

**575.** *A Convenient Synthesis of Dibenz[*a,c*]anthracene and Tribenz[*a,c,h*]anthracene.*

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DIBENZ[*a,c*]ANTHRACENE (I) and TRIBENZ[*a,c,h*]ANTHRACENE (III) are hydrocarbons of low carcinogenic potency;<sup>1</sup> the former, however, has recently acquired biological interest because of its ready fixation on skin proteins.<sup>2</sup> The procedure generally used for their preparation, *i.e.*, Elbs reaction with 9-*o*-toluoyl- and 9-(2-methyl-1-naphthoyl)-phenanthrene,<sup>3</sup> requires the synthesis of phenanthrene derivatives substituted in position 9.

An easier route has now been found, making use of 1,2,3,4-tetrahydrophenanthrene

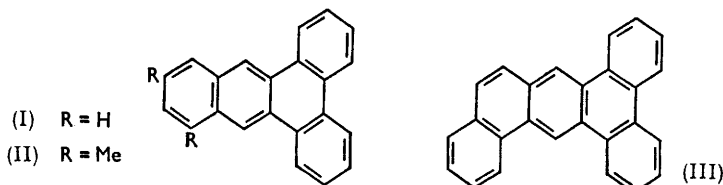
<sup>1</sup> Cook, Hieger, Kennaway, and Mayneord, *Proc. Roy. Soc.*, 1932, *B*, **111**, 455.

<sup>2</sup> Heidelberger *et al.*, *Cancer Res.*, 1951, **11**, 885; 1956, **16**, 442; *J. Amer. Chem. Soc.*, 1955, **77**, 2877; 1956, **78**, 3671.

<sup>3</sup> Bachmann, *J. Amer. Chem. Soc.*, 1934, **56**, 1363; Clar, *Ber.*, 1929, **62**, 350, 1574; Fieser and Dietz, *Ber.*, 1929, **62**, 1827.

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which is known to undergo Friedel-Crafts acylation in the 9-position. 1,2,3,4-Tetrahydro-9-*o*-toluoylphenanthrene underwent Elbs cyclodehydration with partial dehydrogenation, the product being converted into the hydrocarbon (I) by selenium. A similar



reaction sequence was followed with 1,2,3,4-tetrahydro-9-(2,4,5-trimethylbenzoyl)phenanthrene, to furnish 10,12-dimethyldibenz[a,c]anthracene (II). Tribenz[a,c,h]anthracene was prepared in the same way, starting from 2-methyl-1-naphthoyl chloride.

*Experimental.*—1,2,3,4-Tetrahydrophenanthrene, b. p. 167°, m. p. 38°, was readily prepared by Wolff-Kishner reduction of the mixture of 1,2,3,4-tetrahydro-1- and -4-oxophenanthrene obtained by cyclisation of  $\gamma$ -1- and  $\gamma$ -2-naphthylbutyric acid (the mixture of these two acids resulting from reduction of the crude succinylation product of naphthalene). It has since become available commercially. With tetrachlorophthalic anhydride, it formed a pale yellow molecular complex (1 : 1), crystallising from acetic acid as pale yellow needles, m. p. 154°. A similar complex obtained with tetrabromophthalic anhydride formed canary-yellow needles, m. p. 161° (decomp. >140°).

*1,2,3,4-Tetrahydro-9-*o*-toluoylphenanthrene.* To a solution of 1,2,3,4-tetrahydrophenanthrene (15 g.) and *o*-toluoyl chloride (15 g.) in carbon disulphide (150 c.c.), aluminium chloride (16 g.) was added in small portions with stirring, and the mixture left for 15 hr. at room temperature. After decomposition with ice, the organic layer was washed with aqueous sodium hydroxide, then with water, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated and the residue was fractionated *in vacuo*, giving the *ketone* (13 g.), b. p. 277°/15 mm., prisms, m. p. 91° (from hexane) (Found: C, 87.7; H, 6.7. C<sub>22</sub>H<sub>20</sub>O requires C, 88.0; H, 6.7%).

*Dibenz[a,c]anthracene (I).* The foregoing *ketone* was gently refluxed until steam ceased to be evolved, and the residue was distilled *in vacuo*, giving a resin, which was heated for 3 hr. at 320–350° with its own weight of selenium. The product was then taken up in benzene, the benzene solution filtered, and the residue obtained on evaporation was recrystallised from acetic acid, giving needles (10%), m. p. 205° (picrate, m. p. 207°) (lit.,<sup>4</sup> hydrocarbon m. p. 205°, picrate m. p. 208°).

*1,2,3,4-Tetrahydro-9-(2,4,5-trimethylbenzoyl)phenanthrene.* Prepared as above from 2,4,5-trimethylbenzoyl chloride (5 g.), 1,2,3,4-tetrahydrophenanthrene (4.5 g.), and aluminium chloride (5 g.) in methylene chloride (200 c.c.), this *ketone* (4 g.), b. p. 295°/20 mm., formed needles, m. p. 63°, from acetic acid (Found: C, 87.5; H, 7.5. C<sub>24</sub>H<sub>24</sub>O requires C, 87.8; H, 7.4%).

*10,12-Dimethyldibenz[a,c]anthracene (II).* The foregoing *ketone* (3 g.) was pyrolysed as above, giving a resin which was heated with selenium (2 g.) at 300–320° for 4 hr.; the product formed needles (0.2 g.), m. p. 211°, from cyclohexane (Found: C, 94.0; H, 6.0. C<sub>24</sub>H<sub>18</sub> requires C, 94.1; H, 5.9%), and gave a *picrate*, brick red prisms (from cyclohexane), m. p. 228° (Found: N, 8.1. C<sub>30</sub>H<sub>21</sub>N<sub>3</sub>O<sub>7</sub> requires N, 8.1%).

*Tribenz[a,c,h]anthracene (III).* 2-Methyl-1-naphthoyl chloride (7.5 g.) was condensed with 1,2,3,4-tetrahydrophenanthrene (6 g.) by means of aluminium chloride (7 g.) in carbon disulphide (250 c.c.), to give a solid crude *ketone* (3 g.) that was pyrolysed to an orange-red resin; this resin was treated with selenium in the usual way. The product crystallised from benzene as colourless needles (0.3 g.), m. p. 225° (lit.,<sup>5</sup> m. p. 225–228°).

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<sup>4</sup> Cf. Buu-Hoï, Lavit, and Lamy, *J.*, 1959, 1845; see also Clar, *Ber.*, 1929, **62**, 350, 1574.

<sup>5</sup> Bachmann and Pence, *J. Amer. Chem. Soc.*, 1937, **59**, 2339; Fieser and Dietz, *Ber.*, 1929, **62**, 1827.