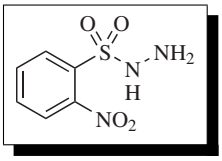
o-Nitrobenzenesulfonylhydrazide



[5906-99-0] $C_6H_7N_3O_4S$ (MW 217.20)

InChI = 1/C6H7N3O4S/c7-8-14(12,13)6-4-2-1-3-5(6)9(10)11/h1-4,8H,7H2

InChIKey = QENBJCMCPIVGMF-UHFFFAOYAL

(reagent used for synthesis of allenes from propargylic alcohols, for the reductive transposition of allylic alcohols, for the deoxygenation of unhindered alcohols, and for the generation of diimide)

Alternate Name: NBSH.

Physical Data: mp 100–101 °C (dec).

Solubility: soluble in acetonitrile, ethyl acetate, *N*-methylmorpholine (NMM), THF, and water; insoluble in benzene and hexanes.

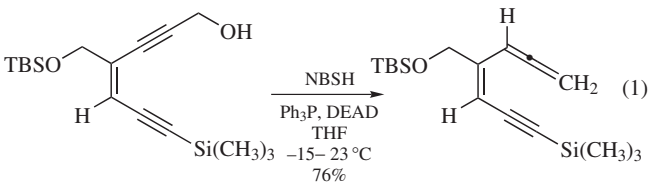
Form Supplied in: off-white solid.

Preparative Methods: prepared in one step from commercially available *o*-nitrobenzenesulfonyl chloride and hydrazine monohydrate in THF at −30 °C.[1]

Purity: a solution of NBSH in ethyl acetate is washed with ice-cold 10% aqueous sodium chloride, dried over anhydrous sodium sulfate, and diluted with hexanes at 23 °C to induce precipitation of NBSH.[1a]

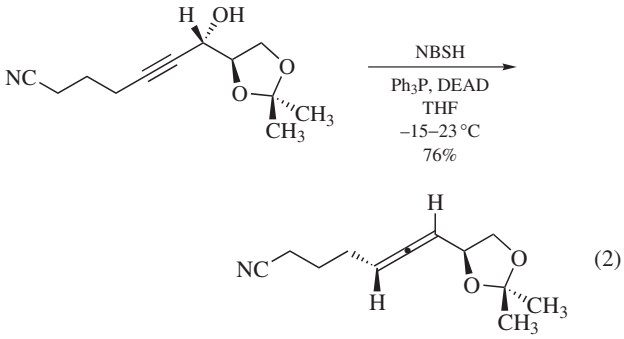
Handling, Storage, and Precaution: stable at ambient temperature for several days, but should be refrigerated (−20 °C) for long-term storage.[1a]

Synthesis of Allenes.[2] The invertive Mitsunobu displacement of propargylic alcohols with *o*-nitrobenzenesulfonylhydrazide (NBSH)[1] occurs within 1–2 h at −15 °C in THF to afford the corresponding *N*,*N*-1-alkyl-1-*o*-nitrobenzenesulfonylhydrazine derivatives. Warming of the reaction mixture to ambient temperature leads to elimination of *o*-nitrobenzenesulfinic acid to give propargylic diazene intermediates that undergo spontaneous sigmatropic loss of dinitrogen to provide the corresponding allenes.[2a] The mild reaction conditions are compatible with a wide variety of functional groups and allow the synthesis of sensitive allene-ene-yne systems (eq 1).[2a] Valuable (trialkylsilyl)allenes, including (trimethylsilyl)allene and (*t*-butyldimethylsilyl)allene, are prepared in a single step from the corresponding *C*-silylated propargylic alcohol derivatives.[2b]



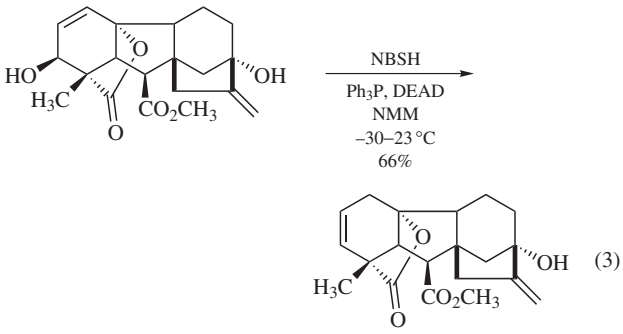
(1)

The overall transformation proceeds with complete stereospecificity and, coupled with the existing methodology for the preparation of chiral propargylic alcohols, provides access to a wide range of optically active allenes (eq 2).[2a]



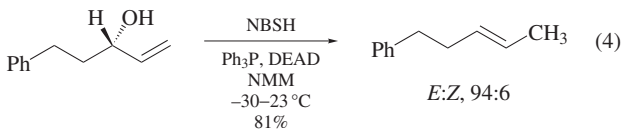
(2)

