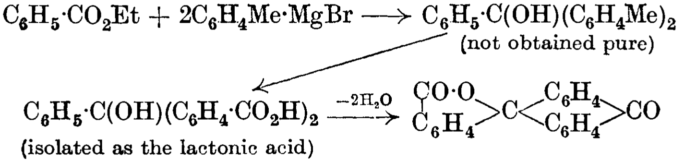
IX.—*A Cyclic Semipinacolin.*

By JAMES WILFRED COOK.

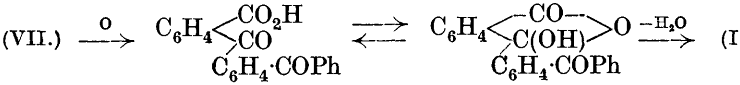
THE action of moist silver oxide on benzylideneanthrone dibromide (VI) leads to a compound, $C_{21}H_{14}O_2$, which gives an acetyl derivative and a coloured sodium salt, but is not 9-benzoylanthrone (Cook, J., 1926, 2164). The structure of this compound has now been more closely examined and it has been established that its formation is due to a semipinacolin change * having converted the central ring of the anthracene complex into a seven-membered ring. The experimental proof of this interpretation is based on the fact that oxidation led to a monobasic acid which must be 2-*benzoylbenzophenone*-2′-*carboxylic acid* (II), since on dehydration it passed into a spirocyclic *lactone* (I), the structure of which was established by its synthesis from ethyl benzoate and magnesium *o*-tolyl bromide as follows :



$$C_6H_5\cdot CO_2Et + 2C_6H_4Me\cdot MgBr \longrightarrow C_6H_5\cdot C(OH)(C_6H_4Me)_2$$

$$C_6H_5\cdot C(OH)(C_6H_4\cdot CO_2H)_2 \xrightarrow{-2H_2O} \begin{matrix}CO\cdot O\\ C_6H_4\end{matrix}\!>C<\!\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}\!>CO$$ (I.)

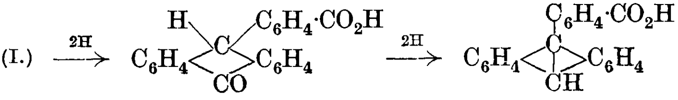
The conversion of the acid (II) into the spirocyclic lactone is doubtless due to the acid being in equilibrium with the hydroxyphthalide (III), a phenomenon that is exhibited by ketonic acids of benzophenone-*o*-carboxylic acid type and accounts for their conversion into acetyl derivatives (compare von Pechmann, *Ber.*, 1881, **14**, 1865; Graebe, *Ber.*, 1900, **33**, 2027), such an *acetate* (derived from III) being formed by the acid under discussion :



$$\text{(VII.)} \xrightarrow{O} C_6H_4<\!\begin{matrix}CO_2H\\ CO\\ C_6H_4\cdot COPh\end{matrix} \rightleftarrows C_6H_4<\!\begin{matrix}-CO-\\ C(OH)\\ C_6H_4\cdot COPh\end{matrix}\!>O \xrightarrow{-H_2O} \text{(I.)}$$

(II.) (III.)

Further confirmation of the structure of the spirocyclic lactone was furnished by its reduction to 9-o-*carboxyphenylanthrone* (IV) and 9-o-*carboxyphenylanthracene* (V) :



$$\text{(I.)} \xrightarrow{2H} C_6H_4<\!\begin{matrix}H\diagdown\ \ \diagup C_6H_4\cdot CO_2H\\ C\\ CO\end{matrix}\!>C_6H_4 \xrightarrow{2H} C_6H_4<\!\begin{matrix}C_6H_4\cdot CO_2H\\ C\\ CH\end{matrix}\!>C_6H_4$$

(IV.) (V.)

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* This term has been used by Tiffeneau and Orékhoff (*Bull. Soc. chim.*, 1921, **29**, 424) to indicate the rearrangement of a *sec. tert.* glycol into a ketone by dehydration and migration. The product of such a change is conveniently termed a semipinacolin.

