# Notes

## Sodium Borohydride Reductions under Phase-Transfer Conditions: Conversion of Halides and Sulfonate Esters to Alkanes

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The hydrogenolysis of carbon–halogen and carbon–sulfonate esters bonds is of considerable importance in organic chemistry; in particular, the ability to reduce alkyl sulfonate esters to alkanes represents a suitable path of conversion of alcohols to hydrocarbons. Many methods are now available to achieve these goals; however, they often require sophisticated reagents and drastic conditions.[1,2] Recently, the use of sodium borohydride as a reducing agent of alkyl halides and sulfonates in dipolar aprotic solvents under anhydrous conditions has been reported.[2]

Halides and sulfonate esters can be advantageously converted to the corresponding alkanes in a two-phase system, according to eq 1.

$$RX \xrightarrow[Q^+Hal^-(cat),\ \Delta,\ solvent]{NaBH_4(aq)} RH \qquad (1)$$

R = alkyl, aryl (activated)
X = Cl, Br, I, $MeSO_3$, $p$-$TolSO_3$
Q = $(alkyl)_4N$, $(alkyl)_4P$

This reaction is carried out by addition of, at the appropriate temperature, the aqueous concentrated solution of $NaBH_4$ to a stirred solution of substrate and catalyst in a suitable solvent (Table I).[3,4] The process can be followed by NMR, GC, or TLC analysis.

Experiments with hexadecyltributylphosphonium bromide and tetraoctylammonium bromide as catalysts indicate that both salts are stable in the reaction mixture in the temperature range 18–80 °C. The catalysts are quantitatively recovered and may be reused as such. It should be noted that quaternary ammonium salts are decomposed to tertiary amines with $NaBH_4$ in anhydrous dipolar aprotic solvents.[2]

Table II shows the factors affecting the reduction of 1-bromohexadecane according to eq 1. The reaction does not proceed in the absence of onium salts (entry 8). Among the catalysts under study, the more lipophilic ones are the more efficient (entries 1–5). *N*-Methyl-*N*-dodecylephedrinium bromide is one of the poorest catalysts, thus confirming that its very high activity in the reduction of carbonyl groups is due to a coordination effect between the catalyst and the substrate rather than to a more favorable extraction coefficient of $BH_4^-$ anions into the organic phase.[6]

Nearly quantitative yields are obtained in the reduction of alkyl halides and sulfonate esters under phase-transfer conditions (PTC) with an excess of hydride[7] (see Tables I and II). The hydrogenolysis of primary alkyl bromides and iodides is an exothermic process which must be controlled, while other less reactive substrates (i.e., primary chlorides, methanesulfonates and toluenesulfonates, and secondary derivatives) require higher temperatures to undergo quantitative reduction.

Primary bromides are more easily reduced than the corresponding chlorides (Table I, entries 2, 3, 5, 6), which is in agreement with their general higher reactivity even under PTC. In the conditions used for alkyl bromides, iodides are only partially converted to alkanes. The reduction becomes quantitative and faster than in the case of bromides only when a large excess of $NaBH_4$ (entry 1) is used. This is likely due to the poisoning effect of $I^-$ connected to a partition coefficient usually much more favorable to the latter than to most other anions. This effect is well-known in the case of nucleophilic displacements.[9] As expected,[1,2] alkyl fluorides do not react under these conditions (entry 4). 1,10-Dibromodecane easily yields decane with an excess of $NaBH_4$ (entry 9), while with 1 mol equiv of reducing agent and 0.01 mol equiv of hexadecyltributylphosphonium bromide, the main product is 1-bromodecane (entry 10). Secondary alkyl halides give alkanes in very high yields (entry 7), requiring, however, more drastic conditions; at 18 °C it is possible to convert 1,10-dibromoundecane into 2-bromoundecane in quantitative yields, according to a very selective process (entry 8). With longer reaction times, cyclododecyl bromide (entry 17) and cyclohexyl bromide (entry 18) are transformed into the corresponding cycloalkanes together with minor amounts of cycloalkenes. Primary alkyl methanesulfonates and toluenesulfonates give the expected alkanes in nearly quantitative yields (entries 11, 13); secondary methanesulfonates undergo hydrogenolysis together with some elimination (entry 12). Benzylic halides are quantitatively and rapidly reduced to toluenes in mild conditions (entries 28–36). Similarly, diphenylmethane is obtained from diphenylchloromethane (entry 27) and phenylethane is obtained from both 1-chloro- (entry 21) and 1-bromo-1-phenylethane (entry 19). The latter, reduced with $NaBD_4$ in $D_2O$, affords 1-phenyl-1-deuterioethane in very high yield (entry 20). 1-Phenyl-3-bromoprop-1-ene mainly gives 1-phenylprop-1-ene (entry 23). Even under

(1) (a) For a review, see: Pinder, A. R. *Synthesis* **1980**, 425. (b) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 849.

