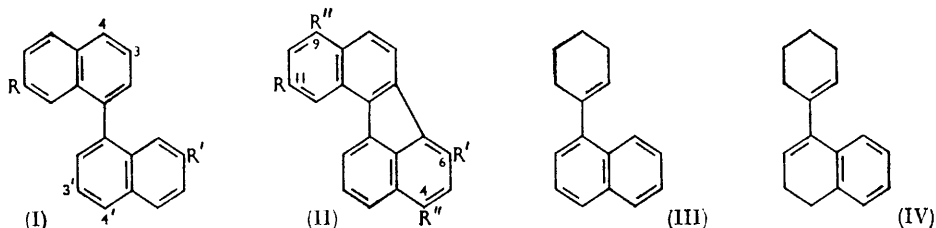


**448.** *A Synthesis of Benzo[j]fluoranthene and its Derivatives, using Palladium-Sulphur as a Cyclodehydrogenating Agent.*

By MALCOLM CRAWFORD and V. R. SUPANEKAR.

3,3',4,4'-Tetrahydro-1,1'-binaphthyl, heated with palladium-charcoal and sulphur at 300° for five minutes, gives a 1 : 1 mixture of 1,1'-binaphthyl and benzo[j]fluoranthene (II; all R's = H). This cannot be achieved by palladium-charcoal or by sulphur separately. Substituted benzofluoranthenes and binaphthyls have also been prepared in this way.

THE effectiveness of a mixture of palladium-charcoal and sulphur as a dehydrogenating agent for polycyclic aromatic systems has been described.<sup>1,2</sup> It is now shown that cyclisation to five-membered rings can accompany the dehydrogenation. Whereas sulphur or palladium-charcoal alone converts 3,3',4,4'-tetrahydro-1,1'-binaphthyl into 1,1'-binaphthyl (I; R = R' = H) on heating at 300—310°, the two reagents employed simultaneously afford, within five minutes, both binaphthyl and benzo[j]fluoranthene (II; all R's = H) in good yield.



By suitably substituting the starting tetrahydrobinaphthyl substituted benzofluoranthenes can readily be obtained, especially with groups at positions 6 and 11, but also at 4 and 9. An unsymmetrically substituted binaphthyl derivative, produced by the mixed pinacol reduction of two different ketones, has also been used, but less successfully. The binaphthyl and benzofluoranthene are readily separated by passing their solution in light petroleum (b. p. 40—60°) through an alumina column; the binaphthyl passes through quickly, but to remove the benzofluoranthene benzene must be added to the eluting solvent. All the binaphthyls prepared were colourless and the benzofluoranthenes yellow. Their identity was checked by examining their characteristic ultraviolet absorptions (see Table).

With the unsubstituted compounds the yield of binaphthyl was 46% and of benzofluoranthene 44%. The presence of substituents affects the yield of benzofluoranthene. With 3,3',4,4'-tetrahydro-7-methoxy-1,1'-binaphthyl the yield is only 21%, and the oxygen atom is replaced by sulphur. From the 7,7'-dimethoxy-compound the yield is 4%, with a corresponding increase in the amount of binaphthyl formed; when two methoxyl groups are present the oxygen is not replaced by sulphur. Two equivalent methyl groups (7,7') are less effective (14% yield). With four methyl groups (5,5',7,7') the yield of benzofluoranthene is still 43% but less binaphthyl (28%) is formed.

The reaction is limited to compounds in which the two relevant double bonds are not part of an aromatic system. Compounds with only one separate double bond, such as 3,4-dihydro-1,1'-binaphthyl and 1-(cyclohex-1-enyl)naphthalene (III) give only biaryls on dehydrogenation. 1,1'-Binaphthyl, which has no separate double bonds, is not dehydrogenated, nor is 1-phenylnaphthalene.

Not only must there be two separate double bonds, but each must be conjugated with

<sup>1</sup> Blair, Crawford, Spence, and Supanekar, *J.*, 1960, 3313.

<sup>2</sup> Crawford and Supanekar, *J.*, 1962, 674.

## Ultraviolet absorption of benzofluoranthenes in 95% ethanol.

Unsubst.		6,11-Dimethyl		4,6,9,11-Tetramethyl		6,11-Dimethoxy	
$\lambda_{\max.}$ (m $\mu$ )	$\epsilon$	$\lambda_{\max.}$ (m $\mu$ )	$\epsilon$	$\lambda_{\max.}$ (m $\mu$ )	$\epsilon$	$\lambda_{\max.}$ (m $\mu$ )	$\epsilon$
223	49,000	226	48,200	232	42,200	—	—
240	45,000	243	47,500	246	55,200	249	44,400
279	13,200	—	—	—	—	—	—
291	19,050	294	19,100	—	—	300	24,200
307	28,200	304	20,900	—	—	313	15,400
318	31,600	317	24,200	321	34,600	333	5400
332	12,900	339	12,700	342	11,300	349	9800
347	4170	352	4600	358	4700	359	5100
365	8130	372	8400	377	10,000	389	12,400
384	12,450	390	10,600	397	13,300	405	13,700

