PRODUCT NO. **D10,620-8**

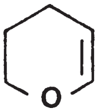
Technical Information Bulletin
Number AL-106

Dihydropyran

(3,4-dihydro-2*H*-pyran)

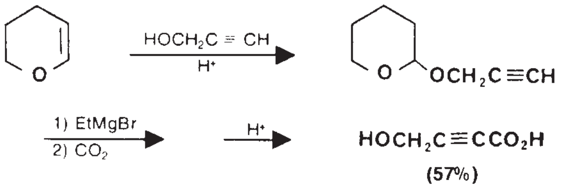
May 1993

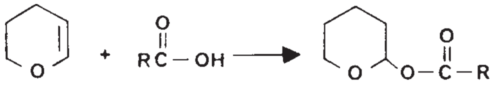
M.W. 84.12
Colorless Liquid
b.p. 86°C
n_D^{20} 1.4400
Purity 97%
Density .922
Flash Point 4°F (-15°C)



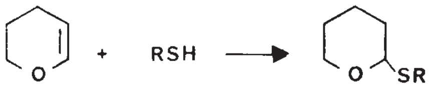
Dihydropyran, a versatile vinyl ether, reacts with alcohols under mild acid catalysis[1] (*p*-toluenesulfonic acid or, more effectively, boron trifluoride etherate[2]) to form tetrahydropyranyl ethers which are extremely useful protecting groups for alcohols.

These ethers are stable to alkali, organolithium and Grignard reagents, Red-Al®, lithium aluminum hydride, acetic anhydride, and chromium trioxide oxidations, yet are easily cleaved by dilute acid to regenerate the alcohol. Typical applications range from the preparation of 4-hydroxy-2-butynoic acid,[3] the protection of sterol hydroxyls,[4,5] the 2'-hydroxyl in ribonucleoside-3'-phosphates,[6] the 6-hydroxyl of methyl α-D-glucopyranoside[7] to the total synthesis of prostaglandins.[8] In addition, dihydropyran can also be used for the protection of carboxyl groups,[1,9a] sulfhydryl groups,[1,9b] secondary amines[9c] and amides.[10]

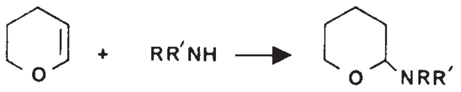




(ref. 1,9a)



(ref. 1,9b)



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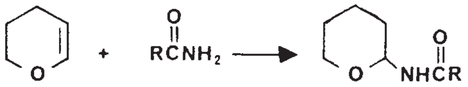
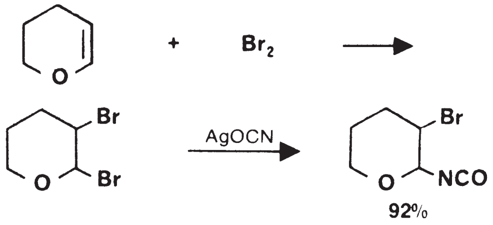


(ref. 10)

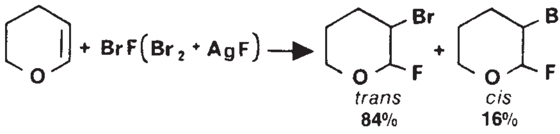
Dihydropyran has potential polymer applications as it can be polymerized either with itself or with other unsaturated compounds. Poly(oxymethylene) polymers have been stabilized against basic media by blocking the terminal hydroxyl groups with dihydropyran.[11]

Hydrochloric and hydrobromic acids add to the highly reactive double bond of dihydropyran to form the corresponding 2-halotetrahydropyrans which, because of their ease of dehydrohalogenation, are used in situ to prepare 2-substituted tetrahydropyrans. For example, they react with silver cyanide to form 2-cyanotetrahydropyran[12] and with Grignard reagents to produce the corresponding 2-alkyltetrahydropyrans. Chlorine and bromine also add to the double bond to yield the 2,3-dichloro- and 2,3-dibromotetrahydropyrans The halogen in the 2-position is more reactive, making possible the synthesis of 3-halo-2-substituted tetrahydropyrans.



(ref. 13)

Other Halogenation Reactions:



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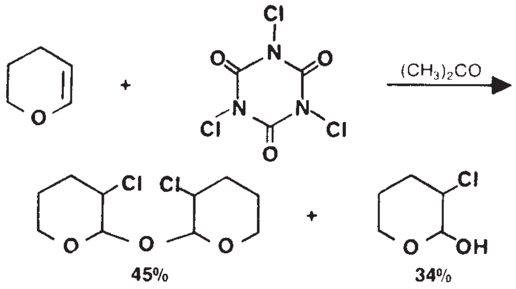

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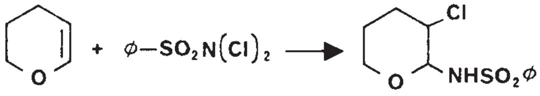
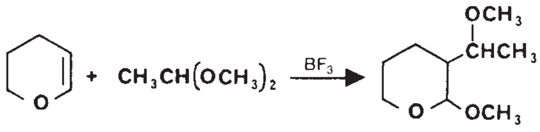


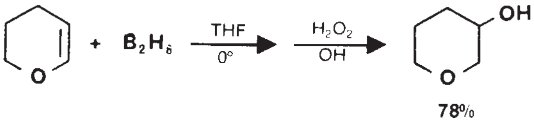
(ref. 16)

Addition of Actetals:



(ref. 17)