That a pinacolin type of rearrangement can be brought about by treatment of a *vic.*-dibromide with moist silver oxide has been shown by Couturier (*Ann. Chim. Phys.*, 1892, **26**, 448), who converted tetramethylethylene dibromide into pinacolin by this means, but it is remarkable that rupture of the anthracene complex should take place under the very mild conditions employed. That the anthracene complex is, in some circumstances, less stable than is generally supposed * is shown by the fact that anthraquinone monoxime undergoes the Beckmann rearrangement with the formation of a seven-membered ring, the oxime of the resulting compound yielding an eight-membered ring by a further Beckmann change (Beckmann and Liesche, *Ber.*, 1923, **56**, 16).

Evidence is found in the literature (*e.g.*, Couturier, *loc. cit.*; Zelinsky and Zelikow, *Ber.*, 1901, **34**, 3249; Thörner and Zincke, *Ber.*, 1878, **11**, 67; Zincke and Tropp, *Annalen*, 1908, **362**, 250; Werner and Grob, *Ber.*, 1904, **37**, 2899; compare Meerwein, *Annalen*, 1913, **396**, 249; 1914, **405**, 129) that the pinacolin change is reversible, the reduction of a β-pinacolin frequently resulting in the formation of a derivative of the pinacol. In the anthracene derivative described above, the change is undoubtedly of a reversible character, since the reduction of the semipinacolin (VII) with hydriodic acid yields 9-benzyl-9 : 10-dihydroanthracene.

The very mild conditions which suffice to convert the six-membered ring in benzylideneanthrone dibromide into the seven-membered ring render it improbable that the change is effected by dehydration of the glycol, and it appears more likely that the reaction consists in the first place in the replacement of one bromine atom by a hydroxyl group, subsequent removal of a molecule of hydrogen bromide from the resulting bromohydrin taking place concurrently with change in ring structure. On Robinson's theory of the mechanism of the pinacolin and Wagner–Meerwein transformations (*Mem. Manchester Phil. Soc.*, 1920, **64**, No. 4) the change can be represented by the following formulæ in which dotted lines represent partial valencies and imply that an electron belonging to one atom participates transiently in the electronic orbits of both atoms to which the first atom is attached by means of partial valencies :

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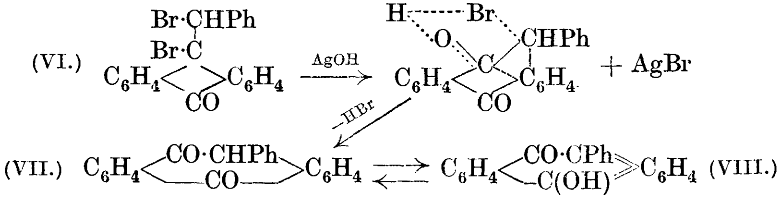
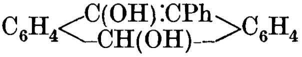
* Robinson, in commenting on the formation of α-anthrapinacolin described by Barnett and Matthews (J., 1923, **123**, 380), has suggested (*Ann. Reports*, 1923, **20**, 122) that the compound is really a β-pinacolin containing a seven-carbon ring. This speculation appears to be devoid of any experimental basis and is not in agreement with facts, as Matthews (private communication) has found that the oxidation of the pinacolin gives anthraquinone in far larger quantity than would be anticipated from Robinson's formula.



The resulting diketone (VII) forms a monoxime, and also yields a monoacetate and hence must be capable of enolisation. This may involve either of the carbonyl groups, but the intense red colour of the alkali-metal salts of the enol renders the orthoquinoid structure (VIII) the more probable.

Reduction of the diketone (VII) led to the formation of a *dihydro-compound.* This did not give an oxime but did give a diacetate and was soluble in sodium hydroxide solution to give a colourless sodium salt and hence is probably represented by the enolic formula



$C_6H_4{<}\genfrac{}{}{0pt}{}{C(OH){:}CPh}{CH(OH)}{>}C_6H_4$ (IX).

Compounds of the phenyldeoxybenzoin type usually undergo hydrolytic fission very readily under the influence of alcoholic potassium hydroxide (compare Cook, J., 1926, 1679). Both the diketone (VII) and its dihydro-compound (IX) resisted attempts to effect ring fission by this means, although six-membered cyclic pinacolins have frequently been found to undergo this hydrolysis (*e.g.*, see Klinger and Lonnes, *Ber.*, 1896, **29**, 2155), and the stability of the seven-membered ring in the compounds now described is in harmony with modern views respecting the stability of *cyclo*heptane derivatives (Mohr, *J. pr. Chem.*, 1921, **103**, 316; Meerwein, *ibid.*, 1922, **104**, 177; Meerwein and Schäfer, *ibid.*, 1922, **104**, 289; Baker and Ingold, J., 1923, **123**, 122).

