European Journal of Chemistry 3 (2) (2012) 208-210

European Journal of Chemistry

Journal homepage: www.eurjchem.com

An efficient and facile ring closure of 2'-hydroxychalcones under irradiation of tungsten light

Sainath Zangade[a,*], Avinash Shinde[b], Arvind Patil[b] and Yeshwant Vibhute[b]

[a] *Department of Chemistry, Madhavrao Patil Mahavidyalaya, Palam, Prabhani, Maharashtra, 431720, India*
[b] *Laboratory of Organic Synthesis, Department of Studies in Chemistry, Yeshwant Mahavidyalaya, Nanded, Maharashtra, 431602, India*

**Corresponding author at: Department of Chemistry, Madhavrao Patil Mahavidyalaya, Palam, Prabhani, Maharashtra, 431720, India. Tel.: +91.246.2254170; fax: +91.246.2253726. E-mail address: drsbz@rediffmail.com (S. Zangade).*

ARTICLE INFORMATION

Received: 27 December 2011
Received in revised form: 01 January 2012
Accepted: 20 February 2012
Online: 30 June 2012

KEYWORDS

2-Pyrazolines
Tungsten light
Photocyclisation
Green chemistry
2-Methoxyethanol
2'-Hydroxychalcones

ABSTRACT

An efficient, green and facile reaction has been reported between 2'-hydroxychalcones and hydrazine hydrate in 2-methoxyethanol in presence of catalytic amount of acetic acid under irradiation of tungsten light to afford 2-pyrazolines. Present methodology presents several advantages including simple reaction procedure, no need of catalyst/special apparatus and short reaction time giving quantitative yields of product.

1. Introduction

Amongst five-membered heterocycles, pyrazolines represent a class of compounds of great importance in heterocyclic chemistry [1-2]. These compounds have intrinsic biological activities and constitute the structural feature of many bioactive compounds [3-7]. Pyrazolines also exhibit excellent film-forming properties [8]. A classical synthesis of these compounds involves the condensation of α,β-unsaturated carbonyl compounds with hydrazines [9]. Pyrazoline also synthesized by using microwave irradiation and ultrasound irradiation [10-11]. Recently various modified method have been reported for the synthesis of 2-pyrazoline by using different catalyst such as $KHSO_4H_2O/SiO_2$ [12], porous calcium hydroxyl appatite [13], mercuric acetate [14], tungsto-phosphoric acid [15], Zn [16] and Lewis acid/bases [17]. The combination of solvents, costly chemicals/catalyst and long reaction time makes these methods environmentally hazardous. Thus utilization of nontoxic chemicals, renewable materials and simple reaction conditions are the key issues of green synthetic strategy. In view of these observations and in continuation of earlier research work [18-20], it was thought worthwhile to develop simple, facile, and efficient methodology for the synthesis of 2-pyrazolines by condensation of 2'-hydroxychalcones with hydrazine hydrate in 2-methoxy-ethanol as reaction solvent under irradiation of tungsten light (Scheme 1). The structures of these compounds were characterized by spectroscopic technique.

2. Experimental

2.1. Instrumentation

Melting points were determined in an open capillary tube and are uncorrected. IR spectra were recorded in KBr pellets on a Perkin-Elmer FT-IR Shimadzu spectrometer. ^1H and ^{13}C NMR spectra were obtained in DMSO-d_6 on Avance 300 MHz spectrometer using TMS as an internal standard. The mass spectra were recorded on EI-Shimadzu-GC-MS spectrometer. Elemental analyses were performed on a Carlo Erba 106 Perkin-Elmer model 240 analyzer.

