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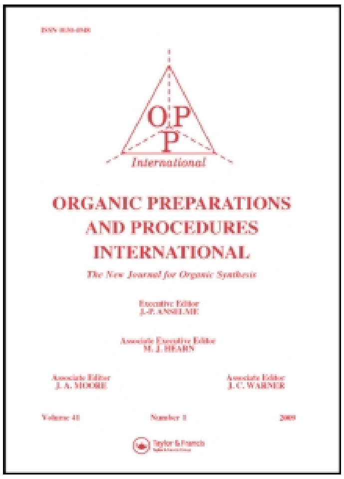

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THE SYNTHESIS OF 1,2,3,7,8,9-HEXAHYDRODIBENZO[*def, mno*]CHRYSENE AND THE USE OF HYDRIODIC ACID-RED PHOSPHORUS IN THE DEOXYGENATION OF KETONES

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ORGANIC PREPARATIONS AND PROCEDURES INT. 8(3), 133-140 (1976)

THE SYNTHESIS OF 1,2,3,7,8,9-HEXAHYDRODIBENZO[*def*,*mno*]CHRYSENE AND THE USE OF HYDRIODIC ACID-RED PHOSPHORUS IN THE DEOXYGENATION OF KETONES

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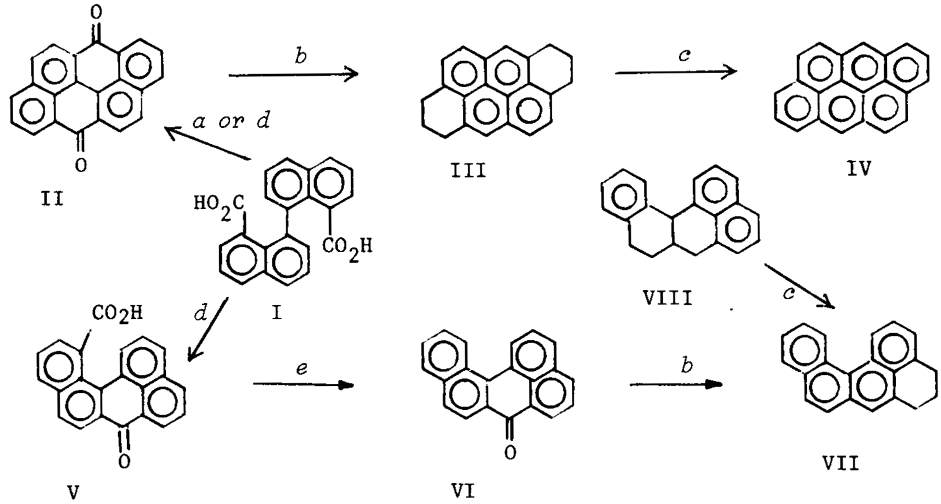
In this paper we describe the synthesis of 1,2,3,7,8,9-hexahydrodibenzo[*def*,*mno*]chrysene (III), a new hydrocarbon. We also report that the hydriodic acid-red phosphorus (HI-P_4) reduction method,[2] which was used in synthesizing III, appears to be the most practical method for deoxygenation of some benzylic ketones.

Hydrocarbon III was isolated during the synthesis of anthanthrene[3] (IV) as shown in Scheme 1. Reduction of anthanthrone (II)[4] with HI-P_4

SCHEME I



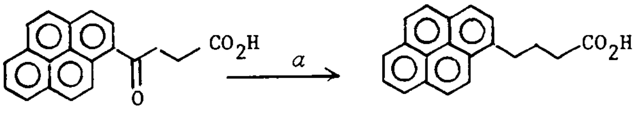
[a] PPA, Δ. [b] HI, P_4, CH_3CO_2H, Δ. [c] Pd/C, Δ. [d] $ZnCl_2$, CH_3CO_2H, Δ.
[e] Cu, quinoline, Δ.

gave III. This structure was determined by comparison of its uv spectrum with that of pyrene. Bathochromic shifts of the absorption maxima were noted, but otherwise the spectra were in good agreement.

Ketone VI is readily reduced to hydrocarbon VII by HI-P_4.[5] This hydrocarbon was prepared to verify the structure of an aromatized product obtained by treating 7a,8,9,13b-tetrahydro-7H-dibenz[*a,kl*]anthracene (VIII)[6] with Pd/C.