The enlargement of ring systems during pinacolin transformations has, of course, been observed, and numerous examples of the conversion of monocyclic five- and six-membered carbon rings into larger rings have been cited by Meerwein and his collaborators (Meerwein and Unkel, *Annalen*, 1910, **376**, 152; Meerwein, *ibid.*, 1913, **396**, 200; 1918, **417**, 255; Meerwein and Schäfer, *loc. cit.*).

A study of the absorption spectra of some of the compounds here described was initiated, but was not proceeded with, as the semipinacolin, its sodium salt and its acetyl derivative all showed only general absorption in the ultra-violet region of the spectrum. The red sodium salt also had an absorption band in the visible region.

The author desires to express his thanks to Messrs. E. B. Robertson, B.Sc., and C. P. Stein, B.Sc., for having photographed the absorption spectra of these compounds.

EXPERIMENTAL.

Rearrangement of Benzylideneanthrone Dibromide.—The conditions already described (Cook, *loc. cit.*) for the preparation of the semipinacolin (VII) were found to give the best results, and the product was conveniently obtained free from anthraquinone by acidifying a filtered aqueous solution of the sodium salt. In one experiment, in which 85 g. of benzylideneanthrone dibromide were treated with moist silver oxide, a 35% yield of the pure semipinacolin was obtained and the residues, on oxidation, gave a 25% yield of 2-benzoylbenzophenone-2′-carboxylic acid (II) and a 30% yield of anthraquinone. The proportion of material converted into the seven-membered ring compound was thus 60%. The use of acetone as a solvent is not essential, since the transformation also occurred in the presence of alcohol.

A *monoxime* was obtained when the semipinacolin (VII; 2 g.) was heated in alcoholic solution (25 c.c.) for 2 hours with hydroxylamine hydrochloride (2 g.) and sodium acetate (3 g.) dissolved in a little water. The resulting solution was diluted somewhat, and the product twice recrystallised from aqueous alcohol. The resulting colourless needles, m. p. 191—193°, contained nitrogen (Found : C, 80·2; H, 4·9. $C_{21}H_{15}O_2N$ requires C, 80·5; H, 4·8%).

Reduction of the Semipinacolin (VII).—(a) The substance (5 g.) was intimately mixed with zinc dust (15 g.) and heated on the water-bath for 3 hours with concentrated ammonia (100 c.c.) diluted with water (50 c.c.). The solid in suspension was collected, dried, and extracted with ether. After removal of the ether, the residue was recrystallised twice from benzene–light petroleum (yield, 3·3 g.), and finally from toluene. The *dihydro-compound* (IX) formed a colourless, crystalline powder, m. p. 186—188° after sintering and becoming yellow at 178°. It gave a colourless solution in boiling aqueous sodium hydroxide, but was unaffected by sodium carbonate (Found : C, 83·9; H, 5·6. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·3%).

This dihydro-compound (1 g.) yielded a *diacetate* when heated on the water-bath for an hour with acetic anhydride (2 c.c.) in pyridine (3 c.c.). After two recrystallisations from alcohol the diacetate formed colourless plates, m. p. 154—156° (Found : C, 78·1; H, 5·3. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·2%).

The dihydro-compound (IX) was recovered unchanged after heating for 2 hours in alcoholic solution with hydroxylamine hydrochloride and sodium acetate, and after boiling for ½ hour with 10% alcoholic sodium hydroxide solution. It yielded a resinous product when reduced with sodium and boiling amyl alcohol. An acid was also formed, but purification was difficult and the amount obtained too small for investigation. Oxidation of the dihydro-compound with chromic acid in boiling acetic acid yielded 2-benzoylbenzophenone-2′-carboxylic acid.

(b) The semipinacolin (1 g.) was heated in a sealed tube at 190° for 7 hours with 50% hydriodic acid (15 c.c.) and red phosphorus (0·6 g.). The resulting solid was extracted with boiling alcohol. The alcoholic filtrate, on cooling, deposited 0·5 g. of pure 9-benzyl-9 : 10-dihydroanthracene, identified by direct comparison with an authentic sample (Cook, J., 1926, 1681).

