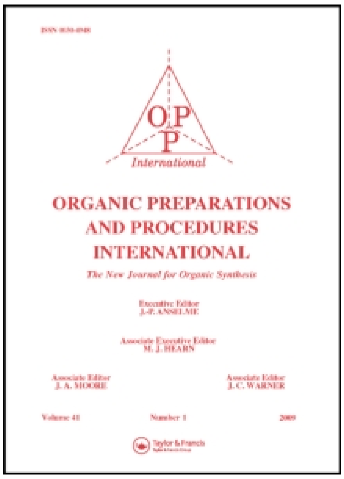

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1,7-DIMETHYLINDAN

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7. Bromine chloride was prepared through dissolution of an equimolar amount of gaseous chlorine in liquid bromine.

8. A dropper with bromine chloride was cooled with Dry Ice to keep the temperature between -20° and -40° (bp. of bromine chloride is +5°). The dropper outlet was immersed in the liquid.

9. The reaction is strongly exothermic. The heat evolved is sufficient to distil the acetyl chloride formed.

1,7-DIMETHYLINDAN

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(1/16/79)

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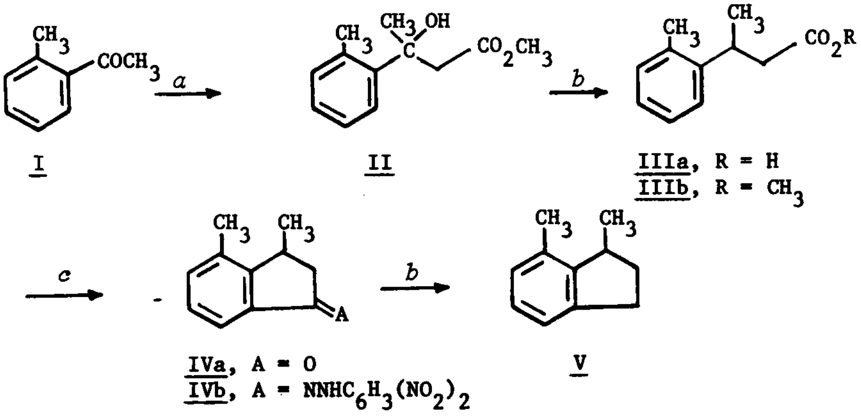
A four step procedure [shown for 1,7-dimethylindan (V, 44% yield)] provides a selective and convenient synthesis of 1,7-substituted indans.



I

II

IIIa, R = H
IIIb, R = CH_3

IVa, A = O
IVb, A = $NNHC_6H_3(NO_2)_2$

V

a) $BrCH_2CO_2CH_3$, Zn(Cu), Ph, Δ. *b)* Pd/C, H_2, HOAc, Δ. *c)* PPA, Δ on IIIa.

Although the yield of II was improved from 32% to 40% by the use of THF and trimethylborate,[1a] substitution of Zn-Cu couple[1b] for activated Zn in the traditional Reformatsky reaction[1a,c] gave II in 70% yield. Since dehydration of II with oxalic acid in boiling toluene resulted in the formation of a mixture of the two olefins,[2] II was hydrogenolyzed directly to III. Indanone IVa, was rigorously purified via preparation, recrystallization and hydrolysis[3] of its 2,4-DNP derivate IVb. Either IVa or IVb may be hydrogenolyzed to give pure V.[4]

EXPERIMENTAL

Melting points are uncorrected. Infrared and ultraviolet spectra were determined on Beckman IR 5A and Cary 14 spectrometers respectively. ^{1}H NMR spectra were obtained on a Varian XL-100 instrument using TMS as internal reference. Mass spectral determinations were made using a CEC 110B spectrometer. A Hewlett-Packard 5750B instrument was used for GC determination.

Methyl 3-hydroxy-3-(2-methylphenyl)butanoate (II).- To a 500 ml 3-necked flask fitted with reflux condenser, magnetic stirrer, addition funnel, and supplied with a nitrogen atmosphere was added 50 g of Zn-Cu couple,[1b,c] 250 ml of dry benzene, and a catalytic amount of iodine. To this was added approximately 10 ml of a solution of freshly distilled I (25 g, 0.19 mol), freshly distilled methyl bromoacetate (45 g, 0.29 mol), and dry benzene (5 ml). The mixture was heated to reflux and the remainder of the solution was added slowly (approx. 20 min) while reflux was continued for 45 min. A red color developed during the reflux period. The reaction mixture was cooled in an ice bath and then poured into 800 ml of ice cold 20% H_2SO_4. The resulting layers were separated and the aqueous layer was extracted with ether. The combined ethereal extracts were washed twice with a saturated solution of sodium bicarbonate, once with a saturated solution of sodium carbonate, dried ($MgSO_4$), and concentrated to a red liquid which was distilled to yield 27 g (70%) of II, bp. 112-115° 2.2 mm; IR (neat): 3500, 1720 cm^{-1}; NMR (neat, TMS): δ 7.28-7.44 (m, 1, Ar-H), 7.00 (d, 3, Ar-H), 4.28 (s, 1, O-H), 3.36 (s, 3, Ar-CH_3), 3.00 (d, 1, methylene proton in unsumm. environment), 2.64 (d, 1, methylene proton in unsymm. environment), 2.48 (s, 3, -CH_2CH_3), 1.54 (s, 3, -CH_3); MS (70-eV): m/z (rel intensity) 134 (45), 119 (91), 91 (100), 74 (14), 65 (22), 43 (73); UV (95% ethanol): λ_{max} (log ε) 210 (3.86) nm.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.75. Found: C, 69.08; H, 7.73.

