Dehydration of alcohols to ethers over Nafion-H, a solid perfluoroalkanesulfonic acid resin catalyst *

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Nafion-H has been found to be a highly efficient solid acid catalyst for the bimolecular conversion of alcohols to ethers in excellent yields.

Keywords: Nafion-H, perfluoroalkanesulfonic acid resin, alcohols, bimolecular dehydration, ethers

To reduce gasoline related emissions, low boiling olefins' (C_4–C_5) and aromatics' content of automobile gasoline are being restricted [2]. Lead and other organometallic octane enhancing additives are also discontinued. Refiners, therefore, turned to alternate sources of octane enhancing additives [3]. Oxygenate additives (such as methyl tert-butyl ether, MTBE) are used extensively to meet increasing octane requirements. Fuel oxygenates can also reduce carbon monoxide (CO) emissions and unburned hydrocarbons in the automobile exhaust and are less photochemically reactive than most unsaturated gasoline range hydrocarbons [4].

Ethers appear to have presently the most favorable properties for reformulating gasoline [5]. Highly branched (high octane) ethers are oxygenates that play an important role in enhancing gasoline octane due to their significantly low blending vapor pressure [3]. Longer straight chain primary ethers can enhance cleaner burning of diesel fuels cetane numbers (ignition quality) [6]. Their preparation is therefore of substantial interest.

The acid catalyzed dehydration of alcohols to ethers is widely used (for a review, see ref. [7]). Generally, elevated temperatures ($> 250°C$) and excess mineral acids are, however, required for such conversions. In continuation of our interest in Nafion-H, a perfluoroalkanesulfonic acid resin, catalyzed synthetic transformations [8], we now report the convenient and efficient preparation of long chain alkyl ethers using Nafion-H as a recyclable catalyst.

Longer chain alkyl ethers were readily prepared by heating the corresponding alcohols in the liquid phase with Nafion-H catalyst. The results are presented in table 1. The method provides excellent yield, easy isolation of the products and ready regeneration of the catalyst. No evidence was obtained for any possible side reactions such as elimination.

The reaction is facile for primary alcohols, yielding the corresponding ethers in quantitative yield. On preparative scale, it was necessary to remove the water as it was formed by azeotropic distillation using toluene as an inert solvent.

The reaction was also applied to secondary acyclic and cyclic alcohols. Results are shown in table 2. In the case of secondary acyclic alcohols, a mixture of structural isomers was formed generally with only low conversion. However, the method proved to be readily adaptable for the etherification of cyclohexanol to dicyclohexyl ether with excellent yield. In this case too, water removal by azeotropic distillation was necessary to achieve 100% conversion. One of the methods of preparation of dicyclohexyl ether has been hydrogenation of diphenyl ether under high hydrogen pressures over noble metal catalysts [9]. Chatterjee and co-workers have also reported the use of bentonite clays in the etherification of cyclohexanol to dicyclohexyl ether with only very low conversion [10a]. This same method also proved facile for the preparation of norbornyl ether from exo-norborneol in excellent yield.

The mechanism for the reaction involves the in situ formation of an oxonium ion, where Nafion-H converts the hydroxyl group of the alcohol into a better leaving group by protonation. The ether is then formed by the nucleophilic attack of alcohol on the oxonium ion in a bimolecular reaction (S_N2 type) as shown in scheme 1. Such a mechanism also explains the low conversion in the case of secondary alcohols due to steric reasons. Such mechanisms have been earlier proposed for secondary alcohol dehydration over alumina [10b].

In summary, the presently developed dehydration method for alcohols to ethers requires no aqueous workup. Filtration of Nafion-H resin followed by distillation of the filtrate gives ethers in good yields. Nafion-

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* Catalysis by solid superacids, Part 31. For Part 30, see ref. [1].

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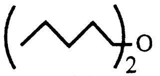
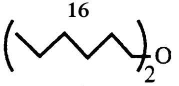
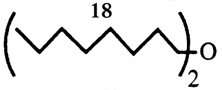
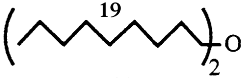
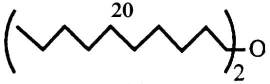
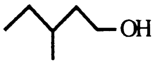
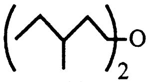
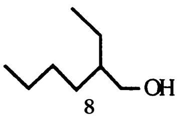
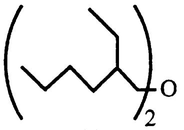
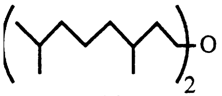
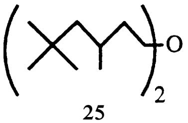
Table 1
Nafion-H catalyzed dehydration of primary alcohols