The deoxygenation of keto acid IX to X with HI-P_4 is shown in Scheme II. Attempts to prepare X, a crucial intermediate in the synthesis of benzo[*a*]pyrene, by other deoxygenation methods (Wolff-Kishner and Pd/C hydrogenolysis) afforded little product and caused some side-chain cleavage.

SCHEME II

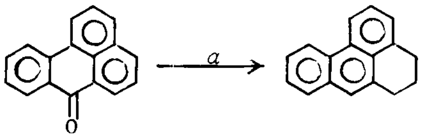


IX X

[a] HI, P_4, CH_3CO_2H, Δ.

Another example of the utility of HI-P_4 is the reduction of benzanthrone (XI)[7] to XII[8a] in 74% yield. Attempts to reduce XI using the Wolff-Kishner method or its modifications, Raney nickel-catalyzed hydrogenation, the Clemmensen procedure, or zinc dust distillation, were reported to be unsatisfactory.[9a] We also found that aluminum chloride-lithium aluminum hydride reduction was ineffective.[9b]

SCHEME III



XI XII

[a] HI, P_4, CH_3CO_2H, Δ.

SYNTHESIS OF 1,2,3,7,8,9-HEXAHYDRODIBENZO[def,mno] CHRYSENE

EXPERIMENTAL[10]

Dibenzo[*def,mno*]chrysene-6,12-dione (II).— A commercial sample (20 g, 0.059 mole) of 1,1'-binaphthyl-8,8'-dicarboxylic acid (I) was added during a 50-min period to 115% polyphosphoric acid (100 ml) which was maintained at 85-95°. The mixture was then heated at 110° for 1.5 hr. The dark, mushy solution was then poured over 750 g of water-ice. A finely dispersed red solid was precipitated which was separated by centrifugation. The resulting solid was stirred with sodium carbonate solution (200 ml saturated sodium carbonate solution diluted with 200 ml of water) and was again separated by centrifugation. Acidification of a portion of the wash yielded no unreacted acid. The red solid was stirred with water (500 ml), centrifuged, stirred with methanol (300 ml), and centrifuged again. Vacuum drying gave 16.3 g (0.053 mole, 90%) of reddish brown II,[4] mp 393-396°, which was used in the reduction procedure. For analysis, a sample of this solid was continuously extracted through neutral alumina (2.5-cm x 2.5-cm column) with benzene eluant and was then sublimed at 250° (0.05 mm) to yield bright orange crystals of II, mp 404-6°, lit.[11] 340°.

Mass spectrum (70 eV) *m/e* (rel intensity) 306, (M^{+}, 100), 278 (8), 250 (9), 248 (8), 125 (8), and 124 (5).

Insolubility of this compound in readily available solvents precluded obtaining pmr data.

1,2,3,7,8,9-Hexahydrodibenzo[*def,mno*]chrysene (III).— A sample of II (9.5 g, 0.031 mole), red phosphorus (8.6 g), 57% hydriodic acid (35 ml) and glacial acetic acid (350 ml) were heated at reflux for 235 hr. The cooled reaction mixture was poured into water (500 ml) and filtered. The collected solid was washed with water (500 ml) and a small amount of 95% ethanol (25 ml). This solid was pumped to dryness, placed in a continuous extractor[12] over Dicalite,[13a] and eluted with ether to give 6.3 g

(0.024 mole, 72%) of yellow-green solid melting at about 200°. Sublimation at 200° (0.07 mm) and recrystallization from methylene chloride gave yellow needles of III, mp 231-233°.

Mass spectrum (70 eV) *m/e* (rel intensity) 282 (M^+, 100), 281 (18), 277 (11), 276 (33), 253 (7), and 126 (12); pmr ($CDCl_3$) δ 8.03-7.85 (m, 2, ArH), 7.81-7.64 (m, 4, ArH), 3.47-3.16 (m, 8, $ArCH_2$) and 2.20 (pentet, 4, $ArCH_2\underline{CH_2}$, J=6 cps); uv max (95% ethanol) 205 nm (log ε 4.60), 213 (4.27), 230 (4.21), 237 (4.58), 247 (4.86), 258 (4.13), 269 (4.43), 280 (4.74), 304 (3.60), 317 (4.00), 332 (4.43), 344 (4.42), 349 (4.61), 364 (3.77), 377 (3.12) and 384 (3.77).

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.49; H, 6.46.

