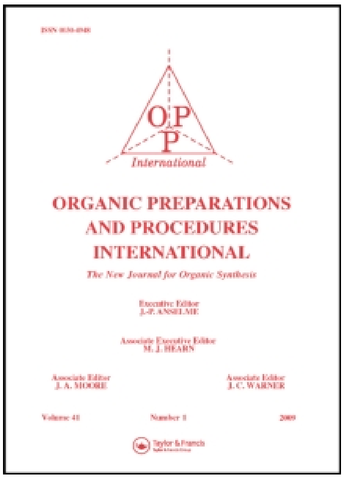

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CONCERNING THE SYNTHESIS OF 4-METHOXYINDAN-1-ONE

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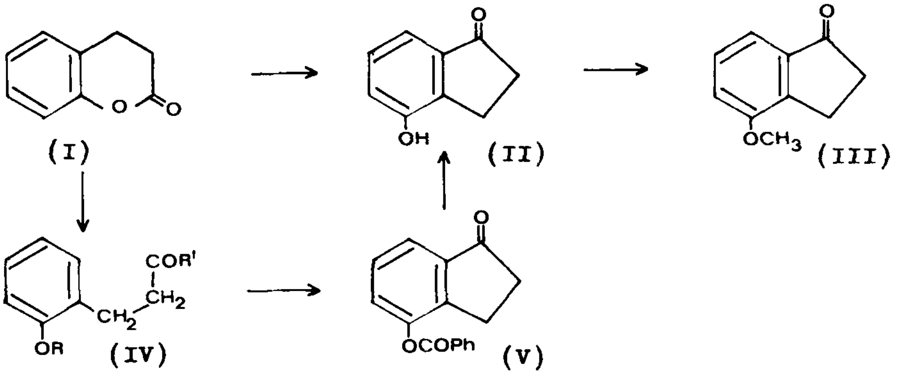
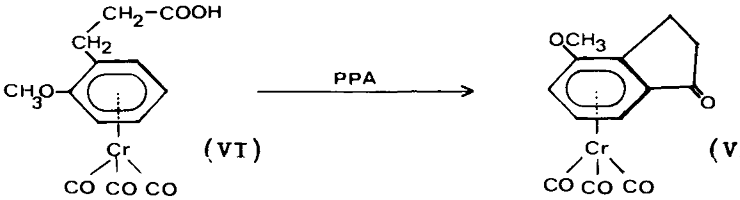
In connection with some synthetic work, a substantial amount of the title compound (III) was required. It had been earlier prepared[1] by the alkylation of 4-hydroxyindan-1-one (II) with methyl iodide in the presence of anhydrous potassium carbonate in acetone solution. Compound (II) can in turn be obtained in 46% yield by fusion of dihydrocoumarin (I) with anhydrous aluminium chloride and isolated from the reaction mixture by steam distillation. Since in our hands, the yield on a large scale was unsatisfactory, we therefore decided to explore the cyclization of 3-(2-methoxyphenyl)-propionic acid (IVa) (R = CH_3, R' = OH) in anhydrous medium



or of the corresponding chloride (IVb) (R = CH_3, R' = Cl) under Friedel-Crafts conditions as a more attractive method for the preparation of III . However, attempts to synthesise III by this route have failed[2,3] and a logical explanation has been suggested[3] involving the chelation of the acylium ion with the oxygen doublet of the methoxy group. More recently[4], it was shown that 3-(2-methoxyphenyl-chromiumtricarbonyl)-propionic acid (VI) afforded a low yield of cyclised product VII by treatment with polyphosphoric acid and this fact was rationalised by considering the electron-withdrawing action of the organometallic complex as reducing the chelate formation.



