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Metal/Ammonia Reduction of Ethers of 3-Decyn-1-ol: Effects of Structure and Conditions on Cleavage and Rearrangement

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Reduction of the THP, ethyl, *tert*-butyl and *tert*-butyldimethylsilyl (TBDMS) ethers of 3-decyn-1-ol with sodium in ammonia/THF results in extensive hydrogenolysis of the carbon–oxygen bond and concomitant bond migration, producing a mixture of 2- and 3-decenes and a very low yield of the desired (*E*)-homoallylic ether. Reduction in the presence of 2-methyl-2-propanol led to excellent yields of the desired (*E*)-3-decenol ethers. The 4- and 5-decyn-1-ol ethers were reduced normally to the (*E*)-decen–1–ol ethers except in the case of the TBDMS ethers which were cleaved to the (*E*)-alcohols under some of the reaction conditions.

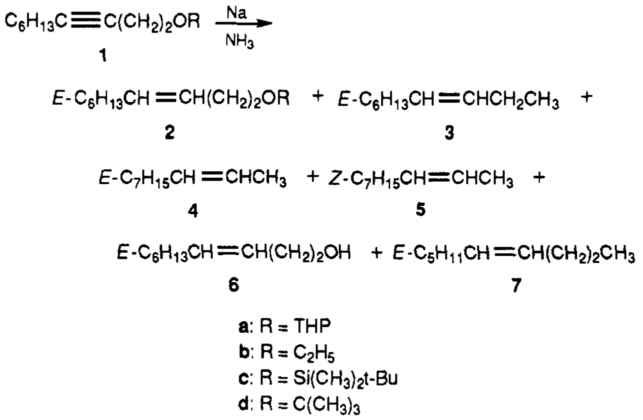
Introduction

The stereoselective reduction of disubstituted alkynes to *E*-olefins with solutions of alkali metals such as sodium and lithium in mixtures of liquid ammonia and nonprotic organic solvents is a widely used, reliable, and thoroughly studied reaction.[1–4] The reduction of functionalized alkynes to *E*-olefins has been used extensively for the preparation of insect sex pheromones.[5–7] These reports have emphasized the high *E*-stereoselectivity of the reduction and minimal formation of byproducts when the sodium is used in a large stoichiometric excess. In the course of the synthesis of the sex pheromones of the lesser peachtree borer, *Synanthedon pictipes* (Grote and Robinson), and the peachtree borer, *S. exitiosa* (Say),[8] sodium/NH_3 reduction of a homopropargylic tetrahydropyranyl ether, even when sodium was used in stoichiometric quantity, resulted in hydrogenolysis of the carbon–oxygen bond with concomitant bond migration to produce a mixture of olefins with the double bonds in the two and three positions. Only traces of desired E-homoallylic tetrahydropyranyl ether (THP) were detected. An investigation of the products from the sodium/NH_3 reduction of several model homopropargylic alcohol ethers under a variety of conditions (from excess sodium to stoichiometrically limited sodium, including proton sources more acidic than ammonia) was undertaken to fully delineate the scope of this reaction.

Results and Discussion

Four ether derivatives of 3-decyn-1-ol were reduced with metallic sodium in a mixture of NH_3 and THF, and the ratios of products were determined by capillary gas chromatographic analysis (CGC). Three of the four ethers chosen are commonly used as protecting groups for alcohols in synthetic applications (Scheme I). The results of the reduction of these ethers are presented in Table I.

