUCTION

Presently, there is a considerable interest in organohypervalent iodine reagents because of their versatile use in solid-state organic reactions

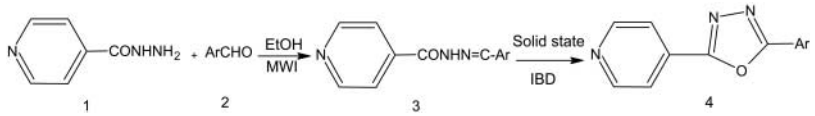
---

[*] Correspondence: V. S. Rao, Chemistry Group, Birla Institute of Technology and Science, Pilani 333 031, Rajasthan, India; E-mail: vsr@bits-pilani.ac.in.

DOI: 10.1081/SCC-120038493
0039-7911 (Print); 1532-2432 (Online)

www.dekker.com

(SSOR).[1] These reagents are used in the synthesis of several heterocyclic compounds in liquid and solid state.[2] Innumerable methods are reported in the literature for the oxidation of acyl hydrazones to 1,3,4-oxadiazoles such as oxidation with lead tetra acetate[3] or electrochemical oxidation of *N*-acylhydrazones.[4] The main drawback of these methods includes long reaction periods, high temperatures, and difficult work-up procedures. Keeping in view the importance of SSOR and biological activities of 1,3,4-oxadiazoles,[5–8] we herein report, simple and efficient conversion of heterocyclyl acylhydrazones to heterocyclyl-1,3,4-oxadiazoles using IBD under solid-state conditions.



RESULTS AND DISCUSSIONS

Conventional synthesis of isonicotinoyl hydrazones[9] has been modified by treating isonicotinic acid hydrazide (**1**) with various aromatic aldehydes (**2**) and subjected to microwave irradiation in domestic microwave oven over a period ranging from 1 to 3 min. After work-up, the resulting hydrazones were triturated with IBD in a pestle and mortar at room temperature without any solvent. After 5 min, sudden exothermic reaction took place with the evolution of nitrogen gas. Completion of reaction is marked by the change of state from solid to semi-solid/liquid with characteristic smell of iodobenzene. All the synthesized compounds (**4a–4l**) were characterized by elemental analysis (CHN) and spectral (IR, ^{1}H NMR) data. Formation of hydrazones (**3a–3l**) were confirmed by previously reported melting points and the absence of primary amino group at ~3350 cm^{-1} in IR spectra. IR spectral analysis of the final compounds (**4a–4l**) shows absorption band at ~1600 and ~1200 cm^{-1} due to C=N and C–O–C functions, respectively. In ^{1}H NMR spectra, peak at δ 7.99–8.33 and 6.95–7.66 indicates the presence of pyridyl ring and phenyl ring, respectively. Elemental (CHN) analysis indicated that the calculated and observed values were within the acceptable limits (±0.4%).

EXPERIMENTAL SECTION

Melting points were determined in open capillaries using Buchi 530 apparatus and are uncorrected. The purity of the compounds was checked

Table 1. Physical constants for compounds **3a–3l**.

Compound number	Ar	Reaction period (min)	Yield (%)	M.p. (lit.)[9] (°C)
3a	C_6H_5	2.0	80	162–164
3b	o-Cl–C_6H_4	1.5	79	210–212
3c	m-NO_2–C_6H_4	1.0	89	269–270 (269)
3d	p-NO_2–C_6H_4	1.0	93	190–191 (190–191)
3e	p-CH_3–C_6H_4	2.5	87	196–197
3f	p-OCH_3–C_6H_4	2.5	91	162–163 (162)
3g	o-OH–C_6H_4	3.0	87	265–266
3h	–CH=CH–C_6H_5	2.5	72	199–201
3i	p-OH–m-OCH_3–C_6H_3	3.0	96	200–202 (200–201)
3j	p-Cl–C_6H_4	2.0	81	212–214
3k	m-CH_3–C_6H_4	2.5	95	206–207
3l	m-Cl–C_6H_4	2.0	89	221–223

Table 2. Physical constants of compounds **4a–4l**.[a]

Compound number	Ar	Yield (%)	M.p. (°C)
4a	C_6H_5	87	152–154
4b	o-Cl–C_6H_4	88	102–104
4c	m-NO_2–C_6H_4	81	123–124
4d	p-NO_2–C_6H_4	80	203–205
4e	p-CH_3–C_6H_4	81	134–135
4f	p-OCH_3–C_6H_4	82	184–185
4g	o-OH–C_6H_4	84	230–233
4h	–CH=CH–C_6H_5	86	151–153
4i	p-OH–m-OCH_3–C_6H_3	93	222–224
4j	p-Cl–C_6H_4	92	174–175
4k	m-CH_3–C_6H_4	90	124–125
4l	m-Cl–C_6H_4	86	142–144

[a] All new compounds show satisfactory C, H, N analysis.

by TLC using silica gel-coated Al plates (Merck). Microwave irradiations were carried out in domestic microwave oven (LG Electronics, model MG-605AP, 2450 MHZ, 900 W). IR spectra were recorded using KBr pellets on a Jasco IR Repot-100 infrared spectrophotometer (ν_{max} in cm^{-1}); ^{1}H NMR spectra on Bruker DRX300 spectrometer using TMS as internal standard

Table 3. IR and ^{1}H NMR spectral data of compounds **4a**–**4l**.