(2) Hutchins, R. O.; Kandasamy, D.; Dux, F.; Maryanoff, C. A.; Rotstein, D.; Goldsmith, B.; Burgoyne, W.; Cistone, F.; Dalessandro, J.; Puglis, J. *J. Org. Chem.* **1978**, *43*, 2259, and references therein.

(3) Usually toluene was used. Similar results were obtained in benzene, xylene, chlorobenzene, dichloromethane, chloroform, and cyclohexane.

(4) Under strictly anhydrous conditions, $Bu_4N^+BH_4^-$ reacts with a number of chemical species, such as alkyl halides and $Me_2SO_4$, generating in situ the diborane.[5]

(5) (a) Brändström, A.; Junggren, U.; Lamm, B. *Tetrahedron Lett.* **1972**, 3173. (b) Brändström, A. "Preparative Ion Pair Extraction"; Apotekarsocieteten, Hässle Läkemedel, 1974; pp 129–132 and 164–166.

(6) For reviews, see: (a) Weber, W. P.; Gokel, G. W. "Phase-Transfer Catalysis in Organic Chemistry"; Springer-Verlag: Heidelberg, 1977; p 215. (b) Starks, C. M.; Liotta, C. "Phase-Transfer Catalysis, Principles and Techniques"; Academic Press: New York, 1978; p 317. (c) Dehmlow, E. V.; Dehmlow, S. S. "Phase-Transfer Catalysis"; Verlag Chemie: Weinheim/Bergstr., Germany, 1980; p 240.

(7) The hydride excess is necessary since $NaBH_4$ is not completely stable in aqueous solution, the decomposition rate depending on the pH of the medium.[8]

(8) Gardiner, J. A.; Collat, J. W. *J. Am. Chem. Soc.* **1965**, *87*, 1692, and references therein.

(9) Starks, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 195.

0022-3263/81/1946-3909$01.25/0 

Table I. Reduction of Halides and Sulfonate Esters with Sodium Borohydride in an Aqueous-Organic Two-Phase System in the Presence of Hexadecyltributylphosphonium Bromide (0.1 mol equiv) as Catalyst