Scheme I



$$C_6H_{13}C{\equiv}C(CH_2)_2OR \xrightarrow[NH_3]{Na}$$

1

$$E\text{-}C_6H_{13}CH{=}CH(CH_2)_2OR + E\text{-}C_6H_{13}CH{=}CHCH_2CH_3 +$$

2, 3

$$E\text{-}C_7H_{15}CH{=}CHCH_3 + Z\text{-}C_7H_{15}CH{=}CHCH_3 +$$

4, 5

$$E\text{-}C_6H_{13}CH{=}CH(CH_2)_2OH + E\text{-}C_5H_{11}CH{=}CH(CH_2)_2CH_3$$

6, 7

a: R = THP
b: R = C_2H_5
c: R = $Si(CH_3)_2t\text{-}Bu$
d: R = $C(CH_3)_3$

The course of the reductions and the distribution of products produced was directly dependent upon the nature of the proton source present in the reaction mixture or the manner in which an additional proton source was introduced to the reaction mixture. When ammonia was the sole proton source, or when a more acidic proton source (methyl alcohol, Table I, entry 2) was rapidly added immediately after the substrate, the THP, ethyl and *tert*-butyl ethers produced mixtures of the desired product **2a**, **2b**, and **2d**, respectively, plus the cleavage product (*E*)-3-decene **3**, as well as the cleavage/rearrangement products (*E*)- and (*Z*)-2-decene **4** and **5** and occasionally traces of (*E*)-4-decen-1-ol. The *tert*-butyldimethylsilyl ether (TBDMS) (entry 4) produced (*E*)-3-decen-1-ol in addition to the olefins **3–5** and no silyl ether reduction product **2c**. In one reaction, a small amount of 3-decyn-1-ol produced by cleavage of the starting ether was identified.

Conversely, when a proton source more acidic than ammonia (2-methyl-2-propanol, Table I, entry 3) was introduced into the reaction mixture just prior to the addition of substrate, a consistently high yield of the desired product **2a** was produced with no evidence of decenes or alcohols. In the case of the TBDMS ether (Table I, entry 7), the inclusion of 2-methyl-2-propanol resulted in a high yield of the desired product **2c** with no production of either (*E*)-3-decen-1-ol or 3-decyn-1-ol.

The data of Table I indicate that these cleavage rearrangement processes that occur when ammonia is the

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Table I. Product Distribution from the Dissolving Metal Reduction of 3-Decyn-1-yl Ethers[a]

		product (%)						
	entry R (products[e,f])	1[a] THP	2[b] THP	3[c] THP	4[a] C_2H_5	5[a] $C(CH_3)_3$	6[a] $Si(CH_3)_2C(CH_3)_3$[d]	7[c] $Si(CH_3)_2C(CH_3)_3$
2	(*E*)-$C_6H_{13}CH{=}CH(CH_2)_2OR$	27.0 (±2.85)	33 (±18)	92.5 (±3.5)	36.0 (±3.65)[g]	62.5 (±11)[g]	0	92 (±4.2)
3	(*E*)-$C_6H_{13}CH{=}CHCH_2CH_3$	17.8 (±3.2)	14.75 (±0.78)	0	16.3 (±2.7)	15.0 (±3.2)	20 (±2.7)	0
4	(*E*)-$C_7H_{25}CH{=}CHCH_3$	12.8 (±2.1)	11.8 (±0.14)	0	11.6 (±1.8)	9.5 (±1.1)	14.5 (±2.1)	0
5	(*Z*)-$C_7H_{15}CH{=}CHCH_3$	3.6 (±0.5)	3.7 (±0.0)	0	3.1 (±0.5)	2.7 (±0.36)	3.7 (±0.55)	0
6	(*E*)-$C_6H_{13}CH{=}CH(CH_2)_2OH$	0	0		0	0	34.5 (±5.3)	0
	total products	61.2	63.25	92.5	67	89.7	72.7	92

[a] Experimental method. The standard reaction conditions were 20 mL of NH_3, 10 mL of THF, 5 mg mmol (2.5 equiv) of Na, 2 mmol of substrate, and reaction for 2 h under NH_3 reflux. [b] Experimental method. The reaction was initiated under standard conditions (footnote *a*) but was immediately quenched after addition of substrate by rapid addition of 4 mmol (162 μL) of methanol. Average of two duplicate reactions. [c] Experimental method. The standard reaction conditions (footnote a) with the inclusion of 6.2 mmol (300 mg) of Na and 11.5 mmol (1.1 mL) of 2-methyl-2-propanol (added a few minutes prior to substrate addition). Average of two duplicate reactions. [d] In one of the four duplicate reactions, we found 6.56% 3-decyn-1-ol. [e] In the cases of the THP, ethyl, and *tert*-butyl ethers, at least one reaction produced traces (<0.5%) (*E*)-4-decene (product 7, Scheme I). [f] Percentages recorded are measured yields of gas chromatographed products present based upon a theoretical yield of 2 mmol of product **2**, ($\bar{x}$ ± SD). [g] Results are from four duplicate reactions.

