

A Convenient Catalytic Method for the Synthesis of Ethers from Alcohols and Carbonyl Compounds

Yasuyuki Fujii,* Hisakazu Furugaki, Eiko Tamura,† Shinji Yano,†† and Katsumi Kita†††

Materials Development Research Laboratories, Kao Corporation, 1334 Minato, Wakayama 640-8580

Received July 30, 2004; E-mail: fujii.yasuyuki@kao.co.jp

Dialkyl ethers and alkyl fluoroalkyl ethers are obtained in excellent yields by the reaction of alcohols and carbonyl compounds in the presence of Pd/C under the atmospheric pressure of hydrogen, when water produced by the reaction is continuously removed by bubbling hydrogen through the reaction mixture.

The Williamson synthesis[1] has been industrially used for the synthesis of ethers, in spite of requiring strongly basic conditions and generating a stoichiometric amount of waste salts. In view of environmentally benign organic chemistry, an alternative catalytic method with minimal waste is desired.[2–5] Diethyl ether and dibutyl ether are catalytically synthesized from the corresponding alcohols in strongly acidic conditions, and MTBE (methyl *tert*-butyl ether) is synthesized from methanol and isobutene using an acidic ion-exchanged resin as a catalyst. The former method is usable only for synthesis of symmetrical ethers with short alkyl chains. The latter method is usable only for the synthesis of *tert*-butyl ethers. On the other hand, a catalytic method for the synthesis of ethers from alcohols and carbonyl compounds under hydrogen atmosphere using PtO_2[6] under acidic conditions or $Pd(OH)_2$[7] as a catalyst has been reported previously, although it could not become a general synthetic method for ethers because of various limitations, as pointed out by Lemaire et al.[8] Recently, Lemaire et al.[8] and we[9] have independently found that ethers can be obtained from alcohols and carbonyl compounds in good yields (>80%) using Pd/C as a catalyst under a hydrogen atmosphere. The proposed methods, however, require a relatively high pressure of hydrogen (>40 atm, where use of an autoclave is unavoidable) and a dilute solution of substrate ($\sim$0.2 mol dm^{-3}). Under a low pressure of hydrogen, the side reactions increase and the yields decrease remarkably: 1-butanol reacted with octanal gave only 39% butyl octyl ether at 10 atm of hydrogen.[10] These limitations are disadvantages not only in laboratories but also especially in industries. Moreover, we found that the removal of water from the reaction mixture was indispensable to the synthesis of ethers, and we reported a useful catalytic method under the atmospheric pressure of hydrogen for the synthesis of ethers (Scheme 1).[11]

In this paper we report our successful results for the synthesis of dialkyl ethers and alkyl fluoroalkyl ethers using our "hydrogen-bubbling method" and discuss the action of Pd/C under hydrogen atmosphere and the reaction mechanism.

Results and Discussion

Synthesis of Ethers under Atmospheric Pressure of Hydrogen. Ethers are not easily obtained from primary alcohols and ketones using Pd/C as a catalyst under atmospheric pressure of hydrogen. On the other hand, when a stream of hydrogen was bubbled through the reaction mixture during the reaction, the conversion of alcohol increased with the increasing flow rate of hydrogen. The relationship between the flow rate of hydrogen and the conversion of alcohol is shown in Fig. 1, when 1-hexadecanol and 4-methyl-2-pentanone as a substrate and neutral-type Pd/C (5% palladium-on-carbon, 8 wt %/1-hexadecanol) as a catalyst were used at 105 °C.

The effusion of water with a stream of hydrogen was observed in a Dean–Stark trap during the reaction. These results indicate that the removal of water with hydrogen-bubbling accelerates the Pd/C-catalyzed etherification to give good yields even under the atmospheric pressure of hydrogen. At more than a 180 mL/min-flow rate of hydrogen, the rate of conversion of alcohols did not increase further. This means that the 180 mL/min-flow rate of hydrogen provides a desirable volume of hydrogen for the reaction conditions. The conversion of 1-hexadecanol is 40% at 116 °C (bp of 4-methyl-2-pentanone) in 8 h under the 180 mL/min-flow rate of hydrogen. The lower reactivity may be attributed to the decrease in the partial pressure of hydrogen. The conversion of 1-hexadecanol was 2% using basic-type Pd/C and was 86% using acidic-type Pd/C at 105 °C in 8 h under the 180 mL/min-flow rate of hydrogen. The selection of the flow rate of hydrogen, the reaction temperature, and the kind of Pd/C is especially important to our hydrogen-bubbling method. We tried the synthesis of various dialkyl ethers under our suitable reaction conditions and verified the generality of our hydrogen-bubbling method (Table 1).

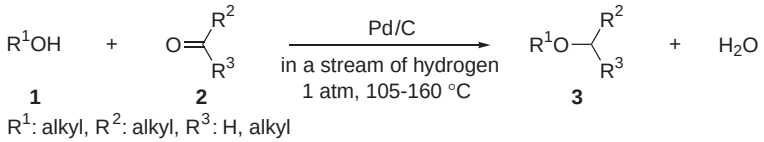
Primary alcohols reacted with ketones or aldehydes to give the corresponding ethers in excellent yields using neutral-type Pd/C as a catalyst under the atmospheric pressure of hydrogen

† Present address: Skin Care Products Research Laboratories, Kao Corporation, 2-1-3 Bunka, Sumida-ku, Tokyo 131-8501

†† Present address: Division for Product Safety, Kao Corporation, 2-1-3 Bunka, Sumida-ku, Tokyo 131-8501

††† Present address: Research Center for Characterization and Analytical Science, Kao Corporation, 2606 Akabane, Ichikai-machi, Haga-gun, Tochigi 321-3497

Published on the web March 11, 2005; DOI 10.1246/bcsj.78.456



Scheme 1.

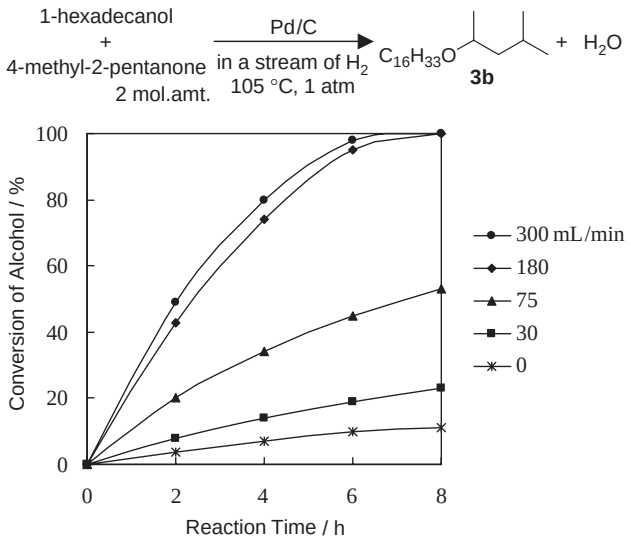


Fig. 1. Effect of the flow rate of hydrogen on the etherification.

