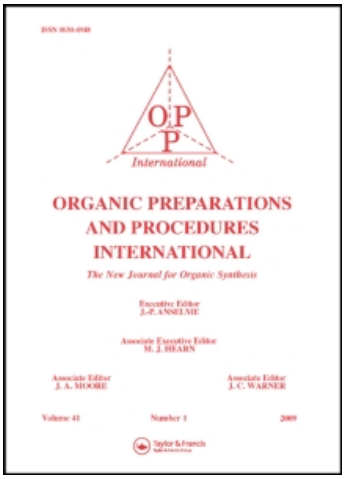

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A SIMPLE PREPARATION OF 1-HYDROXYPYRENE

Raj K. Sehgal[a]; Subodh Kumar[ab]
[a] Great Lakes Laboratory, State University of New York College at Buffalo, Buffalo, NY [b] Department of Chemistry, SUNY College at Buffalo,

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General Procedure for the Oxidation of 4-Chomanones with m-CPBA.- 4-Chromanones (1a-e) (0.01 mol) and m-chroroperbenzoic acid (1.72 g, 0.01 mol) were heated under reflux in dry dichloromethane (50 ml) over a period of 15-18 hrs. The m-chlorobenzoic acid which had precipitated during reflux was removed by filtration and the filtrate was concentrated. The resulting residue dissolved in ethyl acetate and the solution was washed with 2% aqueous sodium bicarbonate (3 x 30 ml) and dried over anhydrous sodium sulphate and evaporated. The colorless semi-solids were crystallized from pet. ether (IIb, c) or benzene (IId, e) to yield colorless needles. IIa was purified by preparative thin layer chromatography to yield a colorless oil.

Synthesis of 3,4-Dihydro-1,5-benzodioxepin-2-one (IIa) from Catechol.- Catechol (1.1 g, 0.01 mol) and β–chloropropionyl chloride (1.2 g, 0.01 mol) was stirred at room temperature in 5% methanolic potassium hydroxide solution (50 ml) for 6 hrs. The solvent was removed under reduced pressure. The residue (1.0 g) was chromatgraghed over silica gel (ACME, 200 mesh, 60 g). Elution with benzene (200 ml) gave a crude liquid which was purified by preparative TLC, to yield 3,4-dihydro-1,5-benzodioxepin-2-one (IIa) as colourless liquid (0.41 g, 20%), identical in all respects (Co-tlc and Superimposable IR) with IIa prepared as described above.

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A SIMPLE PREPARATION OF 1-HYDROXYPYRENE

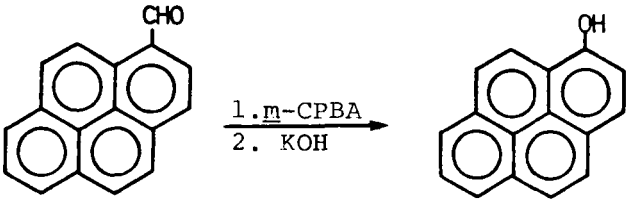
Submitted by (04/04/88)

Raj K. Sehgal and Subodh Kumar*†

Great Lakes Laboratory
State University of New York College at Buffalo
1300 Elmwood Avenue, Buffalo, N. Y. 14222

1-Hydroxypyrene, a metabolite[1] of pyrene, is a valuable intermediate for the synthesis of

various phenolic metabolites of benzo(a)pyrene[2] and other oxygenated derivatives of pyrene.[3] The reported procedures[4,5] for the synthesis of 1-hydroxypyrene are unsatisfactory both because of the very poor yields of 1-hydroxypyrene and the difficulty in its preparation, especially on a large scale (e. g. 50 g). We have recently developed a relatively simple and high yield procedure for the synthesis of 1-hydroxypyrene from pyrene-1-carboxaldehyde using a method anagous to the one originally developed by Godfrey et al.[6] for the synthesis of methoxy phenols. Thus, Baeyer-Villiger oxidation of pyrene-1- carboxaldehyde with an excess



of m-chloroperoxybenzoic acid in boiling dichloromethane followed by hydrolysis of the resultant formate with alkali produced the desired 1-hydroxypyrene in a 90-96% yield.