Alcohol	Temp. (°C)	Time (h)	Product	Yield (%)	m.p. (°) or b.p. (°C) {mmHg}		
					found	reported	ref.
 **1**	reflux	7	 **16**	97	187–188 {760}	190 {760}	[11]
 **2**	145–150	7	 **17**	97	228–229 {760}	73–75 {2}	[12]
 **3**	145–150	overnight	 **18**	95	61–63 {0.38}	82–85 {1.5}	[13]
 **4**	145–150	overnight	 **19**	98	99–101 {0.47}	120–122 {3}	[14]
 **5**	145–150	overnight	 **20**	97	77–79 {0.05}	–	
 **6**	145–150	overnight	 **21**	95	96–98 {0.05}	156–158 {1.7}	[12]
 **7**	reflux	overnight	 **22**	94	68–69 {760}	–	
 **8**	reflux	7	 **23**	93	124–125 {5}	144–146 {13}	[17a]
 **9**	145–150	7	 **24**	93	117–119 {0.35}	144–145 {2}	[17b]
 **10**	145–150	overnight	 **25**	92	87–89 {0.39}	137–138 {9}	[17c]

H can be easily regenerated while maintaining its high catalytic activity.

Materials. The chemicals were purchased from Aldrich Chemical Company and their purity was verified by GC-MS. The solvent toluene was of highest purity available commercially. The Nafion-H catalyst was prepared from commercial (Du Pont) Nafion-K 501 resin with a mesh size of 50. The equivalent weight of such a resin is around 1100.

Conversion of Nafion-K to Nafion-H. All reactions described above were catalyzed by the acid form of the Nafion resin. The acidic form (Nafion-H) was prepared by acid treatment of the potassium form (Nafion-K) according to the literature procedure [8][1].

Regeneration of the catalyst. The filtered catalyst is washed with acetone and deionized water, followed by drying at 105°C overnight. The catalytic activity of regenerated catalyst was as good as that of freshly activated catalyst.

Analysis. Products were analyzed by GC-MS and characterized by ^{1}H- and ^{13}C-NMR. Gas chromatographic analyses were performed with an HP-5890 GC coupled with an HP-5971 mass spectrometer and a 30 m DB-5 capillary column, with helium as carrier gas. The ^{1}H- and ^{13}C-NMR measurements were carried out on a Varian VXR 300 MHz NMR spectrometer in $CDCl_3$ as a solvent with tetramethylsilane standard.

Typical procedure. A stirred solution of the corresponding alcohol (50 mmol) was heated under reflux in the presence of Nafion-H (1 g) under nitrogen atmosphere. Reactions involving alcohols with very high boiling points were maintained at 145–150°C. The reactions were monitored by GC/MS. On completion of the reac-

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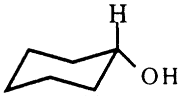
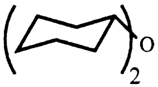
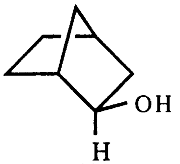
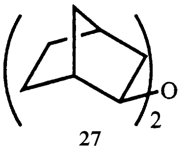
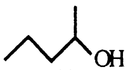
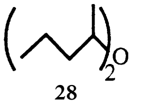
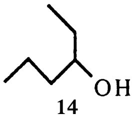
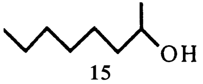
[1] Nafion is a registered trademark of the DuPont Company and commercially available. The active form (Nafion-H) was generated from the potassium salt (Nafion-K) by treatment with 25% nitric acid followed by washing with deionized water and drying at 105°C for 24 h.

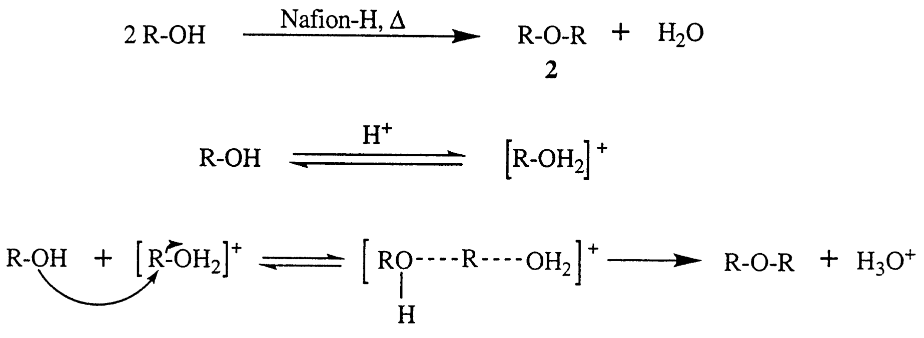
Table 2
Nafion-H catalyzed dehydration of secondary acyclic and cyclic alcohols

