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Reductive cleavage versus hydrogenation of allyl aryl ethers and allylic esters using sodium borohydride/catalytic ruthenium(III) in various aqueous solvent mixtures

James H. Babler *, Nicholas A. White, Eric Kowalski, Jeffrey R. Jast

Department of Chemistry, Loyola University Chicago, Chicago, IL 60660, United States

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ABSTRACT

The reduction of allyl aryl ethers using sodium borohydride in the presence of a catalytic amount of ruthenium(III) chloride in various aqueous solvent mixtures at 0 °C was examined. In aqueous tetrahydrofuran, hydrogenation was the favored pathway (85–100% yield of the corresponding aryl propyl ether); whereas in aqueous *N*-methylformamide, reductive cleavage predominated (4:1 mixture of phenolic product/aryl propyl ether). In order to gain some insight into the mechanism for this process, 3-octyn-1-ol and *trans*-2-decen-1-yl acetate were subjected to similar reductive conditions; and both substrates afforded products inconsistent with a single-electron-transfer mechanism.

Recently we reported[1] an experimentally convenient process for the small-scale hydrogenation of alkenes that avoids the use of a hydrogen cylinder and pressure equipment. The chemoselective reduction of various types of functionalized alkenes (including trisubstituted olefins) was achieved by addition of one molar equivalent (or less) of sodium borohydride to an aqueous *N*,*N*-dimethylacetamide (DMA) solution of the substrate and a catalytic amount of ruthenium(III) chloride at 0 °C, followed by subsequent stirring of this mixture in a stoppered flask at 0 °C for 60 min. Similar conditions ($NaBH_4$/cat. $RuCl_3$) had previously been reported[2] for selective reduction of mono- and disubstituted olefins in aqueous tetrahydrofuran (THF); however, that process resulted in a rapid evolution of hydrogen, loss of color in the liquid phase, and proceeded very slowly at 0 °C. In sharp contrast, when similar reductions were conducted in aqueous DMA, we observed[1] little (if any) release of H_2 and the appearance of a long-lasting (usually 30 min or more) dark blue-green color[3] (sometimes, very dark brown) in the liquid phase. In view of the unexpected behavior of the reductant in aqueous DMA (vs aqueous THF[2]), we decided to investigate this process further to obtain insight into a mechanistic pathway and to extend its synthetic utility.

Our previous Letter[1] reported that the sulfone functionality was inert to $NaBH_4$/cat. $RuCl_3$ in aqueous DMA at 0 °C; however, during that study, in an attempt to reduce the olefin moiety in allyl phenyl sulfone[4] using the latter conditions, only a low isolated yield (<15%) of phenyl propyl sulfone was obtained—an indication that reductive cleavage may have occurred. Since alcohols, phenols, and carboxylic acids can be protected[5] by conversion to the corresponding allyl ethers and esters, we decided to investigate our conditions ($NaBH_4$/cat. Ru^{+3}/aqueous DMA) as a possible method for deblocking such allyl derivatives. Although $NaBH_4$/cat. Ru^{+3}/3:1 (v/v) THF/H_2O has been reported[2] to convert allyl phenyl ether to phenyl propyl ether in quantitative yield, we hoped that our conditions would be more robust and effect the reductive cleavage of various types of allyl derivatives. Such a process could then be useful in protective group chemistry since various sensitive and/or reducible groups (e.g., acetals, allylic alcohols, benzyl ethers, epoxides, esters, halides, nitriles, and sulfones) have been shown[1] to be inert to these reducing conditions.