Table II. Effect of Dilution and Ratio of Sodium to Starting Material on the Reduction of 3-Decyn-1-yl THP Ether

		20[a]			80[b]		
	NH_3 (mL) mmol of Na[c]	5[d]	12.5[a]	20[e]	2[f]	5[e]	20[e]
2	$C_6H_{13}CH{=}CH(CH_2)_2OTHP$	20.1 (±7.64)[g]	16.8 (±3.6)	6.8 (±1.98)	15	23.3 (±6.41)	26.2 (±5.94)
3	$C_6H_{13}CH{=}CH\text{-}CH_2CH_3$	24.7 (±3.35)	16.5 (±6.9)	17.7 (±1.31)	20.65	19.0 (±0.53)	14.4 (±0.42)
4	$C_7H_{15}\text{-}CH{=}CHCH_3$	14.5 (±2.18)	12.0 (±4.6)	11.6 (±0.81)	13.9	13.0 (±1.03)	9.7 (±0.42)
5	(*Z*)-$C_7H_{15}CH{=}CHCH_3$	5.3 (±0.92)	4.2 (±1.8)	3.3 (±0.32)	8.05	6.9 (±0.04)	5.8 (±1.38)
6	(*E*)-$C_5H_{11}CH{=}CH(CH_2)_2CH_3$	6.4 (±3.85)	0	6.15 (±1.34)	0	0	0
	total yield	71 (±10.2)	49.5 (±16.8)	45.4 (±1.91)	57.5	63 (±7.38)	56.4 (±6.15)

[a] These are the "standard" reaction conditions 2/1 NH_3/THF. [b] The ratio of NH_3/THF was 2/1. [c] This is the mmol equiv relative to substrate with the quantity of substrate held at 2 mmol. [d] These results are from four reactions. [e] These results are from two reactions. [f] This is the result from one reaction. [g] ($\bar{x}$ ± SD).

sole proton source can divert a considerable portion of the starting material from production of the desired *E*-ether in the case of the THP, ethyl, and *t*-Bu ethers, while in the case of the silyl ether, none of the desired product is isolated. The stereochemistry of the ether and alcohol products **2–7** were determined (capillary gas chromatography, CGC) to be not less than 95/5 *E*/*Z* in each case.

The effects of varying the stoichiometry of sodium relative to the THP ether substrate and the relative quantities of NH_3 and THF were determined, and the results are presented in Table II.

The data in Table II indicate that when ammonia is the sole proton source, dilution of the reaction mixture and/or increasing the amount of sodium does not significantly affect the overall yield of the desired product or the relative amounts of products.

The acidity of the proton source is clearly the most important factor in determining what course the reaction will take.

When products **2a** and **2d** (Scheme I) were subjected to the reduction conditions they were essentially unaffected, producing only trace amounts of (*E*)-3-decen-1-ol, thus indicating that the cleavage–rearrangement is part of the reduction process. The cleavage of the TBDMS ether **1c** to the alcohol by amide ion was unanticipated, since these ether derivatives are reported[9] to be stable to Na/NH_3 although there is no mention of the exposure of TBDMS ethers to Na/NH_3 in the original report.[10–11] When **2c** was exposed to the reduction conditions, less than 5% of (*E*)-3-decen-1-ol was produced, but otherwise, the starting material was recovered. Also, exposing dec-1-yl TBDMS ether to the conditions of the reduction with ammonia as a proton source led to the recovery of the starting material only. Similarly, when 4-decyn-1-yl THP ether was exposed to the Na/NH_3/THF, the reaction proceeded normally, producing (*E*)-4-decen-1-yl THP ether exclusively in good yield.

By treating (*E*)-3-decen-1-yl TBDMS ether **2c** under the standard reduction conditions with 2 mmol of 3-dodecyne and 2 mmol of additional sodium included, the only product was (*E*)-3-decen-1-ol **6**. When this same substrate ether was added to a suspension of sodium amide in NH_3/THF that had been prepared from 5.21 mmol of sodium the only product isolated was (*E*)-3-decenyl alcohol **6**. Thus, in the experiment run with added 3-dodecyne, the cleavage of the TBDMS ether to the alcohol was effected by the sodium amide present in the reaction mixture.

When (*E*)-4-decen-1-yl TBDMS ether was exposed to these same conditions, (*E*)-4-decen-1-ol was produced quantitatively. The other olefinic ethers **2a**, **2b**, and **2d** were unaffected under these same conditions. When 4-decyn-1-yl TBDMS ether was exposed to the reduction conditions, reduction and cleavage took place to produce (*E*)-4-decen-1-ol in good yield with only traces of the decenes **4** and **5** produced. When 5-decyn-1-yl TBDMS ether was exposed to the reduction conditions, (*E*)-5-decen-1-ol was produced exclusively.