Reductive Transposition of Allylic Alcohols.[3] In direct analogy to the synthesis of allenes from propargylic alcohols, invertive (Mitsunobu) displacement of allylic alcohols with NBSH followed by warming of the reaction mixture to ambient temperature to induce diazene formation and sigmatropic loss of dinitrogen provides reductively transposed alkenes.[3] This methodology has proven to be highly effective for the reductive 1,3-transposition of a wide variety of allylic alcohols (eq 3).[3]



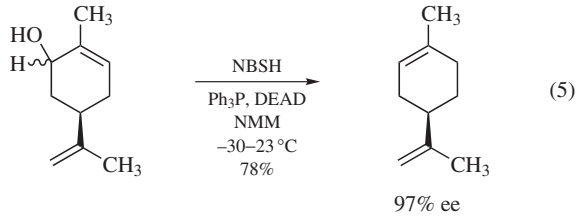
(3)

The rearrangement proceeds with high trans selectivity in the formation of 1,2-disubstituted olefins, an outcome consistent with the minimization of allylic strain during sigmatropic loss of dinitrogen from the allylic diazene intermediates (eq 4). Furthermore, the regioselectivity of the reduction (1,3-transposition versus direct displacement) is complete in all cases studied thus far (eq 5).[3]



(4)

E:*Z*, 94:6

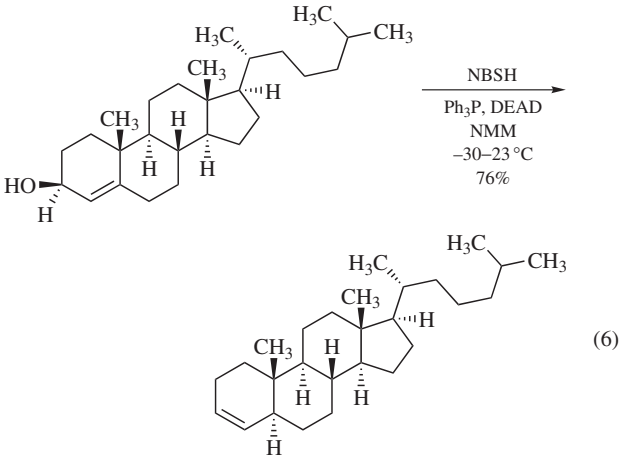


(5)

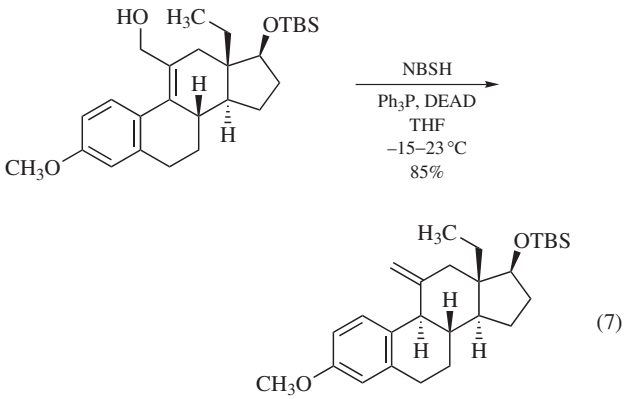
97% ee

The invertive nature of the initial displacement reaction may be utilized in a 1,3-transfer of stereochemistry from the hydroxylic center to the β-olefinic carbon (eq 6).[3] Precedence also exists for

the use of more distant stereocenters to control the stereoselectivity of hydrogen transfer to the β-olefinic carbon (eq 7).[4]

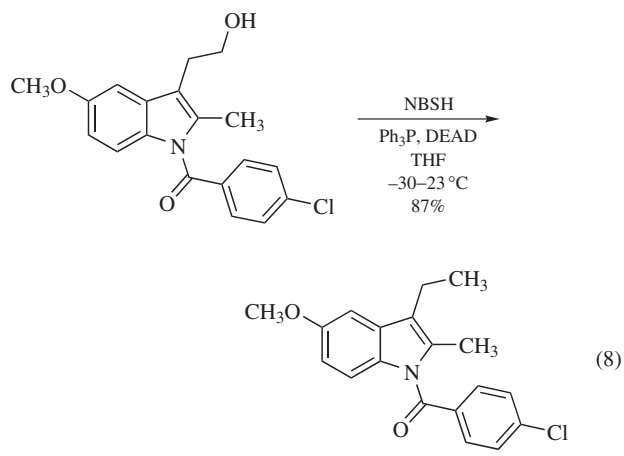


(6)