(Table 1, entries 1–11), except for acetophenone (entry 12), 2,2-dimethylpropionaldehyde (entry 13), and 2,4-dimethyl-3-pentanone (entry 14). Paraldehyde, which could generate acetaldehyde, could be used as a reactant to synthesize ethyl ether (entry 8). A symmetrical ether could also be synthesized (entry 4). A conjugated ketone also reacted with a primary alcohol (entry 11). A secondary alcohol also reacted with an aldehyde in high yields by hydrogen-bubbling (entry 16), whereas the corresponding ether was not obtained with a ketone (entry 17). The low reactivity of 1-octanol with acetophenone may be attributed to the low reactivity of acetophenone due to resonance stabilization (entry 12). Low reactivities of 2,2-dimethylpropionaldehyde (entry 13), 2,4-dimethyl-3-pentanone (entry 14), and 4-methyl-2-pentanone with benzyl alcohol (entry 15) and with 2-octanol (entry 17) may be attributed to steric hindrance. When aldehydes were added dropwise during the reaction, side reactions such as the reduction of aldehyde were minimal in our synthetic procedure. The effusion of water with a stream of hydrogen was observed during the reaction, and an amount of water corresponding to that of the ethers formed was obtained: in the case of entry 1, 3.3 g of water (93% of the theoretical amount) was obtained.

Next, we tried the synthesis of alkyl fluoroalkyl ethers using the hydrogen-bubbling method (Table 2). Alkyl fluoroalkyl ethers were previously synthesized by the Williamson synthesis,[12] the Mitsunobu condensation,[13] and an addition to olefins[14] in laboratories.

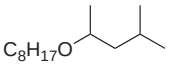
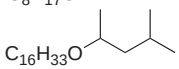
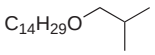
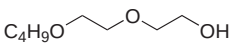
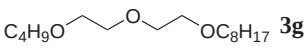
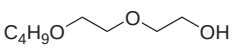
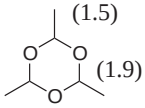
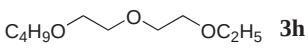
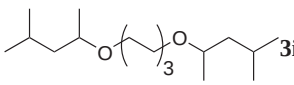
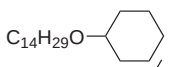
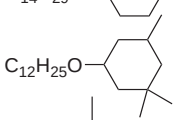
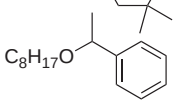
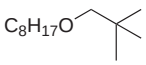
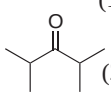
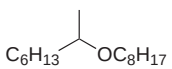
Non-branched 2-(perfluoroalkyl)ethanol reacted with either ketones or aldehydes to give the unique 2-(perfluoroalkyl)ethyl alkyl ethers (Table 2, entries 1–8). The low reactivity of a branched fluoro alcohol (entry 9) may be attributed to steric hindrance. The low reactivities of (fluoroalkyl)methanols (entries 10, 11) may be attributed to the lower compatibility of the high fluoride-substituted alcohols with a ketone. Pd/C-catalyzed etherification may be useful for the industrial synthesis of alkyl fluoroalkyl ethers. Synthesized 2-(perfluoroalkyl)ethyl alkyl ethers **3o–3u** were easily soluble (10% solution) in ethanol, acetone, hexane, and dimethylsiloxane (KF96A-6, Shinetsu Silicone Corp.). Furthermore, **3o**, **3q**, **3t**, and **3u** were also soluble (10% solution) in perfluoropolyether (trifluoromethyl-poly[oxy-2-(3-trifluoromethyl)-trifluoroethylene]-poly(oxydifluoromethylene)-trifluoromethoxy: Fomblin HC/04, Ausimont SpA). Interestingly, **3v** became a gel in ethanol (5% solution) and in dimethylsiloxane (10% solution).

Action of Pd/C under Hydrogen Atmosphere and Reaction Mechanism. Next, we show our proposed reaction mechanism for the formation of ethers in Scheme 2 and we discuss the action of Pd/C in the reaction process. First, Lemaire et al.[10] considered that the main reaction is the formation of hemiacetal **4** which is also dehydrated to the enol ether **6** followed by hydrogenation to the desired ether or by direct hydrogenolysis to ether **3**. Furthermore, they report that the formation of acetal **5** from hemiacetal **4** is irreversible under the reaction conditions (50–100 °C, 40 atm).

We could not obtain the reaction intermediates for hemiacetal **4**, acetal **5**, and enol ether **6** under our conditions (Table 1, 2). When the reaction temperature was 70 °C (Table 1, entry 5), however, we could confirm the acetal (1,1-bis(decyloxy)-butane **5e**) as the reaction intermediate by GC analysis. After 8 h, when the reaction temperature was increased to 160 °C, **5e** was immediately transformed into **3e**. We isolated **5e** using flash column chromatography: **5e** was obtained at 10% of the theoretical amount in 8 h at 70 °C. These results indicate that the reaction will not stop under our reaction conditions even if acetal **5** forms. Because the participation of Pd in the acetalization and the hydrogenolysis was thought to occur under hydrogen atmosphere, we studied the acetalization (synthesis of 4-methyl-2,2-ethylenedioxypentane **5x**) from ethylene glycol and 4-methyl-2-pentanone (Table 3) and the hydrogenolysis from 2,2-bis(octyloxy)propane **5y** to isopropyl octyl ether **3y** and 1-octanol using various Pd catalysts (Table 4).