Inspection of the results presented in Table I reveals that a considerable portion of the starting substrate in each case is unaccounted for in the products. This ranges from about 39% for the THP ether to 10.3% for the *tert*-butyl ether. Extensive CGC examination of the low-boiling components of the reaction mixtures did not reveal the presence of any lower molecular weight products that could account for the missing material balance. Temperature programming of the CGC analyses did not reveal the presence of any higher molecular weight products such as

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dimers or trimers to account for the material balance. 3-Decyn-1-yl THP ether was reduced on a 20 mmol scale (see Experimental Section), and the products were isolated by distillation in order to investigate the fate of the remainder of the starting substrate. A considerable high boiling distillation residue (probably produced by oligermerization) remained after removal of the product **2a** which, together with the lower boiling decenes, may account for the missing material. However, at present, the ultimate disposition of the THP group (that was cleaved from the starting substrate) is unknown.

Conclusion

It is clear from the data in Table I that reduction of the 3-decyn-1-yl THP and TBDMS ethers proceeds in good yield only when a proton source more acidic than ammonia (2-methyl-2-propanol) is included in the reaction mixture. Varying the stoichiometry of the reductant to the substrate (Table II) results in changes in the yield of desired product [(*E*)-3-decen-1-ol THP] but does not produce the product in satisfactory yield. Subsequent cleavage of the ethers to produce (*E*)-3-decen-1-ol is the only method that will conveniently produce this olefinic alcohol free of starting acetylene. Direct reduction of 3-alkyn-1-ols to the olefinic alcohol is very difficult. The method described by Schwarz[7] or the lithium bronze[12] method were unsatisfactory. A modification of the tetrahydroaluminate (LTHA) procedure of Rossi,[11] which may not be applicable to all substrates, was successful (see Experimental Section) but entails the separation of the product from 2-methoxyethyl ether (diglyme). A high dilution method[6] (using sodium in ammonia) resulted in only 80% conversion on the first reduction. The reaction mixture could be repeatedly resubmitted to the conditions of the reaction with the recovered 3-alkyn-1-ol decreasing approximately 5% upon each repetition. Thus, we have established a procedure for the reduction of 3-alkyn-1-ols via an ether derivative and have established, contrary to published reports,[9] that TBDMS ethers are not stable to sodium amide at liquid ammonia temperatures for extended periods but are stable to 2-methyl-2-propoxide.

Experimental Section

General Methods. Proton magnetic resonance spectra were recorded in $CDCl_3$, as 1% solutions, on a Nicolet 300-MHz spectrometer; shifts are in ppm relative to TMS. Infrared spectra were recorded as 2% w/v solutions in CCl_4 with either a Perkin-Elmer Model 467 or Model 1420 or a Nicolet Model 20SXC spectrophotometer. Mass spectra were recorded on a Finnigan 1014SL chemical ionization mass spectrometer using either methane or isobutane as reagent gas or a Finnegan mat ion trap detector interfaced to a Hewlett-Packard Model 5890 gas chromatograph. The CGC was carried out on a Hewlett-Packard Model 5890 gas chromatograph equipped with a Quadrex 50-m × 0.25-mm i.d. 007-1 methyl silicone capillary column operated in the on-column injection mode at a linear flow velocity (He carrier gas) of 18 cm/s. A Hewlett-Packard Model 3396 Series II integrator was used to quantify peak areas. The isomeric decenes were purchased from Chemical Samples Co., Columbus, OH.

Analytical Method. A blank experiment was conducted wherein known amounts of each of the reaction products was added to a standard reaction mixture (see below), and the reaction was run for 2 h and worked up. Quantitation of the products recovered is as follows: (*E*)-3-decen-1-yl THP ether, 102.3%; (*E*)-3-decene, 88%; (*E*)-2-decene, 94.6%; and (*Z*)-2-decene, 89.1%. The quantity of (*E*)-3-decen-1-yl THP ether recovered varied from 70% to 97% in two repeated experiments. In all of these experiments, the recovery of (*E*)-3-decene was consistently higher than 95%, indicating no mechanical losses. Based upon the known tendency of THP ethers to decompose upon CGC analysis we concluded that the poor recoveries of the THP ether are the result of thermal decomposition during CGC analysis.