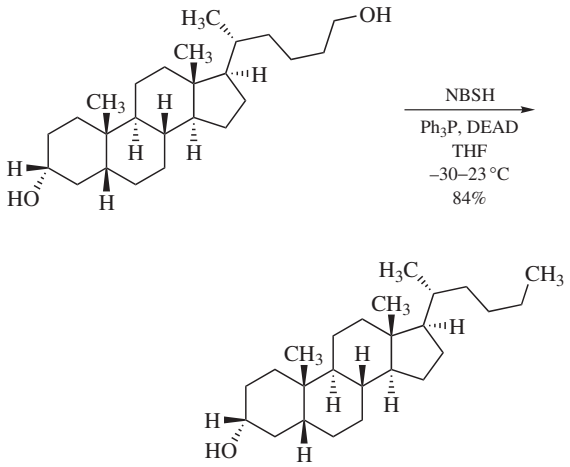


(7)

Deoxygenation of Unhindered Alcohols.[5] The NBSH reagent can be used for the deoxygenation of unhindered primary and secondary alcohols in a single step, without the use of heavy metal hydride reagents and under mild reaction conditions (eq 8).[5] Mitsunobu displacement of saturated alcohols by NBSH followed by in situ elimination of *o*-nitrobenzenesulfinic acid is proposed to provide a monoalkyl diazene intermediate. This monoalkyl diazene intermediate is then proposed to undergo fragmentation by a free-radical mechanism to form dinitrogen and the corresponding alkane.[5] The sensitivity of the initial invertive step to steric effects can be used advantageously in the selective deoxygenation of unhindered alcohols in the presence of other alcohols (eq 9).[5]

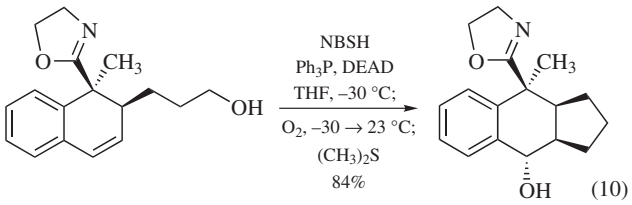


(8)



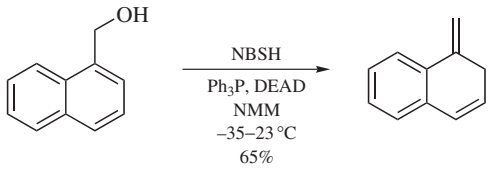
(9)

The proposed free-radical intermediates have been used for ring-formation, for fragmentation, and have been captured by intermolecular trapping (eq 10).[5]



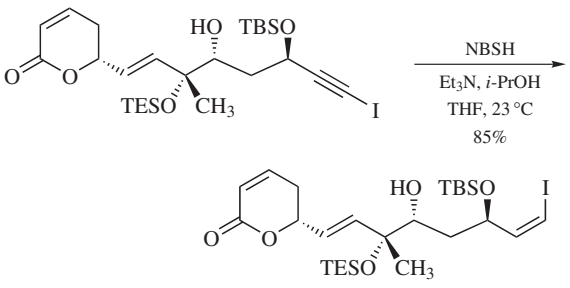
(10)

Deoxygenation of benzylic substrates provides a synthetic route to interesting deconjugated products (eq 11).[5]



(11)

Generation of Diimide. In comparison to other arenesulfonylhydrazines,[6] NBSH undergoes more facile thermal fragmentation (loss of *o*-nitrobenzenesulfinic acid) to form diimide.[1a,7] Simple dissolution of NBSH in water or methanol at ambient temperature leads to the rapid generation of diimide.[1a] The mild nature of this method of diimide generation permits its use with sensitive substrates (eq 12).[8]



(12)

Related Reagents. 2,4-Dinitrobenzenesulfonylhydrazide; Mesitylenesulfonylhydrazide; *p*-Toluenesulfonylhydrazide; 2,4,6-Triisopropylbenzenesulfonylhydrazide.

1. (a) Myers, A. G.; Zheng, B.; Movassaghi, M., *J. Org. Chem.* **1997**, *62*, 750. (b) Dann, A. T.; Davies, W., *J. Chem. Soc.* **1929**, 1050.
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5. (a) Myers, A. G.; Movassaghi, M.; Zheng, B., *J. Am. Chem. Soc.* **1997**, *119*, 8572. (b) Myers, A. G.; Movassaghi, M.; Zheng, B., *Tetrahedron Lett.* **1997**, *38*, 6569.
6. Cusack, N. J.; Reese, C. B.; Risius, A. C.; Roozpeikar, B., *Tetrahedron* **1976**, *32*, 2157.
7. Hünig, S.; Müller, H. R.; Thier, W., *Angew. Chem., Int. Ed.* **1965**, *4*, 271.
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