To initiate this study, we selected 1-methyl-4-(2-propen-1-yloxy)benzene (**1a**)[6] (allyl 4-methylphenyl ether) to ascertain whether our conditions ($NaBH_4$/cat. $RuCl_3$/aqueous DMA) would result in any reductive cleavage[7] of this allyl moiety along with the expected[2] hydrogenation of the allyl group. When the latter ether (**1a**) was subjected to our general procedure[8] [using 10:1 (v/v) DMA/H_2O as the solvent], proton NMR analysis[9] of the isolated product mixture indicated the presence of only two components: 4-methylphenol (**2a**)[10] and 1-methyl-4-propoxybenzene (**3a**)[11] in a ratio of 55:45. Although reductive cleavage of the allyl aryl ether was slightly favored over hydrogenation of the olefin functionality, the recovery of material was only 60%—presumably due to the loss of a substantial amount of 4-methylphenol (**2a**) during the aqueous washes used in the product isolation procedure.

* Corresponding author.
E-mail address: jbabler@luc.edu (J.H. Babler).

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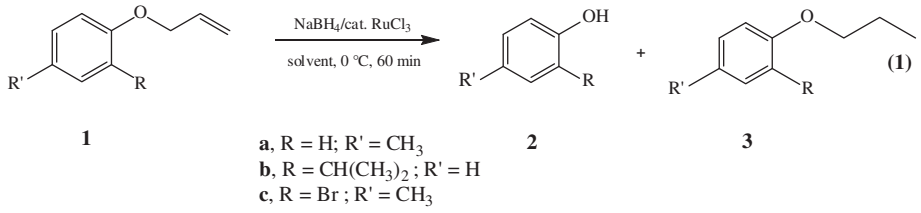


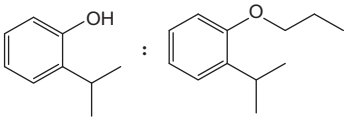
In order to determine more accurately the feasibility of effecting reductive cleavage of an allyl aryl ether (rather than hydrogenation of the allyl moiety), we selected 1-(1-methylethyl)-2-(2-propen-1-yloxy)benzene (**1b**)[12] as the representative substrate and conducted an investigation of the effect various solvent mixtures had on the ratio of the two expected products (**2b** and **3b**[13]). As indicated by the results in Table 1, a wide variation in the product ratio can be obtained as the organic solvent in the aqueous reaction mixture is changed from tetrahydrofuran (which afforded predominantly hydrogenation product **3b**) to the more polar liquid carboxamides, especially the protic, highly polar *N*-methylformamide, which dramatically enhanced the rate of cleavage (**1b** → **2b**). Decreasing the water content of the mixture (Table 1, entry 3 vs entry 1) also favored reductive cleavage of the allyl ether.

To verify the stability of a halide functionality to the conditions used in this reductive methodology, the allyl ether derivative (**1c**) [2-bromo-4-methyl-1-(2-propen-1-yloxy)benzene[14]] of 2-bromo-4-methylphenol[4] was subjected to the general procedure[8] [using 10:1 (v/v) *N*-methylformamide/H_2O as the solvent] and afforded a 77% isolated yield of the deblocked 2-bromo-4-methylphenol (**2c**)[10] and the hydrogenation product (2-bromo-4-methyl-1-propoxybenzene (**3c**)[15]) in a 4:1 ratio,[16] respectively. As expected from our previous work,[1] benzyl ether[4] and alkyl aryl ethers (e.g., 1-ethoxy-3-methylbenzene[17]) were inert to this reductive procedure.

To our surprise, subjection of a simple alkyl allyl ether to the general procedure for reductive cleavage [10:1 (v/v) *N*-methylformamide/H_2O as the solvent] occurred slowly and with poor selectivity. Thus, allyl octyl ether[18] [1-(2-propen-1-yloxy)octane] afforded, after approximately 50% conversion, a 3:2 mixture of octyl propyl ether[19]/1-octanol. In order to increase the solubility of allyl octyl ether in the reaction mixture, this procedure was repeated using 10:1 (v/v) DMA/H_2O as the solvent; and, to our dismay, >80% of the isolated product was 1-propoxyoctane[19] (octyl propyl ether), the product derived from hydrogenation of the allyl moiety.