The capability of Pd to catalyze an acetalization under hydrogen atmosphere has been reported previously: syntheses of acetal from cinnamaldehyde with methanol[15] and from cyclohexanone with ethylene glycol are reported.[16] We also confirmed the formation of acetal in the presence of Pd under hydrogen atmosphere. Especially, the neutral- and acidic-type Pd/C (Table 3, entries 1, 2) showed good activity, the same level as that of *p*-toluenesulfonic acid (entry 7). Basic-type Pd/C, Pd-black, Pd/Zeolite, and Pd/SiO_2–Al_2O_3 had low activities (entries 3–6). The conversion of 1-hexadecanol with 4-methyl-2-pentanone (synthesis of 1,3-dimethylbutyl hexadecyl ether **3b**) was 2% using basic-type Pd/C at 105 °C under the

Table 1. Synthesis of Dialkyl Ethers[a)]

Entry	Alcohol **1**	Carbonyl compound **2** (molar amount)	Product[b)] **3**	Conversion of alcohol/%[c)]	Yield /%[d)]
1[e)]	1-octanol	4-methyl-2-pentanone (2.0)	 **3a**	>99	97
2[e)]	1-hexadecanol	4-methyl-2-pentanone (2.0)	 **3b**	>99	98
3[f)]	1-tetradecanol	2-methylpropanal (1.1)	 **3c**	>99	96
4[f)]	1-octanol	octanal (1.1)	$C_8H_{17}OC_8H_{17}$ **3d**	>99	97
5[f)]	1-decanol	butanal (1.5)	$C_{10}H_{21}OC_4H_9$ **3e**	>99	95
6[f)]	1-hexadecanol	octanal (1.2)	$C_{16}H_{33}OC_8H_{17}$ **3f**	>99	96
7[f)]		octanal (1.5)	 **3g**	97	95
8[f)]		 (1.9)	 **3h**	98	96
9[g)]	1,6-hexanediol	4-methyl-2-pentanone (4.0)	 **3i**	98	94
10[e)]	1-tetradecanol	cyclohexanone (2.0)	 **3j**	>99	96
11[h)]	1-dodecanol	isophorone (2.0)	 **3k**	97	92
12[i)]	1-octanol	acetophenone (2.0)	 **3l**	22	18
13[f)]	1-octanol	 (1.0)	 **3m**	45	41
14[e)]	1-octanol	 (2.0)	—	no reaction	
15[e)]	benzyl alcohol	4-methyl-2-pentanone (2.0)	—	no reaction	
16[f)]	2-octanol	octanal (1.2)	 **3n**	>99	95
17[e)]	2-octanol	4-methyl-2-pentanone (2.0)	—	no reaction	

a) All reactions were carried out under a stream of hydrogen (180 mL/min) using Pd/C (5% palladium-on-carbon, 8 wt %/alcohol **1**). b) All products were characterised by IR, NMR, and mass spectra. c) Determined by GLC. d) Isolated yields based on the starting alcohols. e) 105 °C, 8 h. f) 160 °C, 10 h. Aldehydes were added dropwise during a period of 8 h. g) 105 °C, 48 h. h) 105 °C, 10 h. i) 120 °C, 8 h.

180 mL/min-flow rate of hydrogen. The low conversion may be attributed to the low activity of Pd/C.

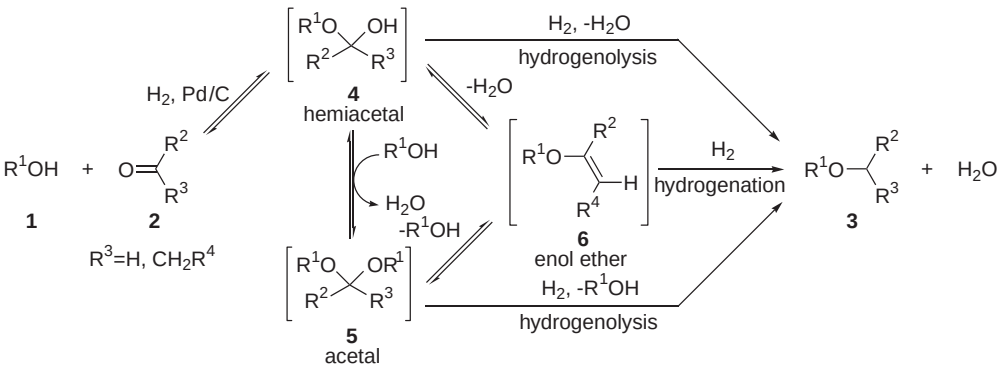
Acetals formed from primary or secondary alcohols with ketones are easily hydrogenolyzed to give the corresponding ethers and alcohols using Rh/Al_2O_3 at 2–4 atm of hydrogen under acidic conditions.[17] 2,2-Bis(octyloxy)propane **5y** was completely hydrogenolyzed at room temperature in 24 h using neutral- and acidic-type Pd/C under atmospheric pressure of hydrogen to give isopropyl octyl ether **3y** and 1-octanol (Table 4, entries 1, 2). Basic-type Pd/C and Pd-black clearly promoted the hydrogenolysis of **5y** at 100 °C (entries 3, 4). These results indicate that the hydrogenolysis of acetal **5** formed with alcohol and ketone is easily promoted under our conditions (Table 1, 2) with any kind of Pd catalyst.

Therefore, it can be concluded that Pd/C catalyzed both the acetalization and hydrogenolysis and that the most suitable catalyst for our etherification was neutral- and acidic-type Pd/C with high activity for acetalization and hydrogenolysis. The removal of water may shift the equilibrium toward the acetal **5** or enol ether **6** from hemiacetal **4**, followed by hydrogenolysis or hydrogenation to the corresponding ether **3** with $Pd/C–H_2$. Now we propose the reaction mechanism (see Scheme 2). Ethers are also directly generated from hemiacetal **4** or acetal **5**, because 2,2-dimethylpropyl octyl ether **3m**, which cannot form the enol ether **6**, forms from 1-octanol and 2,2-dimethylpropionaldehyde (Table 1, entry 13).

Table 2. Synthesis of Alkyl Fluoroalkyl Ethers[a)]

Entry	Alcohol **1**	Carbonyl compound **2** (molar amount)	Product[b)] **3**		Conversion of alcohol /%[c)]	Yield /%[d)]
1[e)]	C_6F_{13}OH	4-methyl-2-pentanone (2.0)	C_6F_{13}O	**3o**	95	92
2[f)]	C_6F_{13}OH	octanal (1.5)	$C_6F_{13}OC_8H_{17}$	**3p**	98	90
3[f)]	C_6F_{13}OH	CHO (1.1)	C_6F_{13}O	**3q**	99	92
4[f)]	C_6F_{13}OH	dodecanal (1.2)	$C_6F_{13}OC_{12}H_{25}$	**3r**	98	92
5[f)]	C_8F_{17}OH	octanal (2.5)	$C_8F_{17}OC_8H_{17}$	**3s**	85	80
6[f)]	C_8F_{17}OH	CHO (1.1)	C_8F_{17}O	**3t**	85	78
7[f)]	$C_{10}F_{21}$OH	octanal (1.7)	$C_{10}F_{21}OC_8H_{17}$	**3u**	87	81
8[f)]	$C_{10}F_{21}$OH	dodecanal (2.0)	$C_{10}F_{21}OC_{12}H_{25}$	**3v**	89	83
9[e)]	C_3F_7, CF_3, F_3C, OH	4-methyl-2-pentanone (2.0)	C_3F_7, CF_3, F_3C, O	**3w**	35	29
10[e)]	$H(CF_2)_8$OH	4-methyl-2-pentanone (4.0)	—		no reaction	
11[e)]	C_7F_{15}OH	4-methyl-2-pentanone (2.0)	—		no reaction	

