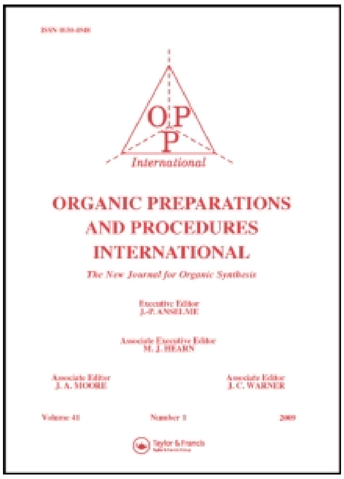

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4-HYDROXYCYCLOHEXANONE

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4-HYDROXYCYCLOHEXANONE

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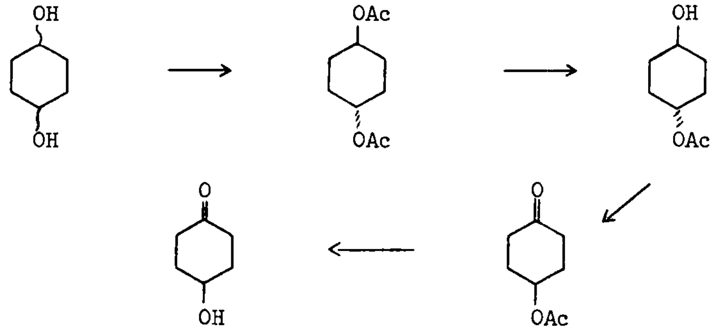
The dual functionality of 4-hydroxycyclohexanone makes this compound an attractive starting point for the elaboration of more complex molecules. The preparation of that compound starting from cyclohexanediol by the scheme below has been reported.(1)



Our initial attempts to carry out this procedure gave very erratic results. We wish to report a set of modified experimental conditions which in our hands have proved very reproducible. The starting material used in this work was a commercial mixture of <u>cis</u> and <u>trans</u> cyclohexanediol whereas in the original report the <u>trans</u> compound was employed. Dilution of the acetylation mixture with water followed by cooling leads to precipitation of only the <u>trans</u> diacetate; this material was used for the subsequent step.(2) Our yield for the acetylation is thus only half of that obtained from <u>trans</u> diol. Largely for that reason the overall yield (16.5%) is lower than that reported previously (30%); the final product was found by GLC to be 96% pure.(3)

Experimental(4)

1,4-Diacetoxycyclohexane A mixture of 50.0 g. (0.43 mole) of 1,4-dihydroxycyclohexane(5) and 175 ml. of acetic anhydride was heated under reflux for 1.5 hrs. and then allowed to cool to 50°. The mixture was poured into 1 l. of water at 50° and allowed to stand at room temperature overnight. The precipitated crystals were recrystallized from aqueous ethanol to afford 37.4 g. (46%) of diacetate m.p. 98-101° (lit.(1) 102-103°).

4-Acetoxycyclohexanol To a stirred solution of the diacetate (67.5 g., 0.337 mole) in 275 ml. of ethanol and 175 ml. of water at 45° there was added over 7 min. 17.6 g. of potassium hydroxide in 35 ml. each of water and ethanol. An ice bath was used to hold the temperature at 49°. Following an additional 15 min. stirring the volume of the mixture was reduced on a rotary evaporator until crystals just came out. This mixture was then cooled to room temperature and the solid (recovered diacetate) collected on a filter. The filtrate was extracted with several portions of chloroform. These extracts were taken to dryness separately and those which melted below 72° combined.(6) This last material was recrystallized from ether: petroleum ether to afford 27.2 g. (51%) of monoacetate, m.p. 67-71.5° (lit.(1) 68-72°).

4-Acetoxycyclohexanone Jones reagent(7) (56.0 ml.) was added to an ice cooled solution of 35.0 g. (0.221 mole) of the monoacetate in 725 ml. of acetone over 7 min. Following an additional 3 mins. stirring the bulk of the acetone was removed in vacuum. The residue was taken up in water and ether. The organic layer was washed once each with water and brine and taken to dryness. The residual oil was distilled to afford 31.9 g. (92.5%) of acetoxyketone, b.p. 71-73° at 0.4 mm. (lit.(1) 110° at 8 mm.).

4-Hydroxycyclohexanone A mixture of 34.0 g. (0.218 mole) of the acetoxy ketone and 18.1 g. of sodium bicarbonate in 170 ml. of methanol was stirred at reflux overnight. The solvent was removed in vacuum and the residue suspended in ether. The solid was collected on a filter and washed well with ether. The filtrates and washes were combined and taken to dryness. The residual oil was distilled at 0.20 mm. to afford 21.2 g (78%) of hydroxycyclohexanone, b.p. 71-76° (lit.(1) 83-85° at 0.6 mm.).

References

(1) J. B. Aldersley, G. N. Burkhardt, A. E. Gillam and N. C. Hindley, J. Chem. Soc., 10 (1940).

(2) An attempt to employ the total crude diacetate gave equivocal results.

(3) Determined on a Carbowax 20M column, isothermally at 200°. The authors are indebted to Mr. L. Reineke of these laboratories for the determinations.

(4) Melting points are uncorrected and recorded as observed on a Thomas-Hoover melting point apparatus.

(5) Aldrich Chemical Co.

(6) Further extraction affords samples contaminated with the diol.

(7) A solution of 26.73 g. of chromium trioxide and 23 ml. of concd. sulfuric acid diluted to 100 ml. with water.

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