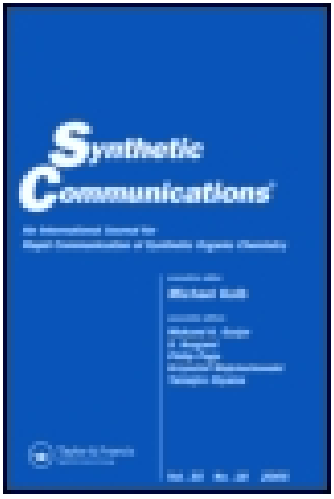


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Sodium Perborate: A Facile Synthesis of 1,2-Benzisoxazole 2-Oxides

Vidyadhar K. Jadhav [a] , Anjali P. Deshmukh [a] , Prakash P. Wadagaonkar [b] & Manikrao M. Salunkhe [a]
[a] Department of Chemistry , The Institute of Science , 15 - Madam Cama Road, Mumbai, 400032, India
[b] Polymer Chemistry Division , National Chemical Laboratory , Pune, 411008, India
Published online: 04 Dec 2007.

To cite this article: Vidyadhar K. Jadhav , Anjali P. Deshmukh , Prakash P. Wadagaonkar & Manikrao M. Salunkhe (2000) Sodium Perborate: A Facile Synthesis of 1,2-Benzisoxazole 2-Oxides, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 30:8, 1521-1527, DOI: 10.1080/00397910008087181

To link to this article: http://dx.doi.org/10.1080/00397910008087181

SYNTHETIC COMMUNICATIONS, 30(8), 1521–1527 (2000)

SODIUM PERBORATE : A FACILE SYNTHESIS OF 1,2-BENZISOXAZOLE 2-OXIDES

Vidyadhar K. Jadhav, Anjali P. Deshmukh, Prakash P. Wadagaonkar[#] and Manikrao M. Salunkhe*

Department of Chemistry, The Institute of Science, 15 - Madam Cama Road, Mumbai-400032, India.
[#] Polymer Chemistry Division, National Chemical Laboratory, Pune-411008, India.

ABSTRACT: An efficient and convenient methodology has been developed for the conversion of 2-hydroxy phenyl ketoxime to 1,2-benzisoxazole 2-oxide with sodium perborate (SPB) in glacial acetic acid under mild reaction conditions. Interestingly when the reaction was carried out under reflux condition deoximation was observed in quantitative yield.

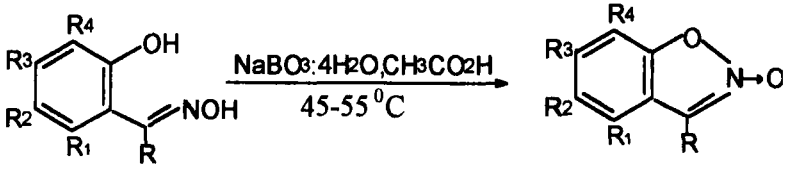
Over the last two decades the use of sodium perborate $NaBO_3 : 4H_2O$ (SPB), an environmentally attractive solid oxidizing agent, in synthetic chemistry has become more and more popular due to its characteristic properties such as, low price, environmental friendly, easy to handle and stable at room temperature.[1,2]

* To whom correspondence should addressed.

There are few methods reported in literature for the formation of 1,2-benzisoxazole 2-oxides from 2-hydroxy phenyl ketoximes using lead tetra acetate,[3] phenyl iodosodiacetate[4] and sodium hypochlorite.[4]

Various aldoximes and ketoximes are oxidized by SPB in glacial acetic acid led to some nitro or aci-nitro compounds.[5] Conversion of oximes to corresponding carbonyl compounds with sodium perborate in glacial acetic acid is also reported.[6] However SPB has not been used for oxidation of 2-hydroxy ketoximes. SPB has recently been used by us for a variety of oxidations.[7, 8]

Various 2-hydroxy phenyl ketoxime **1 (a-h)** on treatment with 2.0 equivalent of SPB in glacial acetic acid at 45-55 °C gave a cyclised product, 1,2-benzisoxazole 2-oxide **2 (a-h)** as shown in Scheme-I. Results are summarised in Table- I.