## Ultraviolet absorption of 1,1'-binaphthyls in 95% ethanol.

Unsubst.*		7,7'-Dimethyl		5,5',7,7'-Tetramethyl		7-Methylthio		7,7'-Dimethoxy	
$\lambda_{\max.}$ (m $\mu$ )	$\epsilon$	$\lambda_{\max.}$ (m $\mu$ )	$\epsilon$	$\lambda_{\max.}$ (m $\mu$ )	$\epsilon$	$\lambda_{\max.}$ (m $\mu$ )	$\epsilon$	$\lambda_{\max.}$ (m $\mu$ )	$\epsilon$
221	92,000	225	107,600	228	100,000	222	49,800	229	89,600
283	13,300	287	12,900	292	14,400	282	9200	278	9100
293	13,000	293	12,900	297	14,500	—	—	289	9400
								319	4900
								334	6400

\* Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1951.

an aromatic ring. 1-(Cyclohex-1-enyl)-3,4-dihydronaphthalene (IV) gives only 1-phenylnaphthalene on dehydrogenation, although Orchin and Reggel<sup>3</sup> obtained fluoranthene in 5—30% yield from 1-phenylnaphthalene and 1-(cyclohex-1-enyl)naphthalene using palladium-charcoal at *ca.* 500° for several hours. Buchta and Maar<sup>4</sup> obtained dibenzo[j]fluoranthene from 1,2-diphenylacenaphthylene by dehydrogenating with palladium at 350—355° for 1 hour, extracting the product with toluene, and dehydrogenating for another 45 minutes. In this dehydrogenation, however, a six-membered ring is formed.

The respective functions of the palladium and sulphur are not clear, but a tentative explanation is that hydrogen atoms are abstracted by the palladium, leaving a diradical which cyclises. Without the sulphur the palladium would rapidly become saturated with hydrogen; the sulphur may act, possibly in free-radical fashion, to remove the hydrogen atoms from the palladium and give hydrogen sulphide. Many hydrogenations are known to be effected by hydrogen transfer, in the presence of a metal catalyst, from substances richer in hydrogen, for example, unsaturated hydrocarbons hydrogenated by cyclohexene.<sup>5</sup> The present reaction represents the converse, namely, dehydrogenation by a substance poorer in hydrogen, *i.e.*, sulphur.

## EXPERIMENTAL

All crystallisations were from light petroleum (b. p. 40—60°) unless otherwise stated.

**Dehydrogenation Procedure.**—A hard-glass test-tube containing an intimate mixture of 3,3',4,4'-tetrahydro-1,1'-binaphthyl (1 g.), sulphur (0.35 g.), and 30% palladium-charcoal (0.1 g.) was placed in a metal-bath at 300—310°. Brisk evolution of hydrogen sulphide occurred for 4 min. The tube was cooled, the contents were warmed with chloroform, and the resulting solution was filtered and evaporated to dryness. The residue was extracted by refluxing light petroleum (b. p. 40—60°), and the extract was chromatographed on alumina. Elution with light petroleum gave 1,1'-binaphthyl (0.463 g.), m. p. 156°, and benzene-light petroleum (1 : 1) gave benzo[j]fluoranthene (0.436 g.), m. p. 160°.

Dehydrogenation without sulphur or without palladium yielded no benzofluoranthene, only unchanged starting material and binaphthyl which were difficult to separate.

At 210° in the presence of both palladium and sulphur, even after 1 hr., the dehydrogenation

<sup>3</sup> Orchin and Reggel, *J. Amer. Chem. Soc.*, 1947, **69**, 505.

<sup>4</sup> Buchta and Maar, *Chem. Ber.*, 1962, **95**, 1826.

<sup>5</sup> Linstead, Braude, Mitchell, Woolridge, and Jackman, *Nature*, 1952, **169**, 100.

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was incomplete and the yield of benzofluoranthene low (14%). At 380° much gummy material was formed and the yield was 6.2% whilst that of binaphthyl was 59.2%.

*Dehydrogenation of 3,4-Dihydro-1,1'-binaphthyl.*—This substance, prepared by the method of Miller and Mann,<sup>6</sup> had m. p. 118—118.5°. Dehydrogenation at 300—310° for 4 min. gave 1,1'-binaphthyl (82%) but no benzofluoranthene.