a) All reactions were carried out under a stream of hydrogen (180 mL/min) using Pd/C (5% palladium-on-carbon, 8 wt %/alcohol **1**). b) All products were characterised by IR, NMR, and mass spectra. c) Determined by GLC. d) Isolated yields based on the starting alcohols. e) 105 °C, 8 h. f) 160 °C, 10 h. Aldehydes were added dropwise during a period of 8 h.



Scheme 2. Proposed mechanism for the formation of ethers.

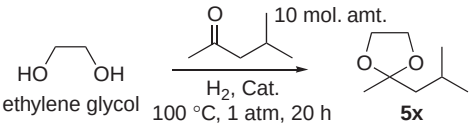
We reported the synthesis of ethers using Pd/C under the atmospheric pressure of hydrogen. From the viewpoint of industrial applications, the advantages of the proposed method are as follows; employing ether synthesis (i) under the atmospheric pressure of hydrogen, (ii) without using an autoclave, (iii) without generating any waste salts, (iv) by using 2-fold amounts of carbonyl compounds without using any co-solvents. Further, the amount of hydrogen used could be reduced to less than that in the autoclave method by circulating hydrogen to reuse it during the reaction. On the other hand, it should be pointed out as a limitation that a water-soluble or low-boiling substrate, e.g., acetone, methanol, etc., may not be applied without an alternative procedure for separating water, instead of the "Dean–Stark trap technique" used here.

In conclusion, the Pd/C-catalyzed etherification assisted by the hydrogen-bubbling dehydration may be useful for the synthesis of ethers from alcohols and carbonyl compounds, especially for environmentally benign industrial production as an alternative method to the Williamson synthesis.

Experimental

General. Melting points were measured on a Mettler EP62. IR spectra were recorded on a Horiba FT-700. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, on a

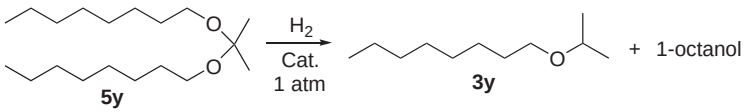
Table 3. Effect of Pd on the Acetalization



Entry	Catalyst (pH)[a)]	Amount of cat. /wt %[b)]	Conversion of ethylene glycol/%[c)]	Selectivity /%[c)]
1	Pd/C[d)] (7.1)	2.0	67	>99
2	Pd/C[d)] (3.8)	2.0	67	>99
3	Pd/C[d)] (10.3)	2.0	3	>99
4	Pd-black	1.7	0	0
5	Pd/Zeolite[d)] (6.5)	2.0	7	>99
6	Pd/SiO_2–Al_2O_3[d)] (8.0)	2.0	0	0
7	*p*-TsOH·H_2O	0.18	77	>99

a) pH of catalyst/water suspension. b) To ethylene glycol. c) Determined by GLC. d) 5% palladium-on-support.

Table 4. Effect of Pd on the Hydrogenolysis



Entry	Catalyst (pH)[a)]	Amount of cat. /wt %[b)]	Conversion of **5y**/%[c)] r.t., 24 h → 100 °C		Selectivity /%[c)]
1	Pd/C[d)] (7.1)	2.0	>99		>99
2	Pd/C[d)] (3.8)	2.0	>99		>99
3	Pd/C[d)] (10.3)	2.0	trace	>99 (3 h)	>99
4	Pd-black	0.69	trace	>99 (15 h)	>99

a) pH of catalyst/water suspension. b) To **5y**. c) Determined by GLC. d) 5% palladium-on-carbon.

VARIAN Mercury 400, using $CDCl_3$ as a solvent and TMS as an internal standard. Mass spectra were recorded on a JOEL SX-102A spectrometer. GC analysis was performed on a Hewlett Packard 4890 with a capillary column (Ultra 1, Hewlett Packard). Flow rates of hydrogen were measured with a Dry Test Gas Meter (Shinagawa Seiki DC-2). For flash column chromatography, Merck Kieselgel 60 (230–400 mesh) was used. The catalysts used, three types of Pd/C (5% palladium-on-carbon), "neutral-type", "acidic-type", and "basic-type", Pd/Zeolite (5% palladium-on-zeolite) and Pd/SiO_2–Al_2O_3 (5% palladium-on-silica–alumina), were purchased from N. E. CHEMCAT Corp. Pd-black was purchased from Aldrich Corp. When 0.2 g of catalyst was suspended in 3 g of water, the pH of the resulting suspension was 7.1 for neutral-type Pd/C, 5.9 for acidic-type Pd/C, 10.3 for basic-type Pd/C, 6.5 for Pd/Zeolite, and 8.0 for Pd/SiO_2–Al_2O_3.

Typical Procedure for the Synthesis of Ethers from Alcohols and Ketones. A mixture of 1-hexadecanol (48 g, 0.20 mol), 4-methyl-2-pentanone (40 g, 0.40 mol), and neutral-type Pd/C (5% palladium-on-carbon 3.8 g, 0.19 g as Pd) was placed in a flask equipped with a tube for introducing hydrogen and a Dean–Stark trap. The mixture was stirred vigorously under a stream of hydrogen (180 mL/min, at atmospheric pressure) at 105 °C. During the reaction, the water produced was eliminated from the effluent, and the substrates that effused were returned continuously to the reaction mixture by the "Dean–Stark trap technique". The reaction was monitored by GLC. After completion of the reaction (8 h), the reaction mixture was filtered. After the excessive 4-methyl-2-pentanone was evaporated, the product was purified by flash chromatography on silica gel (hexane:ethyl acetate = 20:1) to afford 1,3-dimethylbutyl hexadecyl ether **3b** (64 g, 98%).

