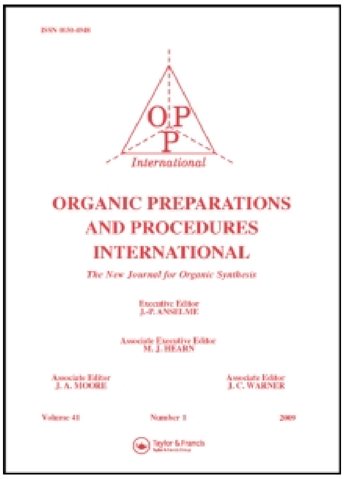

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BENZOYLATION OF TETRALIN. PRODUCT DISTRIBUTION.
PHENYL 5,6,7,8-TETRAHYDRO-2-NAPHTHYL KETONE

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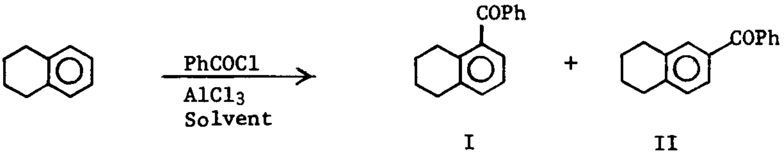
Earlier reports of the benzoylation of tetralin do not give the product distribution of I and II. Although I is known, its formation has apparently not been reported by this route.[2a,b] Pure II was sought as a precursor to 6-benzyl-1,2,3,4-tetrahydronaphthalene (III).



We sought to increase the yield of II by varying the solvent. Nitroethane, the most effective solvent, gave I and II in ratio of 1:22.[3] Other solvents tried were nitrobenzene (1:21),[2c] chloroform (1:13), and carbon disulfide (1:12).[2a,b] Although nitrobenzene and nitroethane are about equally effective, the latter is considerably more convenient to use since it is readily steam distilled. The yield of distilled mixture of ketones I and II ranged from 75-85% irrespective of solvent. The isolation of II is readily accomplished by recrystallization from aqueous methanol. The Wolff-Kishner reduction[4] of II to III is superior to catalytic hydrogenation[5] over Pd/C catalyst.[6,7]

EXPERIMENTAL[8]

Phenyl 5,6,7,8-Tetrahydro-2-naphthyl Ketone (II). The ketone II was prepared[2a,b,c] by addition of $AlCl_3$ (454 g, 3.4 mole) to a cooled (ice water) and well-stirred mixture of nitroethane (1.8 l.), benzoyl chloride

(350 g, 2.5 mole) and tetralin (350 g, 2.7 mole) at such a rate (55 min) as to maintain a temperature of 10-15°. The ice water was removed and water at room temperature was kept around the reaction flask for three hours.[9a] The contents of the flask were poured onto ice and the mixture was extracted with a total of 1200 ml of petroleum ether.[8] This extract was washed with water, dried ($MgSO_4$), filtered and concentrated (rotary evaporation) to remove nitroethane. One l. of petroleum ether[8] was added to the concentrate with stirring and the resulting solution was decanted from a small tarry residue and filtered through Dicalite filter aid.[9a] The filtrate was washed[9b] with 10% NaOH (2 x 200 ml), dried ($MgSO_4$), filtered and distilled to give a first cut, 16 g, bp 25-160° (0.01 mm), a second cut, 466 g (79%), bp 160-180° (0.01 mm) of a mixture of I and II (1:22),[3] and 20 g of pot residue. Methanol (2.5 l.) and then H_2O (0.1 l.) were added with stirring to cut 2 and the suspension was refrigerated. Filtration yielded 427 g (72%) of II.[9c] An additional recrystallization[9c] from methanol gave pure II: mp 40-41°, lit.[2b] 40.4-41.2°, lit.[2c] 40-41°; IR (KBr) 690, 723, 787, 821, 837, and 1660 (C=O) cm^{-1}; NMR (CCl_4) δ 6.85-7.7 (m, 8, Ar$\underline{H}$), 2.5-2.9 (broad m, 4, Ar$C\underline{H}_2$), 1.6-1.9 (broad quintet, 4, β -$C\underline{H}_2$-$C\underline{H}_2$); UV max (95% C_2H_5OH) 201 mμ (ε 35,000) and 268 mμ (ε 17,000). Another run in which CS_2 was used instead of nitroethane gave 529 g (90%) of crude I and II: (1:12).