Alcohol	Temp. (°C)	Time (h)	Product	Yield (%)	m.p. (°C) or b.p. (°C) {mmHg}		
					found	reported	ref.
 **11**	reflux	24	 **26**	91	118–120 {22}	97–98.5 {8}	[15]
 **12**	145–150	3	 **27**	99	m.p. 63–65	m.p. 65–66	[16]
 **13**	reflux	overnight	 **28**	trace			
 **14**	reflux	overnight	mixture of structural isomers				
 **15**	145–150	overnight	mixture of structural isomers				

tion, the reaction mixture was filtered and the residue washed with diethyl ether. The filtrate was dried over anhydrous magnesium sulfate and evaporated. The remaining crude product was purified either by recrystallization or fractional distillation.

Di(2-ethylhexyl) ether. A mixture of 2-ethylhexanol (500 g, 3.84 mol), toluene (100 ml), and Nafion-H (40 g) was refluxed overnight and distilled azeotropicly to remove the water as it was formed. On completion of the reaction, the reaction mixture was filtered and the residue washed with diethyl ether. The filtrate was dried over anhydrous magnesium sulfate followed by fractional distillation to afford 2-ethylhexyl ether. The crude product was purified by distillation in reduced pressure: yield 432 g (93%); b.p. 135–136°C (17 mbar). MS (m/z, 70 eV, EI): 242 (M^+, 0.05), 112 (34.6), 71 (71.3), 57 (100), 43 (33.6); ^{1}H-NMR ($CDCl_3$) δ 0.75–0.90 (m, 12H, CH_3), 1.10–2.10 (broad, 18H, CH, CH_2), 3.10–3.30 (m, 4H, CH_2); ^{13}C-NMR ($CDCl_3$) δ 73.84, 39.73, 30.71, 29.16, 23.99, 23.16, 14.07, 11.07.

Dicyclohexyl ether. A mixture of cyclohexanol (11.56 g, 115 mmol), toluene (7 ml; only 2 ml were actually in the reaction flask and 5 ml in the side arm of the Dean-Stark apparatus), and Nafion-H (2 g) was refluxed for 24 h and distilled azeotropicly to remove the water as it was formed. On completion of the reaction, the reaction mixture was filtered and the residue washed with diethyl ether. The filtrate was dried over anhydrous magnesium sulfate followed by fractional distillation to afford dicyclohexyl ether. The crude product was purified by distillation in reduced pressure: yield 9.57 g (91%); b.p. 118–120°C (22 mmHg). MS (m/z, 70 eV, EI): 182 (M^+, 22.5), 100 (100), 82 (80.7), 67 (31.0), 55 (79.4), 41 (31.5); ^{1}H-NMR ($CDCl_3$) δ 1.00–1.34 (br, 8H, CH_2),



Scheme 1.

1.35–1.59 (br, 4H, CH_2), 1.61–1.90 (br, 8H, CH_2), 3.20–3.35 (br, 2H, CH); ^{13}C-NMR ($CDCl_3$) δ 74.57, 33.27, 25.80, 24.49.

Bis(exo-norbornyl) ether. The exo-norborneol (5.0 g, 45 mmol) was heated at 140–145°C in the presence of Nafion-H (1.0 g) under nitrogen atmosphere. After 3 h, the reaction was completed and was allowed to cool to room temperature. The solid material was dissolved in dichloromethane and filtered. The filtrate was dried over anhydrous magnesium sulfate and evaporated. The remaining crude product was recrystallized from dichloromethane and hexanes: yield 4.55 g (99%); m.p. 63–65°C. MS (m/z, 70 eV, EI): 206 (M$^+$, 2.1), 112 (1.9), 95 (100), 67 (15.3), 55 (3.0); ^{1}H-NMR ($CDCl_3$) δ 0.93–1.10 (m, 6H), 1.27–1.60 (m, 10H), 2.20 (m, 2H), 2.25 (m, 2H), 3.36–3.38 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 80.04, 79.54, 41.03, 40.85, 40.23, 40.11, 35.23, 35.19, 34.92, 34.85, 28.68, 24.86.

Other ethers were prepared following the general procedure and they showed the following spectroscopic data.

Di(n-pentyl) ether. MS (m/z, 70 eV, EI): 158 (M$^+$, 4.1), 71 (100), 55 (21.0), 41 (56.5), 39 (24.9); ^{1}H-NMR ($CDCl_3$) δ 0.90 (m, 6H, CH_3), 1.32 (m, 8H, CH_2), 1.57 (m, 4H, CH_2), 3.39 (m, 4H, CH_2); ^{13}C-NMR ($CDCl_3$) δ 70.78, 29.29, 28.22, 22.39, 13.81.

