An Effective Method for the Preparation of ω-Bromoalkanols from α,ω-Diols

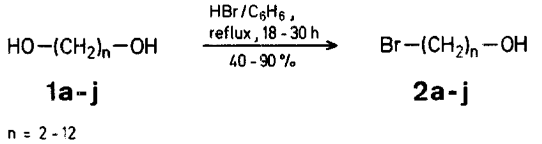
Suk-Ku Kang*, Won-Sup Kim, Byoung-Ho Moon

Department of Chemistry, Sung Kyun Kwan University, Natural Science Campus, Suwon, 170 Korea

Pure ω-bromoalkanols **2** (n = 2-12), not contaminated by any dibromoalkanes or unreacted diols **1**, were prepared in good yields by refluxing a mixture of diols **1**, aqueous (48 %) hydrogen bromide, and benzene using a Dean-Stark water separator.

ω-Bromoalkanols are of special value as intermediates in the synthesis of insect pheromones. The bromide function of the ω-bromoalkanols can be converted to a Wittig reagent by treatment with triphenylphosphine[1-5], or substituted by an acetylenide anion[6,7], or converted to a Grignard reagent with magnesium in tetrahydrofuran[8], after suitable protection of the alcohol group.

The conversion of diols **1** into ω-bromoalkanols **2** is amply described in the literature. Diols **1** have been heated with aqueous hydrogen bromide in ligroin[10], or reacted with aqueous hydrogen bromide using a continuous extraction apparatus employing non-polar solvents such as cyclohexane[7,8], toluene[9], and petroleum ether[1,11,12]. Under these conditions it was difficult to obtain the pure monobromoalkanols **2** uncontaminated by the dibromoalkane or unreacted diol, even after column chromatography or fractional distillation.



In a model experiment conducted by us, a mixture of 1,10-decanediol (**1i**) and aqueous hydrogen bromide (48%) heated to 110 °C was continously extracted with petroleum ether in a liquid-liquid extractor[11]. After removal of the solvent, the G.L.C. analysis (silicon OV 101, 170-230 °C) of the resulting low-melting solid indicated it to be a mixture of 10-bromo-1-decanol (**2i**), 1,10-dibromodecane, and the starting 1,10-decanediol (**1i**) in a ratio of 85 : 13 : 2. Hence a search for more efficient and convenient methods for the preparation of monobromoalkanols from diols is still very worthwhile.

We have now accomplished an efficient conversion of diols **1** into monobromoalkanols **2** by simply refluxing a mixture of

Table. ω-Bromoalkanols **2** prepared

Product No.	n	Reaction time [h]	Yield[a] [%]	b.p. [°C]/torr[b]	Molecular Formula[c] or Lit. b.p. [°C]/torr	^{1}H-N.M.R. (CDCl$_3$/TMS$_{int}$) δ [ppm]
2a	2	20	40	30-33°/5	56-57°/20	2.20 (s, 1H); 3.55 (t, 2H, J = 7 Hz); 3.80 (t, 2H, J = 7 Hz)
2b	3	20	90	52-55°/3	62°/5	1.80 (s, 1H); 2.15 (m, 2H); 3.55 (t, 2H, J = 7 Hz); 3.80 (t, 2H, J = 7 Hz)
2c	4	24	65	57-59°/3	C$_4$H$_9$BrO (153.0)[d]	1.60-2.20 (m, 5H); 3.45 (t, 2H, J = 7 Hz); 3.70 (t, 2H, J = 7 Hz)
2d	5	28	68	66-69°/3	C$_5$H$_{11}$BrO (167.1)	1.40-2.10 (m, 7H); 3.45 (t, 2H, J = 7 Hz); 3.70 (t, 2H, J = 7 Hz)
2e	6	18	60	88-90°/2	97-98°/2.5[4]	1.20-2.10 (m, 9H); 3.45 (t, 2H, J = 7 Hz); 3.70 (t, 2H, J = 7 Hz)
2f	7	20	77	98-100°/2	111-112°/4[9]	1.20-2.00 (m, 11H); 3.40 (t, 2H, J = 7 Hz); 3.65 (t, 2H, J = 7 Hz)
2g	8	18	78	110-119°/2	81°/0.06[7]	1.20-2.00 (m, 13H); 3.40 (t, 2H, J = 7 Hz); 3.65 (t, 2H, J = 7 Hz)
2h	9	20	72	118-120°/3	97-100°/0.06[12]	1.20-2.00 (m, 15H); 3.40 (t, 2H, J = 7 Hz); 3.65 (t, 2H, J = 7 Hz)
2i	10	30	80	125-127°/3	166-169°/10[11]	1.20-2.00 (m, 17H); 3.40 (t, 2H, J = 7 Hz); 3.65 (t, 2H, J = 7 Hz)
2j	12	20	88	155°/4	155°/4[13]	1.20-2.00 (m, 21H); 3.40 (t, 2H, J = 7 Hz); 3.65 (t, 2H, J = 7 Hz)

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[a] Yield of isolated pure product. The yields have not been optimized. H. P. L. C. analysis of the reaction mixture shows that all the products **2** are formed in almost pure state.

[b] Kugelrohr distillation, bath temperature given.

[c] Satisfactory microanalyses obtained: C ±0.33, H ±0.17.

[d] I.R. (Film): ν = 3500, 2900, 1040 cm^{-1}.

the diol **1**, aqueous hydrogen bromide (48%) and benzene using a Dean-Stark apparatus to remove the water formed. This way the reaction mixture is made less polar and pure monobromoalkanols **2** (> 99% by H.P.L.C.) are formed in good to excellent yields.

5-Bromo-1-pentanol (2d); Typical Procedure:

To a solution of 1,5-pentanediol (**1d**; 10.4 g, 100 mmol) and benzene (200 ml) is added hydrobromic acid (48%, 12.5 ml), and the mixture is heated at reflux for 28 h while trapping the water formed using a Dean-Stark water separator. The mixture is washed with 6 normal sodium hydroxide solution (100 ml), 10% hydrochloric acid (100 ml), water (2 x 200 ml), and brine (150 ml). The organic layer is dried with anhydrous magnesium sulfate and evaporated under reduced pressure. The residue is purified by Kugelrohr distillation; yield: 11.4 g (68%); b.p. 66–69°C/3 torr.

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