*Dehydrogenation of 1-(Cyclohex-1-enyl)naphthalene (III).*—This hydrocarbon, prepared by the method of Klibansky and Ginsburg<sup>7</sup> but with dehydration of the intermediate tertiary alcohol by refluxing with acetic acid for 4 hr., had m. p. 47—48°. Dehydrogenation at 300—310° for 5 min., gave 1-phenylnaphthalene (~100% yield). No fluoranthene was detected.

*Dehydrogenation of 1-(Cyclohex-1-enyl)-3,4-dihydronaphthalene (IV).*—The naphthalene (IV) was prepared by pinacol reduction of a mixture of cyclohexanone and 1-tetralone. The crude product, on dehydrogenation at 300—310° for 4 min., gave an oil (73%) which had the ultra-violet spectrum of 1-phenylnaphthalene. No fluoranthene was detected.

*Dehydrogenation of 3,3',4,4'-Tetrahydro-7,7'-dimethyl-1,1'-binaphthyl.*—This diene,<sup>8</sup> dehydrogenated at 260—270° for 12 min., gave 6,11-dimethylbenzo[j]fluoranthene (II; R = R' = Me, R'' = H) (14%) fine yellow needles, m. p. 168.5° (Found: C, 94.0; H, 5.8. C<sub>22</sub>H<sub>16</sub> requires C, 94.2; H, 5.7%). When eluted from the column in the usual way this compound contained small amounts of a sulphur-containing by-product. If benzene was omitted from the eluant the by-product remained on the column but the elution required several days. The reaction also gave 7,7'-dimethyl-1,1'-binaphthyl (66%), very pale yellow crystals, m. p. 157° (Found: C, 93.2; H, 6.6. C<sub>22</sub>H<sub>18</sub> requires C, 93.6; H, 6.4%).

*Dehydrogenation of 3,3',4,4'-Tetrahydro-5,5',7,7'-tetramethyl-1,1'-binaphthyl.*—Dehydrogenation of this diene<sup>9</sup> at 300—310° for 4 min. gave 4,6,9,11-tetramethylbenzo[j]fluoranthene (II; R = R' = R'' = Me) (43%) yellow needles, m. p. 172° (Found: C, 93.1; H, 6.6. C<sub>24</sub>H<sub>20</sub> requires C, 93.5; H, 6.5%), and 5,5',7,7'-tetramethyl-1,1'-binaphthyl (28%), colourless crystals, m. p. 98° (from pentane) (Found: C, 92.9; H, 7.2. C<sub>24</sub>H<sub>22</sub> requires C, 92.9; H, 7.1%).

*Dehydrogenation of 3,3',4,4'-Tetrahydro-7-methoxy-1,1'-binaphthyl.*—The unsymmetrical binaphthyl was obtained by the pinacol reduction of a mixture of 1-tetralone (5 g.) and 7-methoxy-1-tetralone (5 g.), and separated from the symmetrical isomers on alumina, colourless crystals (1.74 g.) m. p. 109° (Found: C, 87.2; H, 6.9. C<sub>21</sub>H<sub>20</sub>O requires C, 87.5; H, 7.0%), Dehydrogenation conditions at 260° for 12 min. gave 7-methylthio-1,1'-binaphthyl (I; R = SMe, R' = H) (47%) m. p. 93—94° (Found: C, 84.0; H, 5.5. C<sub>21</sub>H<sub>16</sub>S requires C, 84.0; H, 5.4%), and a yellow substance (21%), m. p. 110—112°, which was difficult to purify and was probably a mixture of 6- and 11-methylthiobenzofluoranthenes.

*Dehydrogenation of 3,3',4,4'-Tetrahydro-7,7'-dimethoxy-1,1'-binaphthyl.*—Dehydrogenation of the dimethoxy-compound<sup>1</sup> at 300—310° for 4 min. was unsatisfactory because of decomposition. At 260° for 12 min. it gave 6,11-dimethoxybenzo[j]fluoranthene (II; R = R' = OMe, R'' = H), (4%) yellow crystals, m. p. 158.5° (Found: C, 83.9; H, 5.3. C<sub>22</sub>H<sub>16</sub>O<sub>2</sub> requires C, 84.6; H, 5.2%), and 7,7'-dimethoxy-1,1'-binaphthyl (I; R = R' = OMe) (79%), colourless prisms, m. p. 129—130° (Found: C, 83.9; H, 5.7. C<sub>22</sub>H<sub>18</sub>O<sub>2</sub> requires C, 84.0; H, 5.8%).

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<sup>6</sup> Miller and Mann, *J. Amer. Chem. Soc.*, 1951, **73**, 45.

<sup>7</sup> Klibansky and Ginsburg, *J.*, 1957, 1293.

<sup>8</sup> Newman, *J. Amer. Chem. Soc.*, 1940, **62**, 1683.

<sup>9</sup> Bell and Waring, *J.*, 1949, 2689.