3-(2-Methylphenyl)butanoic Acid (IIIa).- A mixture of II (12.3 g, 0.06 mol), 300 ml of acetic acid, and 2 g of 5% Pd/C was hydrogenated[4] at 50 psig until hydrogen uptake ceased. The mixture was then filtered through Dicalite, concentrated, diluted with water and extracted with ether. The ethereal extract was concentrated leaving a clear liquid which was distilled at 132-140°/9 mm to give the methyl ester IIIb. Hydrolysis with 10% sodium hydroxide, extraction with ether to remove neutral impurities, and acidification with 10% hydrochloric acid followed by re-extraction with ether, and concentration yielded 9.47 g (90%) of IIIa; IR (neat): 1710 cm^{-1}; NMR (neat, TMS): δ 9.51 (s, 1, -CO_2H), 7.06-7.22 (m, 4, Ar-H), 3.42-3.64 (m, 1, benzylic proton), 2.58 (d, 1, methylene proton in unsymm. environment), 2.35 (s, 3, Ar-CH_3), 2.28 (d, 1, methylene proton in unsymm. environment), 1.23 (d, 3, -CH_3); MS (70 eV) m/z (rel intensity) M^+ 178 (24), 119 (100), 97 (30), 91 (25), 55 (38), 41 (19); UV (95% ethanol) λ_{max} (log ε) 262 (2.16), 271 (214) nm.

Anal. Calcd for $C_{12}H_{16}O_2$ (IIIa): C, 74.97; H, 8.39. Found: C, 74.79; H, 8.62.

3,4-Dimethyl-1-indanone (IVa).- The acid IIIb (6.1 g. 0.04 mol) was mixed with 29 g of PPA (polyphosphoric acid) at 60° for 30 min. An additional 25 g of PPA was added to the mixture and heating at 75° was continued for 30 min. The product mixture was stirred in a Waring Blender containing ice water and then extracted with ether. The ethereal extract was washed with a saturated solution of sodium bicarbonate, dried ($MgSO_4$), and concentrated, leaving a red liquid which was distilled to yield 5.0 g (88%) of IVa, bp. 80-82°/0.5 mm; IR (neat); 1710 cm^{-1}; NMR (neat, TMS): δ 7.10-7.50 (m, 3, Ar-H), 3.20-3.50 (m, 1, methylene proton in unsymm. environment), 2.62-2.90 (m, 1, methylene proton in unsymm. environment), 2.28 (s, 3, Ar-CH_3), 1.98-2.06 (m, 1, benzylic proton), 1.18 (d, 3, C-CH_3); MS (70-eV): <u>m/z</u> (rel intensity) M^+ 160 (53), 145 (100), 117 (23), 115 (25), 91 (18), 55 (16); UV (95% ethanol): λ_{max} (log ε) 250 (4.40), 290 (3.29) nm.

<u>Anal</u>. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.64; H, 7.55. The red 2,4-dinitrophenylhydrazone (IVb) was prepared[5] (97%) and recrystallized from methanol, mp. 229-230°.

<u>Anal</u>. Calcd for $C_{17}H_{16}N_4O_4$: C, 59.99; H, 4.74. Found: C, 59.91; H, 4.82.

Hydrolysis[3] of IVb with 35% H_2SO_4 afforded pure IVa in 65% yield.

<u>1,7-Dimethylindan (V)</u>.- A mixture of IVa (2.1 g, 0.01 mol, or an equivalent of IVb), 50 ml acetic acid, and 0.2 g of 5% Pd/C was hydrogenated at reflux[6] until the hydrogen uptake ceased. The mixture was then cooled, filtered through Dicalite, diluted with water, and extracted with ether. The ethereal layer was washed with a saturated solution of sodium bicarbonate, dried ($MgSO_4$), and concentrated to yield 1.5 g (80%) of V, bp. 88°/16 mm; IR (neat): 2933, 1548, 1453, 1370, 1068, 763, 749 cm^{-1}; NMR (neat, TMS): δ 6.71-7.00 (m, 3, Ar-H), 2.95-3.30 (m, 1, Ar-C-H), 2.48-2.93 (m, 3, Ar-CH_2-), 2.17 (s, 3, Ar-CH_3), 1.45-2.20 (m, 2, -CH_2-) and 1.02-1.09 (d, 3, -CH_3); MS (70-eV): <u>m/z</u> (rel intensity) M^+ 146 (18), 131 (100), 116 (15), 115 (20), 77 (8); UV (95% ethanol): λ_{max} (log ε) 265 (2.69), 273 (2.69) nm.

<u>Anal</u>. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.40; H, 9.60.

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AN IMPROVED SYNTHESIS OF BENZO[k]FLUORANTHENE

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This synthesis of V was reported[1] as proceeding through the diamide IV. We found that the tedious preparation of IV may be omitted to give V in 60% overall yield.