Quantitation of the products recovered from (*E*)-3-decen-1-yl *tert*-butyl ether: 96% (±3.21) (*E*)-3-decene, 99% (±2.38) (*E*)-3-decen-1-yl *tert*-butyl ether (results from three replicates).

Reduction of ethers of 3-decyn-1-ol; **1a**–**1d**.

Standard Reaction. Anhydrous ammonia (20 mL) was condensed in a dry 50-mL three-necked flask via a "dry ice"/2-propanol reflux condenser. Sodium metal (0.120 g, 5 mmol) was added, producing a deep blue color. Anhydrous THF (distilled from benzophenone ketyl under nitrogen) (5 mL) was added followed by a solution of the 3-decyn-1-yl ether (**1a**–**1d**) (2 mmol) in 5 mL of anhyd THF. The reaction mixture turned a deep red. The mixture was held under reflux for 2 h and quenched by addition of NH_4Cl to give a light yellow mixture. The ammonia was allowed to evaporate, water and hexane were added, and the layers were separated. The aqueous layer was extracted several times with hexane, and the combined hexane extracts were washed with water and saturated brine and dried over Na_2SO_4. The drying agent was removed, the solvent evaporated, and the residual oil analyzed by CGC. Internal standards including *n*-nonane, dodecyl acetate, and decyl acetate (in the TBDMS experiments) were added, the samples were diluted with GC^2 hexane, and aliquots were injected on the CGC column. Quantitation was based on peak areas, predetermined response factors, and dilution. The reduction of **1a** was carried out on a larger scale than the standard reaction in order to look for other possible byproducts. The substrate was 4.73 g of 3-decyn-1-yl THP ether (20 mmol), 1.45 g (63 mmol) of sodium in 750 mL of NH_3, and 100 mL of THF. The weight of distilled product (a mixture of 3-decyn-1-yl THP ether and (*E*)-3-decen-1-yl THP ether) was 1.228 g (26%) with an extensive pot residue remaining.

The standard reaction conditions were modified for entries 2, 3, and 7 of Table I as follows: for entry 2, the reaction was immediately quenched with 4 mmol of methanol after the addition of the substrate; for entries 3 and 7, the quantity of sodium was increased to 6.2 mmol and 11.5 mmol of 2-methyl-2-propanol was added to the reaction mixture a few minutes prior to the substrate.

Preparation, Physical Constants and Spectral Characteristics of Ethers 1a–**1d.** 1a was prepared according to either of two published procedures[13,14] and had bp 110–112 °C/0.02 Torr: ^1H NMR 2.13 (2H, t, $C\mathit{H}_2C{\equiv}C$), 2.46 (2H, t, $C\mathit{H}_2C{\equiv}C$), 3.53 (2H, dt, $C\mathit{H}_2OC$), 3.7–3.95 (2H, m, $C\mathit{H}_2O$), 4.65 (1H, t, $OC\mathit{H}O$); IR (cm^{-1}) 1200, 1135, 1120, 1030 (CO). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.63; H, 10.84. **1b.** Sodium hydride (0.055 mol, 2.21 g of a 57% dispersion in oil) was placed in a 100-mL three-necked flask under a N_2 blanket and washed free of mineral oil with pentane. Then 7.7 g (0.05 mol) of 3-decynyl alcohol and 20 mL of anhydrous THF were added, and the mixture was stirred until the foaming stopped. Anhydrous hexamethylphosphoramide (HMPA) (10 mL) was added, the mixture was chilled (−20 °C), and a solution of 8.58 g (0.55 mol) of ethyl iodide in 10 mol of HMPA was added. The mixture was allowed to come to room temperature and stirred overnight. Dilution with water and extraction several times with hexane, washing the hexane extracts with water and saturated brine, drying (Na_2SO_4), and removal of drying agent and solvent gave 8.47 g (93%) **1b**: bp 96–98 °C/4.8 Torr; ^1H NMR 2.14 (2H, t, $C\mathit{H}_2C{\equiv}C$), 2.43 (2H, t, $C\mathit{H}_2C{\equiv}C$), 3.51 (4H, q, t, $C\mathit{H}_2OC\mathit{H}_2$); IR (cm^{-1}) 1120 (CO). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.77; H, 11.98. **1c** was prepared according to the published procedure[10] and had bp 85 °C/0.09 Torr: ^1H NMR

