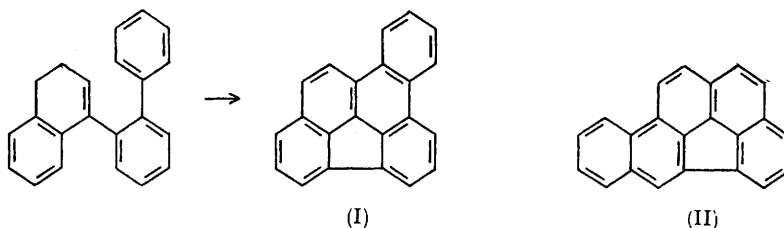


### 339. *The Cyclodehydrogenation of *o*-Terphenyl and 1-2'-Biphenyl-3,4-dihydronaphthalene.*

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Catalytic cyclodehydrogenation of *o*-terphenyl has been shown to give triphenylene in high yield. Under the same conditions, 1-2'-biphenyl-3,4-dihydronaphthalene did not give the expected 1,2-benzochrysene, but two compounds believed to be 1-2'-biphenylnaphthalene and dibenzo[*b,mno*]-fluoranthene. A synthesis of 7-phenylfluoranthene is also described.

THE various previous syntheses of triphenylene give low yields. Allen and Pingert,<sup>1</sup> however, obtained triphenylene (20%) and *p*-terphenyl (7.5%) by the action of a mixture of sodium and aluminium chlorides on *o*-terphenyl at 200°. This ring closure between the two *o*-positions in the terminal phenyl groups is a frequent side-reaction in the chemistry of *o*-terphenyl and is accomplished by most dehydrogenating and condensing agents although the yield of triphenylene is usually low. It has now been found that the passage of a decalin solution of *o*-terphenyl over palladium-platinum-charcoal at 490° gives a much improved overall yield (63%) of triphenylene uncontaminated with *p*-terphenyl. The decalin probably helps to prevent carbonisation by reducing the contact time, and the resulting naphthalene is readily removed from the product by steam-distillation.



In an endeavour to shorten the Bradsher-Rapoport synthesis<sup>2</sup> of 1,2-benzochrysene starting from 1-2'-biphenyl-3,4-dihydronaphthalene, the latter compound was treated in the same way as *o*-terphenyl. After removal of the naphthalene, two substances were isolated. The first, although having almost the same melting point as 1,2-benzochrysene, considerably depressed the melting point of an authentic specimen.<sup>3</sup> Elementary analysis and infrared examination showed the presence of a phenyl group and the absence of aliphatic CH groups, suggesting that the substance is 1-2'-biphenylnaphthalene formed by a normal dehydrogenation. It had been thought that the higher-melting substance

<sup>1</sup> Allen and Pingert, *J. Amer. Chem. Soc.*, 1942, **64**, 1365.

<sup>2</sup> Bradsher and Rapoport, *J. Amer. Chem. Soc.*, 1943, **65**, 1646.

<sup>3</sup> Bergmann and Szmuskovicz, *J. Amer. Chem. Soc.*, 1947, **69**, 1367.

might be 7-phenylfluoranthene, since fluoranthene itself has been obtained by cyclodehydrogenation of 1-phenylnaphthalene.<sup>4</sup> That this was not so was established by comparison with a synthetic specimen and by elementary analysis and infrared examination which showed the absence of phenyl groups and aliphatic CH groups. The last finding suggests that the substance is dibenzo[*b,mno*]fluoranthene (I) formed by loss of hydrogen as shown.

An isomer of the above substance, namely, dibenzo[*k,mno*]fluoranthene (II), and the parent substance, benzo[*mno*]fluoranthene, have been reported by Campbell and Reid.<sup>5</sup>

#### EXPERIMENTAL

Light petroleum refers to material b. p. 60—80°.

*o*-Terphenyl.—A commercial sample, m. p. 55°, crystallised from methanol, gave material of m. p. 57° (Allen and Pingert<sup>1</sup> give m. p. 58°).

