

**657.** *Cyclodehydration of Arylidene- $\alpha$ -tetralones derived from Fluorene, Dibenzofuran, and Dibenzothiophen.*

By G. SAINT-RUF, NG. PH. BUU-HOÏ, and P. JACQUIGNON.

Arylidene- $\alpha$ -tetralones derived from fluorene, dibenzofuran, and dibenzothiophen undergo cyclodehydration to polycyclic compounds when treated with phosphorus pentoxide. Some similar condensed carbazoles have also been prepared.

CYCLODEHYDRATION of 2-benzylidene- $\alpha$ -tetralone to 3,4-benzofluorene under the influence of phosphorus pentoxide<sup>1</sup> has been used for the synthesis of a large number of condensed fluorene hydrocarbons.<sup>2</sup> It has now been extended to arylidene derivatives of 6,7,8,9-tetrahydro-6-oxo-11*H*-benzo[*b*]fluorene (I), a ketone readily prepared from fluorene by the succinic anhydride method.<sup>3</sup> This ketone underwent alkali-catalysed condensation with benzaldehyde and 1-naphthaldehyde, to the corresponding arylidene compounds which were cyclodehydrated in the presence of phosphoric oxide to fluoreno[3,4-*b*]fluorene (II) and benzo[*a*]fluoreno[3,2-*g*]fluorene (III). A heterocyclic analogue was prepared by indolisation of the phenylhydrazone of ketone (I) and dehydrogenation, with chloranil, to fluoreno[2,3-*c*]carbazole (IV).

Oxygen- and sulphur-containing heterocyclic analogues of the ketone (I) are accessible from dibenzofuran<sup>4</sup> and dibenzothiophen,<sup>5</sup> and the cyclodehydration of arylidene derivatives of the ketones (V) and (VI) afforded compounds (VII) and (VIII); similarly, the

<sup>1</sup> Rapson and Shuttleworth, *J.*, 1940, 536.

<sup>2</sup> Buu-Hoï and Cagniant, *Rev. sci.*, 1942, **80**, 319, 384; 1943, **81**, 30; Cagniant, *Compt. rend.*, 1948, **226**, 137; *Bull. Soc. chim. France*, 1949, 382; Buu-Hoï and Saint-Ruf, *J.*, 1957, 3806.

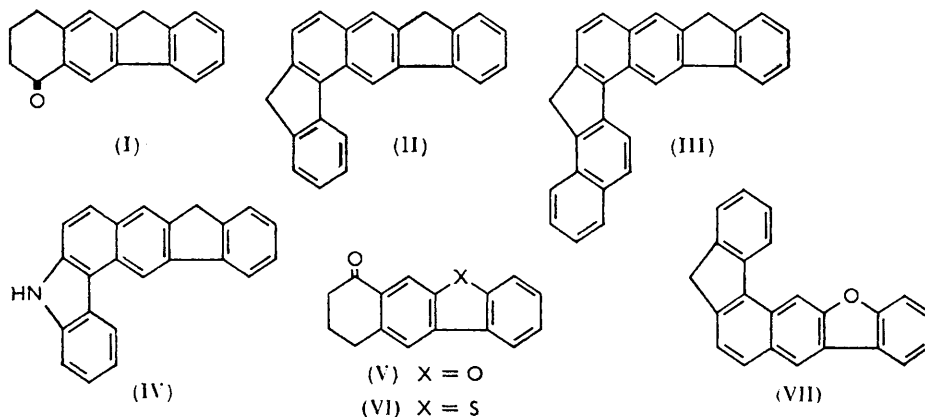
<sup>3</sup> Barnett, Goodway, and Watson, *Ber.*, 1933, **66**, 1876.

<sup>4</sup> Mosettig and Robinson, *J. Amer. Chem. Soc.*, 1935, **97**, 902.