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2.06 (2H, t, $C\mathit{H}_2C{\equiv}C$), 2.29 (2H, t, $C\mathit{H}_2C{\equiv}C$), 3.62 (2H, t, $C\mathit{H}_2OSi$); IR (cm^{-1}) 1255 ($SiCH_3$), 1100 (CO, SiOR). Anal. Calcd for $C_{16}H_{32}OSi$: C, 71.57; H, 12.02. Found: C, 71.64; H, 12.17. **1d** was prepared according to the published procedure[15] and had bp 92–95 °C/2 Torr: ^{1}H NMR 1.19 [9H, s, $C(C\mathit{H}_3)_3$], 2.13 (2H, m, $C\mathit{H}_2C{\equiv}C$), 2.35 (2H, m, $C\mathit{H}_2C{\equiv}C$) 3.43 (2H, t, $C\mathit{H}_2O$); IR (cm^{-1} 1196 (CO), 1085 (CO); MS *m/z* 211 (M + 1), 193 (M + 1 – H_2O), 155 (M + 1 – C_4H_8), 137 (M + 1 – $C_4H_{10}O$).

Preparation, Physical Constants, and Spectral Properties of ethers 2a–2d. These ethers were prepared from (*E*)-3-decen-1-ol (prepared from 3-decyn-1-ol by repeated Na/NH_3 reduction) analogously to **1a**–**1d** and had the following physical constants and spectral properties. **2a**: bp 115 °C/0.02 Torr; ^{1}H NMR 1.98 (2H, dt, $C\mathit{H}_2CH{=}C$), 2.31 (2H, dt, $C\mathit{H}_2CH{=}C$), 4.60 (1H, t, $OC\mathit{H}O$), 5.35–5.6 (2H, m, $\mathit{H}C{=}C\mathit{H}$); IR (cm^{-1}) 3020 (C=CH, 1200, 1140, 1125, 1035 (CO), 975 (*E*-C=C). Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 74.86; H, 11.95. **2b**: bp 60 °C/0.02 Torr; ^{1}H NMR 1.98 (2H, dt, $C\mathit{H}_2CH{=}C$), 2.27 (2H, dt, $C\mathit{H}_2CH{=}C$), 3.4–3.6 (4H, q and t, $C\mathit{H}_2OC\mathit{H}_2$), 5.3–5.6 (2H, m, $C\mathit{H}{=}C\mathit{H}$; IR (cm^{-1}) 3020 (C=CH), 1115 (CO), 975 (*E*-C=C). Anal. Calcd for $C_{12}H_{24}O$: C, 78.20; H, 13.12. Found: C, 77.98; H, 12.91. **2c**: bp 55 °C/0.001 Torr; ^{1}H NMR 1.93 (2H, dt, $C\mathit{H}_2C{=}C$), 2.15 (2H, dt, $C\mathit{H}_2C{=}C$), 3.55 (2H, t, $C\mathit{H}_2OSi$), 5.25–5.5 (2H, m, $\mathit{H}C{=}C\mathit{H}$); IR (cm^{-1}) 3015 (C=CH), 1255 ($SiCH_3$), 1100 (CO, SiOR), 970 (*E*-C=C). Anal. Calcd for $C_{16}H_{34}OSi$: C, 71.03; H, 12.67. Found: C, 71.21; H, 12.49. **2d**: bp 89–91 °C/1.5 Torr; ^{1}H NMR 1.19 (9H, s, $C(C\mathit{H}_3)_3$), 1.98 (2H, dt, $C{=}CHC\mathit{H}_2$), 2.21 (2H, dt, $C{=}CHC\mathit{H}_2$), 3.33 (2H, t, $CH_2C\mathit{H}_2O$), 5.34–5.54 (2H, m, $\mathit{H}C{=}C\mathit{H}$); IR (cm^{-1}) 3020 ($\mathit{H}C{=}C$), 1197 (CO), 1079 (CO), 970 (*E*-C=C); MS 213 (M + 1), 157 (M + 1 – C_4H_8).