Typical Procedure for the Synthesis of Ethers from Alcohols and Aldehydes. A mixture of 1-tetradecanol (43 g, 0.20 mol) and neutral-type Pd/C (5% palladium-on-carbon 3.4 g, 0.17 g as Pd) was placed in a flask equipped with a tube for introducing hydrogen and a Dean–Stark trap and was heated at 160 °C with vigorous stirring under a stream of hydrogen (180 mL/min, at atmospheric pressure). To the reaction mixture 2-methylpropanal (16 g, 0.22 mol) was added dropwise for 8 h. After the addition of 2-methylpropanal, the reaction mixture was maintained under the same hydrogen-bubbling condition for 2 h. During the reaction, the water produced was eliminated from the reaction mixture. The reaction was monitored by GLC. After completion of the reaction, the reaction mixture was filtered. After the low-boiling point compounds were evaporated, the product was purified by flash chromatography on silica gel (hexane:ethyl acetate = 20:1) to afford 2-methylpropyl tetradecyl ether **3c** (52 g, 96%).

1,3-Dimethylbutyl Octyl Ether (3a): Colorless oil; IR (neat) 1095, 1371, 1468, 2856, 2927 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3H, $J = 7.2$ Hz), 0.92 (d, 6H, $J = 6.4$ Hz), 1.11 (d, 3H, $J = 6.8$ Hz), 1.12–1.38 (m, 10H), 1.43–1.60 (m, 4H), 1.77 (m, 1H), 3.20–3.60 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.11, 20.02, 22.60, 22.72, 23.11, 24.71, 26.36, 29.37, 29.54, 30.32, 31.93, 46.48, 68.51, 73.52; HRMS (CI) Found: m/z 215.2366 $(M + H)^+$. Calcd for $C_{14}H_{30}O$: M + H, 215.2375.

1,3-Dimethylbutyl Hexadecyl Ether (3b): Colorless oil; IR

(neat) 1093, 1371, 1468, 2854, 2924 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3H, $J = 7.2$ Hz), 0.92 (d, 6H, $J = 6.4$ Hz), 1.11 (d, 3H, $J = 6.8$ Hz), 1.12–1.38 (m, 26H), 1.43–1.60 (m, 4H), 1.77 (m, 1H), 3.20–3.60 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.28, 20.14, 22.72, 22.91, 23.26, 24.83, 26.50, 29.60, 29.73, 29.86 (2C), 29.90 (2C), 29.94 (4C), 30.46, 32.16, 46.61, 68.65, 73.63; HRMS (CI) Found: m/z 327.3641 $(M + H)^+$. Calcd for $C_{22}H_{46}O$: M + H, 327.3627.

2-Methylpropyl Tetradecyl Ether (3c): Colorless oil; IR (neat) 1117, 1381, 1468, 2854, 2925 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3H, $J = 6.8$ Hz), 0.90 (d, 6H, $J = 6.8$ Hz), 1.19–1.38 (m, 22H), 1.59 (m, 2H), 1.87 (m, 1H), 3.16 (d, 2H, $J = 6.4$ Hz), 3.40 (t, 2H, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.27, 19.58 (2C), 22.91, 26.43, 28.65, 29.60, 29.74, 29.86 (2C), 29.91 (2C), 29.92 (2C), 29.99, 32.16, 71.27, 78.03; HRMS (CI) Found: m/z 271.3029 $(M + H)^+$. Calcd for $C_{18}H_{38}O$: M + H, 271.3001.

Dioctyl Ether (3d): Colorless oil; IR (neat) 1115, 1377, 1468, 2856, 2925 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 6H, $J = 6.8$ Hz), 1.18–1.38 (m, 20H), 1.58 (m, 4H), 3.40 (t, 4H, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.01 (2C), 22.63 (2C), 26.19 (2C), 29.26 (2C), 29.45 (2C), 29.77 (2C), 31.82 (2C), 70.93 (2C). These spectral data agreed with those of an authentic sample (Aldrich).

Butyl Decyl Ether (3e): Colorless oil; IR (neat) 1120, 1377, 1466, 2854, 2925 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, 3H, $J = 7.6$ Hz), 0.90 (t, 3H, $J = 7.6$ Hz), 1.18–1.41 (m, 16H), 1.48–1.59 (m, 4H), 3.33–3.40 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.30, 14.47, 19.81, 23.10, 26.63, 29.75, 29.93, 30.00, 30.04, 30.21, 32.30, 32.32, 70.90, 71.24; HRMS (EI) Found: m/z 214.2290 (M^+). Calcd for $C_{14}H_{30}O$: M, 214.2297.

Hexadecyl Octyl Ether (3f): White solid; mp 28.2 °C; IR (neat) 1117, 1377, 1466, 2854, 2923 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 6H, $J = 7.6$ Hz), 1.18–1.38 (m, 36H), 1.58 (m, 4H), 3.40 (t, 4H, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.26, 14.28, 22.88, 22.91, 26.46 (2C), 29.53, 29.62, 29.72, 29.76, 29.87 (2C), 29.92 (2C), 29.95 (4C), 30.04 (2C), 32.08, 32.17, 71.17 (2C); HRMS (CI) Found: m/z 355.3908 $(M + H)^+$. Calcd for $C_{24}H_{50}O$: M + H, 355.3940.

2-Butoxyethyl 2-(Octoxy)ethyl Ether (3g): Colorless oil; IR (neat) 1119, 1466, 2856, 2925 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3H, $J = 6.8$ Hz), 0.91 (t, 3H, $J = 7.2$ Hz), 1.20–1.43 (m, 12H), 1.57 (m, 4H), 3.46 (m, 4H), 3.55–3.67 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 14.02, 14.19, 19.42, 22.79, 26.26, 29.42, 29.60, 29.81, 31.88, 31.98, 70.26 (2C), 70.81 (2C), 71.30, 71.63; HRMS (CI) Found: m/z 275.2623 $(M + H)^+$. Calcd for $C_{16}H_{34}O_3$: M + H, 275.2586.

2-Butoxyethyl 2-Ethoxyethyl Ether (3h): Colorless oil; IR (neat) 1117, 1350, 1458, 2868, 2933 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, 3H, $J = 7.6$ Hz), 1.16 (t, 3H, $J = 7.2$ Hz), 1.32 (m, 2H), 1.52 (m, 2H), 3.41 (t, 2H, $J = 6.8$ Hz), 3.48 (q, 2H, $J = 7.2$ Hz), 3.52–3.63 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 13.59, 14.83, 18.99, 31.45, 66.30, 69.58, 69.82, 70.36, 70.39, 70.87; HRMS (CI) Found: m/z 191.1633 $(M + H)^+$. Calcd for $C_{10}H_{22}O_3$: M + H, 191.1647.