Di(n-hexyl) ether. MS (m/z, 70 eV, EI): 186 (M$^+$, 0.1), 85 (100), 56 (30.5), 43 (56.8); ^{1}H-NMR ($CDCl_3$) δ 0.89 (m, 6H, CH_3), 1.30 (m, 12H, CH_2), 1.57 (m, 4H, CH_2), 3.39 (m, 4H, CH_2); ^{13}C-NMR ($CDCl_3$) δ 70.86, 31.65, 29.64, 25.79, 22.54, 13.87.

Di(n-heptyl) ether. MS (m/z, 70 eV, EI): 214 (M$^+$, 0.05), 97 (12.0), 70 (26.3), 57 (100), 43 (23.1); ^{1}H-NMR ($CDCl_3$) δ 0.88 (m, 6H, CH_3), 1.20–1.63 (broad, 20H, CH_2), 3.39 (m, 4H, CH_2); ^{13}C-NMR ($CDCl_3$) δ 71.06, 31.97, 29.93, 29.30, 26.30, 22.73, 14.13.

Di(n-octyl) ether. MS (m/z, 70 eV, EI): 242 (M$^+$, 0.06), 84 (27.9), 71 (100), 57 (95.8), 43 (52.9); ^{1}H-NMR ($CDCl_3$) δ 0.88 (m, 6H, CH_3), 1.20–1.63 (broad, 24H, CH_2), 3.38 (m, 4H, CH_2); ^{13}C-NMR ($CDCl_3$) δ 71.08, 32.03, 29.99, 29.66, 29.48, 26.41, 22.82, 14.15.

Di(n-nonyl) ether. MS (m/z, 70 eV, EI): 271 (M$^+$, 0.3), 98 (25.8), 85 (56.5), 71 (100), 57 (86.2), 43 (79.2); ^{1}H-NMR ($CDCl_3$) δ 0.88 (m, 6H, CH_3), 1.21–1.63 (broad, 28H, CH_2), 3.38 (m, 4H, CH_2); ^{13}C-NMR ($CDCl_3$) δ 71.08, 32.08, 29.94, 29.78, 29.70, 29.48, 26.39, 22.83, 14.15.

Di(n-decyl) ether. MS (m/z, 70 eV, EI): 299 (M$^+$, 0.5), 112 (36.9), 97 (51.9), 85 (96.5), 71 (74.2), 57 (93.5), 43 (100); ^{1}H-NMR ($CDCl_3$) δ 0.88 (m, 6H, CH_3), 1.05–1.70 (broad, 32H, CH_2), 3.38 (m, 4H, CH_2); ^{13}C-NMR ($CDCl_3$) δ 71.08, 32.09, 29.98, 29.81, 29.77, 29.69, 29.52, 26.40, 22.84, 14.16.

Di(3-methylpentyl) ether. MS (m/z, 70 eV, EI): 187 (M$^+$, 0.6), 84 (100), 69 (37.8), 56 (37.9), 41 (43.3); ^{1}H-NMR ($CDCl_3$) δ 0.83–0.91 (m, 12H, CH_3), 1.00–1.70 (broad, 10H, CH&CH_2), 3.42 (m, 4H, CH_2); ^{13}C-NMR ($CDCl_3$) δ 69.34, 36.51, 31.62, 29.72, 19.23, 11.31.

Bis(3,7-dimethyl-1-octyl) ether. An equal mixture of two stereoisomers. MS (m/z, 70 eV, EI): 299 (M$^+$, 0.2), 140 (41.7), 85 (66.1), 70 (100), 57 (93.2), 43 (51.8); ^{13}C-NMR ($CDCl_3$) δ 69.27, 69.24, 39.36, 37.46, 37.45, 36.89, 29.99, 29.96, 28.01, 24.74, 22.73, 22.64, 19.73.

Bis(3,5,5-trimethyl-1-hexyl) ether. An equal mixture of two stereoisomers. MS (m/z, 70 eV, EI): 271 (M$^+$, 0.1), 126 (7.7), 83 (13.2), 70 (66.8), 57 (100), 41 (22.5); ^{13}C-NMR ($CDCl_3$) δ 69.17, 69.14, 51.33, 51.29, 39.23, 31.09, 29.99, 26.27, 26.25, 22.86, 22.79.

Registry Nos.: **1**, 693-65-2; **2**, 112-58-3; **3**, 629-64-1; **4**, 629-82-3; **5**, 2456-27-1; **6**, 2456-28-2; **8**, 10143-60-9; **9**, 29053-11-0; **10**, 148598-43- 0; **11**, 4645-15-2; **12**, 61376-57-6; **13**, 56762-00-6; Nafion-H, 63937-00- 8.

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