The reductive cleavage process was successful when applied to a representative allyl ester (allyl nonanoate); although, as expected, benzyl esters (e.g., benzyl octanoate[20]) and alkyl esters (e.g., octyl acetate[4]) were inert to such conditions. Subjection of allyl nonanoate[21] to the general procedure[8] [using 10:1 (v/v) DMA/H_2O to dissolve this fatty ester] afforded cleanly a 4:1 mixture[22] of nonanoic acid/propyl nonanoate,[23] respectively, in 90% yield [isolated yield (reduction products + starting material) 94%].

Table 1
Ru^{+3}-catalyzed reduction[a] of 1-(1-methylethyl)-2-(2-propen-1-yloxy)benzene[b] (**1b**) using $NaBH_4$ in various aqueous solvent mixtures

Entry	Solvent Mixture	Recovery [product(s) + unreacted substrate] (%)	Isolated yield of reduction products (%)	Ratio[c,d] of  (**2b**) : (**3b**)
1	0.60 mL of 5:1 (v/v) DMA[e]/H_2O	74	74	65:35
2	0.60 mL of 5:1 (v/v) $CH_3NHCH{=}O/H_2O$	81	81	2:1
3	0.75 mL of 2:1 (v/v) DMA/H_2O[f]	70	60	1:4
4	0.75 mL of 2:1 (v/v) $CH_3NHCH{=}O/H_2O$	73	63	1.1:1
5	0.50 mL of 5:5:1 (v/v/v) DMA/$CH_3NHCH{=}O/H_2O$	92	92	3:1
6	0.50 mL of 10:1 (v/v) $CH_3NHCH{=}O/H_2O$	93	93	4:1
7	0.50 mL of 25:1 (v/v) $CH_3NHCH{=}O/H_2O$	93	93	3:1
8	0.60 mL of 5:1 (v/v) THF/H_2O[g]	98	98	1:5
9	0.60 mL of 5:1 (v/v) CH_3CN/H_2O[h]	83	37	4:5

[a] All reactions were conducted at 0 °C by addition of $NaBH_4$ (0.24 mmol) to an aqueous solvent mixture of substrate ether (0.19–0.20 mmol) and ruthenium(III) chloride hydrate (0.034 mmol), using the general procedure[8] for reductive cleavage of allyl ethers and esters.

[b] Prepared in 98% yield by reaction of 2-isopropylphenol (**2b**) [commercially available from Sigma–Aldrich (Milwaukee, WI, USA)] with allyl bromide in acetone containing an excess of K_2CO_3 powder at 20 °C. For a previous synthesis of this allyl ether, see Ref. [12].

[c] Structural assignments and product ratios were based on analysis of ^1H NMR spectral data (300 MHz) for these known compounds. For a previous synthesis of 1-(1-methylethyl)-2-propoxybenzene (**3b**), see Ref. [13].

[d] The ^1H NMR spectrum (300 MHz, $CDCl_3$) of 2-isopropylphenol (**2b**) was characterized by signals at δ 4.72 (s, 1H, OH); 3.21 (septet, J = 6.9 Hz, 1H); and 1.26 (d, J = 6.9 Hz, 6H). 1-(1-Methylethyl)-2-propoxybenzene (**3b**) was characterized by signals at δ 3.92 (t, J = 6.6 Hz, 2H, CH_2O); 3.35 (septet, J = 6.9 Hz, 1H); 1.21 (d, J = 6.9 Hz, 6H); and 1.06 (t, J = 7.2 Hz, 3H). Unless indicated otherwise, no unreacted starting ether (**1b**) [characterized by a signal at δ 4.53 (dt, J = 5.1 and 1.5 Hz, 2H, CH_2O)] was detected in the isolated product mixture.

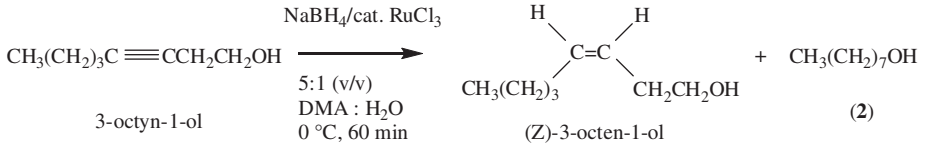
[e] Similar results were obtained when DMA was replaced by DMF, NMP, or DMPU [1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone].