1-2'-Biphenyl-3,4-dihydronaphthalene.—Reaction between 1-tetralone and the aryl-lithium compound prepared from lithium and 2-iodobiphenyl gave the required compound, m. p. 75—76°, in 45% yield.<sup>2</sup>

Cyclodehydrogenation of *o*-Terphenyl.—The apparatus is described elsewhere.<sup>6</sup> In a typical experiment, a solution of *o*-terphenyl (4.5 g.) in purified decalin was passed over palladium-platinum-charcoal<sup>7</sup> at 490° together with hydrogen (7—8 l./hr.) during 3 hr. The product, after removal of naphthalene in steam, crystallised from light petroleum to give triphenylene (2.67 g.) as needles, m. p. 198°, mixed m. p. 198—199°. Chromatography of the liquors on activated alumina (P. Spence, Type "H," 100—200 mesh) gave unchanged *o*-terphenyl (1.04 g.) and triphenylene (0.16 g.) on elution with light petroleum and benzene, respectively. The yield, 82.5% at a conversion of 77%, is the highest recorded for a synthesis of triphenylene.

Cyclodehydrogenation of 1-2'-Biphenyl-3,4-dihydronaphthalene.—This compound (3.3 g.) in decalin (15 ml.) was cyclodehydrogenated in the same way as *o*-terphenyl. Chromatography of the product on alumina gave a white solid (1.35 g.), m. p. 110—111°, and a yellow solid (0.51 g.), m. p. 165—168°, on elution with light petroleum and benzene, respectively. Crystallisation of the former solid from ethanol gave 1-2'-biphenylynaphthalene as prisms (1.10 g., 34%), m. p. 115°, mixed m. p. with 1,2-benzochrysene (m. p. 116°) 92° (Found: C, 94.1; H, 5.9. C<sub>22</sub>H<sub>16</sub> requires C, 94.3; H, 5.7%). Crystallisation of the higher-melting solid from benzene-light petroleum gave dibenzo[*b,mno*]fluoranthene as pale yellow needles (0.35 g., 10.9%), m. p. 179.5° (Found: C, 95.6; H, 4.4. C<sub>22</sub>H<sub>12</sub> requires C, 95.6; H, 4.4%). The hydrocarbon gave a green colour in warm concentrated sulphuric acid. The *picrate* separated from ethanol in orange needles, m. p. 231° (Found: N, 8.0. C<sub>28</sub>H<sub>15</sub>O<sub>7</sub>N<sub>3</sub> requires N, 8.3%).

6b,7,10,10a-Tetrahydro-7-phenylfluoranthene.—According to a British patent<sup>8</sup> this compound can be prepared by the reaction between acenaphthylene and 1-phenylbuta-1,3-diene. Although the instructions were followed closely, only unchanged acenaphthylene and large amounts of polymer could be obtained. The following procedure proved to be more successful.

A solution of 1-phenylbuta-1,3-diene<sup>9</sup> (26 g.), acenaphthylene (30.4 g.), and diphenylamine (0.5 g.) in purified xylene (100 ml.) was refluxed for 15 hr. The solution was then washed with 10% hydrochloric acid, dried (MgSO<sub>4</sub>), and distilled at 1 mm. to give unchanged acenaphthylene (12 g.) at 100°, and an oil (20.7 g.) at 190—200°. The latter fraction partly solidified. Crystallisation from ethanol-benzene gave colourless needles (6.9 g., 20%) of the required product, m. p. 155°.

7-Phenylfluoranthene.—A slow stream of carbon dioxide was passed through a boiling mixture of 6b,7,10,10a-tetrahydro-7-phenylfluoranthene (2 g.), 10% palladium-charcoal (1 g.), and *p*-cymene (30 ml.) for 3 days. The catalyst was then removed by filtration and the solvent by distillation. Chromatography of the resulting yellow fluorescent oil on activated alumina gave

<sup>4</sup> Orchin and Reggel, *J. Amer. Chem. Soc.*, 1947, **69**, 505.

<sup>5</sup> Campbell and Reid, *J.*, 1952, 3281.

<sup>6</sup> Copeland, Dean, and McNeil, following paper.

<sup>7</sup> Baker, Warburton, and Breddy, *J.*, 1953, 4149.

<sup>8</sup> B.P. 646,214.

<sup>9</sup> Grummitt and Becker, *Org. Synth.*, 1950, **30**, 75.

7-phenylfluoranthene (1.70 g., 86%) as colourless prisms (from light petroleum), m. p. 73° (Found: C, 94.9; H, 5.1.  $C_{22}H_{14}$  requires C, 94.9; H, 5.1%). The *picrate* crystallised in yellow needles (from ethanol), m. p. 145° (Found: N, 8.45.  $C_{28}H_{17}O_7N_3$  requires N, 8.3%).

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