

Synthesis of ω -Iodoalkan-1-ols from α, ω -Diols¹

Suk-Ku Kang¹, Won-Sup Kim, and Byoung-Ho Moon

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

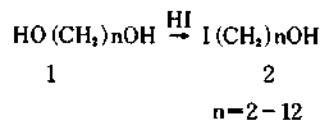
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ω -Iodoalkan-1-ol acetate or ω -iodoalkan-1-ol THP ether, the protected forms of ω -iodoalkan-1-ol is of special value in the synthesis of natural products, particularly in the synthesis of insect pheromones. The iodo-portion of the ω -iodoalkan-1-ol acetate or ω -iodoalkan-1-ol THP ether can be converted to Wittig reagent with triphenylphosphine, substituted by nucleophiles,² or coupled with Grignard reagent.³

ω -Iodoalkan-1-ol acetate and ω -iodoalkan-1-ol THP ether were supposed to be easily prepared from the corresponding ω -iodoalkan-1-ol by acetylation or protection reaction. Unexpectedly, in the literature, ω -iodoalkan-1-ols were not known. Normant reported⁴ the synthesis of 8-iodooctan-1-ol acetate from 8-bromooctan-1-ol⁵ by acetylation with acetic anhydride followed by nucleophilic displacement with sodium iodide. Oku reported⁶ the preparation of 4-iodobutan-1-ol acetate from tetrahydrofuran by reacting with hydriodic acid and acetic anhydride in the presence of zinc dust. No direct conversion of diols into ω -iodoalkan-1-ols was reported.

Search for the preparation of ω -iodoalkan-1-ol and direct method for the preparation of ω -iodoalkan-1-ols from α, ω -diols is very worthwhile.

Now we wish to report an effective synthesis of ω -iodoalkan-1-ol from diol without any diiodoalkane formed or diol remained.



The efficient conversion of diols into monoiodoalkanols was accomplished using Dean-Stark trap apparatus. Refluxing a solution of diol, aqueous HI (55%) and toluene while trapping water with a Dean-Stark water separator by making the reacting bath nonpolar afforded the pure monoiodoalkanol (Table). The purity of the products is greater than 99% by H.P.L.C. analysis.

A typical procedure is as follows. To a solution of 1, 10-decanediol (0.35g) and toluene (40 ml) was added hydriodic acid (55%, 0.27 ml), and the reaction mixture was heated at reflux for 20 hr while trapping water with a Dean-Stark water separator. The solvent was evaporated under reduced pressure and the residue was extracted with ether, washed with H₂O and 10% sodium thiosulfate, and saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The residue was distilled on Kugelrohr to afford 10-iododecan-1-ol (2j) (0.49g, 87%, b.p. : 140–143°C/3 torr). The product was analyzed by H.P.L.C..

References

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TABLE 1: Monoiodoalkanols (2) prepared from Diols (1)^a

Product I (CH ₂) _n OH	Reaction Time [hr]	Yield ^b [%]	b.p. [°C]/torr ^c Observed
2a n=2	20	30	45–47/3
2b 3	4	61	58–60/3
2c 4	4	74	70–72/3
2d 5	6	88	80–82/3
2f 6	6	84	84–87/3
2g 7	20	86	110–112/3
2h 8	20	80	116–119/3
2i 9	20	85	126–129/3
2j 10	20	87	140–143/3
2k 12	20	80	150–153/3

^a Consistent spectral data were obtained on all compounds reported.

^b Yield of isolated pure product. H.P.L.C. analysis of the reaction mixture shows that all the monoiodoalkanols were produced in almost pure state. ^c Kugelrohr distillation (bath temperature given).