[f] The quantities of $NaBH_4$ and $RuCl_3{\cdot}xH_2O$ were decreased to 0.18 mmol and 0.019 mmol, respectively, in this experiment.

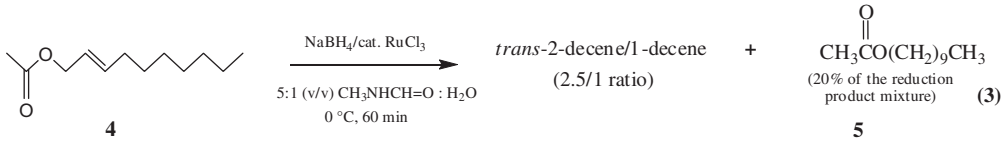
[g] This experiment, which involved the rapid evolution of H_2 gas upon addition of $NaBH_4$ to the mixture, occurred more slowly than reactions conducted in aqueous carboxamides. For consumption of all starting allyl ether, the reaction mixture was stirred in a closed vessel at 0 °C for 60 min, followed by 150 min at 20 °C.

[h] This experiment occurred more slowly than reactions conducted in aqueous carboxamides. The reaction mixture was stirred at 0 °C for 40 min, followed by 75 min at 20 °C. Since the selectivity (reductive cleavage versus hydrogenation) was not encouraging, no attempt was made to repeat this experiment to determine if all starting allyl ether could be consumed.

In order to elucidate a mechanistic pathway for this reductive cleavage process, 3-octyn-1-ol[4] was subjected to similar reaction conditions ($NaBH_4$, cat. $RuCl_3$, aqueous DMA, 0 °C). The experimental conditions were modified to minimize complete reduction of the alkyne moiety in order to ascertain the stereochemistry of the initially-formed alkenol. With this goal in mind, 3-octyn-1-ol (0.20 mmol) in 0.60 mL of 5:1 (v/v) DMA/H_2O was reduced at 0 °C (60 min) using only 3.5 mg (0.10 mmol) of $NaBH_4$ in the presence of 7 mg of $RuCl_3{\cdot}H_2O$.[4] Isolation of the product in the manner described in the general procedure[8] afforded a 73% isolated yield of a mixture of three components shown by careful proton NMR analysis[24] to be a 2.5:1:1 mixture of unreacted 3-octyn-1-ol[10]/(*Z*)-3-octen-1-ol[25]/1-octanol,[10] respectively. The most significant result of the experiment was the failure to detect the presence of any (*E*)-3-octen-1-ol,[24] thereby excluding a mechanism involving the formation of a radical anion intermediate.



The unlikelihood of a single-electron-transfer mechanism was further confirmed by subjection of *trans*-2-decen-1-yl acetate (**4**)[26] to our general procedure[8] for reductive cleavage in order to ascertain what happens to the allylic moiety during this transformation. When the reaction was conducted in 10:1 (v/v) DMA/H_2O using the general procedure,[8] the reduction occurred rapidly (less than 10% allylic acetate **4** was recovered). However, over-reduction of the initial C-10 alkene product(s) was a serious problem; and the major product was decane, accompanied by decyl acetate (**5**).[27] To circumvent this problem of over-reduction, the process was conducted in 5:1 (v/v) *N*-methylformamide/H_2O (in which any initially-formed 1- and/or 2-decene would be insoluble, thereby minimizing subsequent reduction). Isolation of the product mixture using a modified procedure,[28] followed by careful proton NMR analysis of the mixture and comparison of the data with that exhibited by authentic samples of 1-decene,[4] *trans*-2-decene,[29] decyl acetate (**5**),[27] and starting allylic acetate **4**, indicated that unreacted allylic acetate **4** comprised approximately 50% of the isolated product mixture. The reduction products consisted of a 2.5:1:1 mixture of *trans*-2-decene/1-decene/decyl acetate (**5**), respectively. The formation of a mixture of both *trans*-2-decene and 1-decene during the reductive cleavage suggests the involvement of a π-allylruthenium complex in this process, which is consistent with our observations from two separate control experiments.[30]