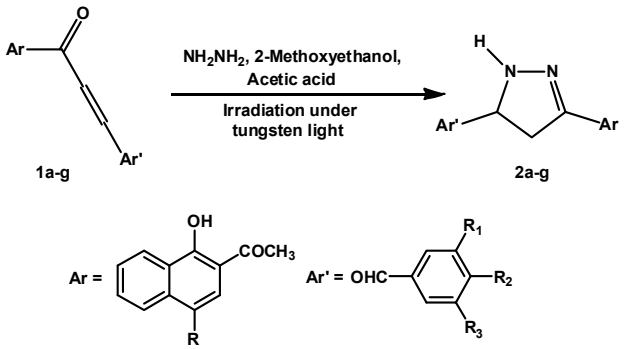
2.2. Synthesis

2.2.1. Synthesis of pyrazolines

In 50 mL beaker, a mixture of 2'-hydroxychalcones **1a-g** (10.0 mmol), hydrazine hydrate (50 mmol) was dissolved in 2-methoxyethanol (20 mL) by warming. To this hot reaction solution 0.001 mmol of acetic acid was added and irradiated under tungsten light (100 Watt) for 25-32 min, and progress of reaction was monitored on TLC. After completion of reaction, the resultant mixture was poured with stirring into water (20 mL). The precipitate formed was filtered through simple büchner funnel, washed with cold water and crystallized from ethanol to yield 2-pyrazolines (Scheme 1).

2-[5-(4-Methoxy-phenyl)-4,5-dihydro-1H-pyrazol-3-yl]-naphthalen-1-ol (**2a**): UV/VIS (λ_{max}, nm): 412, 328. FT-IR (KBr cm^{-1}): 1592 (C=N), 1472, 1542 (C=C), 1232 (C-N). ^1H NMR (300 MHz, DMSO-d_6, δ, ppm): 12.47 (s, 1H, OH), 7.83-7.63 (m, 10H, Ar-H),6.82 (s, 1H, NH), 3.27 (dd, J = 5.0 Hz, 17.5 Hz, 1H, H_A), 3.63 (dd, J = 12.1 Hz, 17.5 Hz, 1H, H_B), 4.81 (dd, J = 5.0 Hz, 12.0 Hz, 1H, H_X), 3.78 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 160.13 (C *of* Ar-OCH_3), 154.83 (C *of* Ar-OH), 152.27 (C *of* C=N), 138.28 (Ar-C), 137.92 (Ar-C), 136.28 (Ar-C), 135.83 (Ar-C), 134.72 (Ar-C), 128.63 (Ar-C), 128.47 (Ar-C), 127.79 (Ar-C), 127.67 (Ar-C), 126.93 (Ar-C), 126.82 (Ar-C), 124.17 (Ar-C), 122.34 (Ar-C), 117.28 (Ar-C), 56.71 (C *of* OCH_3), 52.13 (C *of* CH), 44.75 (C *of* CH_2). MS (EI, *m/z* (%)): 318 (M^+, 100).

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online)
DOI:10.5155/eurjchem.3.2.208-210.581



Compound	R	R_1	R_2	R_3
2a	H	H	OCH_3	H
2b	H	OCH_3	OCH_3	Br
2c	Br	OCH_3	OCH_3	Br
2d	I	H	OCH_3	H
2e	H	H	F	H
2f	H	H	Cl	H
2g	I	OCH_3	OCH_3	Br

Scheme 1

Anal. calcd. for $C_{20}H_{18}O_2N_2$: C, 75.47; H, 5.66. Found: C, 75.58; H, 5.59 %.

