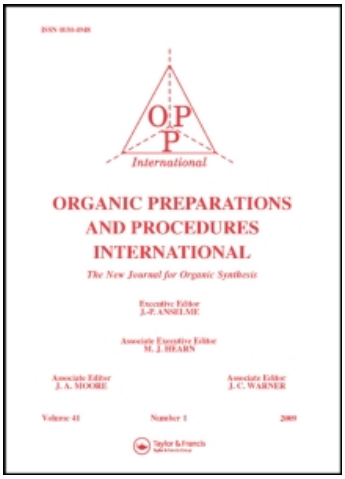


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

1-TERT-BUTYL-1,3-PROPANEDIOL

R. O. Hutchins[a]; Frank J. Dux[a]
[a] Department of Chemistry, Drexel University, Philadelphia, Pennsylvania

To cite this Article Hutchins, R. O. and Dux, Frank J.(1970) '1-TERT-BUTYL-1,3-PROPANEDIOL', Organic Preparations and Procedures International, 2: 4, 291 — 294
To link to this Article: DOI: 10.1080/00304947009458631
URL: http://dx.doi.org/10.1080/00304947009458631

ORGANIC PREPARATIONS AND PROCEDURES, 2(4), 291-294 (1970)

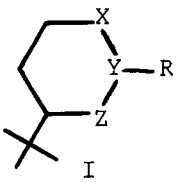
1-TERT-BUTYL-1,3-PROPANEDIOL

R. O. Hutchins and Frank J. Dux
Department of Chemistry
Drexel University
Philadelphia, Pennsylvania 19104

$$(CH_3)_3CCHO + BrCH_2CO_2C_2H_5 \xrightarrow{Zn} (CH_3)_3CCHOHCH_2CO_2C_2H_5$$

$$(CH_3)_3CCHOHCH_2CO_2C_2H_5 \xrightarrow{LAH} (CH_3)_3CCHOHCH_2CH_2OH$$

In recent years, the surge of interest in conformational analysis of heterocycles has created a need for synthetic procedures leading to substituted heterocycles, especially those with one or more t-butyl groups attached. A particularly useful class of precursors to such systems is variously substituted 1,3-propanediols which may be ultimately converted to several important types of heterocycles including 1,3-dioxanes,[1] 1,3-dithianes,[2] 1,3-oxathianes[2] and other derivatives containing an additional heteroatom at position 2. This article describes the preparation of the previously unreported 4,4-dimethyl-1,3-pentanediol (1-t-butyl-1,3-propanediol) which may be utilized to synthesize 4-t-butyl heterocycles of the general type I.



I

X, Z = O, S, N

Y = C, P, B

EXPERIMENTAL

Ethyl 3-hydroxy-4,4-dimethylpentanoate. In a dry 250-ml., 3-necked flask equipped with a magnetic stirrer, dropping funnel and condenser protected with a drying tube is placed zinc dust (20 g, 0.31 mole).

Ethyl bromoacetate (41.7 g, 0.25 mole) and 2,2-dimethylpropanal (26.7 g, 0.31 mole) are dissolved in 40 ml. of benzene and 10 ml. of ether and then placed in the dropping funnel. Approximately 10 ml. of the solution is added and the flask is warmed slightly until reaction is initiated. The remainder of the solution is then added slowly at such a rate that gentle reflux in maintained; about 2 hr. are required. After addition is complete, the mixture is refluxed for 30 min., then poured into 200 ml. of cold 10% aqueous sulfuric acid, filtered, and the aqueous phase is then extracted with 50 ml. of ether. The combined ether-benzene solution is washed successively with two 10 ml. portions of 5% sulfuric acid, 10 ml. of 10% aq. sodium carbonate, again with 10 ml. of 5% sulfuric acid and then dried over anhydrous magnesium sulfate. Solvent is removed at reduced pressure on a rotary evaporator to afford crude ethyl 3-hydroxy-4,4-dimethyl-pentanoate which can be used directly in the reduction step below. If isolation of the hydroxy ester is desired, the crude product is neutralized with alcoholic potassium hydroxide and then fractionally distilled at reduced pressure to give 27.1 g (62%) of pure ester bp 49-51°/0.62 mm. The i.r. spectrum (neat) showed major peaks at 3510, 2981, 1302, 1164, and 1025 cm^{-1}; nmr ($CDCl_3$) in ppm, 0.92 (sing., 9H), 1.27 (triplet, J = 7.2Hz), ca. 2.5 (mult., 2H), 3.74 (doub. of doub., 1H), 4.21 (quartet, J = 7.2Hz, 2H).

Anal. Calcd. for $C_9H_{18}O_3$: C, 62.04; H, 10.42. Found: C, 62.23; H, 10.61.

4,4-Dimethyl-1,3-pentanediol. A dry 3-necked flask fitted with a mechanical stirrer, dropping funnel, nitrogen-inlet tube and condenser

protected with a drying tube is charged with a slurry of lithium aluminum hydride (10.0 g, 0.263 mole) in 350 ml. of anhydrous ether. To this is added dropwise a solution of ethyl 3-hydroxy-4,4-dimethylpentanoate (27.1 g, 0.15 mole) in ca. 100 ml. of anhydrous ether at such a rate that gentle reflux is maintained; approximately 4 hr. is required. After addition is complete, the mixture is hydrolyzed by the cautious dropwise addition of 10 ml. of water followed by 30 ml. of 15% aq. sodium hydroxide and finally 10 ml. of water. The mixture is filtered, the salts washed thoroughly with ether, and the ether solution dried over anhydrous magnesium sulfate. The solvent is removed under reduced pressure, the residue cooled and the white crystalline product filtered and recrystallized from benzene to afford 16.9 g (82%) of 4,4-dimethyl-1,3-pentandiol, mp 65.5-66°C. The i.r. spectrum (KBr) showed major peaks at 3280, 2955, 1362, 1087, 1058 and 970 cm^{-1}; nmr ($CDCl_3$) in ppm, 0.92 (sing. 9H), ca, 1.7 (mult., 2H), ca, 3.22 (broad, 1H), 3.52 (broad mult., 2H), 3.86 (broad triplet, 2H). Repeated recrystallization from benzene gave the analytical sample, mp. 66°C.

Anal. Calcd. for $C_7H_{16}O_2$: C, 63.60; H, 12.20; O, 24.20.
Found: C, 63.75; H, 12.04; O, 24.48.

REFERENCES

1. E. L. Eliel and Sr. M. C. Knoeber, J. Am. Chem. Soc., 90, 3444 (1968), provide general synthetic procedures for preparing 1,3-dioxanes from 1,3-propanediols.

2. For a general procedure for converting 1,3-propanediols, via the ditosylates, to the corresponding dithiols and subsequently to substituted 1,3 dithianes see: E. L. Eliel and R. O. Hutchins, J. Am. Chem. Soc., 91, 2703 (1969). A similar procedure may be used to convert 1,3 diols to 1,3-mercaptoalcohols (via the

monotosyl alcohol) which in turn react readily with aldehydes to afford 1,3-oxathianes. We are currently exploring synthetic methods leading to substituted 1,3-propanediamines for use in preparing 1,3-diazanes and related heterocycles.

(Received July 6, 1970)