| entry | substrate[a] (1 mol equiv) | product | $NaBH_4$, mol equiv | t,[b] h | temp,[c] °C | % yield anal.[d] | % yield isolated |
|---|---|---|---|---|---|---|---|
| 1 | 1-iodohexadecane | hexadecane | 5 | 2 | 18 | 92 | 90 |
| 2 | 1-bromohexadecane | hexadecane | 3 | 6 | 18 | 95 | 92 |
| 3 | 1-chlorohexadecane | hexadecane | 10 | 6 | 80 | 95 | 91 |
| 4 | 1-fluorohexadecane | hexadecane | 3 | 24 | 80 | 0 | |
| 5 | 1-bromododecane | dodecane | 3 | 6 | 18 | 95 | 90 |
| 6 | 1-bromooctane | octane | 3 | 6 | 18 | 94 | |
| 7 | 2-bromohexadecane | hexadecane | 5 | 6 | 80 | 94 | 90 |
| 8 | 1,10-dibromoundecane | 2-bromoundecane | 3 | 6 | 18 | 97 | 95 |
| 9 | 1,10-dibromodecane | decane | 4 | 5 | 18 | 98 | 94 |
| 10 | 1,10-dibromodecane | 1-bromodecane | 1[e] | 4 | 18 | 65 | |
| | | decane | | | | 3 | |
| 11 | 1-dodecyl methanesulfonate | dodecane | 3 | 6 | 40 | 95 | 91 |
| 12 | 2-octyl methanesulfonate | octane | 3 | 48 | 80 | 80 | |
| | | octene | | | | 10 | |
| 13 | 1-dodecyl toluenesulfonate | dodecane | 10 | 5 | 40 | 95 | 91 |
| 14 | 11-bromoundecan-1-ol | undecan-1-ol | 3 | 6 | 18 | 92 | 89 |
| 15 | methyl 11-bromoundecanoate | methyl undecanoate | 3 | 1 | 18 | 100 | 98 |
| 16 | 11-bromoundecanoic acid, *N-N*-dimethylamide | undecanoic acid, *N-N*-dimethylamide | 3 | 1 | 18 | 100 | 98 |
| 17 | bromocyclododecane | cyclododecane | 10 | 90 | 80 | 65 | |
| | | cyclododecene | | | | 7 | |
| 18 | bromocyclohexane | cyclohexane | 10 | 45 | 80 | 83 | |
| | | cyclohexene | | | | 1 | |
| 19 | 1-phenyl-1-bromoethane | phenylethane | 3 | 4 | 18 | 95 | 85 |
| 20 | 1-phenyl-1-bromoethane | 1-phenyl-1-deuterioethane | 3[f] | 6 | 18 | 99 | 90 |
| 21 | 1-phenyl-1-chloroethane | phenylethane | 10 | 3 | 80 | 95 | 85 |
| 22 | β-bromostyrene | styrene | 10 | 24 | 80 | 7 | |
| | | phenylacetylene | | | | 2 | |
| 23 | 1-phenyl-3-bromoprop-1-ene | 1-phenylprop-1-ene | 3 | 0 | 18 | 80 | |
| 24 | 2,4-dinitrochlorobenzene | 1,3-dinitrobenzene | 1 | 0 | 10 | *g* | |
| 25 | 2-chloronitrobenzene | nitrobenzene | 3 | 0 | 18 | *h* | |
| 26 | 4-chloronitrobenzene | nitrobenzene | 3 | 0 | 18 | *h* | |
| 27 | diphenylchloromethane | diphenylmethane | 3 | 6 | 80 | 85 | 77 |
| 28 | benzyl bromide | toluene | 2 | 0 | 18 | 100 | |
| 29 | benzyl chloride | toluene | 3 | 0 | 40 | 96 | |
| 30 | 4-nitrobenzyl bromide | 4-nitrotoluene | 2 | 0 | 18 | 100 | 99 |
| 31 | 4-nitrobenzyl chloride | 4-nitrotoluene | 3 | 0 | 40 | 100 | 99 |
| 32 | 4-bromobenzyl bromide | 4-bromotoluene | 2 | 0 | 18 | 100 | 95 |
| 33 | 4-chlorobenzyl bromide | 4-chlorotoluene | 2 | 0 | 18 | 96 | 91 |
| 34 | 4-fluorobenzyl bromide | 4-fluorotoluene | 2 | 0 | 18 | 100 | 93 |
| 35 | 4-cyanobenzyl bromide[i] | 4-cyanotoluene | 2 | 0 | 18 | 98 | 96 |
| 36 | 1,4-dibromomethylbenzene[i] | *p*-xylene | 4 | 0 | 18 | 100 | 94 |

[a] In toluene (1 mL/g of substrate). [b] From the end of addition of the aqueous phase. [c] Bath temperature. [d] By GC, NMR, or TLC analysis. [e] With 0.01 mol equiv of catalyst. [f] With $NaBD_4$ in $D_2O$. [g] As a complex mixture of products, also containing some 1,3-dinitrobenzene. [h] As a complex mixture of products, also containing some nitrobenzene. [i] Dissolved in 10 mL of dichloromethane/g of substrate.

Table II. Factors Affecting the Reaction between 1-Bromohexadecane[a] (1 mol equiv) and Sodium Borohydride at 18 °C under Phase-Transfer Conditions

| entry | sodium borohydride, mol equiv | catalyst[b] (mol equiv) | t,[c] h | % yield[d] |
|---|---|---|---|---|
| 1 | 3 | A (0.1) | 6 | 95 |
| 2 | 3 | B (0.1) | 24 | 71 |
| 3 | 3 | C (0.1) | 6 | 95 |
| 4 | 3 | D (0.1) | 70 | 40 |
| 5 | 3 | E (0.1) | 70 | 62 |
| 6 | 3 | A (0.05) | 22 | 95 |
| 7 | 3 | A (0.01) | 70 | 69 |
| 8 | 3 | | 48 | 3 |
| 9 | 2 | A (0.1) | 6 | 90 |
| 10 | 1.5 | A (0.1) | 24 | 78 |

[a] A toluene solution (1 mL/g of substrate) is used. [b] A = hexadecyltributylphosphonium bromide, B = tetrabutylammonium bromide, C = tetraoctylammonium bromide, D = triethylbenzylammonium chloride, E = *N*-methyl-*N*-dodecylephedrinium bromide. [c] From the end of the addition of the aqueous phase. [d] By GC analysis.

temperature-controlled conditions, activated aryl halides (i.e., 2,4-dinitrochlorobenzene, 2-nitrochlorobenzene, and 4-nitrochlorobenzene) give a variety of reaction products together with the expected nitroarenes (entries 24–26). Poor results have been obtained under homogeneous conditions.[10] Vinylic halides show a low reactivity (entry 22).