(*Z*)-3-Decen-1-ol was prepared from 3-decyn-1-ol by hydrogenation over "P-2 nickel" catalyst[16] and had bp 120 °C (20 Torr): ^{1}H NMR 2.06 (2H, dt $C{=}CHC\mathit{H}_2$), 2.33 (2H, dt, $C{=}CHC\mathit{H}_2$), 3.64 (2H, t, $C\mathit{H}_2OH$), 5.3–5.4 (1H, dt, $C{=}C\mathit{H}$), 5.5–5.61 (1H, dt, $C{=}C\mathit{H}$); IR (cm^{-1}) 3010 (C=CH), 1100 (CO). Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: 77.10; H, 13.06. (*E*)-3-Decen-1-ol was prepared by repeated reduction of 3-decyn-1-ol with sodium in NH_3/THF[6] and had bp 125 °C (20 Torr) (lit.[11] bp 113–114 °C (15 Torr): ^{1}H NMR 2.01 (2H, dt $C{=}CC\mathit{H}_2$), 2.26 (2H, dt, $C{=}CHC\mathit{H}_2$), 3.62 (2H, t, $C\mathit{H}_2OH$), 5.3–5.5 (1H, m, $C{=}C\mathit{H}$), 5.5–5.65 (1H, m, $C{=}C\mathit{H}$); IR (cm^{-1}) 3015 (C=CH), 1050 (CO), 970 (*E*-C=C); MS 157 (M + 1).

(*Z*)-3-Decen-1-yl ethyl ether (*Z* analog of **2b** was prepared from **1b** by reduction over "P-2 nickel" and had: ^{1}H NMR 2.04 (2H, dt, $C{=}CHC\mathit{H}_2$), 2.33 (2H, dt, $C{=}CHC\mathit{H}_2$), 3.4 (2H, t, $CH_2C\mathit{H}_2O$), 3.49 (2H, q, $OC\mathit{H}_2CH_3$), 5.3–5.42 (1H, dt, $CH_2\mathit{H}C{=}C$), 5.42–5.53 (1H, dt, $CH_2\mathit{H}C{=}C$); IR (cm^{-1}) 3008 (C=CH), 1110, 1125 (CO). Anal. Calcd for $C_{12}H_{24}O$: C, 78.20; H, 13.12. Found: C, 78.06; H, 13.28.

(*Z*)-3-Decen-yl TBDMS ether (*Z* analog of **2c**) was prepared from 3-decyn-1-yl TBDMS ether by hydrogenation over "Lindlar" catalyst[17] and had bp 60 °C (0.002 Torr): ^{1}H NMR 1.98 (2H, dt, $C{=}CHC\mathit{H}_2$), 2.22 (2H, dt, $C{=}CHC\mathit{H}_2$), 3.54 (2H, t, $CH_2C\mathit{H}_2O$), 5.25–5.5 (2H, m, $\mathit{H}C{=}C\mathit{H}$); IR (cm^{-1}) 3020 ($\mathit{H}C{=}C$), 1256 ($SiCH_3$), 1099 (CO, SiOR); MS 271 (M + 1), 213 (M + 1 – C_4H_{10}).

(*Z*)-3-Decen-1-yl *tert*-butyl ether (*Z* analog of **2d**) was prepared from 3-decyn-1-yl *tert*-butyl ether by hydrogenation over "Lindlar" catalyst[17] and had bp 90–92 °C/2 Torr: ^{1}H NMR 1.19 [(9H, s, $C(C\mathit{H}_3)_3$], 2.04 (2H, dt, $C{=}CHC\mathit{H}_2$), 2.27 (2H, dt, $C{=}CHC\mathit{H}_2$, 3.25 (2H, t, $C\mathit{H}_2O$), 5.31–5.5 (2H, m, $CH_2\mathit{H}C{=}C\mathit{H}CH_2$); IR (cm^{-1}) 3020 ($\mathit{H}C{=}C$), 1197 (CO), 1080 (CO); MS 213 (M + 1), 157 (M + 1 – C_4H_8).

4-Decyn-1-yl tetrahydropyranyl ether was prepared by alkylation of 4-pentyn-1-yl tetrahydropyranyl ether with pentyl bromide[7] and had bp 120 °C/0.02 Torr: ^{1}H NMR 2.13 (2H, t, $C\mathit{H}_2C{\equiv}C$), 2.35 (2H, t, $C\mathit{H}_2C{\equiv}C$), 3.50 (2H, dt, $C\mathit{H}_2OC$), 3.6–3.9 (2H, m, $C\mathit{H}_2OC$), 4.59 (1H, t, $OC\mathit{H}O$); IR (cm^{-1}) 1165, 1035 (CO). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.82; H, 10.79.

