mixture was added dropwise and with stirring, 0.6 mole of thionyl chloride. After the addition was complete, the mixture was gradually heated to 100°, in *ca.* 2 hr., and maintained at this temperature for an additional 4 hr. The amber colored mixture was fractionally distilled, yielding 41.2 g. (46.8%) of product at 87–89° (12 mm.), $n^{25}_D$ 1.4539.

*Anal.* Calcd. for $C_7H_9ClO_3$: C, 47.60; H, 5.14; Cl, 20.08. Found: C, 47.69; H, 5.30; Cl, 20.23.

*i-Propyl cyanomethyl fumarate.* This compound was prepared by essentially the method of Mowry.[2a] A mixture of 13.9 g. (0.17 mole as a 37% aqueous solution) of formaldehyde, 8.4 g. (0.17 mole) of sodium cyanide, and 100 ml. of water was cooled to 5–10°. *i*-Propyl fumaryl chloride, 26.5 g. (0.15 mole) was added dropwise and the mixture was allowed to stir overnight. The solution was extracted with ether and the combined ether extracts were washed with dilute sodium carbonate, dilute hydrochloric acid, and finally with water. After drying over Drierite, the material was distilled through a 15-cm. Vigreux column. The bulk of the distillate, 9.4 g., b.p. 112–113° (1.1 mm.), $n^{25}_D$ 1.4534, represented a 31.7% yield of the desired product.

*Anal.* Calcd. for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10. Found: C, 54.80; H, 5.75; N, 6.82.

However, in the forerun, there was obtained 1.3 g. of material of b.p. 40° (0.2 mm.), $n^{25}_D$ 1.4364.

*Anal.* Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.65; H, 7.15; N, 0.26.

*Methyl i-propyl fumarate.* A mixture of 6 g. (0.18 mole) of methanol and 50 ml. of pyridine was cooled to 0°, 12.4 g. (0.07 mole) of *i*-propyl fumaryl chloride was added dropwise and the mixture was allowed to stir overnight. The solution was poured into ice water with stirring. The aqueous solution was extracted with ether and the combined ether extracts were washed with dilute hydrochloric acid and water. The material was fractionally distilled and 7.0 g. (63.4%) of product at 98° (10 mm.), $n^{25}_D$ 1.4354 was obtained.

*Anal.* Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.91; H, 7.12.

The infrared spectra of this material and the above-mentioned forerun were identical.

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## New Synthesis of Dibenzo[a,i]pyrene[1]

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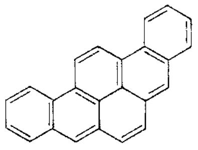
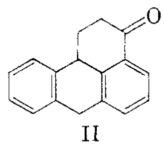
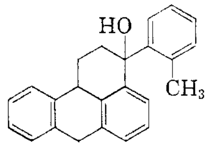
Recently Buu-Hoï and Lavit reported a five-step synthesis of dibenzo[a,i]pyrene (I) from benzo[a]pyrene in approximately 1% over-all yield.[2] Previously, the synthesis of I has been reported by several workers by the reduction of dibenzo[a,i]pyrene-5,8-quinone.[3–5]

A new synthesis of I has been accomplished in 7% over-all yield in this laboratory *via* 3-keto-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (II), an intermediate readily available from previously reported research.[6,7] The ketone II was treated with *o*-tolylmagnesium bromide and the resulting carbinol, III, was dehydrated with Lucas reagent and chromatographed on alumina. The red, oily 3-(*o*-tolyl)-1,11b-dihydro-7H-*meso*-benzanthracene (IV) (or isomers thereof) thus obtained was cyclodehydrogenated with palladium on charcoal to dibenzo[a,i]pyrene (I).

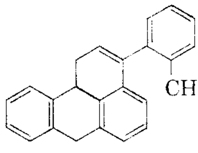

I



II



III



IV

### EXPERIMENTAL

*3-Hydroxy-3-(o-tolyl)-1,2,3,11b-tetrahydro-7H-meso-benzanthracene* (III). A solution of 4.68 g. (0.02 mole) of 3-keto-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (II) in 75 ml. of dry benzene was added dropwise over a period of 30 min. to a stirred ether solution of *o*-tolylmagnesium bromide prepared from 4.28 g. (0.025 mole) of *o*-bromotoluene. After refluxing for 1 hr. the reaction mixture was hydrolyzed with 50 ml. of 10% hydrochloric acid. The organic layer was washed with water and dried over anhydrous sodium sulfate. Removal of the solvent left 3-hydroxy-3-(*o*-tolyl)-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (III) as a viscous brown oil which failed to crystallize.

*3-(o-Tolyl)-1,11b-dihydro-7H-meso-benzanthracene* (IV). The crude carbinol, III, was dissolved in anhydrous benzene and refluxed for 90 min. with 30 ml. of Lucas reagent. The organic layer was washed with water and saturated sodium carbonate solution, dried over anhydrous sodium sulfate, and chromatographed on alumina. Removal of the solvent yielded 5.2 g. of the hydrocarbon IV as a light red oil.

*Dibenzo[a,i]pyrene* (I). The hydrocarbon IV was cyclodehydrogenated by heating with 0.78 g. of 10% palladium on charcoal at 320–400° for 30 min. The crude hydrocarbon was sublimed from the reaction mixture at 275° and 0.05 mm. A toluene solution of the sublimate was chromatographed on alumina and concentration of the eluants yielded 0.42 g. (7% over-all yield from II) of dibenzo[a,i]pyrene (I) as small yellow plates, m.p. 281.5–282.5° uncorr.

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