In addition to the mechanistic insight presented in this Letter, the reductive methodology detailed herein could be useful for deblocking allyl aryl ethers in the presence of benzylic and alkyl aryl ethers, especially if the selectivity (i.e., hydrogenolysis vs hydrogenation of the allyl moiety) can be improved. Selective cleavage of allyl carboxylate esters in the presence of benzylic, methyl, *tert*-butyl, and most other types of esters could also be a useful transformation since the non-hydrolytic conditions are mild and compatible with many common functional groups.

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6. This allyl aryl ether (**1a**) was prepared in 90% yield by treatment of 4-methylphenol (*p*-cresol) with allyl bromide and excess potassium carbonate powder in acetone at 20 °C. Its ^1H NMR spectral data (300 MHz) were identical to those previously reported by: Kong, L.; Lin, Q.; Lv, X.; Yang, Y.; Jia, Y.; Zhou, Y. *Green Chem.* **2009**, *11*, 1108–1111.
7. Reductive deprotection of allyl aryl ethers using the combination of a molar excess of $NaBH_4$ and a catalytic amount of $Pd(PPh_3)_4$ occurs in high yield under non-hydrolytic conditions at 20 °C. See: Beugelmans, R.; Bourdet, S.; Bigot, A.; Zhu, J. *Tetrahedron Lett.* **1994**, *35*, 4349–4350.
8. General procedure for reductive cleavage of allylic ethers and esters: To a 15-mL 1-neck reaction flask fitted with a glass stopper [NOTE: A larger-scale reaction may require use of a pressure vessel and/or addition of $NaBH_4$ in small portions.] were added a small spin bar, 0.19–0.20 mmol of substrate, 0.50 mL of either 10:1 (v/v) *N*-methylformamide/H_2O or 10:1 (v/v) DMA/H_2O, and 7.0 mg (0.034 mmol) of ruthenium(III) chloride hydrate (Sigma–Aldrich catalog no. 206229). After cooling the latter mixture to 0 °C (external ice-H_2O bath), 9.0 mg (0.24 mmol) of $NaBH_4$ powder was added in one portion; and the mixture was subsequently stirred at 0 °C for 60 min. The reaction was then quenched by addition of 2.00 mL of 2 M aqueous HCl to the reaction flask and subsequent stirring of the mixture at 0 °C for 15 min. The product was then isolated by dilution of the reaction mixture with 10 mL of 4:1 (v/v) pentane/dichloromethane; and the solid material was removed by filtration through a small pad of Hyflo Super-Cel® filtering aid. After dilution of the filtrate with 20 mL of 9:1 (v/v) pentane/dichloromethane, removal of the amide solvent was accomplished by washing the organic filtrate with 15% (w/v) aqueous NaCl (4 × 20 mL portions). The organic layer was then dried over anhydrous $MgSO_4$, filtered, and the volatile organic solvents were removed by evaporation at reduced pressure.
9. This ratio was determined by integration of proton NMR signals ($CDCl_3$, 300 MHz, ppm) arising from 4-methylphenol (**2a**)[10] [δ 4.74 (s, 1H, OH)] and 1-methyl-4-propoxybenzene (**3a**)[11] [δ 3.89 (t, J = 6.6 Hz, 2H, CH_2O) and δ 1.02 (t, J = 7.2 Hz, 3H)]. For full spectral characterization (^1H NMR and ^{13}C NMR) of 4-methylphenol, see Ref. 10.
10. The full ^1H NMR spectral data of this compound are freely accessible via the Spectral Data Base System (SDBS) maintained by the Japanese National Institute of Advanced Industrial Science and Technology at: http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng.