<sup>5</sup> Gilman and Jacoby, *J. Org. Chem.*, 1938, **3**, 108; Buu-Hoï and Cagniant, *Ber.*, 1943, **76**, 1269.

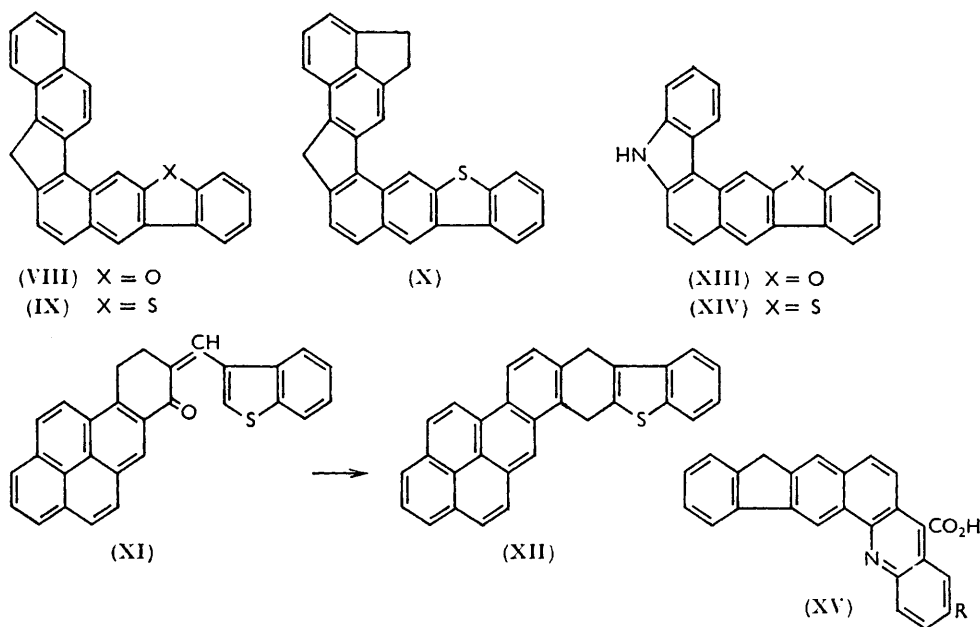
$\alpha$ -naphthylidene and the 5-acenaphthylidene derivatives of ketone (VI) could be cyclodehydrated to the polycyclic compounds (IX) and (X).

A related route to condensed thiophen derivatives is the condensation of 3-formylthionaphthen with polycyclic tetralones, and cyclodehydration of the resulting unsaturated



ketones. For instance, 3-formylthionaphthen<sup>6</sup> gave with 7,8,9,10-tetrahydro-7-oxo-benzo[*a*]pyrene the ketone (XI), which was easily cyclised to the yellow octacyclic compound (XII).

As in the case of the fluorene ketone (I), the furan and thiophen derivatives (V) and



(VI) readily gave the condensed carbazoles, (XIII) and (XIV), which gave coloured 1 : 1 molecular complexes<sup>8</sup> with tetrachloro- and tetrabromo-phthalic anhydride. Pfitzinger reaction of ketone (I) with isatin and 5-bromoisatin led to the polycyclic cinchoninic acids

<sup>6</sup> Cf. King and Nord, *J. Org. Chem.*, 1948, **13**, 635; Buu-Hoï and Hoán, *J.*, 1951, 251.

<sup>7</sup> Saint-Ruf, Buu-Hoï, and Jacquignon, *J.*, 1948, 48.

<sup>8</sup> Buu-Hoï and Jacquignon, *Compt. rend.*, 1952, **234**, 1056; *Bull. Soc. chim. France*, 1957, 488.

(XV; R = H or Br); decarboxylation of the non-halogenated compound yielded 7,8-dihydro-5*H*-fluoreno[2,3-*c*]acridine.

