

Synthetic Methods and Reactions; 99¹. Preparation of Cyclic Ethers over Superacidic Perfluorinated Resinsulfonic Acid (Nafion-H) Catalyst

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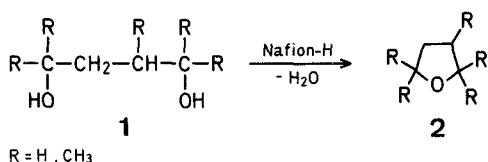
1,4-Glycols readily undergo intramolecular dehydration to yield tetrahydrofurans. Generally, elevated temperatures (>250 °C) and excess of mineral acid are, however, required for such conversions²⁻⁵. It is also known that cyclization of 1,4- and 1,5-glycols take place under similar conditions or on reaction with benzenesulfonyl chloride in the presence of amines⁶, giving, howev-

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er, less satisfactory conversions. More recently, diaryldialkoxysulfuranes⁷, *N*-methyl-*N,N'*-bis[*t*-butyl]carbodiimine salts⁸ and sulfonated polystyrene resin (Amberlyst-15)⁹ were also used as catalysts for these dehydration reactions, however, with limited scope.

We report now the fast, convenient dehydration of 1,4-butanediols (**1**) to the corresponding tetrahydrofurans (**2**) over Nafion-H¹⁰, a solid superacidic perfluorinated resinsulfonic acid catalyst. The method provides excellent yields, easy isolation of the products, and ready regeneration of the catalyst without loss of activity. No solvent is required for the reactions.



1,5-Pentanediol (**1f**), 1,6-hexanediol (**1g**), and diethylene glycol (**1i**) under similar conditions, also dehydrate readily giving tetrahydropyran (**2f**), oxepane¹¹ (**2g**), and 1,4-dioxane (**2i**), respectively in good yields. Furthermore, 1,7-heptanediol (**1h**) also dehydrates readily to give the corresponding oxocane¹² (**2h**) in 51% yield (Table). When ethylene glycol (**1i**) was reacted under the reaction conditions, only the intermolecular condensation product i.e. 1,4-dioxane (**2i**) was obtained in 50% yield.

Tetrahydrofuran (**2a**); Typical Procedure:

A 100 ml round reaction flask containing 1,4-butanediol (**1a**; 50 g, 0.55 mol) and Nafion-H (2.5 g) catalyst is equipped with a Claisen head and receiver, cooled by an ice/water bath. The reaction mixture is heated with good stirring at 135 °C in an oil bath. Product tetrahydrofuran distills over as it is formed. The reaction is completed in 5 h with no appre-

ciable amount of butanediol is left in the reaction flask. Distillation of the crude product gives pure tetrahydrofuran; yield: 36.1 g (91%); b.p. 65–67 °C.

2,2,5,5-Tetramethyltetrahydrofuran (**2e**); Typical Procedure:

A 25 ml round flask containing 2,5-dimethyl-2,5-hexanediol (**1e**; 10 g, 68 mmol) and Nafion-H (1 g) is equipped with a Claisen distillation head. The stirred reaction mixture is heated at 130 °C in an oil bath. The product 2,2,5,5-tetramethyltetrahydrofuran distills over as it is formed. The distillate separates into two layers. After reaction is completed (~2 h), the ether layer is dried with sodium sulfate and distilled to give 2,2,5,5-tetramethyltetrahydrofuran; yield: 8.3 g (95%); b.p. 110–112 °C.

Regeneration of Nafion-H Catalyst:

After filtering, the used catalyst is washed subsequently with acetone and deionized water, then dried overnight at 105 °C. Application of the regenerated catalyst in the preparation of tetrahydrofuran gave identical results with those using fresh catalyst.

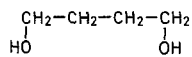

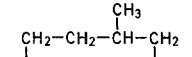

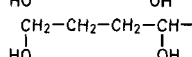

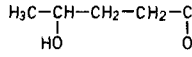

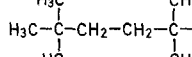

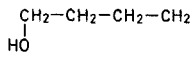

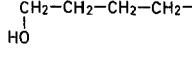

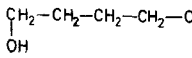

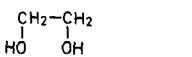

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- For Part 98 see: G. A. Olah, A. P. Fung, *Synthesis* **1981**, 473.
- V. J. Traynelis, W. R. Hergenrother, J. R. Livingston, J. A. Valicenti, *J. Org. Chem.* **27**, 2377 (1962).
- L. F. Schmoyer, L. C. Case, *Nature* **187**, 592 (1960).
- V. J. Traynelis, W. L. Hergenrother, H. T. Hanson, J. A. Valicenti, *J. Org. Chem.* **29**, 123 (1964).
- B. T. Gillis, P. E. Beck, *J. Org. Chem.* **28**, 1388 (1963).
- D. D. Reynolds, W. O. Kenyon, *J. Am. Chem. Soc.* **72**, 1593 (1950).
- J. C. Martin, J. A. Franz, R. J. Arhart, *J. Am. Chem. Soc.* **96**, 4604 (1974).
- R. C. Schnur, E. E. Van Tamelen, *J. Am. Chem. Soc.* **97**, 464 (1975).
- L. T. Scott, J. O. Naples, *Synthesis* **1973**, 209.

Table. Formation of Cyclic Ethers over Nafion-H Catalyst

Diol	Cyclic ether ^a	Yield [%]	b.p. [°C]/760 torr	
			found	reported
1a 	2a 	91	65–67°	
1b 	2b 	93	86–87°	86–87° ¹³
1c 	2c 	90	78–80°	80°/761 ¹³
1d 	2d 	91 ^b	90–92°	91–93° ⁵
1e 	2e 	94	112–115°	115.5–116.5° ⁵
1f 	2f 	86	88°	88°/760 ¹³
1g 	2g 	72	118–119°	117° ⁴
1h 	2h 	51	140–142°	131–142° ¹⁴
1i 	2i 	50	101°	101°/750 ¹³

^a Identity and purity (≥98%) established by G.L.C. (25 ft × 0.25 mm i.d. glass capillary column, OV 101, temperature 40–70 °C), I.R., and ¹H-N.M.R. spectrometry.

^b Mixture of *cis* and *trans* isomers.

- ¹⁰ Nafion is trade name of the DuPont company for a commercially available perfluorinated resin-sulfonic acid. Its activation in the H-form from the commercial potassium salt has been described previously. See G. A. Olah, D. Meidar, A. P. Fung, *Synthesis* **1979**, 270.
- ¹¹ In reference 4, 24% yield of oxepane was reported.
- ¹² L. A. Paquette, R. W. Begland, *J. Org. Chem.* **32**, 2723 (1967).
- ¹³ *Handbook of Chemistry and Physics*, 57th Ed., CRC Press, Cleveland, Ohio 1976-1977.
- ¹⁴ A. Müller, W. Vanc, *Ber. Dtsch. Chem. Ges. [B]* **77**, 669 (1944).

0039-7881/81/0632-0476 \$ 03.00

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