SYNLETT Spotlight 235

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

N-Bromosaccharin (NBSac)

Compiled by Lokesh Kumar Pandey

L. K. Pandey was born in Gorakhpur, Uttar Pradesh, India in 1976. He obtained his B.Sc. degree from St. Andrew's College Gorakhpur in 1994 and M.Sc. (Chemistry) degree from Gorakhpur University in 1997. He joined the Defence Research & Development Establishment in 2002 as Sr. Technical Assistant. Currently he is working under the supervision of Dr. Uma Pathak. His research interests involve synthetic organic chemistry, development of new strategies for organosulfur transformations, and drug research and development.

Synthetic Chemistry Division, Defence Research and Development, Establishment, Jhansi Road, Gwalior 474002, M.P., India. E-mail: lkp1976@gmail.com Dedicated to my research supervisor Dr. Uma Pathak, for her sup-

port and constant encouragement

Introduction

N-Bromosaccharin (NBSac) is a strong oxidizing and chlorinating agent. It is a white powder, easy to handle, with its melting point at 160-170 °C. It is soluble in organic solvents, for example in alcohols, acetonitrile, tetra-chloromethane, ethyl acetate, trichloromethane, acetone, and 1,4-dioxane. *N*-Bromosaccharin has been proven to be a useful and alternative reagent for diverse organic transformations, such as halogenation of aromatic compounds, co-halogenation of alkenes, oxidation of alco-

hols, halogenation of benzylic and carbonylic positions, etc. *N*-Bromosaccharin¹ can easily be prepared by bromination of the sodium salt of saccharin which is commonly available, non-corrosive, and non-toxic.

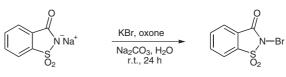


Figure 1

Abstracts

(A) N-Bromosaccharin has been used for regioselective cleavage of NBSac/PPh3 (1.2/1.2) PhOCH₂CH(OH)CH₂Br epoxides to vicinal bromohydrins and dibromides in the presence of r.t., 1% aq MeCN, 3-40 min Ph₃P.² 15-95% NBSac/PPh3 (2.5/2.5) PhOCH₂CHBrCH₂Br reflux, MeCN (75-90%) (B) N-Bromosaccharin in combination with Ph₃P is a highly reactive reagent for the conversion of hydroxyl compounds into the corre-NBSac, PPh₃ ROH RBr sponding bromides using dichloromethane as solvent at room tem-CH₂Cl₂, r.t. perature under neutral conditions.³ (C) N-Bromosaccharin reacts with electron-deficient alkenes such as

(C) *N*-Bromosaccharin reacts with electron-deficient alkenes such as α , β -unsaturated ketones, acids, esters, and nitriles in aqueous organic solvents, yielding the corresponding bromohydrins in good yields. The reaction takes place at room temperature, mostly within short reaction times and with high *anti* stereoselectivity.⁴



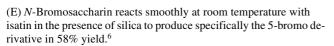
Y = COMe, COPh, COOH, CO₂Me, CN R = H, Me, Et solvent: MeCN or acetone-H₂O

SYNLETT 2008, No. 6, pp 0947–0948 Advanced online publication: 11.03.2008 DOI: 10.1055/s-2008-1032201; Art ID: V24007ST © Georg Thieme Verlag Stuttgart · New York 947

(D) *N*-Bromosaccharin has successfully been used for chemoselective oxidation of thiols to their corresponding disulfides in dichloromethane under microwave irradiation in high yields.⁵

RSH → NBSac CH₂Cl₂, MW, 3–10 min 86–94%

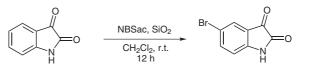
R = alkyl or aryl

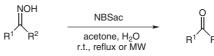


(F) *N*-Bromosaccharin was applied as an efficient reagent for the oxidative cleavage of oximes to the corresponding aldehydes and ketones at room temperature or by conventional heating or microwave irradiation.⁷

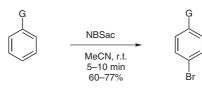
(G) *N*-Bromosaccharin was successfully applied for bromination of electron-rich aromatic compounds (anisole, acetanilide, *N*,*N*-dimeth-

ylaniline). The reaction with N-bromosaccharin gave para-substitut-





 R^1 , R^2 = alkyl or aryl



G = OMe, NHAc, NMe₂

References

ed compounds only.8

- (1) de Souza, S. P. L.; da Silva, J. F. M.; de Mattos, M. C. S. *Synth. Commun.* **2003**, *33*, 935.
- (2) Iranpoor, N.; Firouzabadi, H.; Azadi, R.; Ebrahimzadeh, F. Can. J. Chem. 2006, 84, 69.
- (3) Firouzabadi, H.; Iranpoor, N.; Ebrahimzadeh, F. *Tetrahedron Lett.* **2006**, *47*, 1771.
- (4) Urankar, D.; Rutar, I.; Modec, B.; Dolenc, D. Eur. J. Org. Chem. 2005, 2349.
- (5) Khazaei, A.; Rostami, A.; Aminimanesh, A. J. Chin. Chem. Soc. 2006, 53, 437.
- (6) de Souza, S. P. L.; da Silva, J. F. M.; de Mattos, M. C. S. *Heterocycl. Commun.* **2003**, *9*, 31.
- (7) Khazaei, A.; Aminimanesh, A.; Rostami, A. *Phosphorus* Sulfur Relat. Elem. **2004**, 179, 2483.
- (8) de Souza, S. P. L.; da Silva, J. F. M.; de Mattos, M. C. S. *J. Braz. Chem. Soc.* 2003, *14*, 832.