### EXPERIMENTAL

*Preparation of Ketone (I).*—As an improvement on the Koelsch procedure,<sup>9</sup>  $\beta$ -2-fluorenylpropionic acid was prepared in 87% yield by adding aluminium chloride (55 g.) to an ice-cooled mixture of fluorene (60 g.), succinic anhydride (44 g.), and nitrobenzene (200 c.c.); after 36 hr. at room temperature, the mixture was worked up in the usual way, giving a product (90 g.), m. p. 212—213° (from acetic acid). This keto-acid was best reduced by the Wolff-Kishner method, using Huang-Minlon's technique, and the chloride of the resulting  $\gamma$ -2-fluorenylbutyric acid was cyclised with aluminium chloride in benzene, to ketone (I), b. p. 257—258°/15 mm. (60% yield).

*7-Benzylidene-6,7,8,9-tetrahydro-6-oxo-11H-benzo[b]fluorene.*—An ethanolic solution of the above ketone (3 g.) and benzaldehyde (1.4 g.) was shaken with 4% alcoholic potassium hydroxide (50 c.c.) and left for 3 hr. in the refrigerator. The solid *derivative* was then collected, washed with dilute aqueous acetic acid and with water, and recrystallised from ethanol as yellow needles (3 g.), m. p. 153°, giving a deep red halochromy in sulphuric acid (Found: C, 89.4; H, 5.5. C<sub>24</sub>H<sub>18</sub>O requires C, 89.4; H, 5.6%).

*Fluoreno[3,4-*b*]fluorene (II).*—A solution of the foregoing chalcone (2 g.) in dry xylene (75 c.c.) was refluxed with phosphoric oxide (1.75 g.) for 30 hr.; the hot liquid was filtered off, and the filtrate washed with aqueous sodium hydroxide, then with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated *in vacuo*. The residue was treated with picric acid in ethanol, and the brown picrate (m. p. 99°) was decomposed with aqueous ammonia, giving the *hydrocarbon* (5%), yellowish needles, m. p. 259° (from ethanol-benzene) (Found: C, 94.4; H, 5.4. C<sub>24</sub>H<sub>16</sub> requires C, 94.7; H, 5.3%).

*6,7,8,9-Tetrahydro-7-1'-naphthylidene-6-oxo-11H-benzo[b]fluorene.*—Prepared from ketone (I) (3 g.) and 1-naphthaldehyde (2 g.) in the usual way, this *ketone* formed yellow prisms (3 g.), m. p. 164—165°, from ethanol-benzene, giving a violet halochromy with sulphuric acid (Found: C, 90.1; H, 5.4. C<sub>28</sub>H<sub>20</sub>O requires C, 90.3; H, 5.4%).

*Benzo[a]fluoreno[3,2-*g*]fluorene (III).*—Cyclodehydration of the foregoing chalcone (2.5 g.) with phosphoric oxide (2 g.) afforded a 4% yield of *hydrocarbon*, yellowish needles, m. p. 275° (from ethanol-benzene) (Found: C, 94.9; H, 5.2. C<sub>28</sub>H<sub>18</sub> requires C, 94.9; H, 5.1%).

*5,6,7,9-Tetrahydrofluoreno[2,3-*c*]carbazole.*—A mixture of ketone (I) (1.5 g.) and phenylhydrazine (1 g.) was heated at 120° until steam ceased to be evolved; after cooling, acetic acid saturated with hydrogen chloride (20 c.c.) was added to the crude phenylhydrazone, and the mixture brought to the b. p., then poured in water. The precipitated *carbazole* separating on cooling recrystallised from ethanol as cream-coloured needles (1.7 g.), m. p. 224°, giving a yellow halochromy in sulphuric acid (Found: C, 89.6; H, 5.8. C<sub>23</sub>H<sub>17</sub>N requires C, 89.9; H, 5.5%); the *picrate* formed dark violet needles, m. p. 186—187°, from ethanol (Found: N, 10.6. C<sub>29</sub>H<sub>20</sub>O<sub>7</sub>N<sub>4</sub> requires N, 10.4%). This tetrahydrocarbazole gave with tetrachlorophthalic anhydride a red complex, m. p. 238° (decomp.), in acetic acid, and with tetrabromophthalic anhydride, a red complex, m. p. 249—250°.