1,6-Bis(1,3-dimethylbutoxy)hexane (3i): Colorless oil; IR (neat) 1093, 1371, 1468, 2868, 2956 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (d, 12H, $J = 7.2$ Hz), 1.12 (d, 6H, $J = 6.0$ Hz), 1.15–1.92 (m, 14H), 3.20–3.60 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 19.68 (2C), 22.28 (2C), 22.76 (2C), 24.36 (2C), 25.86 (2C), 29.91 (2C), 46.10 (2C), 68.06 (2C), 73.18 (2C); HRMS (CI) Found: m/z 287.2934 $(M + H)^+$. Calcd for $C_{18}H_{38}O_2$: M + H, 287.2950.

Cyclohexyl Tetradecyl Ether (3j): Colorless oil; IR (neat) 1109, 1363, 1452, 2854, 2925 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, $J = 6.8$ Hz), 1.14–1.42 (m, 27H), 1.46–1.94 (m, 7H), 3.17 (m, 1H), 3.40 (t, 2H, $J = 6.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.47, 23.11, 24.56, 26.32, 26.70, 29.81, 29.95, 30.07 (2C), 30.11 (2C), 30.13, 30.14, 30.68 (2C), 32.35, 32.70 (2C), 68.16, 77.55; HRMS (EI) Found: m/z 296.3067 (M^+). Calcd for $C_{20}H_{40}O$: M, 296.3079.

Dodecyl 3,3,5-Trimethylcyclohexyl Ether (3k): Colorless oil; IR (neat) 1093, 1344, 1456, 2854, 2923 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75–1.08 (m, 2H), 0.86 (s, 3H), 0.86 (d, 3H, $J = 6.4$ Hz), 0.89 (t, 3H, $J = 6.8$ Hz), 1.05 (s, 3H), 1.20–1.44 (m, 20H), 1.48–1.96 (m, 5H), 3.22–3.59 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.55, 23.15, 23.20, 23.60, 26.82, 27.67, 29.85, 30.00, 30.13 (3C), 30.17, 30.66, 31.19, 32.40, 34.63, 39.62, 41.04, 49.31, 60.51, 75.53; HRMS (EI) Found: m/z 310.3204 (M^+). Calcd for $C_{21}H_{42}O$: M, 310.3236.

Octyl 1-Phenylethyl Ether (3l): Colorless oil; IR (neat) 700, 760, 1105, 1452, 2856, 2927 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (t, 3H, $J = 6.4$ Hz), 1.30–1.50 (m, 10H), 1.52 (d, 3H, $J = 6.4$ Hz), 1.67 (m, 2H), 3.38 (t, 3H, $J = 6.8$ Hz), 4.45 (q, 1H, $J = 6.4$ Hz), 7.27–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.63, 23.22, 24.80, 26.78, 29.84, 30.00, 30.53, 32.39, 69.12, 78.33, 126.31 (2C), 127.47, 128.56 (2C), 144.57; HRMS (EI) Found: m/z 234.1996 (M^+). Calcd for $C_{16}H_{26}O$: M, 234.1984.

2,2-Dimethylpropyl Octyl Ether (3m): Colorless oil; IR (neat) 1119, 1466, 2854, 2927 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, $J = 6.8$ Hz), 0.90 (s, 9H), 1.20–1.38 (m, 10H), 1.55 (m, 2H), 3.04 (s, 2H), 3.39 (t, 2H, $J = 6.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.52, 23.10, 26.63, 27.15 (3C), 29.75, 29.91, 30.11, 32.29, 32.46, 71.93, 81.66; HRMS (CI) Found: m/z 201.2206 $(M + H)^+$. Calcd for $C_{13}H_{28}O$: M + H, 201.2218.

1-Methylheptyl Octyl Ether (3n): Colorless oil; IR (neat) 1097, 1373, 1466, 2856, 2927 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 6H, $J = 7.6$ Hz), 1.12 (d, 3H, $J = 6.4$ Hz), 1.19–1.42 (m, 18H), 1.53 (m, 4H), 3.20–3.56 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.24 (2C), 19.90, 22.84, 22.86, 25.81, 26.49, 29.52, 29.63, 29.68, 30.43, 32.06, 32.11, 36.98, 68.63, 75.52; HRMS (CI) Found: m/z 243.2679 $(M + H)^+$. Calcd for $C_{16}H_{34}O$: M + H, 243.2688.

2-(Perfluorohexyl)ethyl 1,3-Dimethylbutyl Ether (3o): Colorless oil; IR (neat) 1146, 1242, 1369, 2962 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (d, 3H, $J = 6.4$ Hz), 0.90 (d, 3H, $J = 6.4$ Hz), 1.14 (d, 3H, $J = 6.0$ Hz), 1.16 (m, 1H), 1.48 (m, 1H), 1.73 (m, 1H), 2.37 (m, 2H), 3.49 (m, 1H), 3.61 (dt, 1H, $J = 9.6$, 6.4 Hz), 3.80 (dt, 1H, $J = 9.6$, 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 19.59, 22.43, 22.91, 24.56, 31.96 (t, $J = 21.4$ Hz), 46.11, 60.05, 74.40, 107.24 (m), 109.60 (m), 112.30 (m), 114.50 (m), 117.21 (m), 119.90 (m); HRMS (CI) Found: m/z 449.1144 $(M + H)^+$. Calcd for $C_{14}H_{17}OF_{13}$: M + H, 449.1150.

2-(Perfluorohexyl)ethyl Octyl Ether (3p): Colorless oil; IR (neat) 1146, 1240, 1365, 2931 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, $J = 7.2$ Hz), 1.20–1.38 (m, 10H), 1.57 (m, 2H), 2.40 (m, 2H), 3.44 (t, 2H, $J = 6.8$ Hz), 3.70 (t, 2H, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$) δ 13.88, 22.72, 26.18, 29.38, 29.53, 29.70, 31.67 (t, $J = 22.2$ Hz), 31.95, 62.56, 71.53, 108.48 (m), 110.98 (m), 113.08 (m), 115.67 (m), 118.36 (m), 121.07 (m); HRMS (CI) Found: m/z 477.1482 $(M + H)^+$. Calcd for $C_{16}H_{21}OF_{13}$: M + H, 477.1463.

