Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2010, 1 (1): 124-128

A selective iodination of some substituted *o*-hydroxychalcones by using iodine and iodic acid

Smita V. Gurav, Archana Y. Vibhute, Sainath B. Zangade, Shyam S. Mokle and Yeshwant B.Vibhute

P. G. Department of Studies in Chemistry, Yeswant Mahavidyalaya Nanded(MS), India

---

ABSTRACT

A variety of ortho hydroxy substituted chalcones were selectively mono or diiodinated using iodine and iodic acid within 20-30 min with excellent yield of products. Iodine do not adds to ethylenic bond of substituted o-hydroxychalcones.

Key words*:* *O*-hydroxychalcones, iodine, iodic acid and selective iodination.

INTRODUCTION

Iodo aromatic compounds are valuable intermediate in organic synthesis, medicine and biochemistry [1-4]. Number of iodinating reagents such as iodine/$Na_2S_2O_8$ [5], iodine-$(NH_4)_2S_2O_8$-$CUCl_2$-Ag_2SO_4[6], NaOCl-NaI [7], Bis (pyridine iodonium (1) tetrafluoro borate-CF_3SO_3H [8], iodine silver sulphate [9], DMSO-H^+-I_2 [10], trichloro-isocyanuric acid/I_2/wet SiO_2 [11] regent have been reported for electrophilic aromatic substitution.

Regioselective iodination of aromatic compounds is reported by using different reagents such as ammonium iodine and oxone [12], iodine and nitrogen dioxide [13], Fe (NO_3) 1.5 N_2O_4/charcoal [14], N- chlorosuccinimide and NaI [15] and KI and tert-butyl hydroperoxide [16]. Selective α-iodination of enaminones using I_2 and Et_3N [17] and of ketones with MnO_2/I_2 [18]. Selective iodination of α, β-unsaturated ketones, without effecting of ethylenic bond is reported by using copper II oxide/iodine reagent [19].

In continuation with our previous work [20-25] iodination of aromatics by using iodine and iodic acid, herein, we report selective iodination of substituted *o*-hydroxychalcones in phenyl ring without effecting ethylenic bond using iodine and iodic acid as iodinating reagent.

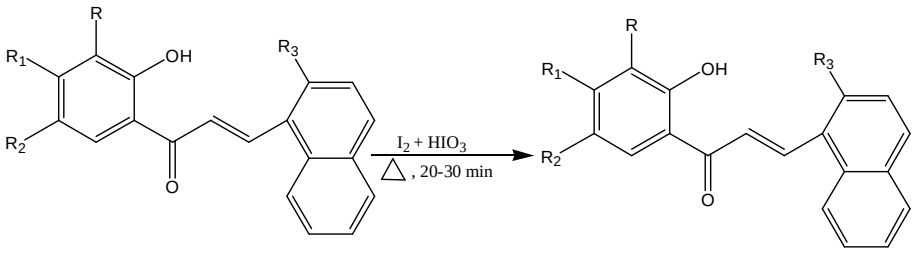
MATERIALS AND METHODS

Experimental

Melting points were determined in open capillaries and are uncorrected. The purity of the compounds was checked by TLC. The IR spectra were recorded on FTIR Perkin-Elmer 1420 spectrometer and PMR spectra ($CDCl_3$) on a varian-300 MH_Z spectrometer using TMS as internal standard. Mass spectra were recorded on VG 7070H mass spectrometer at 70 eV.

General procedure for the iodination of substituted o-hydroxychalcones:

To a mixture of substituted *o*-hydroxychalcones (0.05mol) and iodine (0.02mol) were dissolved in ethyl alcohol (25ml), iodic acid (0.01mol) dissolved in water (1ml) was added while stirring for 5 min. The reaction mixture was then refluxed on hot water bath for 20-30 min (Table). On cooling solid separated. Solid obtained was filtered washed with water and crystallized from glacial acetic acid. Melting point and mixed melting point with authentic sample was not depressed.