2-[5-(3-Bromo-4,5-dimethoxy-phenyl)-4,5-dihydro-1H-pyrazol-3-yl]-naphthalen-1-ol (**2b**): UV/VIS (λ_{max}, nm): 409, 326. FT-IR (KBr cm^{-1}): 1588 (C=N), 1477, 1538 (C=C), 1228 (C-N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 12.55 (s, 1H, OH), 7.73-7.37 (m, 8H, Ar-H), 6.88 (s, 1H, NH), 3.29 (dd, *J* = 5.1 Hz, 17.5 Hz, 1H, H_A), 3.68 (dd, *J* = 12.0 Hz, 17.5 Hz, 1H, H_B), 4.84 (dd, *J* = 5.0 Hz, 12.0 Hz, 1H, H_X), 3.83 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 154.67 (C *of* Ar-OH), 152.56 (C *of* C=N),152.29 (C *of* Ar-OCH_3), 149.47 (C *of* Ar-OCH_3) 138.23 (Ar-C), 137.83 (Ar-C), 128.42 (Ar-C), 127.48 (Ar-C), 127.23 (Ar-C), 125.31 (Ar-C), 124.93 (Ar-C), 121.27 (Ar-C), 118.89 (Ar-C), 116.74 (Ar-C), 115.39 (Ar-C), 113.79 (Ar-C), 109.17 (C *of* Ar-Br), 57.84 (C *of* OCH_3), 56.45 (C *of* OCH_3), 53.28 (C *of* CH), 43.98 (C *of* CH_2). MS (EI, *m/z* (%)): 427 (M^+, 100). Anal. calcd. for $C_{21}H_{19}O_3N_2Br$: C, 59.01; H, 4.44. Found: C, 59.13; H, 4.51 %.

4-Bromo-2-[5-(3-bromo-4,5-dimethoxy-phenyl)-4,5-dihydro-1H-pyrazol-3-yl]-naphthalen-1-ol (**2c**): UV/VIS (λ_{max}, nm): 411, 329. FT-IR (KBr cm^{-1}): 1590 (C=N), 1472, 1545 (C=C), 1231 (C-N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 12.62 (s, 1H, OH), 7.89-7.43 (m, 7H, Ar-H), 6.81 (s, 1H, NH), 3.26 (dd, *J* = 5.1 Hz, 17.5 Hz, 1H, H_A), 3.64 (dd, *J* = 12.0 Hz, 17.5 Hz, 1H, H_B), 4.89 (dd, *J* = 5.1 Hz, 12.1 Hz, 1H, H_X), 3.86 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 155.31 (C *of* Ar-OH), 152.74 (C *of* C=N), 152.39 (C *of* Ar-OCH_3), 149.42 (C *of* Ar-OCH_3) 139.29 (Ar-C), 137.13 (Ar-C), 129.46 (Ar-C), 128.86 (Ar-C), 127.45 (Ar-C), 126.30 (Ar-C), 124.97 (Ar-C), 121.71 (Ar-C), 118.28 (Ar-C), 116.71 (Ar-C), 116.39 (Ar-C), 115.39 (C *of* Ar-Br), 109.22 (C *of* Ar-Br), 57.92 (C *of* OCH_3), 56.42 (C *of* OCH_3), 53.29 (C *of* CH), 43.96 (C *of* CH_2). MS (EI, *m/z* (%)): 506 (M^+, 100). Anal. calcd. for $C_{21}H_{18}O_3N_2Br_2$:C, 49.80; H, 3.55. Found: C, 49.72; H, 3.59 %.

4-Iodo-2-[5-(4-methoxy-phenyl)-4,5-dihydro-1H-pyrazol-3-yl]-naphthalen-1-ol (**2d**): UV/VIS (λ_{max}, nm): 413, 331. FT-IR (KBr cm^{-1}): 1592 (C=N), 1476, 1540 (C=C), 1230 (C-N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 12.58 (s, 1H, OH), 7.81-7.34 (m, 9H, Ar-H), 6.84 (s, 1H, NH), 3.28 (dd, *J* = 5.1 Hz, 17.5 Hz, 1H, H_A), 3.67 (dd, *J* = 12.1 Hz, 17.5 Hz, 1H, H_B), 4.87 (dd, *J* = 5.1 Hz, 12.1 Hz, 1H, H_X), 3.74 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 159.97 (C *of* Ar-OCH_3), 155.14 (C *of* Ar-OH), 152.32 (C *of* C=N), 137.83 (Ar-C), 137.97 (Ar-C), 136.45 (Ar-C), 136.83 (Ar-C), 135.62 (Ar-C), 129.36 (Ar-C), 128.41 (Ar-C), 128.79 (Ar-C), 127.17 (Ar-C), 126.90 (Ar-C), 126.79 (Ar-C), 124.28 (Ar-C), 123.64 (Ar-C), 108.12 (C *of* Ar-I), 56.73 (C *of* OCH_3), 52.17 (C *of* CH), 44.63 (C *of* CH_2). MS (EI, *m/z* (%)): 444 (M^+, 100). Anal. calcd. for $C_{20}H_{17}O_2N_2I$: C, 54.05; H, 3.82. Found: C, 54.17; H, 3.78 %.