*Fluoreno[2,3-*c*]carbazole (IV).*—The tetrahydrocarbazole (1 g.) in dry xylene (50 c.c.) was refluxed with chloranil (2 g.) for 3 hr. The hot liquid was filtered, the filtrate washed first with 15% aqueous sodium hydroxide, then with water, and dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was distilled off *in vacuo*. The residual *base* formed colourless needles (0.5 g.), m. p. >340°, from ethanol-benzene (Found: C, 90.2; H, 4.7; N, 4.7. C<sub>23</sub>H<sub>15</sub>N requires C, 90.5; H, 4.9; N, 4.6%).

*8-Benzylidene-7,8,9,10-tetrahydro-7-oxobenzo[b]naphtho[2,3-*d*]furan.*—Ketone (V) was prepared from dibenzofuran and succinic anhydride according to Mosettig and Robinson's directions,<sup>4</sup> except that the intermediary keto-acid was reduced by Wolf-Kishner-Huang-Minlon's method. Condensing this ketone (3 g.) with benzaldehyde (1.4 g.) gave a *benzylidene derivative* (4 g.), yellowish needles, m. p. 205° (from ethanol), giving a deep red halochromy in sulphuric acid (Found: C, 85.2; H, 5.0. C<sub>23</sub>H<sub>16</sub>O<sub>2</sub> requires C, 85.2; H, 4.9%).

*Fluoreno[3,4-*b*]dibenzofuran (VII).*—Cyclodehydration of the foregoing derivative afforded a 7% yield of a *compound*, crystallising as cream-coloured needles, m. p. 221°, from ethanol (Found: C, 90.2; H, 4.6. C<sub>23</sub>H<sub>14</sub>O requires C, 90.2; H, 4.6%).

<sup>9</sup> Koelsch, *J. Amer. Chem. Soc.*, 1933, **55**, 3885.

7,8,9,10-Tetrahydro-8- $\alpha$ -naphthylidene-7-oxobenzo[b]naphtho[2,3-d]furan.—Prepared from ketone (V) and 1-naphthaldehyde, this *derivative* formed pale yellow prisms, m. p. 225°, from ethanol–benzene, giving a violet halochromy in sulphuric acid (Found: C, 86.8; H, 4.9.  $C_{27}H_{18}O_2$  requires C, 86.6; H, 4.8%).

Benzo[7,8]fluoreno[2,1-b]dibenzofuran (VIII).—Prepared from the above chalcone, this *compound* formed cream-coloured needles, m. p. 278°, from ethanol–benzene (Found: C, 91.3; H, 4.5.  $C_{27}H_{16}O$  requires C, 91.0; H, 4.5%).

5,6-Dihydro(dibenzofurano)[2,3-c]carbazole.—Obtained from ketone (V) (1.5 g.) and phenylhydrazine (1 g.), this *compound* formed colourless needles (1.7 g.), m. p. 251–252°, from ethanol, giving a lemon-yellow halochromy in sulphuric acid (Found: C, 85.5; H, 4.9; N, 4.3.  $C_{22}H_{15}ON$  requires C, 85.4; H, 4.9; N, 4.5%). The *picrate* formed violet needles, m. p. 210° (from ethanol) (Found: N, 10.3.  $C_{28}H_{18}O_8N_4$  requires N, 10.4%); the *addition compound* with tetrachlorophthalic anhydride formed cherry-red needles, m. p. 234–235° (decomp. >212°), from acetic acid (Found: C, 60.4; H, 2.5.  $C_{30}H_{15}O_4NCl_4$  requires C, 60.5; H, 2.5%).