1a-k **2a-k**

Scheme: Iodination of Substituted *o*-hydroxychalcones

1a = R, R_1, R_2, R_3= H
1b = R, R_1, R_2= H, R_3 = OCH_3
1c = R, R_1, R_3= H, R_2= Cl
1d = R, R_1, R_3= H, R_2= Br
1e = R, R_1= H, R_2= Br, R_3 = OCH_3
1f = R, R_1= H, R_2= Cl, R_3 = OCH_3
1g = R, R_1, R_3= H, R_2= CH_3
1h = R, R_1= H, R_2= CH_3, R_3 = OCH_3
1i = R, R_3= H, R_1= CH_3, R_2 = Cl
1j = R = H, R_1 = CH_3, R_2= Cl, R_3 = OCH_3
1k = R, R_2, R_3= H, R_1= OH

2a = R, R_2 = I, R_1, R_3= H
2b = R, R_2 = I, R_1 = H, R_3= OCH_3
2c = R = I, R_1, R_3= H, R_2 = Cl
2d = R = I, R_1, R_3= H, R_2 = Br
2e = R = I, R_1 = H, R_2 = Br, R_3= OCH_3
2f = R = I, R_1 = H, R_2 = Cl, R_3= OCH_3
2g= R = I, R_1, R_3= H, R_2 = CH_3
2h = R = I, R_1 = H, R_2 = CH_3, R_3= OCH_3
2i = R = I, R_3= H, R_1= CH_3, R_2 = Cl
2j = R = I, R_1 = CH_3, R_2= Cl, R_3 = OCH_3
2k = R, R_2 = I, R_3= H, R_1= OH

RESULTS AND DISCUSSION

Substituted *o*-hydroxychalcones were obtained by claisen Schmidt condensation between hydroxy substituted acetophenones and napthaldehyde/2-methoxy napthaldehyde [26-31]. We report here a practical and regioselective aromatic iodination of hydroxy substituted chalcones. A combination of iodine and iodic acid has been found to be an excellent reagent for the regiselective iodination of hydroxy substituted chalcones (Ia-k); without affecting an ethylenic bond. These reactions are carried out at 60-70^{o}c using 95% aqueous ethyl alcohol as a solvent. The iodination occurs regioselectively and iodination took place at ortho or/and at para positions with respect to hydroxy group. Iodination does not occur at ethylenic bond; only nuclear iodination take place. The iodination procedure is very simple, convient, shorter reaction time with excellent yields; chemicals are not hazardous and can be weighed easily.

Structures of newly synthesized compounds were confirmed by compairing m.p. and TLC with authentic samples prepared by reported methods as well as spectral data and elemental analysis.

*1-(5'-Bromo-2'-hydroxy-3'-iodo-phenyl)-3-naphthalen-2-yl-propenone (**2d**):*
Anal. Calcd. For $C_{19}H_{12}O_2BrI$:- C, 47.59; H, 2.50; O, 6.68; X= (Br +I); 43.21. Found: C, 47.70; H, 2.59; X= (Br+I); 43.31. IR (KBr) νmax: 1626 (C=O), 1610-1590 (C=C), 1165 (C–O); ^{1}H NMR ($CDCl_3$): δ 7.6 (d, 1H, J= 16 H_Z =CH), δ 7.85 (d, 1H, J= 16 H_Z =CH), δ 7.51-8.25 (m, 10H, Ar-H), δ 11.45 (s, 1H, OH) ppm.; MS (m\z): M^+ 479.

*1-(2'-Hydroxy-3'-iodo-5'-methyl-phenyl)-3-naphthalen-2-yl-propenone (**2g**):*
Anal. Calcd. For $C_{20}H_{14}O_2I$:- C, 58.11; H, 3.38; O, 7.74; I, 30.75. Found: C, 58.25; H, 3.47; I, 30.88. IR νmax: 1630 (C=O), 1612-1580 (C=C), 1170 (C–O) ^{1}H NMR: δ 2.45 (s, 3H, CH_3), δ 7.58 (d, 1H, J= 16 H_Z =CH), δ 7.94 (d, 1H, J= 16 H_Z =CH), δ 8.44 (m, 10H, Ar-H), δ 12.45 (s, 1H, OH). M^+: 413.

Table: A selective iodination of some substituted *o*-hydroxychalcones by using iodine and iodic acid

Entry	Melting points ^{o}C		Time	Yield
	Found	Reported	(min.)	(%)
2a	213	214[23]	23	82
2b	220	219[23]	26	90
2c	144	146[27]	22	85
2d	161	-----	27	80
2e	190	189[25]	29	86
2f	178	178[25]	24	88
2g	182	-----	20	90
2h	210	211[25]	21	82
2i	145	144[27]	30	87
2j	162	163[25]	25	80
2k	210	211[22]	26	83

CONCLUSION

In summary, a simple and convenient method for the iodination of substituted *o*-hydroxychalcones by using iodine and iodic acid. The advantages of this method include easy and simple procedure, no need of catalyst, nearly quantitative yield; chemicals are not hazardous and can be weighed easily.

Acknowledgement
Authors are thankful to Principal Yeshwant Mahavidyalaya Nanded for providing laboratory facilities and to Director of IICT Hyderabad for providing spectra of samples. Authors are also thankful to UGC for sanctioning major research grant.