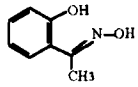
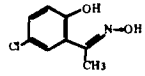
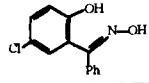
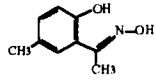
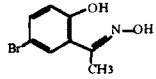
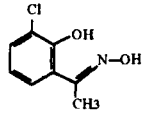
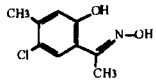
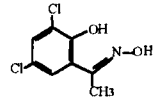


1 (a-h) **2 (a-h)**

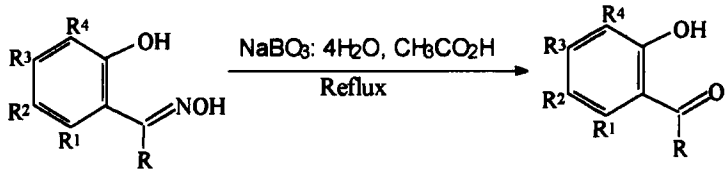
Scheme - I

However, reaction of 2-hydroxy ketoxime **1 (a-h)** with 3 equivalent of SPB in acetic acid under reflux led to the formation of carbonyl compound **3 (a-h)**, as shown in Scheme-II. In this case oxidative cleavage of oximes led to corresponding carbonyl compounds selectively without oxidation of hydroxyl group. These compounds were confirmed by IR, NMR, TLC with authentic samples and physical constants. Results are summarized in Table-I.

Table- I : Synthesis of 1,2-Benzisoxazole 2-oxides and Deoximation of oximes.

Sr. No.	Oximes	Temp.	Time (h)	Product	Yield %	M. P. °C (Literature)[4]
1a.		a	20	**2a**	10	95 (96)
		b	4.5	**3a**	85	
1b.		a	14	**2b**	86	134 (133)
		b	3.5	**3b**	75	
1c.		a	12	**2c**	92	148-151 (150)
		b	4.5	**3c**	80	
1d.		a	20	**2d**	16	72 (74)
		b	5.0	**3d**	78	
1e.		a	18	**2e**	65	116-118 (117)
		b	5.0	**3e**	88	
1f.		a	16	**2f**	60	143-146
		b	5.5	**3f**	82	
1g.		a	18	**2g**	60	148
		b	5.0	**3g**	75	
1h.		a	18	**2h**	72	92-94
		b	5.5	**3h**	80	

a. 45-55 °C
b. Reflux



1 (a-h) **3 (a-h)**

Scheme II

It has been observed in cyclisation reaction that halo- substituted 2-hydroxy acetophenone oxime or 2-hydroxy benzophenone oxime gives better yields, whereas methyl substituted 2-hydroxy acetophenone oxime or unsubstituted 2-hydroxy acetophenone oxime gives poor yield. All these give low yields when carried out at room temperature. Glacial acetic acid has been proved to be the better solvent than acetic anhydride, trifluoroacetic acid and trifluoroacetic anhydride.

IR spectra of compounds **2 (a-h)** show two characteristic absorption bands, in the range of 1575-1650 cm^{-1} (C=N, stretching) and 1200-1300 cm^{-1} (N → 0, stretching).

Analytical data of new compounds are as follows.

2f. 7-Chloro-3-methyl-1,2-benzisoxazole 2-oxide ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25 (s, 3H, $-CH_3$), 7.15-7.65 (m, 3H, Ar-H). Elemental analysis calcd for $C_8H_6NO_2Cl$ C, 52.34; H, 3.30; N, 7.63; O, 17.43. Found C, 52.25; H, 3.39; N, 7.68; O, 17.40. MS m/z (rel. intensity) 183,185 (27, 9, M^+), 153 (5), 125 (24), 117 (41), 99 (17), 89 (100, Base peak), 63 (57).

2g. 5-Chloro-3,6-dimethyl-1,2-benzisoxazole 2-oxide ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (s, 3H, $-CH_3$), 2.60 (s, 3H, $-CH_3$), 7.20-7.60 (d, 2H, Ar-H). Elemental analysis calcd for $C_9H_8NO_2Cl$ C, 54.70; H, 4.08; N, 7.09; O, 16.19. found C, 54.68; H, 4.03; N, 7.00; O, 16.25. MS m/z (rel. intensity) 197, 199 (51, 17, M^+), 152 (9), 167 (29), 139 (100, Base peak), 132 (23), 103 (68), 89 (5), 77 (31), 63 (8).