2-[5-(4-Fluoro-phenyl)-4,5-dihydro-1H-pyrazol-3-yl]-4-iodo-naphthalen-1-ol (**2e**): UV/VIS (λ_{max}, nm): 410, 330. FT-IR (KBr cm^{-1}): 1588 (C=N), 1468, 1542 (C=C), 1228 (C-N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 12.48 (s, 1H, OH), 7.88-7.37 (m, 9H, Ar-H), 6.87 (s, 1H, NH), 3.30 (dd, *J* = 5.2 Hz, 17.6 Hz, 1H, H_A), 3.70 (dd, *J* = 12.1 Hz, 17.6 Hz, 1H, H_B), 4.89 (dd, *J* = 5.2 Hz, 12.1 Hz, 1H, H_X). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 155.23 (C *of* Ar-OH), 152.48 (C *of* C=N), 137.18 (Ar-C), 137.82 (Ar-C), 136.25 (Ar-C), 136.96 (Ar-C), 135.27 (Ar-C), 129.31 (Ar-C), 129.57 (Ar-C), 128.62 (Ar-C), 127.19 (Ar-C), 127.91 (Ar-C), 126.73 (Ar-C), 125.57 (Ar-C), 124.88 (Ar-C),122.65 (Ar-C), 109.98 (C *of*Ar-I), 52.26 (C *of* CH), 44.60 (C *of* CH_2). MS (EI, *m/z* (%)): 432 (M^+, 100). Anal. calcd. for $C_{19}H_{14}N_2OIF$: C, 52.77; H, 3.24. Found: C, 52.84; H, 3.27 %.

2-[5-(4-Chloro-phenyl)-4,5-dihydro-1H-pyrazol-3-yl]-4-iodo-naphthalen-1-ol (**2f**): UV/VIS (λ_{max}, nm): 409, 328. FT-IR (KBr cm^{-1}): 1590 (C=N), 1475, 1552 (C=C), 1232 (C-N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 12.56 (s, 1H, OH), 7.92-7.39 (m, 9H, Ar-H), 6.90 (s, 1H, NH), 3.28 (dd, *J* = 5.1 Hz, 17.6 Hz, 1H, H_A), 3.69 (dd, *J* = 12.1 Hz, 17.6 Hz, 1H, H_B), 4.87 (dd, *J* = 5.1 Hz, 12.1 Hz, 1H, H_X). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 156.14 (C *of* Ar-OH), 152.67 (C *of* C=N), 138.41 (Ar-C), 138.63 (Ar-C), 136.87 (Ar-C), 135.19 (Ar-C), 135.54 (Ar-C), 133.27 (Ar-C), 131.39 (Ar-C), 128.50 (Ar-C), 127.47 (Ar-C), 127.98 (Ar-C), 126.25 (Ar-C), 125.52 (Ar-C), 124.90 (Ar-C), 122.69 (Ar-C) 109.83 (C *of* Ar-I), 53.16 (C *of* CH), 44.65 (C *of* CH_2). MS (EI, *m/z* (%)): 448 (M^+, 100). Anal. calcd. for $C_{19}H_{14}N_2OICl$: C, 50.89; H, 3.12. Found: C, 50.82; H, 3.15 %.