Dibenzo[*def*,*mno*]chrysene (IV).— Catalyst (10% Pd/C,[13b] 0.1 g) and a sample of III (1.0 g) were heated for one hr at 290-300°. Product was separated from catalyst by continuous extraction[12] of the solid mixture with methylene chloride. The solution was evaporated to dryness and the resultant solid was extracted[12] through a 1/2" x 1/2" column of neutral alumina using toluene. Crystallization from this solvent gave amber plates of IV (1.0 g, 100%), mp 263.5-265.5, lit.[14] 261°.

Mass spectrum (70 eV) *m/e* (rel intensity) 276 (M^+, 100), 277 (24), 138 (18), 274 (16), 137 (13), 275 (8), 136.5 (6), 136 (5), 138.5 (4), and 272 (3); uv max (95% ethanol) 209 nm (log ε 4.79), 213 (4.78), 232 (5.16), 242 (s, 4.79), 247 (s, 4.70), 255 (4.71), 259 (4.79), 271 (3.91), 282 (4.31), 294 (4.80), 307 (5.16), 320 (s, 4.05), 363 (3.71), 380 (4.29), 384 (4.29), 396 (s, 4.44), 401 (4.69), 406 (4.71), 421 (4.78), and 430 (5.04).

The compound was not sufficiently soluble in available solvents to obtain pmr data.

7-Oxo-7H-dibenz[*a*,*kl*]anthracene-13-carboxylic acid (V).— Zinc chloride (90 g, 0.82 mole) and a sample of I (50.4 g, 0.147 mole) were heated in refluxing acetic acid (1350 ml) for 5 hr.[5] The cooled solution was filtered to separate a red solid which was then washed with saturated sodium carbonate solution (400 ml) and water (200 ml). The dry, dark red solid (6.0 g, 0.019 mole, 13%) melted at 395° and 396° when mixed with a sample of II prepared by polyphosphoric acid cyclization.

Filtrate and washes were combined and this mixture was diluted with water to a volume of 3.5 ℓ. Filtration gave a solid which was then washed with hot water (1 ℓ). A crude, dried sample of V (38.3 g, 0.118 mole, 81%) was isolated. A sample of this solid (5 g) was eluted through Dicalite[13a] with benzene and then crystallized from this solvent to yield 3.7 g of V, mp 286-288°, lit.[5] 278°.

Mass spectrum (70 eV) *m/e* (rel intensity) 324 (M^+, 10), 306 (31), 280 (100), 278 (25), 252 (33), and 250 (31).

A pmr analysis was attempted, but a suitable solvent was not found. The keto acid V is very insoluble in common solvents at room temperature.

7-Oxo-7H-dibenz[*a*,*kl*]anthracene (VI).— A suspension of crude V (33.3 g, 0.12 mole) and copper powder (17.0 g) in quinoline (200 ml) was heated at reflux for 10 hr.[5] Dilution (1.8 ℓ of H_2O) and filtration of the cooled reaction mixture separated a green solid. This solid was extracted with boiling benzene (3 x 600 ml). The hot benzene washes were filtered through Dicalite[13a] to remove residual copper. The benzene was reduced in volume to ∿100 ml. A dark yellow solid separated. This solid was continuously extracted[12] through Dicalite[13a] with isohexane[15] to give 22.4 g (0.08 mole, 78%) of yellow crystals of VI, mp 185-187°. Sublimation gave yellow needles of VI, mp 186-187.5°, lit.[5] 185°.

Mass spectrum (70 eV) *m/e* (rel intensity) 280 (M^+, 100), 252 (34), 251 (10), 250 (25), 126 (13), and 125 (6); pmr ($CDCl_3$) δ 8.87-8.43 (m, 4, ArH) and 8.36-7.55 (m, 8, ArH).

5,6-Dihydro-4H-dibenz[*a*,*kl*]anthracene (VII).[8b]— Acetic acid (200 ml), hydriodic acid (20 ml), red phosphorus (5 g), and VI (5 g, 0.017 mole) were heated at reflux under a nitrogen atmosphere for 214 hr.[5] A procedure similar to that described for the separation of III was used to isolate 5.9 g of brown oil which showed a 72% yield of VII by glc.[16] This oil was eluted with isohexane[15] through a 2.5-cm x 17-cm column of neutral alumina to give colorless crystals of VII (2.6 g, 0.009 mole, 55%), mp 134-137°. For analysis, further purification was done by sublimation at 125° (0.1 mm) to give VII, mp 138-140°, lit.[5] 139°.