(Dibenzofurano)[2,3-c]carbazole (XII).—Obtained by dehydrogenation of the foregoing product (1 g.) with chloranil (1.6 g.), this *carbazole* formed colourless prisms, m. p. >340° (from ethanol–benzene), giving an orange halochromy in sulphuric acid (Found: C, 86.1; H, 4.2.  $C_{22}H_{15}ON$  requires C, 86.0; H, 4.2%). The *picrate* formed violet needles, m. p. 218–219° (from ethanol–benzene) (Found: N, 10.5.  $C_{28}H_{16}O_8N_4$  requires N, 10.4%); the orange *addition compound* with tetrachlorophthalic anhydride melted at 245° (decomp. >206°).

7,8,9,10-Tetrahydro-8- $\alpha$ -naphthylidene-7-oxobenzo[b]naphtho[2,3-d]thiophen.—Ketone (VI) was prepared from dibenzothiophen and succinic anhydride,<sup>5</sup> the intermediary keto-acid being reduced, in 94% yield, by the Huang-Minlon technique. Condensing this ketone (3.5 g.) with 1-naphthaldehyde (2.5 g.) afforded a *derivative*, crystallising as pale yellow prisms (5 g.), m. p. 197°, from ethanol–benzene, and giving a violet halochromy in sulphuric acid (Found: C, 83.0; H, 4.5.  $C_{27}H_{18}OS$  requires C, 83.1; H, 4.6%).

Benzo[7,8]fluoreno[2,1-b]dibenzofuran (IX).—Cyclodehydration of the foregoing ketone afforded a *compound*, crystallising as colourless needles, m. p. 289° (decomp.), from ethanol–benzene (Found: C, 87.0; H, 4.2.  $C_{27}H_{16}S$  requires C, 87.1; H, 4.3%).

8-5'-Acenaphthylidene-7,8,9,10-tetrahydro-7-oxobenzo[b]naphtho[2,3-d]thiophen.—Prepared from ketone (VI) (3 g.) and 5-acenaphthaldehyde (2.5 g.), this *chalcone* (4 g.) formed yellow prisms, m. p. 238° (from ethanol–benzene), giving a violet halochromy in sulphuric acid (Found: C, 83.6; H, 5.1.  $C_{29}H_{20}OS$  requires C, 83.7; H, 4.8%). Cyclodehydration furnished 15,16-dihydro-4H-acenaphthyleno[5',4':2,3]indeno[4,5-b]dibenzothiophen (X), yellowish needles, m. p. 264°, from ethanol–benzene (Found: C, 87.5; H, 4.6.  $C_{29}H_{18}S$  requires C, 87.4; H, 4.5%).

7,8,9,10-Tetrahydro-7-oxo-8-(3-thionaphthylmethylene)[a]pyrene (XI).—This *derivative*, prepared by condensation of 3-formylthionaphthen (3.5 g.) with 7,8,9,10-tetrahydro-7-oxobenzo[a]pyrene (5.8 g.), crystallised as deep yellow prisms (6 g.), m. p. 262°, from ethanol–benzene (Found: C, 84.0; H, 4.3.  $C_{29}H_{18}OS$  requires C, 84.1; H, 4.3%).

Pyreno[1',2':6,7]indeno[1,2-b]thionaphthen (XII).—Obtained from the foregoing derivative (5 g.), this *compound* formed yellow prisms (0.25 g.), m. p. 276°, from ethanol–benzene (Found: C, 87.9; H, 4.0.  $C_{29}H_{16}S$  requires C, 87.9; H, 4.0%) (*picrate*, brown-red needles from ethanol).