2-[5-(3-Bromo-4,5-dimethoxy-phenyl)-4,5-dihydro-1H-pyrazol-3-yl]-4-iodo-naphthalen-1-ol (**2g**): UV/VIS (λ_{max}, nm): 410, 330. FT-IR (KBr cm^{-1}): 1592 (C=N), 1470, 1560 (C=C), 1234 (C-N). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 12.48 (s, 1H, OH), 7.78-7.34 (m, 7H, Ar-H), 6.92 (s, 1H, NH), 3.32 (dd, *J* = 5.2 Hz, 17.5 Hz, 1H, H_A), 3.70 (dd, *J* = 12.1 Hz, 17.5 Hz, 1H, H_B), 4.88 (dd, *J* = 5.2 Hz, 12.1 Hz, 1H, H_X), 3.88 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 154.88 (C *of* Ar-OH), 152.48 (C *of* C=N), 151.89 (C *of* Ar-OCH_3), 149.50 (C *of* Ar-

OCH_3) 138.37 (Ar-C), 138.86 (Ar-C), 128.25 (Ar-C), 127.92 (Ar-C), 126.13 (Ar-C), 125.75 (Ar-C), 124.40 (Ar-C), 121.27 (Ar-C), 118.59 (Ar-C), 114.94 (Ar-C), 115.80 (Ar-C), 113.19 (Ar-C), 109.22 (C *of* Ar-Br), 57.66 (C *of* OCH_3), 56.40 (C *of* OCH_3), 53.29 (C *of* CH), 43.85 (C *of* CH_2). MS (EI, *m/z* (%)): 553 (M^+, 100). Anal. cacld. for $C_{21}H_{18}O_3N_2IBr$: C, 45.56; H, 3.25. Found: C, 45.64; H, 3.18 %.

3. Result and discussion

In present communication, we have described the photocyclisation of 2'-hydroxychalcones by the reaction of **1a-g** with hydrazine hydrate in presence of catalytic amount of acetic acid using tungsten light irradiation to obtained 2-pyrazolines **2a-g**. A variety of methods have been reported for the preparation of this class of compounds. However in spite of their potential utility, some of the reported methods suffer from drawbacks such as long reaction time, cumbersome product isolation procedure and environmental concerns. The use of tungsten light can be considered as ideal green route for synthesis of 2-pyrazolines since they are not expensive, could be successfully used in place of toxic or expensive chemicals to over come the activation energy in organic synthesis.

Initially we attempted the condensation of 4-bromo-2-[5-(3-bromo-4,5-dimethoxy-phenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-naphthalen-1-ol (**1c**) with hydrazine hydrate using acetic acid in 2-methoxyethanol in combination with tungsten light irradiation. The reaction went completion within 25 min and corresponding product **2c** obtained in 92% yield (Table 1). In view of these results we focus our attention towards variety substituted 2-hydroxychalcones. In all cases reaction proceeds efficiently giving excellent yields of product. Structures of compounds **2a-g** have been elucidated by UV, IR, ^{1}H NMR and^{13}C NMR measurements. Their IR spectra show absence of carbonyl absorption band and the appearance of characteristic absorption band for $\nu_{C=N}$ at 1592-1588 cm^{-1}. In ^{1}H NMR spectra show an ABX spin system was observable, H_A, H_B and H_X appear as pair of doublets near δ 3.29, 3.66 and 4.85 ppm with J_{AB} = 17.5 Hz, J_{AX} = 5.1 Hz, J_{BX} = 12.1 Hz and singlet of 2-H pyrazolines around at δ 6.87 ppm, respectively. In ^{13}C NMR spectra, the chemical shifts value of carbon atoms C-3 (152 ppm), C-4 (44 ppm), and C-5 (53-52 ppm).

Table 1. Synthesis of 2-pyrazolines under irradiation of tungsten light (100 watt).

Product	Time (min)	Melting point (°C)	Yield (%)
2a	32	148-150	82
2b	28	160-163	86
2c	25	177-179	92
2d	30	153-155	84
2e	28	128-130	88
2f	30	136-137	85
2g	26	186-188	90

4. Conclusion

We have developed a simple practical procedure for synthesis of 2-pyrazolines from 2'-hydroxychalcones using tungsten light. The process is simple, efficient, and economical. It is also consistent with the green chemistry approach because it does not need heating.