EXPERIMENTAL SECTION

1-Hydroxypyrene.- Pyrene-1-carboxaldehyde (46 g, 0.2 mol) and m-chloroperoxybenzoic acid (52 g, 0.3 mol) were heated under reflux in dry dichloromethane (800 mL) for 24 hrs under an argon atmosphere. Most of the solvent was removed by distillation under reduced pressure, and the residue was stirred with 10% $NaHCO_3$ (500 mL) until effervescence ceased. The residual dichloromethane was evaporated by using water aspirator, and the resulting crystalline solid was collected, washed with water and dried. The air dried solid was dissolved in a mixture of THF (200 mL) and methanol (200 mL), and then 60 mL of 25% KOH solution was added. The mixture was stirred under argon for 3-4 hrs, most of the solvent was removed by distillation under reduced pressure, and the residue was then diluted with 1 1. of 2% KOH. The unreacted aldehyde and other neutral impurities were extracted with benzene-ether (1:1), and the ice-cooled aqueous phase was acidified to pH 2. The resultant solid was collected, washed with water and then triturated several times with 10% $NaHCO_3$. The gray solid was finally washed with water and dried in vacuo to yield 42.0 g (92%) of 1-hydroxypyrene, mp. 176-178°. A small sample was further purified according to the procedure described earlier [5] to give a pale yellow crystalline solid, mp. 178-180°, lit.[5] mp. 179-180° with a little loss.

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†. Adjunct Associate Research Professor in the Department of Chemistry, SUNY College at Buffalo.

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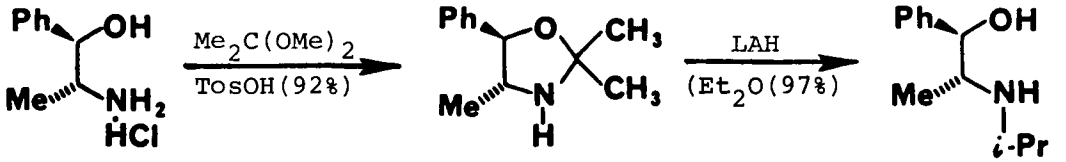
AN IMPROVED SYNTHESIS OF

(1R, 2R)-(-)-a-(1-ISOPROPYLAMINOETHYL)BENZYL ALCOHOL

Submitted by (03/01/88) Duy H. Hua*, Roch Chan-Yu-King, Robert A. Ostrander and Jeffrey A. McKie

Department of Chemistry
Kansas State University, Manhattan, KS 66506

Directed asymmetric synthesis via 1,4-addition reactions of chiral allylphosphonyl anions with cyclic enones is a powerful new synthetic tool.[1] The chiral director (1R,2R)-(-)-a-(1-isopropyl-aminoethyl)benzyl alcohol (1) was originally prepared from the coupling reaction of (1R, 2R)-(-)-norpseudoephedrine hydrochloride (2) with acetone-sodium acetate-sodium borohydride in acetic acid-water at 0° followed by reduction of the resulting (4R, 5R)-(-)-5-phenyl-2,2,4-trimethyl-1,3-oxazolidine (3) with lithium aluminum hydride in ether at room temperature.[1,2] We later found that in the first step, the formation of the intermediate, oxazolidine 3 is very much dependent on the sodium borohydride used. The reaction proceeded to varying degree depending on the lot number of sodium borohydride employed. These undependable results prompted us to explore a different method for the formation of 3. Herein, we now report an improved and simple procedure for the preparation of 1 in excellent yield.



2 3 1

Treatment of amino alcohol 2 with 2,2-dimethoxypropane and anhydrous p-toluene