2h. 5,7-Dichloro-3-methyl-1,2-benzisoxazole 2-oxide ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.35 (s, 3H, $-CH_3$), 7.10-7.65 (m, 2H, Ar-H). Elemental analysis calcd for $C_8H_5NO_2Cl_2$ C, 44.07; H, 2.31; N, 6.42; O, 16.68. Found C, 44.00; H, 2.25; N, 6.40; O, 16.60. MS m/z (rel. intensity) 217, 219, 221 (25, 16, 3, M^+), 187 (6), 159 (30), 151 (51), 123 (100, Base peak), 97 (25), 63 (11).

In conclusion, the present procedures for the preparation of 1,2-benzisoxazole 2-oxides and deoximation are simple and convenient. In addition the reagent used, sodium perborate, is inexpensive, non-toxic, easy to handle and does not involve any effluent or byproduct problem.

EXPERIMENTAL :

2-hydroxy acetophenone and 2-hydroxy benzophenone are prepared according to reported procedure and then converted to corresponding oximes.[9] Melting points were taken in open capillary and are uncorrected. IR spectra were recorded using KBr pellets on Perkin-Elmer-738 FTIR. ^{1}H-NMR spectra were recorded on 500 MHz Bruker instrument in $CDCl_3$ using Me_4Si as an internal reference. Mass spectra were taken on Hewlett Packard G 1800A, GCD system.

General Procedure for preparation of 1,2- benzisoxazole 2-oxide

4 mmol crystalline 2-hydroxy phenyl ketoxime was taken in 100 ml round bottom flask containing 10 ml glacial acetic acid which dissolves completely then 1.23 g. (8 mmol) of SPB was added to the reaction mixture at

once. Reaction mixture was then heated at 45-55°C. After 30 min. SPB dissolves slowly and reaction mixture becomes yellow in color. After completion of the reaction (18-24 h.), mixture was poured on crushed ice with stirring and kept aside for 20 min. Light yellow colored solid obtained was filtered, washed with water (2×20 ml.). Crude product obtained was kept aside for 2h. with dil. NaOH (0.12 g. in 20 ml water) to remove unreacted oxime. Insoluble residue was filtered and washed thoroughly with water (5×20 ml.), dried and was further purified by crystallization from dilute alcohol.

General Procedure for deoximation of 2-hydroxy phenyl ketoxime

4 mmol crystalline 2-hydroxy phenyl ketoxime was taken in 100 ml round bottom flask containing 10 ml glacial acetic acid then 1.85 g. (12 mmol) of SPB was added to the reaction mixture at once. Reaction mixture was then heated to reflux temperature. Progress of reaction was monitored on TLC. After completion of the reaction, final compound was extracted in ethyl acetate (20 ml) washed with water, dried over anhydrous Na_2SO_4, filter and then evaporated under vacuum. Compound was further purified by column chromatography.

REFERENCES

1. Muzart, J. *Synthesis*, **1995**, 1325.
2. Mc Killop, A. and Randerson, W.R. *Tetrahedron*, **1995**, 51 (22), 6145.
3. Boulton, A.J. and Tsoungas, P.G. *J. Chem. Soc. Chem. Commun.*, **1980**, 10, 421.

4. Boulton, A.J., Tsoungas, P.G. and Tsiamis, C. *J. Chem. Soc. Perkin Trans. I*, **1986**, 1665.

5. Olah, G.A., Ramaiah, P., Lee C.S. and Prakash, G.K.S. *Synlett*, **1992**, 337.

6. Bandgar, B.P., Shaikh, S.I. and Iyer, S. *Syn. Commun.*, **1996**, 26 (6), 1163.

7. Jadhav, V.K., Wadagaonkar, P.P. and Salunkhe, M.M. *J. Chinese Chem. Soc.*, **1998**, 45, 831.

8. Deshmukh, A.P., Padiya, K.J., Jadhav, V.K. and Salunkhe, M.M. *J. Chem. Res. (S)*, **1998**, 828.

9. Furniss, B.S., Hannford, A.J., Rogers, V., Smith, P.W.G. and Tatchell, A. R. *"Vogel's Text Book of Practical Organic Chemistry"*, 4th ed., ELBS, **1978**, pp. 750, 1113.

Accepted 7/3/99