Acknowledgements

The authors gratefully acknowledge University Grant Commission New Delhi for sanctioning major research grant (No. 38-267/2009). The authors are also thankful to Principal, Yeshwant Mahavidyalaya, Nanded, for providing laboratory facilities and Director Indian Institute of Chemical Technology (IICT), Hyderabad, for providing necessary instrumental facilities.

References

[1]. Elguero, J. In Comprehensive Heterocyclic Chemistry. Karitzyky, A. R.; Ress, C. W. (Eds.) Pergamon: Oxford, 1984, *5*, 167-303.
[2]. Elguero, J. In Comprehensive Heterocyclic Chemistry II. Karitzyky, A. R.; Ress, C. W.; Scriven, E. F. (Eds.) Pergamon: Oxford, 1996, *3*, 1-76.
[3]. Girisha, K. S.; Kalluraya, B.; Narayana, V.; Padmashree, P. *Eur. J. Med. Chem*. **2010**, *45*, 4640-4644.
[4]. Banday, A. H.; Mir, B. P.; Lone, I. H.; Suri, K. A.; Sampathkumar, H. M. *Streoid* **2010**, 75, 805-809.
[5]. Kaplancikli, Z. A.; Turan-Zitouni, G.; Ozdemir, A.; Can, O. D.; Chevallet, P. *Eur. J. Med. Chem.* **2009**, *44*, 2606-2610.
[6]. Wanare, G.; Aher, R.; Kawathekar, N.; Ranjan, R.; Kaushik, N. K.; Sahal, D. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 4675-4678.
[7]. Shivakumar, P. M.; Seenivasan, S. P.; Kumar, V.; Doble, M. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 3169-3172.
[8]. Zhang, X. H.; Wu, S. K.; Gao, Z. Q.; Lee, S. T.; Kwong, H. L. *Thin Solid Film* **2000**, *371*, 40-46.
[9]. Seebacher, W.; Michi, G.; Belaj, F.; Brun, R.; Saf, R.; Weis, R. *Tetrahedron* **2003**, *59*, 2811-2819.
[10]. Kidwai, M.; Misra, P. *Synth. Commun*. **1999**, *29*, 3237-3250.
[11]. Li, J. -T.; Zhang, X. -H.; Lin, Z. -P. *Beilstein J. Org. Chem*. **2007**, *3,* 13-13.
[12]. Kapoor, K. K.; Ganai, B. A.; Kumar, S; Andotra, C. S. *Synth. Commun*. **2006**, *36*, 2727-2735.
[13]. Atir, R.; Mallouk, S.; Bougrin, K.; Soufiaoui. *Synth. Commun.* **2006**, *36*, 111-120.
[14]. Rai, K. M. L.; Linganna, N. *Synth. Commun*. **1997**, *21*, 3737-3744.
[15]. Fazaeli, R.; Aliyan, H.; Mallakpour, S.; Rafiee, Z.; Bordbar, M. *Chinese J. Catal*. **2011**, *32*, 582-588.
[16]. Alex, K.; Tilack, A.; Schwarz, N.; Beller, M. *Org. Lett.* **2008**, *10*, 2377-2379.
[17]. Krishna, P. R.; Sekhar, E. R.; Morgin, F. *Tetrahedron Lett.* **2008**, *49*, 6768-6772.
[18]. Vibhute, A.; Mokle, S.; Karamunge, K.; Gurav, V.; Vibhute, Y. *Chinese Chemical Lett.* **2010**, *21*, 914-917.
[19]. Zangade, S.; Mokle, S.; Vibhute, A.; Vibhute, Y. *Chem. Sci. J.* **2011**, *2*, 1-6.
[20]. Shinde, A. T.; Zangade, S. B.; Chavan, S. B.; Vibhute, A. Y.; Nalwar, Y. S.; Vibhute, Y. B. *Synth. Commun.* **2010**, *40*, 3506-3513.