The selectivity of the reaction is very high with respect to a relevant number of functional groups, such as carboxylic esters (entry 15) and amides (entry 16), carbon–carbon double bonds in reactive alkyl halides (entry 23), nitroarenes (entries 30 and 31), and nitriles (entry 35).

The mildness of the reaction and its high selectivity, the quantitative recovery of the catalyst, and the simple operative conditions suggest that the present method is advantageously comparable with those previously reported.[1,2]

## Experimental Section

NMR spectra were recorded on a Varian EM-390 90-MHz spectrometer in $CCl_4$ solutions with $Me_4Si$ as internal standard.

(10) Gold, V.; Miri, A. Y.; Robinson, S. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 243, and references therein.

IR spectra were measured as films or Nujol mulls on a Perkin-Elmer 377 grating spectrophotometer using NaCl cells. GC data were obtained on a Hewlett-Packard Model 5850 A gas chromatograph using a 3% SE-30 Chromosorb column; conversions were corrected for detector response. TLC was performed on silica gel plates from Merck.

**Materials.** Sodium borohydride and solvents, commercially available grade reagents, were used as purchased. Catalysts, halides, and sulfonate esters were prepared by standard procedures or were obtained commercially.

**General Procedure for Reduction under PTC.** A solution of $NaBH_4$ in water (2.6 mL/g) was added at the indicated temperature in 30 min with magnetic stirring to a solution of substrate and catalyst in a suitable solvent; the stirring was maintained for the appropriate time (see Tables I and II). The layers were separated, and the product was obtained by distillation of the organic phase. From the distillation residue, the catalyst was recovered in nearly quantitative yields; it may be reused as such.

**Registry No.** 1-Iodohexadecane, 544-77-4; 1-bromohexadecane, 112-82-3; 1-chlorohexadecane, 4860-03-1; 1-fluorohexadecane, 408-38-8; 1-bromododecane, 143-15-7; 1-bromooctane, 111-83-1; 2-bromohexadecane, 74036-96-7; 1,10-dibromoundecane, 74036-98-9; 1,10-dibromodecane, 4101-68-2; 1-dodecyl methanesulfonate, 51323-71-8; 2-octyl methanesulfonate, 924-80-1; 1-dodecyl toluenesulfonate, 10157-76-3; 11-bromoundecan-1-ol, 1611-56-9; methyl 11-bromoundecanoate, 6287-90-7; 11-bromoundecanoic acid *N,N*-dimethylamide, 2732-31-2; bromocyclodecane, 2749-64-6; bromocyclohexane, 108-85-0; 1-phenyl-1-bromoethane, 585-71-7; 1-phenyl-1-chloroethane, 672-65-1; β-bromostyrene, 103-64-0; 3-phenyl-3-bromoprop-1-ene, 70032-14-3; 2,4-dinitrochlorobenzene, 97-00-7; 2-chloronitrobenzene, 88-73-3; 4-chloronitrobenzene, 100-00-5; diphenylchloromethane, 41376-15-2; benzyl bromide, 100-39-0; benzyl chloride, 100-44-7; 4-nitrobenzyl bromide, 100-11-8; 4-nitrobenzyl chloride, 100-14-1; 4-bromobenzyl bromide, 589-15-1; 4-chlorobenzyl bromide, 622-95-7; 4-fluorobenzyl bromide, 459-46-1; 4-cyanobenzyl bromide, 17201-43-3; 1,4-dibromomethylbenzene, 623-24-5; hexadecane, 544-76-3; dodecane, 112-40-3; octane, 111-65-9; 2-bromoundecane, 39563-54-7; decane, 124-18-5; 1-bromodecane, 112-29-8; octene, 62777-59-7; undecan-1-ol, 112-42-5; methyl undecanoate, 1731-86-8; undecanoic acid *N,N*-dimethylamide, 6225-09-8; cyclododecane, 294-62-2; cyclododecene, 1501-82-2; cyclohexane, 110-82-7; cyclohexene, 110-83-8; phenylethane, 100-41-4; 1-phenyl-1-deuterioethane, 1861-02-5; styrene, 100-42-5; phenylacetylene, 536-74-3; 3-phenylprop-1-ene, 300-57-2; 1,3-dinitrobenzene, 99-65-0; nitrobenzene, 98-95-3; diphenylmethane, 101-81-5; toluene, 108-88-3; 4-nitrotoluene, 99-99-0; 4-bromotoluene, 106-38-7; 4-chlorotoluene, 106-43-4; 4-fluorotoluene, 352-32-9; 4-cyanotoluene, 104-85-8; *p*-xylene, 106-42-3; sodium borohydride, 16940-66-2.