(VI)

(VII)

Based upon these considerations, we have prepared 3-(2-p-toluenesulfonyloxyphenyl)-propionic acid (IVc) (R = p-$C_7H_7SO_2$-R' = OH) and 3-(2-benzoyloxyphenyl)-propionic acid (IVd) R = COPh, R' = OH) by acylation in alkaline medium of the available dihydrocoumarin (I), in order that the decreased disponibility of the oxygen doublet compared with the methoxy group would allow the cyclisation. When IVc was treated with polyphosphoric acid or with phosphorus pentoxide-methanesulfonic acid[5] or the corresponding chloride (IVe) (R = p-$C_7H_7SO_2$, R' = Cl) with anhydrous aluminium chloride starting dihydrocoumarin was regenerated. Cyclization of the acid (IVd) under the conditions outlined above gave a low yield of V , owing to the concomitant formation of by-products, whereas treatment of the chloride (IVf) (R = COPh, R' = Cl) in the presence of aluminium chloride proceeded readily leading to the cyclized product V in 65% yield. Saponification of the benzoyl group afforded II which was quantitatively alkylated to the desired compound III following the known procedure.[1]

EXPERIMENTAL

3-(2-Benzoyloxyphenyl)-propionic acid (IVd).- Seventy-four g. (0.5 mole) of dihydrocoumarin (I) were dissolved in 30% sodium hydroxide solution (1 mole) by heating slowly for 10 minutes. Then 70 g. (0.5 mole) of benzoyl chloride were added over 3o minutes under efficient stirring at room temperature. The cooled reaction mixture was acidified with concentrated hydrochloric acid and the precipitated solid collected by filtration, washed with water and dried to yield 148 g. (82%) of IVd . Recrystallization from benzene gave white needles, mp. 140°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22
Found : C, 71.01; H, 5.15

3-(2-p-Toluenesulfonyloxyphenyl)-propionic acid (IVc).- This was prepared as described above, i.e., 95 g. (0.5 mole) of p-toluenesulfonylchloride was substituted for 0.5 mole of benzoyl chloride. An 80% yield of IVc was obtained. Recrystallization from methanol gave white needles, mp. 137-138°.

Anal. Calcd. for $C_{16}H_{16}O_5S$: C, 60.00; H, 5.04
Found : C, 59.91; H, 4.92

4-Benzoyloxyindan-1-one (V).- To a solution of 135 g. (0.5 mole) of the acid (IVd) in 1 l. of methylene chloride was added 150 g. of thionyl chloride and a few drops of N,N-dimethylformamide. The mixture was heated at 50-60° for 4 hrs, then evaporated *in vacuo*. The residue was treated with 100 ml. portions of benzene and concentrated *in vacuo* in order to remove the excess of chlorinating agent. Finally it was dissolved in 200 ml. of methylene chloride and added under efficient stirring to a suspension of 300 g. of anhydrous aluminium chloride in 200 ml. of methylene chloride and the mixture heated gently at reflux for 3 hrs., The cold mixture was poured into 1 l. of ice-water. The organic layer was separated and the aqueous solution extracted several times with methylene chloride. The organic extracts were washed first with 5% aqueous sodium bicarbonate solution, then with water and finally dried over anhydrous magnesium sulfate. Evaporation of the organic solvent yield 82 g. of a brown oil, which on cooling crystallized (65%). Recrystallization from benzene gave V , mp. 85°.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80

Found : C, 76.07; H, 4.72

4-Hydroxyindan-1-one (II).-A suspension of 27 g. (0.1 mole) of V in 60 ml. of 30% sodium hydroxide solution was heated under stirring for 30 minutes until it was completely dissolved. The brown solution was decolorized with carbon and filtered through Celite. The cooled mixture was acidified with concentrated hydrochloric acid and the precipitated solid collected by filtration. The wet solid was triturated with 100 ml. of saturated aqueous sodium bicarbonate in order to remove benzoic acid and the solid filtered, washed with water and dried to give 12.5 g. (85%) of II . Recrystallization from methanol gave 4-hydroxyindan-1-one (II) mp. 239-240°, identical with an authentic sample.[1] Transformation of II into the title compound proceeded without difficulties.[1]

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