Oxidation of the Semipinacolin (VII).—(a) On addition of potassium ferricyanide to a cold aqueous solution of the potassium salt of the semipinacolin the red colour was immediately discharged. The resulting gelatinous precipitate could not be obtained crystalline and was not further investigated.

(b) A boiling solution of the semipinacolin (20 g.) in acetic acid (200 c.c.) was treated slowly with an aqueous solution of chromic acid (50 g.). Boiling was continued for ½ hour, and the solution diluted with water; the precipitate was collected, extracted with sodium carbonate solution, and the filtrate acidified with hydrochloric acid. The precipitate was recrystallised from acetic acid, aqueous alcohol, and finally from xylene. 2-*Benzoylbenzophenone-2′-carboxylic acid* (II) forms colourless needles, m. p. 228° (Found : C, 76·3; H, 4·5. $C_{21}H_{14}O_4$ requires C, 76·4; H, 4·2%). Fusion with potassium hydroxide yielded only benzoic acid.

The *methyl* ester was obtained when the acid (2 g.) was heated on the water-bath for 4 hours with methyl alcohol saturated with hydrogen chloride (20 c.c.). It separated on cooling and after recrystallisation from methyl alcohol formed colourless, glistening needles, m. p. 165° (Found : C, 76·4; H, 4·7. $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·65%). This ester was recovered unchanged after heating on the water-bath for an hour with acetic anhydride in pyridine and was reconverted by hydrolysis into the original acid. These results are in accordance with the structure assigned to the acid, since a hydroxyl group, if present, would scarcely have resisted both methylation and acetylation.

2-Benzoylbenzophenone-2′-carboxylic acid reacted with hydroxylamine in alkaline solution, but the product could not be purified.

An *acetate* (derived from III) was obtained when 2-benzoylbenzophenone-2′-carboxylic acid (1 g.) was heated for an hour on the water-bath with acetic anhydride (1 c.c.) in pyridine (4 c.c.). When the cooled solution was diluted with water an oil separated which slowly solidified. The product was washed with cold dilute sodium carbonate solution and with water and recrystallised from alcohol. o-*Benzoylphenylacetoxyphthalide* forms small, colourless needles, m. p. 171—173° (Found: C, 73·9; H, 4·5. $C_{23}H_{16}O_5$ requires C, 74·2; H, 4·3%).

Reduction of 2-*Benzoylbenzophenone*-2′-*carboxylic Acid.*—With the object of obtaining 1-benzylanthrone, or a derivative by subsequent ring closure, attempts were made to reduce this acid to 2-benzyldiphenylmethane-2′-carboxylic acid. This result appeared to be achieved by reduction with zinc dust and boiling sodium hydroxide solution, but the resulting acid could not be obtained crystalline and dehydration with sulphuric acid was accompanied by considerable oxidation and sulphonation.

Reduction with zinc dust and boiling acetic acid for 4 hours gave a yellow pasty substance which could not be purified, together with a small amount of an acid. This acid was extracted with sodium carbonate solution and then reprecipitated and crystallised twice from benzene. The product formed yellowish, microscopic needles, m. p. 213—214° (Found: C, 79·6; H, 5·2. $C_{21}H_{16}O_3$ requires C, 79·7; H, 5·1%).

Spirocyclic Lactone of 9-o-*Carboxyphenyl*-9-*hydroxyanthrone* (I).—A solution of 2-benzoylbenzophenone-2′-carboxylic acid (10 g.) in concentrated sulphuric acid (100 c.c.) was heated at 160° for $\frac{3}{4}$ hour. After cooling, the solution was poured into water, and the precipitate collected. The precipitate was recrystallised from acetic acid containing a little chromic acid, the purpose of the latter being to destroy a trace of coloured impurity. The product was quite pure (yield, 8 g.), but for analysis a sample was recrystallised from benzene–light petroleum (Found: C, 80·6; H, 3·9. $C_{21}H_{12}O_3$ requires C, 80·7; H, 3·85%). This *lactone* forms colourless needles, m. p. 238—239°; the m. p. was depressed by admixture with 1-benzoylanthraquinone.* The lactone was hydrolysed by boiling alcoholic potassium hydroxide, giving a solution which remained clear on dilution. From this solution the lactone was reprecipitated by the addition of a mineral acid.