Compound number	IR (KBr) (cm^{-1})		
	C=N	C–O–C	^{1}H NMR (CDCl$_3$) δ (ppm)
4a	1,620	1,210	7.31–7.42 (m, 5H, Ar-H) 8.02–8.14 (m, 4H, Py)
4b	1,600	1,180	7.27–7.35 (m, 4H, Ar-H) 8.12–8.22 (m, 4H, Py)
4c	1,650	1,190	7.49–7.57 (m, 4H, Ar-H) 8.06–8.15 (m, 4H, Py)
4d	1,640	1,210	7.57–7.66 (m, 4H, Ar-H) 8.11–8.21 (m, 4H, Py) 2.46 (s, 3H, CH$_3$)
4e	1,590	1,200	7.26–7.38 (m, 4H, Ar-H) 8.02–8.16 (m, 4H, Py) 3.91 (s, 3H, OCH$_3$)
4f	1,610	1,220	7.04–7.26 (m, 4H, Ar-H) 7.99–8.12 (m, 4H, Py) 5.25 (br s, 1H, OH)
4g	1,640	1,200	6.82–6.95 (m, 4H, Ar-H) 8.10–8.21 (m, 4H, Py) 6.65 (s, 2H, –CH=CH–)
4h	1,650	1,200	7.24–7.36 (m, 5H, Ar-H) 8.02–8.11 (m, 4H, Py) 3.82 (s, 3H, OCH$_3$)
4i	1,640	1,220	5.71 (br s, 1H, OH) 6.95–7.21 (m, 3H, Ar-H) 8.12–8.21 (m, 4H, Py)
4j	1,610	1,180	7.25–7.32 (m, 4H, Ar-H) 8.02–8.14 (m, 4H, Py) 2.48 (s, 3H, CH$_3$)
4k	1,620	1,190	7.17–7.26 (m, 4H, Ar-H) 8.21–8.30 (m, 4H, Py)
4l	1,600	1,200	7.27–7.33 (m, 4H, Ar-H) 8.01–8.12 (m, 4H, Py)

(chemical shifts in δ, ppm), and elemental analysis on a Carla Erba 1108 elemental analyzer.

Heterocyclyl acylhydrazones 3: general procedure. Isonicotinic acid hydrazide **1** (5 mmol), corresponding benzaldehyde **2** (5 mmol) in ethanol with a few drops of glacial acetic acid were subjected to microwave irradiation at 60% power output (540 W) for the period indicated in Table 1. After completion of the reaction (monitored by TLC), the reaction mixture was kept in the refrigerator overnight. The resultant product was filtered, washed with water, and recrystallized from ethanol to afford **3** (Table 1).

Oxidation of heterocyclyl acylhydrazones 3 to heterocycyl-1,3,4-oxadiazoles 4: general procedure. A mixture of appropriate heterocyclyl acylhydrazone **3** (2 mmol) and IBD (2.4 mmol) was ground by pestle and mortar at room temperature. After 5 min, evolution of nitrogen gas occurred. The solid was diluted with water, filtered and recrystallized from ethanol to afford **4**. Characterization data is given in Tables 2 and 3.

ACKNOWLEDGMENT

We wish to thank the RSIC, CDRI, Lucknow, India for analytical and spectral data.

REFERENCES

1. Perrin, R.; Lamartine, R.; Perrin, M.; Thozet, A. *Organic Solid State Chemistry*; Desiraju, G.R., Ed.; Elsevier: Amsterdam, 1987; 217.
2. Zhdankin, V.V.; Stang, P.J. Chem. Rev. **2002**, *102*, 2523–2584.
3. Stolle, R. J. Prakt. Chem. **1906**, *73*, 77.
4. Chiba, T.; Mitsuhiro, O. J. Org. Chem. **1992**, *57*, 1375.
5. Sharma, R.S.; Bahd, S.C. J. Indian Chem. Soc. **1982**, *59*, 877.
6. Ramalingam, T.; Deshmukh, A.A.; Sattur, P.B.; Sheth, U.K.; Naik, S.R. J. Indian Chem. Soc. **1981**, *58*, 269.
7. Ram, V.J.; Pandey, H.N. J. Indian Chem. Soc. **1974**, *51*, 634.
8. Ponticello, G.S.; Engelhardt, E.L.; Baldwin, J.J. J. Hetrocyclic Chem. **1980**, *17*, 425.
9. Bayer, A.G. GB Pat. 737271, 1955.

Received in India February 10, 2004

Downloaded by [Washington University in St Louis] at 07:56 23 December 2014

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/ Order Reprints" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Request Permission/Order Reprints

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SCC120038493