Taylor for the infrared measurements, to the Dow Chemical Company for the polystyrene used in most of the experiments, and to the E. I. du Pont de Nemours & Co., Inc. for the sodium oxide.

Department of Chemistry
Massachusetts Institute of Technology
Cambridge 39, Mass.

Preparation of D-Propylene Glycol and Oxide

Nan Shieh and Charles C. Price

Received March 2, 1959

By the reduction of acetol benzoate, readily prepared from chloroacetone and sodium benzoate, with fermenting yeast solution, optically pure D-propylene glycol 1-benzoate was obtained in 65% yield. Saponification produced D-propylene glycol in 60% yield. This contrasts to yeast reduction of acetol itself, which yields L-propylene glycol.[1]

Treatment of the D-glycol with anhydrous hydrogen bromide gave the bromohydrin, $[\alpha]_D^{24}$ +9.90° (in $CHCl_3$), which was converted by alkali to D-propylene oxide, $[\alpha]_D^{21}$ −6.21° (2% in $CHCl_3$).

EXPERIMENTAL

D-*Propylene glycol 1-benzoate.* Into a 3-l. two-necked round-bottomed flask, provided with a gas trap and a mechanical stirrer, a solution of 100 g. of sucrose in 450 ml. of tap water was placed. To this solution, a paste of 40.6 g. of Fleischmann's dry yeast in 140 ml. of tap water was added. The mixture was allowed to stand at room temperature until a lively evolution of gas started. To this vigorous fermenting solution, 4.5 g. of acetol benzoate[2] was added and the mixture was allowed to stand at room temperature until the reaction subsided. The flask was then transferred to an incubator at 32° (or at room temperature for a longer time). The reaction was generally completed when all of the yeast had settled. Most of the clear solution was separated from the yeast by a siphon. The last portion of the solution was filtered. The combined solution was extracted with ether (3 × 150 ml., tech. grade) and the ethereal solution was washed with 3% aqueous sodium carbonate solution, water, and dried. After the removal of the solvent, the yellowish oil was distilled under reduced pressure, b.p. 139–140° (5 mm.). The distillate solidified after cooling. It was recrystallized from ether (Mallinckrodt, anhyd.) as white needles by dissolving the crude product in ether at room temperature and cooling the ethereal solution with an acetone–Dry Ice bath, m.p. 42–42.5°; yield, 64–66%, $[\alpha]_D^{24.2}$ + 21.8° (in $CHCl_3$).

The compound obtained did not give a good analysis, even after it had been purified alternatively by vacuum distillation and recrystallization (each twice).

Anal.: Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 67.17, 67.32, 67.39; H, 6.87, 6.84, 6.77.

D-*Propylene glycol.* Optically-active propylene glycol 1-benzoate (40 g.) was added gradually with constant shaking to 20 g. of 50% alkali solution. An additional 10–15 ml. of water was added and the cakelike sodium benzoate was mashed with a spatula. The reaction mixture was refluxed in an oil bath at 125° for 3 hr. After cooling, 100 ml. of ether was poured in and the mixture was filtered. The precipitate was washed with 10 ml. of absolute ethanol. The filtrate was extracted with ether for 9 hr. The ethereal layer obtained was dried over anhydrous magnesium sulfate and evaporated to yield 10.1 g. (60%) of propylene glycol, b.p. 92° (14 mm.), $n_D^{26.7}$ 1.4334, $[\alpha]_D^{24.2}$ + 30.0° (in $CHCl_3$). (For *l*-propylene glycol, b.p. 86–88° (9–10 mm.), $[\alpha]_D^{24.4}$ −28.6° (in $CHCl_3$); −14.9° (pure state, dm.), d^{24} 1.030, n_D^{24} 1.4355.)

D-*Propylene oxide.* Levene's synthesis[3] for L-propylene oxide was used. D-Propylene bromohydrin was prepared by passing dry hydrogen bromide through D-propylene glycol at 0°; yield, 60%, b.p. 57–58° (19 mm.), n_D^{25} 1.4765 $[\alpha]_D^{24}$ +9.90° (in $CHCl_3$). (For L-propylene bromohydrin, n_D^{25} 1.4775, $[\alpha]_D^{24}$ −10.53° (in $CHCl_3$) or −3.37° (pure bromohydrin), $d^{24.5}$ 1.541.)

The D-propylene bromohydrin was then cyclized to D-propylene oxide with 45% (by weight) aqueous potassium hydroxide, b.p. 35°, $[\alpha]_D^{21}$ −6.21° (2% in $CHCl_3$). [*l*-Propylene oxide, $[\alpha]_D^{21}$ +7.05° (2% in $CHCl_3$); +14.5° (38% in ether)].

Department of Chemistry
University of Pennsylvania
Philadelphia 4, Pa.

---

(1) The reduction of the benzoate in the opposite sense to the glycol was predicted by Dr. V. Prelog (private communication).

(2) For the preparation of acetol benzoate, Adams and Govindacharis' procedure was followed [*J. Am. Chem. Soc.*, **72**, 158 (1950)] with the following modification. The combined ethereal solution was washed with ice-cold 3% sodium carbonate solution, water, and dried. It is very important that no trace of benzoic acid remain in the acetol benzoate. Otherwise the yeast will be killed during the fermentation.

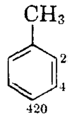
(3) P. A. Levene and A. Walti, *J. Biol. Chem.*, **68**, 415 (1926).

Relative Reactivities of Toluene and Toluene-α,α,α-d_3 in Hydrogen-Deuterium Exchange

W. M. Lauer and C. B. Koons[1]

March 2, 1959

Recent exchange studies[2] carried out in this laboratory have led to the following values for the partial rate factors for hydrogen-deuterium exchange in the case of toluene:



These exchange studies were conducted at 70° in a trifluoroacetic acid medium. Under these conditions, exchange occurs only in the aromatic nucleus. This fact was demonstrated by oxidizing a sample of randomly deuterated toluene to benzoic acid with aqueous alkaline permanganate. There was no loss of deuterium in this transformation. Infrared absorption studies, though less sensitive, also indicated the absence of side-chain deuterium in the randomly deuterated toluene samples. These

---

(1) Abstract of part of Ph.D. thesis submitted to the University of Minnesota, June 1958.

(2) W. M. Lauer, G. Matson, and G. Stedman, *J. Am. Chem. Soc.*, **80**, 6433, 6437, 6439 (1958).