The orange 2,4-dinitrophenylhydrazone of II was prepared[10] and an analytical sample showed mp. 197-198°.

Anal. Calcd for $C_{23}H_{20}N_4O_4$: C, 66.33; H, 4.84; N, 13.46. Found: C, 66.09; H, 4.74; N, 13.66.

Phenyl 5,6,7,8-Tetrahydro-1-naphthyl Ketone (I). The combined concentrated mother liquor (74 g)[9c] from the isolation of II above was subjected to chromatography on a 2" x 36° column of acidic alumina and elution with petroleum ether.[8] The chromatography was monitored with glc analysis.[3] After 15 x 500-ml fractions, 12.5 g of I:II (6:1) was obtained. This fraction was separated by preparative glc on a 0.5-in. x 4-ft column of 10% Carbowax 20M coated on acid-washed Gas Pack W 80/100 mesh at 225°. Distillation of the collected glc fractions gave 2.5 g of I: bp 177° (0.01 mm) IR 670, 689, 705, 724, 767, 779, 802, 817, 832, and 1670 (C=O) cm^{-1}; NMR (CCl_4) δ 6.8-7.7 (m, 8, Ar$\underline{H}$), 2.45-2.9 (broad m, 4, Ar$C\underline{H}_2$), 1.45-1.8 (broad, quintet, 4, β -$C\underline{H}_2$-$C\underline{H}_2$-); UV max (95% C_2H_5OH) 201 mμ (ε 40,000) and 252 mμ (ε 13,500).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.20; H, 6.87. The orange 2,4-dinitrophenylhydrazone was prepared:[10] mp 190-191°

Anal. Calcd for $C_{23}H_{20}N_4O_4$: C, 66.33; H, 4.84; N, 13.46. Found: C, 66.17; H, 5.03; N, 13.34.

Wolff-Kishner Reduction of II to 6-Benzyl-1,2,3,4-tetrahydronaphthalene (III). To a mixture of 47.2 g (0.20 mole) of II, 25 g (0.45 mole) of KOH, and 1 l. of diethylene glycol in a 1.5-l. stainless steel flask was added 30 g (0.80 mole) of 85% aqueous hydrazine.[4] The flask was equipped with a nitrogen inlet and outlet, a thermocouple, and a Dean-Stark trap. The reaction mixture was heated to 231° over 2 hr, by which time 200 ml of condensate appeared. The reaction mixture was steam distilled until 35 l. of condensate were collected. The condensate was extracted with 6 l. of petroleum ether,[8] dried ($MgSO_4$), and concentrated (rotary evaporation), and distilled to give 35.2 g (79%) of III: bp 128° (0.1 mm); UV max (95% C_2H_5OH) 204 mμ (ε 50,000), 270 (ε 1,000), and 280 (ε 1,000); IR 694, 715, 763, 793, and 834 cm^{-1}; NMR (CCl_4) δ 6.96 (s, 5, $C_6\underline{H}_5$), 6.71 (s, 3, Ar$C\underline{H}$), 3.72 (s, 2, C_6H_5-$C\underline{H}_2$-Ar), 2.57 (m, 4, Ar-$C\underline{H}_2$-CH_2-), and 1.62 (m, 4, Ar-CH_2-CH_2-); mass spectrum (70 eV) m/e (rel intensity) 222 (85), 178 (18), 165 (19), 131 (100), 115 (21), and 91 (52).[11]

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(8) NMR line positions are reported as ppm from internal tetramethylsilane. The petroleum ether, bp 60-68°, was distilled before use.

(9) (a) With nitroethane as solvent, heating at reflux temperature (115°) causes reduction in yield (to 60% and lower) and the formation of considerable tarry material which interferes with the workup. However, petroleum ether readily removes the mixture of I and II from the tar which settles out. Filtration through Dicalite filter aid also assists in removing tar; (b) This extract yielded 24 g (8%) of benzoic acid; (c) Filtrates were saved, combined and concentrated for the isolation of I.

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(11) We thank M. C. Hamming, Continental Oil Company, for this mass spectrum.

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