2-(Perfluorooctyl)ethyl 3,5,5-Trimethylhexyl Ether (3q): Colorless oil; IR (neat) 1146, 1240, 1365, 2958 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (s, 9H), 0.93 (d, 3H, $J = 6.8$ Hz), 1.07 (dd, 1H, $J = 14.0$, 6.0 Hz), 1.23 (dd, 1H, $J = 14.0$, 3.2 Hz), 1.36–1.47 (m, 1H), 1.53–1.67 (m, 2H), 2.40 (m, 2H), 3.46 (t, 2H, $J = 6.8$ Hz), 3.69 (t, 2H, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 22.65,

26.23, 29.83 (3C), 31.10, 31.71 (t, $J = 21.4$ Hz), 39.05, 51.29, 62.59, 69.79, 108.48 (m), 110.98 (m), 113.50 (m), 115.67 (m), 118.36 (m), 121.06 (m); HRMS (CI) Found: m/z 491.1582 $(M + H)^+$. Calcd for $C_{17}H_{23}OF_{13}$: M + H, 491.1620.

2-(Perfluorohexyl)ethyl Dodecyl Ether (3r): Colorless oil; IR (neat) 1146, 1240, 1365, 2927 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, $J = 6.8$ Hz), 1.20–1.38 (m, 18H), 1.57 (m, 2H), 2.40 (m, 2H), 3.44 (t, 2H, $J = 6.4$ Hz), 3.70 (t, 2H, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.00, 22.81, 26.22, 22.55, 29.62, 29.75, 29.77, 29.79, 29.83, 29.85, 31.71 (t, $J = 21.3$ Hz), 32.11, 62.60, 71.58, 108.48 (m), 111.00 (m), 113.58 (m), 115.70 (m), 118.39 (m), 121.09 (m); HRMS (CI) Found: m/z 533.2095 $(M + H)^+$. Calcd for $C_{20}H_{29}OF_{13}$: M + H, 533.2089.

2-(Perfluorooctyl)ethyl Octyl Ether (3s): Colorless oil; IR (neat) 1151, 1242, 1381, 2931 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, $J = 6.8$ Hz), 1.20–1.39 (m, 10H), 1.57 (m, 2H), 2.40 (m, 2H), 3.44 (t, 2H, $J = 6.8$ Hz), 3.70 (t, 2H, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$) δ 13.94, 22.69, 26.11, 29.31, 29.46, 29.64, 31.61 (t, $J =$ 22.2 Hz), 31.89, 62.52, 71.50, 108.29 (m), 110.93 (m) (2C), 113.44 (m) (2C), 115.56 (m), 118.26 (m), 120.97 (m); HRMS (CI) Found: m/z 577.1400 $(M + H)^+$. Calcd for $C_{18}H_{21}OF_{17}$: M + H, 577.1399.

2-(Perfluorooctyl)ethyl 3,5,5-Trimethylhexyl Ether (3t): Colorless oil; IR (neat) 1153, 1244, 1367, 2958 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (s, 9H), 0.93 (d, 3H, $J = 6.4$ Hz), 1.07 (dd, 1H, $J = 14.0$, 6.0 Hz), 1.23 (dd, 1H, $J = 14$, 3.6 Hz), 1.36–1.47 (m, 1H), 1.53–1.67 (m, 2H), 2.39 (m, 2H), 3.46 (t, 2H, $J = 7.2$ Hz), 3.69 (t, 2H, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$) δ 22.66, 26.24, 29.83 (3C), 31.11, 31.74 (t, $J = 21.4$ Hz), 39.07, 51.30, 62.60, 69.79, 108.39 (m) (2C), 111.02 (m) (2C), 113.54, 115.64, 118.36, 121.04; HRMS (CI) Found: m/z 591.1569 $(M + H)^+$. Calcd for $C_{19}H_{23}OF_{17}$: M + H, 591.1556.

2-(Perfluorodecyl)ethyl Octyl Ether (3u): Wax; IR (neat) 1151, 1209, 1379, 2927 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, $J = 6.8$ Hz), 1.20–1.39 (m, 10H), 1.57 (m, 2H), 2.40 (m, 2H), 3.44 (t, 2H, $J = 6.8$ Hz), 3.70 (t, 2H, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 13.87, 22.73, 26.19, 29.40, 29.54, 29.72, 31.67 (t, $J =$ 22.1 Hz), 31.96, 62.57, 71.54, 108.34 (m) (2C), 111.84 (m) (3C), 113.54 (m) (2C), 115.63 (m), 118.33 (m), 121.03 (m); HRMS (CI) Found: m/z 677.1328 $(M + H)^+$. Calcd for $C_{20}H_{21}OF_{21}$: M + H, 677.1335.

2-(Perfluorodecyl)ethyl Dodecyl Ether (3v): White solid; mp 40.0 °C; IR (neat) 1151, 1209, 1384, 2919 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81 (t, 3H, $J = 7.2$ Hz), 1.20–1.38 (m, 18H), 1.57 (m, 2H), 2.40 (m, 2H), 3.44 (t, 2H, $J = 6.8$ Hz), 3.70 (t, 2H, $J =$ 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 13.95, 22.78, 26.18, 29.51, 29.59, 29.71, 29.73, 29.76, 29.79, 29.82, 31.65 (t, $J = 22.1$ Hz), 32.07, 62.57, 71.55, 108.33 (m) (2C), 110.82 (m) (3C), 113.54 (m) (2C), 115.61 (m), 118.30 (m), 121.02 (m); HRMS (CI) Found: m/z 733.1996 $(M + H)^+$. Calcd for $C_{24}H_{29}OF_{21}$: M + H, 733.1961.

2-(Perfluoro-1,1-dimethylbutyl)ethyl 1,3-Dimethylbutyl Ether (3w): Colorless oil; IR (neat) 1157, 1219, 1369, 2964 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (d, 3H, $J = 6.4$ Hz), 0.90 (d, 3H, $J = 6.4$ Hz), 1.13 (d, 3H, $J = 2.0$ Hz), 1.16 (m, 1H), 1.46 (m, 1H), 1.71 (m, 1H), 2.46 (m, 2H), 3.48 (m, 1H), 3.57 (dt, 1H, $J = 8.4$, 8.4 Hz), 3.74 (dt, 1H, $J = 8.4$, 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 19.72, 22.41, 22.81, 24.69, 27.98, 46.18, 59.96 (m), 62.46, 74.59, 106.92 (m), 109.62 (m), 112.46 (m), 115.69 (m), 118.55 (m); HRMS (CI) Found: m/z 449.1155 $(M + H)^+$. Calcd for $C_{14}H_{17}OF_{13}$: M + H, 449.1150.

