Pergamon

Tetrahedron Letters, Vol. 35, No. 42, pp. 7861-7862, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01652-6

Tri-*n*-butyltin Hydride Mediated Dehalogenation in Water

Uday Maitra* and Koushik Das Sarma
Department of Organic Chemistry,
Indian Institute of Science, Bangalore-560012, India.

Abstract: *A new methodology has been developed to reduce water soluble and water insoluble organohalides in aqueous medium in high yields using TBTH.*

The application of tin hydride radical chemistry in organic synthesis is well known.[1,2] The solubility of tri-*n*-butyltin hydride (TBTH), however, has previously limited it to organic solvents. A water soluble tin hydride has recently been reported by Breslow[3] for dehalogenation of water soluble substrates. This reagent gave good yields with water soluble substrates, but its multistep synthesis makes it somewhat unattractive. In this communication we report that *TBTH can be used directly in water to effect dehalogenation.*

In order to overcome the solubility problem we explored the possibility of solubilizing TBTH in water using a detergent in order to achieve the dehalogenation of water soluble halides in aqueous media. Using CTAB, SDS or Triton-X-100 as the solubilizing agent we were able to reduce 3-bromobenzoate efficiently. However, a control reaction in the absence of any detergent showed that the same substrate was reduced to benzoate in high yield. We have examined a few other substrates under thermal as well as photochemical conditions and the results are summarized in Table 1.[4] It is interesting to note that for water insoluble substrates such as 9-bromoanthracene the presence of a detergent is necessary, since the reaction carried out without a detergent for 48 hours did not go to completion. However, cholesterol dibromide underwent smooth reduction to cholesterol (84%) in the absence of any detergent with 2.20 equivalents of TBTH.

We feel that our dehalogenation methodology in aqueous medium with TBTH will be of general interest in organic synthesis. We are examining other TBTH mediated synthetic transformations in water and these results will be reported in due course.

Table 1: Reduction of organohalides with TBTH in water[a]

Entry	Substrate	Additive	TBTH equiv.	% Yield
1	3-$BrC_6H_4CO_2H$	$NaHCO_3$	3.1	99
2	3-$BrC_6H_4CO_2H$[b]	$NaHCO_3$	3.1	93
3	4-$BrC_6H_4CO_2H$	$NaHCO_3$	3.1	89
4	2-$IC_6H_4CO_2H$	$NaHCO_3$	3.1	95
5	5-Br uracil	none	3.1	>95[c]
6	9-Br anthracene	$NaHCO_3$[d]	3.1	85
7	Cholesterol dibromide	$NaHCO_3$	2.2	84

[a] Unless otherwise mentioned the temperature and reaction times were 90°C and 24 h, respectively. [b] Photolysis (300 nm) at room temperature. [c] The yield was measured by ^1H NMR using an internal standard. [d] CTAB was also added.

Acknowledgment: We thank Prof. Paul A. Bartlett for a gift of TBTH, and the US Educational Foundation in India for a Fulbright travel grant to UM for a visit to the University of California at Berkeley during summer, 1993.

References and notes:

1 Neuman, W. P. *Synthesis*.**1987**, 665-683.

2 Dowd, P.; Zhang, W. *Chem. Rev.* **1993**, 2091-2115.

3 Breslow, R.; Light, J. *Tetrahedron Lett.* **1990**, *31*, 2957-2958.

4 **General procedure:** All the reactions were done under argon atmosphere in deoxygenated water. ***(a) Water soluble substrates:*** A mixture of 3-bromobenzoic acid (25 mM), $NaHCO_3$ (40 mM) and AIBN (0.30 equiv.) in water was stirred for 15 min. TBTH (3.1 equiv.) was added and the mixture was stirred at *ca.* 90°C for 24 h. The reaction mixture was cooled, made alkaline with 1 M NaOH and washed with $CHCl_3$. The aqueous phase was acidified with conc. HCl and the product was extracted with $CHCl_3$. The $CHCl_3$ extract was dried to yield benzoic acid (99%). ***(b) Water insoluble substrate:*** $NaHCO_3$ (6.3 mg), 9-bromoanthracene (32.4 mg), CTAB (21.2 mg) and AIBN (5.9 mg) were taken in water (5 mL) in an argon atmosphere and stirred for 1 h. TBTH (104 μL) was added and the reaction mixture was stirred at 90°C for 24 h. The reaction mixture was cooled, diluted to 60 mL, $Al_2(SO_4)_3$ (2 g) was added and extracted with $CHCl_3$. The organic extract was washed with 5% aq. NH_3 and the crude product was purified by column chromatography on silica gel using hexane to afford 19 mg of anthracene (85%).

(*Received in UK* 27 *July* 1994; *revised* 24 *August* 1994; *accepted* 26 *August* 1994)