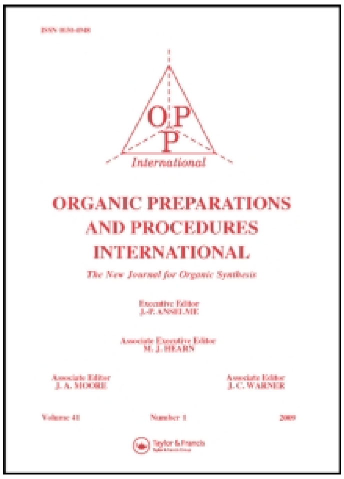

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THE SYNTHESIS OF BENZ[*a*]ANTHRACENE[1]

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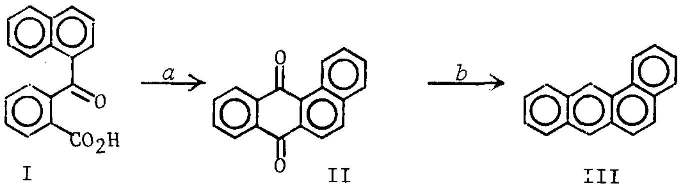
Benz[*a*]anthracene (III), a carcinogenic polynuclear aromatic hydrocarbon widely distributed in the environment,[2-7] is an important reference hydrocarbon in pollution studies. Consequently, a direct and reliable synthesis was developed by the route shown below. Three procedures were tried in the cyclization of 1 to 2. Sulfuric acid (95%) at 80°, with added boric acid to inhibit sulfonation gave considerable tar, and the yield was 54% instead of the reported 94%.[8] With liquid HF, even after 48 hr, the reaction was incomplete and the resulting neutral fraction contained tarry material which interfered with purification. PPA was the most effective catalyst.[9] We also found that commercial aluminum tricyclohexoxide, though active as a reducing agent, was not suitable for the reduction of 2. Picrate formation enabled easy separation of II and III, since 1,2-benzanthraquinone (II) does not form a picrate.



[a]PPA, Δ. [b]Aluminum tricyclohexoxide, cyclohexanol, Δ.

EXPERIMENTAL

2-(1-Naphthoyl)benzoic Acid (I).— The method is an adaptation of that reported by Groggins and Newton.[8] A 2-ℓ fluted flask was equipped with a mechanical stirrer, thermocouple, nitrogen inlet, gas bubbler, and condenser. A solution of naphthalene (83 g, 0.65 mole) and resublimed phthalic anhydride (92 g, 0.62 mole) in 250 ml of *o*-dichlorobenzene was added to the flask and then cooled to 0°. Anhydrous aluminum chloride (182 g; 1.4 mole) was gradually added to the solution over a period of 3 hr with constant stirring at 0°. Stirring was continued (2 hr) until the evolution of HCl ceased. The dark product was then poured onto ice (1 kg) containing 100 ml of conc. hydrochloric acid and left overnight. The reaction mixture was steam-distilled until most of the *o*-dichlorobenzene (242 ml) was removed. The residue was washed with 5% hydrochloric acid, homogenized in a Waring Blendor, filtered and dried *in vacuo*. The crude yellow product (154 g, 0.56 mole, 86%) melted at 110-170°. Four recrystallizations from toluene (800 ml), yielded 92 g (0.33 mole, 53%) of colorless I, mp 174-175°, lit.[8] 170-172°.

IR spectrum (KBr) 3000, 2300, 1670, 1400, 1270, 908, 810, 775, 745, 685, 655 cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) 276 (M$^+$, 41), 232 (63), 321 (38), 155 (100), 127 (76), 9 (48); pmr spectrum (DCCl$_3$, 100 MHz), 9.95 (5, 1, COOH), 8.9 (d, 1, ArH), 7.9 (m, 1, Ar-H), 7.1-7.7 (m, 7, Ar-H).

Cyclization of I to 1,2-Benzanthraquinone (II).— A 50 g (0.18 mole) sample of I was added over 2 hr to 480 g of PPA held at 90° with stirring. The mixture was then heated at 110° for a total of 5 hr. The resulting dark-colored product mixture was cooled and poured onto ice. The resulting greenish-black solid was filtered and washed first with 500 ml of saturated sodium carbonate solution and then with water thoroughly. The dried II (46 g, 0.18 mole, 98%), melted at 130-150°. Distillation at approximately 135-155° at 1 mm in a Kugelrohr apparatus gave 30 g, 0.12 mole (65%, lit.[9] 45%) and two recrystallizations from acetic acid gave 21 g

(45%) of golden-yellow II, mp 167-169°, lit.[8] 169°.

IR spectrum (KBr) 2300, 1650, 1565, 1450, 1370, 1300, 1270, 1160, 845, 765, 755, 708 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 258 (M^+, 100) 230 (33), 228 (28), 202 (48), 200 (28), and 101 (26); pmr spectrum ($DCCl_3$, 100 MHz), δ 9.65 (d, 1, Ar-H), 8.35-8.0 (m, 4, Ar-H), 7.9-7.45 (m, 5- Ar-H).

Reduction of II to Benz[*a*]anthracene (III).[10]— A 40 g (0.16 mole) solution of III in 200 ml of dry cyclohexanol was added to aluminum tricyclohexoxide (prepared from 20 g of aluminum turnings and 400 ml of dry cyclohexanol).[10] The reaction mixture was again refluxed for another 48 hr under nitrogen. The contents of the flask were cooled, poured into cold water, acidified with 10% hydrochloric acid, stirred for 2 hr and then extracted twice with 250-ml portions of benzene. Benzene and cyclohexanol were removed from the combined extracts by steam distillation. The yellow pasty mass was recrystallized three times from ethanol-acetic acid mixture to yield 28 g (0.12 mole, 80%) of pale yellow crystals of benz[*a*]anthracene (III), mp 153-155°. To a clear solution of picric acid (98 g) in ethanol was added 65 g (0.29 mole) of crude III by extraction through a Soxhlet apparatus. The red picrate (120 g, 0.26 mole, 90%) was recrystallized twice from ethanol to give 108 g (0.24 mole, 83%), mp 140-142°, lit.[11a,b] 141.5-142.5°.

The picrate was then decomposed by extracting it in a Soxhlet apparatus through basic alumina (300 g) using 1.5 ℓ of petroleum ether (bp 60-68°) as the solvent.[12] An inert atmosphere (Co_2 or N_2) was maintained throughout the extraction which lasted for 48 hr. On cooling the extract, colorless plates of III, mp 158-159°, were obtained. These were recrystallized from toluene, distilled in a Kugelrohr apparatus and then zone-refined to give III, mp 158.5-159.5°, lit.[13] 159.5-160.5° (corr).

IR spectrum (KBr), 2300, 950, 895, 880, 820, 780, 745, 685 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 228 (M^+ 100), 227 (6), 226 (20), 114 (115), 113 (3), and 100 (10); pmr spectrum ($CDCl_3$, 100 MHz) δ 9.15 (5, 1, ArH), 8.88 (m, 1, ArH). 8.3 (5, 1, ArH), 7.9-7.4 (m, 9. ArH).

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