1,1-Bis(decyloxy)butane (5e): Colorless oil; IR (neat) 1074, 1136, 1466, 2854, 2924 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, 6H, $J = 6.8$ Hz), 0.89 (t, 3H, $J = 7.2$ Hz), 1.15–1.41 (m, 30H), 1.53 (m, 6H), 3.30–3.60 (m, 4H), 4.43 (t, 1H, $J = 5.6$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.12, 14.24 (2C), 18.30, 22.88 (2C), 26.50 (2C), 29.55 (2C), 29.69 (2C), 29.80 (2C), 29.84 (2C), 30.14 (2C), 32.11 (2C), 35.77, 65.52 (2C), 103.07; HRMS (EI) Found: m/z 370.3781 (M^+). Calcd for $C_{24}H_{50}O_2$: M, 370.3811.

Typical Procedure for the Acetalization of Ethylene Glycol with 4-Methyl-2-pentanone. A mixture of ethylene glycol (1.2 g, 20 mmol), 4-methyl-2-pentanone (20 g, 0.20 mol), and neutral-type Pd/C (5% palladium-on-carbon 24 mg, 1.2 mg as Pd) was placed in a flask equipped with a hydrogen balloon and was stirred vigorously at 100 °C (20 h). The conversion of ethylene glycol was determined by GLC. After the reaction mixture was filtered, the filtrate was washed with water. After the excessive 4-methyl-2-pentanone was evaporated, we obtained 4-methyl-2,2-ethylenedioxypentane **5x** (1.6 g, 11 mmol).

4-Methyl-2,2-ethylenedioxypentane (5x): Colorless oil; IR (neat) 1041, 1092, 1186, 1377, 1468, 2873, 2956 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (d, 6H, $J = 6.8$ Hz), 1.21 (s, 3H), 1.44 (d, 2H, $J =$ 6.8 Hz), 1.70 (m, 1H), 3.81 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 24.01 (2C), 24.10, 24.41, 47.41, 64.36 (2C), 110.41; HRMS (EI) Found: m/z 144.1150 (M^+). Calcd for $C_8H_{16}O_2$: M, 144.1150.

Typical Procedure for the Hydrogenolysis of 2,2-Bis(octyloxy)propane 5y. A mixture of 2,2-bis(octyloxy)propane **5y** (3.0 g, 10 mmol) and neutral-type Pd/C (5% palladium-on-carbon 60 mg, 3.0 mg as Pd) was placed in a flask equipped with a hydrogen balloon and was stirred vigorously at room temperature (24 h). The conversion of **5y** was determined by GLC. The reaction mixture was filtered. The product was purified by flash chromatography on silica gel (hexane:ethyl acetate = 20:1) to afford isopropyl octyl ether **3y** (1.7 g, 9.8 mmol). We obtained 2,2-bis(octyloxy)propane **5y** by the exchange reaction of 2,2-dimethoxypropane with 1-octanol using *p*-toluenesulfonic acid as a catalyst.[18]

2,2-Bis(octyloxy)propane (5y): Colorless oil; IR (neat) 1076, 1211, 1378, 1465, 2856, 2927 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, 6H, $J = 7.2$ Hz), 1.20–1.35 (m, 20H), 1.32 (s, 6H), 1.51 (m, 4H), 3.36 (t, 4H, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.27 (2C), 22.88 (2C), 25.20 (2C), 26.60 (2C), 29.53 (2C), 29.75 (2C), 30.33 (2C), 32.07 (2C), 60.87 (2C), 99.69; HRMS (EI) Found: m/z 300.2998 (M^+). Calcd for $C_{19}H_{40}O_2$: M, 300.3028.

Isopropyl Octyl Ether (3y): Colorless oil; IR (neat) 1085, 1128, 1379, 1466, 2856, 2927 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, 3H, $J = 7.2$ Hz), 1.10 (d, 6H, $J = 6.0$ Hz), 1.17–1.45 (m, 10H), 1.51 (m, 2H), 3.35 (t, 2H, $J = 6.4$ Hz), 3.50 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.25, 22.30 (2C), 22.85, 26.41, 29.49, 29.69, 30.38, 32.04, 68.43, 71.41. These spectral data obtained agreed with those in the literature.[10]

We are grateful to Dr. A. Kondo, Dr. Y. Sassa, and Dr. A. Kawamata for helpful discussions and to Mr. M. Uno and Mr. H. Matsumoto for their assistance.

References

1 A. W. Williamson, *J. Chem. Soc.*, **4**, 229 (1851).
2 B. M. Trost, *Science*, **25**, 1471 (1991).
3 R. A. Sheldon, *Chem. Ind. (London)*, **1992**, 903.
4 R. A. Sheldon, *Chem. Ind. (London)*, **1997**, 12.
5 J. H. Clack, *Green Chem.*, **1**, 1 (1999).
6 M. Verzele, M. Acke, and M. Anteunis, *J. Chem. Soc.*, **1963**, 5598.

7 S. Nishimura, T. Itaya, and M. Shiota, *J. Chem. Soc., Chem. Commun.*, **1967**, 422.

8 V. Bethmont, F. Fache, and M. Lemaire, *Tetrahedron Lett.*, **36**, 4235 (1995).

9 Y. Fujii, H. Furugaki, K. Kita, H. Morimoto, M. Uno, and Y. Kajihara, U. S. Patent 6011071 (2000); Priority Application: Jpn. Patent JP 95118309, 17 May 1995; *Chem. Abstr.*, **126**, 61873 (1997).

10 F. Fache, V. Bethmont, L. Jacquot, and M. Lemaire, *Recl. Trav. Chim. Pays-Bas*, **115**, 231 (1996).

11 Y. Fujii, H. Furugaki, S. Yano, and K. Kita, *Chem. Lett.*, **2000**, 926.

12 H. Meinert and U. Geister, *J. Fluorine Chem.*, **68**, 221 (1994).

13 J. R. Falck, J. Yu, and H. Cho, *Tetrahedron Lett.*, **35**, 5997 (1994).

14 M. Fudlicky, "Chemistry of Organic Fluorine Compounds," Pergamon Press Ltd., Oxford·London·New York·Paris (1961).

15 W. S. Millman and G. V. Smith, *Catal. Org. Synth.*, **6**, 33 (1976).

16 J. Ishiyama, K. Esashita, Y. Senda, and S. Imaizumi, *Nippon Kagaku Kaishi*, **1988**, 126.

17 W. L. Howard and J. H. Brown, *J. Org. Chem.*, **26**, 1026 (1961).

18 N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **25**, 521 (1960).