9-o-*Carboxyphenylanthrone* (IV).—A boiling solution of the spirocyclic lactone (I; 2 g.) in acetic acid (25 c.c.) was treated with granulated tin (2 g.) and concentrated hydrochloric acid (4 c.c.), slowly added. After boiling for 1½ hours, the clear yellow solution was decanted from the excess of tin, diluted with a little water, and cooled. The resulting yellow solid was evidently the anthranol, but it passed into the anthrone and became colourless when warmed

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* The crude lactone, but not the purified product, gave a green colour when its solution in sulphuric acid was treated with copper bronze. The green solution yielded a violet precipitate on dilution, and this colour reaction is taken as indicating the presence of a trace of 1-benzoylanthraquinone (formed by loss of water from II) in the crude dehydration product (compare Schaarschmidt, *Ber.*, 1915, **48**, 837).

with benzene. Recrystallisation from benzene gave 9-o-*carboxyphenylanthrone* as colourless needles, m. p. 226—227° (Found: C, 80·2; H, 4·6. $C_{21}H_{14}O_3$ requires C, 80·2; H, 4·5%). This anthrone gave an intense bluish-green colour when warmed with concentrated sulphuric acid, and dissolved in sodium carbonate solution with liberation of carbon dioxide to give the orange-yellow solution characteristic of an anthranol.

9-o-*Carboxyphenylanthracene* (V).—The spirocyclic lactone (I; 2 g.) was intimately mixed with zinc dust (6 g.) and heated on the water-bath with concentrated ammonia (20 c.c.), diluted with water (10 c.c.), for 3 hours. After cooling, the solid was collected, the excess of zinc extracted with hydrochloric acid, and the residue recrystallised from acetic acid containing hydrochloric acid. The resulting colourless, glistening needles were recrystallised from benzene–light petroleum and finally from alcohol and then melted at 250—251° (Found: C, 84·3; H, 4·85. $C_{21}H_{14}O_2$ requires C, 84·6; H, 4·7%). This acid formed sparingly soluble salts with the alkali metals, and dilute solutions of these salts had a violet fluorescence.

Synthesis of the Spirocyclic Lactone (I) *of* 9-o-*Carboxyphenyl*-9-*hydroxyanthrone*.—(a) *Phenyldi*-o-*tolylcarbinol*. Ethyl benzoate (11·5 g.) was added to a Grignard solution prepared from *o*-bromotoluene (34 g.) and magnesium (4·8 g.), cooled in a freezing mixture. After addition of the ester, the ethereal solution was boiled for 3 hours and then decomposed with ice and hydrochloric acid. The ethereal layer was washed, the ether distilled off, and volatile by-products removed from the residue by steam distillation. The resulting viscous oil gave an orange-red solution in sulphuric acid, its solution in light petroleum yielded the corresponding chloride when treated with hydrogen chloride, and the chloride easily reacted with pyridine to give a quaternary salt. None of these products, however, could be obtained in a crystalline condition.

(b) *Lactonic acid of triphenylcarbinol*-2 : 2′-*dicarboxylic acid*. The crude phenyldi-*o*-tolylcarbinol (10 g.), prepared as described above, was suspended in a little potassium hydroxide solution and treated with a solution of potassium permanganate (25 g.) in water (500 c.c.). The whole was boiled for 16 hours, the small amount of residual permanganate removed by the addition of alcohol, and the precipitated hydroxides of manganese, which were contaminated with a considerable amount of unchanged carbinol, removed by filtration. The filtrate was acidified, and the resulting precipitate recrystallised successively from aqueous acetic acid, aqueous alcohol, and aqueous acetic acid (Found: C, 76·4; H, 4·5. $C_{21}H_{14}O_4$ requires C, 76 4; H, 4·2%). This *lactonic acid* formed colourless needles, m. p. 225—227°, and yielded a methyl ester which could not be purified on account of its excessive solubility and tendency to become resinous.

(c) *Dehydration of the lactonic acid.* A solution of the lactonic acid (0·5 g.) in concentrated sulphuric acid (5 c.c.) was heated at 160° for ½ hour. The cooled solution was poured into water and the precipitate was collected, extracted with dilute sodium hydroxide solution, and recrystallised from acetic acid. The resulting colourless needles melted at 238—239° and were shown to be identical with the spirocyclic lactone (I) prepared by dehydration of 2-benzoylbenzophenone-2′-carboxylic acid.

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