11. For access to the ^1H NMR spectrum of 1-methyl-4-propoxybenzene (**3a**), see: Manbeck, G. F.; Lipman, A. J.; Stockland, R. A., Jr.; Freidl, A. L.; Hasler, A. F.; Stone, J. J.; Guzei, I. A. *J. Org. Chem.* **2005**, *70*, 244–250.
12. Marvell, E. N.; Richardson, B.; Anderson, R.; Stephenson, J. L.; Crandall, T. *J. Org. Chem.* **1965**, *30*, 1032–1035.
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14. Prepared in 99% yield by treatment of 2-bromo-4-methylphenol (**2c**) with allyl bromide and excess K_2CO_3 in acetone at 20 °C. For a previous synthesis of this allyl aryl ether (**1c**), see: Bradsher, C. K.; Reames, D. C. *J. Org. Chem.* **1978**, *43*, 3800–3802.
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21. Allyl nonanoate[10] was prepared in 96% yield by treatment of nonanoic acid[4] with allyl bromide in the presence of excess potassium carbonate in 2:1 (v/v) acetone/1-methyl-2-pyrrolidinone at gentle reflux. For a previous synthesis of this ester, see: Kasymova, S. S.; Ergashev, M. S.; Kulakhmatova, M. A. *Uzb. Khim. Zh.* **1982**, *6*, 63–64.
22. This ratio was determined by ^{1}H NMR analysis of the crude reaction product. Approximately 4% unreacted allyl nonanoate[10] [characterized by a proton NMR signal ($CDCl_3$, 300 MHz) at δ 4.58 (dt, J = 7.7 and 1.2 Hz, 2H, CH_2O)] was detected in the latter mixture. Propyl nonanoate was characterized by proton NMR signals ($CDCl_3$, 300 MHz, ppm) at δ 4.03 (t, J = 6.9 Hz, 2H); 0.94 (t, J = 7.2 Hz, 3H); and 0.88 (t, J = 6.6 Hz, 3H).
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25. Complete ^{1}H NMR spectral data ($CDCl_3$, 400 MHz) for both (*E*)- and (*Z*)-3-octen-1-ol can be found in: Kapeller, D. C.; Brecker, L.; Hammerschmidt, F. *Chem. Eur. J.* **2007**, *13*, 9582–9588. The signals for the vinyl hydrogens in (*Z*)-3-octen-1-ol are listed in the latter publication at δ 5.58–5.48 (m, 1H) and 5.40–5.29 ppm (m, 1H).
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28. The product mixture was isolated in the usual manner[8] except that, after the aqueous washes and drying the organic layer over $MgSO_4$, most of the volatile organic solvents were removed by fractional distillation at atmospheric pressure (to minimize loss of C-10 alkenes).
29. Commercially available from ChemSampCo., Inc., Dallas, TX, USA. *trans*-2-Decene was characterized by ^{1}H NMR absorption ($CDCl_3$, 300 MHz) at δ 5.47–5.34 (m, 2H). For a previous synthesis of *trans*-2-decene, see: Julia, M.; Righini-Tapie, A.; Verpeaux, J. N. *Tetrahedron* **1983**, *39*, 3283–3287.
30. As suggested by a reviewer, we conducted a control experiment in which a solution of allylic acetate **4** (0.20 mmol) and $NaBH_4$ (0.24 mmol) in 0.60 mL of 5:1 (v/v) *N*-methylformamide/H_2O was stirred at 0 °C for 60 min. As expected, no reduction of unsaturated ester **4** occurred in the absence of ruthenium(III) chloride. In a separate experiment, a mixture of 1-decene[4] (0.20 mmol) and 0.60 mL of 5:1 (v/v) *N*-methylformamide/H_2O containing 4 mg of $RuCl_3$ and 6 mg of $NaBH_4$ powder was stirred at 0 °C for 60 min. Due to its insolubility in this reaction mixture, 1-decene was reasonably stable under such conditions [i.e., hydrogenation and isomerization (approximately 5% conversion of 1-decene to 2-decene occurred) were minimal].