Mass spectrum (70 eV) *m/e* (rel intensity) 268 (M^+, 100), 267 (21), 266 (13), 265 (18), 253 (11), and 252 (18); pmr ($CDCl_3$) δ 9.18-8.79 (m, 2, ArH at C-1 and C-13), 8.01-7.10 (m, 8, ArH), 3.15 (t, 4, $ArCH_2$, J=6 cps) and 2.07 (q, 2, $ArCH_2\underline{CH_2}$, J=6 cps); uv max (95% ethanol) 200 nm (log ε 4.56), 221 (4.60), 232 (4.38), 248 (4.00), 259 (4.16), 269 (4.47), 277 (4.76), 287 (4.92), 298 (4.20), 308 (4.05), 321 (4.05) and 334 (3.83).

5,6-Dihydro-4H-dibenz[*a,kl*]anthracene (VII) from VIII.[6,8b]— Catalyst (0.2 g of 10% Pd/C)[13b] and VIII (2.0 g, 0.007 mole) were added to a 100-ml round-bottom flask, flushed with nitrogen, and then heated in a molten salt bath at 290-300° C for 45 min. After cooling, the residue was dissolved in benzene (75 ml), filtered to remove catalyst, and rotary-evaporated to give 1.9 g of yellow solid. This solid was passed through a 1.4-cm x 5-cm column of neutral alumina with petroleum ether eluant[15] in a continuous-extraction, glass-fritted apparatus[12] to give 1.8 g (0.0067 mole, 91%) of VII as colorless crystals, mp 138-140°. The mp of a mixture of VII from this source and from VI showed no depression. Instrumental data for samples from both sources were identical.

4-(3-Pyrenyl)butanoic Acid (X).— A sample of IX (25.0 g, 0.09 mole), red phosphorus (11.0 g), and 57% hydriodic acid (20 ml) were heated under nitrogen atmosphere with refluxing acetic acid (400 ml) for 96 hr. The warm reaction mixture was filtered and was then diluted with water (1.5 ℓ), whereupon a precipitate separated. This solid was collected and was then washed with water (5 x 200 ml), dissolved in saturated sodium bicarbonate solution (200 ml), filtered, and reprecipitated by acidification with 10% hydrochloric acid. Recrystallization from toluene-isohexane[15] gave 17.0 g (0.065 mole, 72%) of colorless plates of X, mp 187-188°, lit.[17] 187-188°.

IR (KBr) cm^{-1} 3010, 2940, 1690, 1460, 1430, 1335, 1320, 1275, 1210, 910, 820, 755, 725, and 710; mass spectrum (70 eV) *m/e* (rel intensity) 288 (M^+, 30), 228 (16), 227 (17), 216 (20), 215 (100), and 213 (23); pmr

(DMSO-d_6) δ 8.49-7.94 (m, 9, ArH), 3.38 (t, 2, ArCH_2, J=7 Hz), 2.44 (t, 2, $C\underline{H}_2CO_2H$, J=7 Hz), and 2.05 (pentet, 2, $ArCH_2C\underline{H}_2$, J=7 Hz).

5,6-Dihydro-4H-benz[*de*]anthracene (XII).——A sample (23 g, 0.10 mole) of benzanthrone (XI), red phosphorus (12 g), and 57% hydriodic acid (50 ml) were mixed and were then heated for 96 hr in refluxing glacial acetic acid (450 ml).[7] A procedure similar to that described for III was used to isolate a crude oil which was distilled (Kugelrohr) at 145-155° (0.1 mm) to give 20.9 g of yellow solid. A pot residue of 1.7 g remained. The distillate was eluted with isohexane[15] through a 2.5-cm x 7-cm column of basic alumina using a continuous Soxhlet extractor.[12] Crystallization from this solvent gave colorless XII (16.2 g, 0.074 mole, 74%), mp 84-86°. A second recrystallization from isohexane[15] improved the melting point to 85.5-87°, lit.[7] 81-82°.

Mass spectrum (70 eV) *m/e* (rel intensity) 218 (M^+, 100), 217 (34), 216 (10), 215 (24), 203 (22), and 202 (25); pmr ($CDCl_3$) δ 8.66-8.38 (m, 2, ArH), 7.83-7.21 (m, 6, ArH), 3.06 (t, 4, ArCH_2, J=6 cps) and 2.00 (pentet, 2, $ArCH_2C\underline{H}_2$, J=6 cps); uv max (95% ethanol) 214 nm (log ε 4.50), 225 (4.22), 251 (4.68), 258 (4.76), 271 (4.15), 279 (4.08), 295 (4.05) *and* 302 (4.12).

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   c) Undergraduate Research Assistant, 1974.

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