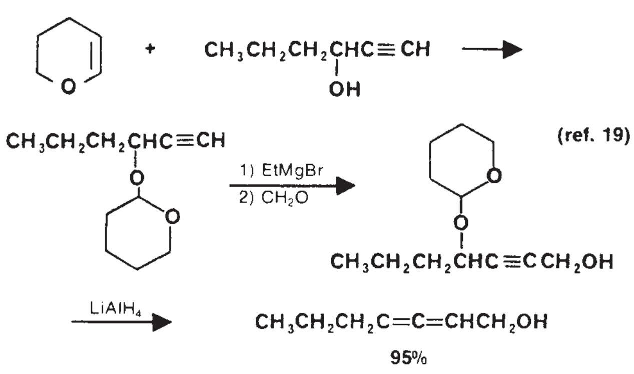
Hydroboration:



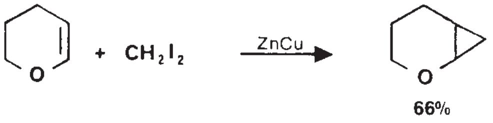
(ref. 18)

☐ See Reverse Side

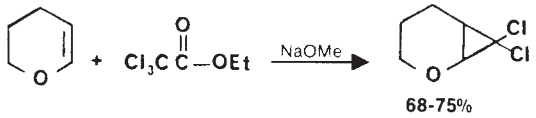
Preparation of allenic alcohols:



Preparation of bicyclic compounds:



(ref. 20)



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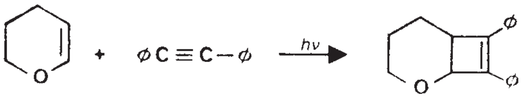

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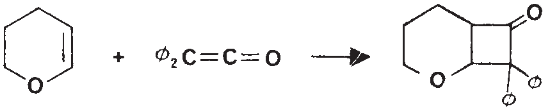

(ref. 23)

References:

1) Fieser, L.F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley and Sons: New York, NY, 1967; Vol.1, p 256.
2) Alper, H.; Dinkes, L. *Synthesis* **1972**, 81.
3) McOmie, J.F.W. *Advances in Organic Chemistry* **1963**, *3*, 218.
4) *Steroid Reactions*; Djerassi, C., Ed.; Holden-Day Inc.: San Francisco, CA, 1963, pp76-79.
5) *Synthetic Methods of Organic Chemistry*; Theilheimer, W., Ed.; S. Karger AG: Basel, Switzerland, 1966; Vol. 20, p 52; 1964, Vol. 18, p 372.
6) Smrt, J.; Sorm, F. *Collect. Czech. Chem. Commun.* **1962**, *27*, 73; *Chem. Abstr.* **1962**, *57*, 3550i.
7) Wolfram, M.L. et al. *J. Org. Chem.* **1971**, *93*, 1490.
8) Corey, E.J. et al. *J. Amer. Chem. Soc.* **1971**, *93*, 1490.
9) *Methoden der Organischen Chemie (Houben-Weyl)*; Mueller, E., Ed.; Verlag: Stuttgart, Germany, 1966; Vol 6, No. 4, (a) 382; (b) 376; (c) 381.
10) Speziale, A.J.; Ratts, K.W.; Marco, G.J. *J. Org. Chem.* **1961**, *26*, 4311.
11) Brinker, K.C.; Schweitzer, C.E. US Patent 3 321 443, 1967; *Chem. Abstr.* **1967**, *67*, 44434g.
12) Zelinski, R.; Yorka, K *J. Org. Chem.* **1958**, *23*, 640.
13) Godefroi, E.F.; Meek, J.S.; Clopton, J.R. *J. Am. Chem. Soc.* **1954**, *76*, 5788.
14) Hall, L.D.; Manville, J.F. *Can. J. Chem.* **1969**, *47*, 361.
15) Juenge, E.C.; Spangler, P.L.; Duncan, W.P. *J. Org. Chem.* **1966,** 31,3836.
16) Otsuki, K. et al. *Chem. Pharm. Bull.* **1970**, *18*, 281.
17) Paul, R.; Tchelitcheff, S. *Bull. Soc. Chim. Fr.* **1952**, 1155.
18) Zweifel, G.; Plamondon, J. *J. Org. Chem.* **1970**, *35*, 898.
19) Cowie, J.S.; Landor, P.D.; Landor, S.R. *Chem. Commun.* **1969**, 541.
20) Shank, R.S.; Shechter, H. *J. Org. Chem.* **1959**, *24*, 1825.
21) Parham, W.E.; Schweizer, E.E.; Mierzwa, Jr., S.A. *Org. Synth.* **1961**, *41*, 76.
22) Rosenberg, H.M.; Serve, P. *J. Org. Chem.* **1968**, *33*, 1653.
23) Brady, W.T.; O'Neal, H.R. *ibid.* **1967**, *32*, 612.

For packaging and pricing information, see current Aldrich Catalog/Handbook. For bulk quantities, please contact our Bulk Sales Department.

Handling

Dihydropyran is a highly flammable colorless liquid. It irritates eyes and skin and may cause dizziness and narcosis in high vapor concentrations. This material should be handled in a well-ventilated hood. Gloves and self-contained or organic-vapor respirator should be worn.

Emergency Procedures

Eye contact Irrigate eyes with water.

Skin Contact Wash skin with soap and plenty of water.

Spill Shut off all possible sources of ignition. Wear a breathing apparatus and gloves. Apply a nonflammable dispersing agent and work into an emulsion with a brush and water. Run to waste and dilute greatly with water.

Fire Extinguish with carbon dioxide on dry powder.

Waste Disposal

Burn in a solvent burner.

Storage

Store in a cool place away from sources of ignition.

Aldrich Chemical Company, Inc.

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