8-Benzylidene-7,8,9,10-tetrahydro-7-oxobenzo[b]naphtho[2,3-d]thiophen.—Prepared from ketone (VI) (3.5 g.) and benzaldehyde (1.5 g.), this *compound* (4 g.) formed pale yellow prisms, m. p. 181–182°, from ethanol–benzene, giving an orange-red halochromy in sulphuric acid (Found: C, 81.0; H, 4.7.  $C_{23}H_{16}OS$  requires C, 81.2; H, 4.7%). Cyclodehydration of this ketone afforded a *compound*, m. p. 187°.

8-5'-Acenaphthylidene-7,8,9,10-tetrahydro-7-oxobenzo[b]naphtho[2,3-d]furan.—Prepared from ketone (V) (2 g.) and 5-acenaphthaldehyde (1.5 g.), this *derivative* (2.6 g.) formed orange prisms, m. p. 209°, from ethanol–benzene, giving a brown-violet halochromy in sulphuric acid (Found: C, 87.2; H, 4.9.  $C_{29}H_{20}O_2$  requires C, 87.0; H, 5.0%).

5,6-Dihydro(dibenzothieno)[2,3-c]carbazole.—This *compound*, prepared from ketone (VI) (1.5 g.) and phenylhydrazine (1 g.), formed colourless prisms (2 g.), m. p. 282–283°, from ethanol (yellow halochromy in sulphuric acid) (Found: C, 81.2; H, 4.6.  $C_{22}H_{15}NS$  requires C, 81.2; H, 4.6%) [*picrate*, violet needles, m. p. 193° (from ethanol) (Found: N, 10.0.  $C_{28}H_{18}O_7N_2S$  requires N, 10.0%)]. The *addition compound* with tetrachlorophthalic anhydride was red, and that with tetrabromophthalic anhydride was vermilion.

*Dibenzohieno*[2,3-*c*]carbazole (XIV).—Prepared by dehydrogenation of the foregoing compound, this *carbazole* formed yellowish prisms, m. p.  $>340^\circ$ , from ethanol (Found: C, 81.6; H, 4.1.  $C_{22}H_{13}NS$  requires C, 81.7; H, 4.0%) (picrate, violet needles, m. p.  $207^\circ$ , from ethanol).

7,8-Dihydro-5H-fluoreno[2,3-*c*]acridine-9-carboxylic Acid (XV; R = H).—A mixture of ketone (I) (2.5 g.), isatin (1.7 g.), and a 20% solution (50 c.c.) of potassium hydroxide in ethanol was refluxed for 18 hr.; after evaporation, the solid was washed with ether and acidified with aqueous acetic acid. The *cinchoninic acid* recrystallised from ethanol as yellowish prisms (2 g.), m. p.  $>350^\circ$  (Found: C, 82.3; H, 4.4; N, 4.1.  $C_{25}H_{17}O_2N$  requires C, 82.6; H, 4.7; N, 3.9%). Thermal decarboxylation of this acid afforded the *acridine* (XV; R = H), yellowish needles, m. p.  $174^\circ$  (from ethanol-benzene) (Found: N, 4.4.  $C_{24}H_{17}N$  requires N, 4.4%) [*picrate*, orange needles, m. p.  $234-235^\circ$  (from ethanol-benzene) (Found: N, 10.0.  $C_{30}H_{20}O_7N_4$  requires N, 10.2%)].

11-Bromo-7,8-dihydrofluoreno[2,3-*c*]acridine-9-carboxylic Acid (XV; R = Br).—Prepared as for the above from ketone (I) and 5-bromoisatin, this *acid* formed yellow needles, m. p.  $335^\circ$ , from ethanol-benzene (Found: N, 3.0; Br, 17.8.  $C_{25}H_{16}O_2NBr$  requires N, 3.2; Br, 18.1%).

This work was done under a grant from the Service d'Exploitation Industrielle des Tabacs et des Allumettes, for which our thanks are due to Dr. J. Cuzin, Scientific Director.

THE RADIIUM INSTITUTE, THE UNIVERSITY OF PARIS.

[Received, April 21st, 1959.]