(*E*)-4-Decen-1-yl tetrahydropyranyl ether prepared from 4-decyn-1-yl tetrahydropyranyl ether by reduction with Na/NH_3 had bp 125 °C/0.02 Torr: ^{1}H NMR 1.97 (2H, dt, $CH_2CH{=}C$), 2.06 (2H, dt, $C\mathit{H}_2CH{=}C$), 4.58 (1H, t, $OC\mathit{H}O$), 5.39–5.43 (2H, m, $\mathit{H}C{=}C\mathit{H}$); IR (cm^{-1}) 3020 (C=CH), 1200, 1140, 1125, 1035 (CO), 975 (*E*-C=C). Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 74.70; H, 11.70.

4-Decyn-1-yl TBDMS ether was prepared[10] from 4-decyn-1-ol and had bp 75 °C/0.007 Torr: ^{1}H NMR 2.07 (2H, m, $C\mathit{H}_2C{\equiv}C$), 2.16 (2H, m, $C\mathit{HC}{\equiv}C$), 3.63 (2H, t, $C\mathit{H}_2OSi$); IR (cm^{-1}) 1256 (Si CH_3), 1105 (CO, SiOR); MS 269 (M + 1); 211 (M + 1 – C_4H_{10}).

5-Decyn-1-yl TBDMS ether was prepared[10] from 5-decyn-1-ol and had bp 75 °C/0.012 Torr: ^{1}H NMR 2.1 (4H, 2t, 2 × $C\mathit{H}_2C{\equiv}C$), 3.58 (2H, t, $-C\mathit{H}_2OSi$); IR (cm^{-1}) 1256 ($SiCH_3$), 1105 (CO, SiOR); MS 269 (M + 1), 211 (M + 1 – C_4H_{10}).

(*E*)-4-Decen-1-yl TBDMS ether was prepared[10] from (*E*)-4-decen-1-ol and had bp 85 °C/0.007 Torr: ^{1}H NMR 2.16 (4H, 2t, 2 × $C\mathit{H}_2CH{=}CH$), 3.56 (2H, t, $C\mathit{H}_2OSi$), 5.27–5.43 (2H, m, $\mathit{H}C{=}C\mathit{H}$); IR (cm^{-1}) 3010 (C=CH), 1255 (Si CH_3), 1102 (CO), SiOR), 968 (*E*-C=C); MS 271 (M + 1), 213 (M + 1 – C_4H_{10}).

(*E*)-3-Decen-1-ol, (*E*)-3-dodecen-1-ol, (*E*)-3-tetradecen-1-ol, and (*E*)-3-hexadecen-1-ol via the reduction of 3-decyn-1-ol, 3-dodecyn-1-ol, and 3-hexadecyn-1-ol were prepared by a modification of the LTHA method. A mixture of diglyme (80 mL or 10 mL) and lithium tetrahydroaluminate (5 g, 0.131 mol or 1.67 g, 0.0436 mol) together with 0.038 mol of either 3-decyn-1-ol or 3-tetradecyn-1-ol or together with 0.013 mol of either 3-dedecyn-1-ol or 3-hexadecyn-1-ol was heated to 100 °C for 8 h. The mixture was cooled, diluted with ether (2 × the diglyme volume), and hydrolyzed with water and 15% sodium hydroxide.[17] The nonhydrated granular aluminum hydroxide was removed by filtration, and the diglyme and product were separated by distillation. The yields are as follows: (*E*)-3-decen-1-ol 77%, (*E*)-3-dodecen-1-ol 87.5%, (*E*)-3-tetradecen-1-ol 95.5%, and (*E*)-3-hexadecen-1-ol 84%. It was not possible to completely separate the (*E*)-3-decen-1-ol from the diglyme whereas the other (*E*)-3-alkenols separated cleanly. The (*E*)-3-alkenols were identified by their IR, ^{1}H NMR, and mass spectra.

(*E*)-5-Decen-1-yl TBDMS ether was prepared[10] from (*E*)-5-decen-1-ol and had bp 90 °C/0.006 Torr: ^{1}H NMR 1.93 (4H, 2t, 2 × $C\mathit{H}_2CH{=}CH$), 3.56 (2H, t-$C\mathit{H}_2OSi$), 5.27–5.42 (2H, m, $\mathit{H}C{=}CH$); IR (cm^{-1}) 3012 (C=CH), 1256 ($SiCH_3$), 1102 (CO, SiOR), 968 (*E*-C=C); MS 271 (M + 1 – C_4H_{10}).

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