REFERENCES

[1] H.O. Wirth, O. Konigslen, W. Kern *Liebigs Ann. Chem.* **1960**, *84*, 634.
[2] E.B. Merkushev, *Synthesis* **1988**; 923.
[3] G.A. Olah, Q. Wang, G. K. Praksh. *J. Org. Chem.* **1993**, *58*, 3194.
[4] B. Abderrazak, F. Franciseu, Y. Miguel. *Tetrahedron Lett.* **1994**, *50*, 5139.
[5] K. Elbs, A. Jaroslawzew. *J. Pract. Chem.* **1913,** *88*, 92.
[6] D.M. Marko, Y.A. Beloyaev, *Khim. Referat. Zhur.* **1941**, *4*, 49.
[7] K.J. Edgar, S.N. Falling, *J. Org. Chem.* **1990**, *55*, 5287.
[8] J. Barluenga, J.M. Gonzalez, M.A. Garcia-Martin, P. Campos, G. Asensio. *J.Org. Chem* **1993**, *58*, 2058.
[9] W.W. Sy. *Tetrahedron Lett.* **1993**, *34*, 6233.
[10] Gundijz, M.; Bilgic, S.; Biligic, O.; Ozognt, D. *Arkivoc* **2008**, *xiii*, 115-121.
[11] B. Akhlaghinia, M. Rahmani, *Turk. J. Chem.* **2009,** *33*, 67.
[12] K.V.V. Krishnamohan, N. Narender, S.J. Kulkarni, *Tetrahedron Lett.* **2004,** *45*, 8015.
[13] Noda, Y.; Kashima, M. *Tetrahedron Lett.* **1997**, *38*, 6225-6228.
[14] H. Firahzabadi, N. Jranpoor, M. Shiri, *Tetrahedron Lett.* **2003,** *44*, 8781.
[15] T. Yamamoto, K. Toyota, N. Morita, *Tetrahedron Lett.* **2010,** *51*, 1364.
[16] K.R. Reddy, M. Venkateshwar, C.U. Maheswari, P.S. Kumar, *Tetrahedron Lett.* **2010,** *51*, 2170.
[17] J. Mikim, J. E. Na, J. N. Kim. *Tetrahedron Lett.* **2003**, *44*, 6317.
[18] G. L. Bras, O. Pruvot, A. Bekaert, J. Peyrat, M. Almi, J- D Briun,. *Synthesis* **2006**, 1537.
[19] Z. Wang, G. Yin, J. Qin, M. Gao, L. Cao, A. Wu. *Synthesis* **2008**, 3675.
[20] B.S. Dawane, Y.B. Vibhute, *J. Indian. Chem. Soc.* **2000**, *77*, 299.
[21] B.R. Patil, S.R. Bhusare, R.P. Pawar, Y.B. Vibhute, *Tetrahedron Lett.* **2005**, *46*, 7179-7181.
[22] B.R. Patil, S.R. Bhusare, R.P. Pawar, Y.B. Vibhute, *Arkivoc*, **2006**, *i*, 104-108.
[23] M.A. Sayyed, S.B. Junne, A.Y. Vibhute, Y.B. Vibhute, *Int. J. Chem. Soc.* **2008**, *6*, 192
[24] A.T. Shinde, S.B. Zangade, S.B. Chavan, A.Y. Vibhute, Y.S. Nalwar, Y.B. Vibhute, *Synth.Commun.* (In Press, LSYC-2009-3474).
[25] A.Y. Vibhute, S.S. Mokle, K.G. Karamunge, V.M. Gurav, Y.B. Vibhute, *Chinese Chemical Letters* (doi:10.1016/j.cclet.2010.04.008).
[26] Y.B. Vibhute, *J. Indian. Chem. Soc.***1976**, *53*, 736-738.
[27] Y.B. Vibhute, M.H. Jagdale, *J. Indian. Chem. Soc.* **1981**, *58*, 1115-1116.

[28] G.R. Subbnwad, Y.B. Vibhute, M.S. Singare, *J. Indian. Chem. Soc.* **1991**, *68*, 570-571.
[29] S.B. Zangade, J.D. Jadhav, Lalpod, Y.B. Vibhute, B.S. Dawane, *J. Chem. Pharm. Research* **2010**, *2*, 310-314.
[30] Y.B Vibhute, M.H. Jagdale, *Acta Ciencia Indica* **1986**, *12* , 223-227.
[31] Y.S. Nalwar, M.A. Sayyed, S.S. Mokle, Y.B. Vibhute, *World. J. Chemistry* **2009**, *4*, 123-126.