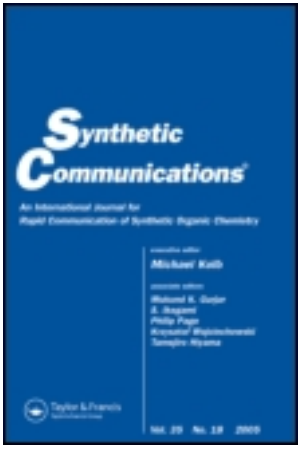

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Bromination of Alkenes Using a Mixture of Sodium Bromide and Sodium Perborate

G. W. Kabalka [a], K. Yang [a], N. K. Reddy [a] & C. Narayana [a]
[a] Departments of Chemistry and Radiology, The University of Tennessee, Knoxville, TN, 37996-1600, U.S.A.
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BROMINATION OF ALKENES USING A MIXTURE OF SODIUM BROMIDE AND SODIUM PERBORATE

G. W. Kabalka*, K. Yang, N. K. Reddy, and C. Narayana

Departments of Chemistry and Radiology
The University of Tennessee
Knoxville, TN 37996-1600, U.S.A.

Abstract: Bromination of alkenes with sodium bromide in the presence sodium perborate provides a simple, high yield route to dibromoalkanes.

Molecular halogens can be difficult to manipulate and have come under increasing scrutiny because of their potential impact on the environment. To overcome these difficulties, alternative methods have been developed for the bromination of alkenes. Solid brominating agents such as pyridine hydrobromide perbromide[1] and tetrabutylammonium tribromide[2] have been used for the bromination of alkenes on a small scale. Phase transfer catalysts have also been used to brominate alkenes using a mixture of aqueous hydrobromic acid and hydrogen peroxide[3]. We wish to report that a mixture of sodium bromide and sodium perborate in acetic acid provides a convenient method for preparing dibromoalkanes from alkenes.

*To whom correspondence should be addressed.

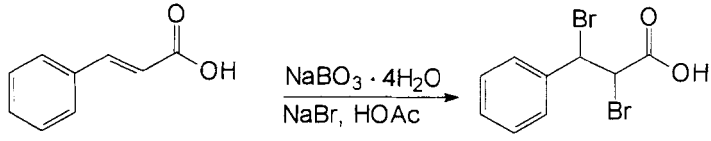
TABLE 1: Bromination of Alkenes with Sodium Bromide-Sodium Perborate

Substrate	Product	Yield(%)[a]	bp(lit)°C
1-Hexene	1,2-Dibromohexane	81	204~205 (82@12 Torr)[5]
1-Octene	1,2-Dibromooctane	83	242~243 (52@15 Torr)[5]
Cyclopentene	1,2-Dibromocyclopentane	72	191~191.7(85~87@23 Torr)[6]
Cyclohexene	1,2-Dibromocyclohexane	87	230~231 (99.6~99.9@13 Torr)[7]
Cyclooctene	1,2-Dibromocyclooctane	81	261~262 (135@15 Torr)[8]
Benzlideneacetophenone	2,3-Dibromo-3-phenylpropiophenone	82	157~158 (156~157)[9]
Methyl 10-Undecenoate	Methyl 10,11-Dibromoundecanoate	82	296~296.8[b,c]
Ethyl *trans*-cinnamate	Ethyl 2,3-Dibromo-3-phenylpropionate	85	71~72[b] (71)[10]
trans-Cinnamic acid	2,3-dibromo-3-phenylpropionic acid	90	200~200.5 (205)[11]

[a] Isolated yields. [b] Melting point. [c] Elemental analysis: Found (Theoretical): C 40.38(40.25) H 6.26 (6.19)

Table 2. N.M.R. Data for Diobromoproducts:	
Product	**^{1}H NMR ($CDCl_3$) δ ppm**
1,2-dibromohexane	4.14 (*m*, 1H), 3.84 (*dd*, 1H), 3.62 (*t*, 1H), 2.15 (*m*, 1H), 1.76 (*m*, 1H), 1.53 (*m*, 1H), 1.36 (*m*, 3H), 0.91 (*t*, 3H)
1,2-dibromooctane	4.18 (*m*, 1H), 3.85 (*dd*, 1H), 3.62 (*t*, 1H), 2.11 (*m*, 1H), 1.75 (*m*, 1H), 1.52 (*m*, 1H), 1.28 (*s*, 7H), 0.88 (*t*, 3H)
1,2-dibromocyclopentane	4.59 (*m*, 2H), 2.65 (*m*, 2H), 2.17 (*m*, 2H), 2.02 (*m*, 2H)
1,2-dibromocyclohexane	4.45 (*t*, 2H), 2.46 (*m*, 2H), 1.82 (*m*, 4H), 1.05 (*m*, 2H)
1,2-dibromocyclooctane	4.59 (*m*, 2H), 2.41 (*m*, 2H), 2.10 (*m*, 2H), 1.83 (*m*, 2H), 1.69 (*m*, 4H), 1.50 (*m*, 2H)
2,3-dibromo-3-phenyl-propiophenone	7.75-7.32 (*m*, 10H), 5.84 (*d*, 1H), 5.55 (*d*, 1H J = 12.5 Hz)
Methyl 10,11-dibromo-undecanoate	4.16 (*m*, 1H), 3.85 (*dd*, 1H), 3.66 (*s*, 3H), 3.60 (*d*, 1H), 2.30 (*t*, 2H), 2.17 (*m*, 1H), 1.76 (*m*, 1H), 1.60 (*m*, 1H), 1.32 (*s*, 9H)
Ethyl 2,3-dibromo-3-phenyl-propionate	7.38 (*m*, 5H), 5.35 (*d*, 1H), 4.83 (*d*, 1H $J_{2,3}$ = 11.8 Hz), 4.35 (*q*, 2H), 137 (*t*, 3H)
2,3-dibromo-3-phenyl-propioninacid	7.37 (*s*, 5H), 5.31 (*d*, 1H), 4.78 (*d*, 1H $J_{2,3}$ = 12 Hz)

Sodium perborate ($NaBO_3 \cdot 4H_2O$) is an inexpensive, stable and easily handled oxidant which has an excellent shelf life. It readily oxidizes sodium bromide in the presence of alkenes to produce the corresponding 1,2-dibromoalkanes in good yields. As an example, the reaction of *trans*-cinnamic acid with a mixture of sodium bromide-sodium perborate in glacial acetic acid for 2 hours gives 2,3-dibromo-3-phenylpropionic acid in 90% isolated yield.



The results of a series of brominations using sodium bromide-sodium perborate are presented in the Table .

The synthesis of 1,2-dibromocyclohexane is representative. Sodium bromide (3.06g, 30.0 mmol) is added to mixture of sodium perborate(2.29g, 15.0 mmol) and cyclohexene (1.11g, 13.5 mmol) in glacial acetic acid (25 ml) and stirred for 2 h. The mixture is then diluted with water, the product extracted into ether and dried over $MgSO_4$. Removal of solvent followed by column chromatography (silica gel, hexanes) gives 1,2-dibromocyclohexane in 87% yield; mp. 230~231 ^{0}C.[5]

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