## Ketenes. 17. Reaction of Thiophosgene with Dimethylketene,[1] a Stable Thio Acid Chloride

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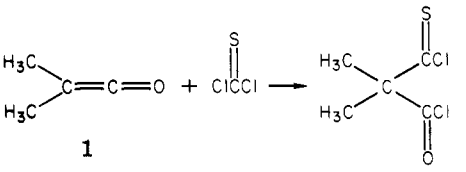
Staudinger reported that thiophosgene did not react with diphenylketene.[2] However, we found that thiophosgene reacted exothermically with dimethylketene (**1**) [2-methyl-1-propen-1-one] to give a high yield of 3-chloro-2,2-dimethyl-3-thioxopropanoyl chloride (**2**, eq 1).

The properties of aliphatic thio acid chlorides have not been reported. Mayer and Scheithauer[3] reported that these compounds cannot be prepared by the methods used

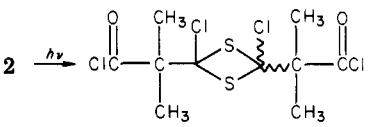


(1)

**1** **2**

to prepare aromatic thio acid chlorides and suggested that the aliphatic compounds are unstable. Thus the stability of **2**, which could be distilled at temperatures as high as 100 °C, is unusual.

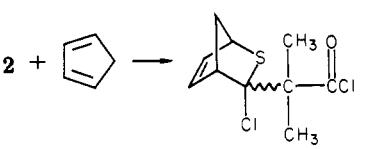
Compound **2** readily dimerized under the influence of sunlight or ultraviolet light to the solid dithietane **3** (eq 2) in a manner similar to the dimerization of thiophosgene.[4] A sample of **2** stored in the dark for several months did not dimerize.



(2)

**3**

Another reaction involving the carbon–sulfur bond of **2**, analogous to the reaction of thiophosgene with cyclopentadiene,[5] was the thermal [4 + 2] cycloaddition of cyclopentadiene to **2** to give the bicyclic adduct **4** of undetermined stereochemistry (eq 3).

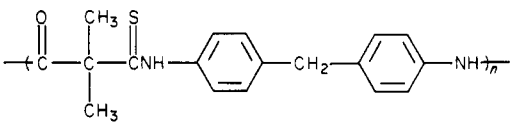


(3)

**4**

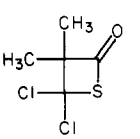
Other reactions of **2** in some ways parallel the reactions of dimethylmalonyl dichloride,[6] although **2** is generally less reactive. Compound **2** reacted readily with active hydrogen compounds, e.g., with phenol to give the diphenyl ester **5**, with methanol to give the dimethyl ester **6**, and with aniline to give the dianilide **7** (Scheme I). Methanethiol (1 equiv) and 1 equiv of sodium hydroxide reacted with **2** to give the ester **8**, and 2 equiv of each afforded the diester **9**. Compound **2** and 1,3-dimethylurea gave the thiobarbituric acid **10** in good yield.

Compound **2** reacted with 4,4′-methylenedianiline under interfacial polymerization conditions to give the polyamide–thioamide **11**.



**11**

When assigning the structure **2** to the adduct of thiophosgene and **1**, it was necessary to consider an alternate structure, **12**. This 2-thietanone could arise from the



**12**

addition of a ketene across a carbon–sulfur double bond,[7]

(1) Paper 16 in this series: R. D. Burpitt, K. C. Brannock, R. G. Nations, and J. C. Martin, *J. Org. Chem.*, **36**, 2222 (1971).
(2) H. Staudinger, O. Göhring, and M. Schöller, *Chem. Ber.*, **47**, 40 (1914).
(3) R. Mayer and S., Scheithauer, *Chem. Ber.*, **98**, 829 (1965).
(4) A. Schönberg and A. Stephenson, *Chem. Ber.*, **66**, 567 (1933).
(5) M. S. Raasch, *J. Org. Chem.*, **40**, 161–172 (1975).
(6) J. C. Martin, K. C. Brannock, and R. H. Meen, *J. Org. Chem.*, **31**, 2966 (1966).

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